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Comparative physicochemical characterisation of thermally modified wood

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Comparative physicochemical characterisation of thermally modified wood

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by

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Con admiración por su compromiso con el trabajo, por el amor a sus hijos, y por su consideración para con mis sueños ....

Quisiera dedicar este trabajo a mi adorada esposa María de Lourdes

I anticipate a day in the foreseeable future, when airplanes will travel exceptional distances, propelled by potent steam engines...

Lord Kelvin, *ca.* 1906[*]

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[*] From the lecture "On the unpredictability of science" by Sir John Meurig Thomas

Abstract

Small matched samples of beech, Scots pine and Norway spruce woods were heat-treated to twenty schedules, at temperatures of 190, 210, 230 and 245 °C for heating periods of 0.3, 1, 4, 8 and 16 h. Following thermal modification, physical changes and chemical composition in thermally modified wood (TMW) were analysed and compared to the characteristics of untreated materials. Most of the analysis were carried out using the heat-induced weight loss values (WL, %) as the independent variable to make the comparisons. Average treatment WL values ranged from 0.3 to 27.0, from 0.6 to 21.5, and from 1.0 to 26.7 for beech, pine, and spruce samples respectively. A major finding of this research was that each characteristic changed following the same profile in the three wood species for all properties studied. Save for hardness in beech, the magnitude and rate of change of each property was often found not to be significantly different between species when relative-to-control values in function of the WL were compared.

The results show that the gravimetric and dimensional changes in the transverse plane are mainly due to chemical breakdown of wood hemicelluloses. On the other hand, the readiness of TMW to dimensional changes and moisture uptake below the FSP was of a much lower concern than in raw wood. Similarly, several mechanical properties were found to be little affected by heat exposure at treatment levels likely to be achieved industrially. Among these were compression strengths parallel and perpendicular to the axis in the tangential direction, and the axial modulus of elasticity in bending (MOE). Other mechanical strength parameters (*e.g.* shear strength, hardness and the modulus of rupture in bending) were reduced at almost any given treatment schedule, but the rate of reduction was mild. It is contended that design practices could make up for the strength loss incurred by the treatment for these properties. On the other hand, parameters related to the energy required to produce failure and also impact strength were greatly diminished at low levels of modification. This may restrict the use of TMW where unpredictable sudden loads may occur. Properties at the limit of proportionality were found to be less reduced than the same property at maximum load. Mechanical properties more affected by heat were found to be those more intimately related to the chemical integrity of the wood material and/or the structural configuration of wood polymers in the cell wall substance, whilst compression strength and hardness were more related to wood density. MOE was proposed to be more dependent of cellulose, microfibril angle and wood density, all of these little altered by wood heating.

Lastly, a description of the colour changes in the test samples was undertaken using image analysis and qualitatively by infrared spectroscopy. It was determined that colour changes in wood were caused mainly by changes in the lignin.

The major input of this work to the state of the art is given by modelling the properties studied using various linear, non-linear and multivariate methods. Properties in TMW were estimated from gravimetric, colour and moisture-related parameters. Solid-state mid-infrared spectra data, treatment parameters and interrelationship between variables were also explored. It is concluded that all changes in small heated samples of wood are amenable to be estimated efficiently in multiple ways, using cost-effective indicators. Remarkably encouraging results for the prediction of physical properties were found for models using colour parameters or by the analysis of the infrared spectra data. Whilst descriptions of the heat-induced changes in wood exist, prediction studies are fairly scarce and not comprehensive. This part of the study is thus very timely, giving the current requirements of quality control and assurance of TMW at the industrial stage. The relevance of these findings to property prediction in larger wood members would depend on the property considered; safety factors will probably be needed for some forms of wood strength in larger heated materials.

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List of Abbreviations and Treatments

ARH	Average relative-to-control hygroscopicity
ASE	Anti-swelling efficiency
CA	Compression strength parallel to the axis
CCA	Copper chrome arsenic
CE	Compression strength perpendicular to the axis
Cell.	Cellulose
CP-MAS	Cross-polarised magic angle spinning
CV	Coefficient of variation
DMDHEU	Dimethylol dihydroxy ethylene urea
DP	Degree of polymerisation
DRIFT	Diffuse reflectance infrared Fourier transform
DVS	Dynamic Vapour Sorption
EMC	Equilibrium moisture content
EW	Earlywood
FTIR	Mid-infrared Fourier transform infrared
GC	Gas chromatography
GC-MAS	Gas chromatography mass spectrometry
GluMan	Glucomannan in hardwoods
GluMan	(galacto)glucomannan in softwoods
GluXylan	Glucuronoxylan
H	Janka hardness on radial face
Hemicell.	Hemicellulose
HW	Hardwoods
IS	Charpy impact strength
LP	Limit of proportionality
LW	Latewood
MOE	Longitudinal modulus of elasticity in bending
MOE_{CA}	Modulus of elasticity in compression strength parallel to the axis
MOE_{CE}	Modulus of elasticity in compression strength perpendicular to the axis
MOR	Longitudinal modulus of rupture in bending
MPa	Mega pascal
ND	Nominal density
NIR	Near infrared
NMR	Nuclear magnetic resonance
OD	Oven-dry
OPI	Overall Performance Index
PDR	Potential decay resistance
R	Resilience or work to the limit of proportionality
RLP	Fibre stress at proportional limit
RH	Relative humidity
R_O	Severity factor

S	Shear strength parallel to the axis
SD	Standard deviation
SEM	Scanning Electron Microscope
SG_{CW}	Oven-dry specific gravity of the cell wall
SG_{OD}	Oven-dry specific gravity of wood
SSLP	Horizontal shear stress at neutral plane at limit of proportionality
SSML	Horizontal shear stress at neutral plane at maximum load
SW	Softwoods
t	Time
T or Temp.	Temperature
TMW	Thermally-modified wood
TW	Total work
UV	Ultraviolet
VOC	Volatile organic compound
WL	Heat-induced weight loss
WML	Work to maximum load

List of heat-treatments used in this study

Temp. °C	Time h	Treatment number
190	0.3	1
	1	2
	4	3
	8	4
	16	5
210	0.3	6
	1	7
	4	8
	8	9
	16	10
230	0.3	11
	1	12
	4	13
	8	14
	16	15
245	0.3	16
	1	17
	4	18
	8	19
	16	20

Chapter 1 Introduction

1.1 General introduction and the need for research

The search for environmentally less aggressive wood treating alternatives has been a central research subject over the last few years in Europe (Militz 2002, Van Acker and Hill 2003, Militz and Hill 2005, Hill *et al.* 2007). Increasingly negative perception from the general public and concerns and restrictions from regulating bodies on current wood treatment technologies, have prompted the need of novel processes for enhancing the bio-deterioration resistance of wood and wood products (Evans 2003, Freeman *et al.* 2003).

The promotion for the development of advanced methods for improving the properties of wood also comes from some sectors of the woodworking industry. This is due to the declining demand in several traditional markets for wood products, which have been lost against possible more environmentally aggressive materials (Hill 2006c). These -mostly synthetic, materials often outperform wood products in applications of varying surrounding moisture conditions or in other situations known to cause the deterioration of solid wood and its surfaces.

Potential treatments that would have made all the impact for reducing the hygroscopic character of wood were traditionally held back by the costs of the process. Already in 1920, when Tiemann in the USA was discussing the colouring of wood when dried at high temperatures, he wrote:

> " Recent experiments carried out at the Forest Products Laboratory have shown that by treating the perfectly dried wood in dry air much higher temperatures can be used with less injury. ... The hygroscopicity and consequently the swelling and shrinkage is reduced by about one-half. The wood however is made more brittle, although its hardness is not greatly reduced. A loss in bending strength of about 15 percent, and in work to maximum load (toughness) of about 30 percent, was found in tests made on this material. ... Its applicability to interior trim and cabinet work, except where brittleness is detrimental, seems promising, except for the cost of treatment" (Tiemann 1920).

However, as industrialised societies become more environmentally conscious and wealthier, and wood modification technologies matured, several processes have been finally commercially realised (Jones 2007). In the last fifteen years or so, modified wood has entered into the building and furniture markets, mostly for non-structural applications such as cladding, decking and garden furniture, but with increasing occurrences in load-bearing situations, mostly in demonstration projects (Homan *et al.* 2003, Bengtsson *et al.* 2003, Christmas *et al.* 2005, Schöftner 2007).

Thermal modification

The thermal modification of wood is commercially by far the most advanced process compared to other wood modification technologies already in the market such as acetylated wood (Kettenbroek 2007), furfurylated wood (Brynildsen and Myhre 2007) and DMDHEU-modified wood (Hill 2006b). Although the most recent technological advances on the thermal modification of wood have developed in Europe, thermal modification processes are being adopted steadily elsewhere (Christmas *et al.* 2005, Shi *et al.* 2007).

Heating of wood in the 140 – 260 °C temperature range for long periods of time causes the irreversible reduction of its capability for moisture uptake (Obataya and Tomita 2002, Gonzãlez-Peña *et al.* 2004). This reduced hygroscopicity is accompanied by the enhancement of other desirable characteristics. Among these are the increased dimensional stability of wood (Krause *et al.* 2004), reduced moist-induced movement in service (Militz and Tjeerdsma 2001), and improved resistance to fungal decay for above-ground applications (Farahani *et al.* 2001, Welzbacher and Rapp 2002). Although the subject has not been thoroughly studied, it is held that the environmental credentials of thermally-modified wood (TMW) in terms of ecotoxicity are superior to that of untreated wood and may surpass that of several man-made materials (Van Eetvelde *et al.* 1998).

Exposing wood to high temperatures however carries its own drawbacks, because some desirable wood properties are negatively affected. It is well established that wood toughness[a] is largely decreased at low levels of modification. Other properties readily reduced are abrasion resistance, cleavage strength and tangential strength perpendicular to the axis. Modulus of rupture (MOR) in both bending and

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[a] Either impact strength, or work to maximum load, total work or resilience in bending.

axial tension, shear strength and hardness are decreased to a somewhat smaller degree (Mayes and Oksanen 2002). Other physical characteristics are also changed by the heat exposure, notably the colour of wood and the response of wood surfaces to light irradiation. Various properties remain largely unaffected (*e.g.* flammability, susceptibility to termite attack). The time-dependent mechanical behaviour of heated woods to any form of stress (*e.g.* creep) is unknown.

The basic characteristics of the process of the thermal modification of wood are well understood. It is known to be an organic acid mediated process whereby hemicelluloses, the most hydrophilic polymers in the wood substrate, are significantly decomposed as soon as the treatment temperature reaches 180 °C. Amorphous regions of the cellulose substance are also rapidly changed structurally leading to molecular configurations less amenable to the reaction with water. Lignin undergoes depolymerisation in a first, fast stage, and then repolymerises trapping some carbohydrate by-products in the process. Crystalline cellulose is largely unaffected at temperatures < 300 °C. The resultant solid residue is a more hydrophobic and stiffer substance (Yildiz *et al.* 2006, Yildiz and Gümüşkaya 2007).

Much less is understood regarding the mechanisms involved in changes - often reduction, in most forms of mechanical strength of wood and in other physical properties. Earlier laboratory-based research carried out in the USA by Stamm and co-workers was limited to the study of a few strength properties and some interactions of wood with water vapour (Stamm 1977 and references therein). Until recently, studies have been more the type of repetitive experimentation (testing species, schedules, treatment atmospheres) rather than basic research on the primary reasons of property change. Most of the latest research has been industrially driven and has concentrated more on the development of end uses in order to consolidate an emerging market. Usually, reports focus more in the prospective benefits of the heat-treatment than on the scientific description of the modification phenomena.

On the other hand, it is recognised that several aspects for the systematic characterisation of TMW have been neglected hitherto. Currently, one of the major ambitions of producers and end-users of thermally modified wood is the standardisation and established quality control and assurance systems of the obtained product (Homan and Tjeerdsma 2003, Sheiding *et al.* 2007). Subjects requiring urgent attention in this regard include the development of methods to compare thermal effects between species and between treatment schedules, and protocols to standardise the product. Additionally, no method exists to find a balance between the heat-induced enhancements and property reduction as a result of the modification.

1.2 Plan of this thesis

The remainder of this thesis is divided into eight chapters. Chapter 2 introduces some background on the subject of study that has not been dealt with in other parts of the document. Relevant references within the scope of this work have been discussed in the corresponding chapters of this thesis.

Chapters 3 presents a detailed account of the methods followed for the experimental part for this research. This covers the selection of the wood species used in this work, the data handling techniques used for all studies included in chapters 4 to 8, the thermal modification, and all subsequent physical and chemical characterisations.

Chapters 4 to 8 contain the main body of this thesis. Chapter 4 describes an investigation on the quantitative changes in the main structural polymers and the extractive contents in the three wood species selected for this work. In this part dimensional and other gravimetric changes such as density and specific gravity of the cell wall are also analysed, and in addition ways to predict these.

Chapter 5 reports on the mechanical responses of the treated material. This is comprised of two main parts. The first part includes the description of the changes in mechanical performance of the material, and the second part introduces the modelling of mechanical and other physical properties.

Chapter 6 was designed to study all the most important aspects of the relationship between modified wood and water, and its prediction. Chapter 7 presents a study of the effects of the treatment on colour changes, as well as the quantitative and qualitative analysis of the relationship between these and chemical changes. The potential to predict several properties of TMW from colour changes was investigated.

Chapter 8 deals with the modelling of most of the properties described in chapters 4, 5 and 6 by a specialised handling of solid state FTIR and DRIFT data. This part also has a detailed qualitative explanation of the chemical changes in treated wood by the analysis of the difference FTIR spectra, and its relationship with physical changes.

Chapter 9 includes a general description of the results from the previous chapters and the contribution of these to the field of knowledge. Conclusions are drawn and areas of further research identified. Finally, Appendices consist of a tabular presentation of a selection of results which were not included in the main text of chapters 4 to 8.

1.3 Aims and objectives

The main objectives of this thesis were:

1. To resolve the effect of weight loss, and temperature and time of treatment on the physical and chemical changes of wood using representative species;

2. To determine the relationship between fundamental characteristics of wood (density and chemical composition) with property change;

3. To establish the primary reasons for large wood strength loss at low values of heat-induced weight loss in some forms of stress; and

4. To assess how well physical properties of thermally-modified wood can be predicted using cost-effective indicators.

Chapter 2 Subject background

2.1 Introduction

The treatment of solid wood to prevent its biological degradation is of ever increasing concern due to the growing scientific and public awareness about the impact of the treating substances in both the human and natural environment. Limitations in the range of wood-based products where arsenic-containing substances can be used have been recently imposed in Europe (Jones 2006). At the end of the last decade, the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) of the European Commission carried out a study on the advantages and drawbacks of the use of arsenic in certain wood treating chemicals (Anon. Undated). The risks identified by the study included those to human health from the disposal of wood treated with wood preservatives containing copper, chrome and arsenic (CCA). In particular risks to children's health from the use of CCA-treated wood in playground equipment were noted. A risk to the aquatic environment in certain marine waters was also recognized. In a further consideration of the health effects of arsenic, the CSTEE concluded that the substance is both genotoxic and a well known carcinogen, and that it may be appropriate to consider that no threshold exists for the carcinogenic effect. Waste CCA-treated wood has been classified as hazardous waste pursuant to Commission Decision 2000/532/EC as of May 3 2000 (*Idem.*). Currently, together with other substances formerly used for treating wood, arsenic-based materials are subject to rigorous commercial restrictions under the EU Marketing and Use Directive 76-769-EEC (and 8th amendment 89/677/EEC) (Jones 2006).

Similar limitations for the use of biocides have also taken place in other developed regions. Public perceptions on the potential arsenic exposure led to a voluntary withdrawal of CCA-treated wood from the residential market in North America in 2004, a share of 68% of all CCA-treated wood in USA and Canada (Freeman *et al.* 2003). In Japan, non-CCA type chemicals have been used to replace CCA preservative since 1997. By 2003, the amount of pressure-treated CCA wood was reduced to zero (Hata *et al.* 2004).

In the short term, restrictions are likely to encompass a wider range of wood treating chemicals. In particular chromium- or copper-containing substances prone to leach from the treated material when exposed to wet conditions in service, or to produce ecotoxic by-products during wood impregnation or landfill disposal, are already under close scrutiny of governmental agencies (*cf.* Jüngel *et al.* 2006)

On the other hand, the advent of fossil-based alternative polymer materials led to a lower demand for wood products likely to be exposed to moist environments in industrialised societies in the third quarter of the 20th century (Dinwoodie 1989). A new wave of wood substitution has been noticed in the recent years, due to the high costs associated with the maintenance of some wood products in outdoors applications. In Germany for instance, the market share of wooden windows has fallen steadily from nearly 8 million units in 1994, to about 4 million pieces in 2002, mainly to the benefit of the plastic windows industry (Eder 2003).

The woodworking industry and in general the scientific community specialized in the subject of wood protection have been engaged in devising effective treatments that can protect wood from biological deterioration without reliance on chemicals that posses high mammalian or environmental toxicity (Evans 2003). Processes to enhance the overall performance of wood under varying moisture conditions have also been investigated intensely during the last decade.

Thermal modification of wood

One way to improve the decay resistance of wood and the response in its interactions with water is by the modification of the wood material. This can be achieved by various ways, notably by changing the nature of the wood substrate. Hill (2006a) listed the most essential requirements for devising a less environmentally aggressive method for wood modification:

- Modified wood should not exhibit toxicity in service;
- Modified wood should not release toxic materials at the end of service life (*e.g.* when incinerated); and
- For biological resistance, the mode of action of the modified wood should be non-toxic (non-biocidal).

The modification of wood substrate by means of subjecting this material to a heat-treatment amply satisfy these requirements. According to the definition accepted by the new installed committee CEN/TC 175/WG3/TG6 preparing a working document for a European standard on thermally modified timber, modified timber is the substance that has endured a treatment during which the cell wall material has changed at the molecular level, in such a way that, dependent on the technology applied, properties of the timber, such as durability and form stability, are improved (Homann and Tjeerdsma 2005).

As introduced in the previous chapter, thermally modified wood (TMW) is a relatively new material option aimed at replacing biocide-treated wood in several above-ground applications. For outdoors its superior durability and dimensional stability makes TMW a good substitute for impregnated softwoods and some tropical hardwoods. However, the reduction of some forms of wood strength gives TMW a low technical profile somehow, with increasing pressure from competing wood modification industries and other sceptics for limiting the use of TMW in several applications (Hill 2006a).

Some 80,000 m^3 of heat-treated timber are currently produced and marketed in Europe, mostly for non-structural applications. The production capacity is nearly three times that of the actual production (Hill 2006a, Anon. 2007). Marketing of TMW started for non-structural purposes, but as appreciation of the benefits of the material have slowly permeated amongst architects, specifiers and the general public, there has been an increased interest to apply this material in load-bearing situations. The pressure from the woodworking industry is also a driving force for varying the applications of wooden materials in order to compete efficiently with other building alternatives. A new consortium of 28 universities, research centres and companies from nine European countries has been recently established to envisage forms to widen the field of uses for TMW made out of European hardwoods to structural applications in particular for an outdoor environment. This 'Holiwood' project is funded by the EC under the 6th Framework Programme; it started in July 2005 and will last until June 2009 with a total budget of €11 million (Schöftner 2007, Widmann *et al.* 2007).

The product already commercialised is however being processed without any European standard or qualified quality assurance method. It is acknowledged that the market needs some type of reliable system for quality and also guidance for proper use in suitable applications (Homan and Tjeerdsma 2003). Enhancements of some properties of TMW are often used as a marketing tool but sometimes misreported outside the scientific community. Conversely, inferiority or misleading claims of material performance are rare but not unknown. For this emerging industry, it is held that the image of TMW could be damaged by inappropriate use of the material. Clarity where TMW can be used and how it should be used is therefore recognised (*Idem.*). From both sides, producers and consumers, the appeal for an ample and universally accepted quality control system is becoming stronger.

The current industrial classification of the ThermoWood® process is probably the most advanced industrially, but it is possibly not the most convenient way for characterizing TMW. This is based on time and temperature of treatment, and only considers the reduction in hygroscopicity in the classification (Mayes and Oksanen 2002). Wood treated at 185 – 190 °C is considered to have an improved stability (the so-called Thermo-S), whilst material treated at 200 – 212 °C (Thermo-D) is supposed to have increased decay resistance due to the most severe treatment conditions. It is possible to correlate time and temperature of treatment with property change using a severity factor approach (this will be demonstrated in chapter 5). This possibility affords for the prediction of residual strength and other properties using a model which combines temperature and time of treatment, but the parameters for this system are species-dependent, and will likely vary with stock size and treatment atmosphere. The use of time and temperature of exposure alone in order to characterise the material is nearly meaningless technically.

In order to maintain consumer confidence and allow the TMW industry to expand, there is a need to further our understanding of the properties of TMW and do this in a rigorous scientific manner. In a similar vein, few reports exist on effective ways to characterise the material in a range of treatment levels regardless of species or secondary treatment parameters. There is an urgent need to elaborate on this and report on efficacious or non-destructive ways for the characterisation of physical properties of TMW to ensure this is adequately treated while retaining sufficient mechanical performance irrespective of species concerned.

In the remaining part of this chapter, a description will be given on the state of the knowledge on the thermal modification of wood at the beginning of this work, with an attempt to address the salient literature in this dynamic area of study. For limitation of space this appraisal is limited to give an overview of the topics dealt with in this research rather that being a meticulous description of all the aspects of thermal modification of wood. Relevant previous investigations on the topics addressed in this research have also been included in the discussion of each respective chapter.

2.2 The thermal modification process

2.2.1 Industrial processes

Several processes have been developed for heat-treating wood at a large scale. Each has its own processing particularities and equipment requirements, but technically they look pretty much the same. There are four main treatments commercially established (Table 2.1). Other treatments carrying out the treatment under vacuum or using other forms of heating the wood (electro-heating, microwave heating, etc.) appear to be in a development stage.

Table 2.1 The four main commercial processes for thermally modifying wood.

Process	Country of development
ThermoWood®	Finland
Retification®/Torrefaction	France
Plato® wood	Netherlands
Menz Holz	Germany

The main difference between treatments comes up from the treating atmosphere. The ThermoWood® process, industrially the most advanced so far, is carried out starting from wood already dried to an equilibrium moisture content (EMC) below the fibre saturation point (FSP). The heating is done in a kiln with a super-heated steam atmosphere. The Plato® process is very similar, although a small variance has been introduced mostly to avoid patent claims from the Finnish industry. In the Plato® system, previous to the drying of the material, there is an hydrothermal step (*i.e.* heating wood in an aqueous environment at 6-8 Bar)[*]. Wood is then dried conventionally, and the subsequent thermal modification is carried out in a steam atmosphere at slightly lower temperatures than the ThermoWood® process. It is held

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[*] Sodium acetate or NaOH are used depending on the species concerned to control the pH

that in this way the mechanical strength is reduced to a smaller degree than the latter, although comparative scrupulous studies to prove this do not exist. The Retification® or Torrefaction process starts from wood in an almost oven-dry condition (Figure 2.1); it is carried out under a nitrogen blanket. The Menz Holz process is different from the previous three treatments in that this is carried out using vegetable oil as the heating medium (Rapp 2001, Militz 2002).

Figure 2.1 The process for the thermal modification of wood in France

All treatments have in common that solid wood is subjected to temperatures from 165 °C to 260 °C, from several hours to a few days, in an atmosphere with low oxygen content. It is held that oxygen accelerates the degradation of wood, although this is seemingly contradictory, because the aim of the treatment is actually to promote the controlled thermal degradation of wood. Probably the deterrence of carrying out the treatment in a oxygen-rich atmosphere comes from the increasing risk of a fire when heating wood in air. At the end of the heating period, wood is conditioned by steaming in all treatments carried out in gaseous environments. The price of the treatment goes from € 60 to 150 per m^3 depending on the method, the Menz-Holz apparently being the least expensive process (Hill 2006b). The technology to produce TMW at a large scale is in all cases quite capital-intensive, though. For instance a 75,000 m^3/year plant would require a capital investment of € 10 to 15 million for the Plato® process (*Idem.*).

Technological research started in Finland in 1992 and a few years later the first pilot plant was installed (Metsä-Kortelainen 2006). Currently the industry for wood modification is more structured also in Finland. An organisation embracing the main actors there, The Finnish ThermoWood Association, was established in December 2000. This association acts as a hub for ten companies treating wood and three kiln manufacturers. The aim of the association is to enhance the use of thermally-modified wood produced by its members and technology transfer. Other important duties of the organisation are quality control of production, product classification and R&D activities. The production in Finland is however dominated by only three major companies, treating two coniferous woods (see below).

In the UK, the production has started just recently in a public organization in central Wales for demonstration of the technology, using a process similar to the ThermoWood system in a kiln of one m^3 capacity (David Jenkins 2005, pers. comm.). It is accepted that the UK lags technologically behind other more advanced EU countries in this respect by at least 10 years.

2.2.2 Main species and principal uses for TMW

Initially, TMW was being basically aimed at some exterior applications such as wall cladding. However, there is an industrial trend to add value to the product in order to make this technology more profitable and competitive against other wood modification processes already in the market. The most basic product (simply treated boards) fell from 67% in 2001, to 56% in 2006 of all the wood treated in Finland using the ThermoWood® process (Anon. 2007). The production has departed from the traditional role of cladding material, to more refined uses such as environmentally friendly prefabricated constructions.

Common exterior uses include decking, windows, door components, garden constructions and furniture, and cladding (Figure 2.2). Poles up to 100 mm in diameter are reported to be treated in the Netherlands using the Plato® process (Boonstra *et al.* 1998). An important application in the context of the Holiwood project is the development of advanced noise barrier systems (Schöftner 2007). Retified beech wood is known to be used for boat decking in substitution of expensive exotic naturally stable woods such as Teak. Other uses reported for Retified wood include street furniture, duck boarding, gates and fences (Gohar and Guyonnet 1998).

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Products for interior application have also evolved from flooring and cladding, to wall and ceiling panelling, interiors of saunas, furnishings and furniture (Metsä-Kortelainen 2006).

As far a load-bearing applications is concerned, the Holiwood project includes the development of a modular system based on prefabricated, self supporting wooden wall elements for house construction. This will be a complete package with cladding, roof elements and detachable parts including optimised domestic techniques for the construction of eco²buildings – efficient in ecology and economy (Schöftner 2007).

The main market of TMW processed with the ThermoWood® process is Europe (90%). Since records began in 2001, the spectrum of modified woods in Finland has steadily narrowed to mainly two species, pine and spruce, with market share of 44% of all the modified material for each species. Other species of secondary importance are birch (3%) and aspen (2%), the remaining 7% shared by a handful of other mostly hardwood species. The demand for product type has remained unchanged in the last four years (2003-2006), with about 30% of the production for Thermo-S material (increased dimensional stability) and 70% for the Thermo-D wood product (increased decay resistance) (Anon. 2007). In New Zealand, it is known that radiata pine is the primary species used for the process, but statistics are still unavailable.

2.3 Effects of thermal modification on physical properties

2.3.1 Mass loss and density

The study of weight changes upon heat-treatment of wood was carried out firstly in a series of papers of McLean (cited by Stamm 1956) and Stamm and co-authors (Stamm *et al.* 1946, Mitchell *et al.* 1953, Seborg *et al.* 1953). The main finding from these experiments was that the weight of modified material is reduced due to the thermal exposure (Stamm 1956). The extent of this reduction was influenced by the nature of the original wood type: smaller mass losses were found for softwoods than for hardwoods heated under similar conditions. The decline in mass was also influenced by the treatment conditions. Larger mass losses were registered for treatments in closed conditions or in air, than in open conditions or oxygen-deprived atmospheres respectively. All other parameters being the same, higher mass losses were also attained when the heating was carried out in moist than in dry conditions (Davis and Thompson 1964, Mitchell 1988).

At all temperatures, the rate of weight loss is greatest at the beginning of the treatment and declines as the treatment continues. Stamm (1956), Lin (1969) and

Chang and Keith (1978) showed all that the log-normal plot of the weight loss on heating time exhibits a linear relationship except for a slight initial curvature. The presence of some strongly adsorbed moisture not removed under normal drying conditions (at 105 °C ± 3 °C, Tsoumis 1991) and/or minute amounts of extractives, resulting in more heterogeneous reactions at the beginning of heating, have been proposed as possible causes for the departure from linearity in the relationship between weight loss and time of treatment.

The results of McLean as well as some results of his own were later used by Stamm (1956) to derive some models for the prediction of WL in a series of treatment atmospheres but this was only for softwoods, and this work was later extended by Millet and Gerhards (1972); this will be discussed in section 2.5.

On the other hand, despite the importance of a density measure at least in untreated wood, heat-induced changes on this parameter have been little studied. Mitchell (1988) reported on changes of the green specific gravity (oven-dry weight/green volume) of wood heated at a lower temperature that that used in modern modification systems. Small samples of loblolly pine were treated at 150 °C for 1 – 16 h in three heating atmospheres (oxygen, nitrogen and air). The experiment was performed departing from samples at three EMC conditions (oven-dry, 12% EMC, and green condition). Slight reductions in specific gravity were found for the samples treated for 4 to 16 h, 2 to 16 h and 8 to 16 h in the green condition in oxygen, nitrogen and air respectively. It was not reported if the reductions were significant, though.

Bohnke (1993, cited by Mouras *et al.* 2002) heat-treated pine wood and found a slight increase in specific gravity up to 220 °C, and then a loss for treatments at 230 °C and up to 270 °C. The initial increment was attributed to a reorganization of macromolecular components, which were reflected into a densification of the cell wall mater. The subsequent reduction was ascribed to the evaporation of breakdown products.

2.3.2 Mechanical strength

On the whole, it is not easy to make generalizations or comparisons between experiments on the effect of the thermal modification on the mechanical performance of wood because of the lack of a harmonized testing methods. As was pointed out for the changes in mass in the previous section (section 2.3.1), the mechanical behaviour of wood is also affected by the heating temperature, heating rate, heating media, atmosphere and pressure of treatment, wood species, the initial EMC of wood, and sample size. A review of the effect of some of these factors on MOE and MOR in bending has been given recently (Hill 2006c). The effect of treatment conditions on wood strength appear to be generally the same as for the foregoing description on weight loss. When reductions in strength occur, these appear to be greater in closed, moist or oxygen-enriched conditions than in open, dry or inert atmospheres, all other factors remaining the same. However, mechanical properties appear not to be affected by heating to the same degree for many different types of stress, which further complicates the analysis.

Many reports have concentrated in the study of a few properties and thus comparisons of results from different reports may be of little utility or even invalid. Apparently the most comprehensive description on mechanical properties of TMW is that in the ThermoWood® Handbook[†] (Mayes and Oksanen 2002), but these will not be considered here because of the lack of scientific rigour in the descriptions.

Two of the most comprehensive reports are described below as an example of the effects of heating on the mechanical performance of TMW (Chang and Keith 1978 and Mouras *et al.* 2002). Results of other investigations on the same properties differ little from these descriptions. All other relevant results of previous research on mechanical properties are included in the discussion of each of the fifteen mechanical strength parameters studied in this work (chapter 5).

Boards of 900 mm × 25.4 mm × 76-162 mm of four hardwoods, namely American beech, sugar maple, rock elm and trembling aspen were heat treated at three target temperatures (Chang and Keith 1978). Treatment time was for 8, 16 and 32 h at 180 °C, for 2, 4 and 8 h at 200 °C and for 0.5, 1 and 2 h at 220 °C. Time of treatment was measured from the average time required for the sample to reach the treatment temperature (40 min for the surface, about 2 h for the board interior). Following thermal modification, samples were machined to final testing dimensions. Samples were tested for static bending strength, toughness, abrasion resistance and glue-line shear strength. Only results for the two first test will be described in this

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[†] Available on-line at www.thermowood.fi

section, whilst results of the other two tests are discussed in chapter 5. Final size for samples for the bending test were 360 mm x 20 mm x 20 mm (*l* × *r* × *t*), whilst for the toughness test these were 280 mm x 20 mm x 20 mm (*l* × *r* × *t*). MOE was found to increase by an average of 8%; the maximum increase was found for the treatment at 180 °C for less than 8 h. At 200 °C the optimum durations were under 2 h for elm and maple, 2 – 4 for aspen and about 8 h for beech. At 220 °C, maximum MOE values were reached at about 2 h. In contrast to MOE, MOR began to decline even after the mildest treatment conditions, while the most severe treatments resulted in significant reductions in all species. Reductions in elm and beech were relatively greater than they were in aspen and maple. Weight losses of 3 – 12% were accompanied by losses in MOR of about 20 – 35%. Toughness of heated elm and beech declined almost 70%, whilst aspen was the least affected species showing an average decline of 40%. The decline in toughness with heating happened rapidly, for all temperatures, most of the damage occurred in the earlier stages of treatment. Toughness loss was much greater than WL, sometimes as much as ten times greater.

Small samples (150 mm × 30 mm × 30 mm, *l* × *r* × *t*) of poplar and Curupixa wood were heated from ambient temperature to 150 °C at 2 °C/min, and then kept there to homogenise the temperature across the full section (Mouras *et al.* 2002). Holding times varied from 30 to 520 min. depending on the species and treatment atmosphere (air or saturated steam). The temperature was raised thereafter at 1 °C/min up to the desired treatment temperature (210 °C, 220 °C or 230 °C). Treatment length varied from 30 min. at 230 °C to 90 min. at 210 °C, with longer periods of exposure when the treatment was in the presence of saturated steam (Table 2.2). Samples were then tested for compression strength parallel to the axis, and for three-point bending strength. Weight losses ranged from 5% to 12% in poplar, and from 1% to 9% in Curupixa.

- *Compression strength parallel to the axis.* Compression strength for untreated samples was of the order of 38 MPa for poplar and of 70 MPa for Curupixa. These authors used the specific gravity to make comparisons between treatments, based on the proposal of Bohnke (1993, cited by Mouras *et al.* 2002). They concluded that compression strength of torrefied wood was equivalent to that of sound wood of the same specific gravity for all treatments tested.

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- *MOE in bending.* No significant reduction in the MOE was found for any of the conditions studied. Results showed increased variation, though.
- *MOR in bending.* Average strength for treatments at the lower temperature and shorter times remained almost unchanged (Table 2.2). More severe treatments (220 °C for 60 min) induced a strength loss of the order of 16.5% and 16.2% for Curupixa and poplar respectively. In poplar, treatments at 220 °C for 60 min in the presence of steam induced a larger decrease in bending strength (33.2%) than heating in air (16.2%), and the coefficient of variation also increased for the treatment in steam. However, the heating up time was longer for the treatment with steam. The reduction in MOR was ascribed to two main phenomena: 1) a change in the lignin structure due to the condensation of degradation by-products, and 2) a change of the state in the amorphous cellulose.

2.3.3 Hygroscopicity and other wood-water interactions

The tendency of wood to adsorb or desorb water vapour under varying moisture conditions below the FSP is reduced by the thermal-induced chemical degradation of the wood substance. This reduced hygroscopicity is dependent on both the time and the temperature of treatment, as well as the heating medium (Hill 2006c). Comparison of different studies is then again difficult given the wide range of experimental conditions used in the investigations. Typical results on the reduction of hygroscopicity from two independent reports are given below as an example of the effect of the treatment, while some other relevant studies on this subject are included in chapter 6.

For the same experiment explained in the previous section on the mechanical strength of four hardwoods (Chang and Keith 1978), Keith and Chang (1978) analysed the hygroscopicity of treated material at three RH conditions (37%, 84% and 97%) at 24 °C over saturated salt solutions. For samples treated at 220 °C for 2 h, the reduction varied from 49 to 52% (average 50%), with no consistent difference between species or RH conditions. Hygroscopicity was generally more reduced for longer treatments or at higher temperatures of exposure. Differences between treatment temperatures were more evident at higher RH conditions. From this limited range of RH conditions studied, these authors showed that the desorption isotherm was nearly flat in the heated material. Similar findings were reported later by Tjeerdsma *et al.* (1998b) on heat-treated beech and Scots pine using the Plato® process 165 °C/180 °C for the hydrothermal/heating cycle. Reductions of about 40% were found for pine at any RH condition, while for beech the hygroscopicity reduction was about 30% at the lower end of the hygroscopic range, and 45% at a RH of 96%.

Lower wood hygroscopicity results in increased dimensional stability and reduced movement in service. Volumetric shrinkage of four hardwoods was reduced by the heat-treatment (Keith and Chang 1978). The largest volumetric shrinkage of control specimens was for beech and the smallest for aspen. In elm, the reduction in volumetric shrinkage was small when the treatment was at 180 °C (averaged over its three heating durations). Larger reductions at 200 °C and at 220 °C brought the elm shrinkages in line with those of the other species. Maple, beech and aspen were characterised by a much smaller difference in shrinkage between 180 °C and 200 °C than between 200 °C and 220 °C.

Tjeerdsma *et al.* (1998b) found that the anti-swelling efficiency (ASE) of beech and pine woods reached a maximum of about 50% for the treatment conditions studied (see above). Both Keith and Chang (1978) and Tjeerdsma *et al.* (1998b) reported a higher reduction in swelling in the tangential than in the radial direction and they considered that this would result in smaller dimensional changes upon moisture stresses. Arnold (2007) also found a small reduction in swelling anisotropy for beech and Norway spruce woods treated at 180 °C or at 220 °C (no treatment time was given), but this reduction was not statistically significant compared to the anisotropy of control samples.

In a comprehensive experiment, beech, Scots pine, Norway spruce and ash woods were all analysed for swelling from the oven-dry condition to the condition at four RH, namely 35%, 65%, 85% at 20 °C, and 50% at 23 °C (Scheiding *et al.* 2005). The moisture uptake at any given surrounding environment was reduced significantly, on average by 50% compared to untreated controls, with no clear effect of the RH setting. Keith and Chang (1978) have previously reported a reduction in swelling in both the radial and the tangential directions at three RH conditions studied. However, they found that the proportional differences in swelling between heated and control samples were greater at higher than at low RH conditions.

2.3.4 Decay resistance

Thermal modification of wood results in an increased resistance to several forms of fungal biodegradation, although the degree of protection afforded by the treatment depends of the type of decay and species concerned. This enhancement has been proved by subjecting various modified woods to pure culture or unsterile soil and various field tests. The origin of this improvement is however not completely clear at present, but it is believed to be the effect of chemical changes in the substrate and/or to the reduced hygroscopicity in the material (Hill 2006c). Apparently, the decay resistance is not linked to biocidal chemicals formed during the thermal process (Kamdem *et al.* 2000). It is also not clear whether the treatment leads to a true deterrence to fungal onset, or if the modification only extends the lag phase typical of fungal colonisation and subsequent polymer breakdown. No method has been devised for testing the enhanced decay resistance of TMW and hence tests have been conducted following protocols designed to either test the toxic threshold of biocides, or the natural resistance of untreated wood. Some inconsistencies arise from applying these methods.

Welzbacher and Rapp (2002) examined the differences in decay resistance of heat treated softwoods from four European industrial processes (those given in Table 2.1). Results from the mini-block test with basidiomycetes showed an increased resistance to decay in all samples studied. Only minor differences in weight losses due to decay were found between processes. The brown rot decay caused by *Oligoporus placenta* was significantly greater than that caused by the white rot fungus *Coriolus veriscolor* in all treatments. Samples treated in the Plato® process and oil-heated woods were classified both as durable, according to the European Standard EN 350-1. ThermoWood® and Retified wood were classified as moderately durable. Based on their results, these authors concluded that TMW is suitable for aboveground exterior applications. The study showed, on the other hand, that materials sampled from the industrial scale processing fell short from the results obtained from samples heat-treated at the laboratory scale. This pointed to the need of the optimization of industrial processes, in order to assure a given quality in service.

In an extension of these investigations (without the Retified wood material included), an outdoor field test above ground (European hazard class 3) was carried out using a horizontal double layer test in Hamburg, Germany (Welzbacher and Rapp 2004). Evaluation was done yearly by rating the extent of decay according to EN 252 as: 0 (sound), 1 (slight attack), 2 (moderate attack), 3 (severe attack) and 4 (failure). A preliminary evaluation of the ongoing experiment showed a substantially improved resistance against biological attack of the thermally modified material compared to controls. No significant differences between the thermally modified materials was found at the last time of the evaluation. None of the thermally modified materials was attacked during the first 0.8 years. First decay was found for ThermoWood® specimens after 1.5 years, similar in its intensity to the decay of oak heartwood (also used as control). After 2.5 years of exposure, all the treated materials showed an incipient decay, giving a rating of 0.2 for TMW from the Plato® and ThermoWood® processes and 0.1 for the oil-treated wood. The significantly highest average evaluation of decay was found for untreated pine sapwood specimens, with a rating of 0.7.

Thirteen variants of TMW from nine European manufacturers including four wood species were investigated on their biological performance, focussing on their use for playground equipment (Scheiding *et al.* 2005). Significant improvements on the decay resistance against wood destroying fungi were observed in all species following pure culture and field tests (Table 2.3). Moreover, results from resistance against mould revealed that although the treatment improved the rating, mould growth was still observed. Microscopic investigations showed that the mycelium did not grow as deeply into the TMW as in untreated wood. Field tests studies according to EN252 were also set up, but these are ongoing. After 12 months of exposure, no attack by wood destroying fungi have occurred in all the TMW specimens (destruction rating 0).

Results from earlier studies on decay resistance of TMW have been discussed recently by Hill (2006c).

Table 2.3 Resistance class according to EN 350-1 and durability class according to ENV 807 for 4 heat-treated woods (control species: Scots pine sapwood for softwoods, beech for hardwoods)[a].

Species	Resistance according to EN 350-1 and EN 113 (without leaching)[b]				Durability class according to ENV 807 (soft rot)[b, c]
	Conipohora puteana	*Gloeophyllum trabeum*	*Poria placenta*	*Trametes versicolor*	
TM Scots pine	1 - 2	1 - 2	2 - 4	NT	3
TM Norway Spruce	1 - 2	1 - 2	2 - 4	NT	3
Norway spruce untreated	5	5	5	NT	4
TM Beech	1	1	NT	1 - 2	1
TM Ash	1-2	1 - 2	NT	1	1 - 3
Ash untreated	3	2	NT	4	4

[a] With data from Scheiding *et al.* (2005)

[b] Individual samples varied in rating, hence ranges appear

[c] Classification against soft rot is based on that period when the controls (Beech and Scots pine sapwood) showed a mass loss of 20%, 16 weeks for Beech, 32 weeks for pine

TM = thermally modified; NT = not tested

2.3.5 Other physical changes

As indicated above, thermal modification has a striking effect on all physical properties of wood materials. Colour changes and surface hydrophobicity are two of the most important physical changes in TMW.

The effect of thermal modification on wood colour has been studied mainly for two reasons. One line of study has been to assess the possibility of establishing the liaison between some physical changes and colour transformation, but the results are inconclusive so far. This subject will be treated in detail in chapter 7.

On the other hand, the stability of the altered colour to light-irradiation has also been reported. Colour in TMW is not stable to UV-light exposure (Ayadi *et al.* 2003, Letourneau *et al.* 2005). Wood samples of 150 mm × 75 mm × 5 mm ($l \times r \times t$) of ash, beech, maritime pine and poplar were treated at 240 °C under anaerobic conditions and then subjected to an accelerated weathering test. Samples were exposed in a chamber to UV light directly at a distance of 5 cm for 835 hours. Each cycle comprised 2.5 h of irradiation at 60 °C followed by 0.5 h of water vapour condensation at 50 °C. Colour changes measured in the CIEL*a*b* system were faster in the untreated material in the first 36 h while in treated material the rate was nearly constant throughout the period of study. The change continued afterwards at seemingly the same rate in treated and untreated material. At the end of the test, total colour change, ΔE^*, was much smaller in the heated material. Untreated samples changed from 25 to 28 ΔE^* units, while treated wood changed from 5 ΔE^* units in ash, to 10.5 ΔE^* units in poplar. In a similar experiment but at 400 h of exposure, faster colour changes were registered in thermally modified jack pine, trembling aspen and white pine than in untreated jack pine (the only control shown) (Letourneau *et al.* 2005). However, colour stabilisation was also faster than in the raw wood. Total colour difference, measured in the CIEL*a*b* colour system was smaller in modified material in the three species ($\Delta E^* < 10$ units) than that in untreated jack pine ($\Delta E^* = 30$). However, no universal behaviour could be observed in the direction of the changes in heated materials. All three woods became more yellow in the b* axis. Softwoods became redder along the a* axis while aspen became greener. Measurements along the L* axis showed that softwoods slightly darkened, while aspen lightened.

Scots pine samples, heat-treated at 225 °C in steam atmosphere and untreated reference samples, were exposed to natural weathering in Espoo, Finland for 7 years, and then examined with FTIR, UV resonance Raman, and ^{13}C CPMAS NMR spectroscopies (Nuopponen *et al.* 2004a). Analyses revealed that the lignin content of the weathered heat-treated and especially weathered reference softwood samples diminished significantly. The surface of the weathered heat-treated sample was still enriched in aromatic and conjugated carbonyl compounds, whereas the surface of the reference sample was rich in cellulose. These results indicated that degradation products of lignin of the reference sample were leached out more easily than in the heated samples. These authors attributed this to the condensed structure of lignin in TMW, which could partly inhibit UV-light–induced free-radical reactions. In addition, the lower equilibrium moisture content of TMW could reduce the leaching out of the degradation products. According to these results, these authors proposed that heat-treated wood is more resistant to natural weathering than untreated wood.

This study however is unlikely to hold for all treated species. Experimental evidence of an improved weatherability was also found for heat-treated beech in earlier research (Feist and Sell 1987), but inconclusive results were found for heated spruce wood.

With regards to surface hydrophobicity, Pétrissans *et al.* (2003) examined the wettability of spruce, beech, Scots pine and poplar woods heat-treated at 240 °C in N_2 for 8 h. Contact angle measurements before and after treatment indicated a significant increase in wood hydrophobicity. Advancing contact angles of a water drop were in all cases systematically higher in heat-treated than in untreated wood. Chemical modifications investigated by FTIR and ^{13}C NMR spectroscopies revealed little chemical change except for the degree of cellulose crystallinity which was considerably higher in heat-treated wood and probably involved with higher contact angles observed. Subsequent experiments carried out in beech wood only treated under the same conditions but at much lower temperature (130 – 160 °C) revealed that either the chemical degradation, the reduced hygroscopicity, or the generation of extractives, were not necessarily the primary causes for the reduced wettability in modified beech (Hakkou *et al.* 2005). They proposed that changes in wettability were more related to modification of conformational arrangement of wood biopolymers due to loss of residual water or more probably to plasticisation of lignin at early stages of the treatment.

The short-term time-dependent behaviour of TMW was investigated in the context of this research and reported elsewhere (Gonzãlez-Peña *et al.* 2005). Small samples of Norway spruce wood were heat-treated at four temperatures for five time periods. Oven-dry weight losses due to the treatment ranged from 1.0% to 31.5%. Blocks were conditioned to 65% RH at 20 °C and then the short-term steady state relaxation was examined in pure compression perpendicular to the grain in the tangential direction. Heat-treated samples were generally characterised by a lower modulus of relaxation. Upon release of the load, modified samples showed smaller delayed elastic recovery and plastic deformation than untreated wood.

2.4 Effects of thermal modification on chemical composition

The matter of the chemical degradation of wood upon heating poses high complexity. The amount of information is overwhelming due to existence of several wood processes employing heat at temperatures higher than 100 °C: high-temperature drying, pyrolysis, gasification, destructive distillation, casks roasting, wood combustion, thermal modification, etc. On the other hand, wood pyrolysis[‡] is not considered to give exactly the same products as would be given by the sum of its three major components pyrolysed separately (Fengel and Wegener 1984). The pyrolysis does not progress at an even rate. It occurs in a step-wise manner with hemicellulose breaking down first at 200 – 260 °C, cellulose next at 240 – 350 °C and lignin at 280 – 500 °C. The rate of reactions also depend upon the atmosphere, pressure and precursor materials (Soltes and Elder 1981).

Overlapping literature is frequent from several processes, but as noted by Hill (2006c), significant differences in degradation kinetics at temperatures > 260 °C and an abrupt change at temperatures > 300 °C do exist. Therefore this section concentrates on studies dealing with solid wood only, treated within the 150 – 260 °C temperature range. Reviews on the effect of heat on individual wood components or on the chemical composition of solid wood at higher temperatures than those used for modern thermal modification processes will not be discussed here. The interested reader is referred to authoritative descriptions (Beall 1971, Shafizadeh and Chin 1976, Soltes and Elder 1981, Fengel and Wegener 1984, Shafizadeh 1984, Elder 1991, Branca *et al.* 2003).

2.4.1 Hemicellulose

Hemicelluloses play an important part both in the thermal modification process and in the subsequent overall behaviour of the treated wood as a building material. Its thermal degradation is of great interest from the standpoint of the increased decay resistance, some forms of mechanical strength and decreased affinity towards water

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[‡] In the strictest definition, pyrolysis of wood is the thermal degradation carried out in the absence of oxygen, so that the matter is converted to solid, liquid and gaseous phases without the combustion of the wood substance (Elder 1991).

vapour in TMW. The chemical degradation mechanisms are intricate but the main characteristics of the process are well understood.

In species from temperate regions, wood is composed of about 40% to 50% cellulose, 20% to 35% lignin, and 12% to 35% hemicelluloses; these components are relatively stable if heated up to about 100 °C for up to 48 h (Fengel and Wegener 1984). Chemical acid hydrolysis is the most typical degradation mechanism upon the heat exposure of wood.

Because hemicelluloses are composed of shorter molecules and have more branched structure than cellulose, they are more accessible in the cell wall material and therefore generally easier to hydrolyze by acids than cellulose (Goldstein 1991). Pentosans (*e.g.* xylan) have been established as the most labile of hardwood hemicelluloses. This difference is explained due to the higher sensitivity of xylan to acids than the other wood polysaccharides. The rate of hydrolysis of xylose glycosides is approximately 4.5 times that of glucose glycosides (Kass *et al.* 1970). Moreover, monosaccharides associated in hemicellulose side-chains such as arabinose and galactose, have been found to be especially sensitive to thermal decomposition (Winandy and Lebow 2001).

Upon heat exposure, acetyl groups are liberated from the chemical structure of wood hemicellulose. These combine with available water to form acetic acid, which in turn acts as a catalyst to increase the degradation rate in the hemicellulose; this also interacts with other wood polymers (Inari *et al.* 2007a). Hardwoods have more acetyl and uronic acid groups than softwoods (Sjöström 1993), and therefore the former has a greater potential to form organic acids and to speed up the degradation. Under similar heating conditions, greater mass loss in hardwoods compared to softwoods has been associated also to the higher hemicellulose content of the former (Zaman *et al.* 2000). Thermal reaction of wood leads to three different phases: a solid brownish residue, a yellowish liquid, and a mixture of non-condensable gases which result from the quenching of the effluent gases (Bourgois and Guyonnet 1988).

In very early research, extracted samples of Douglas-fir wood were heated at 110, 160 and 220 °C for 64 days, 8 days and 16 h respectively in a open system, and for 16 days, 16 h and 4 h respectively in a closed system (Mitchell *et al.* 1953)[§].

[§] Open system, in a container with a constant flow of N_2 or air; closed system in a closed vessel allowing building up of the pressure and volatile products to remain in the treating atmosphere.

Results showed that pentosans degraded to a larger extent than α-cellulose or lignin at any treatment condition. Pentosans decreased more in the closed system than in the open one, with large reductions determined mainly for treatments at 160 °C and 220 °C. At the end of the treatment, samples treated at the harshest conditions had a pentosan content of 2.5% in the open system and 0.7% in the closed system, compared to the 9.1% content in untreated wood.

By heating powdered maritime pine wood at 260 °C for 15 minutes to 4 h under N_2, Bourgois and Guyonnet (1988) established that pentosans decompose very quickly at this temperature, with a half-life time of about 15 min. In an extension of this work, the same material was examined in a larger range of temperatures of exposure (Bourgois *et al.* 1989). Samples were treated at 240, 250, 260, 270 and 290 °C for 30 min. Similar results were reported, with pentosan reduced significantly at any temperature of exposure while an increase of phosphoric-acid lignin was simultaneously observed. Pentosan content fell from 9.61% in control wood, to 5.93%, 3.1% and 1.4% for the samples treated at 240, 260 and 290 °C respectively. In both studies, elemental analysis also showed a decrease in O and H together with an increase in C. These authors concluded that hemicelluloses (pentosan) were the most heat-sensitive polymers in pine wood. The most important reactions took place at the beginning of the treatment, where hemicellulose degraded to give place to a gaseous phase (CO, CO_2, O_2 and N_2), as well as the most important part of the liquid phase (acetic and formic acids, water and methanol). Hemicelluloses also acted as decomposition initiators for the lignin. However, the behaviour of (galacto)glucomannan, the main hemicellulose in pine wood, was not mentioned.

The thermal behaviour of boards of one softwood (Scots pine) and one hardwood (silver birch) heat-treated at 200 – 230 °C under steam atmosphere for 4 to 8 h was compared by Zaman *et al.* (2000). Monosaccharides were analysed by GC on the basis of their per(trimethylsilyl)ated derivatives. Total carbohydrates, computed by difference from lignin and extractives, decreased from 72.3% and 75.6% in untreated pine and birch, respectively, to 57.5% and 56.2% for pine samples treated at 230 °C for 8 h, and birch samples treated at 220 °C for 8 h, respectively. Based on a small increase of the ratio glucose/total-carbohydrates at increasingly higher severe treatment conditions, these authors concluded that hemicellulose were more affected than cellulose upon wood heating. After 8 h of treatment at 205 °C, mass loss in pine was 17.0%, whilst in birch this was 26.7%

(birch was heated at 200 °C, though). They attributed this effect to the higher initial hemicellulose content in birch wood.

Kotilainen *et al.* (2001) investigated the gravimetric changes in small samples of black alder and European aspen heated in N_2 at 150 – 220 °C for 3 h. Oven-dry WL ranged between 1.6 and 19%. From the analysis of the monosaccharide composition, they found that carbohydrates were more susceptible to chemical degradation than the lignin substance. Monosaccharides associated to hemicelluloses (arabinose, galactose, mannose and xylose) were found to be more readily degraded than glucose, so they concluded that this was an indication of the larger degradation of hemicelluloses compared to cellulose. Elemental analysis of the treated samples showed that the mass proportion of carbon increased with the simultaneous decrease in the mass proportion of oxygen as a function of the temperature of treatment. They contend that oxygen-rich carbohydrates degraded faster than the oxygen-poor lignin substance. These authors also noted that relative changes in carbohydrates in both hardwoods at any combination of time and temperature was very similar.

In a similar experiment, Alén *et al.* (2002) heated Norway spruce boards at 180 – 225 °C for 2-8 h under steam atmosphere to give WL between 1.5 to 12.5%. They analysed the material for total lignin content and for individual monosaccharides in the hydrolisate from the Klason lignin determination. The chemical analyses indicated that carbohydrates were more amenable to thermal degradation than lignin. From the determination of the monosaccharide contents, they suggested that cellulose was chemically more stable than hemicelluloses and, on the other hand, that xylan degraded more easily than glucomannan. The mass proportion of carbon in the test samples increased with increasing temperature, and this was accompanied by a corresponding decrease in oxygen and hydrogen. As oxygen-rich aliphatic compounds, carbohydrates were more apt to various degradation reactions than the aromatic moiety-containing lignin fragment.

The analysis of Scots pine boards treated in a two-step process (the Plato® process) using two temperatures for the hydrothermolysis phase (165 °C or 185 °C) followed by conventional drying and the subsequent dry-heating at 180 °C for 4 h, indicated that the hemicelluloses were substantially more degraded than α-cellulose (Boonstra and Tjeerdsma 2006). As expected, calculated hemicellulose content (from holocellulose by difference of α-cellulose) was reduced further when the hydrothermolysis step was at the higher temperature. Hemicellulose content went from 31.9% in control wood to 22.1 and 13.5% (of the final oven-dry weight) in the test samples treated in the hydrothermal step at 165 °C and 185 °C respectively. These authors also noted an increase in the Klason lignin content in both treatment conditions.

Yildiz *et al.* (2006) examined the chemical composition of small specimens of spruce wood (*Picea orientalis*) heat-treated in air at 130, 150, 180 and 200 °C for 2, 6 and 10 h. The hemicellulose content was calculated by subtracting nitric-acid cellulose content from sodium chlorite holocellulose. Invariably, they found that the reduction of hemicellulose was greater than cellulose or lignin at any given combination of time and temperature. Cellulose was reported nearly unchanged for all treatments. Similar accounts were given by Windeisen *et al.* (2007) who studied the chemical composition of small specimens of beech wood heat-treated at 180, 200 and 220 °C for 4 – 6 h. The degradation of sugar units was also reflected by the decrease of acetyl groups and of aliphatic hydroxyl groups in treated samples.

2.4.2 Cellulose

There is general agreement about cellulose changes during the thermal modification process. In the same reports described in the preceding section (section 2.4.1), the findings indicate that gravimetric changes in the cellulose substance are minor and only significant at the most severe treatment conditions. Although it is known that cellulose in wood may decompose for long term exposure at temperatures as low as 120 °C (Fengel and Wegener 1984), it is well established that this fraction is little degraded at temperatures < 300 °C (Kim *et al.* 2001). Most research has focused on changes in cellulose degree of polymerization and microfibril crystallinity. These structural changes will be discussed below (section 2.4.5). Two reports from recent research on gravimetric changes in cellulose are described here, to exemplify the changes in cellulose for the same experimental conditions previously described for hemicellulose.

Boonstra and Tjeerdsma (2006) found that α-cellulose slightly decreased from 49.1 (in % of the final oven-dry weight) in reference Scots pine samples, to 44.9% in samples treated in the two-step protocol at 165 °C/180 °C, while a marginal increase to 49.7% was recorded for the sample treated at the harshest conditions (185

°C/180 °C). Heating of spruce wood between 130 °C and 200 °C for 10 h, led to a small α-cellulose increase for treatments at 130, 150 and 180 °C, while a small decrease was observed by heating at 200 °C (Yildiz *et al.* 2006). Contents went from 54.12% in untreated samples, to 55.85%, 56.32%, 55.45% and 50.39% in samples treated at 130, 150, 180 and 200 °C. In all cases the difference was statistically not significant (at $\alpha = 0.05$).

From thermo-gravimetric analysis, the first change observed in heating of cellulose is the elimination of adsorbed water, which occurs at about 100 °C (Kotilainen 2000, cited by Yildiz *et al.* 2006). By raising the temperature above 200 °C the thermal degradation of cellulose and formation of volatile products proceeds rapidly. Levoglucosan is frequently quoted as the primary degradation product of cellulose, but other anhydroglucoses, furan and furan derivates are also produced (Fengel and Wegener 1984). However, by heating maritime pine at 260 °C, Bourgois and Guyonnet (1988) postulated that furfural was not from cellulose decomposition, but that this was the result from the dehydration of the xyloses.

Some differences in the heat susceptibility of wood polymers may be related to the associations between these in the cell wall material. However, structural changes and the modification of cellulose as it interacts with the matrix substance are poorly described. Regarding the structural association between the cellulose microfibrils and the matrix substance in untreated wood, Shigematsu *et al.* (1994) held that the affinity of cellulose for hemicellulose is greater than that for lignin. On the basis of softening measurements of wood pulp samples, Salmén and Olsson (1998) suggested that in wood, xylan is associated with lignin, whereas glucomannan is more associated with cellulose. Structural similarity as well as the simultaneous response in the dynamic mechanical FT-IR analysis also indicate an intimate association between cellulose and glucomannan in the cell wall of softwoods (Åkerholm and Salmén 2001).

2.4.3 Lignin

Due to its high structural diversity, lignin degrades gradually over a wider temperature range than carbohydrates (Alén *et al.* 2002). However, under heating conditions likely to be used industrially, the most frequent observation is the increase in the acid-insoluble lignin upon heating at 165 – 260 °C, the so-called pseudo-lignin (Nikitin 1966). All the reports described in section 2.4.1 on the degradation of hemicellulose have in common the concurrent weight increase in the acid-insoluble lignin. The obvious source for this gravimetric enhancement is the carbohydrate fraction. This aspect will be elaborated further in chapter 4, section 4.1.1.

Despite the abundant literature on chemical changes in wood upon heating, results on lignin changes in solid wood at the range of temperatures mentioned before under isothermal conditions are somewhat scant. Bourgois and Guyonnet (1988) analysed changes in percent content of Klason lignin and lignin elemental analysis as a function of time for the experiment described above on powdered maritime pine heat-treated at 260 °C. Lignin increased rapidly (faster at the beginning), and to a larger extent, doubling in 1 h, with almost a three-fold increase after 4 h. Carbon content increased, while O and H decreased. Methoxy ratio in lignin decreased with time although in wood the ratio remained almost unchanged; this was because the lignin ratio in the residue increased. They assert that the measurement of methoxy groups in lignin is a good indicator of native lignin loss. Hemicellulose acted as a true decomposition initiator, and promoted lignin degradation. From the analysis of gaseous effluents by GC, these authors determined that the water released was not only from hemicelluloses, but also from the lignin substance. Methanol was also released from lignin and this explained the formation of an ethylenic bond in its FTIR spectra. The release of water and methanol from the lignin molecule affords for the structure stabilisation by π-conjugation. The escape of small molecules takes place in the propane skeleton of phenyl, guaiacyl and syringyl-oxy-propane units. They point out, however, that methanol can also be attributed to the degradation of methoxy groups which belong to the side glucuronic chain of xylan. After a first degradation reaction, a resinification occurs in the lignin which is responsible for the thermal resistance of the solid residue upon further wood heating. This resinification was later explained as a condensation reaction due to molecular rearrangement following the release of the gaseous and liquid phases from both hemicellulose and lignin (Bourgois *et al.* 1989). Based on elemental analysis from their second experiment, they concluded that the nature of lignin at different temperatures was not the same at equivalent levels of the WL. They also found that the rate in which pentosan diminished and the rate of the modification of lignin was roughly the same.

More recently, Windeisen *et al.* (2007) carried out lignin analyses by means of thioacidolysis and acid-insoluble lignins. They found an enrichment of acid-insoluble lignin relative to the carbohydrate fraction in beech wood in the three treatments studied (at 180, 200 and 220 °C for 4 – 6 h). In comparison the relative yields of all thioacidolysis products declined with the severity of the treatment. Compounds detected were predominantly syringyl structures. Guaiacyl lignin went from 206.1 μmol g^{-1} in untreated beech, to 59.6, 53.8 and 0.0 μmol g^{-1} for samples treated at 180, 220 and 220 °C respectively. In the respective order, syringyl lignin was 452.1, 251.1, 233 and 68.8 μmol g^{-1}. Therefore, lignin of the thermally treated samples could not be decomposed by means of thioacidolysis in the same way as the lignin of untreated wood. They attributed this to the significant reduction of the characteristic arylglycerol-β-aryl ether linkages due to the thermal attack. The higher amount of non-hydrolysable substance determined mostly in samples treated at 220 °C were ascribed to lignin-derived compounds. According to them, this confirms that most of the lignin, which is still present in thermally treated wood, cannot be decomposed by means of thioacidolysis in fragments with a molecular mass detectable by gas chromatography. These facts were considered evidence for the occurrence of condensation reactions, leading to the formation of larger cross-linked lignin-derived compounds.

2.4.4 Extractives

To understand the role of acetone-extractable compounds in yellow birch wood on the reduction of wettability, Hemingway (1969) examined fatty acids after air-heating at temperatures between 105 °C and 220 °C. These treatment conditions did not increase the concentration of fatty acids sufficiently to explain the reduced surface wettability observed in heated samples. Unsaturated fatty acids and esters showed a considerable oxidation upon heating, though.

Bourgois *et al.* (1989) found that the presence of extractives accelerates the breakdown of pine wood polymers during heating at 240 – 290 °C. DSC tests showed that the exothermic peaks of the pyrolysis wood reaction were pushed towards the high temperature region when the sample was in the extracted condition. These authors concluded that this demonstrated that extractives acted as a catalyst in the thermal oxidation of the wood material. Extractives may trigger the thermal decomposition of acidic groups in hemicelluloses via radical formation, before these organic acids elicited in turn the degradation of other wood polymers.

Oak wood chips subjected to heat treatment at 120 – 250 °C for up to 6 h revealed two stages in the course of extractive decomposition. At temperatures of between 120 and 185°C, there was an increase in ellagic acid contents from ellagitannins (castalagin) and in cinnamic and benzoic aldehydes from lignins. Above 185 °C, a more intense thermolysis process caused the disappearance and degradation of the previously formed monomer compounds. Increase in treatment time caused an acceleration of all these modifications. Only lyoniresinol remained stable up to 215 °C, but decomposed at 250 °C (Sarni *et al.* 1990).

Similar findings were reported for Scots pine battens heat-treated at 100 – 240 °C using the ThermoWood® process (Nuopponen *et al.* 2003). Cross-sections of wood boards were analysed using infrared microscopy following thermal modification. A typical absorption band of fats and waxes at 1740 cm^{-1} was detected on the sapwood edges in the temperature range of 100 – 160 °C, indicating that fats and waxes moved along the axial parenchyma cells to the surface of the sapwood during the heat treatment. At higher temperatures (> 180 °C) fats and waxes disappeared from the sapwood surface. Resin acids were detected at temperatures up to 180 °C in the middle of the battens. IR spectra of these spots showed a characteristic absorption band of resin acids at 1697 cm^{-1}. At 200 °C resin acids were not detected in the middle of the battens; however, resin acids were detected at distances of 500 and 600 mm from the midpoint of the battens and on the edges of battens. At temperatures higher than 200 °C, resin acids had disappeared from the wood material altogether.

The previous description for the three main polymers and extractives include all the most important studies carried out so far for the chemical characterisation of heated woods in conditions likely to be of any practical relevance for the thermal modification of wood. Except for some instances of the qualitative work given below (section 2.4.5. Solid state studies), it is clear that most of the studies have been limited to one or two species, in a very small range of modifications. Not all results are comparable, because in some instances it is not acknowledged whether the gravimetric determinations are related to the initial oven-dry weight of the sample or to the dry weight of the residue. Comparison of the course of degradation of the two main hemicelluloses of wood have not been attempted, and ways to compare different schedules are also inexistent. These subjects may be of a more scholarly than practical interest, but may also have relevance for the complete understanding of the primary modification events in the material.

2.4.5 Solid-state chemical studies on heat-treated woods

Qualitative chemical modifications occurring during heat treatment are believed to be in great part responsible for the new properties of TMW. These have been investigated using different solid state methods, noticeably by CP/MAS ^{13}C NMR, X-ray diffractometry and FTIR spectrometry (Bourgois and Guyonnet 1988, Tjeerdsma *et al.* 1998, Bhuiyan *et al.* 2000, Sivonen *et al.* 2002, Wikberg and Maunu 2004, Inari *et al.* 2007a, Yildiz and Gümüşcaya 2007). These analyses have served basically to reaffirm the results of the analytical determinations described above for changes in the carbohydrates and lignin fractions in heated solid wood materials. The main deductions from these studies reveal an important degradation of hemicelluloses and molecular reconfiguration, dehydration and/or degradation of amorphous cellulose resulting in an increase of cellulose crystallinity in heated wood. In turn, lignin presents subtle but significant qualitative modifications, mainly due to β-O-4 ether linkage cleavage and aromatic nuclei demethoxylation followed by auto-condensation reactions with formation of methylene bridges.

The thermal degradation of cellulose starts with the molecule cleavage producing alkali-soluble products, and the degree of polymerisation (DP) of the residual cellulose is reduced too (Fengel and Wegener 1984). The DP of isolated cellulose of thermally-treated spruce wood remained constant up to 120 °C, following a rapid decrease with increasing temperature (*Idem.*). The crystalline structure of cellulose is not changed upon heating or can even increase at temperatures as high as 200 °C, depending on the treatment conditions. The crystallinity of the alkali-resistant cellulose from thermally treated spruce wood increased up to a temperature of 200 °C because of a preferred degradation of the less ordered molecules (Yildiz *et al.* 2006). In early research, X-ray spectroscopy showed that cellulose crystallinity of heat-treated maritime pine at 260 °C remained largely unaltered even after 4 h of exposure (Bourgois and Guyonnet 1988). X-ray diffractometry of independent studies of cellulose crystallinity of Norway spruce and Japanese beech heat-treated under dry and moist conditions at 180 – 220 °C also demonstrated a significant increase in crystallinity, more in the moist condition than under dry-heating (Bhuiyan *et al.* 2000). The growth of cellulose crystallites upon heating have been previously noted in Sitka spruce wood heat-treated at 180 °C for 5 hours by X-ray measurements made with the symmetrical transmission technique (Nakao *et al.* 1985). Heat-treatment resulted in the increase in the distortions in both parallel and normal directions to the molecular chain. This indicated that the increase in crystallinity of wood was not due to the improvements in regularity of the structure. As for the crystallite size, this increased in the lateral dimension after the treatment, while in the longitudinal dimension remained unchanged. Nakao *et al.* (1985) concluded that increase in the degree of crystallinity caused by heat treatment was due to lateral growth of cellulose crystallites probably because the crystallisable amorphous region surrounds the crystallites not longitudinally, but laterally. In a recent experiment, the crystallinity of cellulose isolated from heat-treated spruce and beech woods was determined using FTIR spectrometry (Yildiz and Gümüşkaya 2007). This was done by studying the ratio of the peak areas at 1370 and 670 cm^{-1}, or by the ratio of peak heights at 1429 and 897 cm^{-1}, or at 1372 and 2900 cm^{-1}. Heat treatment was applied at 150, 180 and 200 °C, for 6 and 10 h. It was determined that crystallinity of cellulose in wood samples increased with thermal modification, the degree of crystallinity change was related to both temperature and time of the thermal modification.

In another report, ^{13}C CPMAS NMR was used to investigate the crystallinity indices for cellulose (CrI) for four woods heat-treated following the ThermoWood® process (Wikberg and Maunu 2004). Boards of birch, aspen and spruce woods were treated at 195 °C while oak wood was modified at 160 °C. Birch and aspen were treated for a total time of 56 h and spruce for 44 h (no heating time was reported for oak); the actual treatment time at the target temperature was 188 min. for spruce and 130 min. for birch and aspen. The CrI, determined by the spin-locking technique, increased in all woods following heat-treatment (Table 2.4). Similar results were reported previously for Scots pine wood treated following the ThermoWood® protocol (Sivonen *et al.* 2002). The observed increase was proposed to be due to the degradation of the less ordered chains during the thermal treatment rather than to any increase in the amount of more ordered cellulose.

Other important observations from the CP/MAS ^{13}C NMR spectroscopy studies are:

a) For carbohydrates: The shoulder at 102 ppm on the signal of cellulose C-1 at 105 ppm, assigned to hemicelluloses, decreased in the spectrum of heated spruce (Wikberg and Maunu 2004), heated Scots pine (Sivonen *et al.* 2002), or heated beech (Inari *et al.* 2007a) indicating some degradation of hemicelluloses; the shoulder was poorly resolved in the spectra of birch, aspen or oak wood, though (Wikberg and Maunu 2004). In addition, the relative intensity of the signals of methyl (21 ppm) and carboxylic carbons (173 ppm) of acetyl groups attached to hemicelluloses were decreased in the spectrum of every wood after thermal modification (Sivonen *et al.* 2002, Wikberg and Maunu 2004, Inari *et al.* 2007a). By heat-treating the isolated holocellulose fraction of beech wood, Inari *et al.* (2007a) found that signals previously attributed to lignin thermal cross-linking were still noticeable on carbohydrate component. According to these authors, this result suggests that new signals appearing between 125 and 135 ppm and at around 35 ppm on NMR spectra of heat-treated wood are not due to lignin modification, but due to degradation of holocellulose, probably due to the commencement of formation of carbonaceous material. These authors did not detect these signals in isolated Klason lignin heat-treated at 240 °C for 5.5 or 21 h. However, they did not examine the isolated lignin (pseudo-lignin) from the heat-treated material. It is possible that these signals would still be visible therein because some carbohydrate by-products remain trapped in the lignin upon repolymerisation. Whether these by-products contribute to lignin cross-linking is a subject that needs clarification.

b) For lignin: Only fine changes could be identified in the lignin signals attesting for its higher heat stability. After the thermal modification, a reduction in the relative intensity of the signal at 153 ppm (assigned to C-3/5 of syringyl units) and an increase in the relative intensity of the signal at 148 ppm (assigned to syringyl 3/5 carbons in non-etherified units and to guaiacyl 3/4 carbons in the spectra of untreated oak and aspen) were seen in every hardwood spectrum (Wikberg and Maunu 2004). These authors used the relative intensities of these two signals in the heat treated and untreated wood spectra as a measure of the degree to which β-O-4 linkages in lignin are cleaved during the thermal modification. According to this analysis, the majority of the syringyl units in hardwoods included β-O-4 linkages before the thermal modification whilst after the thermal modification a substantial part of the β-O-4 linkages were cleaved. This extensive aryl-ether bond cleavage was credited to the steam used in the heat treatment process. Thermal modification caused a reduction in the relative intensity of the shoulder at 153 ppm for C-4 of guaiacyl units that are etherified, and an increase in the shoulder at 146 ppm for C-4 of non-etherified syringyl units in the dipolar dephasing (DD) spectrum of spruce wood. These changes are an indication of cleavage of β-O-4 linkages in the lignin guaiacyl units. In addition, a broad shoulder appears in the DD spectrum at 128 ppm after thermal modification. This shoulder is assumed to arise from lignin C-5-substituted structures, such as biphenyl (5–5) or diphenylmethane. Its appearance suggests that guaiacyl units are linked by carbon-carbon bonds and hence the content of condensed guaiacyl structures (120–140 ppm) is increased in the thermal modification relative to guaiacyl groups (140–160 ppm) (*Idem.*). The degree of lignin condensation calculated from the same ratio in Scots pine appears to increase during the heat treatment even though the changes appeared to be small (Sivonen *et al.* 2002). The increase of condensed guaiacyl structures observed by Wikberg and Maunu (2004) was further supported by the slight decrease in relative intensity of the methoxyl signal at 56 ppm in the CPMAS spectrum. A similar decrease of the methoxy signal was observed in Scots pine (Sivonen *et al.* 2002), but not for heat-treated Klason lignin (Inari *et al.* 2007a). Demethoxylation of lignin makes more lignin sites available for reaction; a more condensed lignin structure is achieved as a result of this. Neither condensation nor demethoxylation is observed in the DD spectra of hardwood samples, which indicates that only guaiacyl units are condensed by the formation of carbon-carbon bonds at C-5 and C-3 positions in the thermal modification (Wikberg and Maunu 2004). These bonds cannot be formed between syringyl units because a methoxyl group occupies the C-5 and C-3 positions. From the differences in the relative signal intensities in the NMR spectra at 148 and 153 ppm, it appears that the cleavage of the β-O-4 bonds during thermal modification was more extensive in hardwoods than in softwoods (*Idem.*). Additionally, the content of methylene bridges, which connect two phenolic nuclei, increased in pine wood (Sivonen *et al.* 2002). This can be seen as an increase in the peak area at around 30 ppm, which could be assigned to short-chain aliphatics (CH_2). The same increase at 35 ppm was described for heated beech wood (Inari *et al.* 2007a).

Polymer changes following heat treatment studied by solid state FTIR spectroscopy will be discussed in detail in chapter 8 for solid wood (sections 8.3) and chapter 7 for Klason lignin (section 7.3).

2.4.6 Relationship between chemical degradation and mechanical changes

One of the main effects of wood heating is the resultant chemical conversion of wood polymers, and also a clear modification of most of the mechanical properties in TMW. However, the understanding of the relationship between mechanical property and heat-induced chemical changes is rather rudimentary. To the knowledge of the writer, before this thesis there was only one report dealing with the changes in chemical composition and the concurrent modifications in one form of wood strength in TMW (Davis and Thompson 1964). The relationship between hemicellulose degradation and toughness reduction in heat-treated red oak, Douglas-fir and longleaf pine woods, using various heating schedules and processing pressures was investigated. These authors found a close empirical relationship between chemical degradation in the hemicellulose fraction and toughness. However, they ignored the relationships of the wood strength to the concurrent changes in the lignin substance, which became obvious when analysing their data. This is discussed further in section 5.3 (chapter 5).

In a somewhat related study, Winandy and Lebow (2001) studied the empirical relationship between chemical changes and residual MOR strength of small specimens of southern pine wood (*Pinus* spp.). Samples were treated with seven types of fire-retardant substances and then exposed to various environments. Four long-term exposure temperatures (27, 54, 66 and 82 °C) with durations from 3 to 160 days at 54 °C and 82 °C, up to 4 years at 66 °C, and up to 6 years at 27 °C were studied. Samples were then conditioned and subjected to a three-point bending stress test. Chemical studies consisted of the determination of Klason lignin and monosaccharides from the acid-soluble hydrolisate[**].

After a confusing elaboration, these authors failed to demonstrate that monosaccharides associated to hemicellulose side-chains were most critically associated to the reduction of MOR in bending. Two of the three best models computed (in terms of the R^2) have Klason lignin in the equation.

2.5 Modelling of the process and properties in the new material

The modelling of the process in the range of temperatures expected to be of interest industrially for the thermal modification of wood is a subject that has received little attention. Only one mechanistic model has been reported so far (Rajohnson *et al.* 1994). A small sample of pine (or beech) wood was non-isothermally heat-treated in a reactor with a weighing device and temperature and pressure sensors. The reactor was coupled to a FTIR spectrometer for gas analysis. Evolution of temperature, kinetics of weight loss, and evolution of wood internal pressure were recorded. They studied simultaneously heat and mass transfer with chemical reactions. FTIR allowed correlation of the evolved gases of each component with weight loss kinetics at different wood temperatures. The model developed was a combination of high-temperature drying models and wood pyrolysis models. The assumptions in the model neglected the water vapour diffusion in the gaseous phase and the total pressure was considered to be equal to the water pressure. The solid was considered isotropic, homogeneous and in local thermodynamic equilibrium too. Therefore, the water vapour pressure was said to be equal to the product of water activity to the saturated vapour pressure which is estimated from the water sorption curve. For the sample size they used, it allowed consideration of a two-dimension model (radial ×

[**] It is not clear whether the composition reported was related to the initial oven-dry weight or to that after the environmental exposure.

tangential). The model was composed of three balance equations: 1) The humidity balance, which takes into account the diffusion phenomena (Fick's law) and thermo-migration of the liquid phase and the phenomenon of water vapour convection under the total pressure gradient (Darcy's law); 2) The energy balance, which includes the phenomena of thermal conduction (Fourier's law), water vaporization and heat production by exothermal reactions; and 3) The material balance, as a function of initial density, moisture content and final density.

This approach gave a system of non-linear partial differential equations, which were solved by a dynamic simulation code. A good agreement was found between experimental and numerical data. This simulation showed that the system is very sensitive to the gaseous and liquid phase intrinsic permeabilities, the liquid phase diffusion coefficient and the convective and thermal transfer coefficients. The model permitted an analysis of the influence of each process parameter for process optimisation, which it is believed could only be done for one wood species at a time.

On the other hand, the modelling of the properties of TMW has been poorly and not systematically studied.

Alfred Stamm was the first author to study the relationship between mass loss and time and temperature of reaction for thermally-treated wood, by applying models based on the Arrhenius relationship (section 2.3.1). He used some of his own data as well as data of McLean for softwoods heated from 1 min. to 2.4 years at temperatures between 93.5 °C and 300 °C (Stamm 1956, and McLean cited therein). The rate constants of the log-normal plot of mass loss against time were found to obey the Arrhenius relationship, because a linear relationship was found in all cases. Stamm (1956) therefore proposed that weight loss was a first-order reaction, although a heterogeneous one. This work was latter extended by Millet and Gerhards (1972); this is discussed more detailed in section 4.3.1 (chapter 4). Santos (2000) and Bengtsson *et al.* (2002) have both shown the relationship between MOE and MOR in bending for TMW, whilst Mouras *et al.* (2002) found a relationship between density and compression strength in heat-treated wood. These reports will be discussed further in sections 5.1 and 5.2 (chapter 5).

In a recent study, the relationship between MOE and MOR in bending and in tension stress for large beech wood members was evaluated after thermal modification at 180 °C and at another, higher temperature which was not disclosed (Widmann *et al.* 2007). Both dynamic MOE (using two instruments based on acousto-ultrasonic measurements) and static MOE were determined. Dynamic MOE was found effective for predicting static MOE (no statistics given). However, the prediction of bending and tension strength values from MOE was limited, with R^2 varying between 0.03 and 0.49 for bending strength, and $R^2 = 0.41$ for tensile strength.

Other approaches have been explored in order to predict a few properties in TMW, notably from colour changes; these will be discussed at length in chapter 7.

A strong correlation between the amount of free radicals determined by electron spin resonance measurements, and the degree of thermal modification of wooden products has been established (Viitaniemi and Jämsä 2001). They found that it is possible to detect the time and temperature of treatment of any given treated wood sample (from the ThermoWood® process) from the correlation of these parameters with the amount of free radicals determined, even after several years of service. Laser light scattering can also be correlated to the intensity of heat treatments in heated powdered birch and pine woods using the correlation between the light-scattering pattern and the temperature of treatment (Wahl *et al.* 2004).

St-Onge *et al.* (2005) investigated the potential of using acousto-ultrasonic methods for the detection of internal checking in thermally modified balsam fir (*Abies balsamea*) wood. The method was found efficient, with a significant decrease of wave propagation time, only when severe internal checking was present.

A recent proposal for the indirect estimation of WL is a gravimetric method named high-energy multiple impact test (Rapp *et al.* 2006). After ball-milling the sample, the heat-induced weight loss (WL) is predicted from the mass of two opposite size fractions which form the so-called index of resistance to impact milling. These authors speculate that it would then be possible to predict some mechanical properties from the estimated WL.

2.6 Environmental considerations of TMW

Thermally modified wood is a natural product without any chemical additives added during the process. It has a demonstrated increased decay resistance for above ground applications without the use of biocides. This makes TMW arguably an environmentally less aggressive option than traditional systems employing biocides for reducing the decay susceptibility of wood. In this regard TMW also compares favourably against untreated wood, or with some naturally resistant hardwoods sourced from tropical countries with forest management programs of dubious sustainability.

According to the industry literature (Mayes and Oksanen 2002), TMW waste can be handled as with any other untreated wood waste. The material is biodegradable and can be disposed of at the end of its service life by either burning or placing it into the normal waste stream. In the ThermoWood® process, energy is needed mainly for drying wood, which accounts for some 80% of the heat energy used. This energy is produced by burning bark and wood waste. Additional energy is provided with solutions such as natural gas.

Thermally-modified wood has some other characteristics that support a potential environmental benefit compared to other materials. In an study on the toxicity of structural materials, several untreated woods, preserved wood, modified woods as well as other building materials were evaluated for eco-toxicity in aquatic systems (Van Eetvelde *et al.* 1998). The most useful comparisons for the present document are given in Table 2.5. Toxic units[††] obtained for heat-treated beech were the lowest values for all materials examined; heat-treated pine was also among the least ecotoxic materials.

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[††] Toxic unit is defined as the dilution ratio of leaching water giving the EC_{50} value; *i.e.* the more diluted, the higher the TU value (Van Eetvelde *et al.* 1998).

Heat-treated pine rated better than untreated pine for the Algaetox test, while the former was slightly better for the Daphntox and Microtox tests. In all cases heat-treated pine rated better than western red cedar and Azobé, and have comparable ratings to concrete, recycled plastic and furfurylated pine. One reason for the low leachate toxicity of TMW may be that the extractives have already been removed from the material during the thermal conversion (section 2.4.4).

Emission of VOCs of TMW in service are smaller than in untreated wood (Manninen *et al.* 2002, Bengtsson *et al.* 2003). One reason for this is that extractives are no longer present in the treated substance (section 2.4.4). Additionally, it is well established that the potential main source of acetic acid due to its larger acetyl content are wood hemicelluloses; even at room temperature, acetic acid has been detected as the largest emission among all VOCs of untreated hardwoods (Risholm-Sundman *et al.* 1998). These are the most labile of all wood components and are rapidly degraded upon heat-treatment (section 2.4.1). The amount of polar residues after treatment is also smaller in heated wood than in untreated material (González-Peña *et al.* 2004). In particular, a substantially smaller amount of acetic acid was found in heated ash wood. This result is encouraging, because acetic acid is annoying to the sense of smell in humans, eliciting negative emotions such as anger and disgust (Vernet-Maury *et al.* 1999).

One important physical change occurring in wood when heat-treated, is that the substance is coloured throughout, which is useful when further machining is required. This is an alternative to conventional surface staining of light coloured species. This is also useful because there is an increasing requirement for the reduction of the solvent-borne finishes in the woodworking industry. In Europe for instance, the Solvent Emission Directive (Directive 1999/13/EU) sets VOCs emission limit values to which several woodworking industries including wood coating, wood lamination and wood impregnation must comply no later than October 2007 (Fonseca 2004).

In an analysis of the environmental impact for canal linings, TMW treated with the Plato® process was compared to alternative materials such as concrete, aluminium, preservative treated wood, or tropical hardwoods (Boonstra *et al.* 1998). The environmental impact of Plato® treated wood was low for most of the environmental categories used. These included eutrophication of surface waters, ozone depletion, ecotoxicity, energy consumption, green house effect, acidification of water or soil, waste, smog, and human toxicity. Overall performance was comparable to sustainable Azobé. Although this is only an isolated example and cannot be considered representative for all applications of TMW, it highlights the potential benefits of using this material even in some common applications.

There is however the need of a deeper analysis of the ultimate benefits of this technology. All reports so far concentrate on partial appraisals, evaluating some aspects of the environmental performance separately. Much research is required on the production of the treated material itself, regarding the production of VOCs during the thermal decomposition. Reports on the Life Cycle Assessment (LCA) of thermally modified wood are not known to date. The ThermoWood Association announced in its website that an analysis was being elaborated in Imperial College, UK, but this has not been released at the time of writing this thesis.

2.7 Limitations and downside of the thermal modification

Besides the reduction in some forms of strength (section 2.3.2) and the residual susceptibility to light exposure (section 2.3.5), the process for the thermal modification of wood and the treated material itself have other drawbacks and also some limitations. These shortcomings should be considered for a thorough, fair evaluation of the system, so the user is to be in condition to deal with these issues.

Limitations

1. Wood members of large thickness can develop serious internal defects upon heat-treatment. Boards of Sitka spruce, lodgepole pine and Japanese larch were heat-treated under restraint or following the Plato® protocol (Birkinshaw *et al.* 2006). Samples 26 mm thick did not suffer internal checking in any species nor samples 46 mm thick of spruce or pine wood. However, 46 mm thick samples of larch, or 75 mm-thick samples of the three species suffered severe internal checking. Moreover, the EMC in some hardwood species (*e.g.* white oaks) should be well below the FSP in order to be amenable to treatment, to avoid serious shape defects and internal splitting (Mayes and Oksanen 2002). This may limit the size of the members to be treated or the modification of poles.

2. It is held that wood with some defects produces material of very poor quality (Hill 2006b). Wood with knots is held not to be amenable for treatment (Mayes and Oksanen 2002), but there is no concrete proof of this. In the present research, no distortion was noticed by treating some spruce samples with small knots and knots did not drop out as noted elsewhere. Probably a visual grading protocol should be devised for TMW.

3. It is possible that the control of the process for some species with relatively high extractive content (*e.g.* pitch pines and some hardwoods) would be difficult by using colour changes, weight loss, etc. Likewise, boards with heartwood and sapwood in the same specimen are likely to be treated unevenly, although this has not been studied.

4. TMW is not recommended for ground contact (European Hazard Class 4), because it is apparently not resistant to the soft-rot decay type (Militz 2002). However, information in this regard is still limited and the material tested has shown large performance variability (section 2.3.4). Moreover, recent work by Hale *et al.* (2005) indicated considerable improvements in soft rot decay resistance in heat-treated Corsican pine wood at the laboratory scale.

Drawbacks

1. Several studies regarding the behaviour of the material in fire have shown that TMW rates lower than untreated wood in several categories (Mayes and Oksanen 2002), although the information was somewhat inconclusive. In an independent study, the behaviour to fire and flame resistance tests by means of the crib and the two-foot tunnel tests was found to be mostly unchanged in oil-heated spruce wood (Wang and Cooper 2007). Having established that heat-treated pine wood have a higher calorific value than untreated wood (Bourgois and Guyonnet 1988), the smoking potential of retified poplar was examined using a fume-meter. Samples were treated at 260 °C for 45 or 60 min under N_2 and then pyrolysed. The maximum smoke opacity was reached quickly in both materials, faster in retified wood. The level of maximum opacity was similar but slightly larger for the non-heated material, though. The smoking potential was larger for the retified wood below 510 °C, while it was found to be less important than non-heated wood above this temperature (Bourgois *et al.* 1990).

2. Because of a mortality rate of 100% was found in larvae, a good resistance was reported against *Anobium punctatum* in heat-treated Curupixa and poplar woods, but no resistance was found against termite attack (Mouras *et al.* 2002). Several previous reports also conclude that termite resistance is not increased by the thermal modification of wood (Doi *et al.* 1996, 1997, 1999). In fact, it has been proposed that the heat-treatment appears to favour the biological degradation by termites. This may limit the use of TMW in locations of warmer climates. Else, it should be necessary to use some type of biocide, thus compromising the alleged environmentally friendly profile of TMW. Similarly, thermal treatment does not improve the resistance to marine borer attack (Westin *et al.* 2007).

3. Coniferous species with very sharp delimited late- and earlywood boundaries are prone to 'flake' easily upon moisture stresses (Sheiding 2005, pers. comm.).

4. The material is easily machined, but any further operation produces a very fine dust, which may required specialised (though already well established) equipment and facilities for its handling. TMW also splinters easily and some operations require special handling (*e.g.* pre-drilling before nailing) due to the increased brittleness of the material (Mayes and Oksanen 2002).

2.8 Summary

Increased environmental pressures over the last few years led to the development of non-biocidal alternatives to classical wood preservation techniques such as the thermal modification of wood. TMW benefits from new properties like improved decay resistance and higher dimensional stability while some forms of strength are significantly reduced. Modified wood also exhibits lower affinity to water sorption, strongly modified wettability and altered colour. Because of some of these qualities, possible environmental advantages and the un-complicated technology for modification and disposal (compared *e. g.* with acetylation), heat-treatment of wood is currently the technology most developed for wood modification in Europe.

Many of the very basic physical and chemical process of thermally modifying wood are well understood. Until recently, the properties and changes in TMW are being described in more detail, and shortcomings and advantages have been unveiled for a more complete understanding of the material. Current research is targeted at more complex processes of the time-dependent mechanical behaviour of wood or on ways to prevent mechanical strength loss at early levels of treatment. Interests are also focused on the mechanisms behind physical changes to find out ways to enhance some properties without compromising other desirable characteristic in TMW. Assessment of possible structural uses of TMW is matter of intense activity in Europe too.

In complete contrast, potential methods for property prediction and methodical material characterisation are fairly undeveloped. It is accepted that the entry of TMW at the market was somewhat precipitated, mainly motivated by the sudden contraction of several markets after the restriction of some traditional wood preservation ecotoxic substances. In Sweden and other parts of Europe tests are still ongoing to determine the suitability and possible uses of TMW; although some aspects of the behaviour of TMW have been studied at the laboratory scale, protocols to thoroughly evaluate the performance of TMW are yet to be developed. The previous overview has indicated a lack of agreement on several points, a lack of information on basic forms of material description and the importance of having such information.

The industry for the thermal modification of wood is facing major challenges in order to provide consumers with well established standards and ways to characterise and classify the product regardless the process used for modifying the material. Non-destructive methods or techniques not entailing excessive costs may become a key approach for tackling issues of trans-process product characterisation and standardisation.

Chapter 3 Materials and Methods

3.1 Introduction

This chapter presents an outline of the work undertaken in order to gain a more fundamental understanding on the effect of two major treatment factors (time and temperature) in several physical properties of interest of TMW. The chemical changes of the wood species studied were also investigated, in order to resolve the primary relationship between changes in chemical structures and physical property changes. In this work, no comparison of treating media or the effect of wood moisture content was undertaken. This plain approach was adopted in the belief that a more complete understanding of the basic material behaviour could help identify any limiting factors and possibly highlight ways in which performance might be improved, or basic treatment parameters optimised, regardless of wood species or secondary treatment parameters.

Throughout, the properties of thermally modified wood (TMW) are compared with those of untreated material. Every property studied in this work was also determined for untreated solid wood because no comparison could be made on, for instance, mechanical strength values reported in the literature, due to the generally smaller than standard size used for the determinations.

This chapter (Methods) is divided into four sections. The first section (this section) is the Introduction. The second section relates to the thermal modification of wood (section 3.2). The following section (section 3.3) describes the procedures followed for the physical characterisation of TMW, while the last section (3.4) describes the studies for the chemical characterisation of TMW.

A summary for all the studies reported in this thesis is given in Table 3.1. A diagrammatic synopsis of the approach for this research is given in Figure 3.1.

Table 3.1 Summary of the studies carried out in this project, following the thermal modification (20 schedules) of small samples of beech, Scots pine and Norway spruce woods.

STUDY	State	n	Number of treatments (controls included)		
			Beech	Pine	Spruce
Mechanical Properties					
Bending Strength (MOR, MOE, RLP, R, WM, TW)	NC	10	20	21	21
Compression Strength // (MOR, MOE)	NC	8	20	21	21
Compression Strength ⊥ (MOR, MOE)	NC	6	20	21	21
Janka Hardness (ML)	NC	6	20	21	21
Shear strength (ASS)	NC	4	20	21	21
Charpy impact test (IS)	NC	10	20	21	21
Wood-Moisture relationships					
Dimensional stability (Anti-swelling efficiency)	20 °C	10	20	21	21
Anisotropy changes	20 °C	10	20	21	21
Water absorption	20 °C	10	20	21	21
Hygroscopicity (over 5 saturated salt solutions)					
• Adsorption (EMC)	20 °C	4	20	21	21
• Desorption (EMC)	20 °C	4	20	21	21
Hygroscopicity (DVS, 1 sorption loop) (WWP)[a]	20 °C	1	----	----	9
Physical changes					
Size in three planes	OD	44	20	21	21
Volume	OD	44	20	21	21
Colour (CIEL*a*b* system)	NC	10	20	21	21
Weight	OD	44	20	21	21
Nominal density	NC	44	20	21	21
Specific Gravity Cell Wall	OD	1	20	21	21
Chemical characterisation					
Klason Lignin (%, w/w)	OD	1	20	21	21
Acid soluble lignin (%, w/w)	OD	1	20	21	21
Monosaccharides (%, w/w)	OD	1	20	21	21
Fourier-transform infrared spectroscopy of wood	OD	1	20	21	21
Fourier-transform infrared spectroscopy of lignin	OD	1	----	----	11
Diffuse reflectance infrared spectroscopy[a]	NC	1	----	----	11

Key:

MOR	Modulus of rupture	EMC	Equilibrium moisture content
MOE	Modulus of elasticity	WWP	From wood and wood polymers
RLP	Fibre stress at proportional limit	OD	At oven-dry condition
R	Resilience	NC	At nominal condition (65 ± 3% RH at 20 °C)
WML	Work at maximum load	DVS	Dynamic Vapour Sorption
TW	Total work	⊥	Perpendicular to the grain
ML	Maximum load	//	Parallel to the grain
ASS	Apparent mean shear strength	[a]	From samples treated at 210 °C. Not completed due to equipment unavailability
IS	Impact strength	[b]	Only at 210 °C and 230 °C plus controls

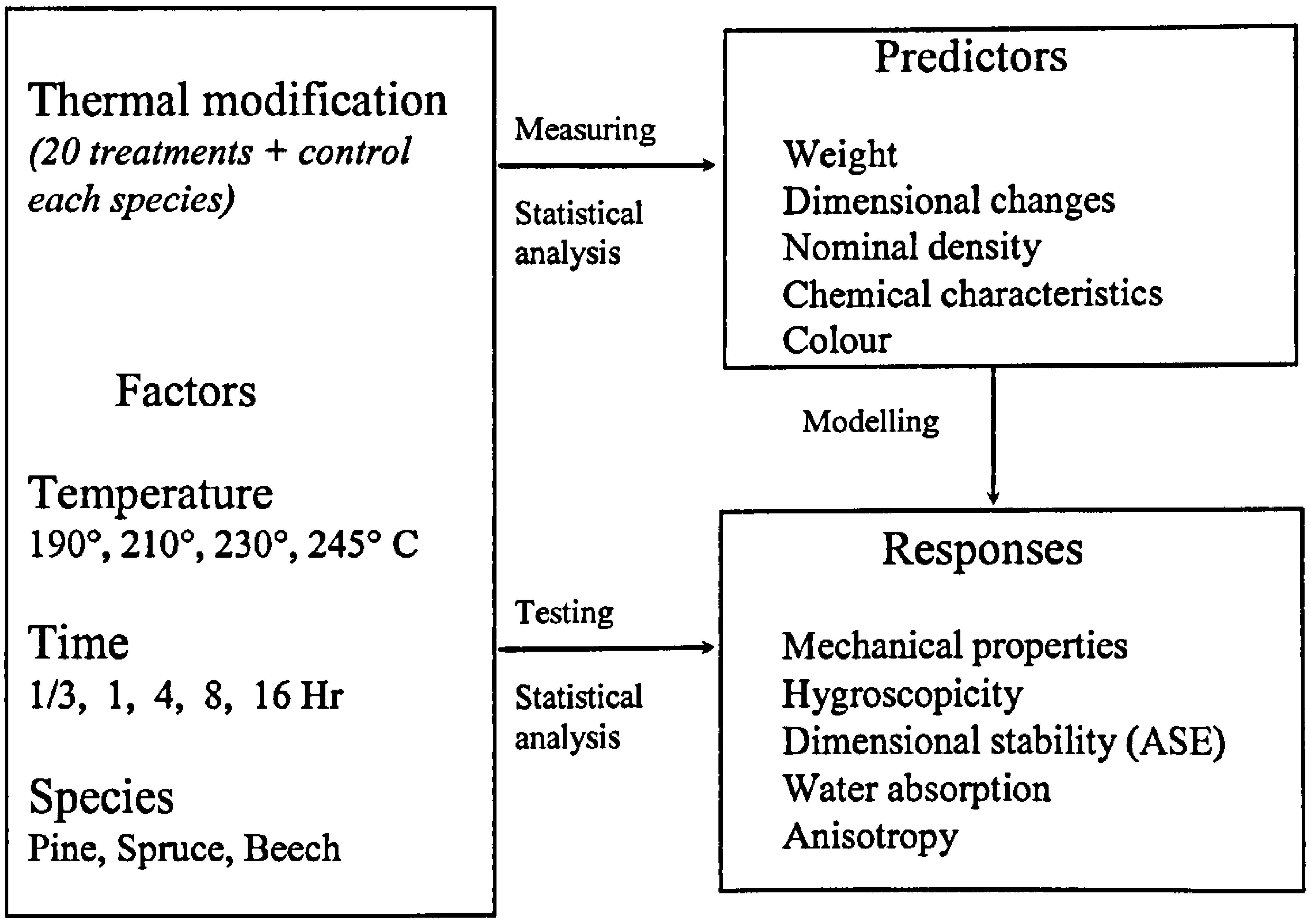

Figure 3.1 Schematic layout of the research approach for this thesis

3.2 Thermal modification of solid wood

3.2.1 Species used for the study and sampling method

3.2.1.1 Species

The focus adopted for the development of this work, was to determine the effect of chemical composition and some of the physical characteristics of solid wood (density, specific gravity) on the properties of the material that resulting from heat treatment (varying two factors only – time and temperature of treatment). Thus, the species for the study were chosen mainly on the grounds of chemical composition and physical characteristics. Published chemical composition, density, specific gravity and movement data from these species are shown in Table 3.2.

Two softwoods and one hardwood species were chosen in order to clarify the differences in the post-treatment behaviour between these two groups, having well-established, different chemical compositions (Sjöström and Westermark 1999).

Softwoods chosen have similar hemicellulose and lignin content, so that the effect of density in the properties under study could be more easily determined. In virtue of the small specimen size used for the dimensional stability and anisotropy studies in this work, species with large movement in service were preferred, in order to get data more easily readable. Ease of supply was a factor when deciding the species examined.

This research was not intended to study variation within a tree or between trees of the same species, neither to establish complete schedules for specific species; the woods selected were those relevant to the use of timber in Great Britain. Initially, British-grown woods were sought, and purchased in central Wales from a single provenance. However, due to the small size of the stock, defects present in the material, mixtures of heartwood and sapwood in pine and the reaction wood in spruce, the softwood material was rated as not suitable for this research. Softwoods were ultimately purchased from a local timber merchant. Both softwoods were imported, of Scandinavian origin.

Softwood boards had moisture content of *ca.* 11% (oven-dry basis) when purchased. No further drying was required before processing. British grown beech (hardwood) was received at the University with an oven-dry-basis moisture content of 16% (as measured with a moisture meter). These boards were then dried in the School's kiln following the conventional schedule for beech (Pratt 1986), to an average moisture content of 6.2% (oven-dry basis). Only one batch was required to dry all the beech boards; the complete drying process took 11 days.

3.2.1.2 Sampling and sample preparation

Several points were taken into consideration before deciding the dimension of the specimens for work. The duration of each treatment, the limited volumetric capacity and size of the oven and the desirability of homogeneity of the treatment throughout smaller samples were major considerations. As well as this, the plan was to keep the emission of fumes and the risk of fire to its minimum. Small sized specimens were used to keep the experimental cost within reasonable limits due to the number of treatments studied.

Machining of the samples was not possible after the thermal modification, because of their small size. Thus, distortion of the samples due to the treatment was avoided by cutting the samples in the radial direction, where possible from straight-grain, defect-free timber: some beech samples were not straight-grained throughout, due to the small-sized stock available.

Preliminary trials were performed to ascertain the best cross-section for the mechanical testing of the pieces, whilst keeping treatment gradients minimal through the whole sample. A section of 20 mm wide (radial face) x 10 mm depth (tangential face) was chosen, and the specimen length was set to 14 times the specimen depth, as prescribed by BS 373 (1957), plus 10 mm of overhanging length for the bending test, which gave an overall length of 150 mm (Figure 3.2).

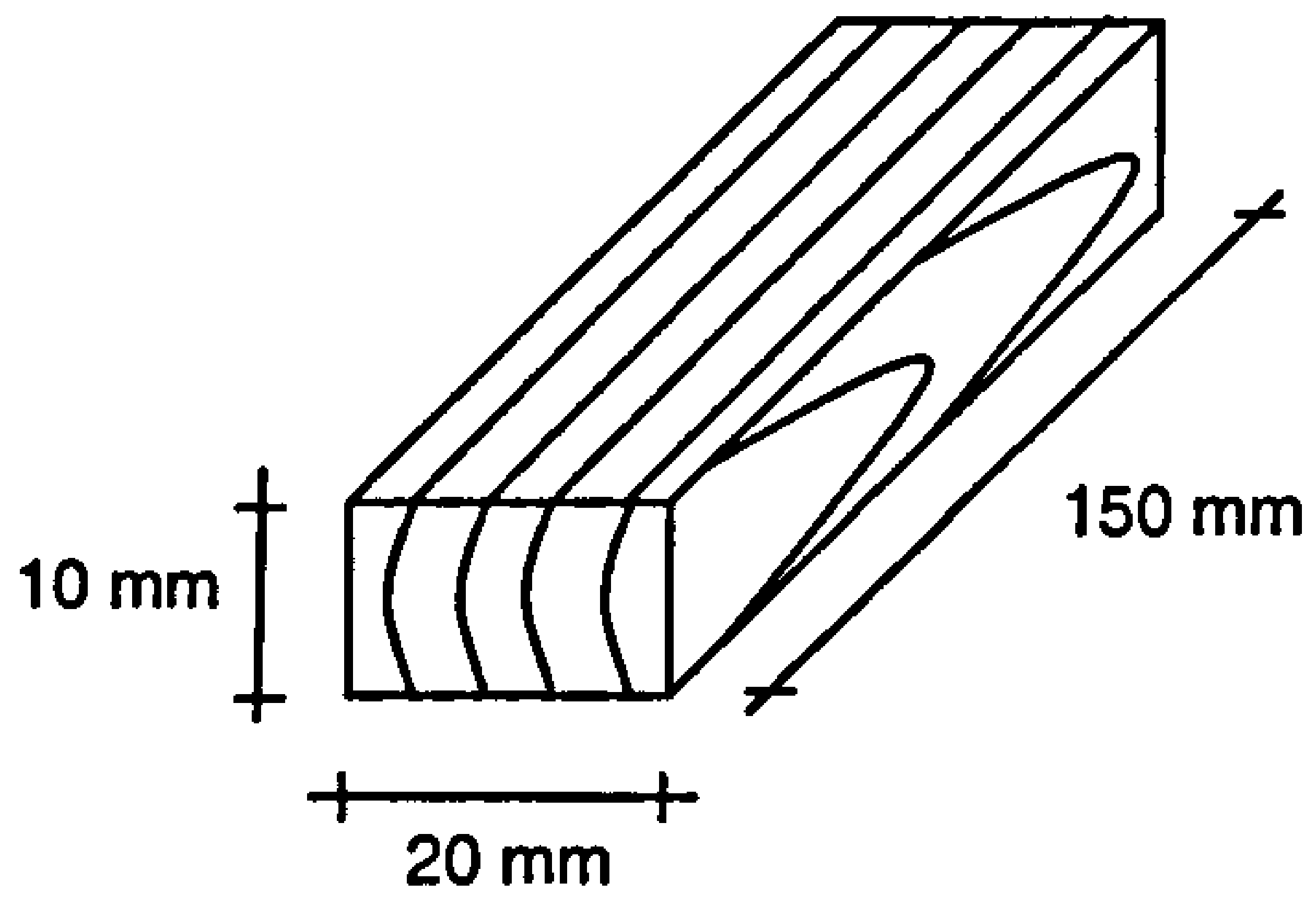

Figure 3.2 Dimensions and cutting planes for samples

This sample size was used for all the thermal treatments. Samples for some studies were further cut following thermal modification (Section 3.3). However, all samples were initially thermally modified at the same size to minimise differences in the extent of the treatment due to sample dimensions (both ends of the sample, irrespective of its length, underwent slightly more modification than the rest of the piece; this was noticeable in the treatments at higher temperatures and longer times).

beech boards were not large enough to produce all the samples for one test for all treatments from the same board. On the other hand, it was found in preliminary trials that density in beech was an important factor for the appearance of data 'outliers' in the weight loss due to the thermal modification. Thus, samples were cut and then conditioned for 4 weeks at 65% RH at 20 °C before being screened within one standard deviation from the average weight at the EMC with that environment. Samples that fell above or below this range were rejected. All beech samples were finally grouped randomly into 21 sets of 44 samples (1 control set and 20 sets for thermal modification), and this sampling was considered to give matched samples for the statistical analysis.

In the case of softwoods, boards were large enough to produce all the samples for one test for all treatments. Some boards were large enough to produce matched samples for several studies. After cutting, samples were screened for defects, such as small knots, curvy grain, and splits or cracks and ultimately by similar early- and latewood content. Finally, 21 matched sets of 44 samples were randomly assigned to each of the 20 treatments and one to control. Samples from all three species were labelled with a pencil prior to modification.

Information exists regarding a small, although significant, effect of extractives on wood degradation during the heat-treatment of wood. Burgois *et al.*

(1989), using differential scanning calorimetry, investigated the thermal reactions of extracted and un-extracted pinewood. The exothermic peaks of the pyrolysis reaction were pushed towards the high temperature region when the sample was an extractive-free wood. They attributed this response to a catalytic effect of the extractives. Evidence also exists on the effect of the presence of extractives on the colour changes undergone for the material due to a thermal modification (Sundqvist and Morén 2002). In the present work, however, no extraction was performed on the samples prior to the thermal modification. Previous research showed that the effect of the extraction procedure overshadowed the effect of the extractives in a study of some properties of modified solid wood (González-Peña *et al.* 2004). The analysis of the influence of the extractives on the hygroscopicity of treated wood was difficult to interpret, due to the effect of the extraction procedure.

In order to minimise the possible effect of extractives in all the responses, all species chosen for this work had small extractive content (Fengel and Grosser 1975, Fengel and Wegener 1984, Sjöström 1993) (Table 3.2). All softwood matched samples were cut from sapwood. The difference between heartwood and sapwood in beech is not always apparent to the eye, although it is well established that this species has a small amount of extractives, and that sapwood may contain a higher amount of extractives than heartwood (Ritter 1953). For the beech stock used, heartwood was readily noticeable, so all samples were cut from sapwood.

3.2.2 Thermal modification

Modifying moist wood by heat has been repeatedly reported to be more deleterious to its mechanical performance than treating wood with low moisture contents or in the absence of water vapour. Information on the damaging effect of oxygen on wood mechanical properties compared to treatments in an inert atmosphere at the same temperature and length of treatment has also been published (Mitchell 1988).

Initially in this study, thermal treatments in synthetic oil were attempted using Scots pine. The aim of this was to avoid the contact of wood with air during the treatment, the oil serving at the same time as a more efficient heat conductor for the thermal modification than a gaseous environment. However, complete removal of oil remaining inside the wood after the treatment was not possible, despite extensive

Soxhlet-extraction with organic solvents. As this effect would have influenced the response of most of the properties under study, leading to complex interactions, the treatment was ultimately performed in a heating chamber under inert atmosphere. Hence, a new, 115 litre vacuum oven-drier (VD115, Binder GmbH, Germany) was commissioned for this research. APTCom© computer software was used to control and monitor the heating schedules in the oven. The electronic controller of the oven allowed the temperature to fluctuate by ± 0.5 °C only, and the maximum internal nominal temperature differential at any two points inside the oven was 3 °C at 200 °C. The oven had a port at the top for connecting the vacuum pump and another port at the bottom for flushing inert gases. A vacuum was applied to eliminate the air inside the oven using a new chemical vacuum pump (CVC 2000-II, Vacuubrand GmbH, Germany). After releasing the vacuum, the port at the top was used for the evacuation of fumes by a continuous, +50 mBar N_2 flow.

Most reports are consistent with the observation that the degradation of the wood substance is dependent of the presence of moisture in the heating medium: the rate of mechanical property loss has been found to be directly related to the amount of wood moisture present (Mitchell 1988, Mouras *et al.* 2002). Nevertheless, the presence of moisture in the heating medium creates complex relationships with other treatment factors. Since a main aim of this research was not to examine differences in relation to the treatment atmosphere or the effect of wood moisture content, wood samples were oven-dried at 105 °C ± 3 °C in a fan-assisted oven, prior to thermal modification.

3.2.2.1 Temperature and length of treatments

It has been proposed that treatment at temperatures lower than 200 °C are normally sufficient to impart dimensional stability to the material. Higher temperatures (>200 °C) are required if decay resistance is desired (Militz 2002). Although this research was not concerned with decay resistance of the modified wood, higher temperatures were also used in order to establish if a similar extent of treatment, measured as Weight Loss (WL), at different temperatures (and consequently at different times), would result in different mechanical properties within and/or between species.

Four temperatures were used for the thermal modification of wood in the present work: 190, 210, 230 and 245 °C. These were chosen so that measurable changes in wood characteristics could be obtained within a reasonable treatment period, taking into consideration the total number of treatments to be applied to each species and the volumetric capacity of the oven. These were also regarded to be of possible practical interest from an industrial standpoint.

For each batch, the temperature on both the surface and the interior of one sacrificial sample located at the middle of the oven was monitored using a differential thermometer. This was fitted with two thermocouples placed inside the oven using a built-in port. A K-type mini-thermocouple (0.50 mm) was inserted into a perforation previously made at mid length to half depth of the sample, and fixed in place with antistatic tape. Another K-type flat attachable thermocouple was fixed onto the sample to monitor the surface temperature.

The temperature of treatment reported was the between-species average temperature reached at the centre of the sample (in all cases below the nominal oven temperature), as proposed by Sailer *et al.* (2000).

It was established in preliminary trials with a few samples of beech treated at 190 °C, that the actual wood temperature remained 10 to 15 °C and 15 to 20 °C below the nominal oven temperature at the surface and in the centre of the sample, respectively. When the first modification experiments took place, though, with the oven at full capacity, the treatment temperature changed differently, in the centre and the surface of the sample, from one temperature of treatment to the other, and also varied substantially from one species to the next. The difference between the minimum temperature and the maximum temperature ranged from -15 °C for the treatment reported at 190 °C, to +11 °C for the treatment reported at 245 °C. Details on treatment temperatures are shown in Table 3.3.

Treatment times were established in preliminary trials, to give weight losses ranging from one to twenty five percent. Treatment times were finally set to 0.33, 1, 4, 8 and 16 h. Length of treatment was counted from the average time the centre of the sample reached the temperature of treatment. As the time to reach the treatment temperature varied from 1.5 h for the treatment at 190 °C, to 0.5 h for the one at 245 °C, this heating-up time was fixed for all schedules to 50 minutes, as an average for the 3 species and 4 temperatures of treatment.

Table 3.3 Nominal temperature of the oven, actual wood temperatures and Reported temperature of treatment (°C). in = inside the sample, out = on the surface of the sample

Oven Temp. (°C)	Minima recorded						Maxima recorded						Reported Temp. (°C)
	Beech		Pine		Spruce		Beech		Pine		Spruce		
	in	out	in	out	in	out	in	out	in	out	In	out	
200	179	180	178	175	184	185	190	188	194	189	193	190	**190**
220	200	203	198	200	205	209	222	220	218	219	216	220	**210**
235	215	212	215	219	230	226	242	236	227	233	233	229	**230**
250	234	227	228	231	240	236	253	253	253	256	250	245	**245**

3.2.2.2 Treatment procedure

Following oven drying, samples were left to cool down, and then weighed before modification on an analytical balance to the nearest 0.1 mg. This weight (g) was labelled as W_1. Dimensions in the three planes were measured to the nearest one µm using an electronic calliper (Mitutoyo, Japan) connected to a computer for the data to be logged into a worksheet. Width and depth were measured at three points along the length (at each end and by the middle) and averaged. Length was measured only once at mid width and recorded as above. Dimensions in the three planes were recorded (cm) as T_1, R_1 and L_1. Initial oven-dry specific gravity [$SG_{(1)}$], was calculated as $W_1/(T_1 \times R_1 \times L_1)/(1 \text{ g cm}^{-3})$.

Before being loaded into the oven, samples were arranged on trays so that samples for every test were at the same location inside the oven. This would minimise the possible differences in the responses due to uneven modification. While the oven had a very precise electronic control for the temperature, it did not have a fan to assist a more even distribution of the heat when it was fully loaded. In exploratory trials, it was found that samples near the rear part of the oven, underwent a slightly higher modification than those placed near the door of the oven (which did not have heating elements). This gradient was increased due to the flush of N_2 at room temperature, which happened to pass by the door from the bottom of the oven upwards. The arrangement of the samples in the tray is depicted in Figure 3.3.

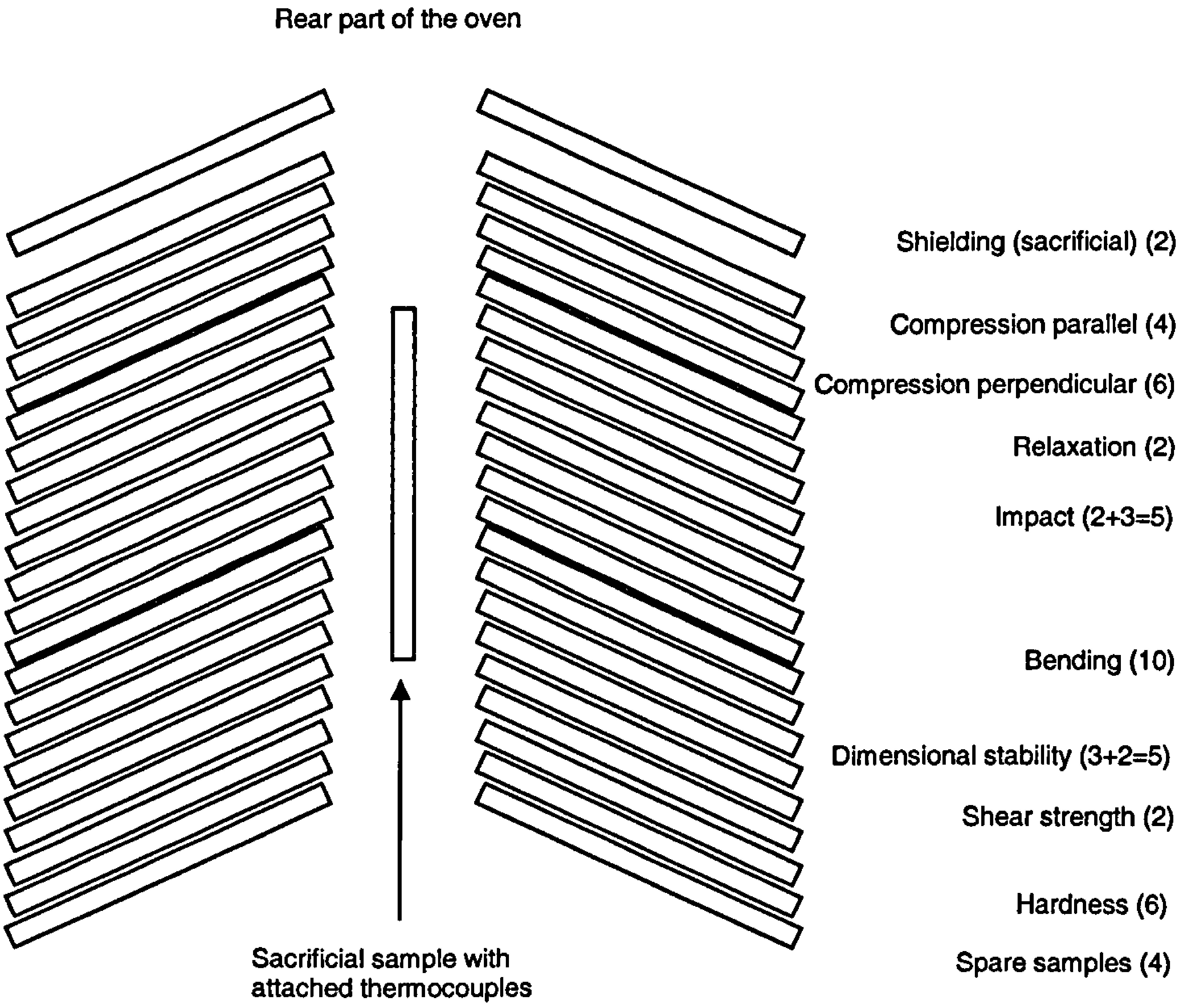

Figure 3.3 Arrangement of samples (showing tangential, 10 mm face) on trays prior to thermal modification

Samples were loaded into the oven previously heated to the reported treatment temperature plus 10 °C for the treatments at 190 °C and 210 °C, or plus 5 °C for the treatments at 230 °C and 245 °C. A vacuum (to 100 mBar) was drawn on the oven for 5 minutes prior to flushing the chamber with nitrogen. Nitrogen was slowly fed through the oven throughout the treatment process to remove pyroligneous gaseous products liberated during heating (+ 50 mBar). A typical treatment schedule is given in Figure 3.4.

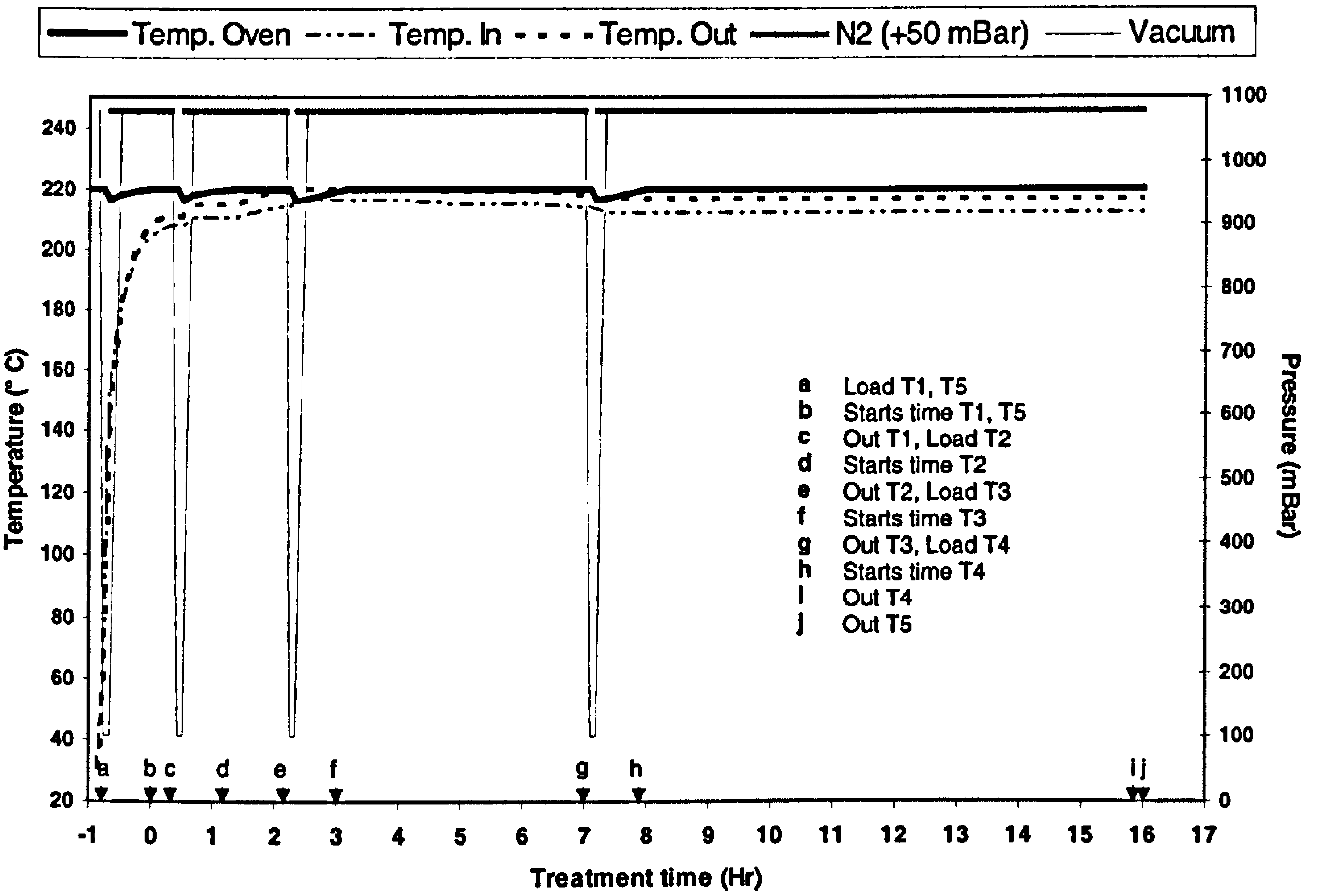

Figure 3.4 Typical schedule of temperature, vacuum and time for the treatment of Norway spruce at 210 °C (reported temperature). In = inner temperature. Out = temperature on the surface. T1, T2, T3, T4 and T5 = treatments at 0.33 h, 1 h, 4 h, 8 h, and 16 h, respectively

At the end of the heating period, the oven was unloaded and the samples were cooled in a desiccator over silica gel. It was considered that the possible degradation suffered for the contact of the sample with the surrounding air at cooling was negligible. Samples of spruce treated at 240 °C for 16 h gave off, though, a cracking sound at the contact with room-temperature air.

The gaseous phase product of the modification during the treatment of beech at 245 °C was very high. The port was just wide enough to exhaust the fumes, even though the load was only ~ 1.3 litres of wood, in a chamber of 115 litres capacity. The set of beech samples for the treatment for 8 hours was aborted midway, due to a damaged chamber seal. Thus, only 19 treatments, plus controls are used throughout this thesis for the studies on beech.

3.3 Physical characterisation of heat treated wood

This section includes the procedures followed for the physicochemical characterisation of the treated material, as compared to the untreated controls. The physical characterisation comprised the determination of weight and dimension changes for the determination the OD specific gravity (SG_{OD}) of solid wood and the measurement of the oven-dry SG of the cell wall substance (SG_{CW}). The study of mechanical properties was also included (Table 3.6, see below), as was the study of the interaction of treated wood with water and water vapour. The physical characterisation included the study of the cell wall micro-porosity, as well as the colour changes of the three species. Table 3.4 summarises the properties studied per treatment for each species. Sample size for the study of the mechanical properties (n), was appointed based on preliminary bending tests on selected treatments.

Table 3.4 Summary of physical parameters determined per species per treatment and number of samples per species. n_1, number of samples for heat-treatment; n_2, number of samples for testing at its ultimate dimensions.

Test	Direction	Size for heat treatments (mm) ($t \times r \times l$)	n_1	Sample size for testing (mm) ($t \times r \times l$)	n_2
SG wood (OD)	---	10 × 20 × 150	--	$10\times20\times150^{a}$	44
SG cell wall (OD)	---		--	$(10\times20\times5^{b})\times 6$	1
Bending	Tangential		10	10×20×150	10
Compression //	Parallel		4	10×x20×45	8
Compression ⊥	Tangential		6	10×20×x35	6
Shear strength	Parallel		2	10×20×20	8^{d}
Hardness	Tangential		6	10×20×60	6
Impact	Radial		5	10×6×48	10
ASE and water absorption	---		5	10×20×75	10
Hygroscopicity	---		--	$10\times20\times5^{b}$	4
Colour	Radial face		--	$10\times20\times150^{c}$	10
Porosity	---		--	$10\times20\times5^{b}$	1
Spare samples and relaxation	---		6	10×20×20	--
Samples per treatment			44	[a] From all samples [b] From the ASE test [c] From the bending test [d] Four in each plane	
× 20 treatments (5 times of exposure x 4 temperatures)			880		
+ controls			44		
Total samples per species			924		

3.3.1 Heat-induced weight loss, specific gravity and nominal density

Following cooling after thermal modification, the samples were measured (T_2, R_2 and L_2) and weighed (W_2) as explained above. Weight Loss (WL) was calculated as the ratio of the difference of the OD weight before W_1 and after treatment W_2 referred to W_1, expressed in percent. Changes in the dimension in the three planes and volume of the samples were calculated in a similar way. Oven dry specific gravity after thermal modification (SG_{OD}) was calculated as $W_2/(T_2 \times R_2 \times L_2)/(1\ g\ cm^{-3})$.

ND was computed as oven-dry weight/ volume at test at 65% at 20°C, only for the samples tested mechanically.

3.3.2 Specific gravity of the cell wall substance

Oven-dry specific gravity values for the wood substance measured *in situ* (SG_{CW}) have been found to range from 1.465 to 1.546 (Walker *et al.* 1993). The oven-dry specific gravity for the three polymers of the wood cell wall varies in the literature from author to author, but it is generally recognised that it is in the order cellulose ≥ hemicellulose > lignin (Stamm and Sanders 1966; Schniewind 1989; Schniewind and Berndt 1991; Walker *et al.* 1993; Mwaikambo and Ansell 2001). The oven-dry specific gravity for each hemicellulose type is not yet available, although Kellogg (1979) gives a higher value for softwood than for hardwood hemicelluloses. This suggests that the specific gravity for hexosan is larger than the one for pentosan. The oven-dry specific gravity values for cellulose, hemicellulose and lignin adopted here are those given by Kellogg (1979) (Table 3.5).

Table 3.5 Specific gravity of the three main polymers of the wood substance (Kellogg, 1979)

Constituent	Specific gravity (oven dry)	
	Hardwoods	Softwoods
Cellulose	1.520	1.520
Hemicellulose	1.457	1.666
Lignin	1.366	1.347

The oven-dry specific gravity of the cell wall substance after heat treatment (SG_{CW}) was calculated to collaborate on the study of the chemical and physical changes suffered during the thermal modification. SG_{CW} was acquired using a gas (helium) displacement pycnometer (AccuPyc 1330, Micromeritics Instrument Corp., USA). For this part of the study, two samples were randomly selected from those used for the determination of the ASE for each treatment-species combination. Three cross-sections of 5 mm thickness were cut at one end of each sample so as to fit them into the pycnometer sample holder. Each set of six pieces was weighed in the oven-dry state, placed into the pycnometer sample holder and then loaded into a cell chamber. The sample identification was given and its weight recorded. The procedure started by admitting the helium gas into the cell chamber, filling the open lumen and pores. The instrument measured the volume and specific gravity of the sample ten times. At the end of the last run, a summary report was printed out giving the values for each run, the averages and the standard deviations.

3.3.3 Mechanical properties

All tests were performed on treated and control samples with an equilibrium moisture content (EMC) at 65% RH (± 3%) at 20 °C (± 2 °C). Before testing the samples, each sample was weighed (W_3, 0.1 mg) and measured (R_3, L_3, T_3, to 1 μm) to determine both the moisture content at testing and nominal density of the samples. No correction in mechanical properties due to dissimilar EMC was done. Tests for mechanical properties assessed in this work are summarised in Table 3.6. Details follow.

Table 3.6 Summary of testing conditions according to BS 373 (1957) and BS EN ISO 179 (1997). These tests were carried out for all 20 treatment + control samples in all three species. //: parallel to the axis, ⊥ : perpendicular to the axis. Sample sizes indicated in Table 3.4.

Test	Loading rate	Output	Notes
Static Bending	6.5 mm/min	Modulus of Elasticity (MOE) Modulus of Rupture (MOR) Fibre stress at proportional limit (RLP) Resilience (R) Work to maximum load (WML) Total work (TW) Horizontal shear stress at neutral plane at limit of proportionality (SSLP) Horizontal shear stress at neutral plane at maximum load (SSML)	Span of 14 × depth, tangential direction
Compression //	0.6 mm/min	Compression strength // (CA) Modulus of elasticity (MOE_{CA})	Slenderness ratio 3:1
Compression ⊥	0.6 mm/min	Compression strength ⊥ (up to the limit of proportionality) (CE) Modulus of elasticity (MOE_{CE})	Pure compression, in tangential direction
Shear //	0.51 mm/min	Shear strength // (S)	Mean of tangential and radial directions
Janka hardness ⊥	6.5 mm/min	Hardness strength (H)	Tangential direction (radial face)
Charpy impact	2.9 m/s	Impact strength (IS)	Normal flat-wise

The mechanical tests carried out in this work were three point flexural bending test in the tangential direction (radial face), compression tests parallel to the grain and perpendicular to the axis (tangential direction), shear test parallel to the axis, Janka hardness test (tangential direction) and Charpy impact test.

The first five tests were done generally in concordance with BS 373 (1957). These five tests were performed using an Instron 1195 Universal Testing Machine with a loading cell of 100 kN (Series 5500, Instron Corporation, USA). The loading device and data capture were controlled by the Merlin© software interface. Data were logged by a computer in an ASCII code format for further analysis. The longitudinal modulus of elasticity in bending was calculated using the Merlin software. The modulus of rupture and horizontal shear stress at neutral plane at maximum load were determined from the maximum load determined from the testing. The load at limit of proportionality was obtained graphically from the stress-strain plot to calculate the fibre stress at proportional limit and the horizontal shear stress at neutral plane at limit of proportionality. Resilience (or work to the limit of proportionality), work to maximum load, and total work were derived from the respective areas of the stress-strain plot. Origin© software was used for integrating the areas.

Two specimens for compression strength parallel to the grain testing were cut from each of the four samples for each species-treatment combination, to give eight testing replicates[†]. For compression testing perpendicular to the grain, only three samples were used out of the four modified. Two samples were cut from each of these, to give six testing replicates. The specimen was then laid flat on its tangential face along its length, and the load was applied in pure compression on its upper surface. In such test, a clearly defined maximum load cannot be obtained (Schniewind 1979), and only a fibre stress at limit of proportionality (or the stress which caused 1% of deformation) was recorded.

For the shear strength testing, four samples were cut from each of two heat-treated samples for each species-treatment combination, to give eight test samples. Four samples were tested in each radial and tangential plane. As the size of the latter (10 mm) did not allow the use of the standardised die for the shearing test, the samples were sandwiched between plywood with hot-melt glue to give the 20 mm required for using the standard application. Values from both directions were averaged to work out the apparent average shear strength of the sample.

One specimen was cut from each sample for the Janka hardness test to give six replicates of TMW for each species-treatment combination. A small piece of untreated beech wood of the same dimensions (10 mm × 20 mm × 60 mm) was placed underneath the test specimen in order to fit it into the standard die.

The Charpy method has been used in the past to determine the impact strength of wood (Dinwoodie 2000). However, the small size of the sample used in this method could result in unrepresentative high values for the material. Larger samples have hence been used in a modified Hatt-Turner machine. However, the specimen size selected for this work did not allow the use of such machine and hence the Charpy test method was adopted. Other authors have used this method in the past and other methods using pendulum machines for the characterisation of the impact resistance of TMW, essentially for comparative purposes (*cf.* Davis and Thompson 1964; Mitchell 1988; Kubojima *et al.* 2000). Impact tests were conducted following

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[†] For ANOVA, no nested design was considered due to fact that two sample replicates were taken from one single modified piece. This was because the samples were all axially matched, and modified to an standard size just to homogenise the extent of the treatment.

the Charpy method according to BS EN ISO 179 (1997). The flat-wise properties of un-notched type 3 specimens were evaluated. The test was carried out using an analogue pendulum impact tester equipped with a 0.5 or 4 J pendulum (Zwick Testing Machines Ltd., England). Prior to testing, samples were cut to the final dimension on a band saw, and detailed to the final width with sanding paper.

3.3.4 Dimensional stability and hygroscopicity

3.3.4.1 Anti-swelling efficiency (ASE)

Farahani (2003) studied the ASE of TMW exposed to five successive cycles of water soaking and drying. He found no change in the swelling coefficient when treated wood was exposed to such cyclic conditions. Thus, for the determination of the ASE in the present work, only two cycles of saturation-drying were used. Following thermal treatments, five samples for the ASE determinations were cut into two parts to give 10 specimens per species-treatment combination. These were soaked in deionised water for seven days at 22 °C and then vacuum-dried overnight at 56 °C at 0.1 Bar, followed for a further drying at room pressure at 105 °C ± 0.5 °C for 8 h. For the second cycle, the saturation procedure was repeated. At the end of the second soaking, excess water was carefully wiped off the samples with paper tissue, and the samples were weighed (for computing water absorption) and measured. Finally, at the end of the second drying procedure, the samples were weighed and measured again.

ASE, in %, was calculated as (Hill 2006c):

$$\mathrm{ASE}\,(\%) = \frac{S_{nh} - S_{h}}{S_{nh}} x 100$$

Where S_{nh} and S_{h} are coefficients of contraction of non-heated or heated samples, respectively, and

$$S = \frac{V_s - V_d}{V_d}$$

Where V_d and V_s are the oven-dry and the swollen volume of the sample, respectively.

Determination of water absorption (WA), in %, was computed according to:

$$\text{MWA}\,(\%) = \frac{\text{W}_s - \text{W}_d}{\text{W}_d} x 100$$

Where:

W_s = Weight of the sample in the soaked condition

W_d = Weight of the sample in the dried condition.

3.3.4.2 Hygroscopicity

At the end of the ASE test, twenty 5-mm cross sections (4 replicates × 5 salts) were cut from 4 randomly chosen ASE samples for each species-treatment combination, to give a total of 420 samples per softwood species and 400 for beech (4 replicates × 5 salts x 21 treatments, 20 for beech). Samples were then vacuum oven-dried and weighed. Using the samples from the ASE test for hygroscopicity studies assured that the stresses brought about by the thermal modification have largely disappeared. A more long-term reproducible hygroscopic behaviour can be expected after the samples have been saturated and dried at least twice after treatment (Keith and Chang 1978).

Control and treated samples were placed in small airtight containers containing saturated salt solutions to produce five relative humidity conditions at 20 °C, namely 11% (LiCl), 33% (MgCl), 44% (K_2CO_3), 75% (NaCl) and 93% (KNO_3). The containers already assembled were placed in a room with controlled temperature at 20 °C ± 2 °C for 16 weeks, when the average change in moisture content from selected samples in 2 subsequent daily weightings was smaller than 0.1%.

The method is based upon the principle that an excess of water soluble salt in contact with its saturated solution and contained within an enclosed space produces a constant relative humidity and water vapour pressure, and it is dependentof the temperature of exposure (Anon. 1996). Deionised water and analytical-grade salts (Aldrich) were used. No monitoring of the actual RH was attempted. The procedure is described in detail by Papadopoulos and Hill (2003).

At the end of the period of exposure in adsorption, the samples were weighed and the moisture content at each relative humidity determined relative to the OD weight of the samples. The samples were then placed over a saturated solution of $CuSO_4 \cdot 5\ H_2O$ for 6 months to attain an EMC of *ca.* 97 %, prior to be placed back into the containers to obtain the EMC on desorption, as just explained for the sorption part of the isotherm.

Additionally, water vapour sorption isotherms of powdered spruce samples and from the three main polymers of the cell wall of these samples, from selected treatments (control samples and wood treated at 210 °C for 1, 4 and 16 h) were scheduled using an automated Dynamic Vapour Sorption (DVS) instrument (Surface Measurement Systems, England). For the determination of lignin isotherms, the Klason lignin from the chemical analysis was used (Section 3.4). α-cellulose was isolated from the samples according to ASTM method D1103-60 (ASTM 1978). Hemicelluloses were isolated following the procedure of Timell (1961). All isotherm determinations were performed at 20 °C ± 0.5 °C, for one adsorption-desorption cycle from the oven-dry condition. An advantage of the DVS instrument over the conventional procedure of the saturated salt solutions, is that it is possible to resolve differences in sorption behaviour at very low relative humidity conditions, which it is not possible by means of conventionally weighing the samples when they are taken off the jars at the end of the sorption process. It has also the added desirable benefit of the speed of the process, whereby it is possible to generate a complete adsorption-desorption cycle in less than 2 weeks, using the same sample for all the measurements. Apart from the relatively high cost of running the instrument due to the consumption of N_2, an apparent disadvantage of the DVS though, is the feasibility for running only one sample at a time, as well as the very small weight of the sample allowed in the micro-balance, which may not be completely representative of the material under study.

A powdered wood (or polymer) sample of *ca.* 10 mg was used in the instrument's microbalance for each run. The schedule for the DVS was set to 11 different relative humidities (0, 3, 5, 10, 20, 40, 60, 72, 82, 90 and 98 %). These environments are generated by mixing dry N_2 and saturated water vapour, using mass flow controllers. Data on mass change was acquired every 20 seconds. At each RH, an inbuilt algorithm was set to consider that equilibrium had been reached when the slope of an adjusted tangent line to the curve of mass change with respect to time for the last five minutes of data was smaller than 0.0001% min^{-1}.

The DVS instrument went out of order before the isotherms of cellulose and hemicelluloses could be obtained. At the time of writing this document, the instrument was still down; only samples of powdered wood and powdered Klason lignin were ultimately obtained.

3.3.4.3 Movement

At the end of the desorption cycle, samples were measured, oven-dried and measured again in the oven-dry status. This measurements were performed only in the tangential and radial directions, while the longitudinal movement was disregarded. Dimensional movement in each direction was calculated for each of the RH conditions by simple difference. With these values, volumetric movement was computed.

3.3.4.4 Anisotropy in swelling

Anisotropy in the response of wood to moisture changes in the cell wall accounts for undesirable shape changes such as diamonding and cupping. Hence, a reduction of wood anisotropy is of particular interest for the user of the material. Changes in wood swelling anisotropy in the plane perpendicular to the axis have been previously noted on heat-treated wood (Keith and Chang 1978, Bekhta and Niemz 2003). In this work, anisotropy was studied to gain a better understanding of the properties of the new material, from the perspective of the changes in its chemical composition.

3.3.5 Colour changes

In this research, colour in TMW was analysed for furthering the assessment of the predictability of physical properties using colour-related parameters, and to understand the relationship between chemical changes and colour change.

In spite of being one of the most important anatomical characters in wood, colour is difficult to define, characterise and further, to determine its origin. In common to other organic materials, colour in wood is a complex phenomenon, with multiple visual effects (*e.g.* dichroism). Colour measurements also fluctuate according to the face of exposure and surface pattern; it is therefore highly variable within the same individual (Chamberlain and Chamberlain 1980). Machine vision systems are common features in several wood processing industries. However, the selection of the colour system and the lighting conditions are essential for reproducible results, because the amount of light reflected from the wood surface depends on the wood fiber angle with that surface (Brunner *et al.* 1990). Typical spectrophotometry arrangements utilize the 45/0° geometry, with the light source at 45° to the plane of the surface and the detector normal to and directly above the surface to be illuminated. This reduces the specular reflectance to the detector, which is useful because the diffuse reflectance contains truer colour information, whilst the former contains more of the illuminant's colour (*Idem.*)

At the time of this research, there was no spectrophotometer in the visible range available locally, and the thermal modification took place before the colour measurements could be done on the unmodified state. This meant that colour parameters before-treatment could not be obtained for the modified samples. After the thermal treatment had taken place, it was decided to follow the approach of others for assessing colour modification (Archer 1985 cited by Keey 2005, Donath 2004). Therefore, the before-treatment colour parameters used for each modified sample were the average of those specimens of the untreated control samples (n = 10) for the respective species.

Image acquisition

Digital images of sample surfaces were recorded on an Epson Perfection 4990 scientific flatbed scanner at ambient temperature. These were carried out on the radial plane of wood samples which had previously been conditioned at 65% RH at 20 °C for at least 4 months in the absence of light. Samples were placed on the scanning surface of the instrument, so that the travelling diffuse light source was at right angles to the exposed surface, and covered. The image of each sample was of *ca.* 3,550 x 450 pixels size, and stored in JPEG format in the standardised RGB system. The image was compressed to a ratio 5:1, to give a suitable handling size (~ 10 MB each). Ten samples per treatment were scanned for each species.

Images were transferred to licensed software (Adobe Photoshop 7.0), and converted to the CIEL*a*b* system. The resolution of the image was 16 bits per pixel. A rectangle of 3500 x 380 pixels was sampled from each wood specimen (83% of the sample surface). Adobe Photoshop software gave the distribution of the measurements for each of the three CIEL*a*b* components (L*, a* and b*). Only the mean value and the SD for each coordinate was registered. The software assigned to each pixel a value in the internal scale of the software, between 0 and 255 for each coordinate. A linear transformation was used to convert the values given by the software to the data range used in the CIEL*a*b* system (100 for L*, and 120 for each a* and b* coordinates, see below).

Complementarily, conditioned Klason lignin samples in powdered (globular) form were scanned and the images stored in a similar way as above, in order to determine its colour parameters. The sample size in pixels was however much smaller. Only one lignin sample per treatment was imaged.

*The CIEL*a*b* colour space*

The choice of standard colour space depends on the nature of the specimen as well as on the application of the measurements. In this work, the surface colour was determined according to the Commission Internationale de l'Eclairage (CIE), using the L*a*b* colour space, which has been utilised in most colour studies in TMW.

In the three-dimensional CIEL*a*b* colour space, each colour can be expressed as a point in the Euclidean space defined by three coordinates correlating with the subjective colour perception (Mononen *et al.* 2002). The vertical coordinate for lightness L* represents the position on the black–white axis (L*=0 for total blackness, L*=100 for pure white), whilst the chromatic coordinates a* and b* describe the position on the horizontal plane. The chrome value a* defines the position on the green-red axis (-60 for green, +60 for red), while b* defines the position on the blue-yellow axis (-60 for blue, +60 for yellow) (Thompson *et al.* 2005) (Figure 3.5).

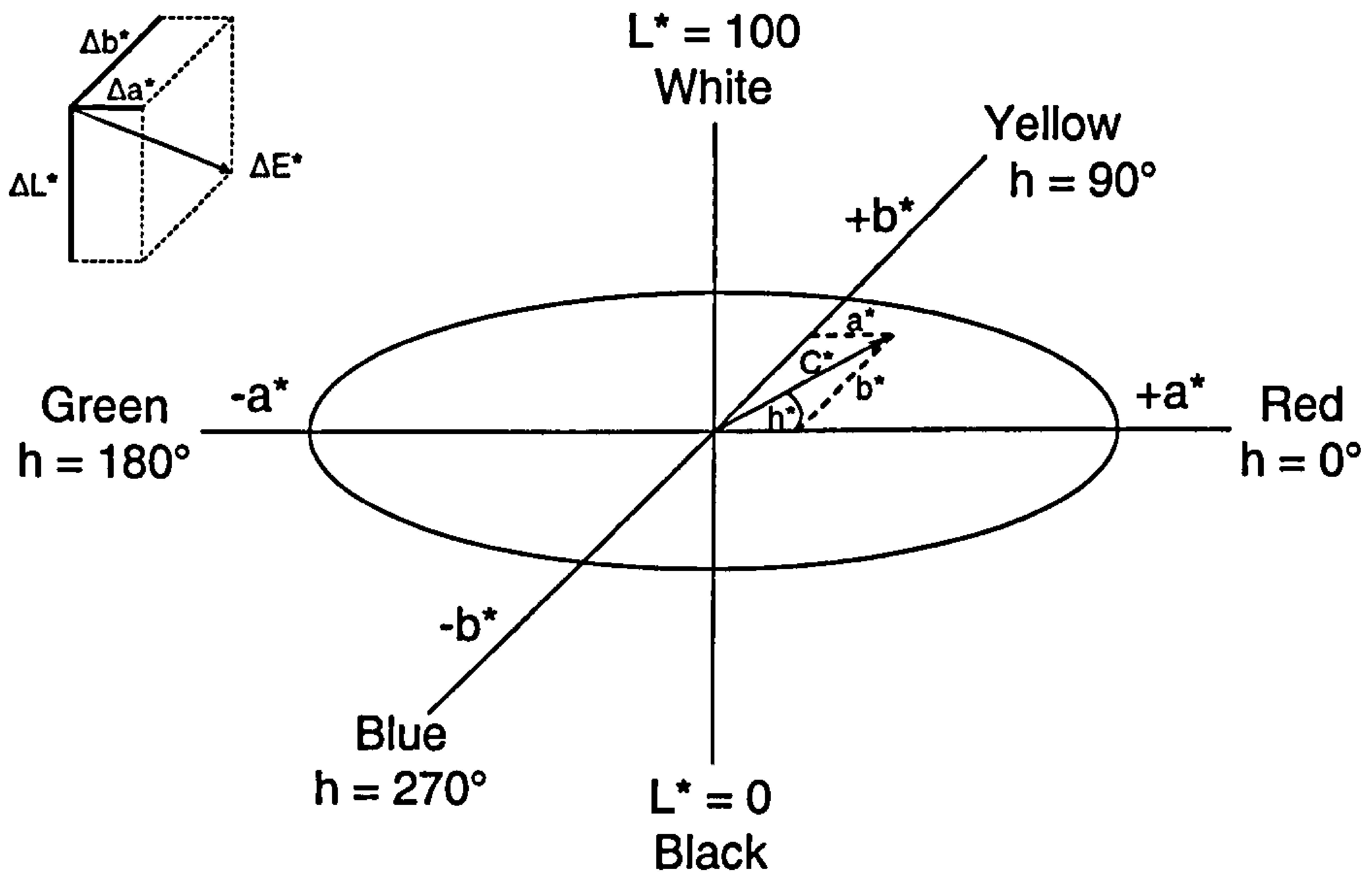

Figure 3.5 The CIEL*a*b* colour space. The deduced colour parameters C* and h* are also included. Insert: the physical interpretation of ΔE*

Loss of lightness is observed as a smaller value of L*. At zero values of a* or b*, there is the absence of greenness-redness or blueness-yellowness; the colour becomes gray, the darkness of this depending on the L* value. A difference in colour called ΔE* is expressed as a distance between two points in the colour coordinate system (Figure 3.5). The equation for the total colour difference ΔE* is (TAPPI 1994):

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$$

where:

ΔL^* is the difference in Lightness = $L^* - L^*_{control}$

Δa^* is the difference in a* coordinate = $a^* - a^*_{control}$

Δb^* is the difference in b* coordinate = $b^* - b^*_{control}$

The smallest colour difference distinguishable to the human eye on wood surfaces is about $\Delta E^* = 2$, whilst the human eye appears to be capable to detect subtler differences in lightness ($\Delta L^*= 1$) (Keey 2005).

Alternatively, a cylindrical coordinate system may be used to describe colour, with the a* and b* values being substituted by the saturation C* and the hue angle h* on the colour circle around the lightness axis L* (Figure 3.5). On the hue circle, h = 0° denotes redness and h = 90° denotes yellowness. Saturation C*, corresponding to the distance between the colour and the centre of the chromaticity plane, is a measure of colour intensity. This subsystem was also explored to find out the best possible predictor of physical changes from colour parameters. From the a* and b* values, the following parameters were calculated (Bourgois *et al.* 1991, TAPPI 1994):

h^* = Hue angle = arctang (b^*/a^*)

C^* = Saturation = $(a^{*2} + b^{*2})^{½}$

ΔC^*_{ab} = Saturation difference = $C^* - C^*_{control}$

ΔC^* = Chromaticity change = $(\Delta a^{*2} + \Delta b^{*2})^{½}$

Data analysis

For the modelling of physical properties using colour parameters as predictors, simple linear regression was used to determine the relationship between ΔE^* or ΔL^* and physical properties. Multiple stepwise regression using all the eleven colour parameters was subsequently explored using SPSS software version 12. Finally, partial least-squares (PLS) regression using the unfiltered data of the eleven colour parameters as independent variables was carried out using SIMCA-P software version 11.0.0.0. For constructing the calibration models for each MOR, MOE, WML, ND and WL using PLS regression, seven samples for each treatment were used (those initially numbered from 4 to 10), whilst samples numbered 1, 2 and 3 from each treatment were left apart for the prediction set. Samples of the calibration set were divided into seven groups for the cross-validation proceedings.

For building the calibration PLS models for each IS, H, S, CA, CE, S, and ASE, mean treatment values were used. This was because colour measurements were only obtained from samples of the bending test (10 samples for each treatment), and these were deemed representative of each batch (each batch comprised the samples for all tests for one treatment). Mean values for treatments 2, 4, 7, 9, 12, 14 and 17 were systematically included in the prediction set, whilst the mean values of the remaining treatments (from a total of 20) were used in the calibration set. A more detailed description of techniques and statistics for the PLS regression is given in section 3.4.6.

3.4 Chemical characterisation of heat treated wood

Following mechanical bending test, three samples from each treatment-species combination were randomly chosen to perform the analysis. The characterisation generally consisted of the quantitative gravimetric determination of the two main groups of components of the cell wall: lignin and polysaccharides. Each analysis was performed once and these were deemed as representative for the full set of treated samples in each treatment-species combination.

Quantification of monosaccharides in the sugar hydrolysate was performed analytically using high performance anion exchange chromatography, following the general methodology established by Pattersen and Schwandt (1991), slightly modified by Worrall and Anderson (1993). The analytical method was deemed as the most suitable one for the rapid determination of monosaccharides from numerous samples. This has the added advantages to avoid derivatisation of sugars prior to injection into the column of the chromatograph, and to have a very high resolution, with detection limits of the order of 10 ng for each sugar. Calculations of ultimate polysaccharide composition followed, based on several assumptions on the structure of the major hemicelluloses, according to the algorithm developed by Janson (1970).

Acid insoluble lignin (Klason lignin) was obtained following the procedure proposed by Effland (1977). Acid soluble lignin (ASL) was done as established in the TAPPI UM 250 (TAPPI 1991). Total lignin content was reported as the sum of Klason lignin and ASL. No correction for ash content was considered in lignin determinations.

Finally, evidence of the chemical degradation mechanism due to heat treatment was complemented by solid state FTIR spectroscopy analysis. Details follow.

3.4.1 Preparation of wood meal

Following flexural testing, three samples were randomly chosen, and lengths of wood were sawn to small pieces (< 10 mm long) to fit into a cross-beater mill (MK II, Glen Creston Ltd., England). The material (*ca.* 20 g) was milled for 30 seconds.

Milled wood was sieved by hand for 30 s using laboratory test sieves (Endecotts Ltd., England). The meal was sifted into three fractions: larger than 30 mesh (0.500 mm aperture as to BS 410-86), 30-60 mesh and smaller than 60 mesh (0.250 mm aperture). The coarse fraction (larger than 30 mesh) was reground for 30 s in order to ensure a good representation of the whole sample, and the product sieved again for 30 seconds. The middle fraction (30-60 mesh) was used for determination of lignin and monosaccharides. The finer portion (smaller than 60 mesh) was discarded. Restricting the powder size to 30-60 mesh for the analysis was intended to maximise the contact of the acid solution with the particles during hydrolysis, without excessive brake up of the cell wall material that could lead to higher than actual lignin content in the wood meal.

In the case of spruce wood, the < 60 mesh fraction was weighed and the > 60 mesh weight obtained by using (weight conditioned at 65% RH at 20 °C in all cases):

> 60 mesh = original weight – weight of the < 60 mesh fraction.

The > 60-mesh fraction was used to correlate this with the parameters of selected mechanical properties of modified samples, in order to assess the feasibility of developing a fast, simple method to evaluate the extent of treatment in TMW.

3.4.2 Extraction

Removal of extractives before polymer isolation of the wood components is particularly important for lignin isolation and determination, as some of the extractives are similar in structure to lignin and therefore would be difficult to differentiate (Fengel and Wegener, 1984).

Initially, it was decided to use organic solvents to remove the extractives only from the control (unheated) wood samples prior to its chemical characterisation. In the case of the heat treated samples, it was initially proposed not to use solvents to extract the material prior to the chemical analysis. It has been shown that lignin in the solid residue resulting from thermal treatments, reaches a maximum breakdown level, and subsequently re-polymerises to give a new lignin of lower molecular weight. This so-called pseudo-lignin is, to different degrees, soluble in organic solvents, including acetone and ethanol (Mitchell *et al.* 1953; Garrote *et al.* 1999).

However, exploratory determinations of chemical composition carried out on treated beech samples revealed that the extractive content was high, and thus total lignin content from non-extracted samples was over estimated. Hence, the Soxhlet extraction was performed using solvents in all treated and control samples of all species.

There are several systems for extractive removal, because extractives are diverse in nature, and the method chosen will depend on the species and the purpose. Usually, at least two solvents of different polarity are used to remove the broad range of extractives present (Holmbom 1999). In this research, a system of three solvents used in other studies was chosen (*cf.* Papadopoulos and Hill 2003): toluene, methanol and acetone in a proportion 4:1:1 (v/v). This mixture was considered adequate to cover the full spectrum of extractive polarities.

3.4.3 Acid-insoluble (Klason) lignin

All ground samples were left to condition to the EMC of the laboratory environment before weighing. A separate sample of 2-3 g was used to determine moisture content by drying at 105 °C ± 2 °C overnight.

Approximately 300 mg of wood flour were hydrolysed with 3 ml of 72% H_2SO_4, for 1 h in a beaker immersed in a water bath set at 30 °C with intermittent stirring, before pouring the sample in a flask for dilution to a concentration of 3% H_2SO_4. The flask was capped with aluminium foil before being autoclaved at 120 °C for 1 h. At the end of the secondary hydrolysis, the flasks were cooled in an ice bath, and the lignin was filtered off through a previously weighed sintered glass crucible (porosity 3) mounted on a Buchner flask. A sample of 1 ml was drawn from the filtrate (for ASL analysis, see below), before the residue was thoroughly washed with

30 ml hot deionised water to completely remove the sulphuric acid and any remaining sugars from the solid residue.

After drying at 105° ± 2 °C overnight, the crucible was cooled in a desiccator and weighed to the nearest 0.1 mg. The acid-insoluble lignin was calculated as percent of extracted, oven-dry samples.

3.4.4 Acid soluble lignin

Acid soluble lignin (ASL) is computed to account for the solubilisation of smaller fragments of lignin that do not condense in the acid fraction during digestion. It also includes the soluble fragments of lignin derived from the thermal treatment process.

The ASL was measured in the retained original filtrate of the Klason lignin, using UV/Visible spectrophotometer (UV1, Thermospectronic, England) at 205 nm, against a blank reference solution of 3% H_2SO_4. Samples were diluted as required with a solution of 3% H_2SO_4 to give an absorbance of between 0.2 and 0.7 in the instrument for the calculation of ASL (TAPPI, 1991). Total lignin in a sample was expressed as the sum of Klason lignin and ASL. No correction for ash content was performed for lignin determinations.

3.4.5 Monosaccharide composition

The hydrolysate from the Klason lignin was made up to 100 ml and diluted 10 times. This final dilution also contained 0.03 mg fucose ml^{-1} of water as internal standard. All samples were frozen after final dilution, and were defrosted overnight in a fridge before further processing when the analytical instrument was made available for use. After defrosting, a sample of approximately 2 ml was drawn from the solution, and passed through a 0.2 μm nylon filter, before being placed in the instrument's auto-sampler.

Monosaccharide composition was carried out by high performance ion exchange chromatography using pulsed amperometric detection in a GP50 gradient pump (BioLC, Dionex, England), ED50 electrochemical detector, AS50 auto-sampler and a Carbopac™ PA1 column. Samples of 20 μl injected into the system were eluted with 4 mM NaOH (carbonate free and purged with helium) with post column addition of 0.3M NaOH at a rate of 1 ml min^{-1}. Run time was 45 minutes, followed by 8 minutes elution with 0.5M NaOH to re-equilibrate the column. Retention times were compared to the standards (see below). After baseline correction, integrated areas were quantified against 3 standard solutions at different concentrations with Chromoleon© software, using fucose as an internal standard. A specimen from a standard solution was injected after every 6 to 8 unknown sample injections, to monitor possible variations in the column or detector. An example of the chromatograph obtained from a single analysis is shown in Figure 3.6.

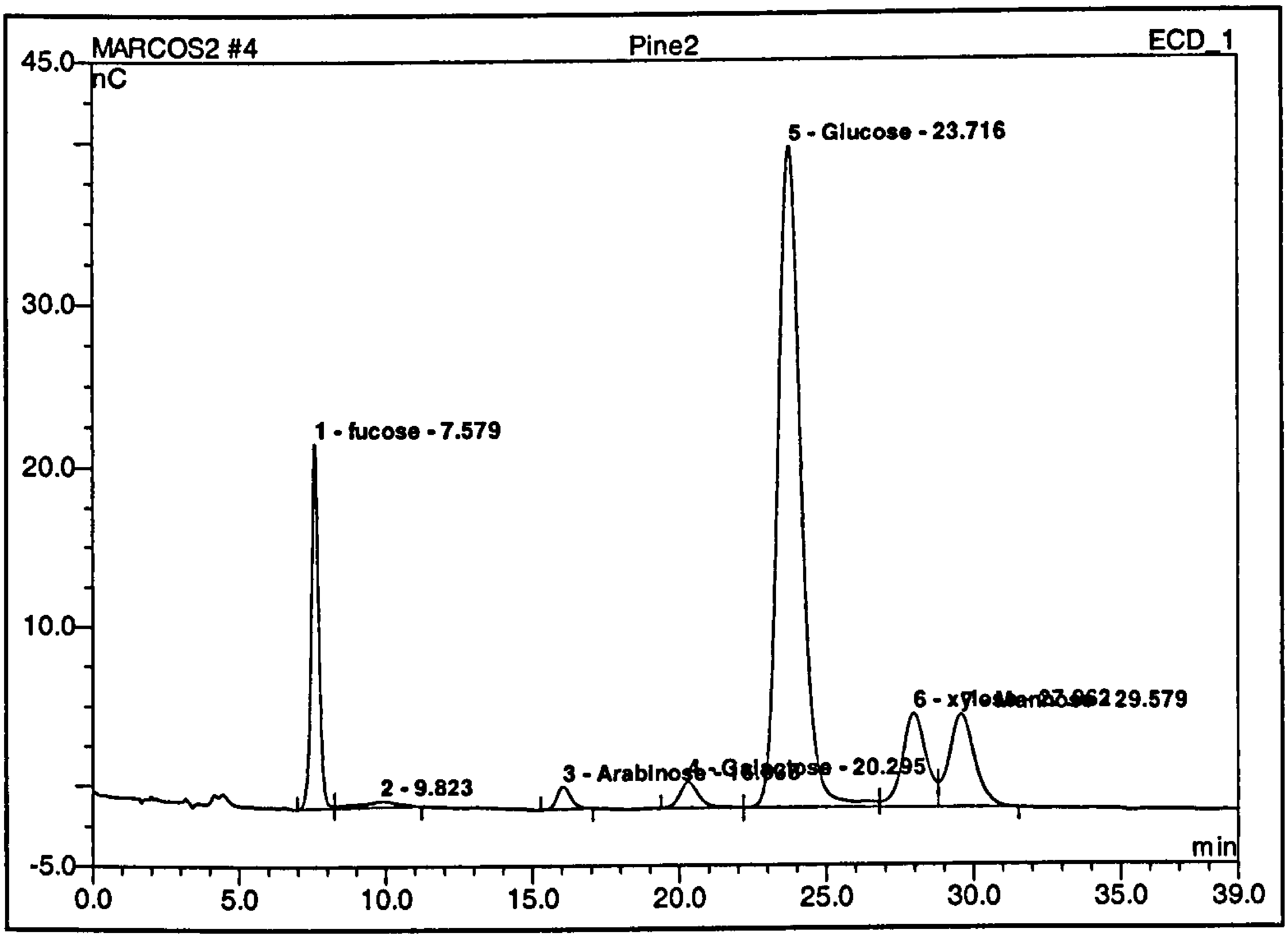

Figure 3.6 Chromatograph of monosaccharide analysis of modified pine at 190 °C for 1 h (High performance pulsed amperometric anion exchange chromatography)

The standard solution was made up of six sugars (rhamnose, arabinose, galactose, glucose, xylose and mannose) in the approximate proportions found in wood, dissolved in deionised water. For the calculation of calibration constants (TAPPI 1994), 10 ml of a standard solution with a total sugar concentration of 30.278 mg/ml were dried, and next subjected to primary and secondary hydrolysis as for the one from the determination of the Klason lignin. After secondary hydrolysis, the solution was made up to 100 ml and diluted 14 times. This final dilution also contained 0.03 mg fucose/ml of water as internal standard. An aliquot of ~ 2 ml was drawn from the final solution, filtered and chromatography-analysed as for the hydrolysate of the wood samples. This procedure was performed three times, and the results averaged. Calibration constants, k, were calculated for each monosaccharide. These constants are computed in order to account for the hydrolysis survival for each component, and were used for all the 62 treatments in this work [(20 treatments + control) × 3 species – 1 treatment for beech].

Based on data of monosaccharides, the carbohydrate content of TMW was calculated. Values were corrected by hydrolysis loss and then multiplied by the conversion factor for monosaccharide to individual oligosaccharides (0.88 for pentoses, 0.90 for hexoses). Total carbohydrate content was finally computed from lignin by difference to give 100% of the extracted oven-dry weight of the sample. From monosaccharide composition, the two main hemicellulose types (glucomannan and glucuronoxylan) as well as cellulose content were calculated based on several assumptions on the structure of the hemicelluloses, according to the algorithm of Janson (1970).

3.4.6 FTIR spectroscopy

Results from the wet chemical characterization and evidence found in the literature on the thermal degradation mechanism were complemented by mid-infrared spectroscopy analyses. Spectra were obtained from the same powdered specimens used for the previous analytical determinations for FTIR spectroscopy, whilst specimens treated at 210 and 230 °C and used for ASE studies of spruce wood were used for DRIFT.

3.4.6.1 Collection of the spectra

Mid-infrared FTIR

Before being pressed under vacuum to form pellets, 11 mg of oven-dried ground wood were mixed with KBr to a 1.1% sample concentration, and ball-milled to a very fine powder in a Mikro-Dismembrator (Sartorius, Germany). The spectra were obtained by accumulating 32 scans prior to the Fourier transformation, in the wavenumber range 4000-400 cm^{-1}, at a resolution of 4 cm^{-1}, on a Bruker spectrophotometer (Tensor 27, Bruker Optik GmbH, Germany), equipped with a RT-DLaTGS detector. The interferograms were Blackman Harris (3-Term) apodized, and the resulting spectra stored in transmission mode. To consider the contribution from the environment, the absorbance peaks from ambient gases (*i.e.* water and CO_2) were eliminated by measuring first the IR spectrum on the empty sample chamber, and then subtracting this spectrum from that of each sample. The resultant spectra were first baseline corrected using inbuilt routines of the OPUS© software (rubber-band mode[‡]), and then converted to absorbance units (using A = Log 1/T), vector normalized[§] with OPUS©, and finally stored in text format for data processing in the specialized multivariate analysis software SIMCA-P©. Only one spectrum was taken from each treatment-species combination.

For the qualitative evaluation of changes in the IR spectra of TMW, the analysis of the differences of relative bands intensities was performed (Tolvaj and Faix 1995). The reference peak chosen for calculating the ratios was the one of the carbohydrate skeleton (CH bending deformation in cellulose, symmetric) at 1374 cm^{-1}. For doing this, each of the original transmittance spectra was converted to absorbance spectra, then baseline corrected by hand by fitting straight lines between wavenumbers 3800, 1875 and 800 cm^{-1}, and finally Mini-max normalized[**], using the closest band to 1374 cm^{-1} (1375.25) as a maximum and 1394.25 cm^{-1} as a minimum. To obtain the difference spectra, the spectra of treated samples were subtracted from the spectrum of the untreated control, using the automatic mode[††] of the OPUS© software. A similar procedure was carried out for the analysis of difference spectra of Klason lignin samples, but the spectra were base-line normalized by hand at 3702, 1851, 709, and 410 cm^{-1}, and then Mini-max normalized using the band at 858 cm^{-1} as a maximum, and 906 cm^{-1} as a minimum.

[‡] For the construction of the baseline, the spectrum is divided into 64 ranges (64 being the number of baseline points) of equal size. The baseline is created by connecting the minima with straight lines. Starting from "below", a rubber band is stretched over this curve. The rubber band is the baseline. The baseline points that do not lie on the rubber band are discharged.

[§] The average y-value of the spectrum is calculated first. This average value is then subtracted from the spectrum so that the middle of the spectrum is pulled down to y = 0. The sum of squares of all y-values is then calculated and the spectrum is divided by the square root of this sum. The vector norm of the result spectrum is 1: $\sum_{i=1}^{NPT}(x_i)=1$

[**] Mini-max normalization. The spectrum is shifted so that the minimum occurring y-value is set to zero. The spectrum is expanded in the y-direction so that the maximum occurring y-values is placed at 2 absorbance units.

[††] In automatic mode, the difference spectrum with automatically determined multiplication factors is calculated from a least squares analysis over the displayed wavenumber range. The range of wavenumbers used is the largest range present in all spectra.

For the prediction of mechanical properties in bending, average strength values of the three samples milled were used for each treatment. As specimens for the bending and Charpy impact strength tests were matched samples from the same boards (in pine and spruce only, see section 3.2), the average values of three samples per treatment with similar levels of WL to those of the bending test, were chosen for the prediction of impact strength.

For the prediction of chemical constituents, results of the analytical determinations were used. For the modelling of galactan in Norway spruce wood, treatment 19 was not included in the calibration set, and treatment 12 was not included in the prediction set for inconsistency in the gravimetric determinations (too high reading).

Diffuse reflectance Fourier-transform mid-infrared spectra (DRIFT)

Another set of treated matched samples was used to investigate the ASE of spruce wood only, for treatments at 210 °C and 230 °C (10 treatments + control), using DRIFT spectroscopy. Spectra were acquired in a Bomem FTIR spectrometer MB100, equipped with a Spectratech diffuse reflectance unit, and a DTGS detector (Figure 3.7).

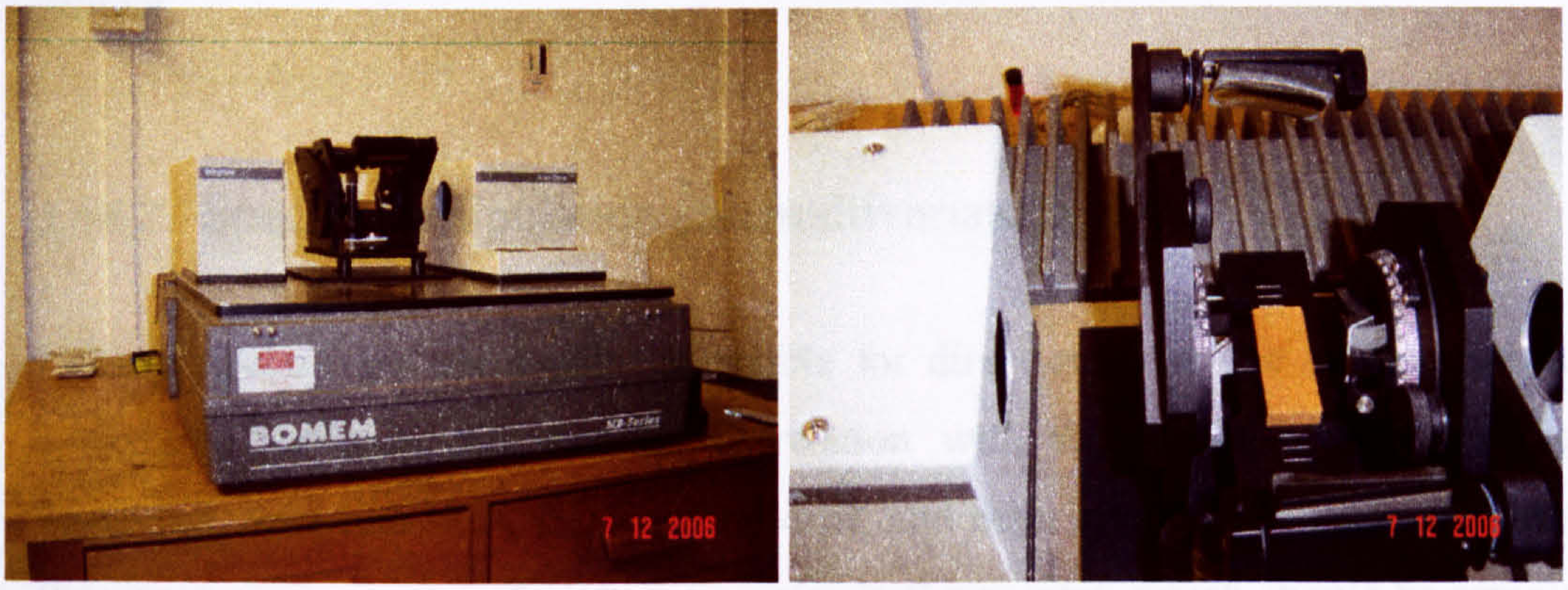

Figure 3.7 Collection of DRIFT spectra in a BOMEM FTIR spectrometer MB100. At the left, a general view of the instrument; on the right, a closer view of the Spectratech diffuse reflectance unit. The thermally-modified wood specimen was scanned without further preparation.

The resolution chosen was 4 cm^{-1}; the grain of the samples was parallel to the irradiating IR beam; two hundred scans were collected. The background spectra were obtained against a silver plate supplied by Spectratech. To minimise scattering contributions to the reflectance spectra, the spectral intensities were calculated in Kubelka-Munk units (cosine apodization) (Ferraz *et al.* 2004). No baseline correction or normalisation was performed before converting the data into ASCII format for multivariate analysis in the SIMCA-P© software. In independent studies (Faix and Böttcher 1992, Tolvaj and Faix 1995, Pandey and Theagarajan 1997), the effect of milling or preparing the surface has been expressly studied using DRIFT spectroscopy. A substantial improvement in the quality of the spectra was obtained by milling the samples to small particle sizes, or by careful sanding off the surface of thin wood wafers. In this study, however, the surface of the sample was scanned without further processing after the ASE analysis, in order to primarily weigh up the suitability of getting the DRIFT spectra without laborious sample preparation. Five samples were used for each treatment and only one spectrum was taken from each sample. Each DRIFT spectrum took ~10 minutes to acquire. The analytical depth of DRIFT is from 40 to 140 μm.

Another set of measurements was taken with a smaller number of scans (24) at reduced resolution (8 cm^{-1}). In this way, the collection of the spectra took 39 s per sample. Only Norway spruce samples treated at 210 °C were analysed. Three samples were used for each treatment; only one spectrum was acquired for each sample.

3.4.6.2 Spectra manipulation and multivariate analysis

Infrared spectra are not usually amenable for direct analysis due to the unwanted systematic variation that has no correlation with the response variable. Light scattering, base line shift, instrumental drift, and path length differences are among the commonest sources of systematic noise in the spectra, which should be removed from the raw spectral signals. Mathematical functions or algorithms for handling such interferences in order to avoid its dominance over chemical signals are used as spectral pre-treatments. The commonest data pretreatments in the study of wood spectra are derivatives (Savitzky and Golay 1964), multiplicative signal correction (Geladi *et al.* 1985) and orthogonal signal correction, OSC (Wold *et al.* 1998). Other approaches to handle systematic variations are described in Næs *et al.* (2002). In the present work, all three corrections were explored, together with the analysis of the raw data. The algorithm that gave the largest improvement for the analysis (better fit and predictive values) and thus the only one reported in this thesis was OSC. Unique among the other spectral filters in one major aspect, OSC takes the response variable into account in its algorithm. This filter is itself based on PLS regression and removes spectral variation orthogonal to the response under the constrain that the covariance between the spectral data and the response should be minimum (Wold *et al.* 1998). Thereafter, components containing unwanted systematic variation are subtracted from the original spectral data (X matrix), to produce a filtered descriptor matrix. For all models in this work, two OSC components were extracted. Prior to PLS regression, principal component analysis (PCA) was carried out on calibration sets as a basis for outlier detection and to get an overview of the data. In no case outliers were removed.

Filtered FTIR (or DRIFT) spectra were subsequently analysed by PLS regression. This technique is particularly useful when the predictors are highly collinear or there are more predictors than observations and ordinary least-squares regression either fails or produces coefficients with high standard errors. PLS regression reduces the number of predictors to a set of uncorrelated components (each component being a linear combination of the original predictor variables) and performs least-squares regression on these components (Miller and Miller 2005).

Digitised FTIR (or DRIFT) spectra and data from mechanical properties as well as WL, ND, SG_{OD}, EMC and chemical constituents (wood polymers or monosaccharides converted to individual oligosaccharides for each treatment), or ASE and WL in the case of the DRIFT spectra, were analysed with the SIMCA-P software version 11.0.0.0 (Copyright: Umetrics AB, Sweden). The spectral ranges used for the PLS regression were 3500-2800 cm^{-1} and 1800-550 cm^{-1}, giving 496 data points for a resolution of 4 cm^{-1}. Additionally, the feasibility of using only a few wavenumbers absorptions on the reliability of the models was assessed. Spectral data (X matrix) were mean-centred, whilst the strength values and physical data (Y matrix) were both mean-centred and scaled to unit variance.

Before carrying out PLS regression, the spectra of the complete set of samples for each species was divided into two groups. One group, containing two thirds of the samples –the training set, was used to construct the so-called calibration model. The remaining one third of samples –the prediction set, was used to evaluate the predictive ability of the calibration model by comparing the actually measured properties, with the predicted properties computed by using the calibration model. Treatments included in the calibration and prediction sets for each species are given in Table 3.7.

Table 3.7 Treatments included in the calibration set for building the PLS models, and treatments included in the prediction set to evaluate the predicting ability of the calibration models for all properties studied*.

Beech[a]		Scots pine		Norway spruce	
Calibration set	Prediction set	Calibration set	Prediction set	Calibration set	Prediction set
1	2	1	3	1	2
3	4	2	7	3	4
5	7	4	8	5	7
6	9	5	13	6	9
8	12	6	14	8	12
10	14	9	15	10	14
11	18	10	18	11	17
13		11		13	18
15		12		15	
16		16		16	
17		17		19	
20		19		20	
		20			

*For treatment numbers see Table 5.4, chapter 5.

[a] No treatment 19 exists for Beech wood.

In order to evaluate the predictive ability of the calibration model for each property, these models were constructed using full cross-validation. The cross-validation method emulates the prediction of unknown samples by using the training data set itself. The validation method involves the systematic removal of one sample from the data set, construction of a model with the remaining samples, and use of the model to predict the value of the Y-variable for the excluded sample. This process continues until each individual sample has been removed from the data set and a fully cross-validated model is constructed (Martens and Næs 1989, Eriksson *et al.* 1999). For each specimen, the difference between the actual and the predicted value is calculated. The sum of squares of these differences is called the predicted residual error sum of squares (PRESS); the closer the value to zero, the better the predictive power of the model. The performance and relevance of PLS models were further evaluated by computing different statistics. The quantitative measure of the *goodness of fit* is given by the parameters R^2_X and R^2_Y, the explained variation for **X** and **Y**, respectively, computed as:

$$R^2_X = 1\text{-SSX [A]/SSX [0]}$$

and

$$R^2_Y = 1\text{-SSY [A]/SSY [0]}$$

where SSX [A] is the sum of squares of the **X**-residuals, SSY [A] is the sum of squares of the **Y**-residuals, after extracting A components; SSX [0] and SSY [0] are the total sum of squares for **X** and **Y**, respectively. After OSC filtering, it was normally found that R^2_X decreases compared to the one determined if raw data were used. However, this effect has little importance in the fitting and predictive ability of the calibration model.

In the present study, the prediction ability of the computed calibration model, the *goodness of prediction*, is also quantified by a parameter called the predicted variation, Q^2, using cross validation sets only. The fraction of the total variation of the **Y**'s that can be predicted by a component Q^2, is computed as:

$$Q^2 = 1 - \text{PRESS/SS}$$

where SS is the residual sum of squares of the previous component (or dimension). This parameter is essential to determine the significance of each model dimension. According to rule 1, if Q^2 due to cross validation is larger than a significant limit, the extracted dimension is considered significant (Umetrics 2006). The cumulative Q^2 (Q^2_{CUM}) for all the extracted components is computed as:

$$Q^2_{CUM} = 1.0 - [\prod_{a=1}^{A} (\text{PRESS/SS})_a]$$

where $\prod_{a=1}^{A} (\text{PRESS/SS})_a$ is the product of PRESS/SS for each individual component, a.

Larger cumulative Q^2 value for a given response indicates that the model for that response is good. As a rule of thumb, a model with $Q^2 > 0.5$ is considered as good, $Q^2 > 0.75$ as very good and $Q^2 > 0.9$ as excellent. The ultimate objective of developing a calibration model is to make predictions in the future. For all the properties studied in this work, the computed calibration models were applied to predict new samples in the prediction sets that were kept aside during calibration models building. Prior to predictions, samples in the prediction set were treated in the same way as the ones in the calibration set (*i.e.* 2-component OSC-filtered). The modelling error of the calibration model and the prediction ability of the model were further evaluated by computing the root mean square error of calibration (RMSEC) and the root mean square error of prediction (RMSEP), respectively. These were computed as:

$$\mathrm{RMSEC} = \sqrt{\frac{\sum_{i=1}^{N_C} (\hat{y}_i - y_i)^2}{(N_C - A - 1)}}$$

where $\hat{y}_i$ is the value of the property of interest for validation sample *i* estimated using the calibration model, y_i is the known value of the property of interest of sample *i*, N_C is the number of samples used to develop the calibration, and A is the dimension of the calibration model; and

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i=1}^{N_P} (\hat{y}_i - y_i)^2}{N_P}}$$

where $\hat{y}_i$ is the value of the property of interest for sample *i* estimated using the calibration model, y_i is the known value of the property of interest of sample *i*, and N_P is the number of samples in the prediction set.

As RMSEE and RMSEP are given in the same units of the property measured (MPa, $kg{\cdot}m^{-3}$ and so on), it is customary to refer these values as ratios of the mean value (M) or the standard deviation (SD) of the property in question to make the comparisons. Another, probably more suitable statistic, is the relative prediction error, RPE (Thumm and Meder 2001)[‡‡], a statistic that is used to compare different sets of data, which have a difference in variance in their Y-data. An RPE value close to one indicates an excellent prediction, whilst a zero or negative value suggest a poor prediction. As most of the after-treatment values for the properties studied in this work cover a relatively large range of data, models with ratios of RMSEP/SD < 0.9 are also considered as robust ones. For a more comprehensive description of theories and applications of PLS regression for multivariate calibration, see Eriksson *et al.* (1999), Wold *et al.* (2001) and Næs *et al.* (2002).

3.5 Data analysis

Partial least-squares regression was used for the prediction of physical properties of TMW using colour parameters or infrared spectral data as descriptors. This has been detailed in sections 3.3.5 and 3.4.6.2, respectively. These analyses were performed using SIMCA-P software (version 11.0.0.0, Umetrics AB, Sweden).

Other statistical analyses carried out in this work included:

- Chapter 4

Least-squares linear regression (LSLR) was used to build models for the prediction of ND and SG_{OD} from WL and dimensional changes.

- Chapter 5

Analysis of variance (ANOVA) was carried out to determine significant differences between heat-treated and untreated wood samples for each strength parameter studied. Analysis of covariance (ANCOVA) was subsequently used to determine if property change was the same at equivalent levels of WL, irrespective of the temperature of treatment, and to determine significant differences between species for each strength parameter. LSLP and least-squares multiple regression (LSML) were used for modelling strength parameters from WL, SG_{OD}, ND, chemical components or from selected strength parameters. Principal component regression (PCR) was also used for models of strength parameters on chemical components. Additionally, non-linear regression (NLR) was used to build the models for the

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[‡‡] RPE = $(SD^2 - MSEP)/SD^2$, where SD^2 is the variance of the Y-data in the calibration model and MSEP = $RMSEP^2$

prediction of wood strength from treatment parameters (time and temperature). Lastly, factor analysis was undertaken to construct an index of the overall performance of TMW.

- Chapter 6

Hygroscopicity isotherm fitting was carried out by NLR, using a single-hydrate form of the Hailwood-Horrobin theory of adsorption. Movement and hygroscopicity isotherms were next modelled using NLR. The prediction of ASE from WL and EMC by LSLR, LSMR and NLR models was also investigated.

- Chapter 7

The prediction of mechanical and other physical properties of TMW from colour parameters was accomplished by means of LSLR, LSMR and PCR. Predictions of ASE from treatment parameters by NLR was also attempted.

All analyses were carried out using SPSS software (version 12.0.1, SPSS Inc., USA).

Chapter 4 Effect of the thermal modification of wood on its gravimetric and dimensional parameters

Heating of wood above 140 °C leads to irreversible changes in all its physical and chemical characteristics. In this chapter, dimensional and gravimetric changes are examined after the thermal modification of wood. Gravimetric changes include the chemical conversion of the three main polymers of the wood substance, weight loss (WL), changes in the nominal density at 65% ± 3% RH at 20 °C ± 1 °C (ND), changes in the oven-dry specific gravity of solid wood (SG_{OD}), and changes in the oven-dry specific gravity of the cell wall substance (SG_{CW}). This chapter ends with the prediction of some properties of possible interest for thermal processing.

4.1 Gravimetric parameters

4.1.1 Chemical composition

Changes in lignin content (Klason lignin + acid soluble lignin)

In all three species, the lignin content in terms of the relative-to-control values (with respect to the initial oven-dry weight of the sample) shows an increase when plotted against the heat-induced weight loss (WL) (Figures 4.1 – 4.3). However, subtle differences exist between beech and the softwoods in the rate of change at low levels of WL. Although the increasing lignin substance in beech wood can be overall efficiently predicted by a curvilinear relationship, the lignin content remains almost unchanged in relative-to-control values from the beginning of the treatment up to WL of around 6% (Figure 4.1). In turn, in softwoods the lignin component increased steadily from the lowest levels of modification (Figures 4.2 and 4.3). In both softwoods, the profile is nearly rectilinear as the WL proceeds.

In view of the different nature of the lignin of TMW from that of the raw material, the lignin from TMW is referred to as TM-lignin in Figures 4.1 to 4.3.

Table 4.1 The effect of thermal modification on gravimetric parameters of solid samples and of the cell wall substance of beech, Scots pine and Norway spruce woods.

Temp.	time	WL (%)		SG_{OD}		ND (kg m^{-3})		SG_{CW}	Extractives	ASL	Klason Lignin	Total lignin	Glu-Xylan	Glu-Man	Hemicell.	Cellulose	Holocell.	Other sugars	Total
(°C)	(h)	x̄	SD	x̄	SD	x̄	SD		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Control beech		0.00	0.00	0.685	0.035	648.83	32.27	1.4258	0.00	1.08	23.42	24.49	23.01	5.16	28.18	42.87	71.04	1.86	97.40
190	0.3	0.33	0.08	0.682	0.036	644.30	32.41	1.4314	-0.28	2.25	20.61	22.86	20.07	2.71	22.79	49.02	71.81	2.38	96.77
	1.0	0.98	0.19	0.681	0.034	648.26	30.68	1.4307	0.34	1.46	24.33	25.79	21.08	3.65	24.73	44.42	69.15	1.54	96.82
	4.0	2.84	0.61	0.680	0.039	651.59	37.18	1.4253	1.09	1.12	23.83	24.95	20.93	3.32	24.25	44.27	68.52	1.21	95.77
	8.0	4.03	0.85	0.684	0.037	656.11	34.18	1.4272	0.72	1.47	22.75	24.22	18.36	1.63	20.00	47.91	67.91	1.29	94.14
	16.0	6.74	1.63	0.668	0.037	642.58	36.35	1.4270	2.33	1.15	24.93	26.08	16.85	1.41	18.26	45.68	63.94	0.71	93.06
210	0.3	1.31	0.29	0.680	0.033	649.43	30.41	1.4226	0.27	0.99	23.28	24.27	21.90	1.65	23.55	46.87	70.42	1.51	96.47
	1.0	6.32	1.65	0.663	0.042	642.84	40.93	1.4289	2.06	1.14	23.13	24.27	15.86	1.23	17.09	49.40	66.49	0.80	93.61
	4.0	9.95	2.12	0.656	0.042	632.97	39.95	1.4275	1.87	0.60	27.78	28.38	11.70	2.23	13.94	44.52	58.46	0.45	89.16
	8.0	13.13	2.09	0.636	0.032	618.34	30.76	1.4162	1.82	0.27	28.52	28.79	9.41	0.60	10.01	45.08	55.10	0.28	86.00
	16.0	16.17	2.40	0.630	0.034	611.62	33.30	1.4283	2.11	0.29	30.03	30.32	7.24	0.99	8.23	42.62	50.85	0.18	83.46
230	0.3	3.84	1.03	0.666	0.033	641.05	32.55	1.4302	1.26	2.81	21.97	24.78	18.27	0.00	18.27	48.64	66.92	2.02	94.98
	1.0	16.36	2.99	0.618	0.029	600.24	27.52	1.4204	3.38	0.45	31.18	31.63	6.51	0.29	6.81	43.02	49.82	0.00	84.83
	4.0	18.01	2.25	0.635	0.038	614.92	35.98	1.4162	1.67	0.25	31.40	31.65	4.55	0.00	4.55	42.96	47.51	0.13	80.96
	8.0	18.88	1.98	0.628	0.035	612.27	34.25	1.4327	1.02	0.18	33.73	33.91	4.12	0.49	4.61	40.28	44.89	0.40	80.22
	16.0	24.47	2.89	0.608	0.038	589.79	34.95	1.4218	0.59	0.16	36.32	36.48	1.71	0.30	2.01	35.19	37.20	0.00	74.28
245	0.3	12.21	3.27	0.650	0.031	630.14	30.18	1.4294	3.93	0.55	26.10	26.65	14.44	0.72	15.16	44.39	59.55	0.42	90.56
	1.0	22.84	3.06	0.608	0.036	590.96	35.48	1.4178	1.31	0.16	32.33	32.49	2.82	0.00	2.82	39.29	42.11	0.21	76.13
	4.0	24.89	2.09	0.600	0.036	578.47	35.28	1.4167	0.96	0.14	34.78	34.92	1.13	0.00	1.13	37.07	38.20	0.00	74.08
	16.0	27.01	2.80	0.606	0.033	586.19	31.56	1.4119	0.43	0.17	38.45	38.62	0.92	0.00	0.92	31.34	32.26	0.00	71.31

Continued over ...

Table 4.1 The effect of thermal modification on gravimetric parameters of solid samples and of the cell wall substance heated woods (*continued...*).

Temp.	time	WL (%)		SG_{OD}		ND (kg m^{-3})		SG_{CW}	Extrac-tives	ASL	Klason Lignin	Total lignin	Glu-Xylan	Glu-Man	Hemicell.	Cellulose	Holocell.	Other sugars	Total
(°C)	(h)	x̄	SD	x̄	SD	x̄	SD		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Control pine		0.00	0.00	0.492	0.066	463.10	58.97	1.4132	-0.14	0.34	28.41	28.75	10.50	15.08	25.58	41.60	67.19	1.96	97.76
190	0.3	0.61	0.09	0.481	0.073	455.12	65.62	1.4264	-0.02	0.30	28.49	28.79	8.24	13.66	21.90	46.29	68.19	0.37	97.33
	1.0	1.26	0.27	0.483	0.065	459.66	58.60	1.4189	-0.02	0.37	28.67	29.03	7.87	14.05	21.92	44.77	66.69	1.09	96.79
	4.0	2.31	0.40	0.479	0.066	456.55	60.83	1.4092	-0.09	0.36	29.48	29.84	5.13	11.05	16.19	49.71	65.89	0.20	95.84
	8.0	3.00	0.45	0.477	0.064	456.37	58.04	no calc.	-0.20	0.43	29.74	30.18	4.99	10.98	15.96	49.25	65.21	-0.11	95.07
	16.0	4.48	0.86	0.472	0.063	452.85	58.14	1.4199	0.00	0.48	30.79	31.27	4.25	11.13	15.38	47.38	62.76	0.12	94.15
210	0.3	2.30	0.54	0.476	0.070	459.63	63.03	1.4303	-0.19	0.27	28.83	29.10	7.25	12.82	20.07	45.17	65.24	1.72	95.88
	1.0	3.12	0.64	0.483	0.067	461.22	62.78	1.4215	-0.03	0.17	29.51	29.68	8.45	13.88	22.33	42.36	64.68	0.88	95.22
	4.0	7.20	1.05	0.472	0.064	456.20	60.76	1.4291	0.12	0.22	31.13	31.36	7.68	12.12	19.80	39.13	58.94	1.05	91.46
	8.0	7.95	1.42	0.460	0.069	443.05	67.43	1.4269	-0.07	0.56	31.50	32.06	7.51	11.68	19.19	38.94	58.13	0.97	91.09
	16.0	10.01	1.75	0.459	0.063	445.21	60.09	1.4181	0.17	0.45	32.29	32.75	5.64	10.25	15.89	39.11	55.00	1.13	89.05
230	0.3	2.99	0.57	0.475	0.071	455.92	64.96	1.4243	-0.08	0.32	29.78	30.10	6.87	12.89	19.75	44.04	63.80	1.55	95.37
	1.0	5.15	1.36	0.474	0.068	457.57	63.42	1.4043	0.01	0.40	30.33	30.73	6.55	12.41	18.96	43.12	62.08	0.74	93.56
	4.0	9.39	1.17	0.461	0.065	448.23	61.00	1.4189	0.01	0.57	32.79	33.36	3.26	8.07	11.32	44.19	55.51	0.44	89.32
	8.0	11.40	1.14	0.453	0.074	441.74	71.61	1.4189	0.21	0.45	34.28	34.73	3.66	8.18	11.84	40.84	52.68	0.03	87.64
	16.0	13.95	2.41	0.440	0.063	426.84	59.92	1.4228	0.03	0.70	34.52	35.23	2.78	6.97	9.75	40.10	49.84	0.27	85.36
245	0.3	5.59	1.23	0.467	0.061	450.23	56.04	1.4224	-0.02	0.57	31.37	31.94	5.44	10.67	16.11	44.31	60.42	1.18	93.52
	1.0	11.50	1.47	0.450	0.058	434.33	58.41	1.4153	0.26	0.44	33.97	34.41	2.61	7.48	10.10	42.89	52.99	0.19	87.85
	4.0	16.06	2.15	0.439	0.067	427.01	64.78	1.4122	0.12	0.52	36.05	36.57	1.26	3.78	5.05	41.66	46.71	0.01	83.41
	8.0	21.80	4.02	0.420	0.067	409.52	63.44	1.4114	0.18	0.29	37.64	37.94	0.39	1.71	2.11	37.76	39.86	0.17	78.15
	16.0	21.53	2.53	0.421	0.051	408.08	49.90	1.4185	0.09	0.30	39.13	39.43	0.00	0.42	0.42	37.56	37.97	-0.02	77.48

Continued over ...

Table 4.1 The effect of thermal modification on gravimetric parameters of solid samples and of the cell wall substance heated woods (*concluded*).

Temp.	time	WL (%)		SG_{OD}		ND (kg m^{-3})		SG_{CW}	Extrac-tives	ASL	Klason Lignin	Total lignin	Glu-Xylan	Glu-Man	Hemicell.	Cellulose	Holocell.	Other sugars	Total
(°C)	(h)	x̄	SD	x̄	SD	x̄	SD		(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Control spruce		0.00	0.00	0.406	0.024	380.73	22.50	1.4480	-0.67	0.83	28.22	29.06	8.19	14.67	22.86	44.85	67.71	1.13	97.23
190	0.3	1.05	0.12	0.401	0.023	379.06	20.42	1.4468	-0.30	0.25	27.44	27.69	7.08	13.35	20.43	47.81	68.24	1.01	96.64
	1.0	1.50	0.23	0.403	0.023	380.34	20.98	1.4396	-0.50	0.46	27.06	27.52	8.47	14.01	22.48	45.93	68.40	0.67	96.09
	4.0	1.99	0.35	0.399	0.020	379.28	19.82	1.4364	-0.60	0.32	28.08	28.40	6.71	14.04	20.76	46.46	67.22	0.52	95.53
	8.0	2.87	0.41	0.396	0.028	377.78	25.67	1.4279	0.25	0.19	29.06	29.26	6.95	14.33	21.28	43.99	65.27	0.75	95.53
	16.0	3.64	0.77	0.399	0.026	381.08	23.79	1.4237	0.26	0.28	30.06	30.34	6.43	13.63	20.06	43.29	63.35	0.86	94.81
210	0.3	1.39	0.24	0.402	0.027	382.02	24.99	1.4422	-0.30	0.11	28.21	28.32	6.92	13.82	20.74	46.70	67.44	0.90	96.37
	1.0	2.85	0.44	0.393	0.020	373.90	18.33	1.4441	0.18	0.14	28.97	29.11	7.41	14.48	21.89	43.75	65.64	0.46	95.38
	4.0	5.21	0.75	0.392	0.025	374.53	24.65	1.4398	0.58	0.26	30.12	30.38	6.17	12.63	18.80	43.44	62.24	0.43	93.63
	8.0	6.24	0.94	0.393	0.021	375.68	20.04	1.4305	0.45	0.30	30.51	30.81	5.13	11.72	16.86	44.00	60.86	0.31	92.43
	16.0	9.02	1.90	0.388	0.032	370.25	31.37	1.3883	0.96	0.36	31.66	32.02	3.66	9.28	12.94	44.29	57.22	0.09	90.30
230	0.3	3.59	0.66	0.398	0.029	378.42	28.92	1.4249	0.72	0.17	28.19	28.35	6.09	13.41	19.49	46.34	65.84	0.41	95.31
	1.0	6.27	1.28	0.388	0.031	370.96	28.48	1.4334	0.76	0.27	30.17	30.45	5.11	10.49	15.60	43.76	59.36	2.28	92.85
	4.0	8.93	1.49	0.386	0.029	370.84	27.33	1.4264	1.15	0.28	31.73	32.01	3.55	9.27	12.82	44.26	57.08	0.22	90.46
	8.0	11.05	1.85	0.377	0.025	363.88	24.26	1.4155	1.12	0.28	32.93	33.21	3.01	7.45	10.45	43.64	54.10	-0.03	88.40
	16.0	15.42	3.27	0.364	0.031	350.47	29.72	1.4104	0.47	0.36	36.80	37.16	1.43	4.34	5.77	40.16	45.93	-0.14	83.43
245	0.3	7.74	1.60	0.376	0.027	362.54	27.36	1.4161	1.09	0.25	30.40	30.66	4.47	10.66	15.13	44.89	60.02	0.18	91.94
	1.0	11.08	2.03	0.379	0.027	365.44	25.57	1.4285	1.36	0.25	32.59	32.84	2.83	7.65	10.48	44.31	54.79	-0.19	88.80
	4.0	15.54	2.32	0.365	0.029	353.08	28.28	1.4217	1.17	0.24	34.91	35.15	1.17	4.22	5.39	42.65	48.04	-0.06	84.29
	8.0	18.12	2.49	0.352	0.027	339.26	27.76	1.4258	0.75	0.24	37.80	38.05	0.60	1.89	2.49	39.47	41.96	0.61	81.36
	16.0	26.68	4.99	0.335	0.039	324.21	37.93	1.4204	0.52	0.17	44.21	44.38	0.30	0.93	1.23	26.47	27.70	0.03	72.63

Lignin and carbohydrates represent the content (in %) with respect to the initial oven-dry weight of the sample.

Total carbohydrate content was computed from lignin by difference. Beech wood not tested at 245 °C for 8 h.

WL, weight loss; ND, nominal density (at 65% RH at 20 °C); SG_{OD} oven-dry specific gravity of solid wood; SG_{CW} oven-dry specific gravity of the cell wall substance; ASL, acid soluble lignin.

WL, SG_{OD} and ND are the mean values and the standard deviations (SD) of 44 replicates. The other values are a single determination. Abbreviations for chemical components as in Figure 4.1

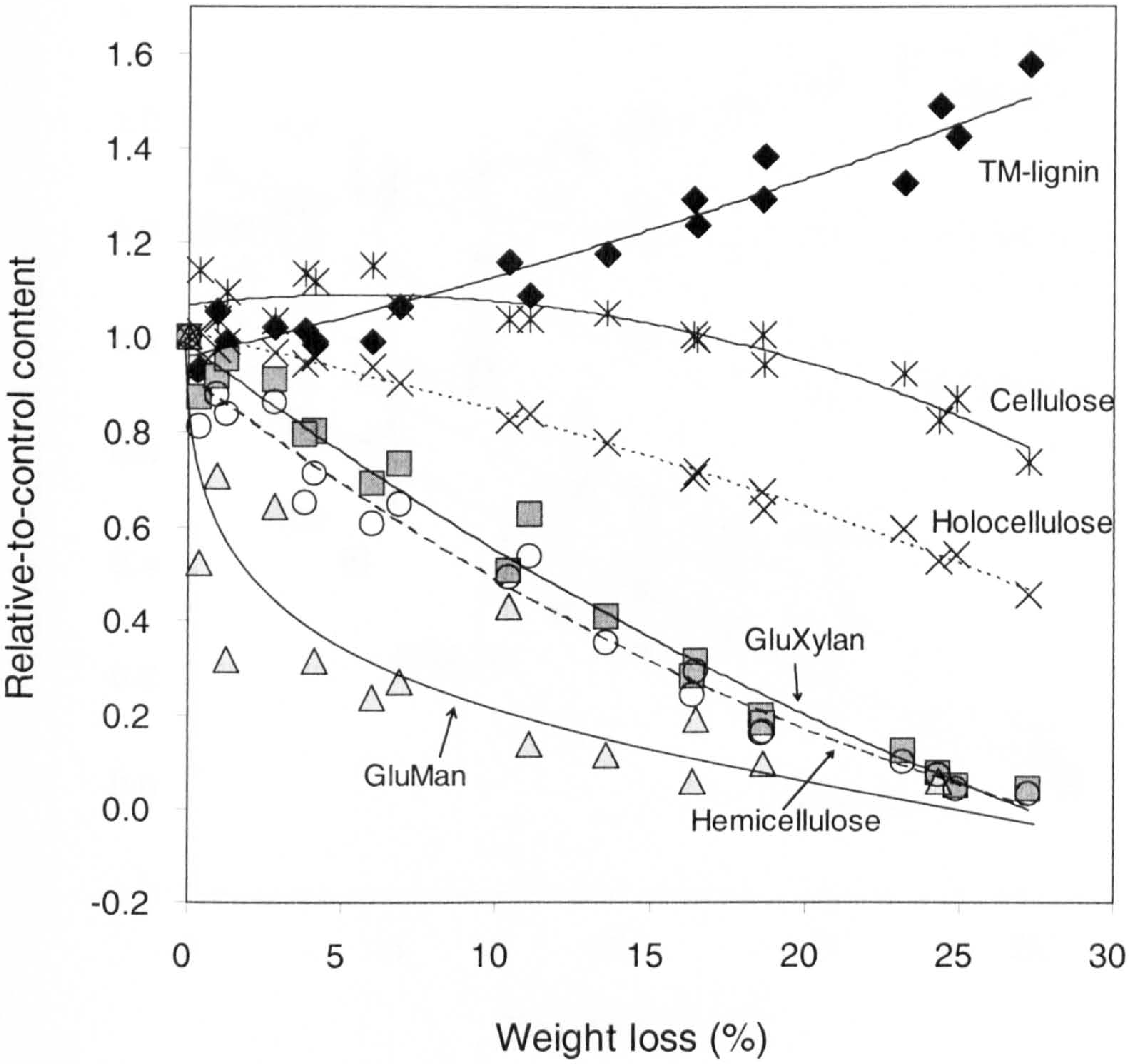

Figure 4.1 Degradation of the main polymers of beech wood upon heating at 190 °C – 245 °C for 0.3 to 16 h. Relative-to-control values of the before-treatment oven-dry weight *vs.* weight loss. ♦ TM-lignin; ■ GluXylan = Glucuronoxylan; △ GluMan = Glucomannan; ○ hemicellulose; ✳ cellulose; × holocellulose

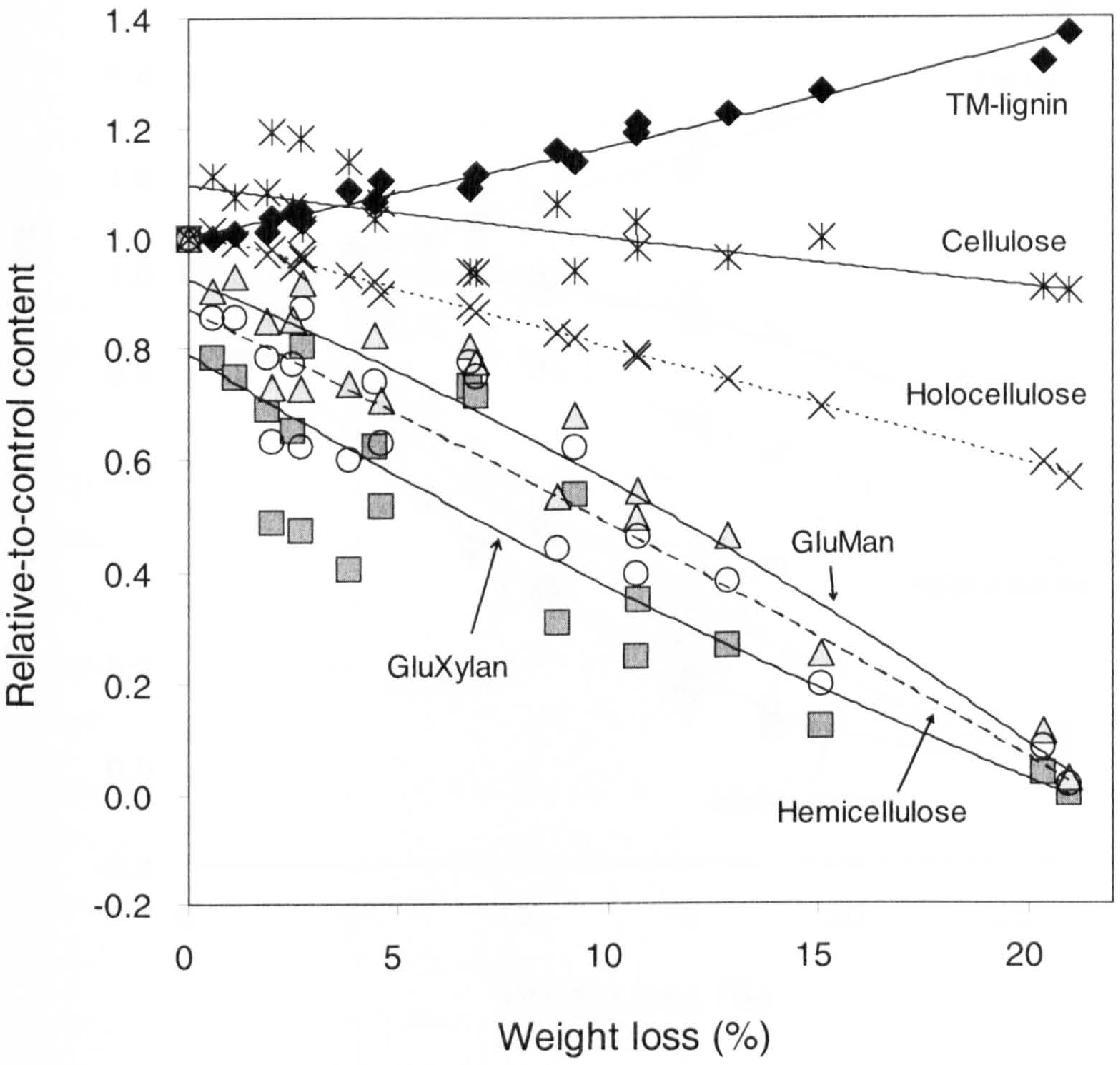

Figure 4.2 Degradation of the main polymers of Scots pine wood upon heating at 190 °C – 245 °C for 0.3 to 16 h. Relative-to-control values of the before-treatment oven-dry weight *vs.* weight loss. ◆ TM-lignin; ■ GluXylan = Arabinoglucuronoxylan; △ GluMan = (Galacto)glucomannan; ○ hemicellulose; ✳ cellulose; × holocellulose

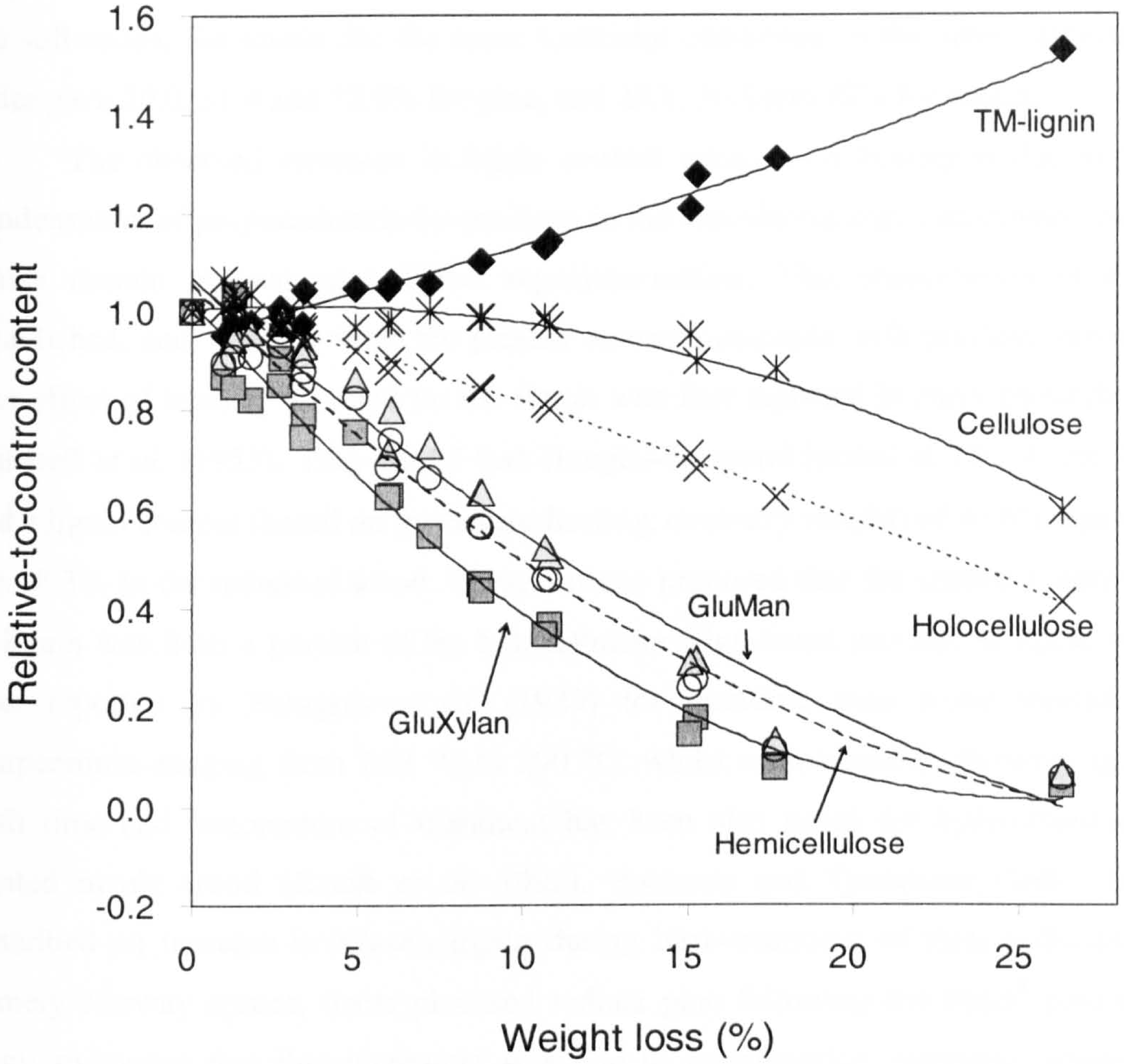

Figure 4.3 Degradation of the main polymers of Norway spruce wood upon heating at 190 °C – 245 °C for 0.3 to 16 h. Relative-to-control values of the before-treatment oven-dry weight *vs.* weight loss. ♦ TM-lignin; ■ GluXylan = Arabinoglucuronoxylan; △ GluMan = (Galacto)glucomannan; ○ hemicellulose; ∗ cellulose; × holocellulose

In beech, the lignin[†] content went from 24.5% in control specimens, to 28.4 and 30.3 % in heated samples for 4 and 16 h at 210 °C respectively (Table 4.1). In the softwoods, the results for the same treatment conditions in the same respective order gave 29.0, 31.4 and 32.8% for pine, and 29.1, 30.4 and 32% for spruce.

The observed increases in lignin content upon wood heating is due to the condensation of polysaccharide by-products in the reticulating lignin macromolecule, which remain trapped upon lignin repolymerisation. This phenomenon is well established, and findings from the present research coincide with previous reports. The effect of heating of wood on the lignin was first reported in early research by Mitchell *et al.* (1953). They found that Douglas-fir wood heated at 200 °C for 4 h had a lignin content (based on the before-heating, oven-dry weight) of 44.6%, against the 28.3% in the unheated wood. These authors proposed that the apparent increase in lignin was from a portion of the holocellulose. Significant increase in lignin was later reported by Bourgois *et al.* (1989) for maritime pine wood treated at temperatures ranging from 240 °C to 290 °C, whilst an increase in dioxane lignin with time and temperature of treatment has been also noted for hydro-thermally treated maple wood (Kacik *et al.* 1992). Boonstra and Tjeerdsma (2006) also described an increase in Klason lignin during heat–treatment of three softwoods, namely Norway spruce, Scots pine and radiata pine following the Plato® process. They suggested that this increment was due to condensation reactions, whereby hemicellulose by-products are available and can contribute to the polymerisation of lignin. Lignin can undergo both depolymerisation and repolymerisation reactions upon heating, specially in aqueous media (Garrote *et al.* 1999). Lignin solubilisation involves both the breaking of lignin-carbohydrate bonds and lignin depolymerisation reactions. For a given temperature, the fraction of solubilised lignin increases with the reaction time to reach a maximum and then decreases. In a first, fast stage, lignin fragments with low molecular weight and high reactivity are solubilised by breaking lignin-carbohydrate bonds. In a subsequent, slower stage, lignin repolymerisation occurs in the presence of organic acids released by the treatment to yield insoluble condensation products. Sugars and sugar degradation products (such as furfural) also react with lignin. The new repolymerised lignin (so-called pseudo-lignin) results in an increased acid-insoluble lignin content in the solid residue (*Idem.*).

[†] The term lignin for TMW is used in this document to describe the acid-insoluble substance plus the substance detected by UV spectrometry at 205 nm, but it is recognised that is not the native lignin.

The quantification of the reduction of the native lignin in the resultant solid residue was not attempted, although this decline could in principle be monitored by the reduction of the methoxyl content (Bourgois and Guyonnet 1988) or by the determination of lignin fractions by thioacidolysis (Windeisen *et al.* 2007).

Changes in the polysaccharides

In beech, changes in all carbohydrate components could be described by a curvilinear profile, except for glucomannan (GluMan), which was fitted to a double first-order non-linear exponential decay model (model not shown) (Figure 4.1). In beech, changes in glucuronoxylan (GluXylan) proceeded steadily in line with the weight loss at any combination of time and temperature, whilst the GluMan content decreased somewhat fast for WL up to 5%, and then kept on declining at a seemingly constant rate, reaching values of zero at a WL of about 20%. The faster degradation of GluMan compared GluXylan in beech was up to certain point unexpected, because xylan is reported to be the most labile hemicellulose in the wood substance (Kass *et al.* 1970), although Rajohnson *et al.* (1994) found clear evidence that pine hemicellulose degraded at a lower temperature (150 °C) than beech hemicellulose (180 °C) heated under identical conditions. Possibly, the chemical breakdown of the GluMan hemicellulose is accelerated by the presence of organic acids liberated in the course of the degradation of the GluXylan fraction, which initially is nearly five times as abundant as the hexosan counterpart. The determinations of GluMan in beech have a relatively large scatter. Thus the apparent greater effect of heat on GluMan could also be the result of the determination procedure, yet the large scatter may in turn arise from differences in polymer breakdown at different temperatures at equivalent levels of WL. The gradual reduction in the total hemicellulose component in beech could be then ascribed to the very similar pattern observed in the dominating fraction of hemicelluloses (GluXylan). Cellulose content in beech remains at comparable levels to that of control samples; changes are recorded up to very high treatment regimes (at WL levels of 16.5 – 18.5%). Hemicelluloses were more rapidly degraded upon heat exposure than cellulose; their greater susceptibility is a result of their amorphous nature and lower molecular weights compared to cellulose (Goldstein 1991). The steady decrease in holocellulose is therefore mostly an effect of the declining hemicellulose component.

The change in polysaccharide composition of softwoods induced by the thermal modification was in essence similar to the corresponding changes induced in beech, but in finer respects different. In softwoods, changes are gradual in all components, and these are defined by a curvilinear profile (Figures 4.2 and 4.3). In comparison to beech wood, the GluMan[‡] change was steady in line with the weight loss at any combination of time and temperature; the same was observed for GluXylan[§]. GluXylan was reduced slightly faster at the beginning of the reaction than GluMan at equivalent levels of WL in both softwoods. Indeed, the reduction of GluMan in spruce wood did not start until the WL of the material reached 2.7%. The rate of reduction was seemingly the same for both hemicellulose types after a WL of about 2.7% in both softwoods; changes in GluXylan show a large scatter in pine, though. The steady reduction in the hemicellulose component could be then credited to the concurrent gradual reduction of each individual hemicellulose type. In contrast to beech wood, the increase of lignin starts at very low levels of modification in softwoods, and the increase is almost rectilinear. On the other hand, the cellulose content remains also at comparable levels to that of control samples, as observed for beech wood. In pine wood, only a small reduction could be observed at the higher WL attained in this study for this species (21% WL). In spruce wood the reduction starts at WL > 15%. In both cases, the decrease in holocellulose is therefore an effect of the declining hemicellulose component for WL < 15%. The observation of uniformity in the nature of the effects of heat on the polysaccharide fraction of Norway spruce wood as a function of WL concords with a similar conclusion drawn from a more limited data by Zaman *et al.* (2000) and Alén *et al.* (2002).

It can be concluded that the weight loss registered in all the three species upon heating was caused mostly by the decomposition of wood hemicelluloses at WL < 15%; at higher WL values the decrease is predominantly due to the reduction of all the polysaccharide fraction. Obviously, the explicit increase in the lignin component in the three woods is at the expense of the holocellulose component, and both profiles act as a mirror images, the lignin increases in relative-to-control values nearly at the same pace as holocellulose declines. It is important to emphasize that the plots in Figures 4.1 to 4.3 are for relative-to-control values, and that the initial content of holocellulose is 2.5 to 3 times higher than the initial lignin element. Not

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[‡] GluMan in softwoods is (galacto)glucomannan

[§] GluXylan in softwoods is arabinoglucuronoxylan all the holocellulose fraction was converted to pseudo-lignin. A similar rate of the pentosan content reduction to that of the lignin increase has been previously reported for small samples of heat-treated maritime pine (Bourgois *et al.* 1989).

Although the reduction of the two main hemicellulose types has not been reported previously for TMW, results from the present study on the changes in the polysaccharide fraction upon heating for both softwoods and hardwoods are in general agreement with previous reports on samples treated in the 140 – 260 °C temperature range (Bourgois *et al.* 1989, Kamdem *et al.* 1999, Zaman *et al.* 2000, Kotilainen *et al.* 2001, Alén *et al.* 2002, Boonstra and Tjeerdsma 2006, Yildiz *et al.* 2006, Inari *et al.* 2007b, Windeisen *et al.* 2007).

In Table 4.1, it can be seen that the sum of the wood components in relation to the initial oven-dry weight of the samples (plus the WL) do not sum up to 100%. A variation of up to ± 3% subsists in most determinations, particularly in softwoods. This is due to the assumptions in the algorithm for computing hemicelluloses from the determination of individual monosaccharides (Janson 1970). An important note on the application of Janson's method in the present study is that the molar ratio of uronic acids is considered to remain unchanged in hemicelluloses upon heating. Although the subject has received little attention, the reduction of these carboxylic groups may be apparently faster than the overall degradation of wood hemicelluloses exposed at temperatures up to 280 °C (Shimizu *et al.* 1971).

Changes of monosaccharides (converted to individual oligosaccharides) have been presented elsewhere (González-Peña and Hale 2007a) and will not be reproduced here for reasons of compactness. A summary of the data for the analysis of monosaccharides is given in Appendix 1.

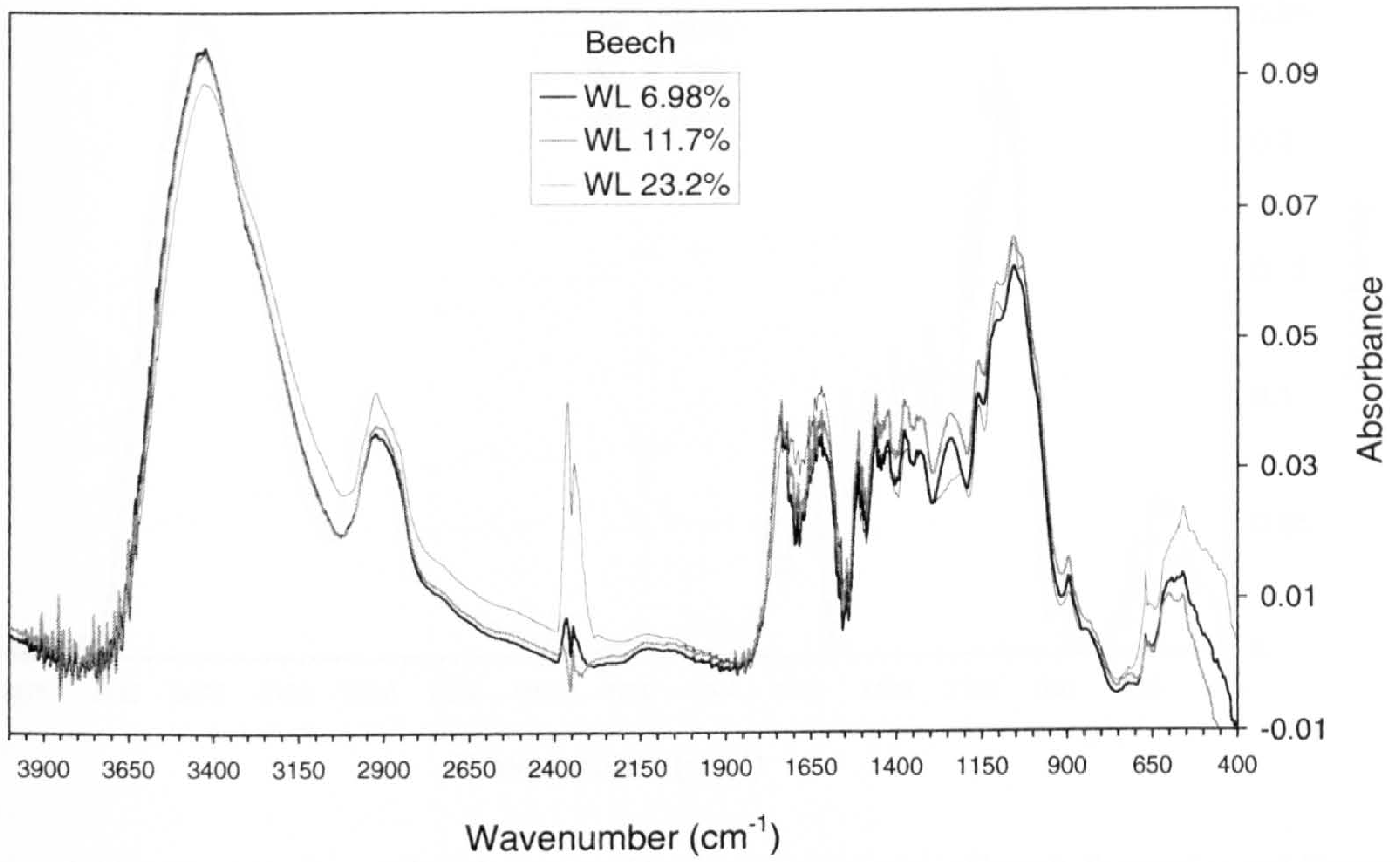
Changes in extractable substances

Despite careful measurements, extractive content after Soxhlet-extraction gave, in some instances, small negative values (most determinations were carried out twice). These results cannot be credited to the experimental error of the measurements, and are considered to be real effects upon the extraction procedure using the standardised solvent combination toluene:methanol:acetone 4:1:1 (v/v). Some solvent molecules probably remained strongly adsorbed to the wood substance and could not be removed by conventional drying at 103 °C ± 2 °C.

No extractives were detected gravimetrically in any of the untreated woods. Significant amounts of extractable compounds were only found in heated beech wood as soon as the WL exceeded 0.50%. These substances increased in synchrony to the severity of the treatment to reach a maximum of about 4% at WL values of about 13.5%. The extractive content declined afterwards at higher levels of WL. In softwoods a similar profile was observed, but the amount of extractable substances was much smaller. In a preliminary experiment (González-Peña *et al.* 2004), it was determined by GC that the main remaining polar substance in heated Ash wood following water extraction was acetic acid. Non-polar extractives were not evaluated, but according to Nuopponen *et al.* (2003), non-polar fats and waxes disappear from heat treated softwoods from 120 to 180 °C; at 200 °C all the resin acids disappear from the heated material. Hence, the extractable compounds were most likely breakdown products remaining somehow in the residue after the thermal modification.

Monitoring chemical changes from FTIR spectroscopy

Despite the overall aspect remaining unchanged, the FTIR spectra of treated wood samples indicate that a number of spectral changes developed due to the thermal modification (Figure 4.4). Two main changes observed in the spectra were an increase in the absorption in the carbonyl region in the range 1750 – 1600 cm^{-1} and, on the other hand, the reduction in the broad, strong OH stretching band centered at around 3400 cm^{-1}. The increased absorption arising from carbonyl groups is attributed to several concomitant changes principally the oxidative carboxylation of polysaccharides (Chow 1971). Lignin condensation at the expense of conjugated carbonyl groups in lignin vibrating at 1654 cm^{-1} (Funaoka *et al.* 1990), and the formation of carbonyl groups due to the opening of the aromatic ring in detriment of the aromatic band at 1508 cm^{-1} (see chapter 7) also contribute to the increased absorbance in the carbonyl region. On the other hand, the band with decreasing absorption centered at 3400 cm^{-1} is for the OH stretching vibration due to intermolecular hydrogen bonding in cellulose (Baeza and Freer 2001). The general reduction in this band may be the manifestation of the loss of OH groups following dehydration upon heating (Tolvaj and Faix 1995).



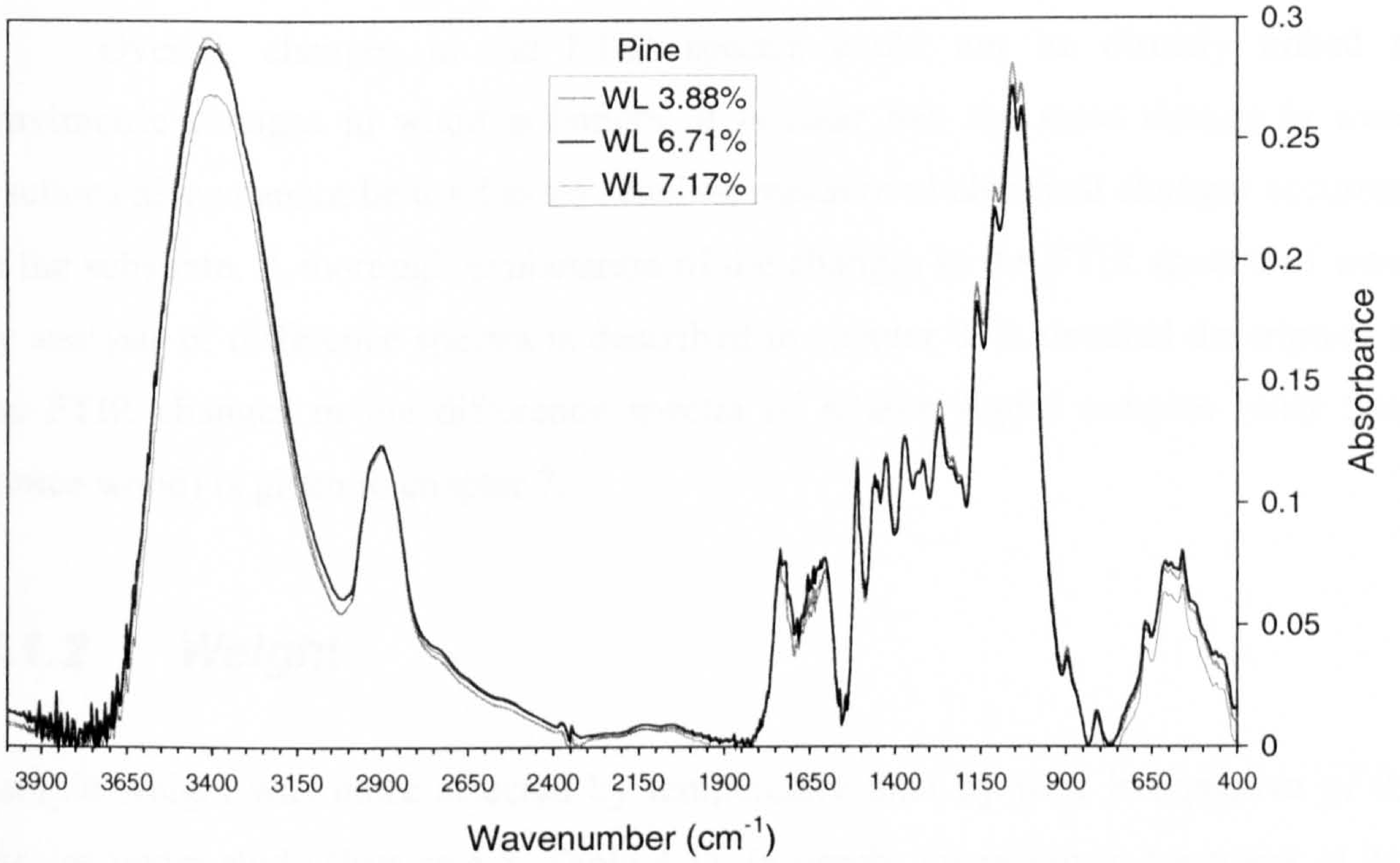


Figure 4.4 Fourier transform infrared spectra of heat-treated samples of beech, Scots pine and Norway spruce samples.

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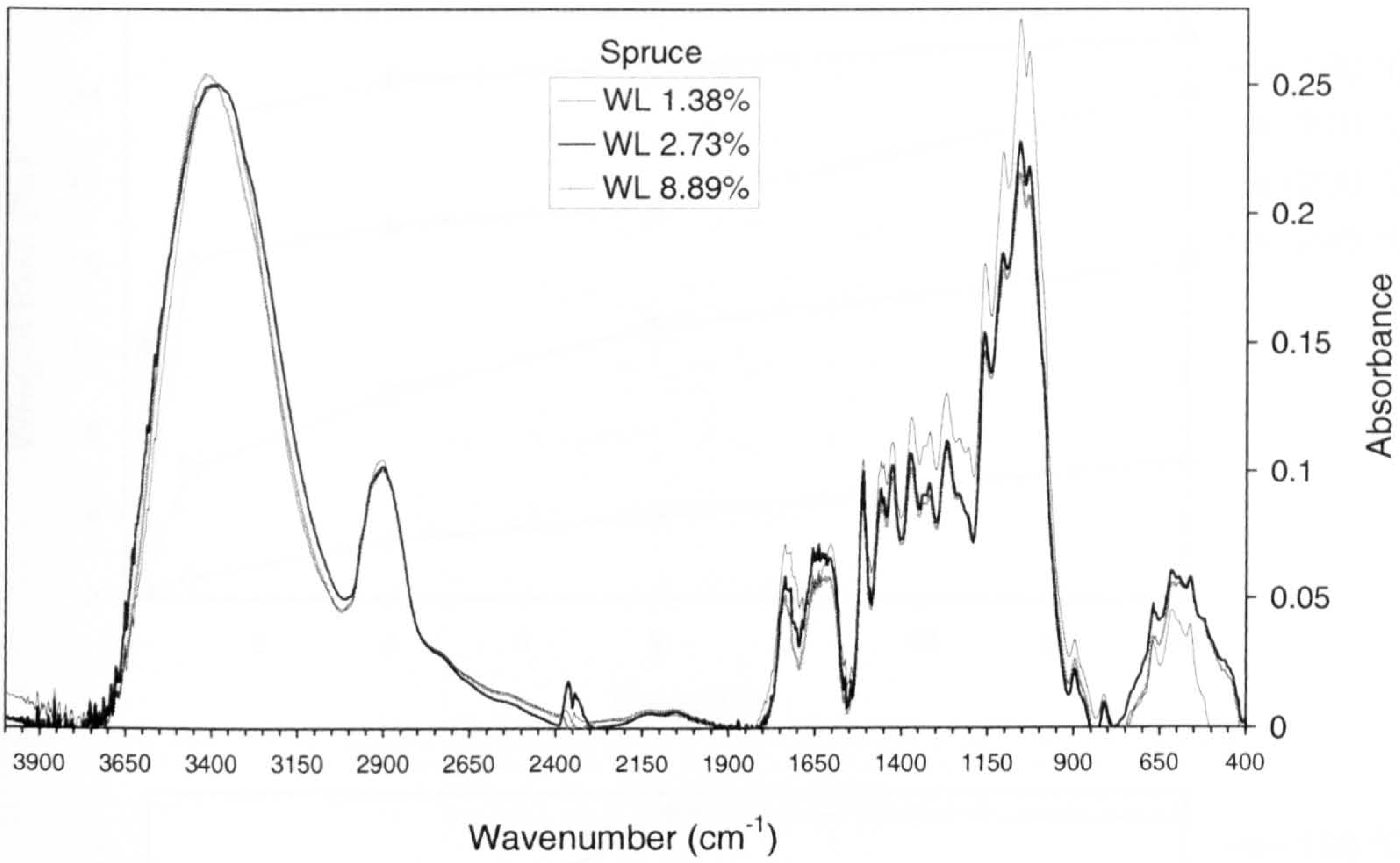
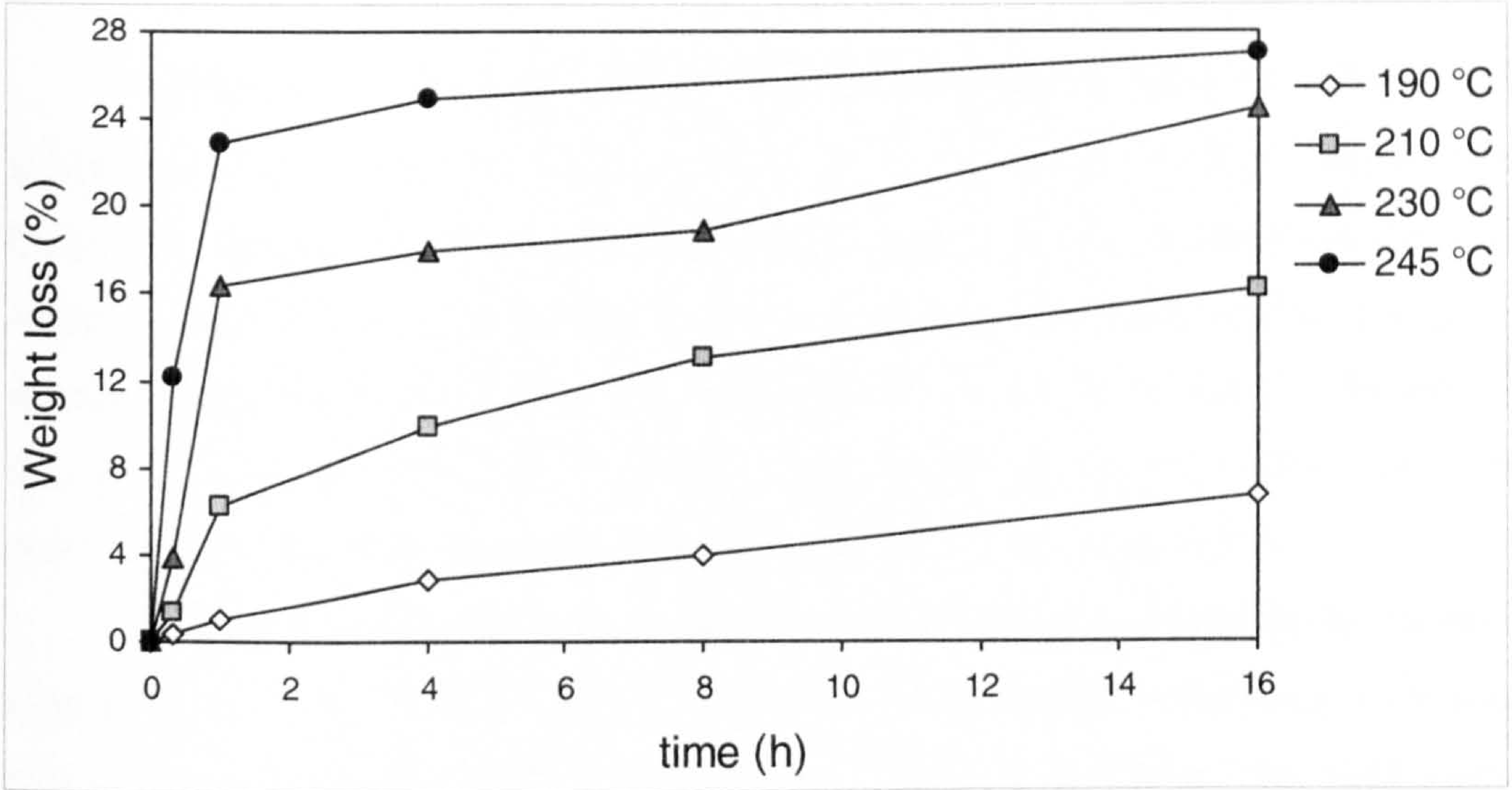


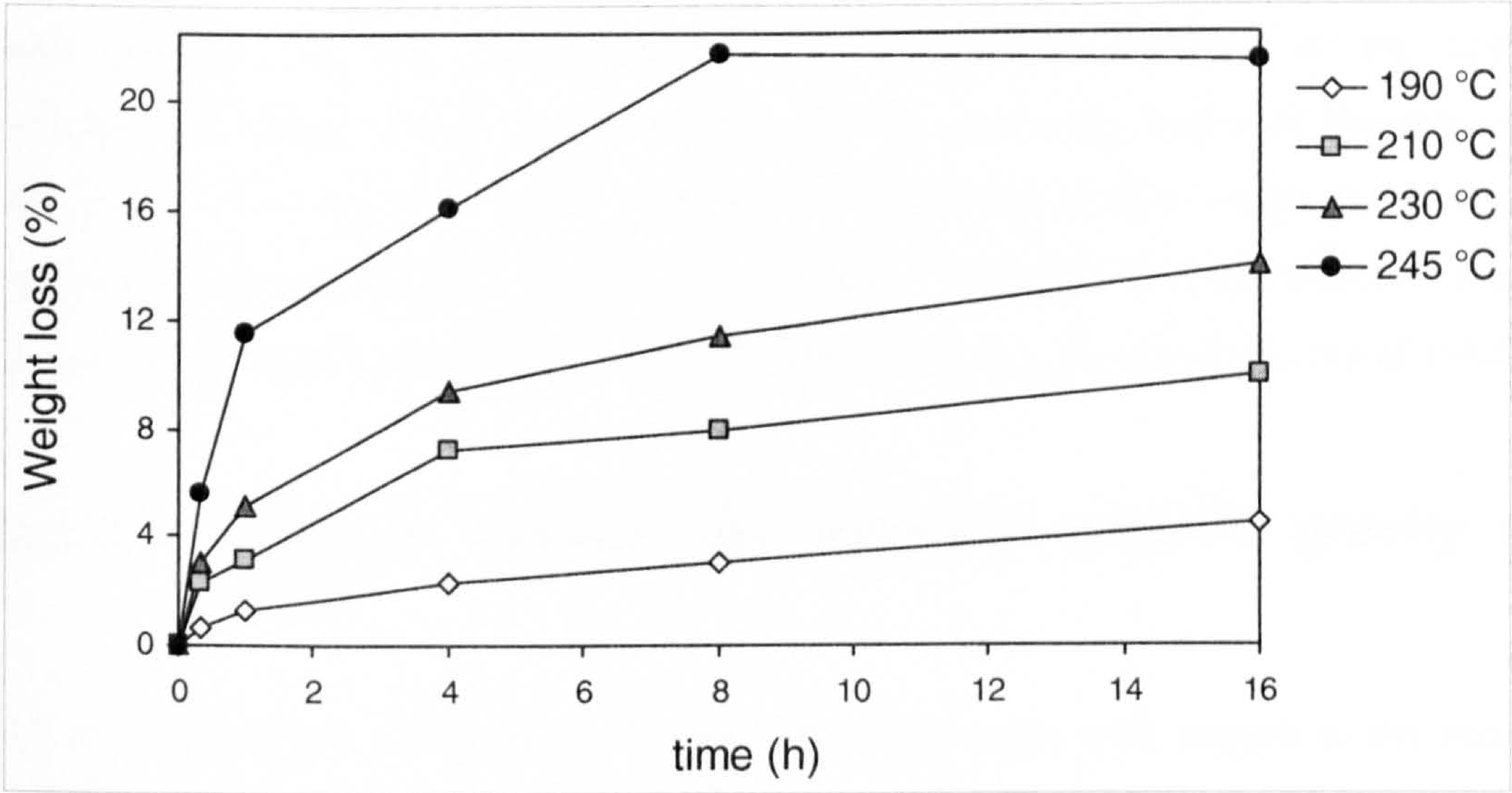
Figure 4.4 Fourier transform infrared spectra of heat-treated samples of beech, Scots pine and Norway spruce samples (*Continued*)

Overall, changes in the FTIR spectra could not be directly linked to gravimetric changes in wood polymers. It is clear that the mass change in wood fractions alone cannot be used as an absolute measure of chemical changes occurring in the substrate. A thorough explanation of the changes in the FTIR spectra of wood by analysis of difference spectra is described in chapter 8. A detailed description of the FTIR changes in the difference spectra of Klason lignin samples (only from spruce wood) is given in chapter 7.

4.1.2 Weight

Sample weight was more affected by temperature than by time irrespective of the species under study (Figure 4.5, Table 4.1). In beech, for instance, treatment at 210 °C for 16 h led to a WL of 16.2%; at 230 °C, the same loss occurs after 1 h. WL between softwoods was similar at equivalent levels of treatment, although spruce wood showed slightly lower levels of WL at any given combination of time and temperature than pine wood. In the softwoods, WL was significantly smaller than that in beech (Table 4.1).





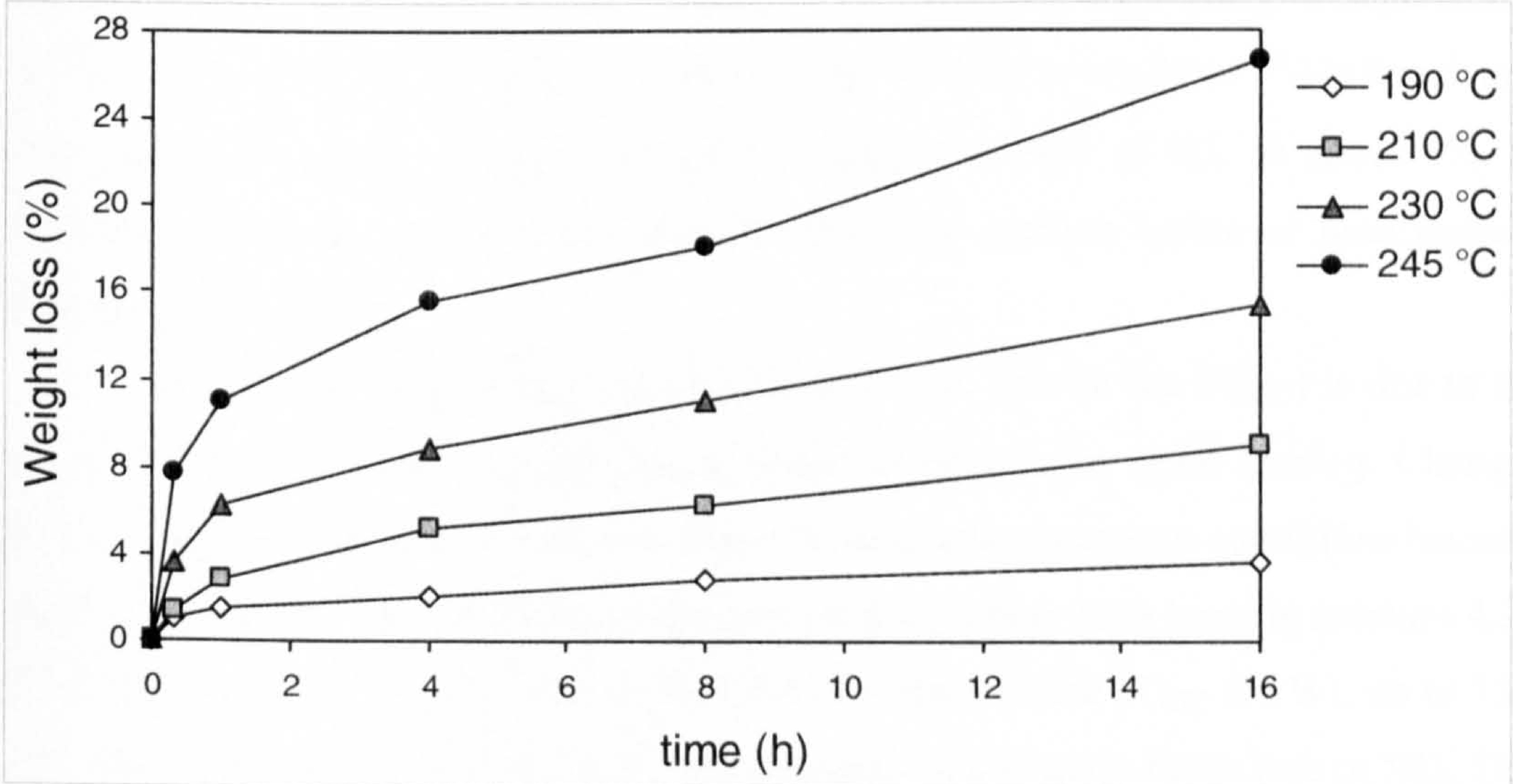


Figure 4.5 The effect of time of heating on the weight loss (%) of beech, Scots pine and Norway spruce woods (from top to bottom) treated at 190, 210, 230 and 245 °C in N_2. Each symbol is the mean value of 44 replicates. Error bars omitted for clarity (shown in plots in Appendix 2)

Apparently, the larger WL in beech compared to that in softwoods at equivalent conditions was basically linked to its proportionally larger initial GluXylan content. Moreover, the initial higher lignin is also involved in the lower thermal susceptibility of softwoods, since a higher initial lignin content retards the thermal degradation of other wood components (Sawabe *et al.* 1968). The ratio of WL to ND change was approximately 3:1, because specimens shrank due to the treatment partially making up the volume of the mass loss (section 4.2).

Regardless of the species, weight loss at any given temperature levels off at longer times of exposure (Figure 4.5). This has been reported previously for heat-treated woods (Bourgois and Guyonnet 1988, Zaman *et al.* 2000). The input energy and possibly the heat energy emitted by exothermic reactions at the upper temperature range breaks the weakest bonds first, at early stages of the reaction (Bourgois and Guyonnet 1988). After a first depolymerisation stage the material undergoes repolymerisation reactions in the lignin molecule. This resinification leads to an increasingly heat-stable structure (Nikitin 1966, Bourgois and Guyonnet 1988).

4.1.3 Nominal density and oven-dry specific gravity of wood

The nominal density of wood (ND) changed curvilinearly with respect to the extent of the treatment in all three species, whilst SG_{OD} declined rectilinearly in dependence of the WL (Figure 4.6). Changes are fairly small for WL up to about 7% in beech and pine, while in spruce wood ND reductions appear to start at WL of about 4%. In contrast, the SG_{OD} was reduced steadily from the earliest levels of modification attained in this study.

As indicated above, the reduction in ND (and also in the SG_{OD}) is due to the mass loss caused by the evaporation of wood carbohydrates upon heating. Changes in ND and SG_{OD} were much smaller than WL at similar treatment conditions because the wood material also shrinks in the transversal direction upon heating (section 4.2). The reduction of ND occurs at a slightly slower rate than the SG_{OD} for WL up to 13 – 15% (Figure 4.6), and then the reduction proceeds at a slightly faster rate in ND. This behaviour has a complex background, because the wood material becomes increasingly hydrophobic as the extent of the treatment increases (chapter 6).

Therefore, the water adsorbed at 65% RH, 20 °C (in % of the oven-dry weight of the sample) is reduced in line with the WL, and the ND is therefore not only reduced by the change in mass, but also due to wood's increasingly hydrophilic character. On the other hand, inasmuch as the SG_{OD} declines due to an increasing overall void space in the solid wood material, the thermal conversion is also accompanied by a slight densification of the cell wall substance at low levels of modification (section 4.1.4), resulting in the overall complex comparison of the profiles observed in these two density parameters. Mean comparisons between control and individual treatments showed that most of the differences in ND and SG_{OD} were not significant, though. This will be discussed further in section 5.1.1, chapter 5.

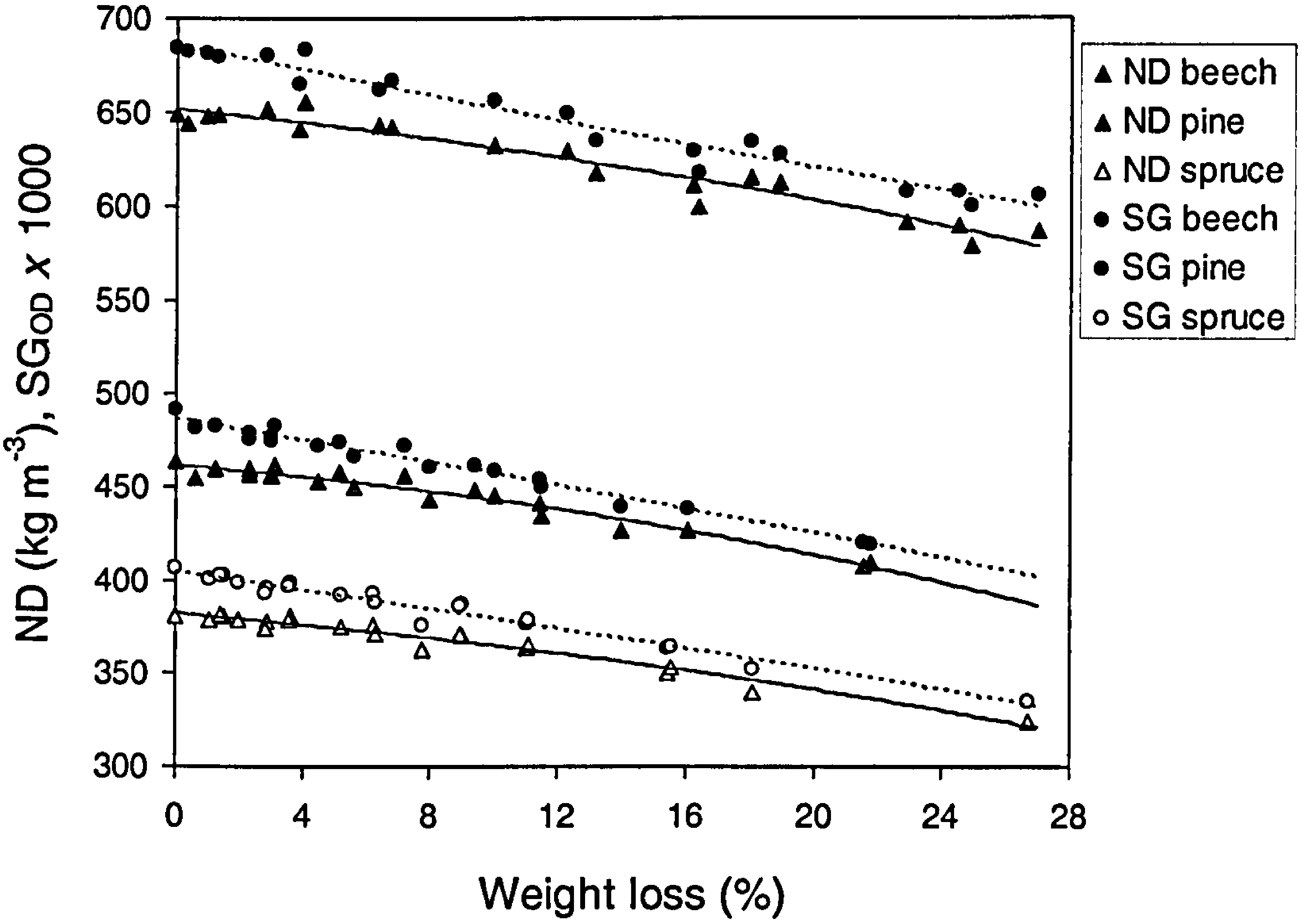


Figure 4.6 The effect of heat-induced weight loss in nominal density (ND) and oven-dry specific gravity (SG_{OD}) in small samples of beech, Scots pine and Norway spruce wood treated in the 190 – 245 °C temperature range for 0.3 to 16 h in N_2 atmosphere. Each symbol is the mean value of 44 replicates. Error bars omitted for clarity

4.1.4 Specific gravity of the cell wall substance

Changes in the specific gravity of the cell wall substance, SG_{CW}, did not show a very clear modification pattern, and the behaviour was species-specific. In beech and pine, no change could be discerned for WL up about 16 – 19%. In spruce, the changing profile was complex; this parameter declined following a sigmoid profile, falling somewhat rapidly by 1.5% at WL values up to 5%, and then remained nearly unchanged up to the most severe treatment tested in this work.

Although the reason for this behaviour is difficult to assign in each species, it is evident that it does not follow the same profile as for the reduction of the carbohydrate fraction (nearly rectilinear with the increase in WL, Figures 4.1 to 4.3), neither follows the trend of the lignin content in the solid residue, because the latter increases directly with the WL also in a closely rectilinear manner. Thus other factors should be involved in the changes observed.

If the oven-dry specific gravity of each of the main constituent of the cell wall substance are used (Kellogg 1979), and the final chemical make up of the residue utilised for computations, the theoretical SG_{CW} change in this parameter is remarkably similar to that measured for pine wood (Figure 4.7), but with somewhat larger variations in the other two species. As seen in Figure 4.7 the changes measured are fairly small, and this can account for the difficulties in determining the changes in beech and spruce woods.

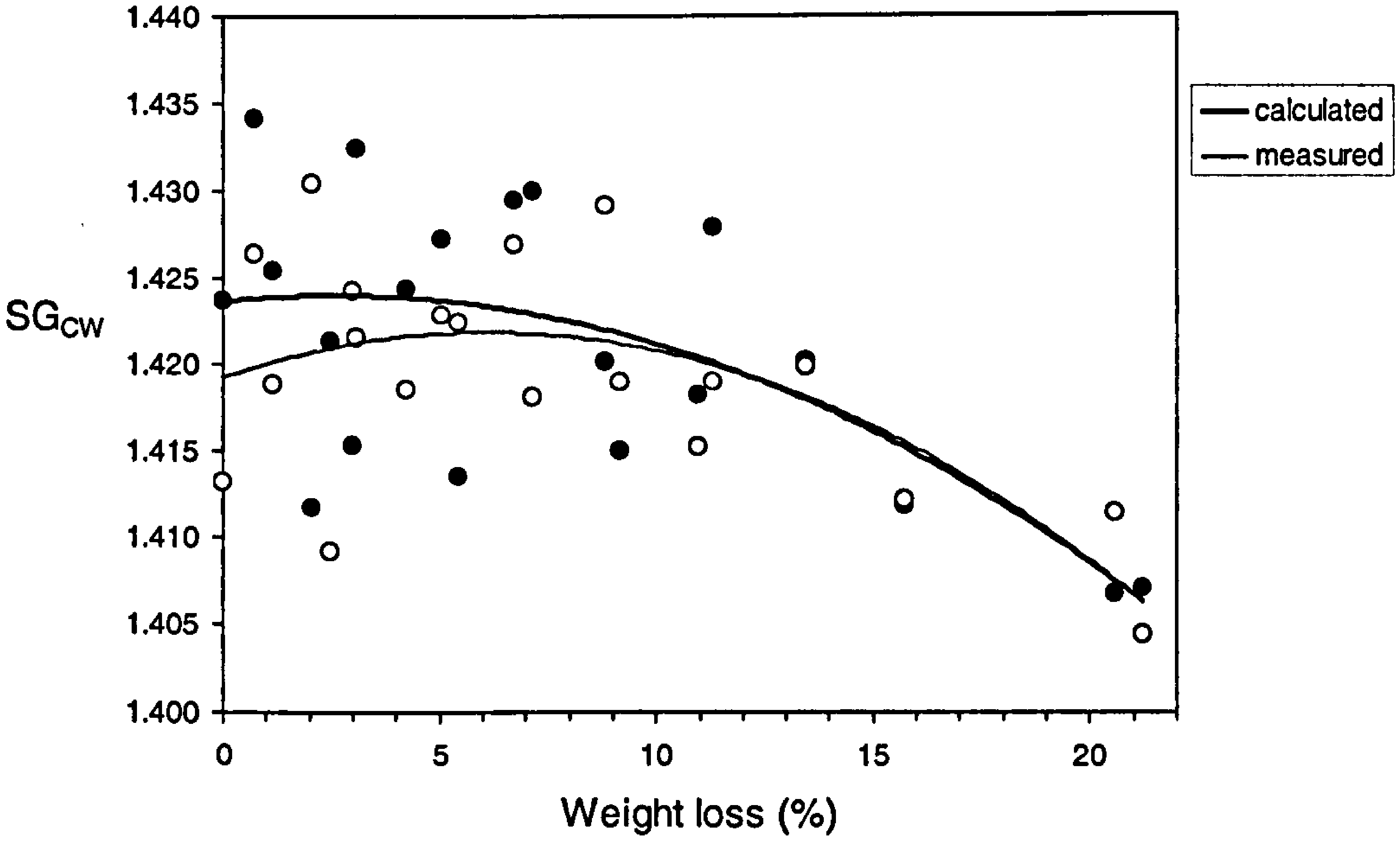


Figure 4.7 Changes in the specific gravity of the cell wall substance SG_{CW} in function of the heat-induced weight loss in samples of Scots pine wood. O measured, ● calculated from the specific gravity of individual wood polymers given by Kellogg 1979

Based on the measured values in pine wood, the SG_{CW} appears to increase slightly up to WL of about 7.2%, and then tends to decline to reach control values at a WL of about 16% (Figure 4.7). This indicates that the cell wall substance suffers somewhat a slight densification upon heating for WL up to 16% in pine wood, although this appears to be more linked to the resultant make up of the material that to structural changes in the arrangement of the wood polymers. However, the measured SG_{CW} displays a clear tendency to increase at early levels of modification, opposite to the profile for the theoretical SG_{CW}, which remains mostly unchanged and then declines slowly after reaching a WL of about 6%. Possible causes for this slight densification are that the reduction of intermolecular spaces has taken place (*i.e.* the densification of the cell wall as a whole) and/or that each component has suffered a densification on its own whose density increase was transmitted to the overall densification of cell wall material.

4.2 Dimensional changes due to heating

4.2.1 In the transverse plane

Changes in dimensions in the radial and tangential planes in relation to the heat-induced WL are shown in Figure 4.8. Heating of wood decreased the oven-dry transverse dimensions of the test specimens. The reduction in both the radial and tangential directions was rectilinear as a function of the WL. Reduction in the transverse plane was nearly two times greater than that of the radial plane, as seen from the slopes of the regression equations of trend lines in Figure 4.8. These results are in good agreement with previous observations of Seborg *et al.* (1953), McGinnes *et al.* (1971), Fung *et al.* (1974) and Chang and Keith (1978). The reduction in the transverse dimensions show the same order of anisotropy (a ration 2:1 in the tangential to radial plane) to those changes observed in response to the reduction of the EMC below the FSP (Dinwoodie 2000). Many factors have been put forward for being responsible for the movement anisotropy in untreated wood, but most of them do not appear to apply to all species. The dominant factor for this phenomenon is probably the differential chemical composition at both planes in the sclerenchyma cells (Boyd 1972, 1982).

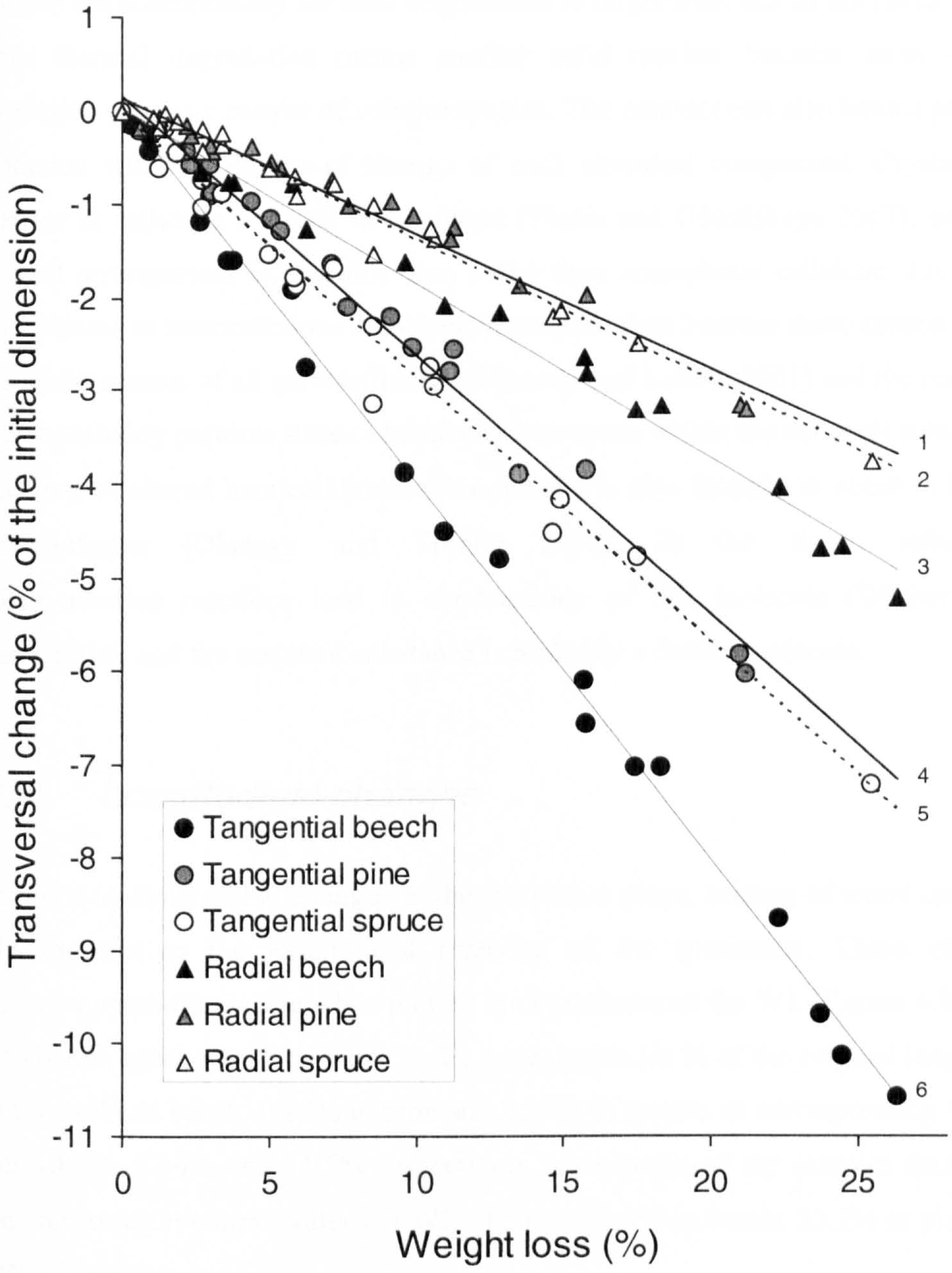


Figure 4.8. Changes in the transverse plane in dependence of weight loss for thermally-modified samples of beech, Scots pine and Norway spruce woods. Each symbol is the mean value between 36 and 44 sample replicates. Solid line, pine; broken line, spruce; hairline, beech. Lines slopes: 1 = -.015, 2 = -0.15, 3 = 0.19, 4 = -.028, 5 = -.028, 6 = -0.40

The dimensional changes caused by the heat treatment appear to support Boyd's postulates that the chemical make up of the wood tissue at each plane is the primary factor behind the anisotropy in adsorption, beyond and above the arrangement of the wood tissues or the presence of rays in the wood tissue. In the radial walls cells may have more lignin than in the tangential walls (Boyd 1982). It follows that the carbohydrate fraction at the tangential plane is probably greater and therefore the susceptibility for heat degradation is larger than that at the radial plane. Larger thermal degradation means smaller solid residue, because most of the degradation products consist of volatile species. The contractions also have a primary connection with the degree of change of each chemical component. Crystallinity increases in cellulose are well documented (Yildiz and Gümüşkaya 2007), and this modified arrangement is probably less bulky than amorphous cellulose. Likewise, sugars related to hemicellulose branches decompose first because these consist of the most labile species of all carbohydrates (Winandy and Lebow 2001) and the resultant product probably requires stereo-chemically less space within the cell wall substance. Annealing of altered hemicelluloses upon heating is also thought to occur in heated lignocellulosics (Obataya and Tomita 2002). In the lignin substance, repolymerisation reactions lead to condensation of this molecule (Wikberg and Maunu 2004), and the resultant substance is probably a denser molecule.

4.2.2 Longitudinal changes

In contrast to dimensional changes in the transverse plane, heating of wood caused a slight increase in the longitudinal direction of the specimens. These changes followed a parabolic profile when plotted in dependence of the WL (Figure 4.9). The length of the specimens increase to reach a maximum (in % of the original length) of about 0.045% in beech, 0.12% in pine and 0.14% in spruce, at corresponding WL of about 10.1%, 12.4% and 11.5% respectively. The length of the samples decreased thereafter to reach control values at WL of about 20.9% in beech, 23.2% in pine and 21.2% in spruce.

The expansion in the longitudinal direction appears to be strongly correlated with the magnitude of the changes in the transverse direction for WL up to about 10%. A multiple linear regression of the longitudinal increase of both the radial and transversal planes for WL ≤ 10%, leads to the finding that the change in the longitudinal direction could be significantly predicted from the changes in the transverse direction in each softwood, and from changes in the tangential direction in beech wood. In spruce wood, for instance, the coefficients for the model were of 0.022 and 0.020 for the radial and the tangential direction respectively.

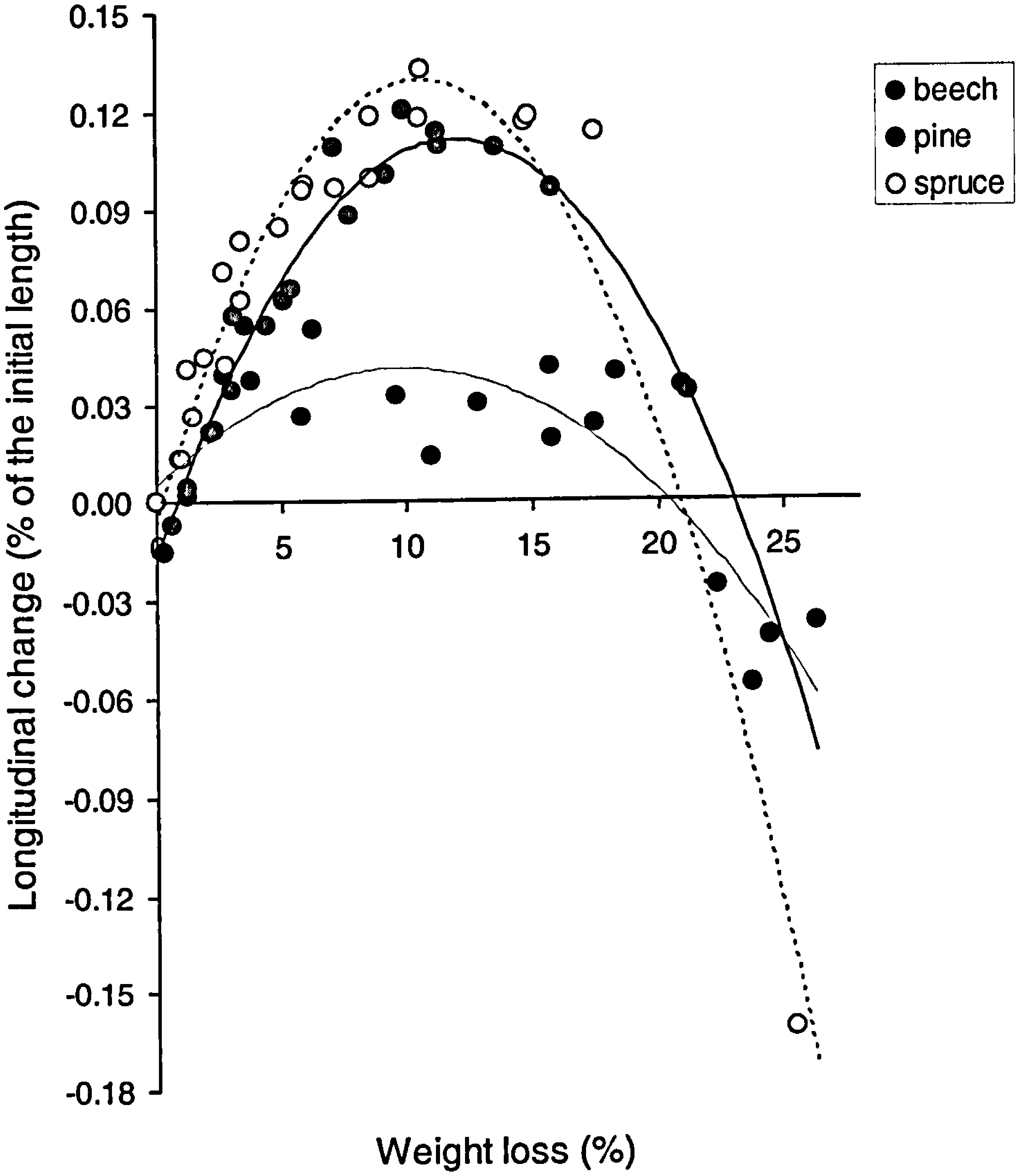


Figure 4.9. Longitudinal changes in small samples of heat-treated beech, Scots pine and Norway spruce woods. Each symbol is the average value between 36 and 44 sample replicates. Solid line, pine; broken line, spruce; hairline, beech

Interestingly, these values are of the same kind of magnitude of the Poisson ratios** for the radial and tangential plane of solid wood when it is stressed in tension along the longitudinal axis, $\nu_{RL} = 0.041$ and $\nu_{TL} = 0.033$ respectively (Bodig and Jayne 1982). In pine similar coefficients in the model were found, but in beech these coefficients were one order of magnitude smaller than in softwoods; the measurements were more difficult to perform in the latter species due to a marginal

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** When wood is subject to a mechanical stress causing for instance a longitudinal elongation, lateral contraction occurs in the sample. The deformation in the direction of the force, *a*, is sometimes termed active deformation, whilst the normal to the direction of the force, *b*, is the passive deformation. The ratio of passive to active strain $\gamma b/\gamma a$ is defined as the Poisson's ratio, denoted by ν_{ab}.

deformation of the material as a result of the treatment, though. These findings provide some evidence that the heat-treatment keeps the cell wall material in a permanent, irreversible strained state. A similar suggestion was made in earlier research by Chang and Keith (1978), who also found a small longitudinal increase in their study of four heat-treated hardwood species (elm, aspen, maple and beech).

Increasingly higher levels of treatment resulted in specimen shortening. This effect was observed at very high levels of WL (> 20%) and is related to the overall pyrolysis of the material (Bellais *et al.* 2003) or to the offset of the stress-induced longitudinal expansion due to increasingly higher levels of thermal degradation.

4.3 Modelling gravimetric changes

4.3.1 Weight loss (WL)

In chapter 5, modelling of WL from process parameters (T and t) is carried out by using the severity factor approach, a novel method for the determination of physical and chemical changes in thermally modified woods. In this section, WL is modelled using the Arrhenius empirical equation relating the rate of change to temperatures between 190 and 245 °C.

The Arrhenius equation can be written as (Equation 4.1);

$$\log R = k_1 + k_2/\mathrm{T} \qquad \text{[Eq. 4.1]}$$

where R is the rate of change of the oven-dry weight due to the thermal exposure, T is the absolute temperature, and k_1 and k_2 are model constants. R can also be the time necessary for a given fractional change in the weight to occur. Then the value of R at any given temperature within the temperature range used in this study can be determined by interpolation. The value of R can alternatively be estimated at both lower or higher temperatures than that used in this work by extrapolation.

The Arrhenius plot of the influence of temperature on the time required to attain a WL of 5% is given in Figure 4.10 for the three wood species studied. Equations for the fitted lines are given in Table 4.2. The data points were obtained by simple linear interpolation using the data in table 4.1 to determine the times required to sustain a WL of 5% at any given temperature of treatment, except for the WL of 5% at 190 °C, which were found by extrapolation in pine and spruce. The data obtained for the four temperatures of exposure is in reasonably good alignment, and could be used for forecasting the weight loss incurred at treating temperatures ideally within the range used in this work. Data in Table 4.1 can be used to compute the equations for a family of curves for the time required to attain any given level of WL within the range of WL obtained in this study.

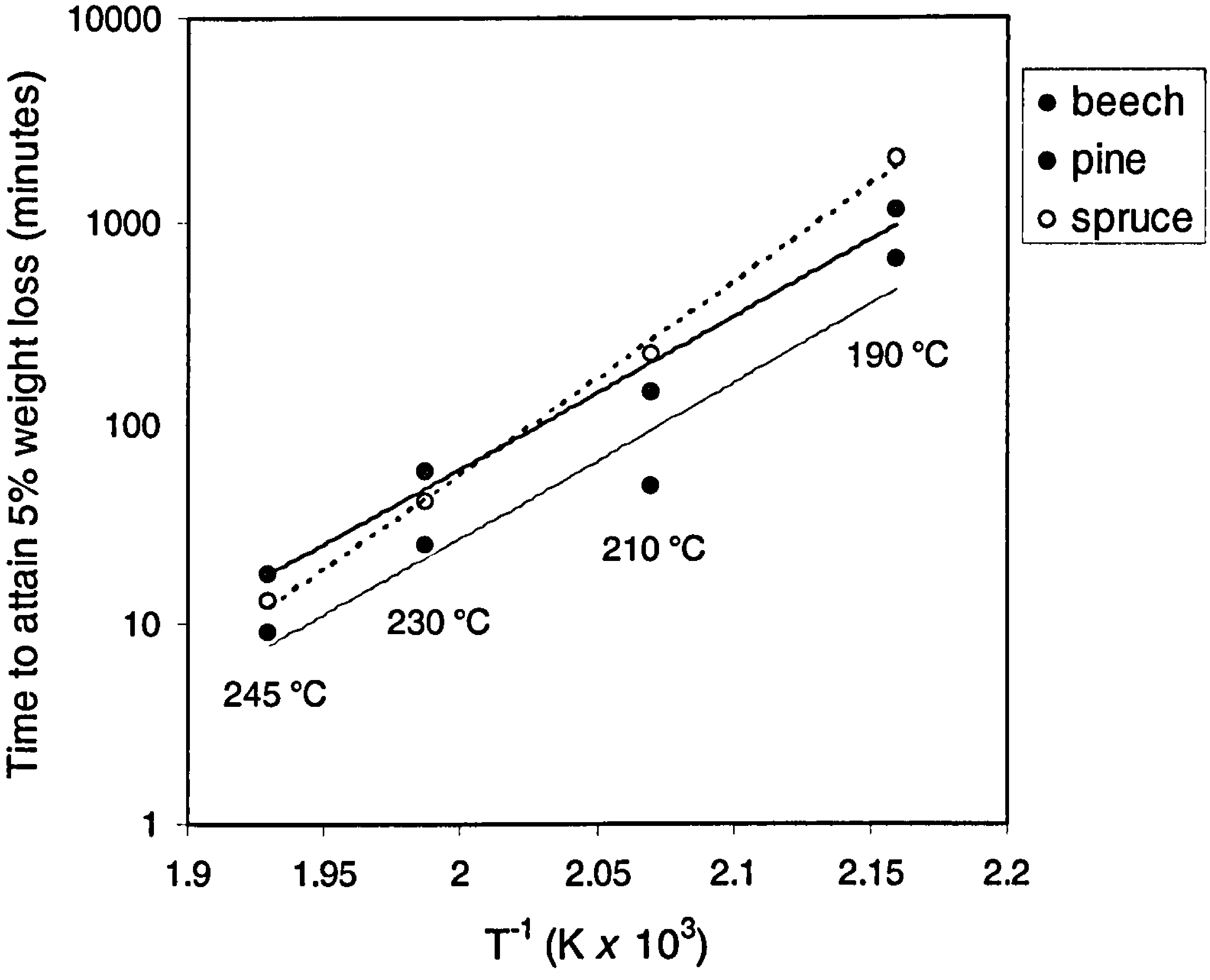


Figure 4.10. The influence of temperature of the time required to attain a WL of 5% in small samples of beech, Scots pine and Norway spruce woods. Each point is the mean value of 44 replicates

Table 4.2. Models derived form the Arrhenius relationship to estimate time to reach 5% WL in three heated woods.

Species	Response[a]	Predictor	R^2	b0	b1
Beech	$\log_{10} R_{.05WL}$	Temperature (K)	0.944	-13.998	7,715.8
Scots pine	$\log_{10} R_{.05WL}$	Temperature (K)	0.982	-13.268	7,525.3
Norway spruce	$\log_{10} R_{.05WL}$	Temperature (K)	0.998	-17.242	9,495.3

[a] $\log_{10} R_{.05WL}$ = the 5% WL lifetime in minutes

All models of the form y = b0 + b1·1/x

A model from the same type of analysis carried out previously for a set of small specimens of four softwoods and two hardwoods, heated at lower temperatures of exposure (115 – 175 °C) than in this work gave, for instance, that the time required at 190 °C to attain a WL of 5% is 629 minutes (Millet and Gerhards 1972). This compares reasonably well to the values obtained for beech wood in this study (650 min.) but underestimates the time required to get a 5% WL for each softwood, 1121 and ~2000 minutes for pine and spruce, respectively. At higher temperatures the model of these authors tend to be more in line with the times calculated for softwoods in the present study, but overestimates the time required to reach the 5 % WL in beech wood. As pointed before, Millet and Gerhards used lower temperatures than the ones in this work, so the extrapolation at much higher temperatures may introduce some error in the predictions using their model. However, the largest source of variation in the results using their model compared to the ones computed in this work is that they averaged the results of hardwoods and softwoods for building their equation. As it has been shown in Table 4.1 and Figure 4.5, the weight loss in beech is significantly larger than the one in softwoods at any given temperature, regardless the time of exposure.

Green *et al.* (2003) have previously compared the experimental results of heat-exposed large wood members to extrapolations using an analogous model obtained by Millet and Gerhards (1972) for residual MOR in bending. Green *et al.* also found that the model of Millet and Gerhards underestimated the loss incurred when samples of solid-sawn lumber, LVL or LSL were exposed by long periods of time at temperatures of 66 °C at 75% RH or at 82 °C at 30% RH. This may indicate that the models of Millet and Gerhards obtained from a mixed set of species do not directly apply to other woods treated at different combinations of time and temperature.

4.3.2 Nominal density and specific gravity of wood

The prediction of the ND or the SG_{OD} of wood is an important subject of study, because in untreated material, density is perhaps the single most important physical characteristic in solid wood (Saranpää 2003). This is because wood density is directed related to many of its physical properties and it can be used indirectly to determine some moisture-related interactions in solid wood specimens (Walker *et al.* 1993, Dinwoodie 2000).

It has been shown graphically in Figure 4.6 that there is a strong relationship between WL and density parameters (ND and SG_{OD}) in small samples of heated woods. Table 4.3 shows the models and statistics for a linear regression of these parameters on WL and on dimensional changes in the transverse direction.

Table 4.3. Least-squares linear models for the prediction of density parameters from weight loss and from changes in dimensions in the transverse plane in small samples of heated beech, Scots pine and Norway spruce woods (*** $p < 0.001$)

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	n^a
Beech	ND	WL	0.941	135.1 ***	651.80	-1.627	-0.040	6.44	20
	ND	TCh	0.932	247.5 ***	64.47	672.83	-----	6.69	20
	ND	RCh	0.924	219.3 ***	653.87	1,421.2	-----	7.08	20
	SG_{OD}	WL	0.959	425.9 ***	0.686	-0.00325	-----	0.0062	20
	SG_{OD}	TCh	0.951	352.1 ***	0.685	0.820	-----	0.0068	20
	SG_{OD}	RCh	0.932	246.9 ***	0.684	1.722	-----	0.0081	20
Pine	ND	WL	0.954	186.2 ***	461.38	-1.279	-0.055	3.67	21
	ND	TCh	0.954	397.1 ***	463.60	900.81	-----	3.56	21
	ND	RCh	0.963	497.9 ***	462.59	1,711.9	-----	3.19	21
	SG_{OD}	WL	0.974	722.9 ***	0.487	-0.00308	-----	0.0033	21
	SG_{OD}	TCh	0.970	624.4 ***	0.485	1.126	-----	0.0036	21
	SG_{OD}	RCh	0.961	473.9 ***	0.484	2.121	-----	0.0041	21
Spruce	ND	WL	0.957	198.1 ***	382.55	-1.460	-0.031	3.34	21
	ND	TCh	0.910	192.5 ***	384.55	778.28	-----	4.67	21
	ND	RCh	0.923	227.8 ***	382.55	1,462.5	-----	4.33	21
	SG_{OD}	WL	0.965	520.6 ***	0.406	-0.00268	-----	0.0036	21
	SG_{OD}	TCh	0.928	246.3 ***	0.405	-0.956	-----	0.0051	21
	SG_{OD}	RCh	0.931	257.4 ***	0.403	1.788	-----	0.0050	21

[a] each element in n is the mean value of 44 samples for WL, and from 36 to 44 samples for TCh and RCh.

ND = Nominal density at 65% at 20 °C; SG_{OD} = oven-dry specific gravity; WL = weight loss; TCh = dimensional change in the tangentail direction; RCh = radial change in the radial direction

Units: ND, kg m^{-3}; SG_{OD}, unitless; WL, %; tangential and radial changes, % of the initial oven-dry measurement

Model for ND on WL of the form $ND = b0 + b1 \cdot ND + b2 \cdot ND^2$

All other models, of the form $y = b0 + b1 \cdot x$

All coefficients significant at $p < 0.05$, except for b2 in the model for ND on WL in Beech, $p < 0.10$

In terms of the coefficient of determination, R^2, WL was in general the best predictor of each density parameter. However, the reductions in the tangential and radial plane have a predictive power comparable to WL; in fact, changes at the radial plane in pine wood gave marginally better predictions of ND than WL (Table 4.3). The good relationship between WL and density changes is attributed to the dependence of these parameters on the mass change of the treated material.

4.4 Conclusions

Upon thermal modification, small samples of three wood species behaved in a similar way in their gravimetric and dimensional changes. All three woods presented reductions in their oven-dry weight in line with the severity of the treatment. This reduction was more marked by increasing the temperature of exposure than by longer periods of treatment. It is demonstrated that the mass loss in the solid wood material is mostly the result of the reduction of the polysaccharide fraction. Beech samples exhibited higher weight losses than softwoods at equivalent periods of treatment regardless of the exposure temperature. This difference was explained by the larger hemicellulose content of beech wood. The lignin increased with the severity of the treatment at the expense of the carbohydrate component.

Corresponding reductions in ND and SG_{OD} were about one third of that for WL at any combination of time-temperature of treatment. This was attributed to the reduction in the dimensions in the transverse direction of the samples following thermal modification. All three species showed this transverse contraction upon heating. Concurrently, heated specimens exhibited a length-wise increment to reach maxima of about 0.05 – 0.10% of the original length of the sample at WL of around 10 – 12%. Net longitudinal shortening was observed only at very high levels of WL. It is concluded that the reduction in the transverse plane of the wood specimens is due to a suite of physical and chemical changes. These include the volatilisation of wood components and a slight densification of the cell wall substance. Some evidence to support this was presented from measurements of the density of the cell wall material by helium pycnometry, and by the strong correlation of the length-wise increase with the contraction in the transverse plane in the samples upon heating.

Solid wood density parameters (ND, SG_{OD}) were readily predicted by measurements of the heat-induced weight loss or by changes in the tangential or radial planes with highly significant models. In turn, the prediction of discrete steps of WL from treatments parameters (time and temperature) can be efficiently accomplished in the each species using a model derived from the Arrhenius relationship.

Chapter 5 Mechanical performance of TMW and its relationship with chemical changes

5.1 Introduction

During the thermal modification of wood, the response of wood strength to various combinations of temperatures, heating periods and media of treatment has been the subject of a number of studies in the recent years (Mitchell 1988, Kim *et al.* 1998, Kubojima *et al.* 2000, Bekhta and Niemz 2003, Shi *et al.* 2007). While the nature of the heat-induced changes in chemical structures has also been examined by a number of authors (Bourgois and Guyonnet 1988, Bourgois *et al.* 1989, Zaman *et al.* 2000, Kotilainen *et al.* 2001, Alén *et al.* 2002, Boonstra and Tjeerdsma 2006), little information is available on the relationship between the progressive changes in mechanical properties to the concurrent changes in chemical composition. To the knowledge of the author, only the work of Davis and Thompson (1964) has partly dealt with this matter; they studied the effect of chemical changes on the toughness of modified wood.

The primary concern of this chapter is to present the results and discuss the effect of thermal modification on the mechanical properties, and examine the relationship of these with chemical changes. Six properties were measured to describe the mechanical behaviour of the material, according to BS 373 (BSI 1957) and BS EN ISO 179 (BSI 1997): Janka hardness (H), shear strength (S), Charpy impact strength (IS), compression strength parallel and perpendicular to the axis (CA and CE respectively), and bending strength. From bending strength, modulus of elasticity (MOE), modulus of rupture (MOR), resilience (R), work to maximum load (WML) and total work (TW) were computed. The mechanical characterisation also included other secondary bending strength parameters, namely the horizontal shear stresses on the neutral plane at the limit of proportionality (SSLP) and at maximum load (SSML), and the fibre stress at the limit of proportionality (RLP). Weight loss due to the treatment (WL) was used as the independent variable for the comparisons.

Firstly, mechanical strength changes resulting from the thermal conversion are presented for each property at a time. This presentation follows the same format for each property and thus some repetition may be unavoidable. Then the relationship between mechanical changes and the correspondent changes in chemical composition is described. The second half of this chapter considers the prediction of mechanical strength properties, starting from gravimetric determinations: WL, after-treatment nominal density at 65% RH at 20°C (ND) and after-treatment specific gravity (SG_{OD}). Mechanical properties are further modelled using changes in chemical constituents. Complementary to this, modelling of mechanical properties from treatment parameters (temperature, T and time, t) is shown. The modelling finishes with the prediction of some mechanical properties from other properties that may be more easily determined. This chapter ends with the proposal of an overall performance index for TMW using multivariate analysis.

One point to bear in mind is that this study was carried out using small, defect-free specimens of wood. In clear wood samples, mechanical properties are mainly a function of density, chemical composition and microfibril angle. In larger samples, wood strength is influenced by other wood characteristics such as grain angle, and some wood defects like knots. Thus, although some of the findings may or may not be applicable to wood in usage dimension, some of the fundamental observations described herein, can certainly be transported to explain the behaviour of larger TMW members. For many years, the derivation of wood strength for structural applications was based on the values derived from small samples testing. It is therefore not ineffectual to study the strength on small specimens, because in this way it can be more economical; it also has some practical relevance for the prospective assessment of the use of TMW for structural applications.

Another major consideration is that the comparison of the strength properties between treated and untreated samples was done in samples with dissimilar moisture content, even though both groups were conditioned to the same testing atmosphere. Irrespective of the relative humidity conditions, the equilibrium moisture content (EMC) of modified samples gradually reduces as the weight loss due to the treatment increases (chapter 6). The correlation of moisture content below the fibre saturation point and several forms of wood strength has been noted by Dinwoodie (2000). No correction factors for differences in moisture content were applied though, because the relationship between EMC and mechanical property changes are unknown for TMW. Thus, it is possible that some of the properties may be somewhat overestimated, whereas others (particularly impact resistance) may be slightly underestimated in this study. It was however considered that the EMC attained by the modified samples are likely to be that found in service, and so comparisons in the actual condition of the samples to be suitable in practical terms.

A final factor to take into account is that the after-treatment dimensions of the wood samples change in line with the thermal modification (chapter 4). Chang and Keith (1978) used the specimen's prior-to-heating dimensions for the calculations of mechanical properties, and in this way the strength characteristics analysed by these authors were slightly smaller than if the properties were computed using the actual dimensions of the samples at test. This approach would probably be valid if the member in question were put in service before the thermal modification take place. However, in the case of TMW, the material is typically modified and then cut to usage dimensions, so the reduction of size due to the conversion has no practical importance. In this study, it was decided to use the dimensions of the specimens at test, so the properties computed as for the equations in BS373 (BSI 1957) and BS EN ISO 179 (BSI 1998) were obtained using the final (after-treatment, conditioned) sample dimensions.

5.2 Bending strength

Strength in static bending is an important mechanical property, because in most applications wood is subject to loads which cause it to bend, even for non-structural applications. Under the action of an external force acting transversely to its axis, three axial stresses develop inside a wood member: tension, compression and shear. Tension stresses tend to stretch the wood fibres, whilst compression stresses induce fibres to become shorter. In a member supported over its two extremes, shear stresses tend to make the upper part of the beam slide over its lower part. Tension stresses develop at the lower part of the member, whereas compression stresses are higher at the upper part, both of them gradually diminishing towards the centre, and are zero at the neutral plane. Inversely, shear stresses are highest in the neutral plane and zero at the upper and lower surfaces (Tsoumis 1991).

Mode of failure

The consequence of this behaviour has relevance on the way in which TMW fails when the material is subject to bending stresses. There was a tendency towards brash failure which became increasingly evident with the severity of the treatment. As shown in section 5.3, the result of thermal modification in compression strength was an increase of this form of strength up to high levels of treatment. Three-point bending strength was lowered by a combination of same-compression strength (at the upper face), and increasingly reduced tensile strength at the lower face of the sample in test. During the bending process, the energy of the applied load was stored in the lower plane (because the specimen was not failing in compression at the upper face), and failure became sudden due to the almost instantaneous release of most of the stress mainly at the (lower) tension plane. This mode of failure is opposed to sound wood, where some energy is dissipated by compression failure at the upper face during the bending testing.

During the bending process of untreated and beech treated at 190 °C, the breaking point was typically accompanied by a splintering sound. In most untreated control samples, failure was first in compression and then in tension, followed by short shear failure along the axis, limited to one tenth of the sample length. Following the first loud fracture, energy is stored and another splintering sound was recorded after reaching the maximum load; always a short shear failure was required to arrest the crack propagation. After the point of maximum load, by the middle of the total strain, it was clear that the material was still failing in tension.

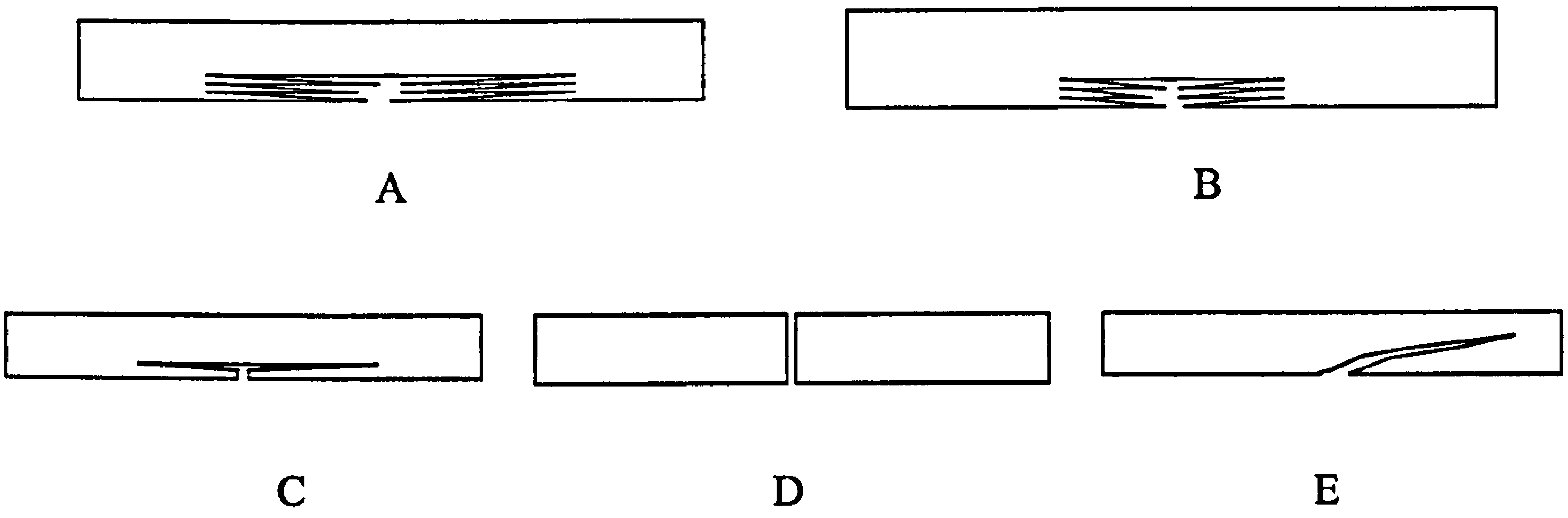


Figure 5.1 Failure types of thermally modified wood in three-point bending with span parallel to the grain. A) Splintering tension; B) Short multiple tension; C) Horizontal shear; D) Brash tension; E) Cross-grain tension.

As the severity of the treatment at 190 °C increases, the failure of the beech samples was more striking; the sample typically failed in tension followed by multiple shear failures, up to two thirds of the sample depth, and the shear failures increased from one tenth to one third of the sample length (failure mode A, Figure 5.1). Splinters were also finer and sharper.

For the samples treated at 210 °C, for processing times ≤ 4 h, the failure was similar to those samples treated to 190 °C. After that, the plastic deformation was small; at the end of the elastic deformation the failure was fast, but the material still withstood the load after failing: the stress-strain plot followed a hyperbolic path after the initial failure. At this level of treatment, tension failure was more evident, with small lines (one fifth) along the length (failure mode B, Figure 5.1). According to Bodig and Jane (1982), this manner of failure usually occurs in wood with low moisture content. When a larger load was stored, the failure was almost across all the sample depth, in mode B or combined mode A + B. This is as if the release of the energy could not be stopped by failing either in tension or shear. The zone immediate to the head's loading point started to bear most of the load, so the stress was not handed over by shear to the remaining body of the specimen. From the treatment leading to a WL above 12%, there was no evident compression failure or buckling at the upper part of the sample, and the splinters in tension failure were blunter. The material was also failing rather catastrophically. Also, as the treating time increased, the failure became less audible, because the maximum load and the total strain is small. As soon as the sample broke, the test ended, because the sample was almost separated into two halves.

In the treatment at 230 °C, the behaviour was similar to the samples treated at 210 °C, but when the weight loss exceeded *ca.* 18%, the beech samples no longer failed as normal wood. The same was true for samples treated at 245 °C, except for the beech samples treated for 0.3 h. There were two characteristic failure types for samples with a WL above this threshold: one type was the failure in tension followed by failure in horizontal shear (failure mode C, Figure 5.1). Samples had a stiff character, and the load-bearing capacity after reaching the point of maximum load was almost zero. Another type of failure was the complete separation of the sample into two pieces at the breaking point (failure mode D, Figure 5.1). In some instances, sample pieces flew apart to some distance from the instrument at failure.

A noticeable feature during testing of beech was that approximately one sample in each set of ten, either in control samples or treated ones, failed more or less catastrophically, so that both the point at maximum load and the total area was reduced by some 30% compared to the rest of the samples (failure mode E, Figure 5.1). This was attributed to the complex anatomical composition and small wavy grain, as well as the presence of brash -probably reaction, wood. In these specimens, the failure seems to run somewhat in line with the waving grain of the wood, not in the longitudinal but in the tangential direction. However, this feature has apparently no effect on the MOE.

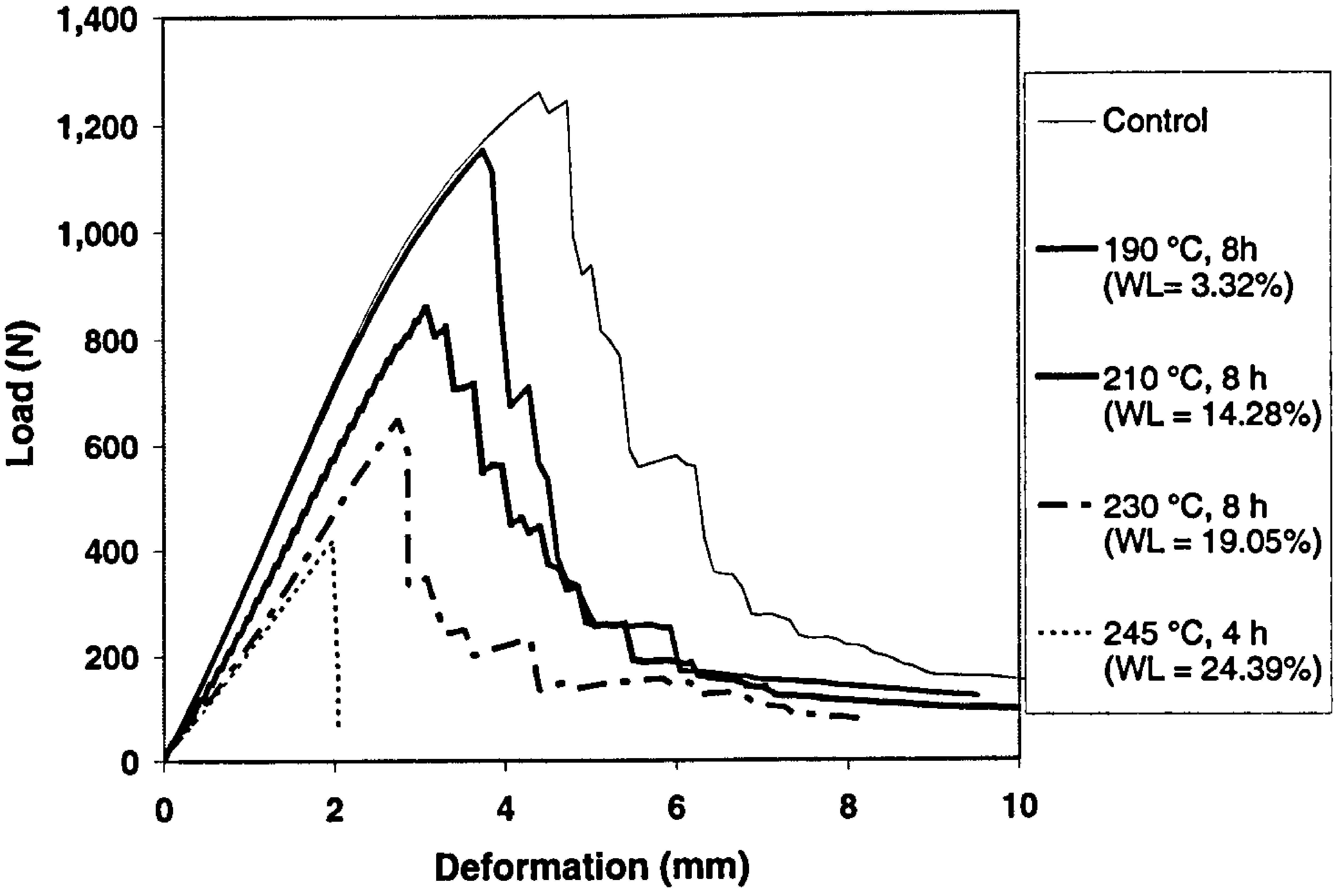


Figure 5.2 Stress-deformation plots for untreated and selected samples of thermally modified beech wood tested in a three-point bending test

The failure behaviour could be better explained with the aid of the stress-deformation plot of the treated samples (Figure 5.2). This plot shows that at the start of loading all control and treated wood specimens exhibited a linear elastic behaviour; the stress being directly proportional to the strain. After the stress reached the limit of proportionality, the plastic part of the curve ran to a larger deformation in the untreated material, and is diminished progressively as the extent of the treatment increased. This was close to zero for the treatment at 245 °C. After the point at maximum load, the untreated sample still had some load bearing capacity; it was evident that the specimen is still able to store some amount of energy as the failure proceeded, since the stress-deformation plot had a positive slope at various points after the breaking point. This load-bearing capacity after the point of maximum load was also steadily reduced as the treatment proceeded, and at high levels of treatment, this was close to zero.

In the case of softwoods, the failure mechanism showed similarities to that of beech, but the material showed the failure characteristics of untreated wood only to slightly lower levels of modification. In spruce, compression failures were noticed in most of the samples at any treatment but for treatment 20, though. This was probably due to the low density of the material. After a WL of about 14.5% (treatments 15, 18, 19 and 20), the failure mode change from B or A+B (as untreated wood fails) to failure mode C (Figure 5.1). With the exception of these last 4 treatments, failure started with the release of various subtle cracking sounds probably from earlywood, followed by a sudden failure in the latewood with a brisk, splintering sound, and crack arrest by shear failure. Shear failure was invariably developed at the interface of early- and latewood. This zone probably acted as a weakness plane due to uneven modification for initial chemical differences at the boundary. The mode of failure of pine was almost the same as in spruce, but the shear failures at the boundary of EW and LW following the tension failure were somewhat longer than in spruce. All modified samples of pine had the failure character of untreated wood (failure modes A, B or A+B) except for those modified at WL > 16% (treatments 18, 19 and 20), which failed mostly in modes C or D. Compression failures were less conspicuous as the severity of the treatment proceeded, but some of the pieces modified up to very high levels of WL (< 16%) still developed compression failures at the upper face of the sample.

In both softwoods, the failure after the maximum load was accompanied by cracking sounds, probably the product of tension failures followed by crack arrests in shear. When these cycles reached about one half of the sample depth, the failure was almost instantaneous, probably because the upper half of the sample had already failed in compression. The splintering sounds after failure contrast with the featureless failure of beech after the failure at maximum load. The difference could be derived from the longer fibers and more distinct growth rings in softwoods than in beech.

5.2.1 Modulus of elasticity

Analysis of variance (ANOVA) with Tukey's test was carried out for each species and for each strength property in bending. The result shows that the MOE of the test specimens was not changed significantly by the treatment at 190 °C or 210 °C in any species. At 230 °C, MOE is significantly reduced only in beech and spruce when the treatment was for 16 h (Figure 5.3, Table 5.1). For treatment at 245 °C, the MOE in beech remained unchanged when wood was treated for 0.3 or for 4 h, being significantly smaller to control MOE for the treatment at 1h or 16 h. At 245 °C, Scots pine and Norway spruce MOE was significantly reduced only when the treatment was for 8 h or longer.

In beech, if the WL was smaller than 16.5%, treating the samples at temperatures up to 210 °C generally lead to marginally larger -although insignificant, increases in MOE compared to control. This small augment in MOE could be an artifact of the reduced EMC of treated samples, though. Modifying the samples above 210 °C, the referred increment followed a more complicated pattern: at 230 °C, MOE rose at the beginning of the treatment, followed by an insignificant reduction for treatment for 1 to 4 h, just to increase marginally for the treatment at 8 h, and to finally fall significantly for the treatment at 16 h. For the treatment at 245 °C, the MOE showed a modest though insignificant increment at the beginning of the treatment (0.3 h), and then was significantly reduced as the treatment time reached 1 h, to be insignificantly smaller than control when the treatment was for 4 h.

In both softwoods, insignificant increments on MOE took place even when the treatment was at a temperature of 230 °C, provided the heat-induced WL was not greater than 10.7% in pine and 10.8% in spruce. In pine, MOE followed an unsystematic trend when the treatment was at 245 °C: at the beginning, MOE was marginally reduced, and then increased modestly after 1 h of treatment. It was subsequently significantly reduced in treatments for 8 h or longer. In spruce, only the treatment for 0.3 h at 245 °C gave a modest increase in MOE, and it then followed a small decrease for the 1 h and 4 h treatments, just to fall significantly afterwards for longer treatment periods.

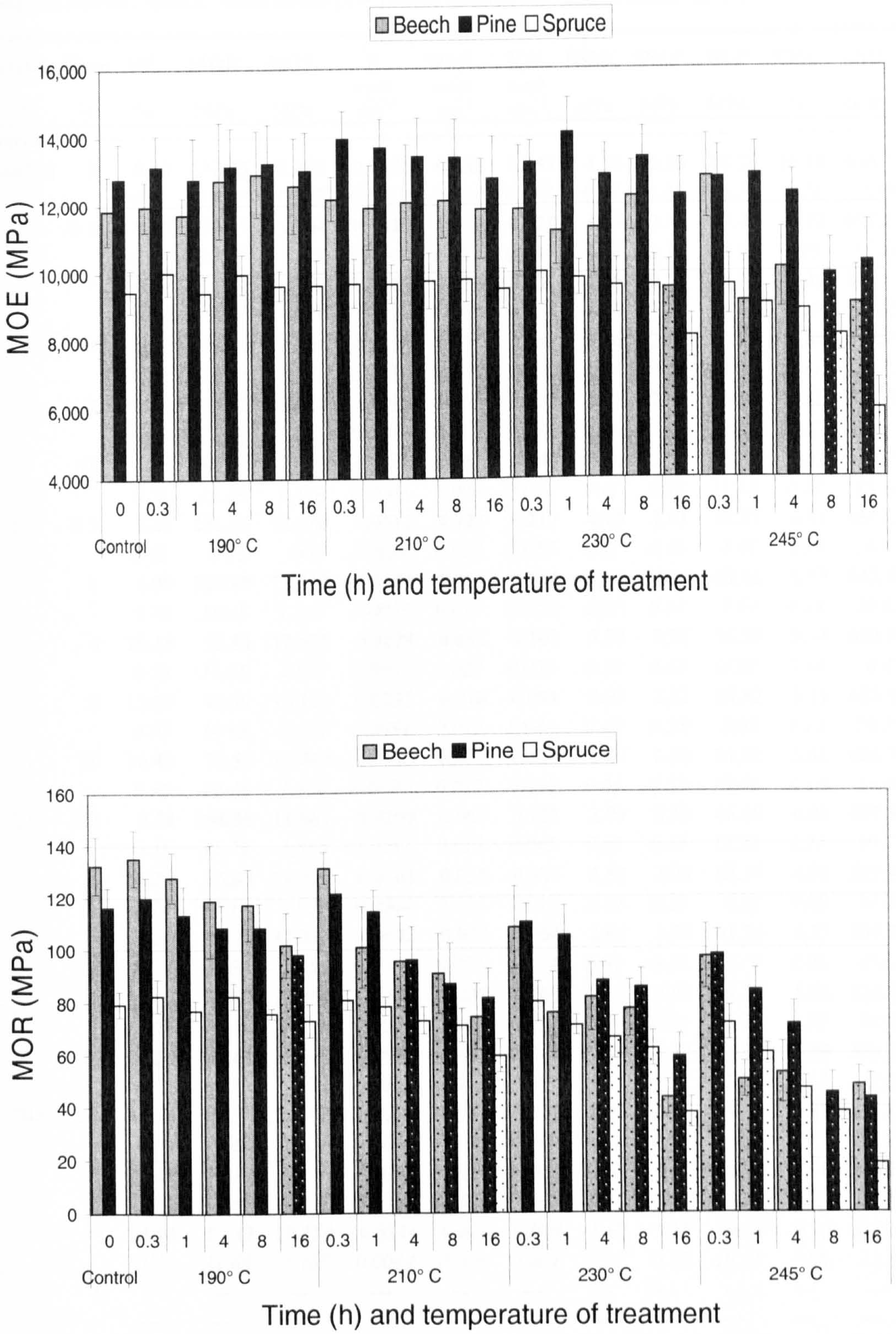


Figure 5.3 Effect of thermal modification on modulus of elasticity in bending (MOE, top) and modulus of rupture (MOR, bottom) on samples of beech, Scots pine and Norway spruce. Each column represents the mean value of ten replicates. Mottled bars: treatment significantly reduced. Error bars = ± 1 SD

Table 5.1 Effect of thermal modification on bending strength parameters on specimens of beech, Scots pine and Norway spruce. Mean values ($n = 10$) are in bold, standard deviation in italics.

Temp.	Time	WL	MOR	MOE	R	WML	TW	SSML	SSLP	RLP	EMC	ND
°C	h	%	MPa	MPa	$\frac{mmN}{mm^3}$	$\frac{mmN}{mm^3}$	$\frac{mmN}{mm^3}$	MPa	MPa	MPa	%	kg m^{-3}
Beech												
Control	0	**0.00**	**132.35**	**11,858**	**0.0346**	**0.152**	**0.257**	**4.78**	**2.93**	**81.23**	**10.15**	**636.24**
		0.00	*10.97*	*1,015*	*0.0059*	*0.034*	*0.075*	*0.37*	*0.28*	*8.29*	*0.16*	*38.06*
190	0.3	**0.36**	**135.19**	**11,964**	**0.0313**	**0.176**	**0.328**	**4.83**	**3.13**	**87.46**	**9.22**	**652.22**
		0.08	*10.67*	*733*	*0.0042*	*0.053*	*0.087*	*0.38*	*0.37*	*9.94*	*0.19*	*35.86*
	1	**0.94**	**127.81**	**11,731**	**0.0289**	**0.126**	**0.231**	**4.58**	**2.76**	**76.83**	**8.35**	**646.48**
		0.08	*9.66*	*501*	*0.0034*	*0.028*	*0.043*	*0.35*	*0.21*	*5.73*	*0.19*	*31.85*
	4	**2.79**	**118.76**	**12,746**	**0.0251**	**0.077**	**0.148**	**4.16**	**2.62**	**74.80**	**6.86**	**647.91**
		0.22	*21.60*	*1,707*	*0.0059*	*0.022*	*0.063*	*0.74*	*0.45*	*13.11*	*0.11*	*40.73*
	8	**4.08**	**117.22**	**12,921**	**0.0206**	**0.076**	**0.128**	**4.07**	**2.38**	**68.52**	**6.59**	**639.83**
		0.48	*13.68*	*1,263*	*0.0045*	*0.011*	*0.041*	*0.46*	*0.37*	*10.57*	*0.17*	*33.41*
	16	**6.85**	**101.82**	**12,572**	**0.0208**	**0.052**	**0.094**	**3.50**	**2.32**	**67.46**	**5.92**	**643.78**
		0.51	*12.28*	*1,398*	*0.0063*	*0.009*	*0.031*	*0.41*	*0.45*	*13.33*	*0.13*	*35.18*
210	0.3	**1.23**	**131.36**	**12,180**	**0.0312**	**0.124**	**0.217**	**4.70**	**2.91**	**81.27**	**8.11**	**654.85**
		0.21	*6.13*	*651*	*0.0029*	*0.017*	*0.035*	*0.22*	*0.16*	*4.41*	*0.19*	*36.63*
	1	**6.00**	**100.89**	**11,919**	**0.0194**	**0.059**	**0.114**	**3.48**	**2.19**	**63.52**	**5.57**	**642.48**
		0.76	*15.45*	*1,233*	*0.0035*	*0.019*	*0.057*	*0.51*	*0.25*	*7.64*	*0.14*	*39.62*
	4	**10.38**	**95.56**	**12,075**	**0.0279**	**0.053**	**0.101**	**3.22**	**2.57**	**76.29**	**5.34**	**650.88**
		0.70	*16.85*	*1,691*	*0.0067*	*0.022*	*0.057*	*0.55*	*0.45*	*14.02*	*0.10*	*30.45*
	8	**13.58**	**90.77**	**12,124**	**0.0231**	**0.048**	**0.091**	**3.01**	**2.32**	**69.82**	**5.21**	**623.59**
		0.92	*14.95*	*1,104*	*0.0054*	*0.012*	*0.044*	*0.49*	*0.28*	*8.65*	*0.15*	*29.32*
	16	**16.48**	**74.50**	**11,869**	**0.0183**	**0.032**	**0.074**	**2.45**	**2.02**	**61.21**	**5.41**	**606.73**
		0.96	*12.43*	*1,477*	*0.0049*	*0.012*	*0.030*	*0.41*	*0.35*	*10.66*	*0.10*	*24.40*
230	0.3	**3.78**	**108.05**	**11,867**	**0.0209**	**0.067**	**0.121**	**3.79**	**2.32**	**66.09**	**6.01**	**637.87**
		0.46	*15.79*	*1,856*	*0.0051*	*0.013*	*0.045*	*0.57*	*0.45*	*12.72*	*0.21*	*30.73*
	1	**16.37**	**75.87**	**11,225**	**0.0203**	**0.035**	**0.084**	**2.50**	**2.05**	**62.37**	**4.92**	**587.46**
		0.76	*15.16*	*999*	*0.0044*	*0.014*	*0.032*	*0.49*	*0.29*	*8.82*	*0.08*	*31.84*
	4	**18.59**	**81.79**	**11,322**	**0.0192**	**0.035**	**0.064**	**2.64**	**1.98**	**61.26**	**5.17**	**609.32**
		0.74	*12.86*	*1,353*	*0.0036*	*0.007*	*0.024*	*0.41*	*0.26*	*8.14*	*0.06*	*40.65*
	8	**18.69**	**77.29**	**12,251**	**0.0180**	**0.030**	**0.069**	**2.51**	**2.00**	**61.70**	**5.28**	**614.45**
		0.66	*10.61*	*1,036*	*0.0042*	*0.010*	*0.054*	*0.34*	*0.26*	*8.34*	*0.13*	*34.30*
	16	**24.34**	**43.61**	**9,541**	**0.0093**	**0.012**	**0.016**	**1.38**	**1.22**	**38.57**	**5.80**	**581.11**
		0.58	*6.73*	*821*	*0.0030*	*0.003*	*0.008*	*0.22*	*0.22*	*6.71*	*0.12*	*42.50*
245	0.3	**11.06**	**96.94**	**12,809**	**0.0288**	**0.051**	**0.129**	**3.25**	**2.68**	**79.76**	**5.11**	**614.06**
		1.19	*12.18*	*1,231*	*0.0048*	*0.016*	*0.040*	*0.41*	*0.30*	*8.98*	*0.15*	*35.88*
	1	**23.19**	**50.37**	**9,149**	**0.0135**	**0.016**	**0.020**	**1.61**	**1.47**	**45.89**	**5.96**	**578.81**
		1.08	*6.89*	*1,302*	*0.0035*	*0.003*	*0.009*	*0.23*	*0.22*	*6.76*	*0.13*	*29.70*
	4	**24.93**	**53.12**	**10,124**	**0.0144**	**0.016**	**0.019**	**1.67**	**1.57**	**50.09**	**5.78**	**582.60**
		0.62	*11.66*	*1,168*	*0.0044*	*0.006*	*0.009*	*0.37*	*0.33*	*10.26*	*0.06*	*23.58*
	8	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**—**	**—**
		—	—	—	—	—	—	—	—	—	—	—
	16	**27.23**	**48.49**	**9,069**	**0.0132**	**0.015**	**0.016**	**1.53**	**1.44**	**45.58**	**6.18**	**569.45**
		1.22	*6.67*	*1,087*	*0.0027*	*0.003*	*0.003*	*0.20*	*0.19*	*6.29*	*0.11*	*30.69*

Beech not tested at 245 °C for 8h. For abbreviations, see foot at the end of the table.

Continued over ...

Table 5.1 Effect of thermal modification on bending strength parameters on specimens of beech, Scots pine and Norway spruce. Mean values (n = 10) are in bold, standard deviation in italics. (*Continued...*)

Temp.	Time	WL	MOR	MOE	R	WML	TW	SSML	SSLP	RLP	EMC	ND
°C	h	%	MPa	MPa	$\frac{mmN}{mm^3}$	$\frac{mmN}{mm^3}$	$\frac{mmN}{mm^3}$	MPa	MPa	MPa	%	kg m^{-3}
Pine												
Control	0	**0.00**	**116.27**	**12,791**	**0.0215**	**0.106**	**0.192**	**4.08**	**2.43**	**69.17**	**10.34**	**518.28**
		0.00	*7.58*	*1,025*	*0.0028*	*0.017*	*0.035*	*0.27*	*0.22*	*6.26*	*0.06*	*19.73*
190	0.3	**0.56**	**119.86**	**13,142**	**0.0203**	**0.094**	**0.210**	**4.20**	**2.39**	**68.36**	**9.79**	**524.08**
		0.05	*7.90*	*914*	*0.0036*	*0.013*	*0.046*	*0.26*	*0.27*	*7.73*	*0.04*	*14.86*
	1	**1.11**	**113.36**	**12,777**	**0.0218**	**0.083**	**0.148**	**3.95**	**2.41**	**69.30**	**9.30**	**510.30**
		0.11	*10.91*	*1,207*	*0.0058*	*0.015*	*0.053*	*0.38*	*0.42*	*12.05*	*0.05*	*22.32*
	4	**2.01**	**108.47**	**13,152**	**0.0206**	**0.073**	**0.130**	**3.75**	**2.37**	**68.51**	**8.66**	**520.15**
		0.20	*8.55*	*1,126*	*0.0045*	*0.023*	*0.048*	*0.31*	*0.30*	*8.34*	*0.11*	*17.60*
	8	**2.68**	**108.29**	**13,227**	**0.0209**	**0.063**	**0.117**	**3.71**	**2.38**	**69.53**	**8.38**	**510.82**
		0.18	*9.27*	*1,153*	*0.0045*	*0.010*	*0.034*	*0.32*	*0.35*	*10.15*	*0.09*	*23.36*
	16	**3.83**	**98.01**	**13,013**	**0.0221**	**0.047**	**0.103**	**3.35**	**2.41**	**70.50**	**7.95**	**517.26**
		0.23	*6.80*	*1,133*	*0.0049*	*0.005*	*0.030*	*0.22*	*0.22*	*6.52*	*0.07*	*20.54*
210	0.3	**1.88**	**121.47**	**13,947**	**0.0244**	**0.083**	**0.181**	**4.19**	**2.66**	**77.20**	**8.54**	**536.67**
		0.36	*7.15*	*813*	*0.0030*	*0.010*	*0.023*	*0.26*	*0.18*	*5.25*	*0.19*	*7.00*
	1	**2.71**	**114.38**	**13,685**	**0.0279**	**0.073**	**0.155**	**3.93**	**2.79**	**81.21**	**7.74**	**523.90**
		0.20	*8.30*	*845*	*0.0048*	*0.017*	*0.041*	*0.29*	*0.26*	*7.52*	*0.08*	*18.86*
	4	**6.70**	**96.02**	**13,413**	**0.0216**	**0.057**	**0.122**	**3.24**	**2.40**	**71.04**	**6.39**	**521.04**
		0.61	*12.54*	*1,139*	*0.0039*	*0.024*	*0.038*	*0.41*	*0.25*	*7.34*	*0.17*	*23.44*
	8	**6.88**	**86.86**	**13,390**	**0.0173**	**0.039**	**0.097**	**2.93**	**2.12**	**62.69**	**6.30**	**523.68**
		0.42	*15.35*	*1,123*	*0.0065*	*0.015*	*0.037*	*0.53*	*0.48*	*14.16*	*0.10*	*25.32*
	16	**9.22**	**81.45**	**12,767**	**0.0198**	**0.035**	**0.078**	**2.71**	**2.21**	**66.27**	**6.08**	**510.66**
		0.65	*11.00*	*1,230*	*0.0046*	*0.012*	*0.030*	*0.37*	*0.32*	*9.61*	*0.10*	*19.95*
230	0.3	**2.50**	**110.08**	**13,240**	**0.0228**	**0.073**	**0.172**	**3.81**	**2.51**	**72.44**	**7.67**	**526.91**
		0.13	*6.98*	*643*	*0.0054*	*0.019*	*0.044*	*0.22*	*0.27*	*8.36*	*0.08*	*18.02*
	1	**4.44**	**105.00**	**14,120**	**0.0222**	**0.058**	**0.126**	**3.58**	**2.52**	**74.04**	**7.17**	**533.45**
		0.57	*11.49*	*1,004*	*0.0037*	*0.016*	*0.037*	*0.39*	*0.26*	*7.82*	*0.18*	*16.10*
	4	**8.77**	**87.75**	**12,867**	**0.0154**	**0.041**	**0.086**	**2.93**	**1.96**	**58.53**	**5.95**	**508.46**
		0.94	*6.79*	*920*	*0.0039*	*0.011*	*0.021*	*0.22*	*0.27*	*7.94*	*0.10*	*19.55*
	8	**10.69**	**85.44**	**13,392**	**0.0149**	**0.034**	**0.087**	**2.84**	**1.96**	**58.92**	**5.77**	**522.13**
		0.47	*6.85*	*879*	*0.0036*	*0.005*	*0.020*	*0.22*	*0.29*	*8.76*	*0.09*	*20.41*
	16	**12.83**	**59.28**	**12,284**	**0.0137**	**0.019**	**0.051**	**1.94**	**1.76**	**53.95**	**5.64**	**497.85**
		0.77	*8.52*	*1,065*	*0.0035*	*0.007*	*0.023*	*0.30*	*0.29*	*8.49*	*0.08*	*32.77*
245	0.3	**4.60**	**97.74**	**12,769**	**0.0215**	**0.061**	**0.129**	**3.34**	**2.36**	**69.15**	**6.79**	**510.20**
		0.35	*9.12*	*938*	*0.0048*	*0.023*	*0.039*	*0.30*	*0.31*	*9.33*	*0.12*	*23.86*
	1	**10.64**	**84.20**	**12,873**	**0.0146**	**0.035**	**0.073**	**2.80**	**1.91**	**57.39**	**5.52**	**504.05**
		0.56	*8.22*	*937*	*0.0030*	*0.009*	*0.024*	*0.29*	*0.24*	*7.19*	*0.08*	*16.98*
	4	**15.06**	**71.66**	**12,329**	**0.0154**	**0.024**	**0.045**	**2.34**	**1.89**	**57.79**	**5.28**	**502.36**
		0.72	*8.37*	*648*	*0.0033*	*0.005*	*0.011*	*0.27*	*0.23*	*7.09*	*0.07*	*13.28*
	8	**20.36**	**45.36**	**9,942**	**0.0118**	**0.012**	**0.014**	**1.46**	**1.46**	**45.10**	**5.51**	**469.94**
		1.21	*7.65*	*1,012*	*0.0032*	*0.003*	*0.004*	*0.25*	*0.25*	*7.57*	*0.07*	*22.48*
	16	**20.95**	**43.44**	**10,300**	**0.0091**	**0.011**	**0.012**	**1.40**	**1.28**	**39.93**	**5.54**	**471.54**
		1.25	*9.04*	*1,192*	*0.0038*	*0.004*	*0.005*	*0.29*	*0.33*	*10.26*	*0.09*	*19.81*

For abbreviations, see foot at the end of the table.

Continued over...

Table 5.1 Effect of thermal modification on bending strength parameters on specimens of beech, Scots pine and Norway spruce. Mean values (n = 10) are in bold, standard deviation in italics. (*Concluded*)

Temp. °C	Time h	WL %	MOR MPa	MOE MPa	R $\frac{mmN}{mm^3}$	WML $\frac{mmN}{mm^3}$	TW $\frac{mmN}{mm^3}$	SSML MPa	SSLP MPa	RLP MPa	EMC %	ND kg m^{-3}
Spruce												
Control	0	**0.00**	**79.38**	**9,460**	**0.0115**	**0.065**	**0.109**	**2.81**	**1.47**	**41.54**	**11.43**	**368.91**
		0.00	*4.82*	*627*	*0.0015*	*0.005*	*0.010*	*0.16*	*0.10*	*2.73*	*0.15*	*13.10*
190	0.3	**0.99**	**82.67**	**10,026**	**0.0138**	**0.078**	**0.129**	**2.92**	**1.74**	**49.34**	**10.50**	**373.95**
		0.05	*6.17*	*664*	*0.0017*	*0.012*	*0.017*	*0.22*	*0.14*	*3.97*	*0.09*	*19.95*
	1	**1.33**	**77.22**	**9,435**	**0.0131**	**0.062**	**0.100**	**2.71**	**1.64**	**46.78**	**9.73**	**362.05**
		0.07	*3.60*	*497*	*0.0016*	*0.006*	*0.011*	*0.12*	*0.10*	*2.96*	*0.15*	*6.16*
	4	**1.80**	**82.48**	**9,975**	**0.0142**	**0.061**	**0.088**	**2.88**	**1.74**	**49.85**	**9.19**	**371.38**
		0.07	*4.86*	*582*	*0.0012*	*0.005*	*0.015*	*0.18*	*0.09*	*2.33*	*0.09*	*13.64*
	8	**2.68**	**75.89**	**9,634**	**0.0128**	**0.051**	**0.080**	**2.64**	**1.62**	**46.78**	**8.94**	**363.83**
		0.08	*2.02*	*430*	*0.0013*	*0.006*	*0.008*	*0.05*	*0.09*	*2.66*	*0.14*	*7.67*
	16	**3.43**	**73.14**	**9,649**	**0.0112**	**0.041**	**0.065**	**2.54**	**1.52**	**43.63**	**8.35**	**369.38**
		0.20	*6.24*	*737*	*0.0014*	*0.006*	*0.014*	*0.22*	*0.14*	*4.14*	*0.19*	*17.71*
210	0.3	**1.26**	**80.94**	**9,692**	**0.0132**	**0.068**	**0.109**	**2.84**	**1.66**	**47.45**	**9.03**	**369.32**
		0.07	*3.66*	*717*	*0.0015*	*0.011*	*0.023*	*0.12*	*0.11*	*3.27*	*0.14*	*11.82*
	1	**2.75**	**78.48**	**9,674**	**0.0098**	**0.052**	**0.082**	**2.74**	**1.43**	**40.89**	**8.29**	**367.01**
		0.17	*3.45*	*572*	*0.0010*	*0.004*	*0.013*	*0.12*	*0.09*	*2.70*	*0.13*	*15.46*
	4	**4.95**	**73.10**	**9,757**	**0.0066**	**0.040**	**0.064**	**2.50**	**1.16**	**33.94**	**7.29**	**360.43**
		0.33	*5.14*	*815*	*0.0013*	*0.006*	*0.012*	*0.18*	*0.15*	*4.46*	*0.40*	*12.72*
	8	**6.05**	**71.21**	**9,794**	**0.0047**	**0.036**	**0.058**	**2.44**	**0.94**	**27.56**	**7.11**	**366.66**
		0.23	*6.38*	*662*	*0.0015*	*0.007*	*0.012*	*0.22*	*0.17*	*4.91*	*0.16*	*12.00*
	16	**8.74**	**59.57**	**9,518**	**0.0037**	**0.029**	**0.046**	**2.02**	**0.82**	**24.34**	**6.40**	**359.83**
		0.47	*6.34*	*593*	*0.0009*	*0.008*	*0.008*	*0.22*	*0.12*	*3.51*	*0.15*	*15.95*
230	0.3	**3.37**	**80.02**	**10,022**	**0.0108**	**0.053**	**0.090**	**2.76**	**1.51**	**43.64**	**7.60**	**371.28**
		0.15	*7.51*	*997*	*0.0018*	*0.011*	*0.024*	*0.24*	*0.17*	*5.33*	*0.13*	*17.50*
	1	**5.94**	**71.17**	**9,839**	**0.0084**	**0.037**	**0.064**	**2.44**	**1.30**	**38.05**	**6.77**	**366.01**
		0.35	*3.73*	*522*	*0.0008*	*0.006*	*0.007*	*0.13*	*0.08*	*2.35*	*0.15*	*21.45*
	4	**8.77**	**66.47**	**9,612**	**0.0066**	**0.033**	**0.051**	**2.25**	**1.13**	**33.19**	**6.26**	**359.73**
		0.42	*8.05*	*807*	*0.0014*	*0.009*	*0.010*	*0.27*	*0.14*	*4.20*	*0.11*	*14.67*
	8	**10.85**	**62.32**	**9,630**	**0.0087**	**0.026**	**0.044**	**2.09**	**1.27**	**38.02**	**5.79**	**360.99**
		0.41	*6.71*	*879*	*0.0021*	*0.006*	*0.008*	*0.21*	*0.19*	*5.89*	*0.06*	*20.23*
	16	**15.26**	**37.79**	**8,122**	**0.0038**	**0.013**	**0.024**	**1.26**	**0.77**	**23.06**	**5.73**	**344.55**
		0.80	*5.88*	*639*	*0.0011*	*0.006*	*0.008*	*0.19*	*0.12*	*3.68*	*0.19*	*16.09*
245	0.3	**7.20**	**71.91**	**9,626**	**0.0115**	**0.041**	**0.065**	**2.46**	**1.51**	**44.11**	**6.20**	**360.87**
		0.44	*6.50*	*885*	*0.0019*	*0.005*	*0.012*	*0.20*	*0.18*	*5.52*	*0.10*	*13.36*
	1	**10.68**	**60.71**	**9,068**	**0.0083**	**0.027**	**0.043**	**2.04**	**1.21**	**36.07**	**5.55**	**348.56**
		0.52	*3.31*	*475*	*0.0014*	*0.004*	*0.013*	*0.10*	*0.11*	*3.42*	*0.11*	*15.60*
	4	**15.09**	**47.15**	**8,894**	**0.0070**	**0.015**	**0.028**	**1.55**	**1.07**	**32.59**	**5.37**	**350.31**
		0.51	*4.45*	*741*	*0.0013*	*0.002*	*0.005*	*0.14*	*0.12*	*3.70*	*0.08*	*22.65*
	8	**17.66**	**38.06**	**8,147**	**0.0067**	**0.010**	**0.016**	**1.24**	**0.99**	**30.41**	**5.27**	**336.02**
		0.40	*3.87*	*500*	*0.0014*	*0.002*	*0.005*	*0.12*	*0.10*	*2.95*	*0.08*	*10.19*
	16	**26.34**	**18.38**	**5,987**	**0.0029**	**0.003**	**0.004**	**0.59**	**0.55**	**17.07**	**5.53**	**329.89**
		1.27	*2.88*	*854*	*0.0009*	*0.001*	*0.001*	*0.09*	*0.11*	*3.55*	*0.07*	*20.36*

WL: weight loss; MOR: modulus of rupture; MOE: modulus of elasticity; R: resilience; WML: work to maximum load; TW: total work; SSML: horizontal shear strength at neutral plane at maximum work; SSLP: horizontal shear strength at neutral plane at limit of proportionality; RLP: fibre stress at limit of proportionality; EMC: equilibrium moisture content at 65% relative humidity at 20 °C; ND: nominal density = oven dry weight/conditioned volume at test.

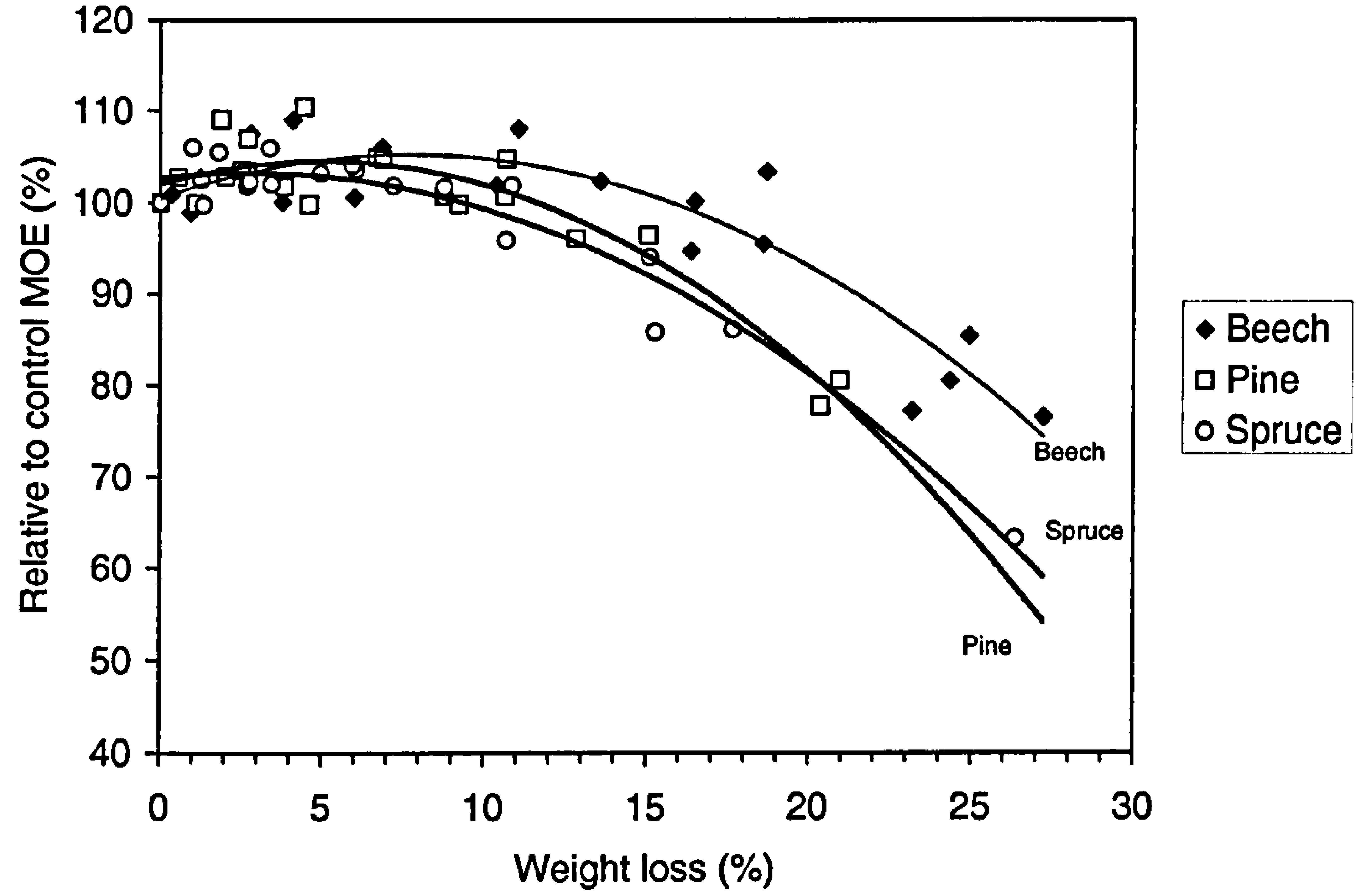


Figure 5.4 Relative (to control) MOE in bending for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements. Error bars omitted for clarity.

The relative-to-control average MOE values plotted against the WL (Figure 5.4), showed changes following the same pattern for the three species: the ratio follows a parabolic trajectory, increasing insignificantly at the beginning as the WL increases up to about 8% for beech, 6% in pine and 2.5% for spruce, and then falling to reach control values at a WL of *ca.* 9%, 12% and 16% for spruce, pine and beech, respectively. The property change pattern was very similar for pine and spruce; softwoods MOE being affected at slightly lower levels of treatment than beech MOE does. Similar results were reported for MOE in tension by Rusche (1973), who studied the effect of thermal treatment in beech and pine in presence and absence of air. This author found that the relationship between relative MOE in tension and substance loss was similar for both species, beech being affected at slightly larger levels of WL.

Reasons for MOE changes

In untreated defect-free wood specimens, it is generally recognized that MOE is closely related to density and fiber properties such as microfibril angle and cell wall dimensions, these three factors representing most of the variation in MOE in both hardwoods and softwood species. For instance, in his study to estimate MOE of Finish-grown Scots pine from wood fiber properties using linear regression, Verkasalo (1992) found that the longitudinal MOE in bending was positively related to nominal density at 12% moisture content (R^2 = 0.904), and inversely related to growth ring width (R^2 = 0.91), and to the coefficient of cell flexibility (lumen diameter/tracheid diameter) in the tangential direction (R^2 = 0.952). In an independent study, when measuring stiffness of a set of 104 alpine ash (*Eucalyptus delegatensis*) samples, Evans and Ilic (2001) established that MOE can be efficiently predicted from measurements of wood density and microfibril angle, these two characteristics accounting for 96% of the variation in MOE. Similarly, Yang and Evans (2003) determined that microfibril angle and density accounted for 92% of the variation of MOE in *E. nitens* and *E. regnants.*

Having establish this, it follows that during the thermal conversion of wood its nominal density (ND) and oven-dry specific gravity (SG_{OD}) are little affected, because as the weight loss increases, there is also a contraction in the transverse plane of the wood material (chapter 4), the dimensional reduction accounting for some of the mass loss due to the modification. ND is significantly reduced only at very high levels of WL (at WL = 23.2%, 20.4% and 17.7% for beech, pine and spruce, respectively). Evidently, this is in clear concordance with the findings of the levels of WL at which changes in MOE become significantly different form untreated samples. Furthermore, the comparison of MOE on a SG_{OD} basis (using the ratio MOE/SG_{OD}) gives that, irrespective of the temperature or length of treatment, the MOE of heat-treated beech is at least equivalent to that of sound wood of the same SG_{OD} at any treatment condition tested here. In the case of softwoods, significant reduction in the ratio MOE/SG_{OD} is found when the treatment was at 245 °C, but only when the exposure period was for 8 h for pine and for 16 h for spruce.

Chemical changes are undoubtedly involved in changes in the MOE. However, the function of the individual chemical components on wood elasticity is not completely understood. The persistent association between wood constituents *in situ* makes difficult to isolate any of them without altering their characteristics somewhat. In turn, this difficulty complicates the precise determination of the role of each chemical constituent in the MOE of wood. If we consider the elastic constants in the axial direction that have been calculated by Salmén (1986, cited by

Schniewind and Berndt 1991) for the three main constituents of the cell wall, 134, 8 and 4 GPa for cellulose, lignin and hemicelluloses, respectively, it is clear that the stiffness of the framework (structural polysaccharide, principally cellulose) is so great compared to the stiffness of the matrix (hemicellulose and lignin) that it will vastly predominate in the macroscopic behaviour of the wood, as would also prevail over the effects of cellular geometry. Therefore, elastic models for the behaviour of cellulose have commonly been used for understanding the behaviour of wood (Mark 1972). Since the microfibril is mainly cellulose, the mechanical properties of the crystalline substance are in turn used exactly as for the properties of the microfibril (Mark 1981). Several studies point to the importance of cellulose and its crystallinity in the elasticity of wood. For instance, Tsuchikawa and Fujimoto (2007) established that the NIR absorption bands due to OH group in the semi-crystalline or crystalline regions in cellulose strongly governed the bending stiffness of hybrid larch. This was also suggested from the result that both α-cellulose content and cellulose crystallinity showed a highly positive correlation to wood stiffness. From the relation between Young's modulus and moisture content, Kubojima *et al.* (1998) concluded that the Young's modulus is increased by cellulose crystallization and the reduction of EMC in thermally-treated spruce wood.

In view of these premises, and since it has been already confirmed that cellulose is stable up to temperatures of 300 °C without inducing thermal decomposition (Kim *et al.* 2001), with overwhelming evidence pointing out to the increase in cellulose crystallinity at low to moderate levels of thermal degradation (Hirai 1972, Nakao *et al.* 1985, 1989, Kubojima *et al.* 1998, Bhuiyan *et al.* 2000, Wikberg and Maunu 2004, Hakkou *et al.* 2005, Yildiz and Gümüşkaya 2007), it is proposed that wood MOE is scarcely affected by wood heating because elasticity is closely related to density and to the physical condition of cellulose microfibrils, these two factors being little altered by treatments for up to 16 h at temperatures between 190 °C and 245 °C.

The results of this study are consistent with other reports that have highlighted the fact that the MOE is little affected at early stages of thermal modification of wood and, in some instances, modest increases in this property have also been documented. For instance, Mouras *et al.* (2002) reported from their study on the strength of two non-durable wood species, namely poplar (*Populus robusta*) and Curupixa (*Micropholis* spp. Brésil), following heat modification. Samples of 150 mm × 30 mm × 30 mm were subjected to controlled pyrolysis using several combinations to heat up wood, and three final temperatures (210, 220 and 230 °C); the experiment also included the comparison of the results whether the treatment was in the presence or absence of water vapor. Weight losses for poplar ranged from 5% to 12% and from 1% to 9% for Curupixa. For all the treatments tested, these authors did not find any significant reduction of MOE with respect to control, even if the modification was in the presence of water vapor. Bekhta and Niemz (2003) found no effect of treatment temperature on MOE in thermally treated spruce wood treated at temperatures of 200 °C for up to 24 h. In the same way, Poncsák *et al.* (2006) found that the effect of the high temperature treatment on the modulus of elasticity of small specimens of birch was almost imperceptible, following several holding times, environment of exposure and heating rates. Moreover, in beam-sized softwood specimens heat-treated at a maximum temperature of 220 °C for four days, MOE was found to decrease subtly but insignificantly (Bengtsson *et al.* 2002). Similar results for 3.6 m long specimens of lodgepole pine, Sitka spruce and Japanese larch were reported by Birkinshaw *et al.* (2006), who found no reduction for the first two species when treated under mechanical restrain in vacuum, and for larch when heated using the Plato® process. MOE of premium graded balsam fir and jack pine lumber modified by three industrial technologies remained also unchanged compared to that of kiln-dried wood (Tremblay and Lihra 2005). Controversially, reductions of 10% and 20% in MOE for radiata pine treated in dimension lumber (3.6 m long) at 170 °C and 230 °C respectively using the ThermoWood® process were found, although it was not reported if such reductions were significant (Christmas *et al.* 2005). These authors suggest that it would be still possible to use TMW in building applications (*e.g.* house framing), and that the reduction in stiffness could be offset by allowances in the design or by specifying stiffer timber than would be required. The exposure of wood for long periods at lower temperatures, but still within the range known to cause reductions in wood strength (> 66 °C) resulted in unchanged MOE in solid lumber and small reductions in LVL and laminated strand lumber (Green *et al.* 2003).

The confirmation that the MOE was found not to be significantly reduced by thermal processing up to very high WL is promising, because wood stiffness is of primary value for many applications of TMW, such as flooring, stairs and decking (Bengtsson *et al.* 2002). For instance, when TMW is used for flooring, deflection rather than carrying capacity is the key performance criterion, because deflection becomes increasingly apparent well before the stress developed reaches that which would cause failure.

5.2.2 Modulus of rupture

Contrarily to MOE, MOR is negatively affected at early stages of treatment (Table 5.1, Figure 5.3), the magnitude of these reductions being influenced both by the time and temperature of treatment imposed and by species of wood.

Beech

Analysis of variance (ANOVA) using Tukey's HSD test, shows that in the case of beech, the MOR of the test specimens was not changed significantly by the treatment at 190 °C and 210 °C if the WL was smaller than about 6%. In the treatment at 190 °C, there was an insignificant increase for the treatment at 0.3 h (probably and artifact of the reduced EMC); afterwards, the MOR decreased gradually; the change being significantly different to control only for the treatment at 16 h (to 6.85% WL). At this point, the maximum decrease in mean MOR reached 23.1%.

For the treatment at 210 °C, beech MOR remained unchanged only when the exposure period was 0.3 h, and then decreased very fast up to 1 h of treatment; the reduction was subsequently almost linear with time. The maximum decrease in MOR at 210 °C was 43.7% (to 16.5% WL). Treatments at 230 °C or 245 °C led to significant changes in all cases, MOR decreasing very fast at the beginning for up to 1 h, and then decreased somewhat linearly with time of exposure. At equivalent time of treatment, modification at 245 °C was more deleterious to bending strength than treatment at 230 °C, with the exemption of the treatment for 16 h, which was statistically the same at both temperatures. Maximum reductions of MOR were 63.4% and 67.1% at 230 °C and 245 °C, respectively (to WL of 24.3% and 27.2% in the same order).

Effect of time and temperature in beech

Increasing the temperature of treatment, led to larger MOR losses at equivalent treatment time, but for the treatment at 230 °C and 245 °C for 16 h, where the reduction was statistically the same. In general, the effect of temperature was more marked than the length of exposure (Figure 5.5). Timber heated at 190 °C for 16 h loss about 23% of its strength; at 210 °C the same loss in strength occurs only after 1 h (Table 5.1).

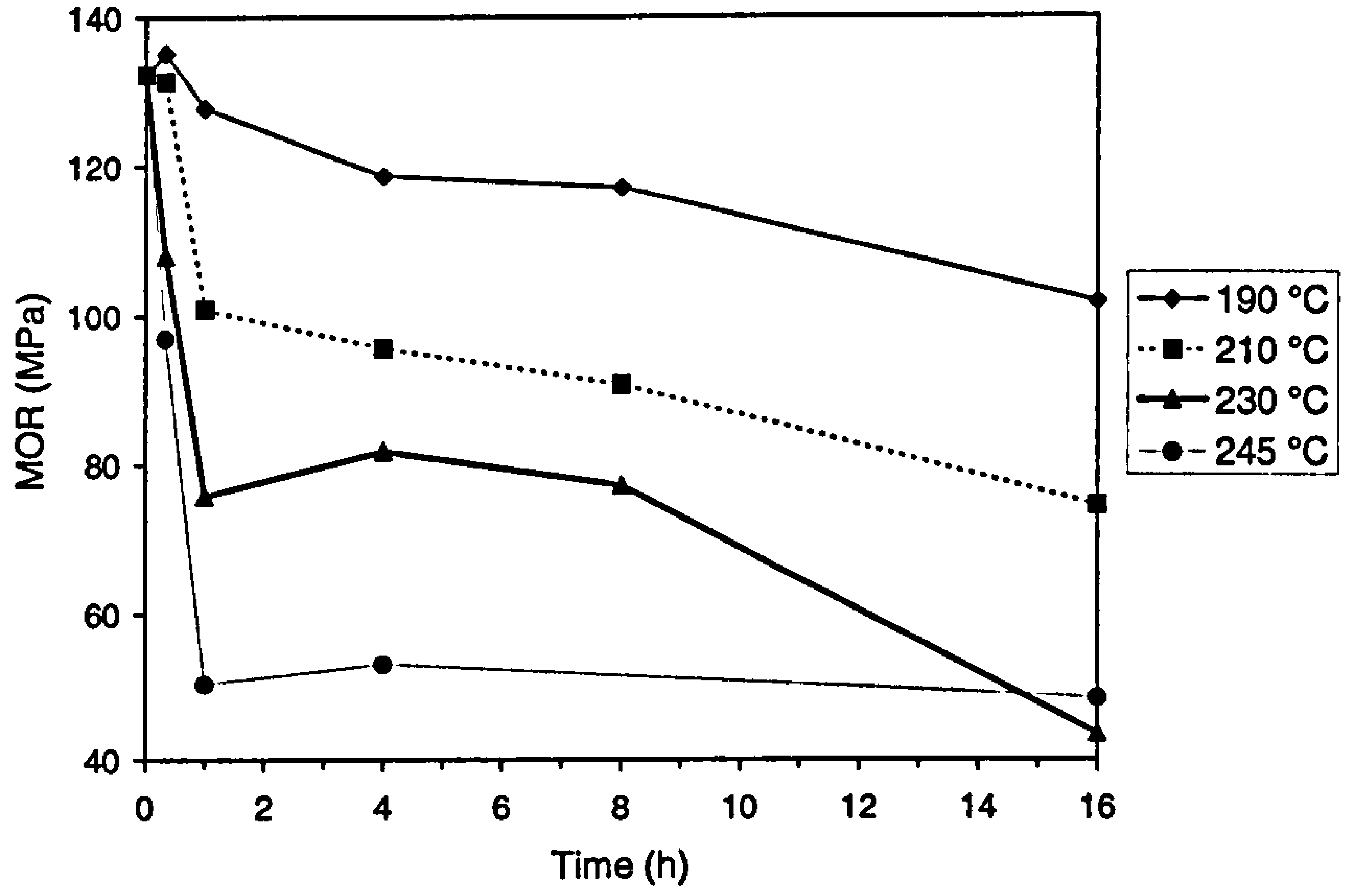


Figure 5.5 The effect of time and temperature in MOR change in beech. Each point represents the average value of ten replicates.

In beech, the most noticeable effect of time of treatment was the reduction MOR at increasing exposure periods, but the effect of treatment time varied with the temperature of exposure (Figure 5.5). At the lowest temperature, the MOR rate reduction was almost linear with time. At 210 °C and 230 °C, the reduction in MOR was very fast at the beginning, for treatments up to 1 h long, and then the reduction rate was constant somewhat. At the highest temp, the reduction was fast and large, so that by 1 h of treatment, the reduction in bending strength had already reached the maximum recorded in this study, a decrease of around 65%, the further reduction being only marginal.

Softwoods

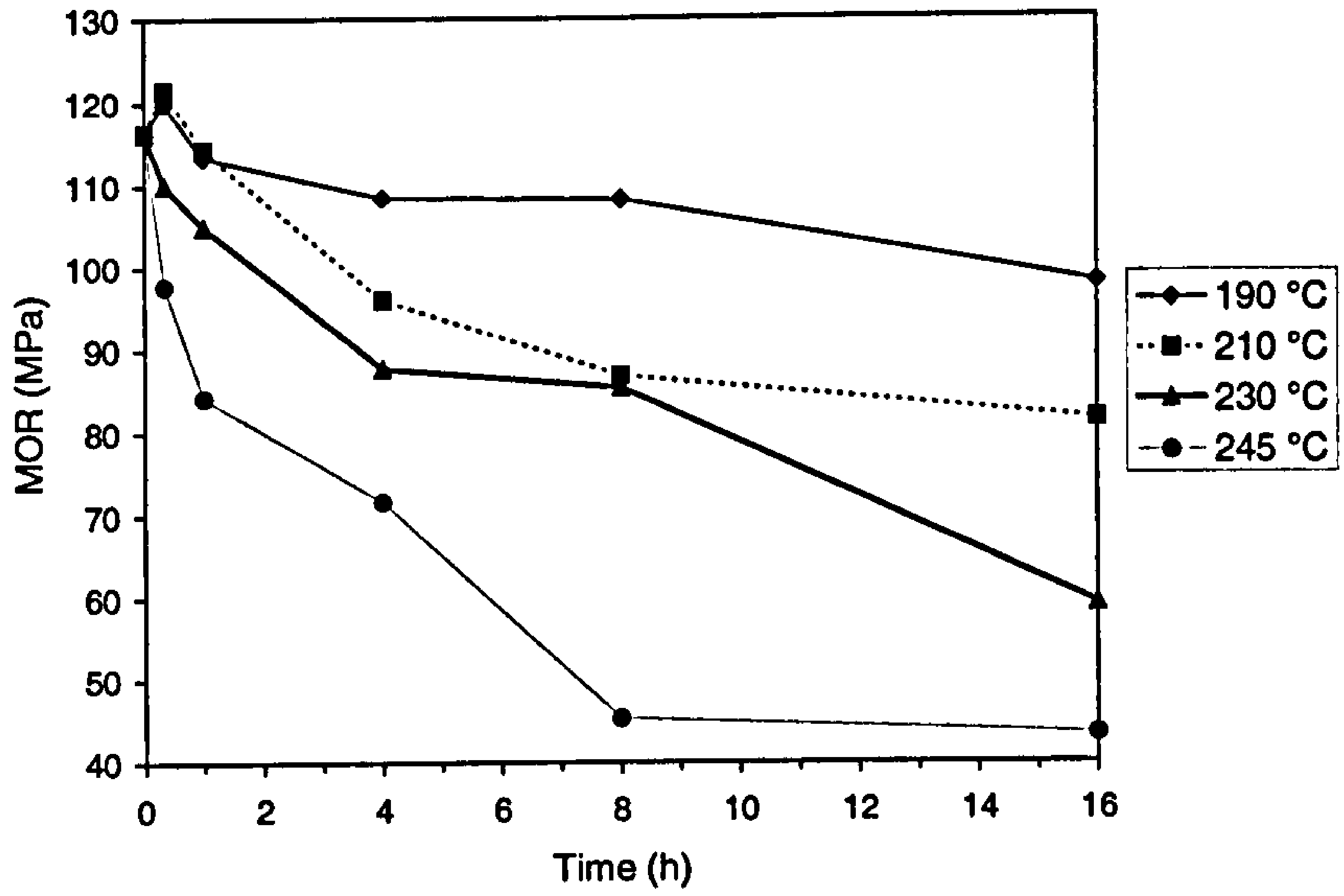
At the lowest treatment temperature, MOR was not changed significantly in both softwoods species, but for the treatment for 16 h in pine, the significant difference being 15.7% at a WL of 3.8% (Figure 5.2). Treatment at 210 °C led to significant MOR changes in pine when the treatment was for 4 h or longer. In contrast spruce MOR was significantly reduced (by 25.0%) only when the treatment was for 16 h, leading to a WL of 8.74%. At 230 °C, both pine and spruce were not significantly changed for treatments up to 1 h long. Afterwards, MOR was significantly reduced, to reach a maximum of 49.0% and 52.4% in pine and spruce, respectively. At 245 °C, all the treatments led to significant reduction in pine MOR, whereas in spruce reductions occurred when the time of treatment was longer than 0.3 h, to WL equal or greater than 10.7%. At the highest temperature of exposure, the maximum reduction of MOR was 62.6% and 76.9% for pine and spruce, respectively. One difference between pine and spruce treated at 245 °C was that spruce MOR continued decreasing with time, to very low values, whereas in pine once the reduction in MOR reached *ca.* 60%, at 8 h of treatment, any further reduction was very small, and statistically not significant.

Effect of time and temperature in softwoods

In the case of softwoods, MOR followed generally the same changing pattern in both species, spruce exhibiting slightly better mechanical performance after most of the temperatures of treatment (Figure 5.6). Regardless of the temperature of treatment, pine MOR was significantly different from control as soon as the WL was 3.83%. In spruce this property was significantly reduced only when the WL was 8.74%.

Increasing the temperature or time of treatment led in most cases, to reductions in MOR in softwoods -not in all cases significant ones though, but the effect was less striking than in beech. Contrarily to beech, the MOR of softwoods was in no case reduced dramatically, the change in property being almost curvilinear with time in both species despite of the temperature of treatment. The effect of temperature is more marked than time in property change in softwoods. Softwoods heated at 190 °C for 16 h suffer about the same strength loss as the one that occurs only after 4 h at 210 °C (Table 5.1).

In all the three species the reduction of MOR was progressive, in line with the time of exposure but for two exceptions. One was spruce treated at 190 °C, where the MOR reduction appears to stabilize after 16 h of treatment. The second exception was in beech treated at 245 °C, where the reduction was very fast at the beginning of the treatment, and then appears to become stagnated. The difference between beech and softwoods was the fast decline in beech MOR at the beginning of the modification, particularly at temperatures > 200 °C, whilst in softwoods the reduction was gradual in all cases.



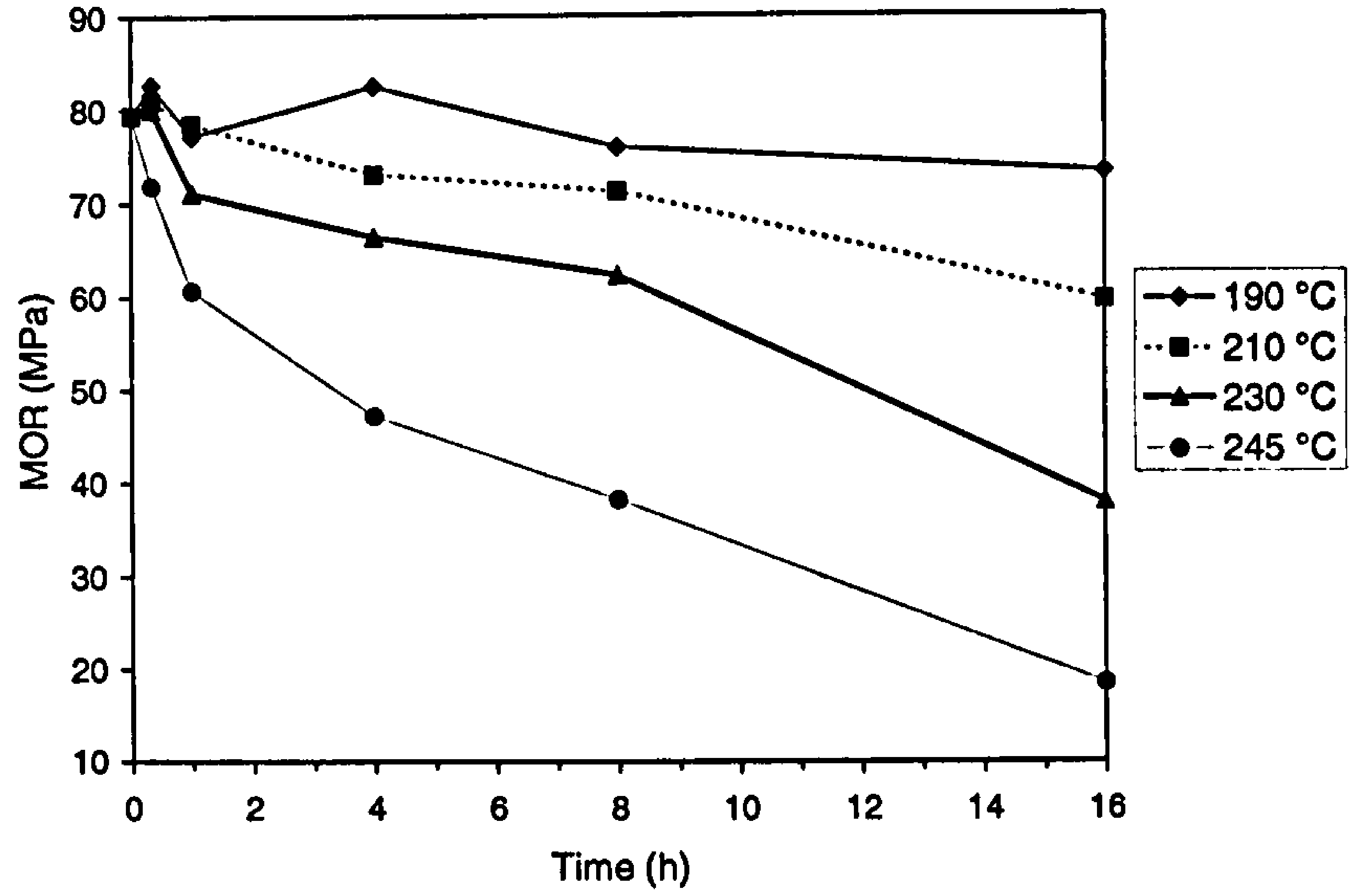


Figure 5.6 The effect of time and temperature in MOR change in Scots pine (above) and Norway spruce (below). Each point represents the average value of ten replicates. Error bars omitted for clarity.

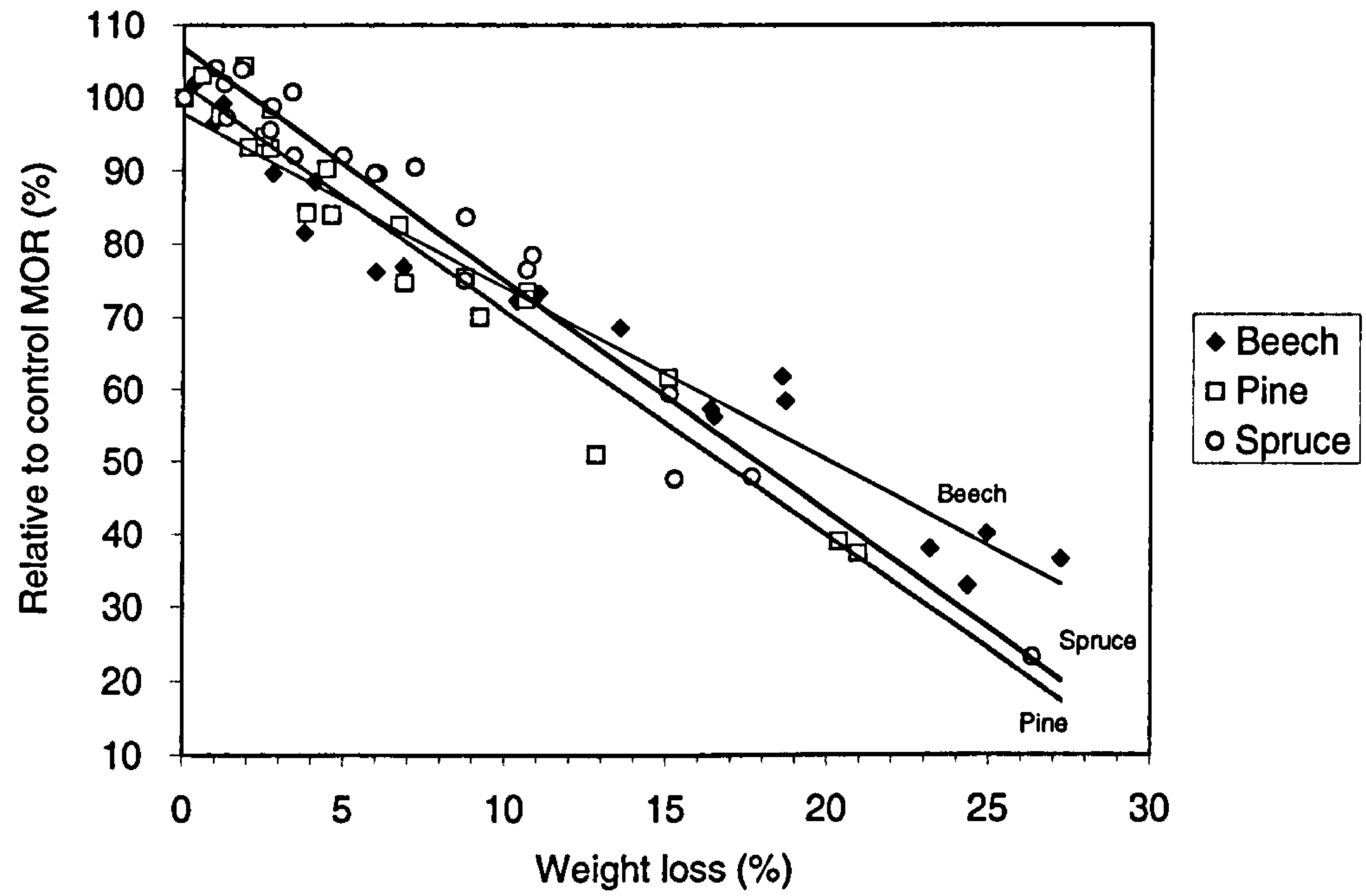


Figure 5.7 Relative (to control) MOR in bending for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements. Error bars omitted for clarity.

The relative-to-control average MOR values in bending plotted against the WL follows the same pattern for all the three species: the ratio shows a rectilinear trajectory, decreasing as the heat-induced WL proceeds (Figure 5.7). Property change pattern is very similar for pine and spruce, the latter having a slightly better performance than pine at comparable levels of treatment. Beech relative MOR follows a similar trend as softwoods' does, but its behaviour is mixed. It is more affected than softwoods' MOR at lower levels of treatment, the reduction being greater than that of pine and spruce at weight losses of 5% and 10% respectively. After that point beech relative MOR is less affected by the treatment than softwoods'.

Similar results were reported for relative MOR in tension by Rusche (1973), who studied the effect of thermal treatment in beech and pine in presence and absence of air. This author found that the relationship between relative MOR in tension and substance loss was similar for both species, following a rectilinear trajectory between ~0.8% and 30% of substance loss. He did not find significant differences between pine and beech, though.

On the change in the coefficient of variation of MOR

Whilst the MOR changes significantly at moderate WL for spruce and beech (8.74% and 6.85%, respectively) and at slightly lower levels in pine, contrarily to the MOE, the coefficient of variation (CV) of MOR gradually increases in all the three species as the severity of the treatment intensifies (Figure 5.8). On average, CV almost doubles as soon as the WL reaches 10%, from a CV of *ca.* 5%, 6.5% and 8% in control spruce, pine and beech, respectively, to 10%, 13% and 17% in average for treated samples, in the same order. Beech variability increases very fast at the beginning, and levels off at a WL of about 11%. The variability in pine and spruce follows the same pattern, increasing almost linearly with the thermal-induced WL. The larger MOR variability in treated samples compared to untreated ones could be due to the known heterogeneity of the wood substance. Unevenness in chemical composition and cell wall density in different cell types (parenchyma, fibres, and tracheids) or different tissues (latewood and earlywood in softwoods, rays and sclerenchyma in beech), probably leads to differential levels of treatment in diverse zones, rendering a more variable material in strength properties.

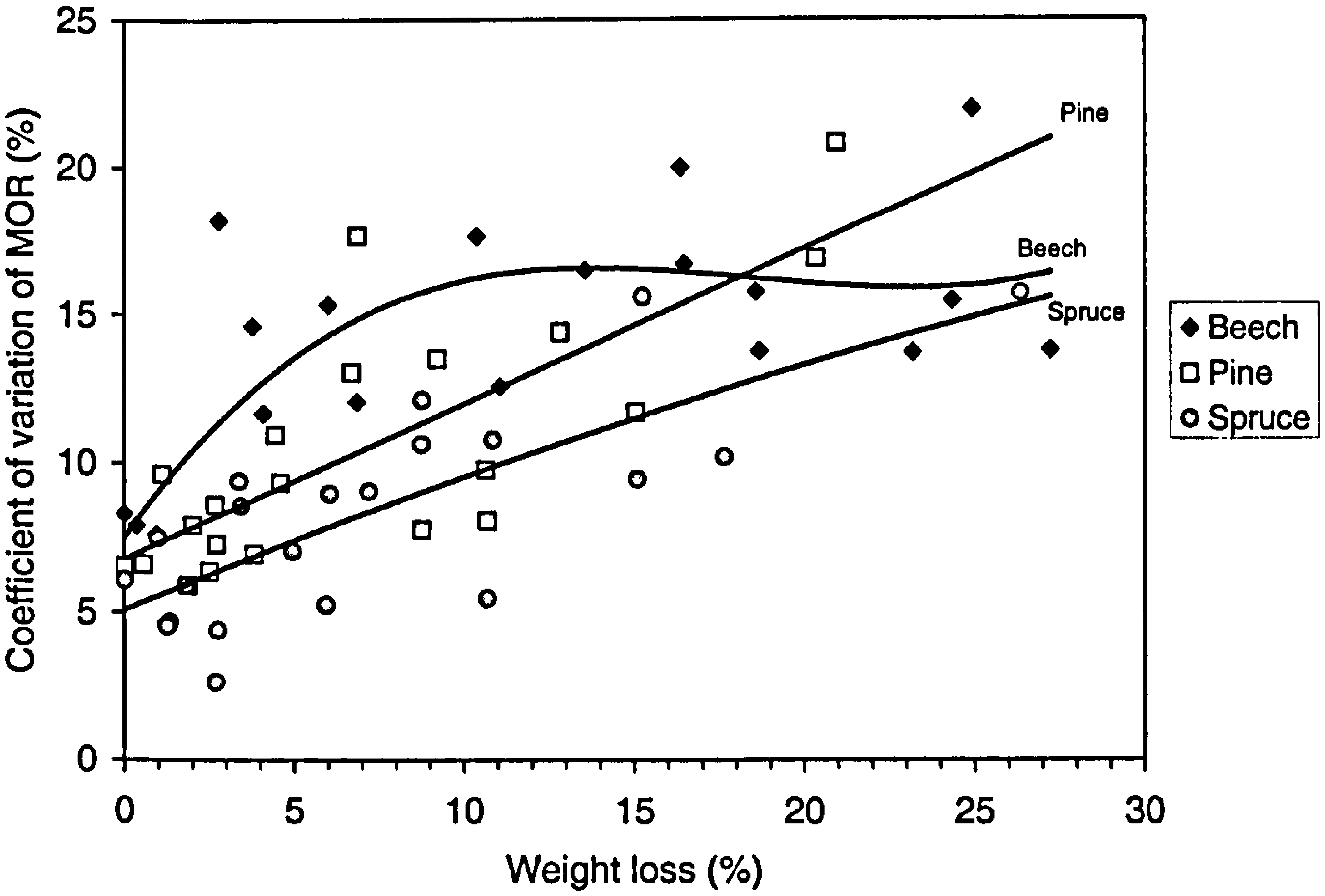


Figure 5.8 Coefficient of variation (CV) for MOR in bending for beech, Scots pine and Norway spruce. Each point represents the mean value of ten replicates

Since the standpoint of the increased variability, a comparison of the parametric 5th percentile value shows that this was 119.2, 106.1 and 72.4 MPa for untreated beech, pine and spruce, respectively (Table 5.2). At a weight loss of say 8%, estimated MOR decreased by ~ 21%, 23% and 19% in the same order, irrespective of the temperature of treatment. In turn, the reduction in the 5th percentile value was substantially greater in beech and pine, to an estimated 83.3 MPa and 75.3 MPa, respectively, a decrease in the parametric value of about 30% in the former and 29% in the latter. The decrease in this value in spruce was only marginal, to 56.6 MPa (22% of control 5th percentile). Analogous behaviour was found when the WL was 12%, the decrease of the 5th percentile value being always greater than the decrease in mean MOR. This higher variability may limit somewhat the applicability of TMW in load bearing situations; this may not however preclude its use for these purposes. Similar effect of the thermal modification but greater reductions in the 5th percentile value for MOR was recorded by Bengtsson *et al.* (2002). These authors also found that the reduction in the 5th percentile value was larger in spruce than in pine, probably because, contrarily to this study, they were working with beams instead of defect-free wood specimens.

Table 5.2 Bending strength and parametric 5th percentile value for treated and untreated wood at two levels of heat-induced weight loss. Mean MOR values are shown for untreated samples. Estimated mean MOR and 5th percentile values (as a function of WL) are shown for treated samples.

Weight loss (%)	Descriptor (MPa)	Beech	Pine	Spruce
0	MOR	132.4	116.3	79.4
	5th percentile MOR	119.2	106.1	72.4
8	MOR	104.2	89.7	64.5
	5th percentile MOR	83.3	75.3	56.6
12	MOR	91.7	75.2	54.4
	5th percentile MOR	71.7	60.6	46.7

Reasons for changes in MOR

Evidently, the underlying factors for changes in MOE and MOR in TMW are very different, since these two strength parameters behave differently in both the manner and the magnitude of change at equivalent levels of modification. As it was pointed out above, MOE is dominated by the mass of the specimen, as well as the microfibril angle and cellulose crystallinity, all of them little changed by most of the treatments carried out in this study. In defect-free wood specimens, it was traditionally hypothesized that MOR was closely related to density and particularly to the physical state (degree of polymerisation and crystallinity) of cellulose and to microfibril angle. However, in the light of relatively recent findings, it is now increasingly recognized that the composite nature and all the three main chemical constituents of the cell wall play a major role in MOR in bending.

As it was pointed out at the beginning of section 5.2, one possible reason for the reduction of MOR in bending strength was the increased resistance to compression strength in treated wood (section 5.3), opposite to the immediate reduction of tensile strength. An implication of this dichotomy is that the material does not dissipate energy by means of a gradual compression failure at the upper face of the beam. This behaviour has been noted previously in brash wood (Dinwoodie 1970). A characteristic of this type of wood is its low ratio of tensile to compression strength along the grain. In normal wood, the ratio is about five to one and failure occurs slowly on the compression side of a beam stressed in bending. In brash wood however there is a lower differential between tensile and compressive strengths because failure in tension occurs at lower level of stress. Complete failure of the beam will be associated with lower deflection and energy absorption.

Two possibly complementary explanations have been proposed to explain the strength loss in MOR. The first involves the relationship between chemical and MOR changes. Leopold and McIntosh (1961, cited by Davis and Thompson 1964) reported that reductions in the tensile strength of hydrolysed loblolly pine tracheids were correlated with decreases in xylan-based hemicelluloses. They postulated that this hemicellulose fraction is located between fibrils, and that its removal reduces interfibrillar bonding, thus causing a reduction in the internal strength of the fibre. This role of interfibrillar adhesive of hemicelluloses could also influence other mechanical properties, but the evidence points that the effect of heat-induced changes in this fraction is primarily manifested in impact resistance and this will be dealt with in section 5.4.

In more recent research, Winandy and Lebow (2001) hypothesized that bending strength losses occur in hydrolyzed wood at low levels of WL because of changes in wood chemical composition. Side-chain sugars of hemicellulose were found to be the most susceptible to acid hydrolysis, followed by sugars associated with the hemicellulose backbone; the extent of their degradation proved to be a sensitive predictor of early stages of strength loss. These authors reasoned that the load-sharing capability between hemicellulose chains is reduced as side-chain hemicellulose moieties (arabinose and galactose) and subsequently main-chain hemicellulose constituents (xylose and mannose) are degraded. Upon further degradation, interpolymeric load-sharing capacity among the three components of the cell wall is gradually reduced and overall wood strength diminished. Contingent evidence of the relative importance of hemicelluloses in wood strength is given when wood is exposed temporarily to temperatures which only cause reversible reductions in strength (below 95 °C). This is because the glass transition temperature for hemicelluloses is lower than that for cellulose and lignin. Transient reductions are also influenced greatly by increased moisture content. As hemicelluloses are the most hydrophilic polymers in the wood substance, the temporary disruption of hemicellulose's structure upon wetting highlights the relevance of hemicelluloses in wood strength.

Mouras *et al.* (2002) hypothesized that the reduction of MOR in TMW was linked to two main phenomena: a change in the lignin structure due to the condensation of degradation by-products, and due to changes of the state in the amorphous cellulose. This second suggestion is part of the second explanation for the reduction of MOR in TMW, which is more related to the after-treatment physical state of the cell wall material.

González-Peña and Hale (2007b) suggested that the main cause behind the reduction in the ultimate fiber stress in bending was the after-treatment physical state of the cell wall substance in modified wood. The shrinkage of the cell wall leaves the treated material in a permanent state of strain, where the reduction of transversal dimensions concurs with the lengthwise increase in specimen dimensions –the Poisson effect. This permanent shrinkage reduces firstly the capability of the cell wall for elastic deformation, lowering the limit of proportionality and, thereafter, drastically lowers the ability of the cell wall polymers for plastic flow, leading to failure at significantly lower levels of strain. This was somewhat supported by previous research of Mark (1952). He was testing the tensile strength of cellulose fibrils and postulated that, if the material was considered to have mixed crystalline and amorphous areas, some of the chains, particularly those in the most adverse positions would take most of the load upon stress, and may break or slip along each other at early stages of deformation. Others, which are curled or wound up may straighten out and gradually become parallel, which leads to an increase in crystallization. This in turn increases the internal viscosity and allows the gradual accumulation of potential energy in the material. When the stress becomes even higher, the aligned chains start to slip along one other and produce a flow, the consequence of this being the gradual reduction of the transversal cross-section of the material. This leads to an increase of the stress and eventually to the rupture.

Therefore, the reduced MOR strength in TMW is likely to be a consequence of a reduced capability of wood polymers for uncoiling or slippage under stress, derived from the permanent shrinkage of the cell wall and to the well established increase in crystallinity of cellulose, and annealing of remaining hemicellulose polymers along cellulose chains.

Results from the present research coincide with reports of previous studies in diverse thermally treated woods. For instance, Chang and Keith (1978), Mitchell (1988), Kim *et al.* (1998), Kubojima *et al.* (2000), Mouras *et al.* (2002) and Bekhta and Niemz (2003) have all found that MOR is more sensitive to heat than MOE, without regard to the atmosphere or other treatment conditions. In all cases, the temperature of treatment had a more important role in property loss than time of exposure and some instances of incipient increase in MOR at low levels of modification have been observed (Kubojima *et al.* 2000). Relative-to-control beech and pine MOR in tension appear to be modified to the same extent at equivalent levels of WL (Rusche 1973), although the topic has been poorly studied.

5.2.3 Fiber stress at limit of proportionality

Whilst the determination of MOR is of major relevance as far as current standards is concerned, whereby most of the characteristic values for design purposes are drawn from the maximum bending strength, in practical terms, users depend upon the performance of the wood not just at the failure level, but in fact well below the proportional limit, since we depend on the elastic performance of the wood. For instance, it is expected that floor joists would straighten up when the applied live load (people) has been removed from the floor. Therefore, it is important that the fiber stress at limit of proportionality (RLP) to be described and considered if this can justify the performance of a product in which wood is used (Figure 5.9).

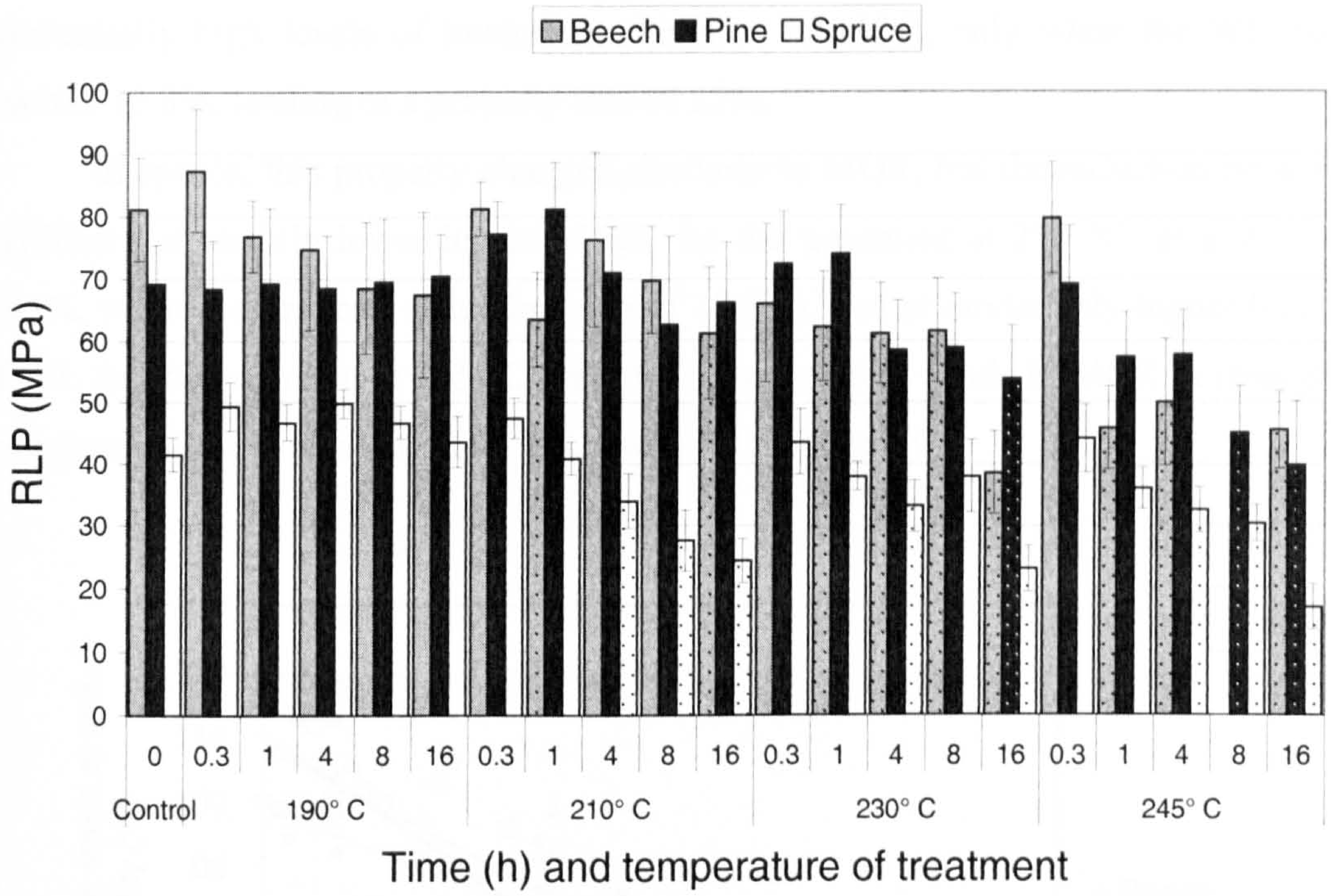


Figure 5.9 Effect of thermal modification on fiber stress at limit of proportionality in bending (RLP) on samples of beech, Scots pine and Norway spruce. Each column represents the mean value of ten replicates. Mottled bars = treatments significantly reduced. Error bars = ± 1 SD.

In beech, the performance of this property was slightly better than the one for MOR, but with increased variability and with a trend not as clear as MOR as far as the relationship with WL is concerned. None of the treatments at 190 °C caused significant reduction in this property. At 210 °C, the reduction was only for the treatment at 1 h and 16 h. The treatment for 1 h was an irregular reading, because this caused significant reduction, when the treatments for 4 h and 8 h did not. For the treatments at 230 °C and 245 °C, the strength was reduced significantly in treatments for 1 h or longer.

The significant reduction in RLP in beech was, in general, at higher severity treatments than in MOR, but these varied with the temperature of treatment. RLP was significantly reduced at increasingly higher WL as the temperature of treatment increased. At 210 °C, the significant reduction was by 21.8%, at a WL of 6.0%; at 230 °C, these values where in the order of 23.2% and 16.37%, whilst at 245 °C, they where 43.5% and 23.19%, respectively.

In the case of pine, RLP was clearly less affected than MOR. The only significant change took place when the treatment was carried out at 230 °C for 16 h and at 245 °C for 8 h or longer. This property became different from control at substantially high levels of treatment compared to MOR, only when the WL had reached 12.8%, leading to a property loss of 22%.

In spruce, this property changed similarly to MOR, but the reduction became significant at slightly lower levels of WL for the treatment at 210 °C (at a WL of 4.95%, when the property reduction was of 18.3%), and at moderately higher levels of WL for the treatment at 245 °C than the correspondent levels in MOR (a strength reduction of 21.6% at a WL of 15.1%, Table 5.1, Figure 5.9).

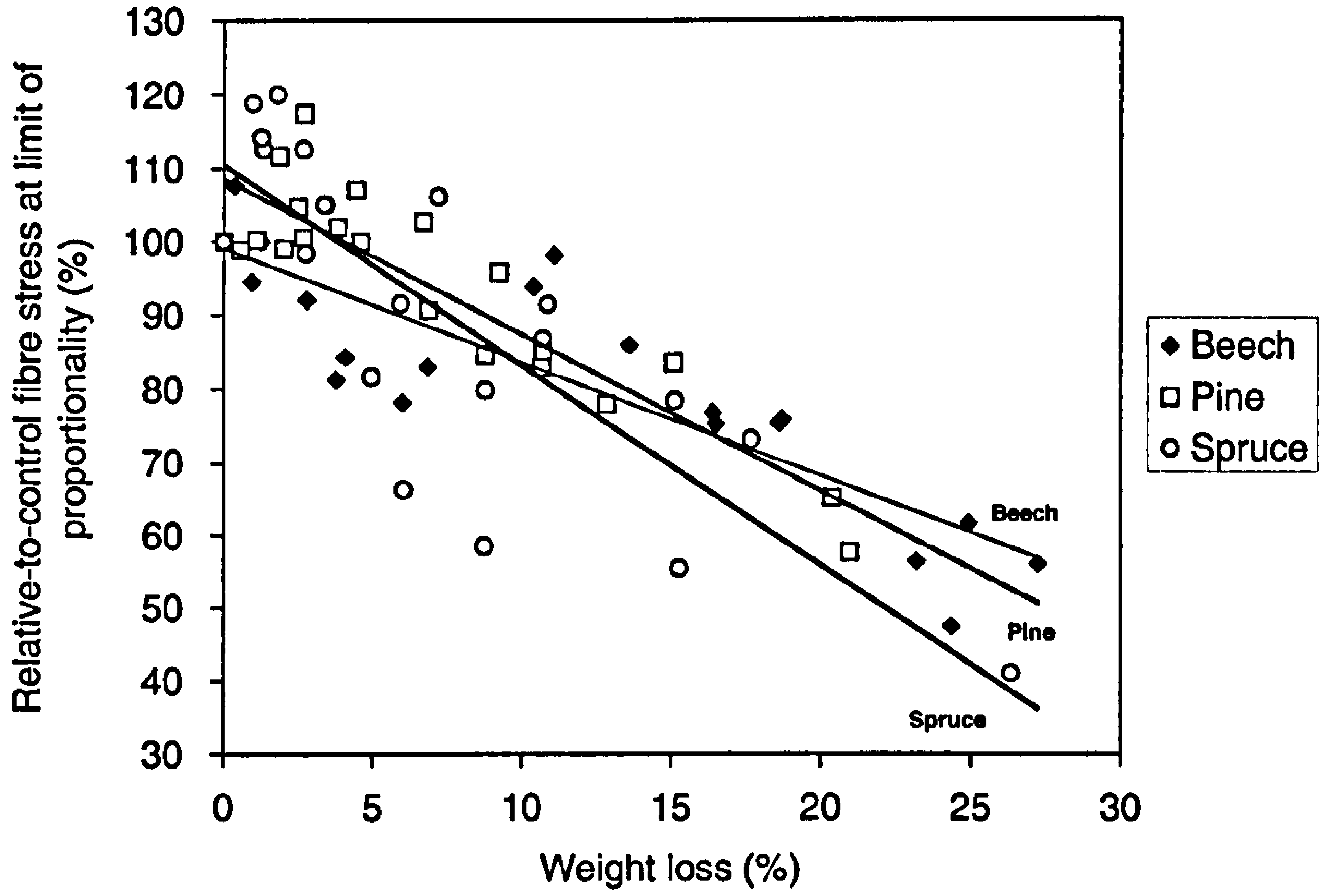


Figure 5.10 Relative (to control) fiber stress at proportional limit in bending for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements.

For the relative-to-control average RLP values in bending in dependence of the WL after the heat treatment (Figure 5.10), this property changed in the same pattern for all the three species: the ratio follows a linear trajectory. Property change pattern is very similar for pine and spruce; softwood RLP being affected at slightly lower levels of treatment than beech RLP. In general, this property was attended by more variation in beech and spruce compared to the MOR, and the relationship of RLP with the WL was not as clear as was between MOR and WL, although the relative reduction was in general smaller than that of MOR at equivalent levels of treatment. This is a key finding, because it implies that an important part of the reduction of MOR takes place after the limit of proportionality has been reached, and consequently, that the material is somewhat more reliable in normal conditions of service (*i.e.* within the elastic range) that it would be perceived if the bending strength would be derived from the values of MOR.

Reasons for changes in RLP

Although the rationale behind the smaller strength reduction in fiber stress at the proportional limit compared to the ultimate fiber stress at correspondent levels of WL is not completely clear at this time, apparently the fiber stress at maximum load is composed of two separated mechanisms. One may be related to the elastic behaviour of the material, probably governed by the concourse of different molecular rearrangements in the cell wall material, to some extent less affected by heat (*e.g.* cellulose crystallinity, lignin content) and more closely related to the RLP and there is another phenomenon which is more related to the plastic absorption of energy, which has no connection with the elasticity of the wood, and which is a component more affected by the treatment (*e.g.* hemicellulose degradation). No studies have been published on the effect on thermal modification on RLP.

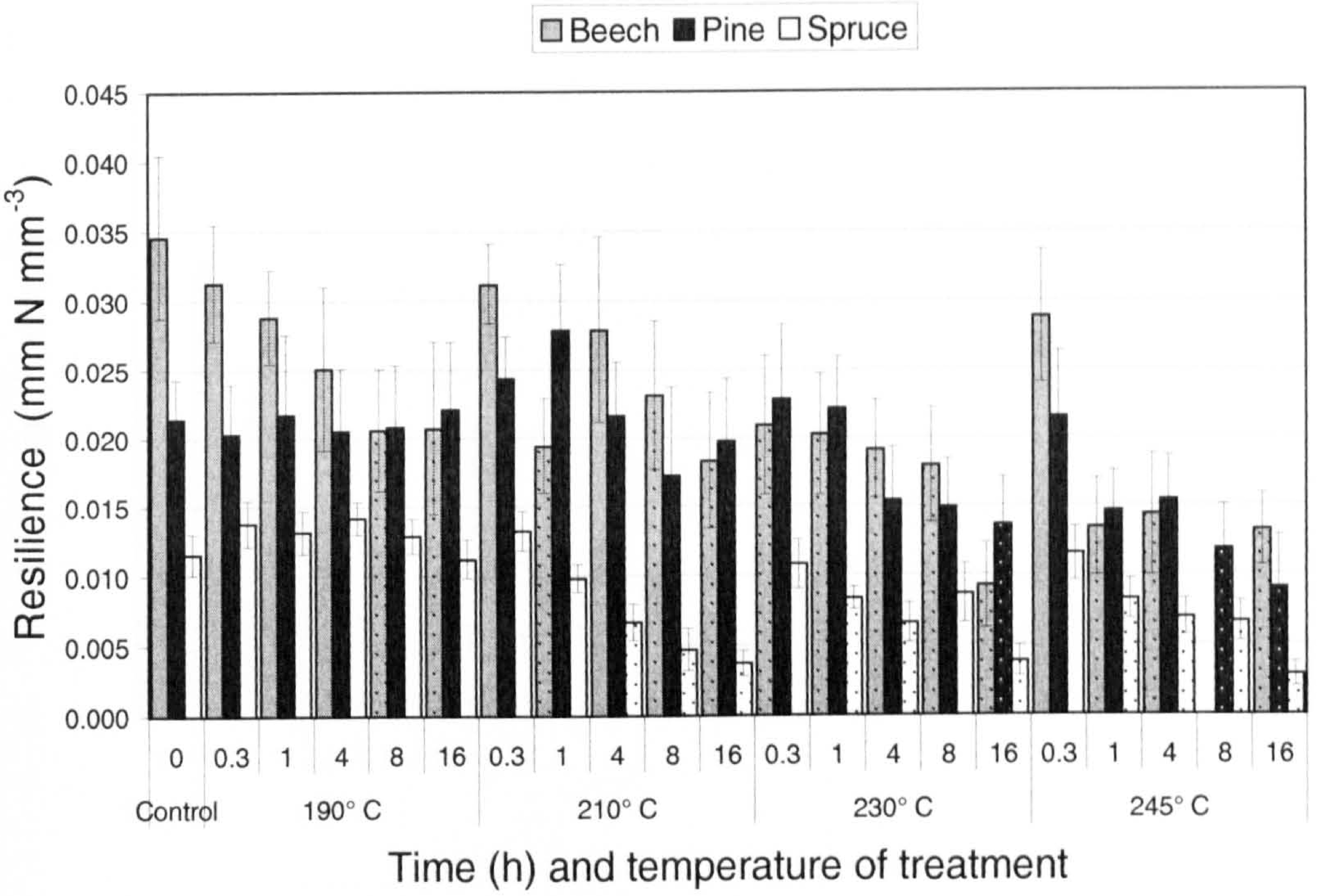
5.2.4 Resilience, work at maximum load and total work

Resilience is the amount of work done upon a body in deforming it. Within the elastic limit, it is also a measure of the potential energy stored in the material and represents the amount of work the material would do upon being released from a state of stress. This amount of work can be applied repeatedly, and is perhaps the best measure of toughness of wood as a working quality though it is not synonymous of toughness. According to Gordon (1991), the quality of being able to store strain energy and be deflected elastically under load without breaking is called resilience, and it is a very valuable characteristic in a structure.

Work to maximum load (WML) is a measure of the energy expended in failure and is determined from the area under the load-deflection curve up to the point of maximum load. Consequently, this parameter is also a measure of the toughness of timber, as is also Total Work (TW), where the area under the load-deflection curve is read to complete failure (Dinwoodie 2000). From a practical point of view, reduced toughness in a material is not a desirable characteristic: for example, in instances were a sudden load is applied to the material, the reduced ability to withstand the work is reduced, and the whole structure compromised.

The ANOVA was carried out after a logarithmic (linear) transformation of property values of R, WML and TW, due to the curved nature of the original data with respect to WL. For all three species, the results for R were substantially more spread than that of all other properties studied (Table 1, Figure 5.11).

Resilience was also the energy-related parameter less affected during the bending testing. In fact, in pine, this property was significantly different to control only at a very high degree of modification at the most severe treatment regimes, at 230 °C and 245 °C for more than 8 and 4 h respectively, when the WL had reached at least 12.83%, causing a property loss of at least 36%. In the case of beech and spruce, resilience was less affected than WML and TW, but this difference was not as striking as in pine. In beech, R was significantly reduced at any temperature of treatment, but the reduction was dependent upon the time of exposure. At 190 °C, R was reduced when the treatment was for 8 h or longer (at WL $\geq$ 4.1%); at 210 °C, the reduction took place when the treatment was for 1, 8 or 16 h (at WL $\geq$ 6.0%), at 230 °C the reduction was for any treatment time (at WL $\geq$ 3.8%), and at 245 °C the reduction was significant for treatment times of 1 h or longer (at WL $\geq$ 23.2%).



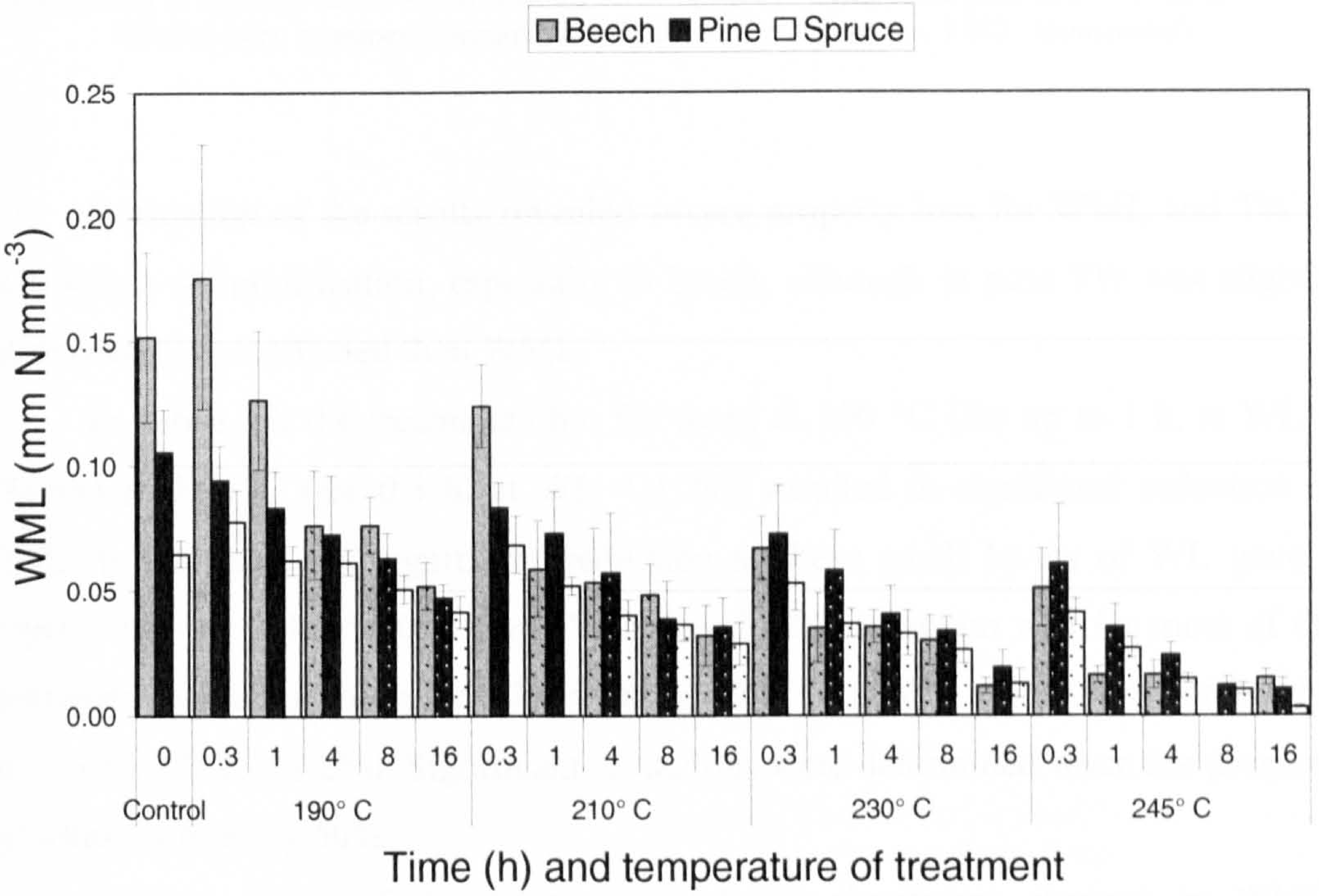


Figure 5.11 Effect of thermal modification on resilience (R), work to maximum load (WML) and total work (TW) in bending (from top to bottom) on samples of beech, Scots pine and Norway spruce. Each bar represents the mean value of 10 replicates. Mottled bars: treatments significantly reduced. Error bars = ± 1 SD

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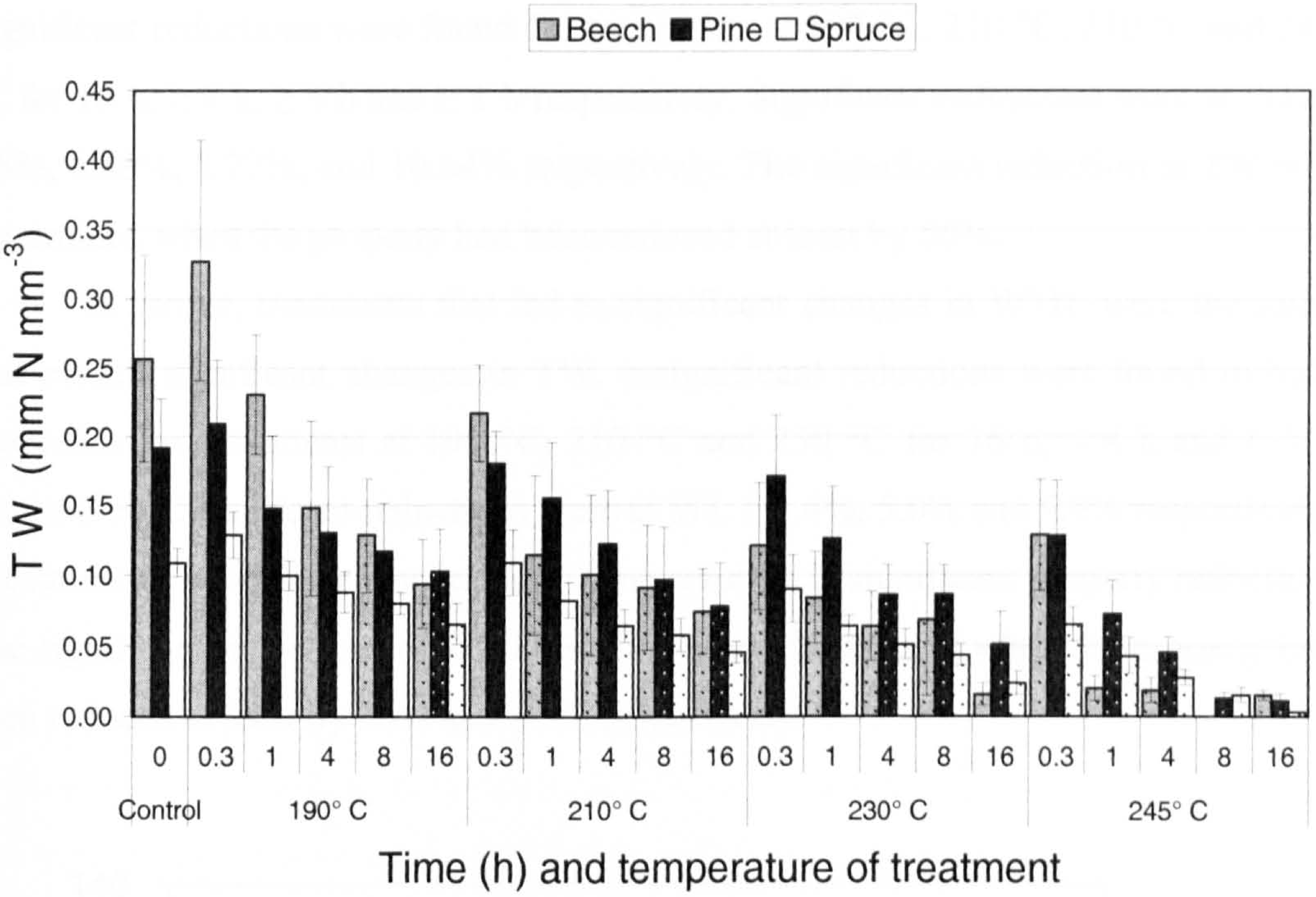


Figure 5.12 Effect of thermal modification on resilience (R), work to maximum load (WML) and total work (TW) in bending (from top to bottom) on samples of beech, Scots pine and Norway spruce. Mottled bars: treatments significantly reduced. Error bars = ± 1 SD (*concluded*)

Evaluation of the results revealed severe property loss for WML and TW at early stages of modification, especially in beech, although in pine TW was slightly but definitely less affected than WML.

In beech, all the treatments but for those at 190 °C (for up to 1 h, at WL < 2.8) and at 210 °C (for 0.3 h, at WL < 1.2%) resulted in significant reduction of WML. In all cases the significant reduction at these small levels of WL gave a property loss of at least 50%. For TW in beech, the reduction was for most of the treatments except for those for 4 h or less at 190 °C (at WL < 2.8%) and at 210 °C (for 0.3 h, at WL < 1.2%). Significant reductions were determined when the property had fallen at least by 50%.

In pine, most of the treatments induced significant changes in WML. Treatments with significant changes were at 190 °C, 210 °C and 230 °C for ≥ 8 h, ≥ 4 h and ≥ 1.0 h respectively, at WL < 2.7%, 6.7% and 4.4% (in the same order); at 245 °C all times resulted in significant decreases. These significant early WL gave WML losses of at least of 40%. Also in pine, significant reductions in TW occurred at any treatment temperature, but the results varied according to the time of exposure. Significant reductions were found for treatments at 190 °C, 210 °C, 230 °C and 245 °C for 16 h, ≥ 8 h, ≥ 4 h and ≥ 1 h respectively. Significant reductions were at WL ≥ 3.8%, 6.88%, 8.77%, and 10.64% respectively. The significant reduction in TW was determined when the property had been reduced at least by 56%.

In spruce, treatments that led to significant changes in WML were the same that caused significant changes in TW. Insignificant reductions were found in both properties for treatments at 190 °C, 210 °C and 230 °C for 16 h, < 4 h and < 1 h respectively. Significant reductions were at WL ≥ 3.4%, 5.0% and 5.9% respectively. Treatment at 245 °C for any period of time resulted in significant property reduction. The significant reductions in WML and TW were determined when the property had been reduced at least by 36% and 40%, respectively.

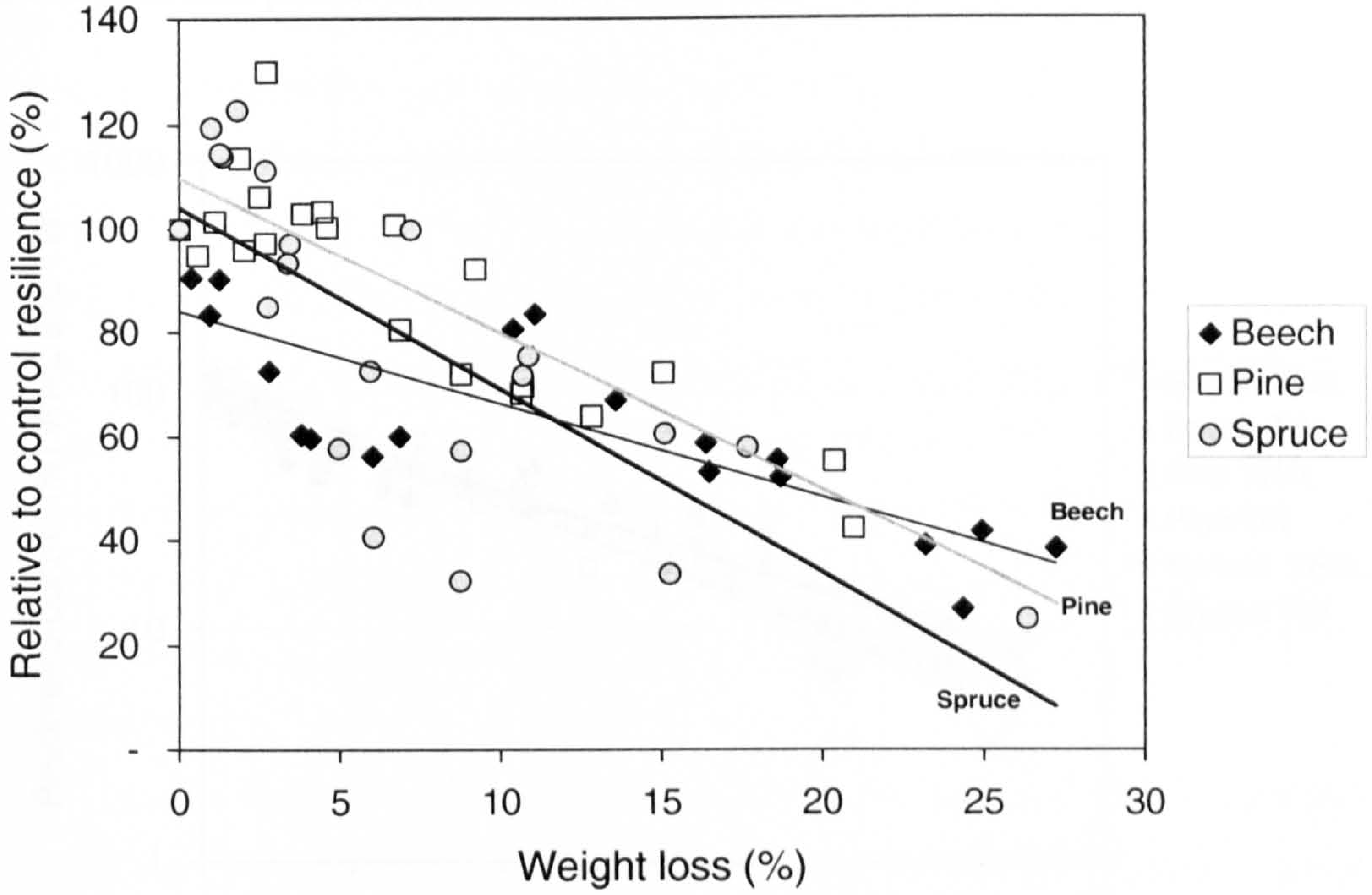


Figure 5.12 Relative to control resilience (R) in bending for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements.

The relative-to-control average R values in bending in dependence of the WL after the heat treatment (Figure 5.12) followed the same pattern although there is a large scatter of the data. For all the three species the ratio follows a rectilinear trajectory, with small increments at the beginning of the treatment for softwoods and then falling to reach control values at a WL of *ca.* 2% and 3.5 for spruce and pine, respectively. Beech R is somewhat reduced at low levels of modification, but the rate of change with respect to WL is smaller than in softwoods. The R pattern is very similar for pine and spruce; softwoods R being affected at slightly higher levels of treatment than beech's R do for WL up to about 12% in spruce and 22% in pine. After these levels of modification, R in beech is less affected by the heat-induced WL.

Changes in relative-to-control WML and TW plotted against WL also followed a rectilinear trajectory (Figure 5.13) in a log-normal plot. The changing pattern was remarkably similar for these two strength parameters for all the three species. Both properties are reduced at low levels of WL, although the changing rate in beech was slightly smaller. The absolute reduction was smaller in beech than in softwoods for WL above 7% for both properties. Spruce WML and TW were slightly less reduced than pine at equivalent levels of WL.

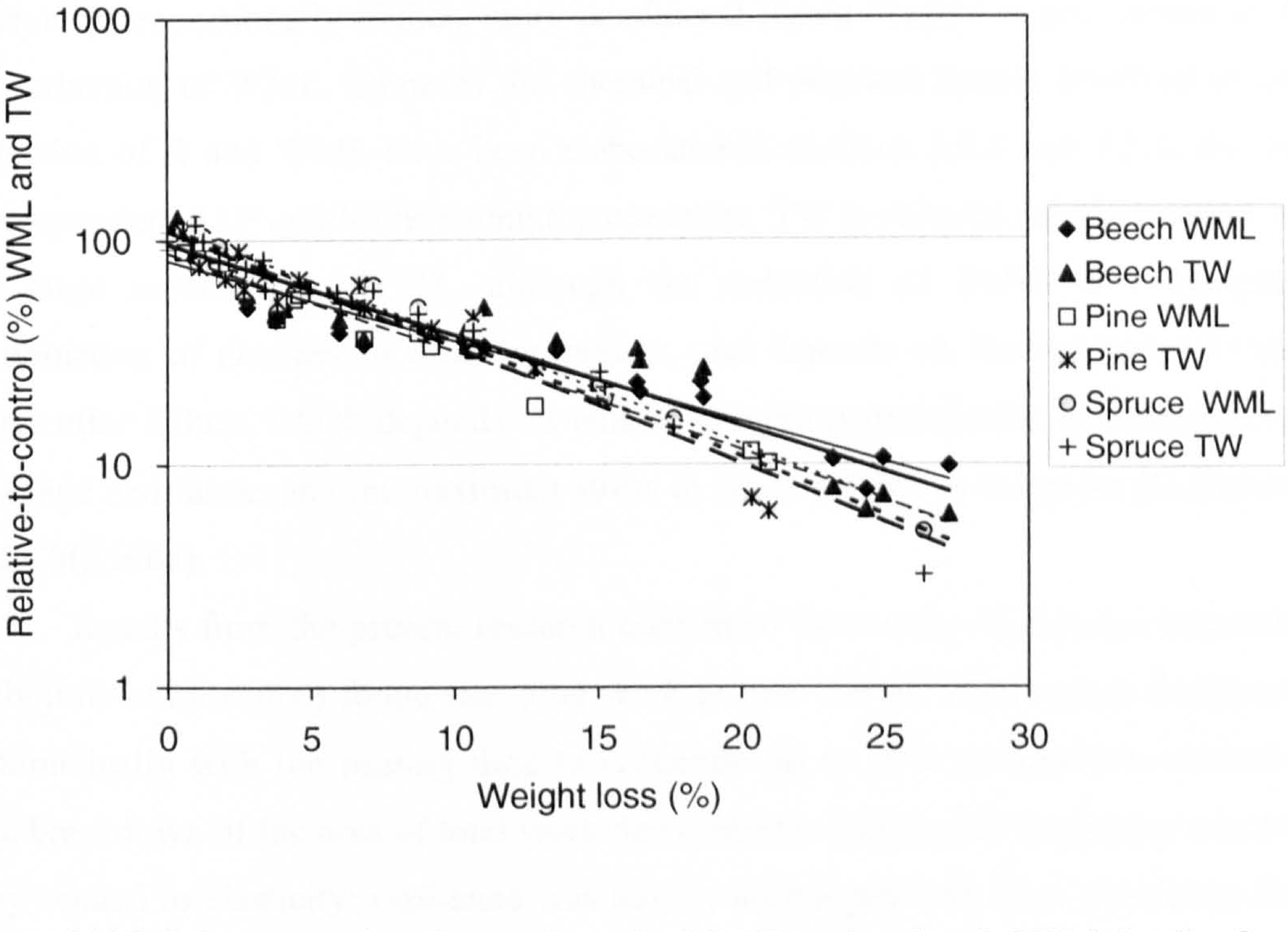


Figure 5.13 Relative to control work to maximum load (WML) and total work (TW) in bending for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements. Thicker lines: TW; thinner lines: WML. Solid lines: beech; broken lines: Scots pine; small broken line: Norway spruce.

Reasons for the reduction in Resilience, WML and TW

It is proposed that the reduction in resilience is more related to changes in the crystallinity of cellulose fibrils and lining up of hemicelluloses along the cellulose crystallites. Rather than the ultimate stress reduction at maximum load, the dramatic fall in WML is a consequence of that drastic decrease of the strain at failure: in a typical stress-strain plot, a reduction of 5% in the maximum load could lead to reductions of 33% in WML, because the latter is dependent on both stress and strain (Winandy and Rowell 2005). Thus the reduction in WML is a direct consequence of the sharp reduction of the viscoelastic portion of the energy expended in failure determined from the area under the load-deflection curve from the limit of proportionality up to the point of maximum load work. The reduction in this plastic work may be a consequence of the densification of the cell wall, as well as the degradation of plastic hemicelluloses. The commonly reported dramatic, brash fracture of TMW in bending could also partially be explained due to the differential change in compression and tension strengths, whilst the smaller EMC and the gradually proportionally higher, more condensed lignin content is also involved in the reduction of WML. Some of the chemical and physical factors involved in the reduction of R and WML have been elaborated in sections 5.2.3 and 5.2.2, for the correspondent RLP and MOR strength parameters. TW is reduced mainly because of the large reduction in WML, although the reduction of TMW is a complex combination of changes in many properties, and depends on the resistance of the fibres after failure, which depends on tensile strength perpendicular to the grain, on cleavage resistance, and on maximum stress in shear parallel to the grain (Kollmann and Côté 1968).

Results from the present research confirmed the results of previous research: Kubojima *et al.* (2000) found that total work in heat treated Sitka spruce decreased arithmetically with the heating time (a reduction up to 30% compared to control). The breakdown of the area of total work demonstrates that timber toughness was not very related to elasticity: resilience was almost unchanged with time. However, the area for R was the smallest of all the sections of the area under the line (*i.e.* it has little influence in the total behaviour). The work represented by the area after the breaking point, of little physical/mechanical significance, did not change significantly compared to control and this area was also small. The area representing the net viscoelastic behaviour (from the limit of proportionality up to the point of maximum load), was the largest and the most affected by the modification, meaning that the delayed elastic and plastic behaviour is more important in wood toughness than resilience.

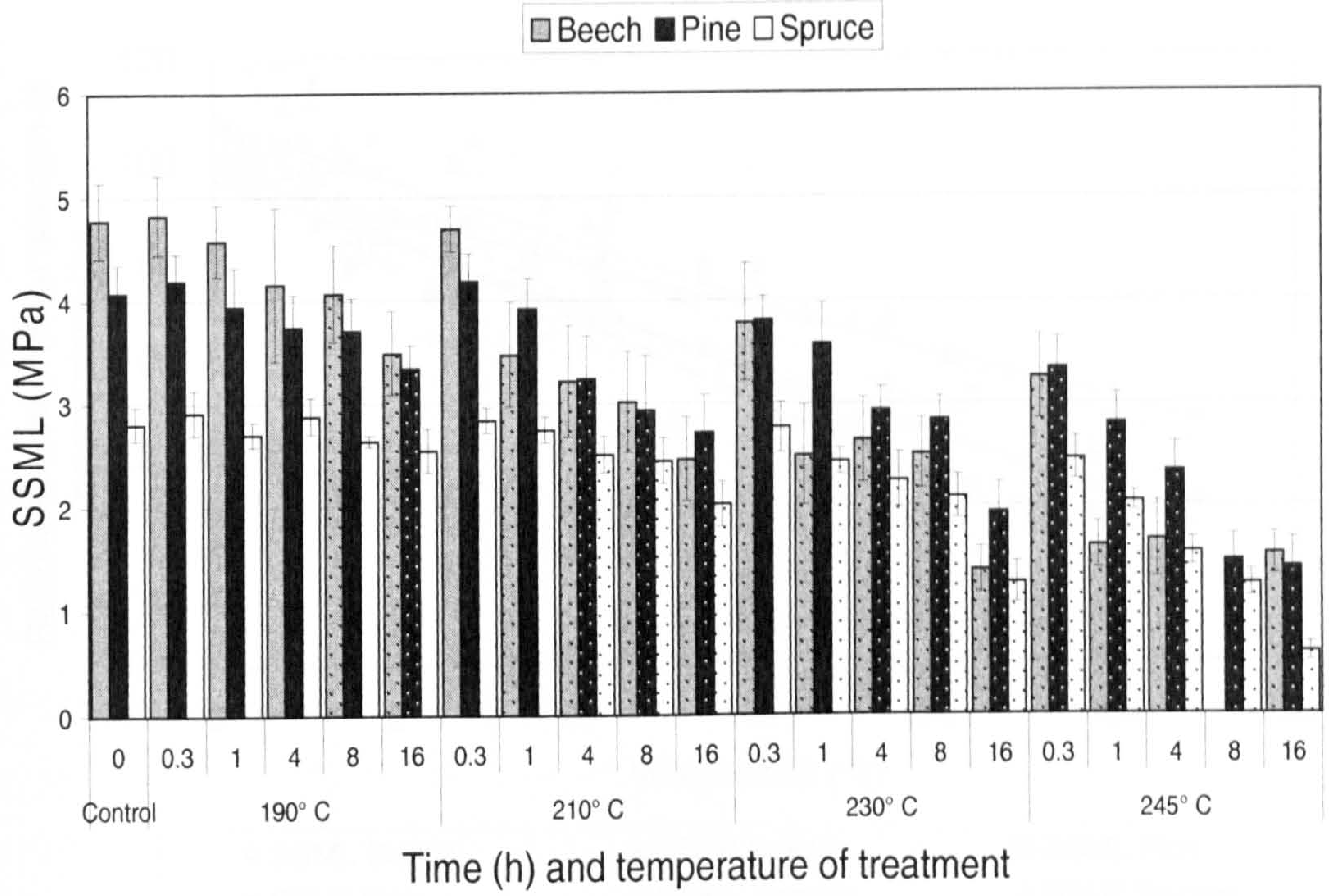
5.2.5 Horizontal shear strength at neutral plane at maximum load and at limit of proportionality

Table 5.1 and Figure 5.14 show that changes in SSML were greater than changes in SSLP in all three species, particularly in pine wood.

In beech, most of the treatments at temperatures greater than 190 °C lead to significant changes in SSML. Only the treatments for less than 8 h at 190 °C (to WL < 4.1%) and for 0.3 h at 210 °C (to WL < 1.2%) resulted in insignificant reductions in SSML in beech. SSLP remained insignificantly modified under these treatment conditions; the treatments at 210 °C for 4 and at 245 °C for 0.3 h (to WL < 11.05%) also resulted in insignificant changes.

In softwoods SSML and SSLP were less affected than in beech. In pine, SSML was modified at any treatment temperature, but the reduction varied according to the time of exposure. Only the treatment for 8 h or less at 190 °C (to WL < 2.7%), and for 1 h or less at 210 °C or 230 °C (to WL < 2.7% or < 4.4%, respectively) resulted in insignificant changes in SSML. In contrast, most of the treatments resulted in insignificant changes in SSLP. Significant changes took place in pine only at 230 °C for 16 h (to WL ≥ 12.8%) and at 245 °C when the treatment was longer than 0.3 h (to WL ≥ 10.6%).

In spruce, no time of exposure at 190 °C gave reductions in SSML or SSLP. At 210 °C, treatments for 1 h or less (to WL < 5.0) gave no reduction in both properties. At 230 °C, the reductions were significant for SSML when the treatment was for 1 h or longer (to WL ≥ 5.9%) and at 245 °C all the treatments conduced to reductions of SSML. The response of SSLP at 230 °C was somewhat irregular, because treatments at 0.3, 1 and 8 h gave no significant reduction, whereas treatments at 4 h (to WL ≥ 8.8%) or 16 h (to WL ≥ 15.3%) did. At 245 °C treatments for 1 h or longer (to WL ≥ 10.7%) lead to significant changes of SSLP.



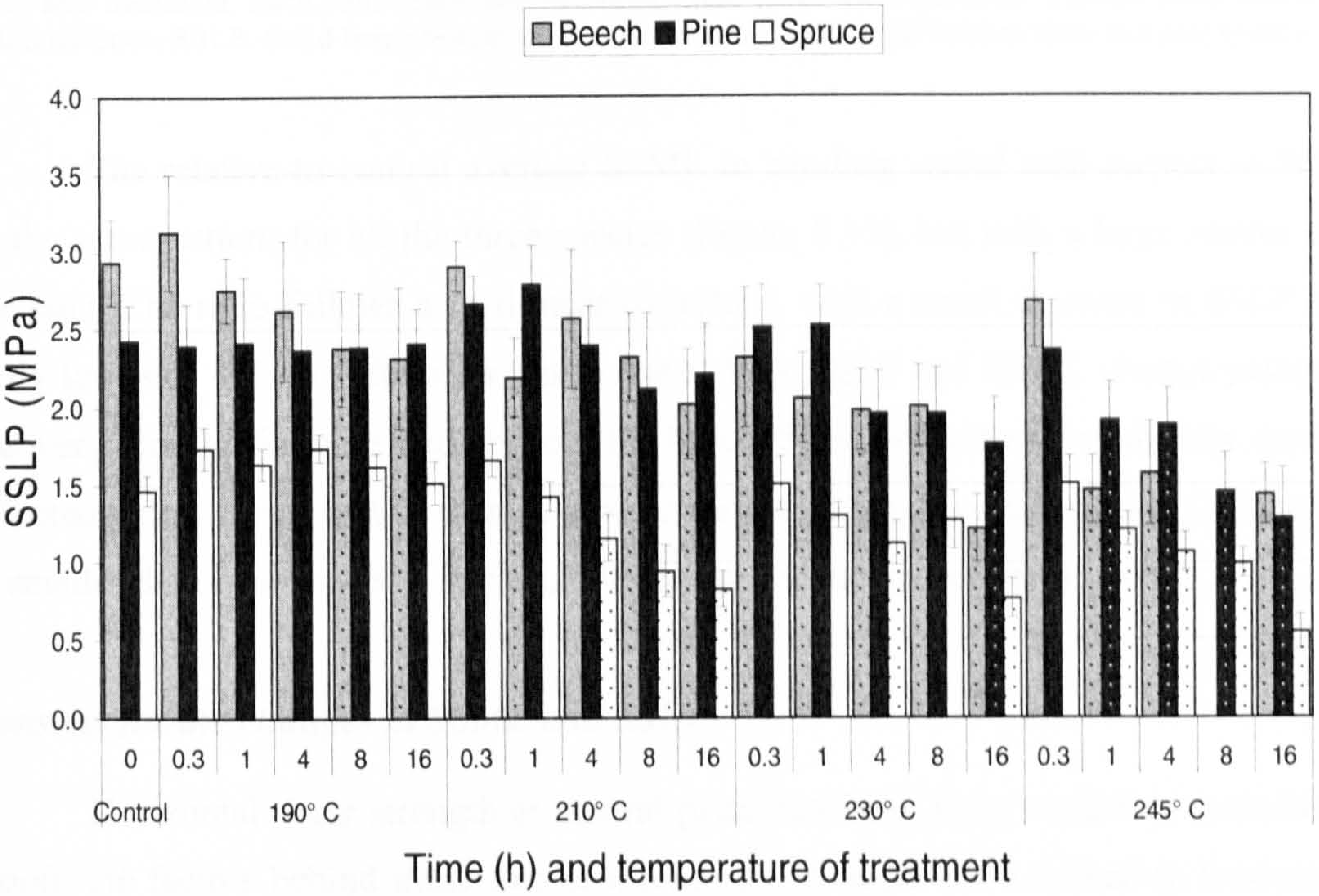


Figure 5.14 Effect of thermal modification on horizontal shear strength at neutral plane at maximum load (SSML, top) and at limit of proportionality (SSLP, bottom) on samples of beech, Scots pine and Norway spruce (from top to bottom). Each bar represents the mean value of ten replicates. Mottled bars = treatments significantly reduced. Error bars: ± 1 SD.

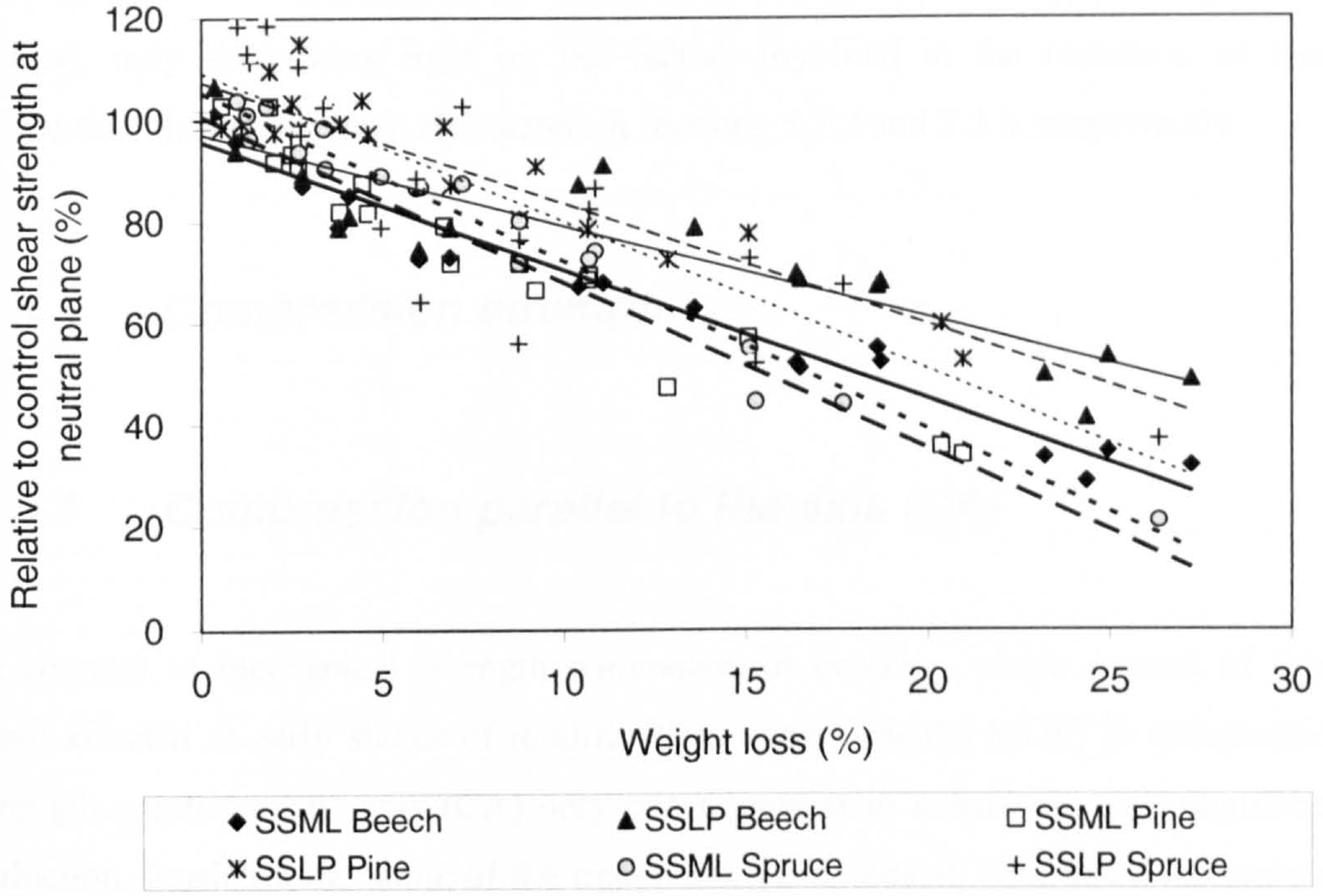


Figure 5.15 Relative to control horizontal shear strength at neutral plane at maximum load and at limit of proportionality in bending (in %) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements. Thicker lines: SSML; thinner lines: SSLP. Solid lines: beech; broken lines: Scots pine; small broken line: Norway spruce.

The relative-to-control average SSML in bending varied with respect to WL in the same pattern for all the three species (Figure 5.15), but with a large scatter of the data. The ratio follows a rectilinear trajectory, with a small increase in SSLP at early levels of WL in softwoods (up to about 3%). SSLP and SSML change pattern are very similar for pine and spruce; for beech these properties are slightly more affected at low levels of WL than in pine or spruce, but as the changing rate in beech is smaller than in softwoods, this trend is reversed at moderated levels of WL.

Reasons for the changes in SSML and SSLP

Horizontal shear strength at neutral plane has been little studied in untreated wood; the factors behind these two properties are thought to be related to torsional strength which in turn is related to the modulus of rigidity in the longitudinal-radial and longitudinal-tangential directions (Kollmann and Côté 1968). It is also thought to be dependent on moisture content on a similar manner to other mechanical strength properties, but the study of these parameters is problematic due to the superposed, mostly bending stresses. The markedly similar behaviour of SSML and SSLP to the correspondent fibre stress parameters (MOR and RLP, respectively) (see Figure 5.34 below), may shed some light on the factors involved in the reduction of these properties; these have been elaborated in sections 5.2.2 and 5.2.3, respectively.

5.3 Compression strength

5.3.1 Compression parallel to the axis (CA)

In contrast to mechanical strength parameters in bending, where several of these were affected at early stages of modification, except for the MOE, in compression strength parallel to the axis (CA) only one treatment in softwoods gave significant reduction. Furthermore, some of the treatments gave, indeed, significant increases in compression strength in beech and Norway spruce (Table 5.3, Table 5.4, Figure 5.16). Only pine treated at 245 °C for 8 h and spruce for 16 h reported significant reductions in CA with respect to control. Several treatments gave significantly higher CA, the largest increases being 26% for beech (to WL = 5%) and 14% for spruce (to WL= 6%).

Similarly, the modulus of elasticity in compression perpendicular to the axis (MOE_{CA}) was only reduced by the treatment at very high levels of treatment, to WL > 25% in the three species (Table 5.4, Figure 5.16). The reduction was only for long treatments at 245 °C in softwoods, whereas in beech, significant reductions were found at this temperature and at 230 °C (for 16 h). As in the case of CA, several treatments lead to increases in MOE_{CA}, but these were significant only in spruce (Table 5.4); the maximum increase being 32% (to WL = 5.85%). As it was noted for the MOE in bending, elasticity in compression parallel to the axis is highly dependent on density and also related to the physical condition of cellulose microfibrils and microfibril angle, all these factors being little altered by treatments for up to 16 h at temperatures up to 245 °C.

Table 5.3 Effect of thermal modification on compression strength parallel (CA) and perpendicular (CE) to the axis on specimens of beech, Scots pine and Norway spruce. Each mean value is the average of eight (CA) and six replicates (CE). Mean values are shown in bold, Std. Dev. in italics.

Temp. °C	**Time** h	CA					CE				
		WL %	CA MPa	MOE$_{CA}$ MPa	EMC %	ND kg m^{-3}	WL %	CE MPa	MOE$_{CE}$ MPa	EMC %	ND kg m^{-3}
Beech											
Control	0.0	**0.00**	**56.85**	**5,360**	**10.02**	**633.36**	**0.00**	**7.67**	**293.71**	**10.57**	**663.66**
		0.00	*5.97*	*525*	*0.06*	*26.99*	*0.00*	*0.95*	*32.12*	*0.09*	*13.99*
190	0.3	**0.32**	**56.73**	**5,137**	**9.09**	**626.74**	**0.31**	**7.30**	**247.57**	**9.33**	**628.12**
		0.04	*2.66*	*265*	*0.12*	*22.50*	*0.05*	*1.51*	*47.10*	*0.16*	*35.75*
	1.0	**1.21**	**63.95**	**5,321**	**8.05**	**648.28**	**1.13**	**8.81**	**286.33**	**8.58**	**645.56**
		0.09	*3.99*	*500*	*0.13*	*18.92*	*0.05*	*0.98*	*35.00*	*0.14*	*23.40*
	4.0	**3.35**	**65.28**	**4,748**	**6.71**	**686.03**	**3.41**	**9.76**	**265.22**	**6.93**	**662.78**
		0.23	*8.51*	*1,084*	*0.17*	*26.78*	*0.21*	*1.90*	*51.78*	*0.12*	*37.88*
	8.0	**4.72**	**71.73**	**5,999**	**6.38**	**673.89**	**4.64**	**8.88**	**277.65**	**6.71**	**646.99**
		0.23	*5.37*	*444*	*0.11*	*29.05*	*0.34*	*1.45*	*37.49*	*0.18*	*37.37*
	16.0	**8.42**	**65.87**	**5,017**	**5.71**	**649.62**	**7.78**	**8.89**	**278.99**	**5.94**	**630.77**
		0.23	*3.51*	*473*	*0.18*	*38.34*	*0.43*	*0.97*	*42.64*	*0.20*	*40.03*
210	0.3	**1.50**	**67.31**	**5,618**	**7.75**	**656.27**	**1.36**	**9.06**	**279.73**	**7.95**	**643.91**
		0.08	*3.32*	*332*	*0.14*	*9.45*	*0.17*	*1.65*	*42.48*	*0.15*	*40.34*
	1.0	**7.97**	**65.74**	**5,482**	**5.34**	**645.99**	**7.54**	**9.59**	**316.18**	**5.61**	**656.65**
		0.53	*9.46*	*695*	*0.07*	*42.55*	*0.74*	*1.10*	*28.97*	*0.27*	*43.48*
	4.0	**11.45**	**67.93**	**5,288**	**4.98**	**648.19**	**11.40**	**7.81**	**250.33**	**5.36**	**604.74**
		0.17	*4.72*	*434*	*0.05*	*30.80*	*0.77*	*1.62*	*54.66*	*0.06*	*30.65*
	8.0	**14.63**	**64.48**	**4,899**	**5.04**	**602.82**	**14.67**	**7.31**	**269.60**	**5.52**	**619.05**
		0.48	*4.19*	*391*	*0.14*	*10.41*	*0.36*	*1.38*	*38.97*	*0.06*	*35.25*
	16.0	**17.37**	**60.08**	**4,373**	**5.26**	**597.09**	**18.12**	**7.53**	**230.37**	**5.66**	**610.40**
		0.41	*7.14*	*349*	*0.14*	*42.34*	*0.65*	*1.24*	*33.84*	*0.08*	*38.25*
230	0.3	**5.04**	**71.09**	**5,811**	**5.82**	**670.48**	**4.26**	**7.88**	**283.07**	**5.88**	**627.16**
		0.18	*1.04*	*379*	*0.11*	*25.97*	*0.37*	*1.35*	*40.10*	*0.15*	*39.48*
	1.0	**18.05**	**62.64**	**4,684**	**5.01**	**592.22**	**18.57**	**7.75**	**239.25**	**5.34**	**620.44**
		0.63	*5.66*	*717*	*0.14*	*36.06*	*0.52*	*0.89*	*25.74*	*0.07*	*14.20*
	4.0	**19.99**	**67.67**	**4,904**	**4.72**	**629.02**	**19.34**	**8.11**	**257.50**	**5.47**	**604.99**
		0.59	*3.23*	*475*	*0.05*	*16.00*	*0.80*	*1.37*	*30.12*	*0.11*	*44.52*
	8.0	**20.42**	**62.52**	**4,536**	**4.89**	**619.87**	**20.36**	**7.48**	**247.37**	**5.63**	**596.53**
		0.57	*4.17*	*523*	*0.11*	*33.96*	*0.56*	*2.04*	*50.64*	*0.08*	*39.98*
	16.0	**25.28**	**56.09**	**4,099**	**5.30**	**604.30**	**26.38**	**6.20**	**197.99**	**6.18**	**587.97**
		1.13	*8.95*	*686*	*0.20*	*32.04*	*0.82*	*1.50*	*40.94*	*0.09*	*45.85*
245	0.3	**16.04**	**66.94**	**4,914**	**4.77**	**622.71**	**14.46**	**9.16**	**273.69**	**5.21**	**652.58**
		0.84	*5.65*	*696*	*0.04*	*25.17*	*0.57*	*1.72*	*18.69*	*0.08*	*35.39*
	1.0	**24.29**	**58.87**	**4,365**	**5.40**	**590.36**	**25.02**	**6.97**	**206.73**	**6.46**	**595.78**
		0.45	*6.65*	*678*	*0.09*	*45.95*	*1.09*	*1.59*	*36.20*	*0.22*	*25.76*
	4.0	**25.66**	**53.54**	**3,535**	**5.21**	**553.21**	**26.81**	**7.36**	**213.76**	**5.91**	**579.22**
		0.74	*5.81*	*749*	*0.11*	*35.71*	*1.02*	*1.56*	*57.01*	*0.08*	*39.57*
	8.0	—	—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—	—
	16.0	**28.57**	**60.17**	**4,065**	**5.02**	**600.77**	**29.27**	**6.25**	**200.78**	**6.59**	**569.63**
		0.29	*6.44*	*299*	*0.05*	*35.45*	*1.32*	*1.53*	*38.50*	*0.08*	*36.02*

Beech not tested at 245 °C for 8 h. For abbreviations see footnote at end of the table

Continued over...

Table 5.3 Effect of thermal modification on compression strength parallel (CA) and perpendicular (CE) to the axis on specimens of beech, Scots pine and Norway spruce. Each mean value is the average of eight (CA) and six replicates (CE). Mean values in bold, Std. Dev. in italics (*Continued...*)

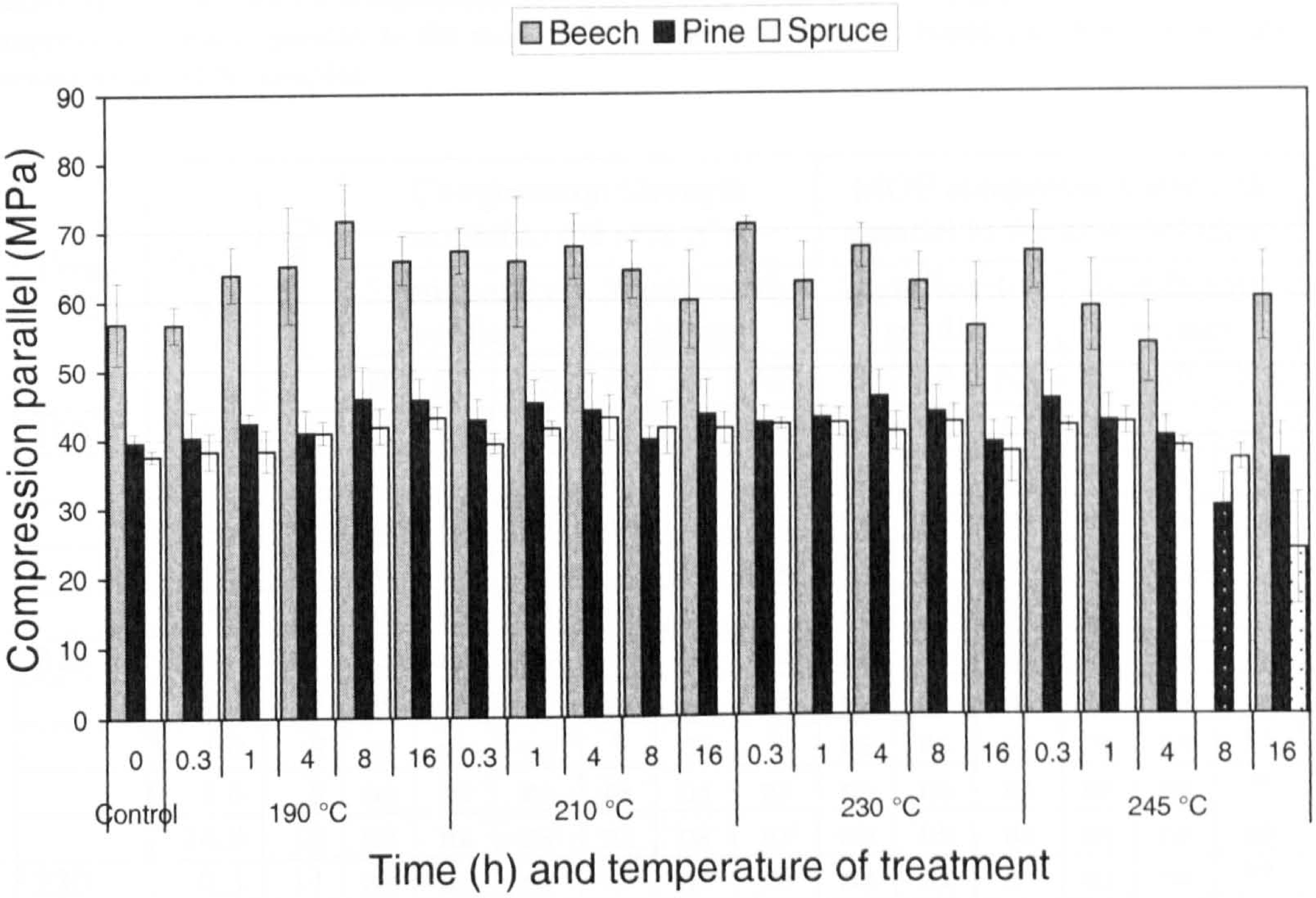
Temp.	Time	CA					CE				
°C	h	WL	CA	MOE$_{CA}$	EMC	ND	WL	CE	MOE$_{CE}$	EMC	ND
		%	MPa	MPa	%	kg m^{-3}	%	MPa	MPa	%	kg m^{-3}
Pine											
Control	0.0	**0.00**	**39.58**	**3,615**	**8.92**	**417.23**	**0.00**	**4.21**	**135.67**	**10.10**	**423.41**
		0.00	*1.33*	*186*	*0.35*	*5.26*	*0.00*	*0.43*	*26.74*	*0.38*	*23.75*
190	0.3	**0.70**	**40.34**	**3,443**	**7.97**	**394.21**	**0.64**	**4.71**	**167.91**	**9.52**	**427.04**
		0.11	*3.57*	*479*	*0.19*	*22.52*	*0.03*	*1.13*	*36.71*	*0.11*	*19.39*
	1.0	**1.48**	**42.35**	**3,926**	**7.36**	**414.49**	**1.45**	**4.16**	**154.49**	**9.06**	**411.33**
		0.12	*1.32*	*158*	*0.11*	*8.81*	*0.07*	*0.33*	*21.12*	*0.09*	*8.73*
	4.0	**2.88**	**40.99**	**3,424**	**7.02**	**410.91**	**2.63**	**4.56**	**166.04**	**8.47**	**418.43**
		0.14	*3.16*	*393*	*0.16*	*19.90*	*0.06*	*0.85*	*35.79*	*0.11*	*23.44*
	8.0	**3.53**	**45.79**	**4,070**	**6.70**	**422.15**	**3.59**	**4.45**	**158.85**	**8.25**	**411.48**
		0.16	*4.73*	*346*	*0.07*	*25.98*	*0.12*	*0.42*	*22.16*	*0.05*	*11.34*
	16.0	**5.81**	**45.63**	**3,776**	**6.18**	**410.15**	**5.23**	**4.55**	**189.05**	**7.74**	**417.99**
		0.50	*3.09*	*524*	*0.14*	*15.84*	*0.17*	*1.07*	*21.50*	*0.10*	*24.15*
210	0.3	**2.80**	**42.72**	**3,549**	**6.88**	**424.45**	**2.69**	**4.51**	**160.73**	**8.30**	**416.16**
		0.02	*2.97*	*472*	*0.27*	*23.13*	*0.04*	*0.56*	*27.17*	*0.07*	*17.05*
	1.0	**3.95**	**45.20**	**3,741**	**6.20**	**419.70**	**3.91**	**5.05**	**150.71**	**7.66**	**413.02**
		0.04	*3.31*	*622*	*0.21*	*11.84*	*0.14*	*0.72*	*39.87*	*0.09*	*22.72*
	4.0	**8.46**	**44.07**	**3,570**	**4.99**	**402.37**	**8.47**	**5.09**	**182.41**	**6.43**	**415.44**
		0.13	*5.43*	*615*	*0.45*	*28.81*	*0.51*	*0.75*	*22.84*	*0.08*	*19.77*
	8.0	**9.73**	**39.82**	**3,396**	**5.20**	**379.02**	**9.23**	**4.28**	**171.45**	**6.23**	**391.51**
		0.19	*1.80*	*273*	*0.13*	*17.76*	*0.37*	*0.49*	*12.85*	*0.05*	*9.03*
	16.0	**12.52**	**43.47**	**3,488**	**4.83**	**392.21**	**11.57**	**4.84**	**192.51**	**6.07**	**408.50**
		0.73	*5.01*	*488*	*0.20*	*19.10*	*0.45*	*0.73*	*38.60*	*0.10*	*17.42*
230	0.3	**3.90**	**42.21**	**3,659**	**6.26**	**401.47**	**3.44**	**4.45**	**172.20**	**7.27**	**410.00**
		0.15	*2.36*	*544*	*0.08*	*24.29*	*0.15*	*0.45*	*21.94*	*0.10*	*9.81*
	1.0	**6.81**	**42.87**	**3,625**	**5.61**	**402.00**	**6.89**	**4.93**	**173.67**	**6.75**	**408.17**
		0.56	*1.55*	*395*	*0.38*	*7.25*	*0.45*	*0.75*	*35.47*	*0.11*	*20.68*
	4.0	**11.00**	**45.89**	**3,630**	**4.78**	**405.37**	**10.48**	**4.74**	**168.15**	**6.03**	**406.49**
		0.36	*3.66*	*400*	*0.41*	*20.64*	*0.18*	*0.49*	*20.34*	*0.02*	*8.34*
	8.0	**12.52**	**43.65**	**3,844**	**4.69**	**378.67**	**13.02**	**4.74**	**150.70**	**5.80**	**399.70**
		0.08	*3.73*	*235*	*0.42*	*19.39*	*0.32*	*1.13*	*40.95*	*0.06*	*15.27*
	16.0	**16.78**	**39.15**	**3,200**	**4.86**	**374.15**	**16.47**	**4.27**	**171.04**	**5.80**	**384.39**
		0.12	*3.07*	*333*	*0.08*	*26.61*	*0.28*	*1.16*	*17.23*	*0.06*	*22.70*
245	0.3	**7.62**	**45.50**	**3,395**	**5.16**	**402.30**	**6.07**	**4.76**	**155.79**	**6.50**	**418.83**
		0.71	*3.82*	*462*	*0.18*	*15.75*	*0.36*	*0.76*	*30.70*	*0.04*	*19.81*
	1.0	**12.98**	**42.33**	**3,642**	**4.42**	**373.91**	**13.04**	**4.50**	**161.14**	**5.52**	**397.20**
		0.15	*3.65*	*246*	*0.39*	*21.59*	*0.33*	*0.54*	*30.80*	*0.02*	*20.49*
	4.0	**19.02**	**40.04**	**3,015**	**4.14**	**361.32**	**17.60**	**3.89**	**135.11**	**5.46**	**387.38**
		1.15	*2.73*	*287*	*0.28*	*7.51*	*0.33*	*0.59*	*24.61*	*0.06*	*24.16*
	8.0	**27.16**	**29.97**	**2,262**	**4.79**	**340.89**	**25.48**	**3.48**	**110.38**	**5.93**	**359.00**
		0.49	*4.48*	*230*	*0.12*	*26.07*	*0.85*	*1.16*	*47.69*	*0.15*	*29.31*
	16.0	**23.71**	**36.70**	**2,913**	**4.55**	**364.18**	**24.39**	**3.92**	**142.64**	**5.93**	**366.66**
		0.34	*5.04*	*469*	*0.07*	*23.08*	*0.93*	*0.27*	*25.57*	*0.11*	*18.93*

Continued over ...

Table 5.3 Effect of thermal modification on compression strength parallel (CA) and perpendicular (CE) to the axis on specimens of beech, Scots pine and Norway spruce. Each mean value is the average of eight (CA) and six replicates (CE). Mean values in bold, Std. Dev. in italics (*Concluded*)

Temp.	Time	CA					CE				
°C	h	WL %	CA MPa	MOE$_{CA}$ MPa	EMC %	ND kg m^{-3}	WL %	CE MPa	MOE$_{CE}$ MPa	EMC %	ND kg m^{-3}
Spruce											
Control	0.0	**0.00**	**37.62**	**2,907**	**9.74**	**388.19**	**0.00**	**4.29**	**171.95**	**11.56**	**362.70**
		0.00	*0.87*	*310*	*0.05*	*11.62*	*0.00*	*0.41*	*23.04*	*0.05*	*11.84*
190	0.3	**1.25**	**38.32**	**2,947**	**8.61**	**374.17**	**0.98**	**4.74**	**179.12**	**10.43**	**373.68**
		0.08	*2.68*	*387*	*0.04*	*14.07*	*0.05*	*0.35*	*27.73*	*0.07*	*7.97*
	1.0	**1.81**	**38.32**	**2,886**	**8.09**	**377.92**	**1.61**	**4.71**	**175.46**	**9.77**	**382.90**
		0.15	*3.07*	*332*	*0.02*	*11.18*	*0.04*	*0.33*	*35.68*	*0.08*	*16.72*
	4.0	**2.48**	**40.93**	**3,485**	**7.78**	**380.83**	**1.93**	**4.90**	**190.26**	**9.10**	**388.32**
		0.10	*1.67*	*336*	*0.09*	*5.11*	*0.05*	*0.38*	*26.96*	*0.03*	*20.46*
	8.0	**3.33**	**41.80**	**3,542**	**7.38**	**372.31**	**3.03**	**4.37**	**187.23**	**8.89**	**358.84**
		0.12	*2.56*	*187*	*0.04*	*17.09*	*0.07*	*0.14*	*23.60*	*0.04*	*11.07*
	16.0	**4.51**	**43.04**	**3,682**	**6.88**	**379.57**	**4.00**	**4.68**	**189.66**	**8.08**	**362.78**
		0.13	*1.55*	*177*	*0.09*	*6.23*	*0.22*	*1.03*	*18.41*	*0.15*	*7.90*
210	0.3	**1.69**	**39.31**	**3,190**	**7.53**	**366.53**	**1.38**	**5.04**	**188.28**	**8.96**	**378.58**
		0.08	*1.45*	*338*	*0.05*	*12.46*	*0.09*	*0.48*	*34.41*	*0.04*	*12.39*
	1.0	**3.13**	**41.47**	**3,311**	**6.93**	**371.71**	**2.89**	**4.88**	**168.35**	**8.09**	**361.59**
		0.09	*1.01*	*257*	*0.06*	*7.60*	*0.20*	*0.34*	*31.71*	*0.14*	*13.20*
	4.0	**5.85**	**42.99**	**3,838**	**6.21**	**369.63**	**5.56**	**4.99**	**172.64**	**7.29**	**375.22**
		0.11	*3.26*	*243*	*0.11*	*15.22*	*0.13*	*0.94*	*27.57*	*0.08*	*27.63*
	8.0	**7.22**	**41.46**	**3,555**	**5.97**	**366.14**	**6.70**	**4.85**	**180.29**	**7.11**	**371.85**
		0.16	*3.76*	*446*	*0.07*	*16.83*	*0.19*	*0.52*	*18.08*	*0.06*	*7.39*
	16.0	**10.64**	**41.38**	**2,973**	**5.36**	**354.96**	**10.06**	**3.95**	**153.60**	**6.24**	**359.46**
		0.22	*2.24*	*286*	*0.07*	*13.82*	*0.43*	*0.55*	*35.95*	*0.12*	*26.38*
230	0.3	**4.43**	**41.94**	**3,647**	**6.33**	**369.30**	**3.70**	**4.55**	**179.04**	**7.54**	**355.59**
		0.17	*0.81*	*188*	*0.08*	*10.57*	*0.20*	*0.71*	*30.68*	*0.07*	*11.37*
	1.0	**7.40**	**42.12**	**3,658**	**5.75**	**365.42**	**7.10**	**4.47**	**165.97**	**6.73**	**356.71**
		0.42	*2.08*	*288*	*0.08*	*13.34*	*0.09*	*0.26*	*17.76*	*0.08*	*3.45*
	4.0	**10.23**	**40.81**	**3,088**	**5.22**	**354.11**	**9.35**	**4.96**	**198.02**	**6.27**	**362.39**
		0.23	*2.74*	*312*	*0.08*	*12.55*	*0.35*	*0.18*	*31.64*	*0.12*	*9.16*
	8.0	**12.91**	**42.18**	**3,129**	**4.87**	**357.44**	**11.87**	**4.51**	**173.99**	**5.70**	**358.75**
		0.34	*2.40*	*463*	*0.07*	*14.28*	*0.50*	*0.55*	*37.69*	*0.04*	*27.23*
	16.0	**17.85**	**37.89**	**2,768**	**4.93**	**343.99**	**17.30**	**3.59**	**141.03**	**5.83**	**328.82**
		0.48	*4.62*	*613*	*0.19*	*11.84*	*0.37*	*0.59*	*20.83*	*0.12*	*25.69*
245	0.3	**9.60**	**41.59**	**3,625**	**5.08**	**355.61**	**8.41**	**3.98**	**151.77**	**6.03**	**339.79**
		0.15	*1.00*	*202*	*0.08*	*6.09*	*0.20*	*0.67*	*31.01*	*0.02*	*19.35*
	1.0	**13.06**	**42.09**	**2,884**	**4.68**	**359.05**	**12.22**	**5.25**	**205.15**	**5.43**	**368.68**
		0.34	*1.93*	*258*	*0.08*	*11.06*	*0.48*	*0.73*	*17.41*	*0.04*	*24.29*
	4.0	**17.58**	**38.55**	**2,709**	**4.56**	**333.91**	**16.90**	**4.24**	**185.40**	**5.42**	**354.06**
		0.31	*1.13*	*253*	*0.11*	*8.95*	*0.54*	*0.43*	*24.05*	*0.08*	*25.34*
	8.0	**20.35**	**36.79**	**2,830**	**4.39**	**324.30**	**20.07**	**3.90**	**153.87**	**5.39**	**318.34**
		0.28	*1.77*	*251*	*0.05*	*10.60*	*0.20*	*0.34*	*35.92*	*0.05*	*9.57*
	16.0	**30.59**	**23.65**	**1,992**	**4.54**	**301.78**	**30.32**	**2.90**	**116.25**	**5.81**	**293.14**
		0.59	*8.10*	*469*	*0.25*	*12.90*	*0.20*	*0.36*	*20.47*	*0.08*	*4.76*

WL: weight loss; CA: modulus of rupture; MOECA: modulus of elasticity in compression strength parallel to the axis; CE: compression strength perpendicular to the axis; MOE$_{CE}$: modulus of elasticity in compression perpendicular to the axis; EMC: equilibrium moisture content at 65% relative humidity at 20 °C; ND: nominal density = oven dry weight/volume at test.



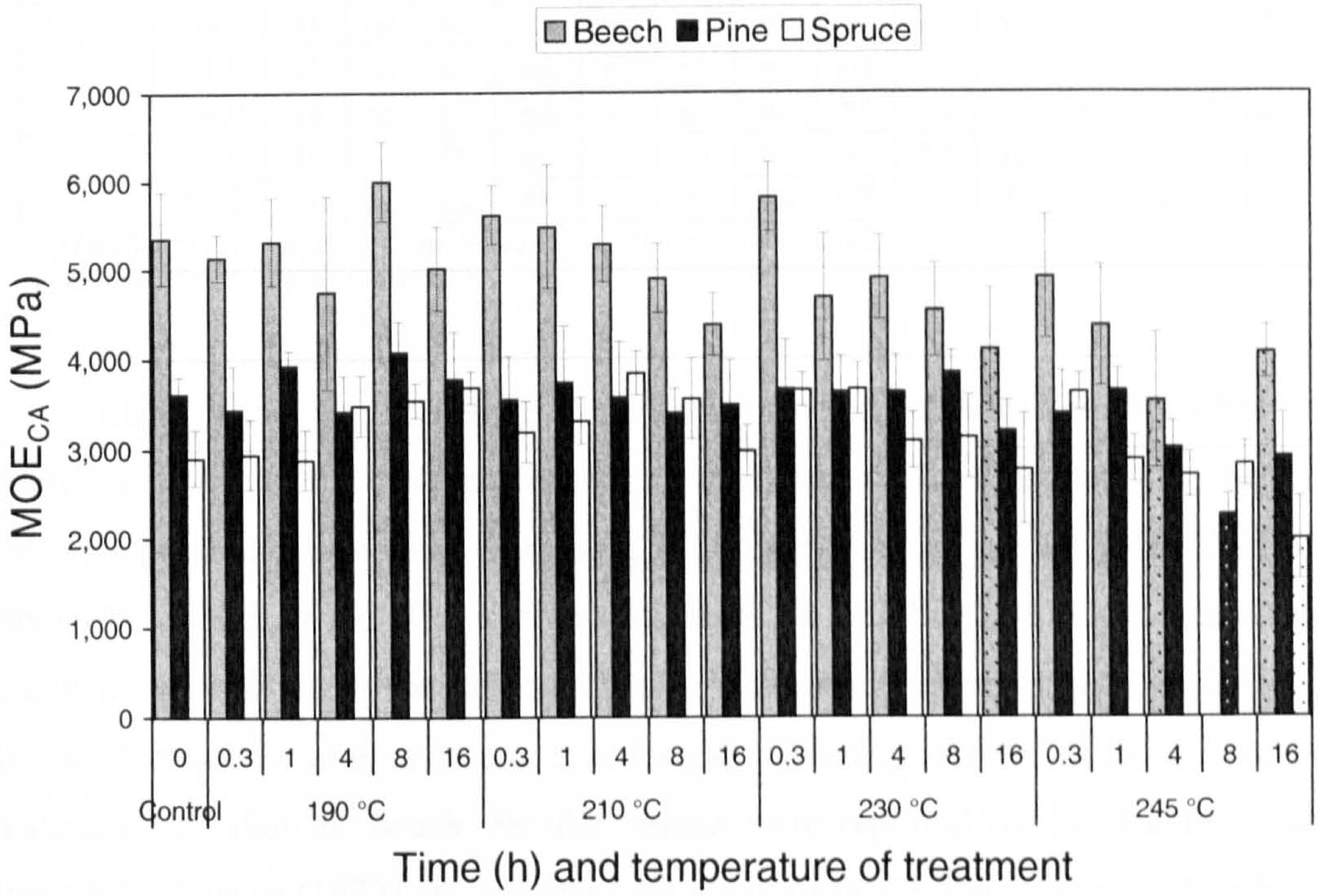


Figure 5.16 Effect of thermal modification on compression strength parallel to the axis (CA, top) and Modulus of Elasticity in compression parallel (MOE$_{CA}$, bottom) for beech, Scots pine and Norway spruce. Each bar represents the mean value of 8 replicates. Mottled bars = treatment with significant reduction. Error bars represent ± 1 SD

Table 5.4 Results from Tukey's multiple comparison tests following ANOVA of untreated samples against treated samples for compression strength parallel to the axis (CA) and modulus of elasticity of compression strength parallel to the axis (MOE_{CA}) on treatment, for beech (B), Scots pine (SP) and Norway spruce (NS) samples.

Temp. °C	Time h	Treatment	Compression Strength parallel to the axis (CA)						MOE compression strength parallel to the axis (MOE_{CA})					
			Significantly smaller			Significantly greater			Significantly smaller			Significantly greater		
			B	SP	NS	B	SP	NS	B	SP	NS	B	SP	NS
190	0.3	1	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	1.0	2	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	4.0	3	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	8.0	4	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	*
	16.0	5	ns	ns	ns	ns	ns	*	ns	ns	ns	ns	ns	**
210	0.3	6	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	ns
	1.0	7	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	4.0	8	ns	ns	ns	*	ns	*	ns	ns	ns	ns	ns	**
	8.0	9	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*
	16.0	10	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
230	0.3	11	ns	ns	ns	**	ns	ns	ns	ns	ns	ns	ns	**
	1.0	12	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**
	4.0	13	ns	ns	ns	*	ns	ns	ns	ns	ns	ns	ns	ns
	8.0	14	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	16.0	15	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns
245	0.3	16	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**
	1.0	17	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
	4.0	18	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns
	8.0	19	--	**	ns	--	ns	ns	--	**	ns	--	ns	ns
	16.0	20	ns	ns	**	ns	ns	ns	**	ns	**	ns	ns	ns

* Significant to $p < 0.05$; ** Significant to $p < 0.01$; ns = not significant
Beech not tested at 245 °C for 8.0 h

Relative-to-control average CA values in dependence of the WL after heat treatment change in the same pattern for all the three species (Figure 5.17); the ratio follows a parabolic trajectory, increasing at the beginning as the WL increases up to about 12% for beech and 10% in pine and spruce, then falling to reach control values at a WL of *ca.* 27%, in beech and 20% in softwoods. Property change pattern is almost identical for pine and spruce; softwood CA being affected at lower levels of treatment than that for beech. Similar results were reported for axial compression strength by Rusche (1973), who studied the effect of thermal processing in beech and pine in presence and absence of air. This author found that the relationship between relative CA and substance loss was similar for both species, beech being negatively affected at larger levels of WL.

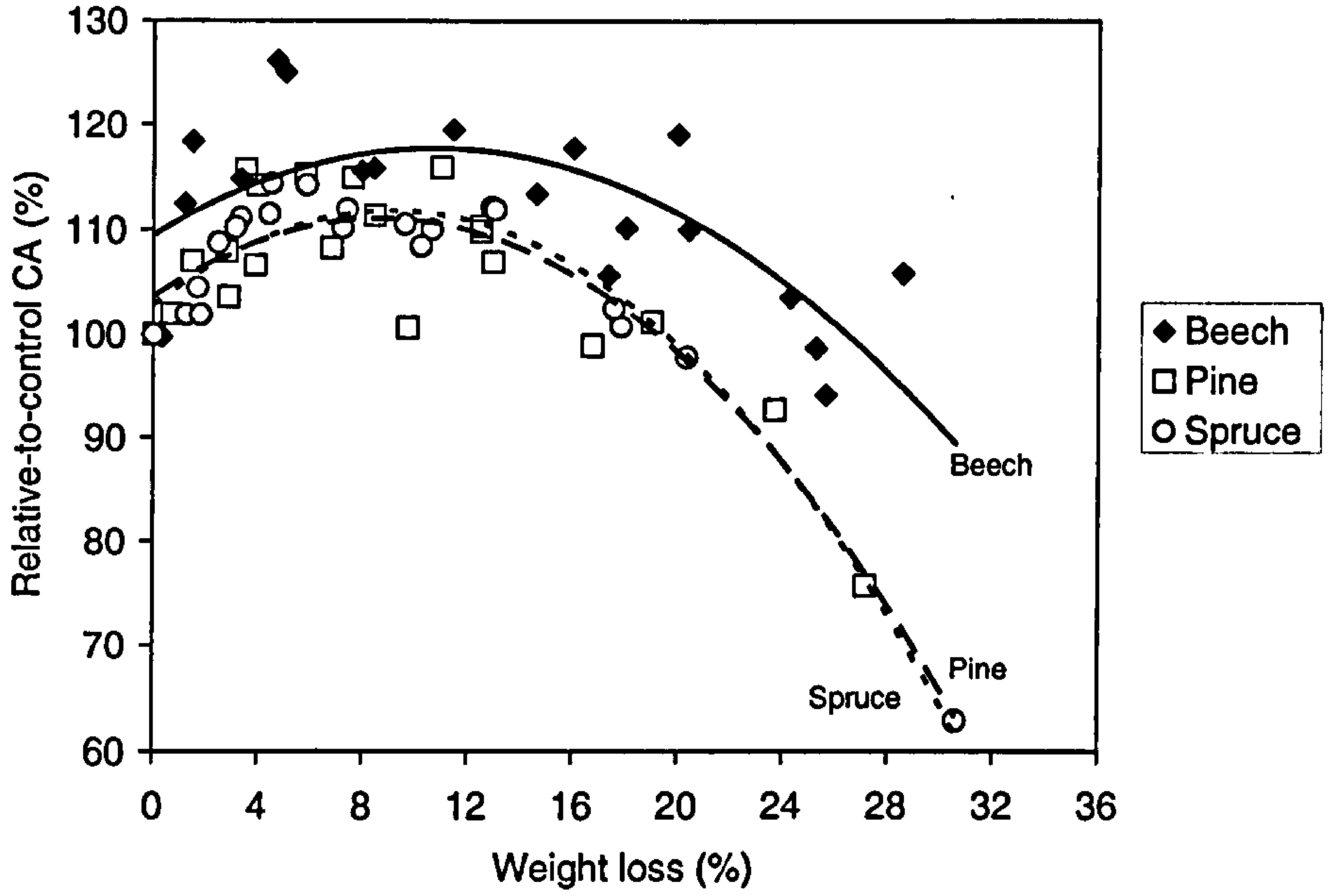


Figure 5.17 Relative-to-control (%) compression strength parallel to the grain (CA) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of eight measurements.

Reasons for changes in CA

In untreated wood, second to bending strength CA is the mechanical property most affected by the moisture content at test (Lavers 1983), and thus one factor explaining the behaviour encountered in the results from this test may be the reduced moisture content of the treated wood, which acts favourably against the CA strength of untreated samples. CA strength is also highly dependent to the cell wall thickness and therefore to wood density: modelling the axial and transverse compression strength of balsa wood, Easterling *et al.* (1982) found theoretical and experimental evidence that CA was linearly related to the ratio of wood density to the density of the dry cell wall material, and the transverse strength to the square of this ratio. Both of those characteristics are little changed due to the thermal conversion of wood (chapter 4). An illustration of the importance of the wood density in CA strength is given by Kaya and Smith (1993), who found that the best combination of two independent variables for predicting maximum crushing strength of untreated radiata pine were specific gravity and tracheid length, although the former alone accounted for 91% of the variation. Similarly, Gindl and Teischinger (2002) found that 84% of the variability of axial compression strength of untreated Norway spruce wood was explained by density. Complementarily, compression strength along the grain in untreated wood has been found to be affected by the degree of lignification not between the cells, but instead within the cell walls, when all other variables are kept constant (Dinwoodie 2000). Clarke (1939, cited by Kollmann and Côté 1968) found that tropical woods with high lignin content had higher axial compression strength than woods from temperate zones of equivalent specific gravity. In a recent study, Gindl (2002) found no reduction of CA in reaction wood of Norway spruce compared to untreated normal wood, despite the high microfibril angle of the former; he proposed that the observed high lignification in compression wood compensates the high microfibril angle and increases the resistance of the cell walls to compression failure. The same situation could be applicable to TMW, where the relative proportion of lignin increases in line with the heat-induced mass loss (section 5.8). Gindl and Teischinger (2002) concluded that the failure of untreated spruce wood in axial compression is by buckling and kinking of the microfibrils caused for the misalignment on the vicinity of the rays; they also found a significant although small effect of lignin content on the compression strength. The thermal modification process does not affect the arrangement of the different cells on the wood tissue, nor affects to a noticeable extent the microfibril angle, so no major changes in axial compression strength could be expected.

Findings from several previous reports are consistent with the results of the present study (Schneider 1971, Syrjänen and Kangas 2000, Mouras *et al.* 2002). Debatably, Unsal and Ayrilmis (2005) determined statistical differences at relatively mild levels of thermal modification, although they reported no significant difference in *Eucalyptus* sp. wood treated for 2 h at temperatures up to 180 °C. Contrarily to the present study, these authors used the CA values corrected by moisture content at 12%.

Results from compression strength parallel to the axis are promising, because this property is less affected by knots and other wood defects than properties in the bending mode (Kollmann and Côté 1968). Therefore the behaviour encountered in small specimens is likely to represent the performance of large-sized specimens. Dinwoodie (2000) gives for instance the CA strength values for untreated small- and structural-sized Norway spruce specimens, to be 36.5 MPa and 45.8 MPa respectively, highlighting the limited importance of the size at test for determining this property. Thus, short columns in which the ratio $L/d < 11$ (L is the unsupported length and d is the shortest dimension) the strength of TMW could be considered suitable even for load-bearing purposes, because the stresses in such columns is in pure compression. Longer columns could also be used in load bearing applications, because in these, the stress in the columns is dependent on both crushing strength and MOE in bending (Kollmann and Côté 1968).

5.3.2 Compression perpendicular to the axis (CE)

Below 24% WL the thermal modification had little negative mechanical effect in CE strength or MOE_{CE} in the three wood species (Table 5.3, Figure 5.18). Several schedules led to small but insignificant increases in both CE and MOE_{CE} strength parameters. Only spruce treated at 245 °C for 16 h (to WL = 30%) showed significant reduction in CE, whereas three treatments resulted in significant decrease of MOE_{CE} in beech (to WL >25%).

As in CA, relative-to-control average CE values plotted against WL shows a similar pattern for all the three species (Figure 5.19). The ratio follows a parabolic trajectory in all species, increasing insignificantly at low levels of WL and then falling to reach control values at a WL of *ca.* 22.3%, 19.3% and 14.7% for beech, pine and spruce, respectively. The changing pattern is very similar for pine and beech; spruce CE being affected at slightly lower levels of treatment than beech and pine did.

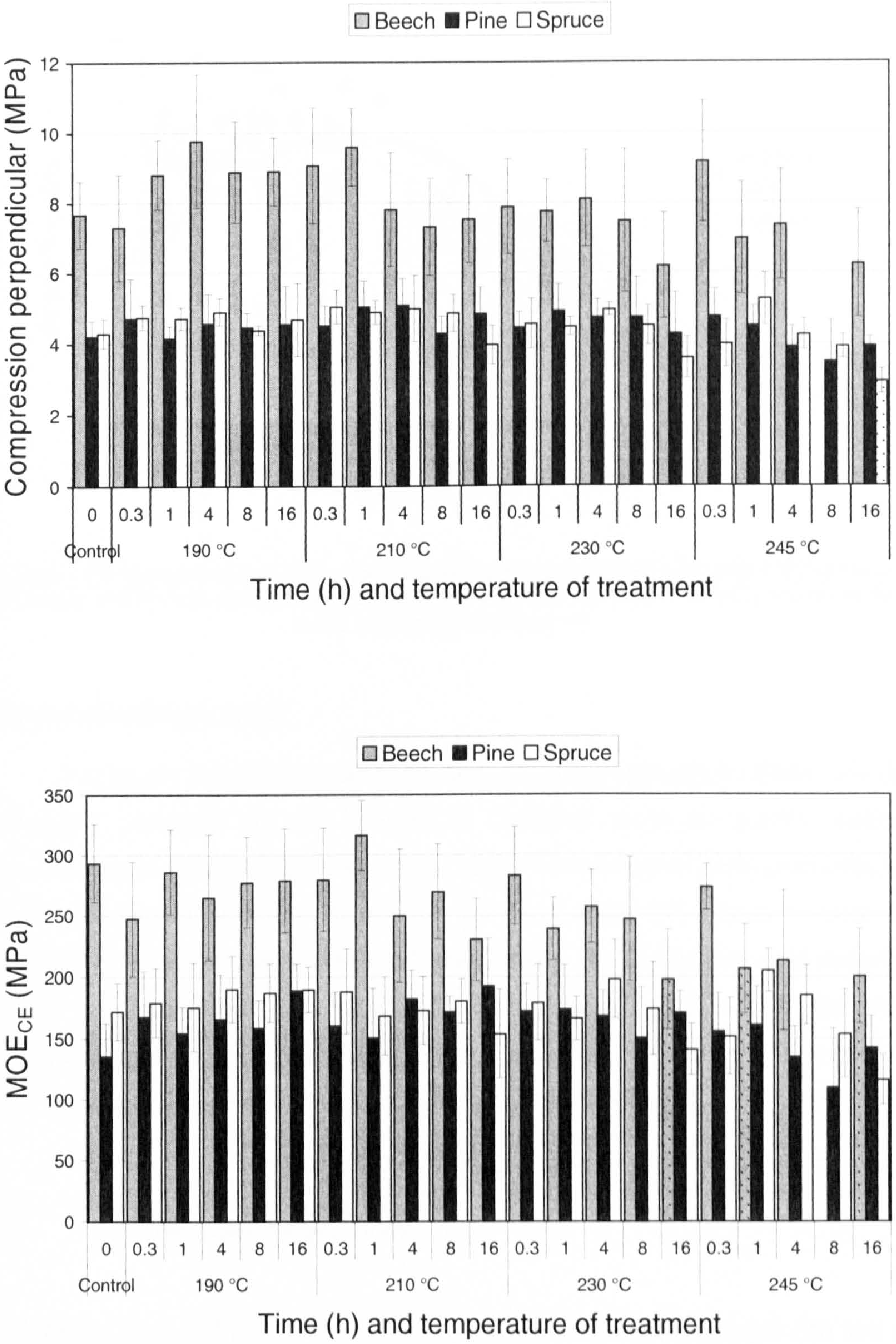


Figure 5.18 Effect of thermal modification on compression strength perpendicular to the axis (CE, top) and Modulus of Elasticity in compression perpendicular (MOE$_{CE}$, bottom) for beech, Scots pine and Norway spruce. Each bar represents the mean value of 6 replicates. Mottled bars = treatments significantly reduced. Error bars = ± 1 SD

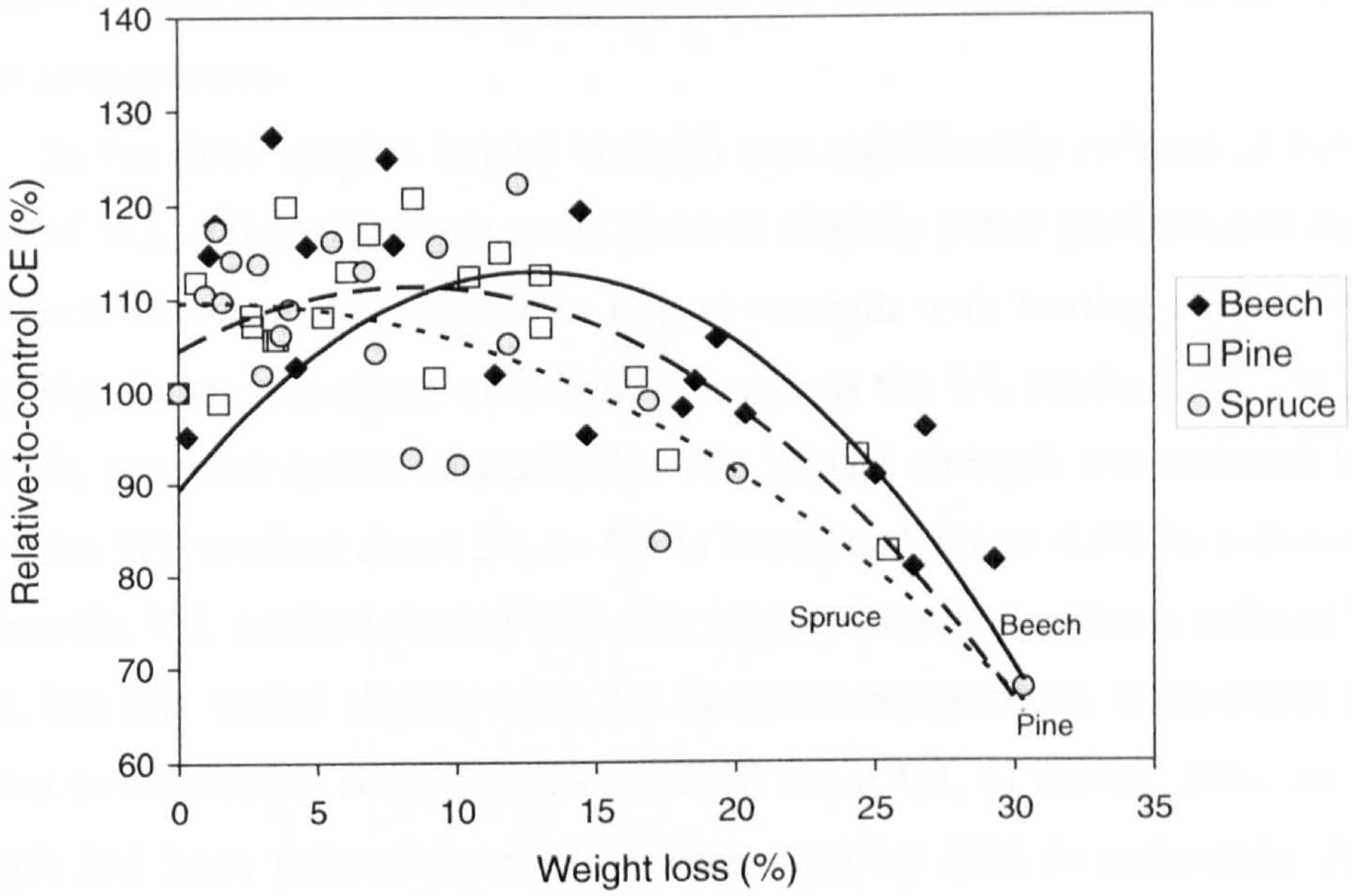


Figure 5.19 Relative-to-control (%) compression strength perpendicular to the grain (CE) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of six measurements.

Reasons for changes in CE

Results for this property have not been previously reported for TMW, and the underlying principles for CE strength in untreated wood are poorly studied. However, the main phenomena behind the degree of retention of these properties are proposed to be similar to the CA strength. As noted above, CE is linearly related to square of the ratio of wood density to the density of the dry cell wall material; density is little modified due to the treatment (chapter 4). As most of the other strength parameters, MOE_{CE} and CE are also positively influenced by the reduced EMC at test of the treated samples compared to untreated controls.

5.4 Impact strength (IS)

The results given in Table 5.5 and Figure 5.20 show the impact strength (IS) loss of TMW within the temperature range and heating periods studied. In contrast to all other mechanical properties, this strength property was found to be more sensitive to the effects of heating at early levels of modification, with clear changes in this property depending upon the temperature of treatment. A noticeable feature is that at equivalent levels of WL, the reduction at 190 °C was slightly larger in beech than at higher temperatures.

In the three species impact strength was significantly reduced at very early values of WL, although spruce wood showed slightly better performance than pine and beech. However, the decline in impact strength with heating happens rapidly; highly significant reductions were found as soon as the WL reached 3%, 2% and 4% in beech, pine and spruce respectively. The impact strength was reduced by 50% before the WL reached about 3% to 4% in beech and 4% to 4.5% in softwoods. By the time the WL reached around 10%, the impact strength had been reduced by two thirds, but this varied slightly with the treatment temperature. Subsequent heating resulted in continuous additional decreases in IS: at WL of around 20%, the impact strength had been reduced by 80% in beech and by 88% in softwoods. Previous studies on the impact resistance of several timbers show close similarities to the results of this work (Davis and Thompson 1964, Chang and Keith 1978, Kubojima *et al.* 2000).

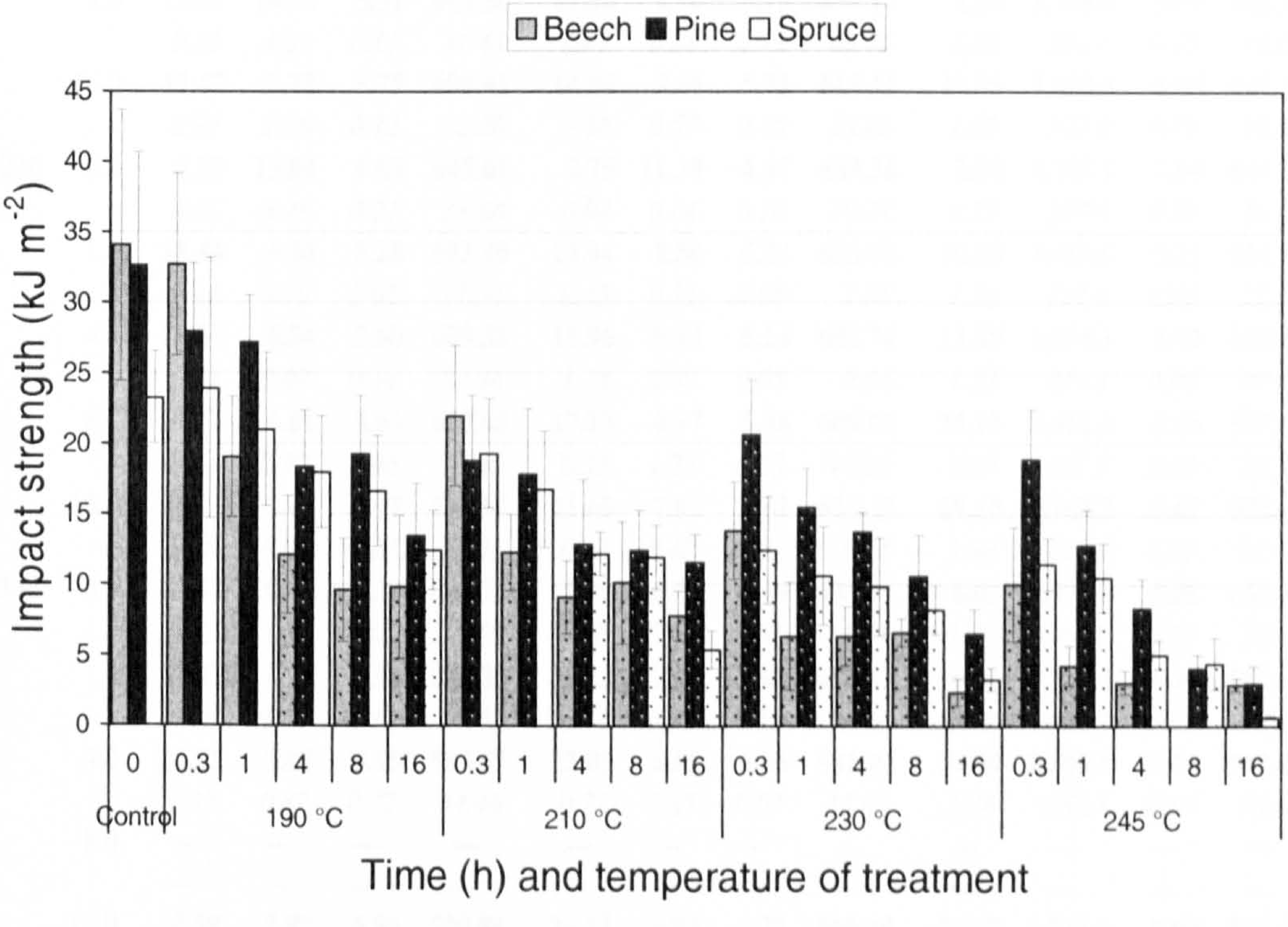


Figure 5.20 Effect of thermal modification on impact strength (IS) for thermally modified beech, Scots pine and Norway spruce woods. Each bar represents the mean value of 10 replicates. Mottled bars = treatments significantly reduced. Error bars = ± 1 SD

Table 5.5 Effect of thermal modification on Charpy impact strength (IS), shear strength (S) and Janka hardness (H) on specimens of beech, Scots pine and Norway spruce. Each value is the mean value of ten (IS), four (S), and six replicates (H). Mean values are shown in bold, with SD in italics.

Temp.	Time	IS				S				H			
°C	h	WL %	IS kJ m^{-2}	EMC %	ND kg m^{-3}	WL %	S MPa	EMC %	ND kg m^{-3}	WL %	H N	EMC %	ND kg m^{-3}
Beech													
Control	0.0	**0.00**	**34.07**	**10.50**	**682.64**	**0.00**	**10.11**	**10.36**	**612.78**	**0.00**	**5,552.1**	**10.50**	**643.27**
		0.00	*9.62*	*0.10*	*4.00*	*0.00*	*0.61*	*0.11*	*0.04*	*0.00*	*712.9*	*0.12*	*27.92*
190	0.3	**0.38**	**32.70**	**9.57**	**658.74**	**0.20**	**11.85**	**9.49**	**665.62**	**0.28**	**5,254.4**	**9.64**	**632.42**
		0.05	*6.47*	*0.10*	*29.38*	*0.02*	*0.44*	*0.03*	*9.15*	*0.07*	*690.9*	*0.21*	*35.26*
	1.0	**0.98**	**19.06**	**8.61**	**647.21**	**0.79**	**11.11**	**8.74**	**648.26**	**0.68**	**5,564.8**	**9.10**	**655.63**
		0.08	*4.30*	*0.28*	*45.67*	*0.04*	*0.85*	*0.05*	*25.97*	*0.12*	*621.6*	*0.24*	*31.30*
	4.0	**3.05**	**12.12**	**6.90**	**631.62**	**2.33**	**10.76**	**7.68**	**643.02**	**1.66**	**5,256.0**	**8.02**	**639.62**
		0.18	*4.20*	*0.13*	*36.05*	*0.14*	*0.63*	*0.03*	*5.99*	*0.32*	*594.4*	*0.21*	*31.66*
	8.0	**4.38**	**9.62**	**6.90**	**657.14**	**2.99**	**12.23**	**7.15**	**663.06**	**2.48**	**5,360.9**	**7.62**	**662.34**
		0.35	*3.69*	*0.13*	*39.94*	*0.09*	*0.72*	*0.13*	*2.50*	*0.44*	*820.0*	*0.34*	*36.89*
	16.0	**7.35**	**9.83**	**6.02**	**635.18**	**4.60**	**10.23**	**6.48**	**640.15**	**3.70**	**4,564.0**	**7.06**	**656.94**
		0.26	*5.07*	*0.16*	*34.74*	*0.26*	*0.93*	*0.07*	*50.68*	*0.76*	*939.9*	*0.46*	*33.93*
210	0.3	**1.56**	**21.97**	**8.11**	**647.81**	**1.05**	**10.94**	**8.50**	**616.94**	**0.92**	**5,796.5**	**8.80**	**661.14**
		0.25	*4.95*	*0.22*	*31.08*	*0.10*	*0.74*	*0.02*	*29.42*	*0.19*	*556.2*	*0.13*	*18.47*
	1.0	**7.11**	**12.28**	**5.60**	**636.35**	**4.24**	**10.56**	**5.97**	**645.40**	**3.46**	**4,385.8**	**6.56**	**634.54**
		0.34	*2.71*	*0.08*	*47.26*	*0.11*	*0.26*	*0.05*	*34.29*	*0.63*	*730.4*	*0.27*	*44.90*
	4.0	**10.83**	**9.09**	**5.50**	**621.32**	**8.14**	**9.51**	**5.58**	**605.01**	**5.50**	**4,131.3**	**6.14**	**649.12**
		0.68	*2.57*	*0.13*	*46.69*	*0.80*	*0.18*	*0.10*	*23.35*	*1.18*	*965.2*	*0.50*	*48.60*
	8.0	**13.87**	**10.14**	**5.51**	**603.56**	**11.24**	**9.90**	**5.79**	**634.14**	**8.84**	**3,748.4**	**5.99**	**643.63**
		0.52	*4.34*	*0.11*	*31.43*	*0.47*	*0.68*	*0.19*	*23.63*	*1.38*	*252.4*	*0.18*	*35.15*
	16.0	**17.47**	**7.78**	**5.75**	**608.41**	**14.06**	**9.40**	**5.71**	**616.12**	**11.35**	**3,623.5**	**5.84**	**642.72**
		0.87	*1.76*	*0.12*	*32.28*	*0.86*	*0.57*	*0.15*	*13.66*	*1.86*	*502.0*	*0.19*	*30.34*
230	0.3	**4.23**	**13.84**	**6.03**	**645.61**	**2.75**	**11.38**	**6.41**	**639.36**	**2.02**	**4,743.1**	**7.04**	**614.53**
		0.66	*3.46*	*0.21*	*33.68*	*0.08*	*0.64*	*0.10*	*10.74*	*0.27*	*207.8*	*0.16*	*16.50*
	1.0	**18.44**	**6.34**	**5.28**	**593.40**	**13.94**	**8.80**	**5.24**	**633.78**	**10.00**	**3,465.5**	**5.21**	**601.05**
		0.23	*3.79*	*0.05*	*11.34*	*0.45*	*0.21*	*0.08*	*1.05*	*1.53*	*411.0*	*0.08*	*22.79*
	4.0	**18.57**	**6.34**	**5.60**	**609.33**	**15.96**	**9.13**	**5.24**	**608.74**	**13.49**	**3,674.1**	**5.42**	**628.84**
		0.83	*2.07*	*0.14*	*37.36*	*1.28*	*0.09*	*0.05*	*0.66*	*1.33*	*819.3*	*0.08*	*49.81*
	8.0	**19.92**	**6.61**	**5.53**	**629.63**	**17.13**	**8.97**	**5.38**	**609.65**	**15.13**	**2,911.4**	**5.46**	**587.06**
		0.64	*0.97*	*0.06*	*19.92*	*0.33*	*1.74*	*0.05*	*47.05*	*1.85*	*471.7*	*0.09*	*30.76*
	16.0	**27.17**	**2.40**	**6.07**	**584.57**	**21.60**	**7.82**	**5.62**	**622.43**	**19.10**	**2,708.7**	**5.67**	**573.67**
		1.10	*0.94*	*0.03*	*18.95*	*0.03*	*0.62*	*0.02*	*16.64*	*2.36*	*215.7*	*0.11*	*34.49*
245	0.3	**13.58**	**10.07**	**5.32**	**620.20**	**9.89**	**10.01**	**5.49**	**639.41**	**6.03**	**4,273.6**	**5.85**	**654.78**
		0.63	*4.07*	*0.09*	*17.59*	*0.20*	*0.18*	*0.01*	*1.15*	*1.25*	*706.7*	*0.22*	*24.80*
	1.0	**24.87**	**4.26**	**6.51**	**586.30**	**20.13**	**7.98**	**5.94**	**631.52**	**16.56**	**2,775.0**	**6.20**	**587.93**
		0.98	*1.39*	*0.16*	*36.02*	*0.44*	*0.92*	*0.13*	*19.16*	*2.06*	*493.7*	*0.19*	*37.03*
	4.0	**26.21**	**3.07**	**6.15**	**587.57**	**23.05**	**6.85**	**5.86**	**581.03**	**20.90**	**2,835.5**	**5.73**	**587.64**
		1.13	*0.82*	*0.12*	*44.46*	*0.72*	*0.85*	*0.07*	*15.08*	*1.34*	*266.7*	*0.10*	*36.46*
	8.0	—	—	—	—	—	—	—	—	—	—	—	—
		—	—	—	—	—	—	—	—	—	—	—	—
	16.0	**28.59**	**2.92**	**6.59**	**599.84**	**24.13**	**6.93**	**6.33**	**599.40**	**21.57**	**2,711.9**	**5.98**	**579.67**
		0.43	*0.45*	*0.08*	*12.13*	*0.15*	*0.80*	*0.18*	*23.99*	*2.29*	*368.2*	*0.17*	*37.53*

Beech not tested at 245 °C for 8 h. For abbreviations, see footnote at end of the table.

Continued over...

Table 5.5 Effect of thermal modification on Charpy impact strength (IS), shear strength (S) and Janka hardness (H) on specimens of beech, Scots pine and Norway spruce. Each value is the mean value of ten (IS), four (S), and six replicates (H). Mean values in bold, with SD in italics. (*Continued...*)

Temp.	Time	IS				S				H			
°C	h	WL %	IS kJ m^{-2}	EMC %	ND kg m^{-3}	WL %	S MPa	EMC %	ND kg m^{-3}	WL %	H N	EMC %	ND kg m^{-3}
Pine													
Control	0.0	**0.00**	**32.63**	**10.50**	**522.39**	**0.00**	**6.46**	**9.89**	**413.43**	**0.00**	**1,752.9**	**10.38**	**393.04**
		0.00	*8.06*	*0.22*	*28.56*	*0.00*	*0.30*	*0.18*	*8.30*	*0.00*	*224.0*	*0.40*	*17.92*
190	0.3	**0.54**	**27.91**	**10.00**	**520.13**	**0.60**	**6.30**	**9.51**	**391.04**	**0.69**	**1,568.8**	**9.78**	**383.83**
		0.05	*4.88*	*0.06*	*22.87*	*0.04*	*0.17*	*0.11*	*17.30*	*0.09*	*210.0*	*0.12*	*14.07*
	1.0	**1.08**	**27.19**	**9.45**	**527.24**	**1.10**	**6.19**	**9.28**	**401.42**	**1.42**	**1,861.5**	**9.48**	**409.99**
		0.12	*3.34*	*0.07*	*22.60*	*0.02*	*1.13*	*0.22*	*40.51*	*0.51*	*123.1*	*0.16*	*23.25*
	4.0	**2.18**	**18.40**	**8.81**	**515.47**	**2.38**	**5.67**	**8.78**	**378.84**	**1.91**	**1,711.8**	**9.19**	**403.17**
		0.12	*4.00*	*0.06*	*26.07*	*0.15*	*0.61*	*0.25*	*10.25*	*0.39*	*282.3*	*0.32*	*22.74*
	8.0	**2.92**	**19.30**	**8.54**	**518.87**	**2.89**	**5.57**	**8.55**	**387.87**	**2.46**	**1,660.2**	**8.95**	**397.62**
		0.19	*4.16*	*0.09*	*16.47*	*0.05*	*0.41*	*0.09*	*11.39*	*0.35*	*238.6*	*0.21*	*20.42*
	16.0	**4.25**	**13.49**	**8.00**	**501.03**	**3.81**	**5.92**	**8.39**	**389.23**	**3.87**	**1,741.1**	**8.84**	**399.41**
		0.46	*3.72*	*0.16*	*39.24*	*0.06*	*0.59*	*0.12*	*5.77*	*0.50*	*247.0*	*0.22*	*24.93*
210	0.3	**2.24**	**18.83**	**8.64**	**509.80**	**2.28**	**5.63**	**8.76**	**382.92**	**2.08**	**1,674.7**	**9.03**	**389.10**
		0.64	*4.60*	*0.31*	*24.99*	*0.09*	*0.18*	*0.12*	*5.93*	*0.73*	*103.0*	*0.28*	*8.15*
	1.0	**2.95**	**17.86**	**7.85**	**529.46**	**3.04**	**6.19**	**8.07**	**391.18**	**2.23**	**1,614.9**	**8.57**	**393.27**
		0.20	*4.62*	*0.06*	*7.62*	*0.38*	*0.85*	*0.07*	*4.82*	*0.23*	*301.4*	*0.25*	*15.60*
	4.0	**7.11**	**12.87**	**6.57**	**515.59**	**5.76**	**6.40**	**7.11**	**386.86**	**6.19**	**1,629.8**	**6.79**	**407.94**
		0.34	*4.61*	*0.09*	*9.88*	*0.05*	*0.57*	*0.02*	*0.07*	*0.68*	*307.9*	*0.20*	*17.24*
	8.0	**8.25**	**12.47**	**6.34**	**500.21**	**7.50**	**3.91**	**6.50**	**369.88**	**5.89**	**1,796.3**	**7.14**	**399.12**
		0.60	*2.85*	*0.07*	*27.31*	*0.04*	*0.39*	*0.00*	*6.52*	*1.22*	*158.2*	*0.37*	*13.35*
	16.0	**9.95**	**11.60**	**6.12**	**500.22**	**8.35**	**5.78**	**6.27**	**383.56**	**7.63**	**1,744.5**	**6.79**	**392.94**
		0.38	*1.97*	*0.05*	*32.83*	*0.17*	*0.29*	*0.05*	*0.22*	*1.06*	*261.9*	*0.27*	*23.11*
230	0.3	**2.59**	**20.66**	**7.81**	**520.58**	**3.04**	**4.82**	**7.56**	**380.72**	**2.77**	**1,768.4**	**7.84**	**398.47**
		0.18	*3.87*	*0.12*	*12.64*	*0.04*	*0.22*	*0.07*	*16.92*	*0.45*	*159.1*	*0.09*	*11.11*
	1.0	**5.10**	**15.52**	**7.17**	**509.52**	**4.28**	**6.12**	**7.46**	**393.97**	**3.34**	**1,862.4**	**8.20**	**402.21**
		0.78	*2.74*	*0.18*	*26.53*	*0.18*	*0.88*	*0.07*	*6.98*	*0.60*	*350.5*	*0.30*	*19.92*
	4.0	**9.17**	**13.80**	**6.11**	**510.06**	**8.92**	**5.63**	**6.04**	**381.90**	**8.02**	**1,542.8**	**6.39**	**380.93**
		0.08	*1.39*	*0.06*	*20.63*	*0.78*	*0.80*	*0.41*	*8.92*	*0.84*	*252.6*	*0.25*	*23.85*
	8.0	**11.15**	**10.62**	**5.94**	**506.65**	**11.06**	**5.13**	**5.82**	**375.37**	**10.42**	**1,335.4**	**6.25**	**362.94**
		0.57	*2.94*	*0.08*	*22.22*	*0.17*	*1.02*	*0.31*	*3.03*	*1.67*	*175.8*	*0.33*	*16.16*
	16.0	**14.58**	**6.52**	**5.79**	**469.25**	**12.64**	**5.18**	**5.70**	**379.75**	**9.81**	**1,487.8**	**6.03**	**374.84**
		0.66	*1.74*	*0.06*	*20.73*	*1.21*	*1.13*	*0.39*	*30.18*	*1.22*	*199.3*	*0.44*	*23.60*
245	0.3	**4.69**	**18.94**	**6.82**	**503.29**	**5.83**	**6.69**	**6.73**	**398.92**	**5.37**	**1,804.4**	**7.16**	**391.37**
		0.24	*3.50*	*0.08*	*22.43*	*0.02*	*0.51*	*0.00*	*11.87*	*1.13*	*107.5*	*0.32*	*17.52*
	1.0	**12.10**	**12.82**	**5.56**	**482.05**	**9.89**	**5.65**	**5.85**	**386.68**	**9.46**	**1,716.6**	**5.96**	**388.07**
		0.71	*2.55*	*0.06*	*27.66*	*0.12*	*0.39*	*0.12*	*5.77*	*1.19*	*205.7*	*0.24*	*14.63*
	4.0	**16.27**	**8.34**	**5.50**	**484.19**	**14.34**	**5.03**	**5.43**	**365.26**	**13.03**	**1,621.7**	**5.42**	**374.50**
		1.14	*2.06*	*0.05*	*30.12*	*0.08*	*0.41*	*0.09*	*3.46*	*1.54*	*205.9*	*0.31*	*20.82*
	8.0	**21.86**	**4.06**	**5.80**	**477.01**	**18.94**	**4.80**	**5.39**	**382.47**	**15.17**	**1,288.4**	**5.42**	**356.41**
		1.65	*0.97*	*0.05*	*20.11*	*0.03*	*0.47*	*0.05*	*4.62*	*2.16*	*232.3*	*0.48*	*13.46*
	16.0	**21.96**	**3.01**	**5.80**	**443.03**	**20.29**	**4.84**	**5.45**	**369.57**	**16.83**	**1,465.1**	**5.60**	**369.69**
		0.89	*1.20*	*0.08*	*21.08*	*0.86*	*0.30*	*0.47*	*7.93*	*1.74*	*201.1*	*0.28*	*13.23*

Continued over...

Table 5.5 Effect of thermal modification on Charpy impact strength (IS), shear strength (S) and Janka hardness (H) on specimens of beech, Scots pine and Norway spruce. Each value is the mean value of ten (IS), four (S), and six replicates (H). Mean values in bold, with SD in italics. *(Concluded)*

Temp.	Time	IS				S				H			
°C	h	WL	IS	EMC	ND	WL	S	EMC	ND	WL	H	EMC	ND
		%	$\mathrm{kJ\,m^{-2}}$	%	$\mathrm{kg\,m^{-3}}$	%	MPa	%	$\mathrm{kg\,m^{-3}}$	%	N	%	$\mathrm{kg\,m^{-3}}$
Spruce													
Control	0.0	**0.00**	**23.26**	**11.42**	**371.93**	**0.00**	**7.42**	**11.26**	**421.38**	**0.00**	**1,775.0**	**11.59**	**396.12**
		0.00	*3.26*	*0.10*	*18.14*	*0.00*	*0.12*	*0.15*	*3.63*	*0.00*	*271.2*	*0.05*	*24.44*
190	0.3	**1.08**	**23.93**	**10.33**	**366.70**	**0.91**	**6.86**	**10.59**	**413.03**	**1.02**	**1,664.5**	**10.85**	**397.44**
		0.01	*9.24*	*0.09*	*5.48*	*0.07*	*0.32*	*0.02*	*18.35*	*0.04*	*262.0*	*0.12*	*22.67*
	1.0	**1.59**	**21.03**	**9.62**	**371.54**	**1.21**	**6.75**	**9.94**	**401.14**	**1.31**	**1,775.0**	**10.31**	**412.29**
		0.12	*5.43*	*0.08*	*12.59*	*0.03*	*0.25*	*0.02*	*19.47*	*0.14*	*199.1*	*0.16*	*18.35*
	4.0	**2.25**	**18.00**	**9.01**	**365.15**	**1.69**	**6.64**	**9.37**	**387.42**	**1.49**	**1,787.2**	**9.84**	**399.45**
		0.06	*3.97*	*0.05*	*18.75*	*0.05*	*0.76*	*0.02*	*28.55*	*0.15*	*215.1*	*0.18*	*17.27*
	8.0	**3.16**	**16.65**	**8.75**	**370.74**	**2.43**	**6.83**	**9.24**	**422.95**	**2.23**	**1,861.7**	**9.64**	**408.84**
		0.15	*3.93*	*0.04*	*17.95*	*0.01*	*0.41*	*0.16*	*3.89*	*0.29*	*238.8*	*0.20*	*26.20*
	16.0	**4.11**	**12.44**	**8.01**	**373.32**	**2.71**	**6.53**	**8.88**	**432.90**	**2.30**	**1,720.3**	**9.34**	**399.29**
		0.25	*2.83*	*0.07*	*12.72*	*0.13*	*0.51*	*0.02*	*8.10*	*0.36*	*265.2*	*0.19*	*22.60*
210	0.3	**1.59**	**19.32**	**8.81**	**370.85**	**1.13**	**7.04**	**9.44**	**439.78**	**1.04**	**1,843.5**	**9.59**	**407.42**
		0.11	*3.88*	*0.06*	*5.10*	*0.03*	*0.36*	*0.01*	*0.20*	*0.07*	*239.8*	*0.16*	*16.98*
	1.0	**3.34**	**16.77**	**8.02**	**368.18**	**2.35**	**6.90**	**8.50**	**418.31**	**2.13**	**1,520.5**	**9.03**	**380.52**
		0.12	*4.11*	*0.07*	*8.18*	*0.03*	*0.27*	*0.08*	*6.09*	*0.31*	*126.1*	*0.24*	*9.02*
	4.0	**5.83**	**12.18**	**7.14**	**358.62**	**4.46**	**6.36**	**7.79**	**408.70**	**3.87**	**1,618.7**	**8.32**	**407.61**
		0.12	*1.55*	*0.04*	*15.61*	*0.05*	*0.12*	*0.02*	*1.91*	*0.54*	*260.9*	*0.30*	*14.64*
	8.0	**6.83**	**11.96**	**6.85**	**364.63**	**5.16**	**6.40**	**7.48**	**406.53**	**4.53**	**1,521.9**	**8.01**	**405.09**
		0.18	*2.28*	*0.11*	*7.35*	*0.09*	*0.31*	*0.06*	*1.88*	*0.59*	*133.8*	*0.29*	*16.59*
	16.0	**10.44**	**5.38**	**6.16**	**352.36**	**6.82**	**6.66**	**7.08**	**432.77**	**5.39**	**1,498.2**	**7.62**	**406.96**
		0.49	*1.34*	*0.16*	*11.37*	*0.13*	*0.41*	*0.12*	*1.32*	*0.78*	*154.2*	*0.30*	*26.30*
230	0.3	**4.03**	**12.45**	**7.31**	**368.07**	**2.71**	**6.82**	**8.18**	**441.56**	**2.58**	**1,650.9**	**8.31**	**400.43**
		0.07	*3.84*	*0.08*	*25.34*	*0.26*	*0.24*	*0.12*	*9.09*	*0.26*	*214.2*	*0.20*	*17.49*
	1.0	**7.24**	**10.63**	**6.62**	**349.13**	**4.51**	**6.79**	**7.41**	**427.33**	**4.07**	**1,481.0**	**7.78**	**399.65**
		0.18	*3.53*	*0.08*	*7.92*	*0.37*	*0.44*	*0.26*	*10.70*	*0.47*	*168.5*	*0.31*	*29.65*
	4.0	**10.12**	**9.86**	**6.06**	**361.97**	**7.14**	**6.20**	**6.79**	**439.03**	**6.28**	**1,570.9**	**7.19**	**389.43**
		0.51	*3.47*	*0.02*	*5.28*	*0.46*	*0.28*	*0.10*	*3.90*	*1.14*	*206.8*	*0.32*	*24.55*
	8.0	**12.15**	**8.23**	**5.64**	**345.07**	**9.15**	**5.77**	**6.25**	**383.02**	**7.48**	**1,562.9**	**6.74**	**401.03**
		0.34	*1.76*	*0.05*	*12.35*	*0.39*	*0.17*	*0.02*	*14.44*	*1.12*	*94.4*	*0.35*	*11.27*
	16.0	**17.92**	**3.29**	**5.66**	**330.03**	**11.24**	**5.43**	**5.97**	**392.01**	**9.17**	**1,592.1**	**6.59**	**397.02**
		1.08	*0.81*	*0.07*	*15.59*	*0.60*	*0.33*	*0.02*	*7.26*	*1.09*	*228.5*	*0.25*	*17.04*
245	0.3	**8.74**	**11.48**	**5.89**	**347.53**	**6.29**	**6.42**	**6.57**	**414.67**	**4.79**	**1,596.6**	**7.15**	**387.60**
		0.21	*1.87*	*0.07*	*25.36*	*0.09*	*0.42*	*0.05*	*5.85*	*0.78*	*192.1*	*0.30*	*20.69*
	1.0	**12.40**	**10.51**	**5.35**	**348.58**	**8.63**	**6.02**	**5.92**	**394.88**	**7.40**	**1,820.3**	**6.44**	**407.29**
		0.42	*2.44*	*0.10*	*6.27*	*0.84*	*0.43*	*0.17*	*13.31*	*1.11*	*189.2*	*0.26*	*15.31*
	4.0	**16.98**	**5.02**	**5.37**	**334.76**	**14.01**	**5.41**	**5.46**	**391.06**	**10.82**	**1,515.2**	**6.04**	**387.49**
		0.16	*1.02*	*0.09*	*19.03*	*0.33*	*0.22*	*0.14*	*3.65*	*1.77*	*176.2*	*0.25*	*26.25*
	8.0	**19.57**	**4.41**	**5.25**	**324.00**	**15.13**	**5.67**	**5.49**	**399.97**	**13.57**	**1,513.3**	**5.69**	**370.51**
		0.36	*1.80*	*0.05*	*16.30*	*0.45*	*0.36*	*0.06*	*11.61*	*1.79*	*156.2*	*0.20*	*11.86*
	16.0	**29.87**	**0.63**	**5.63**	**297.17**	**20.07**	**5.17**	**5.53**	**383.43**	**17.51**	**1,334.3**	**5.70**	**381.35**
		1.54	*0.13*	*0.06*	*14.45*	*1.39*	*0.49*	*0.06*	*23.24*	*2.87*	*119.8*	*0.06*	*21.44*

WL: weight loss; IS: Charpy impact strength; S: shear strength parallel to the axis; H: Janka hardness (on radial face); EMC: equilibrium moisture content at 65% relative humidity at 20 °C; ND: nominal density = oven dry weight/conditioned volume at test

The relative-to-control average IS values in dependence of the WL changed in the same pattern for all the three species (Figure 5.21): the ratio follows a rectilinear trajectory in a log-normal plot. Property change pattern is very similar for pine and spruce; softwoods were affected less in magnitude in proportional-to-control values than beech at equivalent levels of WL for WL up to about 14%. After this threshold, beech IS is less affected than softwoods.

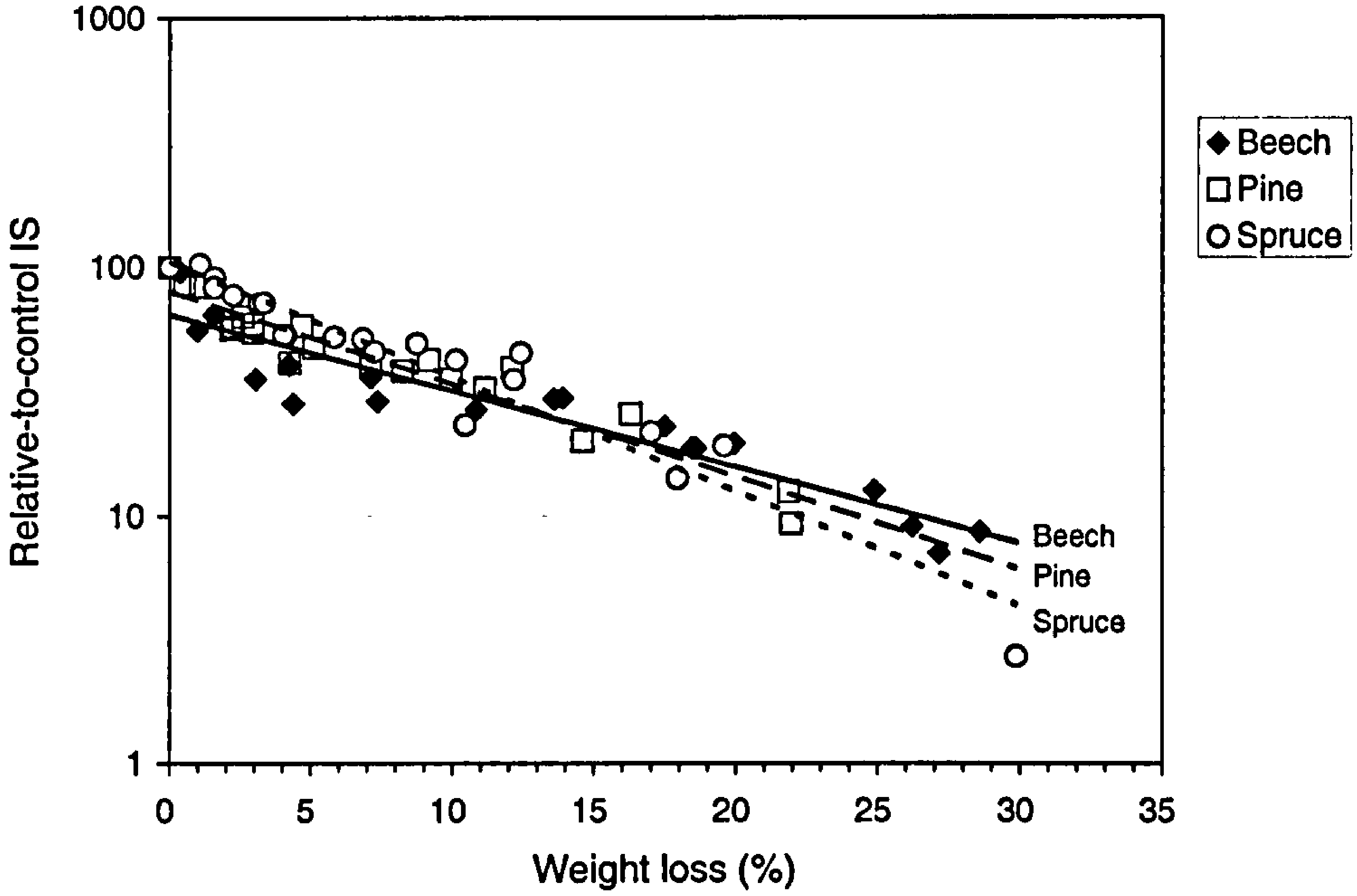


Figure 5.21 Relative-to-control (%) Charpy impact strength (IS) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of ten measurements

Untreated wood and wood modified for 0.3 h, with high shock resistance, showed long splits and coarse splinters. Often, on the compression side, a layer of several fibres thick remained intact. Modified wood at early levels of WL developed rather shorter, more fibrous splinters which were usually longer on the tensile than on the compression side. Splinters in softwoods were produced at the interface EW-LW at low to moderate levels of treatment. In modified wood at high levels of WL (> 12%) the fractured surfaces are rather smooth, occasionally wavy or stepped like a staircase. This last behaviour is typical of brash wood, which goes to failure with very small deformations and very quickly, whereas the fracture in tough wood is accompanied by rather large deformation and vibration (Kollmann and Côté 1968).

Reasons for changes in IS

The amount of shock resistance of a solid body depends directly on its ability to absorb energy and to dissipate it by deformation; high shock resistance of wood is equated to toughness, while low shock resistance with brashness or brittleness (Dinwoodie 2000). Toughness in wood is attributed to the presence of interfaces resulting from the cellular nature of timber and the layered structure of the cell wall (Gordon 1968). Several studies on mechanical testing of TMW have pointed out that the reduction in WML is larger than other bending properties (Millet and Gerhards 1972, Rusche 1973, Kubojima *et al.* 2000). This is explained by the close correlation between toughness, impact strength and WML, the latter being equal to the total energy absorbed in impact bending (Kollmann and Côté 1968). WML is influenced by MOE in bending, the position of the proportional limit, the MOR in bending, which depends itself on the crushing strength and tensile strength, the deflection at the proportional limit, and at the moment of failure, and on the resistance of the fibres after failure, which depends on tensile strength perpendicular to the grain, on cleavage resistance, and on maximum stress in shear parallel to the grain (*Idem*).

Clearly, uncovering the factors behind the reduction of impact strength is a complex subject; differences in IS values are not fully understood even in untreated wood. The situation is aggravated in TMW, due to the concurrent changes in the physical state of the cell wall material and the cell wall polymers, as well as the chemical changes in the wood substance.

Previously to this work, only simplistic explanations have been put forward pointing out to the chemical degradation of hemicelluloses as the main cause of IS reduction in TMW (*e.g.* Davies and Thompson 1964). If beech wood treated at 190 °C for 8 h is considered as an example (WL = 4.38%), IS is reduced by 72%. But at this WL, there is still 80% remaining of GluXylan in the treated wood (chapter 4). Even if the large reduction in the side chain arabinan is considered (62% loss at this conditions, Appendix 2), it is difficult to accept that a 0.65% content of arabinan in untreated beech can account for most of the impact strength in this species.

Some of the main factors proposed to be affecting the IS of TMW in no particular order, are:

1. Residual thermal stresses. As in man made fibre composites, stresses developing on cooling down between different polymers can significantly degrade the strength of the material, resulting in debonding, matrix cracking, reduced fracture toughness, and delamination (Zhao and Cameron 1998). Thermal expansion coefficient of wood cellulose crystallites cannot explain alone the proportionally larger longitudinal thermal expansion observed in solid wood (Hori and Wada 2005), but the coefficients of thermal expansion of lignin and polyoses are unknown. Although speculative at this time, it is undoubted that the thermal expansion coefficients of the three main polymers of wood substance are different. Because of the probably higher thermal expansion coefficient of lignin and hemicelluloses compared to that of cellulose crystals in the axial direction, the shrinkage of the lignin and residual hemicelluloses upon cooling from processing temperature will result in tensile residual stresses in the polymeric matrix. The superposition of these thermal stress and mechanical stresses (point 2 below) will result in increased microstress in the material. Cracks propagate more easily through stressed materials because the release of stress energy adds up to crack's energy, exceeding the energy necessary to produce new surfaces and thus facilitating the self-propagation of the crack.

2. Residual mechanical stresses. Seborg *et al.* (1953) noticed that the weight changes upon heating of Sugar maple and Sitka spruce and volume changes were of the same order of magnitude, a fact regarded as unexpected. On drying wood, the percentage volume change is generally less than 50% that of the percentage weight change, so they assumed that in addition to a loss in volume due to the removal of wood substance there was a decrease in volume in the cell cavities, which decrease was transmitted to the external volume of the wood. After an elaborate experiment they could not demonstrate the hypothetical reduction in cell cavities, except for a small reduction in the hardwood vessels dimensions upon heating. Negligible changes of the transversal dimension of tracheid cells of heat-treated wood were more recently reported by Hietala *et al.* (2002). However, at it was shown in chapter 4, the reduction of transversal dimensions coincides with the lengthwise increase in specimen dimensions –the Poisson effect, which indicates that the cell wall matter is densified somewhat upon heating. Hence, a major reason behind the reduction in the impact stress is the after-treatment physical state of the cell wall substance in modified wood. The shrinkage of the cell wall leaves the

treated material in a permanent state of mechanical strain: the irreversible shrinkage reduces firstly the capability of the cell wall for instantaneous elastic deformation and drastically lowers the ability of energy absorption through viscous deformation of the cell wall polymers. The reduced viscous deformation of TMW was demonstrated indirectly by its reduced relaxation (González-Peña *et al.* 2005): samples of heat-treated spruce showed a smaller plastic deformation than untreated controls upon releasing a compression load held for 180 s. As the treatment causes structural changes and lining up of the hemicelluloses along the microfibrils, and cellulose microfibrils to increase their crystallinity (largely in the form of lateral crystallite growth), the smaller plastic deformation of modified wood was ascribed to the incapability of wood polymers for uncoiling and/or slippage under stress. Plastic deformation is essential for high impact strength in untreated wood (Dinwoodie 2000). Prior to fracture, cells separate in the fracture area and on further stressing these individual and unrestrained cells buckle inwards generally assuming a triangular shape. In this form they are capable of extending up to 20% before final rupture, thereby absorbing a large quantity of energy. SEM observations of fractured surfaces of thermally modified spruce wood (Modes I and III) revealed only very few pulled out fragments and clear cut cell walls, whereas the fracture surface of the raw material was much more deformed and parts of the cell walls were pulled out (Reiterer and Sinn 2002).

3. Chemical degradation: Wood is generally resistant to a large number of chemicals but under prolonged very acidic or alkaline conditions permanent weakening of the timber results (Dinwoodie 1970). In the case of TMW, the relationship between chemical and mechanical changes has been poorly described, although the reduction of IS had been hypothetically ascribed principally to the rapid degradation of hemicelluloses. Only Davis and Thompson (1964) have presented empirical evidence of the relationship between the thermal degradation of hemicelluloses and holocellulose and the reduction of impact toughness in Red oak, Douglas fir and Longleaf pine woods. Toughness in all the three species was related to changes on the carbohydrate fraction of the specimens, where holocellulose content was a marginally better predictor than hemicellulose content, suggesting the minimum contribution of α-cellulose in the prediction of toughness. However, a linear regression of impact strength on lignin content using the oak data of these authors gives a better predictive ability ($R^2 = 0.87$) than that they computed for

hemicelluloses ($R^2 = 0.82$). The significant correlation between IS and gravimetric changes in chemical constituents of TMW and the correlation between themselves was noted by González-Peña and Hale (2007b), so it is not straightforward to deconvolute the effect of each chemical constituent in property change (see section 5.8). Leopold and McIntosh (1961, cited by Davis and Thompson 1964) postulated that the hemicellulose fraction is located between fibrils, and that its removal reduces interfibrillar bonding, thus causing a reduction in the internal strength of the individual fibres. The interfibrillar and interpolymer bonding role of hemicelluloses has been described at length by Koshijima and Watanabe (2003). Reduction of hemicelluloses could influence other mechanical properties, but the evidence points to the effect of heat-induced changes in this fraction are primarily manifested in shock resistance. Evidence from other forms of chemical degradation attribute the reduction of hemicelluloses as the main cause of the reduction of impact strength. Kass *et al.* (1970) described the relationship between the strength of thirteen wood species with the original pentosan composition and residual pentosan content after alkaline and acidic treatments. They found that high initial pentosan content correlated well with work to maximum load retention following alkaline degradation. Recent work on hydrolytic chemical agents (biocide or fire retardant treated wood) and enzymatic decay has indicated that early degradation of hemicelluloses, specially the degradation of shorter branched monomers of D-galactose and L-arabinose along the hemicellulose main chains seems primarily responsible for the earliest portion of strength loss in wood following biological or chemical exposures (alone or combined with heating at less than 100 °C) (Curling *et al.* 2002, Winandy and Rowell 2005). Toughness of wood appears to be particularly sensitive to chemical degrade in all scenarios; even the smaller changes in chemical make up causes noticeable reductions in toughness. Naturally occurring wood with modified chemical composition (increased lignin content in compression wood) is also known for its brashness (Dinwoodie 1970). It is unquestionable the responsibility of the chemical changes in TMW in the reduction of the IS, but the implications have more than one edge. In softwoods, latewood contains more cellulose and galactoglucomannan as compared to earlywood, but earlywood contains more arabinoglucouranoxylan and lignin (Sjöström and Westermark 1999, Rowell *et al.* 2005). All the cell wall layers and wood tissues (parenchyma and sclerenchyma) have different chemical composition (Saka 2001): ray cells and vessels have more lignin than tracheids and fibres, but these have more cellulose and glucomannan; rays also have more glucouranoxylan. In hardwoods, the lignin in the secondary wall of the fibres and the ray parenchyma cells is largely of the syringyl type, while that in the vessel wall is of the guaiacyl type (syringyl units have been reported as the most susceptible to heat exposure, mainly in the presence of moisture by Garrote *et al.* 1999). Hence the differential chemical degradation in tissues and cell wall layers due to their different composition cannot be dismissed. These differences may cause localized zones of weakness and also contribute to the after-treatment micro-stresses referred to in point 1 above. As lignin content in modified wood is higher than in raw wood, the reduction in IS should be manifest even if all other factors remained the same.

4. Different moisture content at test. Studies on moisture content have examined untreated wood from oven-dry to green condition, but the information from impact tests is inconclusive, and no general statements can be produced. Apparently, at EMC larger than 10% to the FSP, the impact strength is independent of the moisture content. Rein (1943, cited by Kollmann and Côté 1968) investigated the toughness of notched specimens of fir wood and found a rather steep decrease in toughness with decreasing moisture content below 5%. Kollmann and Côté (1968) concluded that toughness is dependent upon both strength and pliability; some woods become rather rigid, less pliable and brittle upon drying to approach the oven-dry state. This latter observation may be related somewhat to the dimensional changes elaborated in point 2 above. The issue appears to be better studied in the engineering approach to fracture, and although it may not be directly applicable to IS, some remarks are worth the space: the Mode I fracture toughness of untreated wood increases from the oven-dry condition reaching a maximum between 6% to 8% moisture content, decreasing gradually afterwards although other studies point to a slight increase or constant strength (Conrad *et al.*, 2003). The reduction of Mode I fracture toughness at low moisture contents is due to the differential shrinkage on the radial, tangential and longitudinal directions (drying stresses), which lead to radial micro-cracks and subsequent reduction in fracture toughness (Sobue *et al.* 1985), whereas the increase with moisture content is due to the viscoelastic behaviour of wood leading to greater energy absorption through viscous deformation and an increased toughness (Mindess 1977, cited by Conrad *et al.* 2003). From Table 5.5 it is clear that the moisture content at test was greatly reduced in all the three species, where most of the treated samples had EMC < 8%.

Final considerations on impact strength

According to Kollmann and Côté (1968), two phases should be distinguished in a diagram of the temporal course of the reaction force needed to split a specimen: the event prior to the ultimate load and the event after this threshold. For the first phase, the ability of a material to absorb energy and to convert it into heat is critical; in the second phase, the type of failure controls the further progress to complete failure. In this phase splinters and splits cause unpredictable friction resistance. Kubojima *et al.* (2000) using an acceleration transducer in the hammer for a Charpy impact test of heat-treated Sitka spruce found that the absorbed energy increased slightly at the beginning of the modification, thereafter gradually reducing to about 75% of control samples, for a density change of *ca.* 6% (the harshest treatment tested). They concluded that the reduction in IS was caused more by the decrease in the second phase (*i.e.* the ability of dissipate energy by deformation) than for the initial ability of absorbing energy. They also proposed that treated material was more brittle because of the large reduction in the 'plastic' work (*i.e.* WML minus Resilience) and therefore the main factors contributing to the work needed to fracture were viscosity and plasticity, not elasticity.

From a practical point of view, increased brittleness in a material is not a desirable characteristic. Wood members of aircrafts, vehicles, machines, sports goods, ladders and tool handles fail more frequently under the influence of impact stresses than under static overloading (Kollmann and Côté 1968). However, in spite of the large reduction in impact strength at early stages of conversion, emphasis should be made on the relative low importance of this property for most non-structural applications of TMW (with the obvious exception where the application includes the impact of a falling body). As explained before for the energy parameters in bending, resilience is less affected than the correspondent parameter at maximum load (WML), so a compromised performance upon sudden loads cannot be expected within the limit of proportionality when provisions had been made to maintain the limit state of service. On the other hand, in load-bearing applications ultimate impact strength of wood is only relevant in extreme situations of usage, such as earthquakes or tornadoes, where sudden loads beyond the proportional limit are applied to the material and the reduced ability to withstand the work results in a whole structure failure. In spite of the foregoing, most of the failures in wooden structures in the course of extreme meteorological events lay on defective building foundations or failures at junctions or fasteners (Whitaker 1979). Although not investigated in this work, thermal modification has been reported to be particularly deleterious to the cleavage and tension perpendicular to grain strengths (Syrjänen and Kangas 2000); research should probably be conducted to devise ways to improve fastening of TMW and on designing practices that could compensate the reduced capacity of absorption of sudden loads for load-bearing situations.

5.5 Shear strength

Compared to untreated control, changes in this mechanical property are minor; probably comparable to elasticity, but varied depending on the wood species (Table 5.5, Figure 5.22). Beech and pine were almost not significantly reduced, whereas the effect in spruce was observed at moderate to high levels of modification. In all cases, samples conserved the same wood character at failure as untreated controls, with a noticeable banging at failure; from the stress-strain plot it was clear that the treatment has good reproducibility despite the complexity of this property.

In beech, the reduction was significant only for the treatments at 230 °C for 16 h (at WL $\geq$ 21.6%) and for treatments at 245 °C for more than 0.3 h (to WL $\geq$ 20.1%). The reduction in all cases was significant when the strength property had fallen more than 20%. At 190 °C for 8 h (at WL = 3.0%), this property was significantly larger than control shear.

In pine, only two treatments lead to significant reductions of this property: at 210 °C for 16 h and (at WL $\geq$ 8.4%) and at 245 °C for 8 h (at WL $\geq$ 18.9%). The significant reduction was when the property has been reduced by 10.5% and 25.7% respectively.

In spruce, the reduction of this property occurred at significantly lower WL than pine, and occurred at temperatures of exposure > 190 °C. At 210 °C, the reduction was for treatments at 4 h (to WL $\geq$ 4.5%) and 8 h (to WL $\geq$ 5.2%). At 230 °C, treatments for more than 4 h (at WL $\geq$ 7.1%) lead to reductions, whilst all the treatments at 245 °C resulted in significant changes. Significant reductions took place when the property had been reduced at least by 13.7%.

The relative-to-control average S plotted against the WL shows the same profile for all the three species (Figure 5.23): the ratio follows a rectilinear trajectory at very similar changing rates, although the intercept for beech is at substantially higher relative-to-control vales. S in beech apparently is increased at very small levels of modification, and it is steadily reduced reaching control values at a WL of about 7.5%. Property change pattern is very similar for pine and spruce, although the changing rate of pine is somewhat smaller.

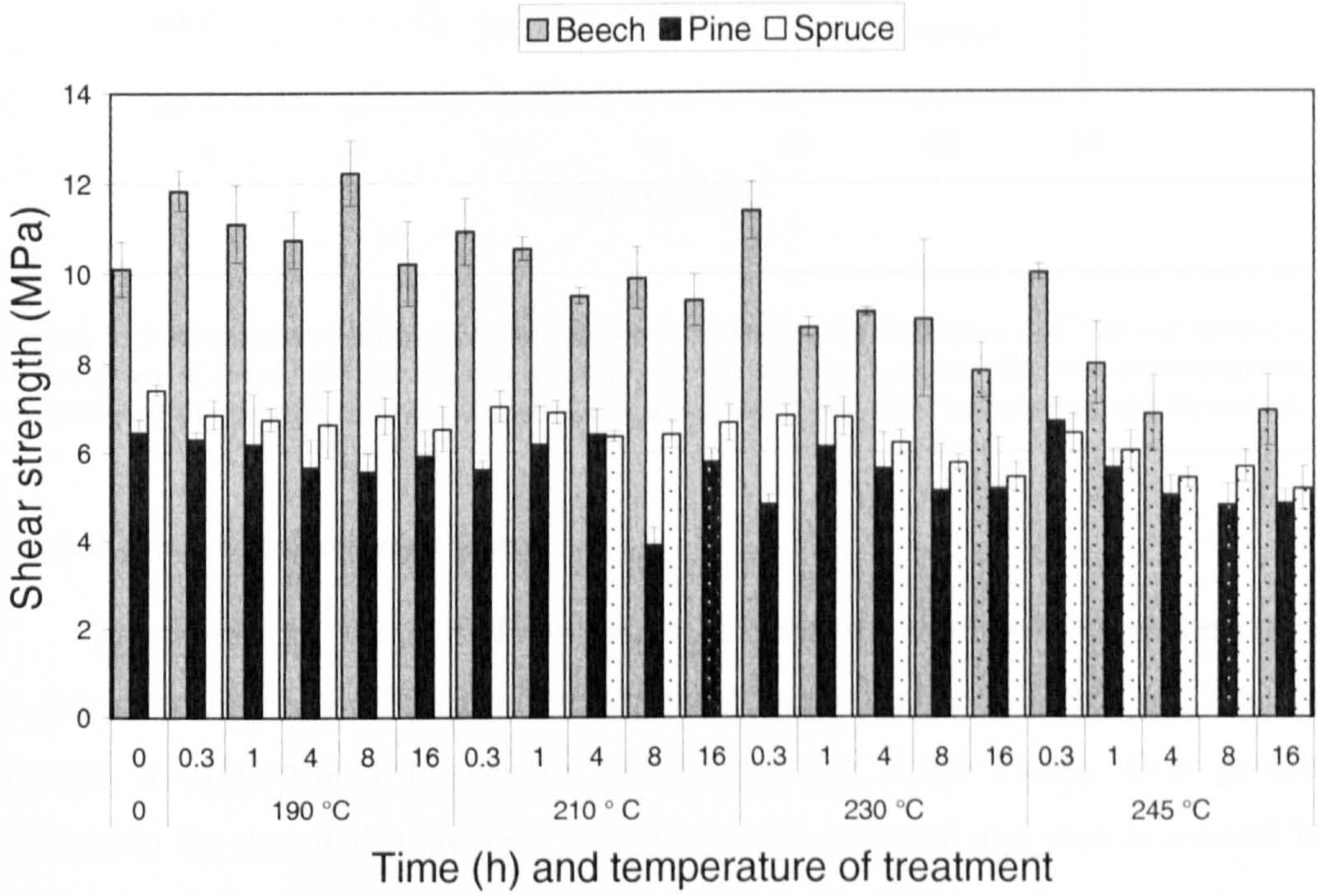


Figure 5.22 Effect of thermal modification on shear strength parallel to the axis (S) for thermally modified beech, Scots pine and Norway spruce woods. Each bar represents the mean value of 4 replicates. Mottled bars = treatments significantly reduced. Error bars = ± 1 SD

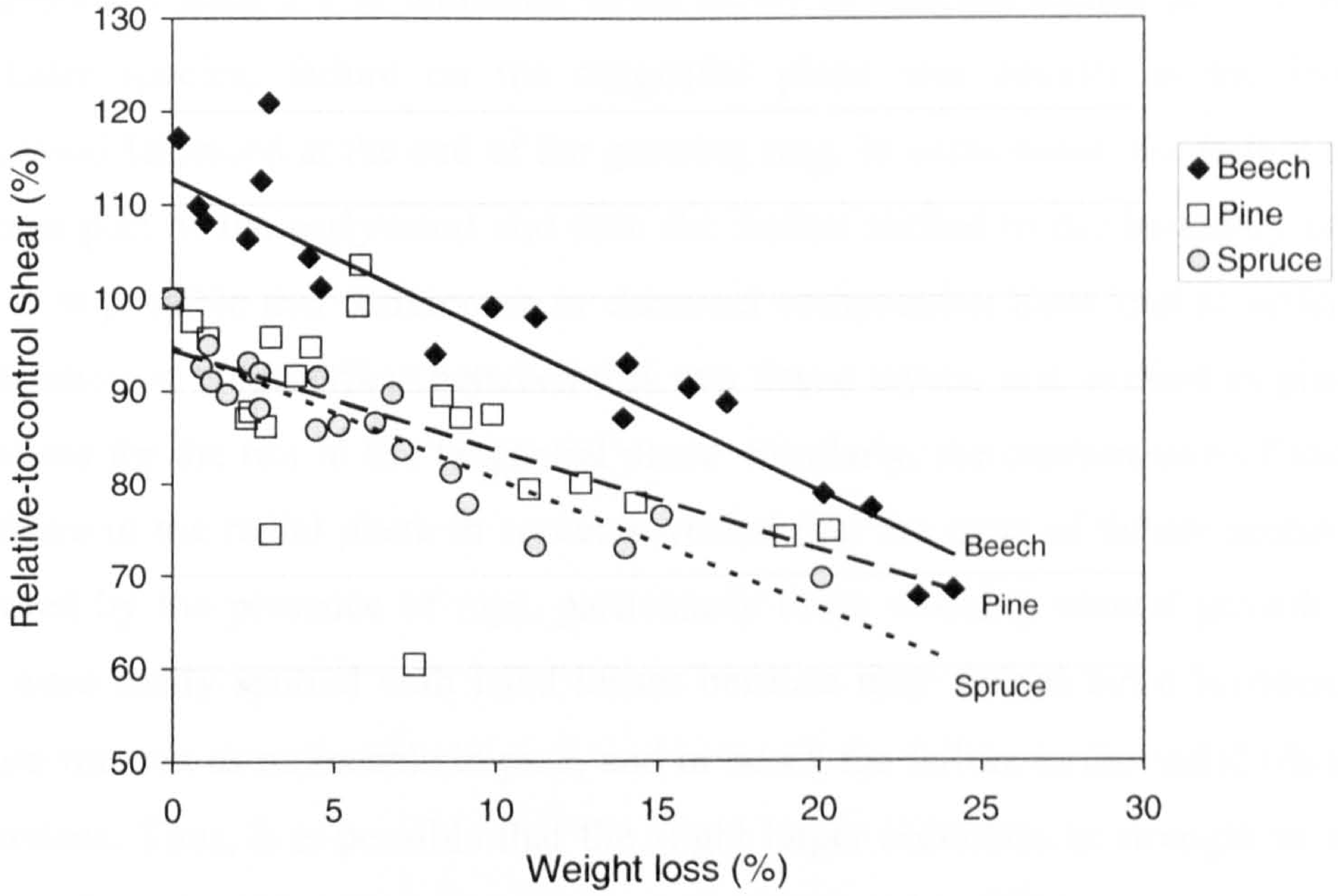


Figure 5.23 Relative-to-control (%) shear strength (S) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of 4 measurements (each being the average of two specimens, one in the radial and other in the tangential direction).

Reasons for the reduction in shear

Shear strength is a complex strength property in wood material and currently the chemical and physical factors behind this property are poorly described. Shearing strength is proportional to density (Kollmann and Côté 1968). One possible explanation for the small reduction in this property in beech and pine is a small but gradual reduction of ND in line with the treatment. Significant reductions only occur at considerable levels of WL in beech and pine. This performance could be favourably related to the reduced wood EMC at test. In untreated wood this property reaches a maximum at moisture content between 6 and 11% and then decreases as the moisture content approaches the oven-dry condition (*Idem.*).

The reasons for the greater reduction in spruce at similar treatment conditions compared to pine and beech are probably related to differential changes in chemical composition. According to the BS373 (BSI 1957), the shear test is made on matched pairs of specimens in the radial and tangential plane and averaged to give an ultimate shear strength. In beech, the ratio between radial and tangential plane strengths remained constant at 1.5:1. In pine, the same ratio increased slightly with the severity of the treatment from 2.2:1 to 2.8:1. In contrast, in spruce the ratio increased progressively from 2:1 in untreated wood to 4:1 in samples treated at 20% WL. In the latter species, failure on the tangential plane was usually at the interface earlywood-latewood at the end of the growing ring. In some cases, the failure started in some part of the earlywood and then the failure shifted to the boundary of EW-LW. It is possible that differences in chemical composition have lead to differential degradation at the interface between this two tissue layers, and worked as planes of weakness for the test in the tangential plane. Similarly, the examination of the zone of failure in the radial plane in spruce revealed that the zone of failure seems to be favoured by the presence of rays, particularly those crossing several growth rings; rays were easily spotted with hand lenses because they looked more lustrous. This feature was not as noticeable in pine, and in beech the failure in the radial plane was featureless. Thus, it is possible that the slight larger reduction in strength in spruce compared to the other two species is also favoured by differences in anatomical composition.

Examples on the reduction of shear strength in TMW are scant, and only indirect measurements are reported in the literature. Bohlen (1972) reported that heating the surface of Douglas-fir lumber at temperatures between 193 °C to 260 °C immediately before gluing weakened the fibres adjacent to the glueline; this reduced shear strength, although the percent of wood failure remained high. These results were partially confirmed by the study of Chang and Keith (1978). They modified four hardwoods at temperatures between 180 °C and 220 °C for times ranging from 0.5 to 32 h and then conducted a glueline shear strength test. Generally, glueline shear strength declined with increasingly severe conditions of treatment, but reductions varied considerable, from about 10% in aspen to 50% in elm. Although these authors found that shear strength declined, the glueability of woods (expressed as the percentage of wood failure) suffered apparently little effect, because the percentages of wood failure for treated samples were generally high, in some instances exceeding the values of control samples. Heated elm samples, for instance, sustained high percentages of wood failure depending on the adhesive employed (86% for urea-formaldehyde, 95% for PVA) while glueline shear strength declined on the average 43% and 30% below control specimens. Clearly, results in the glueline shear strength are more associated to the general reduction of wood strength than to the production of inferior glue bonds, but the direct reduction of shear strength has not been previously reported for TMW.

5.6 Janka hardness

In softwoods, Janka hardness was unaffected by any level of treatment, except for spruce treated at 245 °C for 16 h (to WL ≥ 17.5%). At this level of modification, spruce hardness was reduced by 24.8%. This property was the least affected in softwoods, only comparable to compression strength and MOE. In beech, significant changes took place at WL ≥ 5.5%, but this varied with the temperature of exposure (Table 5.5, Figure 5.24). No treatment at 190 °C caused significant reductions in beech hardness. Modification at 210 °C for four h or more (to WL ≥ 5.5%) and at 230 °C and 245 °C for 1 h or longer (to WL ≥ 10.0% and 16.6% respectively) resulted all in significant reductions of this property. Significant reductions were found when this form of strength had fallen by 25.6%, 37.6% and 50.0% at 210 °C, 230 °C and 245 °C respectively.

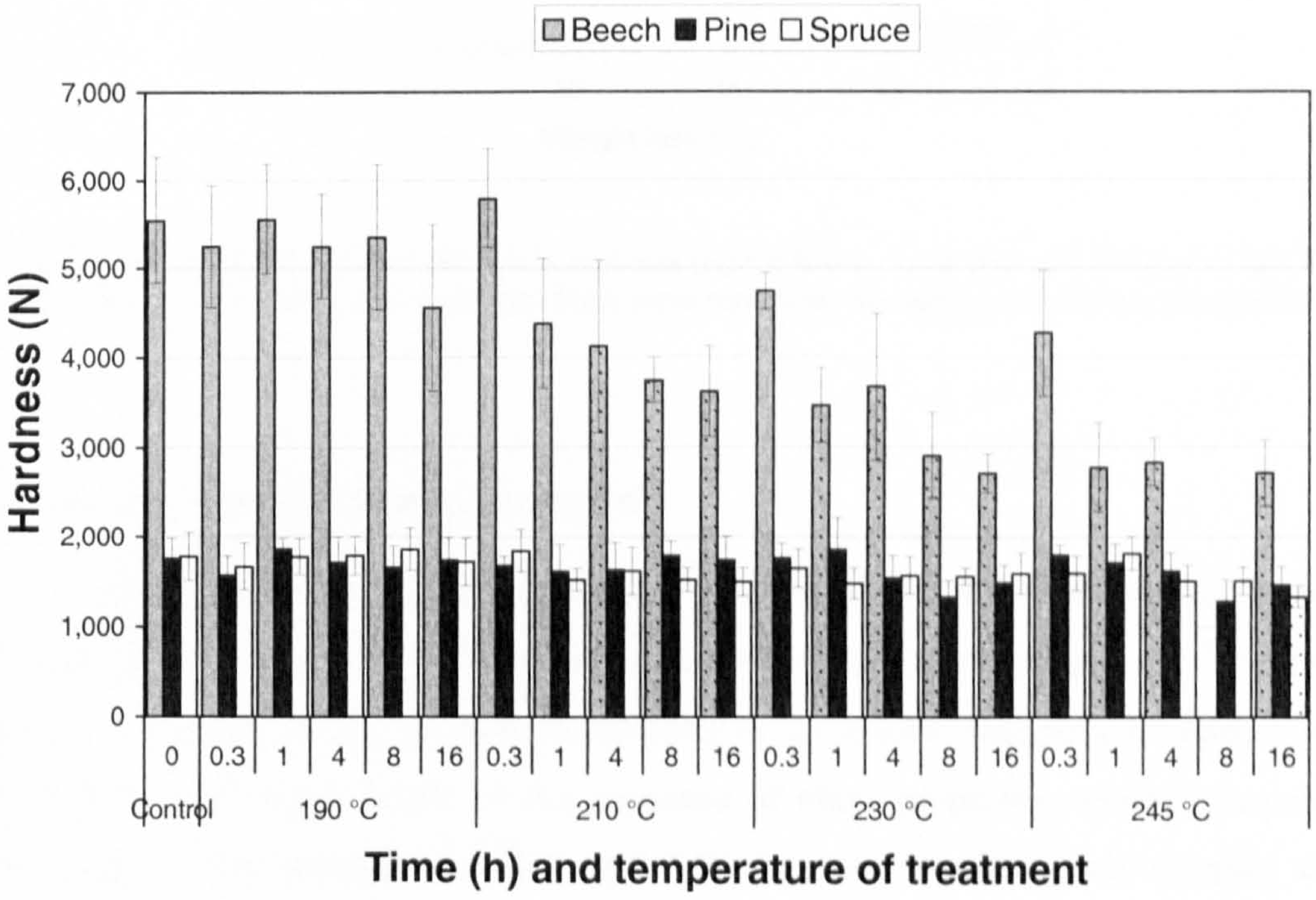


Figure 5.24 Effect of thermal modification on Janka hardness on the radial face (H) for thermally modified beech, Scots pine and Norway spruce woods. Each bar represents the mean value of 6 replicates. Mottled bars = significantly reduced treatment. Error bars = ± 1 SD

The relative-to-control average hardness strength values in dependence of the WL after the heat treatment changed in the same pattern for all the three species (Figure 5.25): the ratio follows a rectilinear trajectory, increasing slightly in pine at the beginning of the treatment and then gradually reduced. Property change pattern is very similar for pine and spruce, but contrarily to all other strength parameters studied in this work, the rate of change in beech was considerably larger than in softwoods.

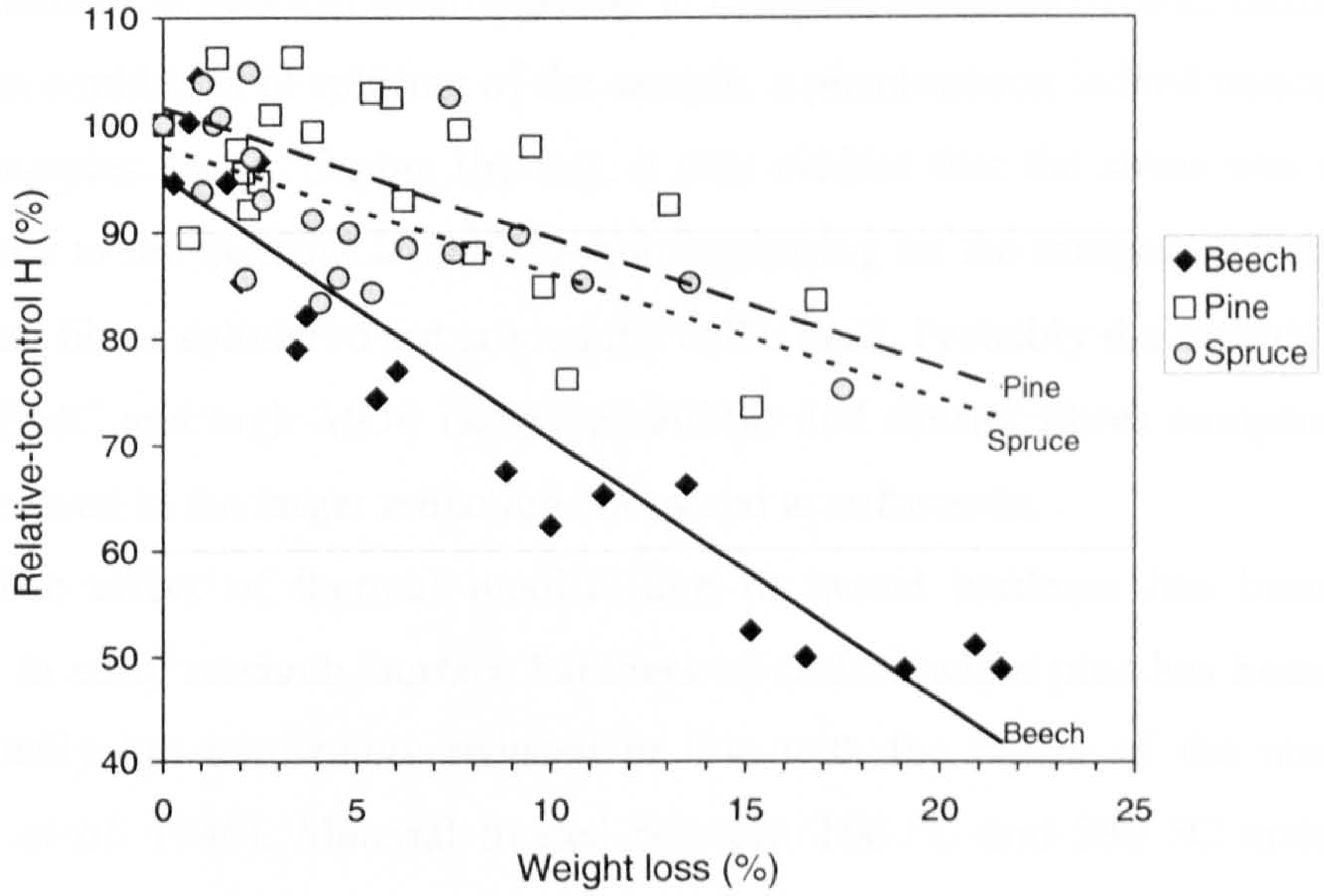


Figure 5.25 Relative-to-control (%) Janka hardness (H) for beech, Scots pine and Norway spruce in dependence of WL after heat treatment. Each point represents the mean value of 6 measurements

Reason for changes in hardness strength

Hardness has a strong correlation with wood density, and density is not dramatically changed by the treatments carried out in this work (chapter 4). This may explain in part the nearly unchanged property in softwoods. Insignificant reductions observed in softwoods could be the response of other properties, mainly cleavage resistance at the boundary of EW and LW, because in almost all samples the indentation of the hemispheric die led to sample splitting. As it was elaborated above (section 5.4), different chemical composition at the boundary of earlywood-latewood may bring about zones of weakness; insignificant but gradual reductions could also be related to the reduced pliability of the material derived from the reduced EMC and unchanged MOE.

In beech, the reasons behind the significant reductions in hardness at moderate levels of WL (≥ 5.5%), and the noticeable difference in behaviour compared to softwoods remains to be clarified. Even if the reduction in density is greater than SW at equivalent levels of WL (chapter 4), this probably does not totally explain the large differences. Probably the relative larger reduction compared to SW is coupled with the dissimilar chemical composition, because the reduction in hemicelluloses in beech is clearly greater at comparable levels of WL. Hemicellulose reduction could lead to splitting of the sample, a phenomenon indeed noticed in 93% of the samples tested. During the test, it was evident that the stress was not being transferred to the material around the hole appearing on the sample surface, and that individual fibres splintered out around the ball's head. Probably the combined effects of low EMC and high MOE (lower pliability) and shorter fibres compared to SW were involved in the larger reduction compared to softwoods.

The effect of thermal modification on wood hardness has been scantily studied. In early research, surface hardness of eastern white pine has been found to be gradually but moderately reduced in line with the extent of the modification (Stamm *et al.* 1946). Material treated between 160 °C and 280 °C under molten metal for 2 h, was found to retain about 73% of hardness (of untreated control) at an ASE of 50%, equivalent to a WL of approximately 17.5%. In the present report, a WL of 17.5% in spruce resulted in a relative-to-control hardness of 75%.

Some of the results from this work partially concord also with an early study of Seborg *et al.* (1953). They found that birch hardness heat-treated at 300 °C to give an ASE of about 20% was reduced by 2.6%, although treatment at 250 °C to an ASE of 20% caused an increase of 5.0% for this property. In the present work, the reduction of hardwood hardness was readily apparent from WL > 2.5%, and significantly reduced at WL > 5.5%. Similarly to the present research, these authors did not find a significant change of hardness strength in the softwood species studied (Douglas-fir).

In partial agreement with the present report, Yilditz *et al.* (2004) found that the Brinell hardness of heat treated beech (*Fagus orientalis* Lipsky) modified at 180 °C for 10 h, with a reduction in specific gravity of about 16%, was reduced by

41.8%. A reduction of specific gravity in beech of about 13.3% in this work resulted in a significant reduction in Janka hardness of around 50%.

In large-sized specimens modified using the ThermoWood® process at temperatures between 202 °C and 212 °C for up to 41 h, hardness on the radial face was found to increase up to 7%, 19% and 36% in spruce, jack pine and birch respectively, although pine hardness decreased up to 24% for two process schedules (at 202 °C for 25 h and at 200 °C for 34 h); aspen hardness decreased by 26% in the single treatment tested (at 200 °C for 46 h) (Shi *et al.* 2007). Hardness in the longitudinal direction is less affected than in the tangential or radial faces, the response of these two faces being mixed: treatments which led to increases in the radial face, led to higher increases in the tangential direction, but schedules that resulted in decrease in hardness in the radial face, led to higher reductions in the tangential one (*Idem.*).

High wood hardness is commonly associated in untreated wood with abrasion resistance, but in TMW it has been determined that this relationship no longer exists (Seborg *et al.* 1953). Samples of yellow birch and Douglas-fir wood treated at an ASE of 20% had no reduction in hardness strength, but the wear due to abrasion in a Navy abrader increased 20% in the softwood and 150% in yellow birch. At an ASE of 40% hardness decreased by less than 3%, but the wear almost doubled in Douglas-fir and increased 3.5 times in birch. Similar accounts have been given for modified silver fir (Brischke *et al.* 2005).

5.7 Property changes at different temperatures at equivalent levels of WL

An analysis of covariance, ANCOVA, shows that the MOR at equivalent heat-induced WL was the same irrespective of the temperature of treatment for beech or spruce woods (Figure 5.26). This remark may have some practical relevance, because the loss in MOR could be estimated from the WL, regardless of the temperature of exposure if the modification were performed in the range of temperatures used in the present work (190 °C to 245 °C). In the case of pine, the ANCOVA shows that MOR changes at equivalent WL are the same independently of the temperature of exposure only when samples with WL $\geq 2.5\%$ are included in the analysis. The difference in pine with respect to the other woods could be derived from the rather chaotic property change at the beginning of the modification, whereby a relatively large WL derived from a possible loss in extractives, brings about no significant change in bending strength.

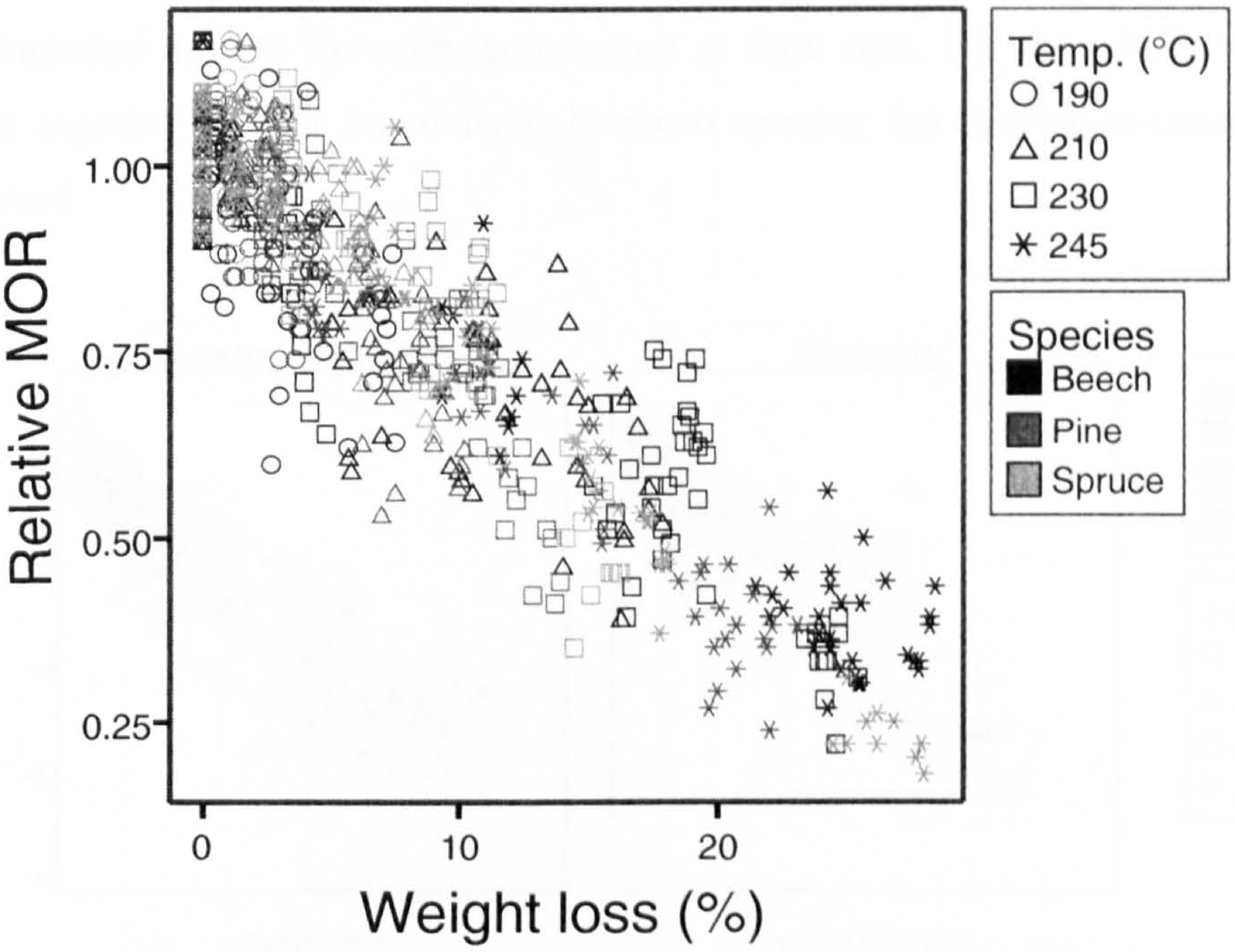


Figure 5.26 Relative-to-control modulus of rupture (MOR, in proportion) in dependence of weight loss at four different temperatures, for treated beech, Scots pine and Norway spruce

ANCOVA also shows that the relative-to-control MOR at equivalent heat-induced WL was statistically the same irrespective of the temperature of treatment if the data of all the three species is considered together.

The behaviour was significantly different between the three species. ANCOVA of the relationship between changes in relative MOR in dependence of heat-induced WL led to the finding that MOR changes have different slopes and intercepts between beech and softwoods, whereas pine and spruce have significantly statistically the same slope but different intercept. This means that the changing rate of MOR with respect to untreated samples is the same in softwoods, whilst in beech the rate is significantly different (smaller) at equivalent WL, although the reduction starts at slightly lower levels of modification in beech than in softwoods.

Similar analyses of covariance were performed for other 9 strength properties when the relationship between WL and property change was rectilinear. Table 5.6 shows the results of the analyses, whereas Figures 5.27 and 5.28 display graphically the relationship between relative-to-control property change in dependence of the WL at all four temperatures of exposure for the three species plotted together. For the analysis within species and for that of all species together, data from control samples were included as data for each temperature at time zero. For the ANCOVA for all species together and for the analysis between species, the relative-to-control values were used.

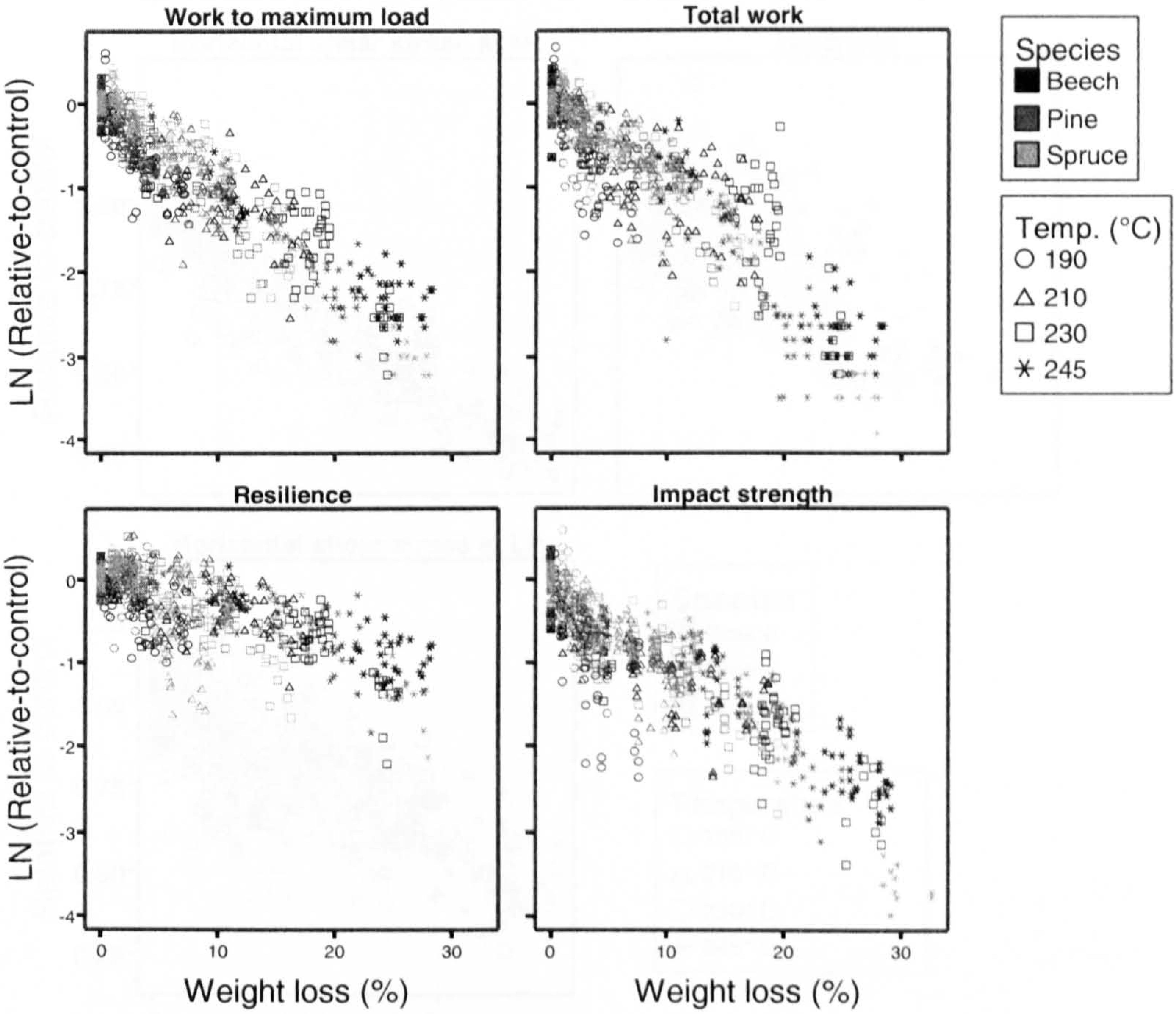


Figure 5.27 Relative-to-control (in proportion) work to maximum load (WML), total work (TW) resilience (R) and Charpy impact strength in dependence of weight loss at four treatment temperatures, for modified beech, Norway spruce and Scot pine woods

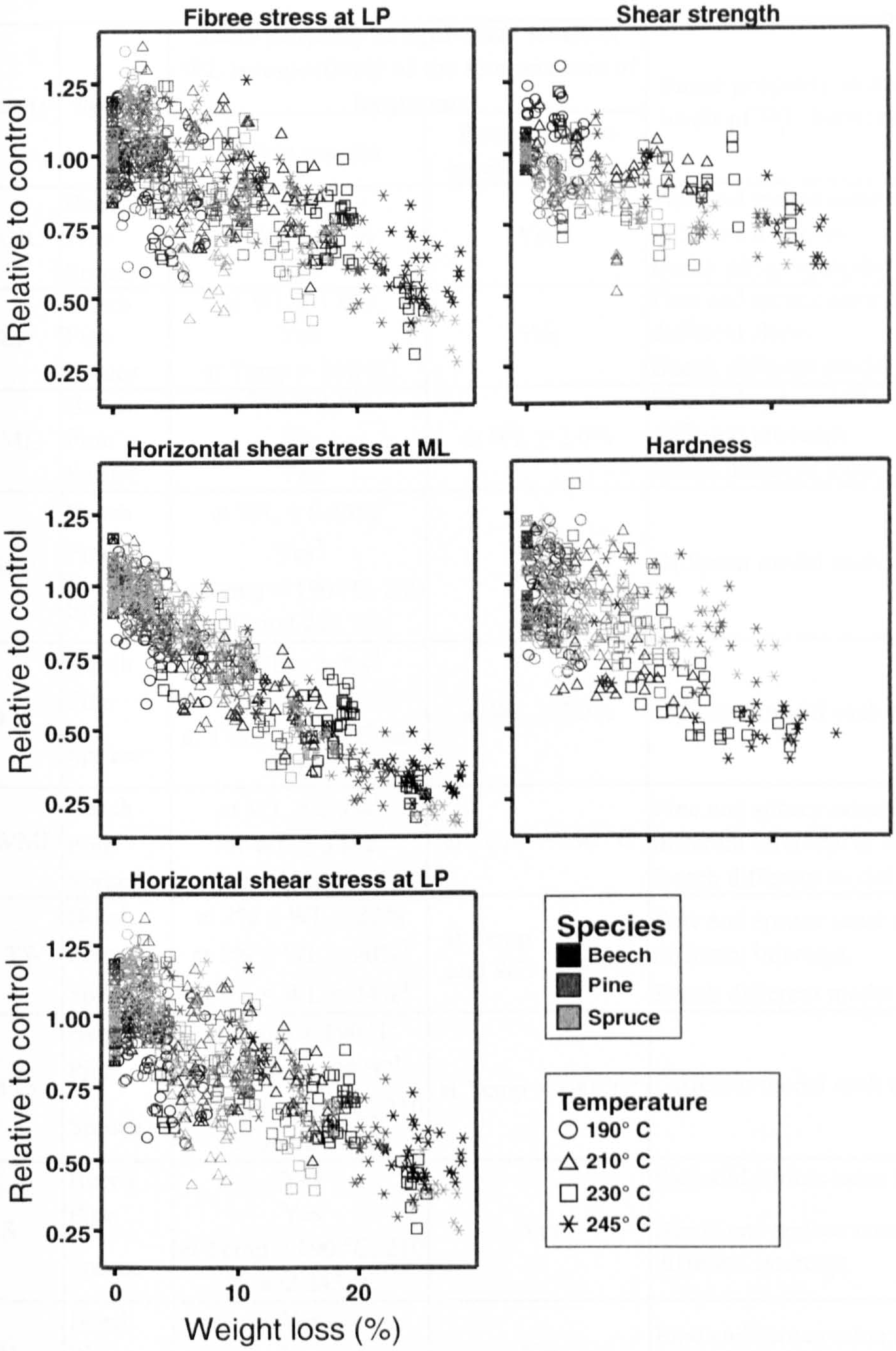


Figure 5.28 Relative-to-control (in proportion) fiber stress at limit of proportionality (RLP), horizontal shear strength at neutral plane at maximum load (SSML) and at limit of proportionality (SSLP), ultimate shear strength parallel to the axis (S) and hardness (H) in dependence of weight loss at 4 temperatures, for modified beech, Norway spruce and Scot pine woods

Table 5.6 ANCOVA for strength property at equivalent levels of WL at different temperatures for each species and for the data of all species together. ANCOVA for the differences between species at equivalent levels of WL. The level of significance in all tests was $\alpha = 0.05$. Type I sum of squares was used for the models.

Property	Species	Same property at equivalent levels of WL irrespectively of the temperature of treatment		Same property at equivalent levels of WL between species
		Within species	Data all three species together	
MOR	Beech	Yes	Yes	Pine and spruce same slope, different intercept. Beech different model
	Pine	at $WL \geq 2.5\%$		
	Spruce	Yes		
RLP	Beech	at $WL \geq 1.0\%$	Yes	Pine and spruce same intercept, different slope. Beech different model
	Pine	Yes		
	Spruce	at Temp > 210 °C		
SSML	Beech	at $WL \geq 1.0\%$	at $WL \geq 2.0\%$	Pine and spruce same slope, different intercept. Beech different model
	Pine	No		
	Spruce	Yes		
SSLP	Beech	at $WL \geq 0.45\%$[†]	Yes	Different model each species
	Pine	Yes[†]		
	Spruce	at Temp = 190 °C, 230 °C and 245 °C		
Ln R	Beech	at $WL \geq 2.0\%$[†]	at $WL \geq 2.0\%$	Different model each species
	Pine	Yes		
	Spruce	at Temp = 210 °C and 230 °C		
Ln WML	Beech	at $WL \geq 2.0\%$[†]	at Temp > 190 °C	Pine and spruce same slope, different intercept at $WL \geq 4\%$ Beech different model
	Pine	at $WL \geq 3.8\%$		
	Spruce	Yes		
Ln TW	Beech	at $2\% \leq WL \leq 22\%$	at Temp > 190 °C and $WL \leq 19.2\%$	Pine and spruce same slope, different intercept. Beech different model
	Pine	at $1\% \leq WL \leq 20\%$[†]		
	Spruce	at $1\% \leq WL \leq 24\%$[†]		
Ln IS	Beech	at Temp > 190 °C	at Temp > 190 °C[†]	Different model each species
	Pine	at Temp > 190 °C[†]		
	Spruce	at Temp = 190 °C, 210 °C and 245 °C		
S	Beech	Yes	Yes	Pine and spruce same model Beech and spruce same slope, different intercept
	Pine	Yes		
	Spruce	at Temp = 190 °C, 210 °C and 245 °C		
H	Beech	Yes	Yes	Pine and spruce same model Beech different model
	Pine	Yes		
	Spruce	Yes		

[†] Slightly different intercepts

Property changes within each individual species was generally the same at equivalent levels of WL irrespective of the temperature of exposure (Table 5.6). This is particularly true when the WL is somewhat larger than about 3%. At earlier stages of modification, the mechanical response is probably obscured by a small WL due to the loss of any residual moisture content and minute amounts of extractives which are not matched with quantifiable changes in mechanical strength. In any case, predictions from WL and other gravimetric parameters (section 5.9.1) were performed considering all the data together for each species, in the belief that larger data sets could possibly vanquish the intrinsic variability at the beginning of the treatment.

For MOR, RLP, S and H, a single model would have sufficed for the property prediction at equivalent levels of WL regardless of the temperature of treatment for beech, pine or spruce if the models were developed using the data from the three species together (Table 5.6). However, for the modelling in section 5.9.1, equations are presented for each species separately, because there was a significant difference between the behaviour in beech and softwoods for all forms of strength at equivalent levels of WL; although pine and spruce had in many instances statistically the same slope (changing rate), the intercepts in the model for each species was significantly different in most mechanical parameters except for S and H (Table 5.6).

5.8 Relationship between chemical degradation and mechanical changes

The nature of the heat-induced changes in chemical structures as well as the differences between softwoods and beech have been presented in chapter 4. In this section, those results are used to analyse the relationship between the progressive changes in mechanical properties and the concurrent changes in chemical composition. The prediction of mechanical strength parameters from changes in chemical composition is given in section 5.9.2.

For correlation analysis, the GluMan content for beech treatment 11 and the GluXylan and cellulose content for spruce treatment 20 were not included for inconsistency (too low value). The galactan content for spruce treatments 12 and 19 was not included in the correlation analysis, for inconsistency (too high value).

For correlation analysis, inverse transformation was attempted for the linearization of the relationship between MOE, CA and CE with chemical constituents, but the significance of the correlation did not change.

Strength properties were positively correlated with the hemicelluloses and cellulose and negatively correlated with the lignin substance.

In beech, no correlation was found between changes in hemicelluloses and CA and only weak correlation between CA and lignin (Table 5.7). CE had also no correlation to GluMan. Hemicelluloses had generally the strongest correlation with most strength parameters in beech, probably reflecting the large correlation between strength and GluXylan, which was generally second to hemicelluloses. Ln TW, S and CE were more strongly correlated to lignin than to polysaccharides and, generally, lignin had strong correlation with most mechanical properties. Cellulose had the weakest correlations with most mechanical properties, but it had the strongest correlation with MOE and CA.

Table 5.7 Correlation of chemical constituents[a)] and strength parameters after thermal modification (Significance: *, $p<0.05$; ** $p< 0.01$; *** $p<0.001$: NS, not significant)

	MOR	MOE	RLP	Ln R	Ln WML	Ln TW	SSLP	SSML	H	S	Ln IS	CA	CE
BEECH													
Lignin	-.930(**)	-.779(**)	-.847(**)	-.810(**)	-.915(**)	-.906(**)	-.878(**)	-.926(**)	-.921(**)	-.933(**)	-.900(**)	-.482(*)	-.730(**)
GluXylan	.964(**)	.716(**)	.846(**)	.821(**)	.941(**)	.898(**)	.896(**)	.970(**)	.979(**)	.889(**)	.911(**)	NS	.691(**)
GluMan	.810(**)	.474(*)	.712(**)	.726(**)	.813(**)	.744(**)	.766(**)	.827(**)	.812(**)	.627(**)	.807(**)	NS	NS
Hemicell	.963(**)	.697(**)	.850(**)	.830(**)	.944(**)	.897(**)	.900(**)	.970(**)	.976(**)	.862(**)	.915(**)	NS	.663(**)
Cellulose	.802(**)	.800(**)	.752(**)	.701(**)	.795(**)	.840(**)	.760(**)	.785(**)	.755(**)	.904(**)	.781(**)	.600(**)	.692(**)
PINE													
Lignin	-.970(**)	-.773(**)	-.913(**)	-.919(**)	-.975(**)	-.943(**)	-.939(**)	-.973(**)	-.651(**)	-.558(**)	-.946(**)	NS	-.542(*)
GluXylan	.851(**)	.694(**)	.825(**)	.828(**)	.882(**)	.859(**)	.849(**)	.857(**)	.591(**)	.493(*)	.847(**)	NS	.513(*)
GluMan	.930(**)	.812(**)	.910(**)	.910(**)	.946(**)	.951(**)	.929(**)	.931(**)	.663(**)	.540(*)	.922(**)	NS	.611(**)
Hemicell	.908(**)	.772(**)	.885(**)	.887(**)	.930(**)	.924(**)	.907(**)	.911(**)	.641(**)	.526(*)	.901(**)	NS	.577(**)
Cellulose	.683(**)	.486(*)	.546(*)	.550(**)	.646(**)	.599(**)	.573(**)	.683(**)	NS	NS	.647(**)	NS	NS
SPRUCE													
Lignin	-.985(**)	-.930(**)	-.827(**)	-.783(**)	-.993(**)	-.989(**)	-.842(**)	-.983(**)	-.647(**)	-.881(**)	-.963(**)	-.722(**)	-.757(**)
GluXylan	.923(**)	.720(**)	.727(**)	.674(**)	.945(**)	.941(**)	.766(**)	.937(**)	.536(*)	.900(**)	.924(**)	NS	.471(*)
GluMan	.959(**)	.808(**)	.778(**)	.726(**)	.944(**)	.912(**)	.805(**)	.967(**)	.633(**)	.919(**)	.890(**)	.572(**)	.663(**)
Hemicell	.947(**)	.776(**)	.784(**)	.735(**)	.936(**)	.902(**)	.812(**)	.958(**)	.634(**)	.924(**)	.886(**)	.524(*)	.641(**)
Cellulose	.859(**)	.816(**)	.721(**)	.642(**)	.883(**)	.885(**)	.740(**)	.855(**)	.479(*)	.705(**)	.804(**)	NS	.555(*)
SOFTWOODS[b)]													
Lignin	-.974(**)	-.845(**)	-.832(**)	-.756(**)	-.985(**)	-.957(**)	-.856(**)	-.974(**)	-.608(**)	-.681(**)	-.951(**)	-.610(**)	-.659(**)
GluXylan	.884(**)	.673(**)	.740(**)	.652(**)	.912(**)	.873(**)	.777(**)	.893(**)	.526(**)	.631(**)	.884(**)	NS	.474(**)
GluMan	.946(**)	.793(**)	.805(**)	.728(**)	.944(**)	.927(**)	.835(**)	.951(**)	.626(**)	.694(**)	.895(**)	.500(**)	.626(**)
Hemicell	.930(**)	.751(**)	.792(**)	.712(**)	.934(**)	.905(**)	.823(**)	.936(**)	.605(**)	.685(**)	.882(**)	.437(**)	.593(**)
Cellulose	.615(**)	.540(**)	.535(**)	.542(**)	.572(**)	.594(**)	.554(**)	.616(**)	.416(**)	.438(**)	.588(**)	NS	.344(*)

a) Expressed on the basis of the original amount of each component in untreated wood
b) For softwoods, realtive-to-control values used

In softwoods, all the constituents appear to be strongly correlated with most of the strength parameters except for the CA. Lignin has the largest correlation with most properties except for MOE, H and CE in pine and S for spruce, which favoured the hemicellulose fraction of the polysaccharides. Lignin has its largest correlation with WML in both softwoods, whilst hemicelluloses have their largest correlations with properties at maximum load (MOR, WML and SSML). Cellulose had its largest correlation with MOR in pine and with TW in spruce, although the largest correlations of cellulose are also for the properties at maximum load. In pine, cellulose content has the weakest correlation with only 9 parameters and no correlation with other 4 strength parameters. In spruce, cellulose generally shows the smallest correlation in 10 parameters and no correlation with CA.

In softwoods, highly significant correlations of chemical compounds with MOR, WML, and SSML indicate that most of the strength changes at maximum load could be explained by changes in the chemical composition of TMW. Conversely, other factors (microfibril angle, density) are probably involved in the description of properties with the lowest correlation with chemical constituents such as CA, CE, and H. Chemical changes account for an important part of change in properties at the limit of proportionally (RLP, R, SSLP), but other mechanisms are probably involved in changes in these properties, such as changes in the physical condition of the cell wall.

As the main constituents had comparable levels of correlation with each mechanical property in all the three species, this is perhaps an indication that the changes in wood polymers, mainly hemicelluloses and lignin, still had a proportional effect on the strength of treated wood as they do in untreated wood. In other words, if untreated wood were hypothetically found with the chemical make up of the treated wood, these two materials would probably show comparable levels of strength, at least in those properties where the behaviour is largely explained by chemical composition. The assumption that hemicellulose degradation is mainly responsible for the mechanical strength loss in bending is probably insufficient, because as it has been shown, the increase of lignin is also clearly involved in the reduction of all strength parameters except for CA in beech and pine[*]. As chemical constituents are strongly correlated between themselves and these appear to be significantly related to most changes in mechanical properties, deconvolution of the effect of each chemical constituent in property change is complex. Furthermore, the correlation of chemical

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[*] It should be cautioned that the increase in lignin and the close relationship of these changes with changes in several forms of mechanical strength of TMW may be merely circumstantial. The ultimate underlying factor of strength change is perhaps the net reduction of hemicellulose.

changes with WL, and the fact that lignin increases at the expense of hemicelluloses breakdown, makes the analysis still more difficult.

In beech, path analysis shows that the significant zero-order correlation between most of the mechanical properties and lignin (except for MOE and S) is due to the correlation of these two with hemicellulose: the partial correlation controlling for hemicelluloses is negligible and not statistically significant ($p > 0.05$) (Table 5.8). In turn, in softwoods, there remains an important pure contribution of lignin change in the reduction of all strength parameters but for H and S. On the other hand, the zero-order correlation between all mechanical properties and hemicelluloses in softwoods (except for CA) is due to the correlation of these two with lignin change, whilst in beech there is a significant pure effect of hemicellulose change in the reduction of MOR, WML, SSLP, SSML, H, and IS when the effect of lignin in property change is removed.

Table 5.8 Partial correlation of chemical constituents[a] and strength parameters after thermal modification (Significance: *, p<0.05; ** p< 0.01; *** p<0.001: NS, not significant).

Species	Control Variable	Variable	MOR	MOE	RLP	Ln R	Ln WML	Ln TW	SSLP	SSML	H	S	Ln IS	CA	CE
Beech	Hemicell.	Lignin	NS	-0.492*	NS	NS	NS	NS	NS	NS	NS	-0.702**	NS	NS	NS
Pine	Hemicell.	Lignin	-0.842***	NS	-0.495*	-0.530*	-0.816***	-0.612**	-0.592**	-0.852***	NS	NS	-0.669**	NS	NS
Spruce	Hemicell.	Lignin	-0.881***	-0.901***	NS	NS	-0.944***	-0.945***	NS	-0.869***	NS	NS	-0.819***	-0.753***	-0.573**
Softw.[b]	Hemicell.	Lignin	-0.814***	-0.652***	-0.420**	-0.361*	-0.889***	-0.780***	-0.423**	-0.793***	NS	NS	-0.757***	-0.628***	-0.384*
Beech	Lignin	Hemicell.	0.733***	NS	NS	NS	0.634***	NS	0.48*	0.793***	0.837***	NS	0.499*	NS	NS
Pine	Lignin	Hemicell.	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Spruce	Lignin	Hemicell.	0.487*	-0.667**	NS	NS	NS	NS	NS	0.644**	NS	0.601**	NS	-0.585**	NS
Softw.[b]	Lignin	Hemicell.	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	-0.468**	NS

[a] Expressed on the basis of the original amount of each component in untreated wood

[b] For softwoods, realtive-to-control values used

The correlation of property changes with monosaccharides (converted to individual oligosaccharides) did not give a clearer overview of the relationship of chemical changes and TMW strength (correlations not shown). In general, xylan had equivalent or slightly higher correlation coefficients than lignin with property change in beech, whereas in softwoods the opposite was found. In most cases, the correlation between both the individual oligosaccharides and lignin and strength parameters was high except for compression strength in all the three species, and for MOE in beech. However, path analysis showed that the pure effect of xylan in the reduction of mechanical properties when the effect of lignin is removed is only significant in hardness and strength properties at maximum load in bending (MOR, WML and SSML). In softwoods, the pure effect of xylan was significant only for MOE and CE. Similar results in both species were found for arabinan and mannan; no significant pure contributions were found for galactan or glucan. On the other hand, in softwoods there remains an important pure contribution of lignin change in the reduction of MOR, MOE, WML, TW, SSML, IS and CA when the effect of all 5 main individual sugars in property change is removed.

Cluster analysis also gives some evidence on the relationship between chemical conversion and strength changes. For instance, in both softwoods and beech, MOR is more intimately related to the amount of hemicelluloses and individual polysaccharides linked to these in the solid residue, particularly to GluXylan in beech, and in general to all hemicelluloses in softwoods, whereas MOE has more connection to cellulose and glucan and less so to lignin in both beech and softwoods (Figure 5.29).

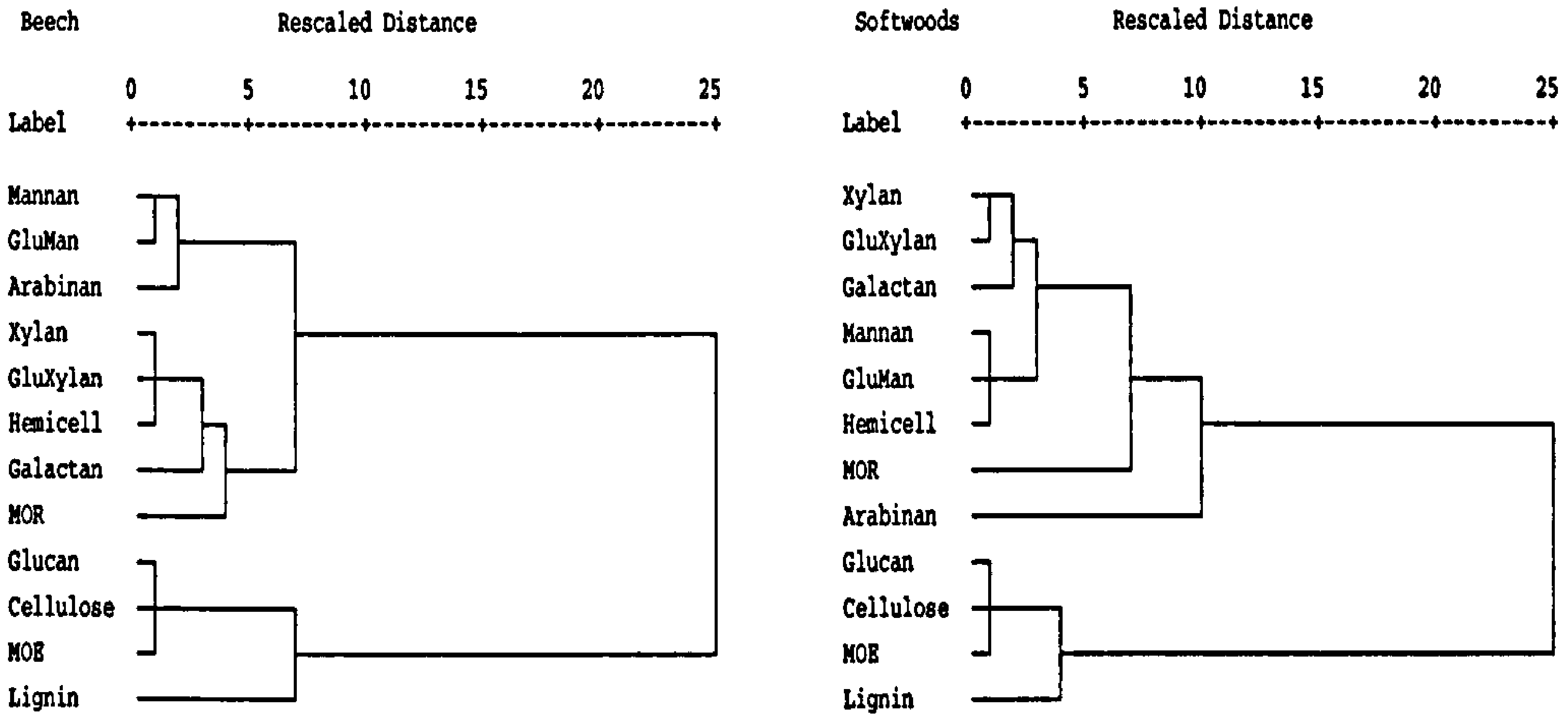


Figure 5.29 Dendrogram for the relationship between individual polysaccharides, hemicelluloses, cellulose and lignin and MOR and MOE in beech (left) and softwoods (right). Relative-to-control values used for the analysis. Method: Between-groups linkage; measure: Squared Euclidean distance.

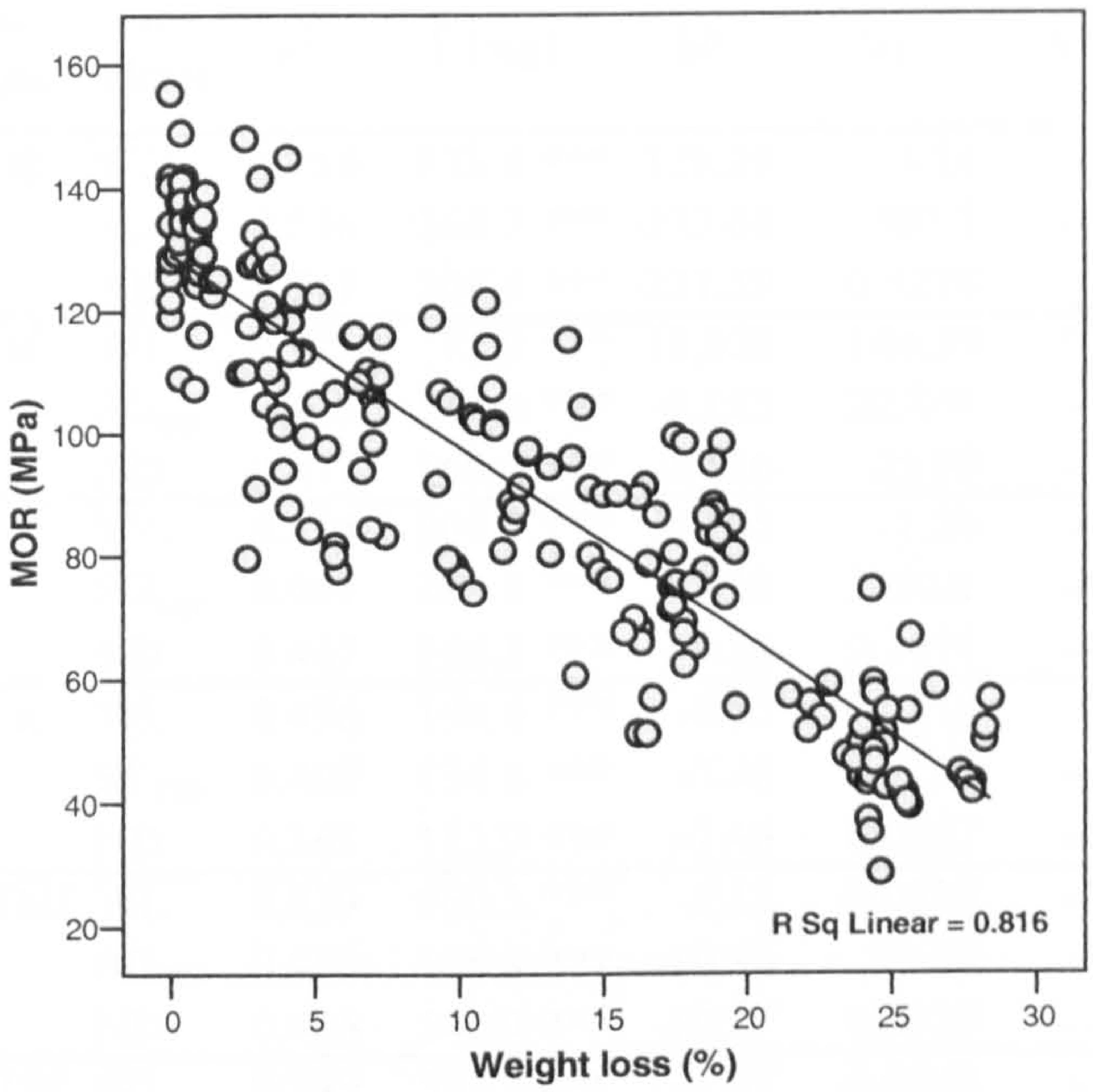
To sum up, the relationship between strength properties and chemical changes upon heating is not limited to changes in a single polymer, but it is the result of the concurrent changes in hemicellulose and lignin, and to a much lesser extent to the gravimetric modification of cellulose. The relationship with each chemical constituent is dissimilar depending upon the strength parameter in concern. The relationship between changes in mechanical properties and chemical changes differ between softwoods and beech probably because of their different initial composition. In beech, hemicelluloses showed high correlation with several properties even if the contribution of lignin was removed, whilst in softwoods this was not the case, probably because of their lower initial hemicellulose content. Cellulose showed little influence in strength changes in all three species, but this does not mean that cellulose has no bearing on the wood strength at early stages of property loss.

5.9 Modelling strength

5.9.1 From weight loss, specific gravity and nominal density

As is has been illustrated throughout the previous sections of this chapter, the reduction in weight due to the heat processing appears to be an useful descriptor of most of the changes in the mechanical properties examined. However, the simple task of measuring weight change in a hygroscopic material such as TMW is not easily accomplished industrially. This involves the determination of moisture content before and after the treatment (at the end of conditioning) in order to measure the actual change in mass. In modern wood drying operations, it is common practice using scales inside the kiln, in order to monitor the weight change due to the reduction of moisture, as well as automated devices for measuring the moisture content of wood at the beginning and end of the operation. In heat-treatment processing, it is plausible that this type of operations could be eventually adopted, and therefore the prediction of TMW properties from WL might have practical relevance.

As an example the nature of the relationship between gravimetric determinations on wood strength, Figure 5.30 represents the relationship of WL and ND with beech's MOR. Table 5.9 presents the results of the linear regression to estimate thirteen mechanical strength parameters using WL, SG_{OD} or ND as predictors.



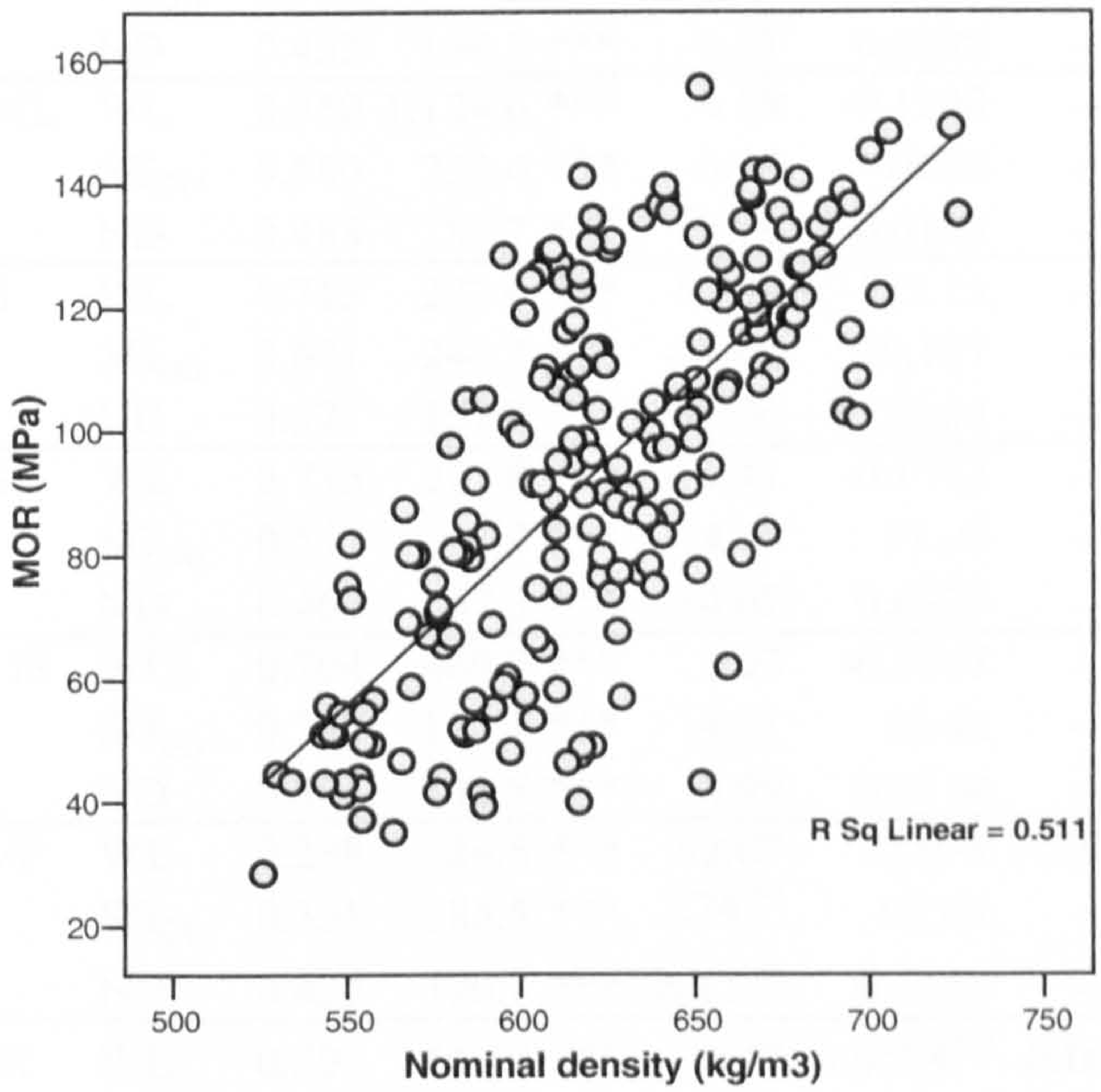


Figure 5.30. Fitted curves to represent the relationship between MOR (MPa) and WL (above) or ND (below). Data represents 20 treatments (19 modifications plus control), 10 replicates for each treatment.

Table 5.9 Linear regression analysis to estimate mechanical strength parameters of TMW using WL, ND or SG_{OD} as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$, NS = not significant).

Species	Res-ponse	Pre-dictor	R^2	F (sig)	b0	b1	b2	SE	n
Beech	MOR	WL	0.816	875.4 ***	129.29	-3.14	----	13.45	200
		SG_{OD}	0.576	268.7 ***	-233.68	507.3	----	20.40	200
		ND	0.511	206.8 ***	-231.59	0.5228	----	21.90	200
	MOE	WL	0.425	72.9 ***	11,928	144.39	-9.49	1,248	200
		SG_{OD}	0.423	144.9 ***	-3,123	22,804	----	1,248	200
		ND	0.457	166.3 ***	-4,536	25.93	----	1,211	200
	RLP	WL	0.514	209.3 ***	80.55	-1.26	----	11.06	200
		SG_{OD}	0.481	183.8 ***	-85.39	235.01	----	11.42	200
		ND	0.447	160.1 ***	-87.88	0.2478	----	11.80	200
	Ln R	WL	0.496	194.6 ***	-3.53	-0.0318	----	0.289	200
		SG_{OD}	0.405	134.8 ***	-7.46	5.54	----	0.314	200
		ND	0.365	113.9 ***	-7.46	0.0057	----	0.325	200
	Ln WML	WL	0.829	960.3 ***	-2.12	-0.0830	----	0.340	200
		SG_{OD}	0.488	188.5 ***	-10.98	12.26	----	0.589	200
		ND	0.416	140.9 ***	-10.77	0.0124	----	0.629	200
	Ln TW	WL	0.749	592.3 ***	-1.45	-0.0949	----	0.495	200
		SG_{OD}	0.414	139.9 ***	-11.29	13.58	----	0.756	200
		ND	0.367	114.7 ***	-11.22	0.0140	----	0.786	200
	SSLP	WL	0.627	333.3 ***	2.86	-0.0531	----	0.369	200
		SG_{OD}	0.503	200.5 ***	-3.66	9.16	----	0.426	200
		ND	0.453	164.3 ***	-3.67	0.0095	----	0.447	200
	SSML	WL	0.850	1,124.6 ***	4.58	-0.1208	----	0.457	200
		SG_{OD}	0.560	252.4 ***	-8.98	18.88	----	0.783	200
		ND	0.488	188.7 ***	-8.79	0.0193	----	0.845	200
	H	WL	0.713	292.6 ***	5,289	-137.15	----	637.8	120
		SG_{OD}	0.671	240.2 ***	-9,002	20,187	----	682.9	120
		ND	0.571	157.2 ***	-8,896	20.84	----	779.0	120
	S	WL	0.736	217.8 ***	11.41	-0.1702	----	0.837	80
		SG_{OD}	0.557	97.9 ***	-14.38	37.00	----	1.09	80
		ND	0.463	67.3 ***	-14.07	0.0379	----	1.19	80
	Ln IS	WL	0.704	469.9 ***	3.03	-0.0707	----	0.439	200
		SG_{OD}	0.383	123.1 ***	-4.61	10.46	----	0.633	200
		ND	0.344	103.8 ***	-4.99	0.0114	----	0.653	200
	CA	WL	0.238	24.6 ***	62.07	0.938	-0.0433	6.43	160
		SG_{OD}	0.351	85.5 ***	2.24^{NS}	93.47	----	5.92	160
		ND	0.432	120.1 ***	-6.12^{NS}	0.1106	----	5.54	160
	CE	WL	0.201	14.69 ***	8.37	-0.0694^{NS}	-0.0050	1.50	120
		SG_{OD}	0.554	146.7 ***	-9.06	26.44	----	1.11	120
		ND	0.602	178.3 ***	-10.66	0.0300	----	1.05	120

Units: MOR, MOE, RLP, SSLP, SSML, CA, CE, S = MPa. R, WML, TW = mm N mm^{-3}.

IS = kJ m^{-2}. H = N. WL (%), SG (unitless), ND (kg m^{-3})

The model is of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$

All coefficients significant at $p < 0.05$ unless otherwise indicated

Abbreviations as in Tables 5.1, 5.3 and 5.5

Continued over...

Table 5.9 Linear regression analysis to estimate mechanical strength parameters of TMW using WL, ND or SG_{OD} as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$, NS = not significant) (*Continued...*)

Species	Res-ponse	Pre-dictor	R^2	F (sig)	b0	b1	b2	SE	n
Pine	MOR	WL	0.830	1,018.7 ***	118.68	-3.62	----	9.96	210
		SG_{OD}	0.586	294.5 ***	-241.94	626.9	----	15.56	210
		ND	0.457	175.4 ***	-233.67	0.6375	----	17.82	210
	MOE	WL	0.477	94.4 ***	13,071	123.85	-12.89	1,003	210
		SG_{OD}	0.726	550.8 ***	-8,494	39,901	----	724	210
		ND	0.750	625.0 ***	-11,102	46.69	----	691	210
	RLP	WL	0.497	205.1 ***	75.40	-1.50	----	9.18	210
		SG_{OD}	0.525	229.8 ***	-104.75	317.29	----	8.92	210
		ND	0.476	188.6 ***	-113.35	0.3476	----	9.37	210
	Ln R	WL	0.491	200.3 ***	-3.73	-0.0416	----	0.258	210
		SG_{OD}	0.401	139.0 ***	-8.16	7.75	----	0.280	210
		ND	0.345	109.5 ***	-8.26	0.0083	----	0.293	210
	Ln WML	WL	0.831	1,021.4 ***	-2.40	-0.1029	----	0.282	210
		SG_{OD}	0.496	204.9 ***	-11.87	16.37	----	0.487	210
		ND	0.371	122.6 ***	-11.47	0.0163	----	0.544	210
	Ln TW	WL	0.793	795.0 ***	-1.58	-0.1208	----	0.376	210
		SG_{OD}	0.593	303.1 ***	-13.94	21.51	----	0.526	210
		ND	0.488	198.5 ***	-13.96	0.0225	----	0.590	210
	SSLP	WL	0.573	278.6 ***	2.61	-0.0585	----	0.307	210
		SG_{OD}	0.544	248.3 ***	-4.07	11.73	----	0.317	210
		ND	0.475	187.9 ***	-4.27	0.0126	----	0.341	210
	SSML	WL	0.850	1,175.9 ***	4.11	-0.1331	----	0.341	210
		SG_{OD}	0.575	281.2 ***	-8.89	22.55	----	0.573	210
		ND	0.438	162.3 ***	-8.45	0.0227	----	0.658	210
	H	WL	0.146	21.1 ***	1,775	-20.34	----	239.6	126
		SG_{OD}	0.563	159.6 ***	-1,562	7,972	----	171.4	126
		ND	0.590	178.7 ***	-1,840	8.97	----	165.9	126
	S	WL	0.208	21.6 ***	6.11	-0.0699	----	0.782	84
		SG_{OD}	0.404	55.7 ***	-6.97	31.41	----	0.678	84
		ND	0.503	83.2 ***	-9.15	0.0383	----	0.619	84
	Ln IS	WL	0.797	818.7 ***	3.25	-0.0877	----	0.288	210
		SG_{OD}	0.503	210.6 ***	-4.00	12.52	----	0.452	210
		ND	0.426	154.1 ***	-4.18	0.0134	----	0.486	210
	CA	WL	0.425	60.9 ***	40.94	0.691	-0.0394	3.75	168
		SG_{OD}	0.445	133.2 ***	-2.36^{NS}	108.51	----	3.67	168
		ND	0.484	155.7 ***	-4.71^{NS}	0.1179	----	3.54	168
	CE	WL	0.162	11.3 ***	4.40	0.0701	-0.0041	0.735	120
		SG_{OD}	0.429	88.5 ***	-3.42	18.93	----	0.604	120
		ND	0.495	115.9 ***	-4.61	0.0225	----	0.568	120

Continued over...

Table 5.9 Linear regression analysis to estimate mechanical strength parameters of TMW using WL, ND or SG_{OD} as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$, NS = not significant) (*Concluded*)

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	n
Spruce	MOR	WL	0.887	1,634.7 ***	84.81	-2.53	----	5.95	210
		SG_{OD}	0.568	273.0 ***	-161.76	606.7	----	11.65	210
		ND	0.496	204.7 ***	-170.63	0.6575	----	12.58	210
	MOE	WL	0.626	173.5 ***	9729	33.08^{NS}	-6.77	687	210
		SG_{OD}	0.606	320.1 ***	-5,595	39,689	----	704	210
		ND	0.611	327.1 ***	-7,324	46.21	----	699	210
	RLP	WL	0.583	291.4 ***	45.93	-1.14	----	6.33	210
		SG_{OD}	0.364	118.9 ***	-63.40	268.73	----	7.82	210
		ND	0.326	100.6 ***	-68.66	0.2949	----	8.05	210
	Ln R	WL	0.529	234.0 ***	-4.40	-0.0563	----	0.350	210
		SG_{OD}	0.254	70.9 ***	-9.21	11.68	----	0.440	210
		ND	0.219	58.5 ***	-9.35	0.0126	----	0.450	210
	Ln WML	WL	0.926	2,591.2 ***	-2.59	-0.1136	----	0.212	210
		SG_{OD}	0.476	189.2 ***	-12.60	24.40	----	0.563	210
		ND	0.394	135.4 ***	-12.70	0.0257	----	0.605	210
	Ln TW	WL	0.899	1,846.8 ***	-2.08	-0.1196	----	0.264	210
		SG_{OD}	0.466	181.2 ***	-12.65	25.78	----	0.607	210
		ND	0.390	133.0 ***	-12.81	0.0274	----	0.649	210
	SSLP	WL	0.630	354.6 ***	1.61	-0.0429	----	0.216	210
		SG_{OD}	0.383	129.1 ***	-2.47	10.02	----	0.280	210
		ND	0.336	105.2 ***	-2.63	0.0109	----	0.290	210
	SSML	WL	0.906	2,009.5 ***	2.96	-0.0928	----	0.197	210
		SG_{OD}	0.570	276.0 ***	-6.01	22.04	----	0.421	210
		ND	0.491	200.5 ***	-6.26	0.0237	----	0.458	210
	H	WL	0.171	25.6 ***	1,740	-21.18	----	211.6	126
		SG_{OD}	0.410	86.1 ***	-898	6,073	----	178.5	126
		ND	0.396	81.2 ***	-1,069	6.79	----	180.7	126
	S	WL	0.686	178.9 ***	7.03	-0.1058	----	0.380	84
		SG_{OD}	0.539	95.7 ***	-2.15	19.81	----	0.460	84
		ND	0.433	62.7 ***	-2.05^{NS}	0.0205	----	0.510	84
	Ln IS	WL	0.851	1,187.1 ***	3.16	-0.1065	----	0.331	210
		SG_{OD}	0.657	399.1 ***	-7.57	26.20	----	0.502	210
		ND	0.520	225.1 ***	-6.96	0.0260	----	0.594	210
	CA	WL	0.660	160.2 ***	38.66	0.748	-0.0410	2.86	168
		SG_{OD}	0.392	106.9 ***	-5.60^{NS}	121.16	----	3.82	168
		ND	0.431	125.7 ***	-10.46	0.1393	----	3.69	168
	CE	WL	0.341	31.78 ***	4.72	0.0019^{NS}	-0.0021	0.604	126
		SG_{OD}	0.467	108.6 ***	-2.04	17.47	----	0.541	126
		ND	0.570	164.2 ***	-2.93	0.0207	----	0.486	126

Regression models in Table 5.9 consider the data for all the temperatures together in the same model. An examination of Table 5.9 shows that the WL is the best predictor for all the properties in beech but for CA, CE and MOE, where ND was better, although WL was almost as good predictor of MOE as was ND. In softwoods, WL was also the best predictor for most strength parameters. In pine, MOE, H, S, CA and CE were best predicted by ND, whilst RLP was better estimated by SG_{OD}, although WL was almost as good as SG_{OD} or ND for predicting RLP and CA. In spruce, all but H and CE were predicted best by WL. In beech, coefficients of determination (R^2) for the best predictor ranged from 0.850 for SSML to 0.432 for CA, whereas in Scots pine this varied from 0.850 for SSML, to 0.484 for CA, and R^2 in spruce went from 0.906 for SSML to 0.410 for H; all models were highly significant.

It is well established that MOE, CA, CE and H are highly dependent on wood density (Dinwoodie 2000) and from this the higher R^2 for these parameters for ND compared to WL. The fact that CE and CA were better predicted by ND than by WL concords with the findings of the correlation analysis (Tables 5.7 and 5.8), where these strength parameters were only weakly or not significantly correlated to chemical changes; WL is closely related to chemical changes.

Although wood density or specific gravity are able to explain large part of the variation of mechanical properties in untreated wood, these serve only as a relative measure of wood cell wall materials per unit volume. These gravimetric characteristics are unable to reflect some wood anatomical features (*e.g.* microfibril angle, fibre morphology) and chemical composition. Changes in the latter are, however, closely related to the variation in the mechanical properties of TMW. ND or SG_{OD} are not as markedly modified as WL (chapter 4), because the reduction in mass is accompanied by a reduction in transversal dimensions. Therefore, the strength response of TMW sometimes cannot be entirely explained in terms of the modified wood density, and WL becomes a better predictor of strength because this reflects both the chemical changes and the reduction of density in the treated material. Properties that were more related to WL probably reflect the significance of chemical changes for property change. The variation not explained by the models for most of the parameters may reflect the relevance of other changes undergone in the material (*e.g.* moisture content), or other factors not measured in the present study, probably physical changes in the cell wall.

Information on modelling the mechanical strength of TMW from changes in WL, SG or ND is scant. Although the thermal degradation of wood is conveniently measured by its declining weight, very few examples exist regarding the prediction of mechanical properties from WL. Most models in the public domain relate the changes in wood properties as a function of temperature and time of treatment (*e.g.* Mitchell 1988, Kubojima *et al.* 2000), but this approach is arguably not as good as the one using WL as predictor, by virtue that the effect of time and temperature of exposure will vary according to the size of the specimen, species concerned and atmosphere of treatment.

In one example of the relationship between WL and mechanical changes, Seborg *et al.* (1953) pictured a relationship between relative-to-control toughness and WL for ponderosa pine sapwood heat-treated at 300 °C. For WL (in %) up to about 20%, the relationship was rectilinear with a slope of about -3.50, irrespective of the heating media. This contrasts with the results in this work, where the relationship between IS or WML was curvilinear at early stages of WL. However, if a regression analysis is run for the relative-to-control values of IS *vs.* WL using the data of the two softwoods species together, gives a regression line with a slope of -3.22; the R^2 is however much lower (0.626) than the one for the regression of Ln (relative-to-control IS) on WL ($R^2 = 0.820$).

Also in early research, Stamm (1956) compared WML and MOR of coniferous woods at equivalent levels of WL, and concludes that the rate of loss of MOR is some ten times that of WL, with the rate of loss of WML being still greater. Later, Rusche (1973) depicted diagram-wise the helpful relationship of WL with MOR, MOE and CA, but no models were given. More recently, Mouras *et al.* (2002) found that ND was a good predictor of CA of heat-treated wood when the data of both species studied (poplar and Curupixa) were considered together ($R^2 = 0.84$). Repellin and Guyonnet (2003) studied the relationship of MOR with WL for small specimens of beech wood modified by the Retification® process, and they concluded that the dry weight loss seem to be suitable to characterise modified wood when the time parameter remained fixed. They conjectured that the relationship may not be suitable for other wood species, particularly those with high extractive content or when the process have stages with variable duration; no models or statistics were given, though.

In large-sized specimens of heat-treated Norway spruce and Scots pine woods, the oven-dry density is a good predictor of MOE (R^2 = 0.64 and 0.71 respectively) and a fair predictor of MOR (R^2 = 0.18 and 0.36) (Bengtsson *et al.* 2002). The coefficients of determination for MOE are very similar to the ones found for SG_{OD} in the present work, but the ones found for MOR are evidently smaller than the ones in this study. This is not unexpected, because MOR is more affected by wood defects than is MOE in large-sized specimens.

Stepwise multiple linear regression using WL and ND as possible predictors of the mechanical properties showed that the addition of a further predictor to the already significant one improved significantly the coefficient of determination in most strength parameters. For instance, the addition of ND as a predictor for MOR added 4.6%, 3.8% and 3.6% for beech, pine and spruce respectively, to the coefficient of determination already produced by WL (81.6%, 83.0% and 88.7% in the same order). However, the addition of another factor made it more difficult to interpret the model in physical terms, and the statistics show that there are moderate to severe problems of collinearity between the two variables (last eigenvalue ≈ 0 and Condition index > 30 in all cases where both WL and ND entered in the model); the use of two variables as predictors of any particular strength parameters is therefore not warranted, because small changes in the data values may lead to large changes in the estimates of the coefficients.

The regression models described in this section are only useful for wood specimens with low extractive contents. If heartwood were included in the analysis, the coefficients of determination would have probably decreased, because the relatively higher content of extractives would account for significant reductions in mass upon treatment without the corresponding change in mechanical property. However, it is also likely that the predictions would be poor at low treatment levels, but better at higher levels of modification, because at the latter stage extractives would have already volatised.

5.9.2 From changes in chemical composition

The results of the regression analyses of mechanical strength parameters on chemical constituents are summarized for beech (ND of untreated specimens between 612.8 kg·m^{-3} and 663.7 kg·m^{-3}) and softwoods (ND of untreated specimens between 362.7 kg·m^{-3} and 522.4 kg·m^{-3}) in Table 5.10. Average values per treatment were used for each parameter, because the chemical analyses were performed only once (from samples for the bending test, see chapter 3. Methods). GluXylan and cellulose values for treatment 20 in Norway spruce (T = 245 °C, t = 16 h) were excluded from the analyses because these single, very extreme values makes the relationships too curved and not suitable for parametric analysis. GluMan for treatment 11 in beech (T = 230 °C, t = 0.3 h) was also excluded for inconsistency. For pine, mean CA for treatment 19 (T = 245 °C, t = 8 h) was not considered either in the regression analysis for inconsistency. Models were obtained using relative-to-untreated values (in proportion) of strength properties and chemical composition[†].

As an example the nature of the relationship borne by mechanical strength parameters and GluXylan, GluMan, hemicelluloses, cellulose and lignin, Figure 5.31 displays the relationship of these 5 constituents to softwoods MOR.

[†] Data of chemical composition on a w/w basis with respect of the initial oven-dry weight of the sample.

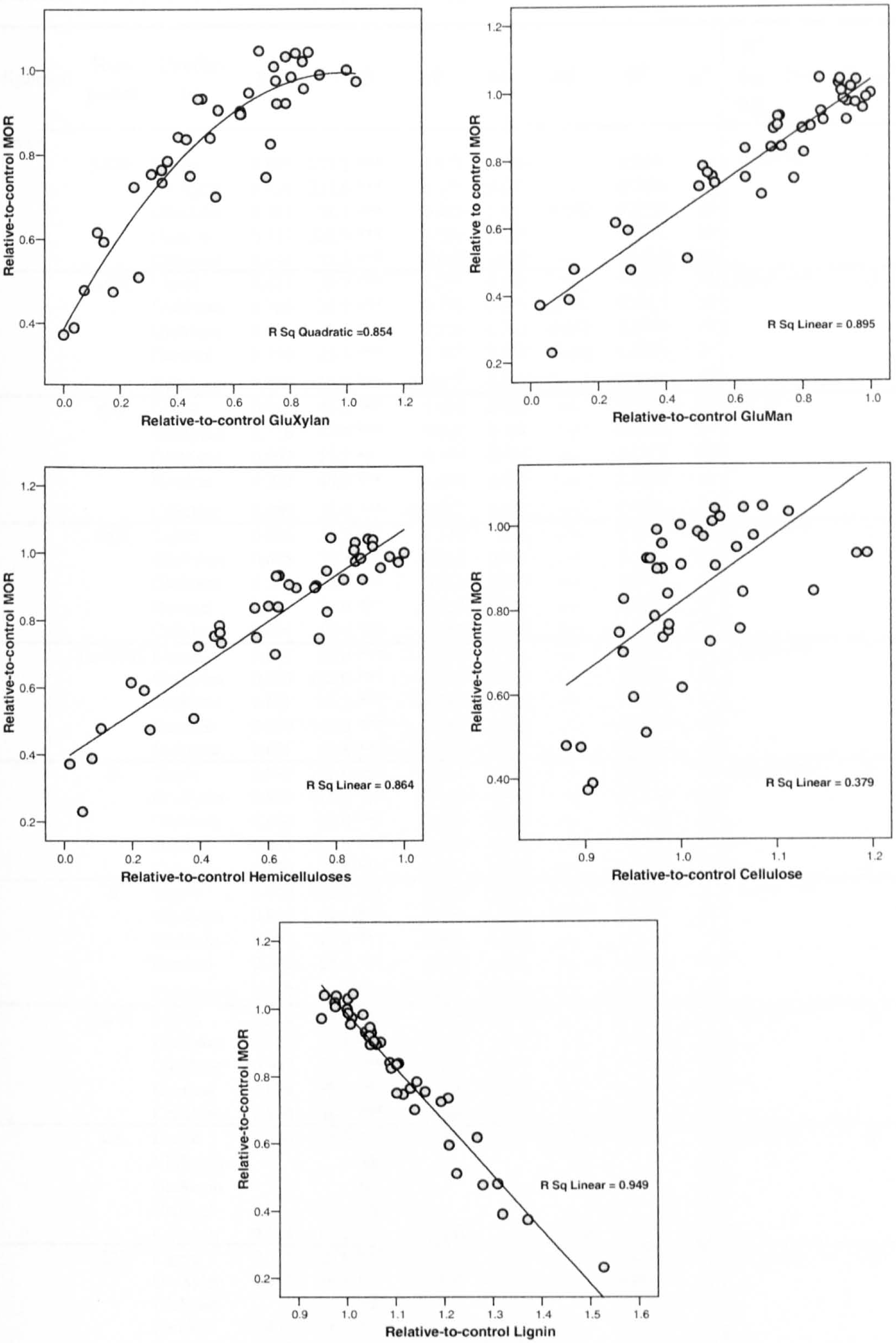


Figure 5.31 Fitted lines to represent the relationship of relative-to-control values of MOR (in proportion) of thermally modified softwoods using relative-to-control content (in proportion) of GluXylan, GluMan, cellulose, hemicelluloses or lignin as predictors

Table 5.10 Linear regression analysis to estimate mechanical strength parameters of TMW using chemical constituents as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$, NS = not significant).

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	$n^{a)}$	R^2 for WL	(sig)	$Type^{b)}$
Beech												
	MOR	Lignin	0.865	115.2 ***	1.972	-1.080	—	0.0841	20	0.960	***	L
		GluXylan	0.930	237.8 ***	0.375	0.627	—	0.0607	20			
		GluMann	0.781	28.5 ***	0.445	1.453	-0.942	0.1127	19			
		Hemicel	0.927	228.9 ***	0.386	0.669	—	0.0618	20			
		Cellulose	0.644	32.5 ***	-0.940	1.629	—	0.1365	20			
	MOE	Lignin	0.631	30.7 ***	1.211	-0.166	—	0.0618	20	0.844	***	Q
		GluXylan	0.760	26.9 ***	0.774	0.857	-0.640	0.0513	20			
		GluMann	0.517	8.5 **	0.876	0.717	-0.643	0.0749	19			
		Hemicel	0.750	25.5 ***	0.787	0.848	-0.662	0.0524	20			
		Cellulose	0.640	32.0 ***	0.246^{NS}	0.723	—	0.0611	20			
	RLP	Lignin	0.717	45.6 ***	1.660	-0.722	—	0.0893	20	0.755	***	L
		GluXylan	0.716	45.4 ***	0.601	0.404	—	0.0894	20			
		GluMann	0.507	17.5 **	0.698	0.426	—	0.1213	19			
		Hemicel	0.722	46.8 ***	0.607	0.433	—	0.0885	20			
		Cellulose	0.565	23.4 ***	-0.318^{NS}	1.121	—	0.1107	20			
	Ln R	Lignin	0.655	34.2 ***	1.170	-1.428	—	0.2039	20	0.703	***	L
		GluXylan	0.675	37.3 ***	-0.932	0.811	—	0.1981	20			
		GluMann	0.527	18.9 ***	-0.749	0.898	—	0.2460	19			
		Hemicel	0.689	39.9 **	-0.923	0.876	—	0.1937	20			
		Cellulose	0.491	17.4 ***	-2.687	2.161	—	0.2478	20			
	Ln WML	Lignin	0.836	92.0 ***	3.251	-3.754	—	0.3271	20	0.929	***	L
		GluXylan	0.885	138.0 ***	-2.292	2.163	—	0.2747	20			
		GluMann	0.661	33.2 ***	-1.805	2.330	—	0.4818	19			
		Hemicel	0.890	146.2 ***	-2.260	2.318	—	0.2677	20			
		Cellulose	0.631	30.8 ***	-6.915	5.704	—	0.4910	20			
	H	Lignin	0.849	101.0 ***	1.835	-0.923	—	0.0767	20	0.940	***	L
		GluXylan	0.959	419.3 ***	0.463	0.549	—	0.0400	20			
		GluMann	0.660	33.0 ***	0.593	0.566	—	0.1175	19			
		Hemicel	0.953	361.6 ***	0.473	0.585	—	0.0430	20			
		Cellulose	0.570	23.8 ***	-0.583	1.322	—	0.1295	20			L
	S	Lignin	0.870	120.3 ***	1.820	-0.731	—	0.0557	20	0.855	***	
		GluXylan	0.864	54.1 ***	0.680	0.927	-0.529	0.0585	20			
		GluMann	0.393	11.0 **	0.863	0.333	—	0.1195	19			
		Hemicel	0.743	52.1 ***	0.770	0.404	—	0.0782	20			
		Cellulose	0.817	80.3 ***	-0.290^{NS}	1.238	—	0.0661	20			
	Ln IS	Lignin	0.810	76.6 ***	2.742	-3.455	—	0.3300	20	0.875	***	L
		GluXylan	0.830	87.8 ***	-2.343	1.959	—	0.3119	20			
		GluMann	0.651	31.7 ***	-1.919	2.154	—	0.4555	19			
		Hemicel	0.838	93.0 ***	-2.315	2.103	—	0.3045	20			
		Cellulose	0.610	28.1 ***	-6.606	5.242	—	0.4726	20			
	CA	Lignin	0.246	5.9 *	1.246	—	-0.094	0.0799	20	0.456	**	Q
		GluXylan		NS					20			
		GluMann		NS					19			
		Hemicel		NS					20			
		Cellulose	0.364	10.3 **	0.849	—	0.256	0.0734	20			
	CE	Lignin	0.533	20.6 ***	1.636	-0.506	—	0.0932	20	0.564	**	Q
		GluXylan	0.477	16.4 **	0.901	0.268	—	0.0987	20			
		GluMann		NS					19			
		Hemicel	0.439	14.1 **	0.911	0.275	—	0.1022	20			
		Cellulose	0.479	16.5 **	0.196	0.838	—	0.0985	20			

The models from chemical constituent are of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$

a) Each element in n is the mean value of 4 to 10 replicates

b) Model type: L = linear, Q = quadratic

Abbreviations as in Tables 5.1, 5.3 and 5.5

Continued over...

Table 5.10 Linear regression analysis to estimate mechanical strength parameters of TMW using chemical constituents as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$) (*Concluded*)

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	n[a)]	R^2 for WL	(sig)	Type[b)]
Softwoods												
	MOR	Lignin	0.949	748.0 ***	2.587	-1.601	----	0.0470	42	0.943	***	L
		GluXylan	0.854	111.1 ***	0.38626	1.234	-0.628	0.0732	41			
		GluMann	0.895	342.3 ***	0.341	0.698	----	0.0675	42			
		Hemicel	0.864	254.5 ***	0.388	0.681	----	0.0770	42			
		Cellulose	0.379	23.8 ***	-0.803	1.620	----	0.1490	41			
	MOE	Lignin	0.853	112.9 ***	-0.459^{NS}	-1.526	3.022	0.0347	42	0.905	***	Q
		GluXylan	0.800	76.1 ***	0.817	0.684	-0.503	0.0313	41			
		GluMann	0.823	90.4 ***	0.713	0.818	-0.512	0.0381	42			
		Hemicel	0.815	85.7 ***	0.731	0.848	-0.572	0.0390	42			
		Cellulose	0.551	23.4 ***	-4.736	10.680	-4.924	0.0469	41			
	RLP	Lignin	0.692	90.0 ***	2.292	-1.241	----	0.1051	42	0.702	***	L
		GluXylan	0.548	47.3 ***	0.683	0.448	----	0.1164	41			
		GluMann	0.648	73.8 ***	0.553	0.539	----	0.1123	42			
		Hemicel	0.627	67.4 ***	0.589	0.526	----	0.1156	42			
		Cellulose	0.287	15.7 ***	-0.370^{NS}	1.292	----	0.1463	41			
	Ln R	Lignin	0.572	53.5 ***	2.360	-2.358	----	0.2590	42	0.614	***	L
		GluXylan	0.425	28.8 ***	-0.670	0.809	----	0.2696	41			
		GluMann	0.530	45.0 ***	-0.940	1.017	----	0.2716	42			
		Hemicel	0.507	41.1 ***	-0.868	0.989	----	0.2782	42			
		Cellulose	0.294	16.2 ***	-2.924	2.683	----	0.2988	41			
	Ln WML	Lignin	0.970	1,300 ***	5.313	-5.495	----	0.1225	42	0.948	***	L
		GluXylan	0.874	132.4 ***	-2.114	3.629	-1.592	0.2230	41			
		GluMann	0.892	329.5 ***	-2.372	2.363	----	0.2332	42			
		Hemicel	0.873	274.8 ***	-2.222	2.323	----	0.2527	42			
		Cellulose	0.327	19.0 ***	-5.701	4.951	----	0.5097	41			
	H	Lignin	0.370	23.5 ***	1.384	-0.411	----	0.0681	42	0.429	***	L
		GluXylan	0.276	14.9 ***	0.850	0.150	----	0.0697	41			
		GluMann	0.392	25.8 ***	0.801	0.189	----	0.0669	42			
		Hemicel	0.367	23.1 ***	0.815	0.182	----	0.0683	42			
		Cellulose	0.173	8.2 **	0.455	0.475	----	0.0745	41			L
	S	Lignin	0.464	34.6 ***	1.429	-0.510	----	0.0696	42	0.507	***	
		GluXylan	0.398	25.8 ***	0.755	0.204	----	0.0717	41			
		GluMann	0.482	37.2 ***	0.706	0.233	----	0.0684	42			
		Hemicel	0.469	35.3 ***	0.721	0.228	----	0.0693	42			
		Cellulose	0.192	9.3 **	0.301^{NS}	0.564	----	0.0831	41			
	Ln IS	Lignin	0.904	375.4 ***	5.124	-5.424	----	0.2250	42	0.903	***	L
		GluXylan	0.781	139.3 ***	-1.815	1.808	----	0.2738	41			
		GluMann	0.801	160.7 ***	-2.432	2.290	----	0.3237	42			
		Hemicel	0.777	139.5 ***	-2.282	2.242	----	0.3422	42			
		Cellulose	0.346	20.6 ***	-5.641	4.794	----	0.4737	41			
	CA	Lignin	0.795	73.9 ***	-2.170	5.937	-2.693	0.0419	41	0.819	***	Q
		GluXylan		NS					40			
		GluMann	0.575	25.7 ***	0.787	0.946	-0.689	0.0604	41			
		Hemicel	0.578	26.1 ***	0.809	0.957	-0.743	0.0602	41			
		Cellulose		NS					40			
	CE	Lignin	0.434	30.6 ***	1.711	-0.596	----	0.0865	42	0.575	***	Q
		GluXylan	0.405	12.9 ***	0.871	0.704	-0.521	0.0775	41			
		GluMann	0.392	25.8 ***	0.879	0.254	----	0.0896	42			
		Hemicel	0.351	21.7 ***	0.902	0.239	----	0.0926	42			
		Cellulose	0.118	5.2 *	0.582	0.476	----	0.0932	41			

The models from chemical constituent are of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$

a) Each element in n is the mean value of 4 to 10 replicates

b) Model type: L = linear, Q = quadratic

Abbreviations as in Tables 5.1, 5.3 and 5.5

Table 5.10 shows that most of the relationships between chemical constituents and strength parameters where of a rectilinear nature, and the best models were linear, except for MOE and CA which were best described by a curvilinear (parabolic) trajectory. The coefficient of regression (b1) presented in Table 5.10 shows that all mechanical strength properties decrease with the decrease in GluXylan, GluMan, hemicellulose or cellulose content, and reduce with increase in lignin content, although the relationship with the polysaccharide constituents and some forms of strength was parabolic, so the direct relationship between these reaches a maximum and then decreases. When the relationship is linear, the coefficient of regression b1 gives the rate of change of the mechanical property to the correspondent change in the chemical component. For instance, in softwoods, the increase in 1.00% in lignin will result in a decrease of 1.6% in MOR, 1.24% in RLP, 0.60% in CE and so on. Therefore, having established the strength properties and chemical composition of other untested species, many of them published (for this work given in chapters 4 and 5), and obtaining the after-treatment content of the chemical constituent of interest, it is possible to make predictions using the models in Table 5.10[‡].

In beech, all best models except in CA (R^2 of best model = 0.364) were highly significant and, apart from CA, very good estimation statistics for all other mechanical parameters were obtained using simple linear regression. The coefficient of determination (R^2) ranged from 0.959 for H, followed by MOR ($R^2 = 0.930$), to 0.533 for CE. GluXylan was the best predictor for three strength properties, and when it was not the best predictor it was the second best, generally to hemicelluloses. This probably indicates the close relationship between changes in GluXylan and changes in most properties, except for compression strength, where the GluXylan model was the third best predictor for CE; the model for CA using GluXylan was also not significant. Lignin generally ranked as the third best predictor after GluXylan and hemicelluloses, except in CA (second best) and CE and S, where it was the best. GluMan had lower prediction ability than hemicelluloses GluXylan and lignin in all cases and in compression strengths has no prediction power. Cellulose generally ranked as the less effective predictor for most mechanical strength

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[‡] For instance: Total lignin content in radiata pine = 26.8% (Fengel and Wegener 1984). MOR of radiata pine at 12% moisture content = 85.0 MPa (Lavers 1983). If radiata pine were hypothetically treated to a lignin content of 30% (based on the original dry weight of the sample), MOR in that specimen would be = $[-1.601 \times (30/26.8) + 2.587] \times 85.0 = 67.6$ MPa.

parameters, except for CA and CE, where it was the best and second best predictor respectively.

The fact that GluXylan is better predictor than GluMan probably reflects the initial chemical composition of beech. Hemicellulose is the largest polysaccharide component apart from cellulose (not significantly reduced below WL > 20%), the second largest is GluXylan, and the least abundant is GluMan, so if hypothetically both hemicelluloses were labile to the same degree, the effect of the thermal treatment would be more prominent and easily and accurately detectable in GluXylan because of their proportionally higher content in beech wood. This in turn may result in a stronger link between the changes in strength parameters to changes in GluXylan. Another, more plausible explanation is that GluMan showed a larger scatter of the data against WL (if WL is considered as a measure of the extent of the treatment), and their relationship was not rectilinear (see Figures 4.1, chapter 4). Likewise the relationship between lignin or cellulose and WL was not rectilinear, and this may influence the fitting ability of these polymers for mechanical properties, in virtue that most of the mechanical strength parameters have a rectilinear relationship with WL (Table 5.9). The relationship between hemicellulose change and WL in beech wood is rectilinear, and the coefficient of determination of the regression of hemicelluloses on WL is very similar ($R^2 = 0.963$) to the one for GluXylan ($R^2 = 0.976$)[§]; consequently GluXylan and hemicelluloses had the best predictive ability for most mechanical parameters.

The multiple stepwise regression using all five chemical components (Lignin, Hemicel, Cell, GluXylan and GluMan) as possible predictors of strength in beech, showed that cellulose added 2.7% to the highly significant coefficient of determination ($R^2 = 89\%$) of Ln WML already produced by hemicellulose. Thus Ln WML can be more significantly predicted by using the equation $\text{LnWML} = -3.853 + 1.890 \cdot \text{hemicellulose} + 1.792 \cdot \text{cellulose}$ ($R^2 = 0.917$, $F = 88.31$, $S = 0.2459$). In all other strength parameters, no additional predictor was incorporated into the model.

In softwoods, all best models were highly significant and, apart from H (R^2 of the best model = 0.392), very good estimation statistics for all other mechanical parameters were obtained using simple linear regression. The coefficient of determination (R^2) ranged from 0.970 for Ln WML, followed by MOR ($R^2 = 0.949$),

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[§] This coefficients of determination are for the relationship between chemical components and WL in the plot of Figure 4.1, chapter 4.

to 0.434 for CE. Lignin was the best predictor in 8 out of 10 mechanical parameters, and second best in one. GluMan was the second best predictor, with best models for 2 properties and second best in other 6 parameters. Hemicelluloses generally ranked third in their prediction capability after lignin and GluMan. GluXylan had lower prediction ability than lignin in all cases, and lower prediction ability than GluMan and hemicelluloses but in CE and Ln IS where it was the second and third best predictor respectively; GluXylan had no prediction power for CA. Cellulose had the lowest prediction capability for all strength properties, and in CA its model was not significant. Then again, the largest importance of lignin and GluMan over GluXylan is probably a reflection of the initial chemical composition of softwoods, where GluMan is the largest component in hemicelluloses. As lignin is generally the best predictor and the fact that cellulose is little and not rectilinearly changed (*vs.* WL, Figures 4.2 and 4.3 chapter 4) suggest that the initial chemical composition plays an important role in the prediction ability of the chemical constituents, as does the pattern and magnitude of change of the polymers with respect to WL.

The model for MOR in softwoods using multiple stepwise regression was only marginally improved by including cellulose into the model, which added 0.4% to the already highly significant model using lignin as predictor ($R^2 = 94.9\%$). Thus MOR can be more significantly predicted by using the equation $MOR = 2.267 - 1.579 \cdot \text{lignin} + 0.291 \cdot \text{cellulose}$ ($R^2 = 0.953$, $F = 387.61$, $S = 0.0414$). In other three strength properties (MOE, Ln R and CA), another predictor was significantly incorporated into the models, but the resultant model was less effective than the parabolic model for the estimation the strength property. In the remaining six strength parameters, no additional predictor was included into the model.

Principal component regression (PCR) using all the 5 chemical constituents (Lignin, Hemicelluloses, GluXylan, GluMan and Cellulose) reduced the data to only one dimension in both beech and softwoods. In beech PCR improved marginally the prediction of MOR ($R^2 = 0.941$), RLP ($R^2 = 0.779$), R ($R^2 = 0.733$), WML ($R^2 = 0.916$), and Ln IS ($R^2 = 0.872$); in softwoods, no prediction was improved by using PCR. Notably, PCR scores had the largest Pearson correlation with WL than to any strength property ($r = -0.995$ in beech, $r = -0.983$ in softwoods), and therefore the single component extracted is very likely exposing the underlying association between chemical changes and WL. Hence WL is probably a better predictor of mechanical strength than any individual chemical constituent. An analysis of WL as predictor for strength properties using the relative-to-control average values per treatment (Table 5.10)[**] reveals that effectively WL is the best descriptor for all mechanical properties but for H and S in beech, and MOR, Ln WML and Ln IS in softwoods, where it has comparable R^2 statistics to the ones produced by chemical constituents.

As it was pointed out at the beginning of section 5.8, no report exists on the modelling of mechanical strength from changes in chemical composition in TMW, but for the report of Davis and Thompson (1964) on their study of toughness resistance of heat-treated (in air or steam) longleaf pine, Douglas-fir and southern red oak woods. Using their relative-to-control data for air-treated specimens ($n = 7$), toughness in oak could be significantly predicted by using Ln Toughness = -1.425 + 1.341 × hemicelluloses ($R^2 = 0.904$, $F = 47.3$, $SE = 0.077$). The rate of change of toughness is smaller compared to the one of Ln IS calculated in this work for beech ($b1 = 2.103$), although contrarily to this work, the maximum temperature of treatment used by Davies and Thompson (1964) was 200 °C, only relatively short times of treatment were used (20 and 60 minutes) and the equipment for the mechanical test (the Forest Products Laboratory's toughness-testing machine) was different to the one used in this work.

Although strictly not comparable, from Table 5.9 and Table 5.10, it is evident that ND is a better predictor than any chemical constituent of CA and CE in beech, and probably better predictor of CE in softwoods. This was not unexpected, because in untreated wood, compression strength is typically closely related with density: For instance, for 117 Malaysian timbers, Ong (1988) found that $CA = -5.42 + 75.69\ ND$ ($R^2 = 0.87$). Working with 11 clones of *Eucalyptus* sp. wood, Lima (1999) also established that ND was better predictor of CA than four anatomical characteristics, grain angle and microfibril angle, and found that CA could be significantly predicted by $CA = 16.6 + 68.6\ ND$ ($R^2 = 0.502$).

In chapter 8, another approach will be presented, where the chemical conversion reflected in changes in the infrared spectra of the treated samples are used to develop models for predicting mechanical properties by multivariate methods.

[**] The coefficient of determination for the prediction of strength properties from WL are smaller in Table 5.9 than the one in 5.10, because the models in the former include all the observations in each treatment (ranging from 4 to 10 replicates per treatment), whilst in Table 5.10 models were obtained using average values per treatment (42 treatments in total for softwoods, 20 for beech) (see Theorem of the Central Limit).

5.9.3 From treatment parameters

No reference exists for the prediction of property change by using a single model that includes simultaneously a range of temperatures and times of exposure. Mitchell (1988) modelled the strength response to different process conditions for small specimens of loblolly pine heat-treated only at 150 °C. He used non-linear equations, because the relationship between property change and time was sufficiently curved and not adequately described by first-order reaction kinetics. The model proposed was of the form: $RP = B2 - B0\ [1-e^{-(B1 \cdot t)}]$, where RP was the residual property, B1, B2 and B3 equation parameters, and t the time of exposure. This function was selected because the treatment reflected a reaction rate type of process; the model indicates that the magnitude of property change was given by B0 and, with increasing processing time, the residual property approached asymptotically the value of B2-B0, where B2 was the untreated value. Differentiation of the equation, B1 was suggested to be a measure of rate of loss according to $dRP/dt = -B1 \times [RP - (B2-B0)]$. Although no statistics of the goodness of fit were given, graphically it was clear that the model described very well residual EMC, reflectance and MOR and in some instances MOE, for times of exposure of up to 16 h. Extrapolation to lengthier exposures was not advised because of the possibility of inaccurate predictions.

In a similar study, Kim *et al.* (1998) modelled the bending strength parameters of small specimens of radiata pine sapwood heat-treated at three temperatures (120 °C, 150 °C and 180 °C) in the green and air-dried conditions. They used Mitchell's model as well as a second linear model of the type $RP = B0 \cdot e^{B1 \cdot t}$. They recommended the use of the second model, even though the initial rapid loss in property was not fitted as good as that of the first model. The coefficient of determination (R^2) values for the second model ranged from 0.78 to 0.97; one equation was calculated for each temperature of exposure.

The severity factor utilised in the processes of other lignocellulosic materials provides a suitable way for comparing results among experiments carried out under different conditions of temperature and time. The severity factor proposed in this work is closely related to other parameters used for similar purposes in pulping processes (Montané *et al.* 1994, Martínez *et al.* 1997). The severity factor, R_O, is defined by the equation:

$$R_O = t \times \exp\left[\frac{T(t) - T(ref)}{\omega}\right]$$

where *t* is the reaction time in minutes, T(*t*) is the reaction temperature in °C which may vary with time (*t*) in non-isothermal conditions, T(*ref*) is the reference temperature (normally chosen in the middle of the experimental conditions used or alternatively that temperature at which no significant reaction occurs, in this work set at 115 °C) and ω is the parameter expressing the importance of temperature in the specific reaction considered (for instance a value of 14.5 indicates that the rate of reaction has doubled ten degrees above a reference temperature of 100 °C, all the other variables remaining the same) (Montané *et al.* 1994). The mathematical interpretation of the reaction in terms of the R_O is based in the following differential equation (Garrote *et al.* 1999):

$$d(PX)/dR_O = -K \times (PX)$$

which assumes a first-order dependence between the percent of the property (or compound) X remaining in the solid phase (PX) and R_O involving a parameter K independent from the severity of the reaction, but dependent of the wood species in concern. The results are commonly presented as a function of $\log_{10}R_O$, the optimum processing conditions corresponding to a narrow range of $\log_{10}R_O$.

This method was chosen because most of the relative-to-control values are generally the same at equivalent levels of WL regardless of the temperature of treatment for each species, and therefore considered suitable for the analysis using this phenomenological approach. The expression of the severity parameter R_O and the general form of the relationship between Ln R_O and the residual property in question were used to calculate the optimal values for the model parameters (ω, b0, b1, b2). The optimal values were obtained by minimizing the square deviations between experimental and model-predicted values for wood strength using the non-linear regression algorithm of Levenberg-Marquardt (SPSS 2002). For plotting the results, both the experimental and predicted values of the remaining property for ten forms of mechanical strength and the remaining weight of modified softwoods, expressed as relative-to-control values (in %), are plotted as customary in dependence of the $\log_{10}R_O$ (Figure 5.32). It is important to emphasize that the severity factor is different for each mechanical strength property and for each species or group of species.

Table 5.11 shows the optimal values of the constants for the models for predicting residual oven-dry weight and remaining relative-to-control strength properties of TMW (in %) from the severity factor R_O, and the optimal ω parameter for computing R_O. Results in Table 5.11 show that this approach gives a better description of the WL, MOR and WML than the IS, RLP, MOE and R, with coefficients of determination values of $R^2 > 0.9$ and $R^2 > 0.7$ respectively, contrasting with the fitting for CA, CE, H and S, where the coefficient of determination was generally below 0.70. This is not surprising since the CA, CE and H have been found to be more strongly correlated to the material's density than to changes in chemical constitution. Chemical components are more affected by the thermal treatment than density, and therefore the combined effect of temperature and time cannot describe completely the changes in compression strengths and H. In the case of S, the scatter in the data could be probably partially attributable to the small sample size used in this work (n = 4 per treatment) and partly to the inherent variability and complexity of this property.

beech models have generally lower R^2 than those for pine or spruce, in part probably due to the larger heat-induced weight changes at any given temperature and in part to the greater anatomical and chemical variability of this species compared to pine or spruce. It is also important to notice that with two exceptions, the value of 9 to about 16 found for the ω is rather similar for most strength parameters, and denotes an increasing importance of temperature in the specific mechanical properties in each species. Values of ω in beech were consistently smaller than the respective values in pine or spruce. Instead of expressing the smaller importance of temperature on the reaction of beech, the smaller ω value possibly reflects the differences in chemical composition between this species and softwoods.

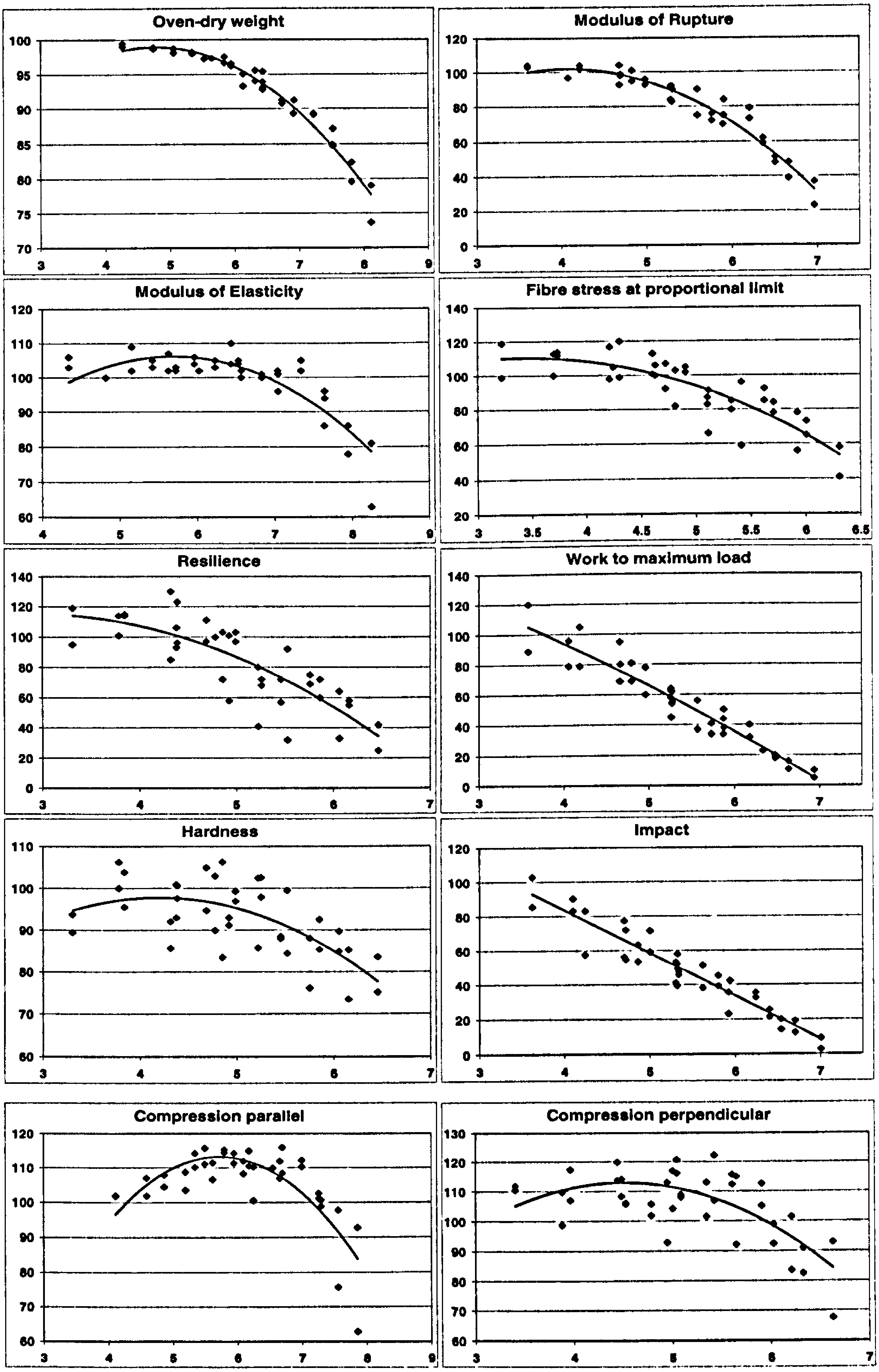

Figure 5.32 Percent relative-to-control property retention *versus* $\log_{10} R_O$ (R_O = severity factor) for oven-dry weight and selected strength properties in modified softwoods. The line represents the fitted model. Each point represents the mean experimental value of *n* samples. Oven-dry weight, *n*=10; II, *n*=6; IS, *n*= 10; CA, *n*=8; CE, *n*=6; MOE, *n*=10; RLP, *n*=10; MOR, *n*=10; WML, *n*=10; R, *n*=10.

Table 5.11 Model parameters for predicting residual oven-dry weight and remaining relative-to-control strength properties of TMW from the severity factor R_O, and the optimal ω parameter for computing R_O

Property	Species	b0	b1	b2	ω	R^2
Weight[a)]	Beech	105.93	1.22	-0.147	9.61	0.927
	Pine	62.64	7.01	-0.338	11.53	0.963
	Spruce	48.97	8.66	-0.376	10.55	0.974
	Softwoods	55.73	7.86	-0.358	11.01	0.966
MOR	Beech	168.62	-4.60	-0.112	9.68	0.886
	Pine	21.87	19.78	-1.211	14.96	0.956
	Spruce	-90.16	38.01	-1.869	13.58	0.951
	Softwoods	-34.07	29.04	-1.551	14.17	0.937
E	Beech	-20.51	14.48	-0.419	6.87	0.669
	Pine	-36.34	16.38	-0.469	7.32	0.745
	Spruce	-34.91	24.48	-1.060	12.92	0.775
	Softwoods	-28.77	20.62	-0.788	10.72	0.735
RLP	Beech	120.32	0.47	-0.249	12.15	0.705
	Pine	-63.45	28.46	-1.194	11.42	0.877
	Spruce	84.97	12.58	-1.114	19.04	0.754
	Softwoods	28.33	20.73	-1.307	16.98	0.732
R	Beech	138.00	-5.14	-0.105	14.90	0.683
	Pine	-92.08	35.29	-1.570	11.89	0.821
	Spruce	192.46	-6.48	-0.318	16.70	0.702
	Softwoods	65.55	15.26	-1.165	16.22	0.663
WML	Beech	501.91	-59.55	1.807	12.52	0.958
	Pine	146.22	-4.90	-0.313	16.45	0.977
	Spruce	219.25	-9.98	-0.154	12.83	0.977
	Softwoods	182.60	-7.56	-0.222	14.27	0.912
IS	Beech	149.80	-9.75	----	14.38	0.804
	Pine	160.29	-10.16	----	16.69	0.915
	Spruce	207.04	-11.56	----	12.30	0.947
	Softwoods	183.67	-10.86	----	14.03	0.900
H	Beech	155.04	-3.35	-0.103	9.30	0.859
	Pine	-12.00	22.15	-1.099	16.55	0.532
	Spruce	78.37	4.40	-0.247	12.29	0.427
	Softwoods	28.74	14.31	-0.741	16.26	0.447
S	Beech	83.41	6.77	-0.343	8.45	0.840
	Pine	73.47	6.48	-0.523	23.43	0.382
	Spruce	42.80	9.10	-0.414	11.01	0.891
	Softwoods	64.99	7.15	-0.449	15.97	0.488
CA	Beech	-36.85	20.22	-0.664	9.11	0.482
	Pine	-60.88	24.08	-0.837	9.99	0.572
	Spruce	-131.35	40.78	-1.693	13.51	0.725
	Softwoods	-96.69	31.86	-1.210	11.58	0.642
CE	Beech	-30.42	27.58	-1.320	14.45	0.600
	Pine	-81.51	15.30	-0.300	4.70	0.537
	Spruce	-41.75	45.96	-3.374	39.70	0.621
	Softwoods	-16.53	24.93	-1.200	15.48	0.488

a) from bending samples

All models of the form: Property = b0 + b1 (Ln R_O) + b2 (Ln R_O)^2

Abbreviations as in Tables 5.1, 5.3 and 5.5

The optimal conditions are not the same for all the properties studied. In softwoods, the optimal treatment conditions for CA, MOE, and CE are for a $\log_{10}R_O$ of about 5.75, 5.7 and 4.7 respectively (Figure 5.32). For MOR, R, RLP and H, the optimum covers a small range of $\log_{10}R_O$ at the beginning of the reaction, but in IS, WML and less so in S there was no optimum, because the mildest reactions tested in this work produced immediate reductions in these properties. The maximum reaction severity that causes no reduction in properties can be derived from plots in Figure 5.32: for instance CA is not affected negatively for $\log_{10}R_O$ values up to about 7.2; for MOE, the reduction becomes qualitatively noticeable for values of $\log_{10}R_O$ greater than about 7.

On the other hand, the scatter of the remaining oven-dry weight *vs.* the $\log_{10}R_O$ is fairly small, and the expression for the severity factor R_O and the curvilinear model proposed predict this property best (Table 5.11). This suggests that under the treatment conditions used in this work, the remaining weight in the heated woods (and therefore the WL) is insensitive to other characteristics of the material (*e.g.* wood density, thermal conductivity), and are closely related only to treatment parameters.

In beech the pattern of the changing properties with $\log_{10}R_O$ is similar to those in softwoods (plots not shown), although in S there was a small range where it did not decrease (up to $\log_{10}R_O$ of about 7.1), and the $\log_{10}R_O$ range where no reduction of H and RLP took place was much smaller than in softwoods. Like in softwoods, WML and IS, R was reduced in beech even at the mildest combination of time and temperature used in this work. The optimal treatment conditions for CA, MOE, and CE were to $\log_{10}R_O$ values of 6.6, 7.5 and 4.7 respectively.

In a somewhat related work, Repellin *et al.* (2005) examined the time-temperature equivalence for the heat-treatment of wood using thermo-gravimetric analysis (TGA). Small samples of pine and beech wood were heated from 160 °C to 260 °C, and by differentiation of the thermograms they found a relationship for the equivalence of time and temperature of treatment only in the 200 °C – 220 °C temperature range for pine wood. These authors could not find an equivalence for beech wood.

5.9.4 Relationship between strength properties

No difference in the average mechanical behaviour was found between species at equivalent levels of WL (Figures 5.33 and 5.34). The magnitude of change in the mechanical properties in each species, expressed as relative-to-control values (in proportion), were in the order: I ≥ MW ≥ TW > R ≥ SSML > MOR > SSLP > RLP > S > H > MOE > CE > CA. The exception was hardness, H, in beech, which was significantly different from the behaviour in softwoods; H and S in softwoods being somewhat slightly more affected at early levels of modification (WL < 5%) than most other properties, though.

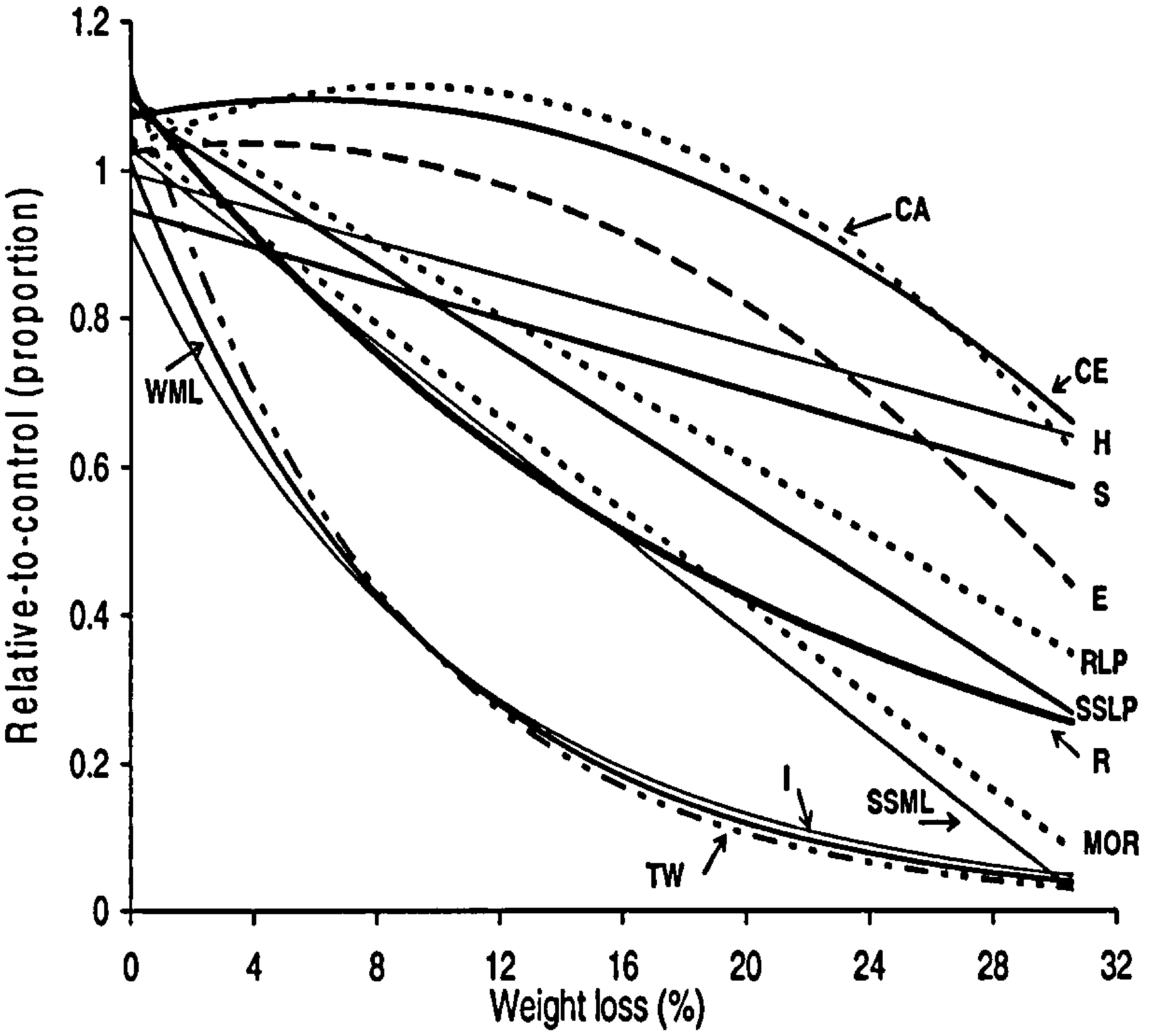

Figure 5.33 Relative-to-control average strength values (in proportion) versus average WL (in %) for the properties plotted together for heat-treated softwoods. Data points removed for clarity

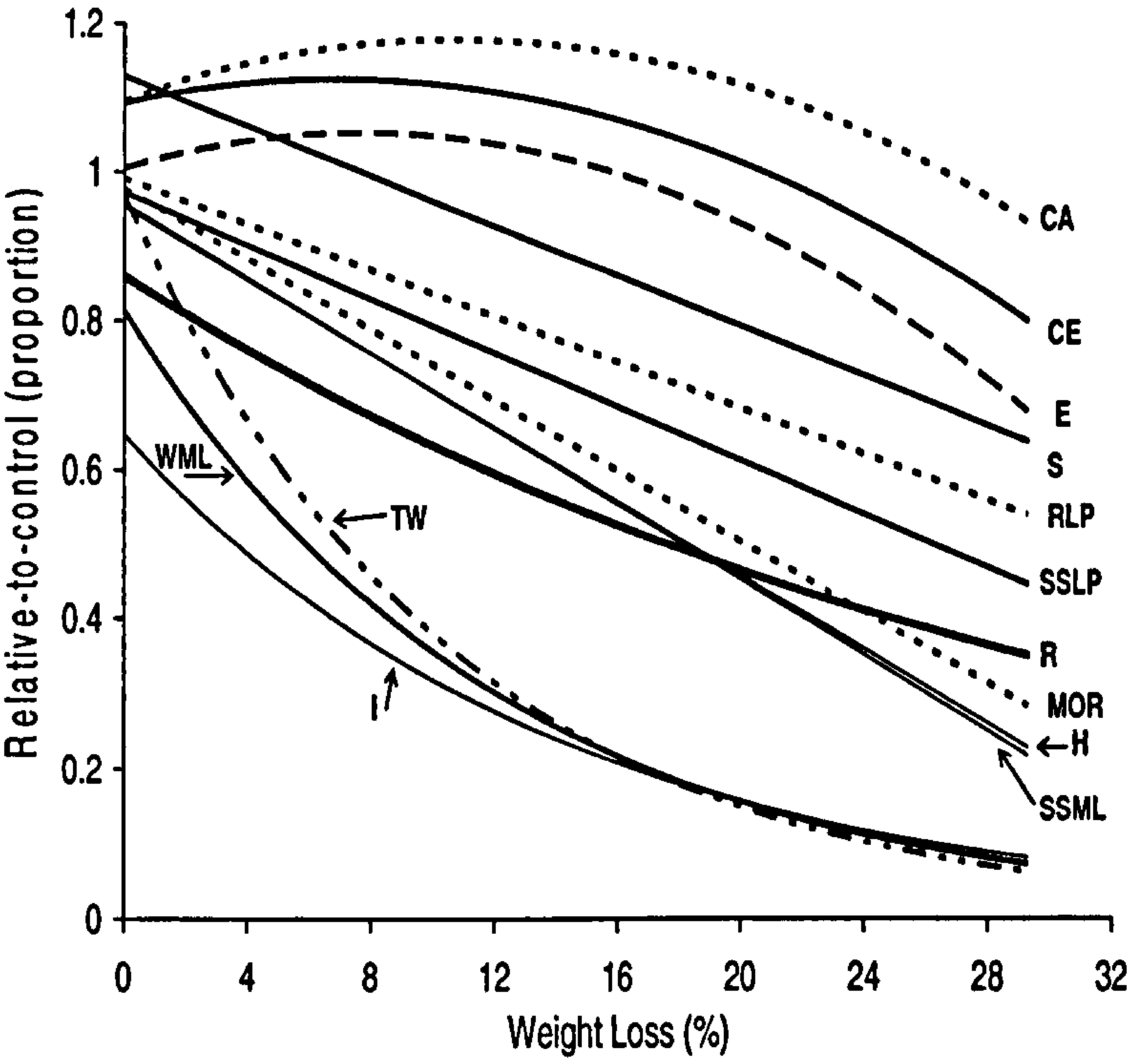

Figure 5.34 Relative-to-control average strength values (in proportion) versus average WL (in %) for the properties plotted together for heat-treated beech. Data points removed for clarity

The reduction in bending strength parameters was smaller at the limit of proportionality that the correspondent property at maximum load at equivalent levels of WL (Figures 5.33 and 5.34). This is an important result, because in practical terms, we normally rely upon the performance of timber not just at maximum load, but in fact well below the proportional limit; in most scenarios, we are depending on the performance of wood within the elastic limit rather than on the ultimate strength parameters. Thus, TMW would perform somewhat better in normal situations of service than it would be expected from the calculated behaviour based on the ultimate strength values, even for toughness.

Studies on softwoods heated in water at much lower temperatures for longer times show some similarities with the findings in the present research. Bending strength properties of Douglas-fir and Sitka spruce heated for up to 400 days at temperatures of 93.3 °C, show a curvilinear relationship with time of exposure, and the magnitude of property reduction in the order WML >> MOR > RLP >> MOE (Anon. 1955, cited by Green and Evans 2001). Results from several independent reports on small specimens also support the findings from the present study (Stamm *et al.* 1946, Thunell and Elken 1948, cited by Chang and Keith 1978, MacLean 1953, 1954, 1955 cited by Chang and Keith 1978, Seborg *et al.* 1953, Mitchell *et al.*, 1953; Stamm 1956, Lin 1969, Schneider 1971, Millet and Gerhards 1972, Rusche 1973, Chang and Keith 1978; Mitchell 1988, Kim *et al.* 1998, Kubojima *et al.* 2000, Mouras *et al.* 2002, Bekhta and Niemz 2003, Brischke and Rapp 2004). In large-sized specimens, noticeable similarities in the behaviour of small specimens have been documented (Syrjänen and Kangas 2000, Bengtsson *et al.* 2002, Green *et al.* 2003, Christmas *et al.* 2005, Tremblay and Lihra 2005, Birkinshaw *et al.* 2006, Shi *et al.* 2007), although most reports from large specimens refer to strength parameters from bending testing only.

According to previous reports, impact strength of TMW is generally found to be the property most affected compared to any other form of stress, whilst H and MOE are the least affected. Other properties are situated somewhere in between in the order WML > MOR > RLP > H ≥ CA ≥ MOE (from most to least). However, no previous example exists for the study of all the properties in matched specimens as described in this work. Other reports have dealt with other mechanical properties not investigated in the present research, though. Despite the difficulty of comparing results from several experiments because of the divergent conditions of treatment, available data indicates that the magnitude of change of cleavage (CL), tension perpendicular to the grain (TE), tension parallel to the grain (TA) and abrasion resistance (AR) is in the order AR >> TE > CL > TA, all of these reduced to a larger extent than MOR, and less than IS (except probably for abrasion resistance). Relative-to-control values appear to be a good way to describe the relationship with WL in order to find a more universal mechanical behaviour independently of other wood characteristics such as density or chemical composition (Seborg *et al.* 1953, Rusche 1973).

The prediction of some mechanical properties from others determined non-destructively may have practical relevance, as may the prediction of some properties from others which may require the destruction of one part of the stock, but could serve for characterising the full batch of treated material by characterising only one property. The correlation between ten mechanical strength properties is presented in Table 5.12.

Table 5.12 Pearson correlation between mechanical strength parameters of TMW

Species	Property	Ln MOR	Ln MOE	Ln R	Ln WML	Ln RLP	Ln IS	Ln H	Ln S	Ln CA	Ln CE
Beech	Ln MOR		**	**	**	**	**	**	**	*	**
	Ln MOE	0.847		**	**	**	**	**	**	**	**
	Ln R	0.914	0.756		**	**	**	**	**	NS	**
	Ln WML	0.978	0.740	0.919		**	**	**	**	NS	**
	Ln RLP	0.945	0.850	0.982	0.926		**	**	**	NS	**
	Ln IS	0.945	0.699	0.910	0.978	0.907		**	**	NS	*
	Ln H	0.961	0.750	0.849	0.955	0.866	0.905		**	*	**
	Ln S	0.921	0.825	0.737	0.882	0.811	0.846	0.903		**	**
	Ln CA	0.500	0.608	0.362	0.357	0.431	0.275	0.474	0.602		**
	Ln CE	0.724	0.767	0.604	0.611	0.660	0.545	0.725	0.684	0.638	
Pine	Ln MOR		**	**	**	**	**	**	*	*	**
	Ln MOE	0.870		**	**	**	**	**	NS	**	**
	Ln R	0.911	0.794		**	**	**	**	**	**	**
	Ln WML	0.983	0.789	0.899		**	**	**	**	NS	**
	Ln RLP	0.938	0.878	0.988	0.908		**	**	*	**	**
	Ln IS	0.963	0.761	0.848	0.978	0.861		**	**	NS	*
	Ln H	0.650	0.590	0.660	0.645	0.666	0.657		NS	NS	NS
	Ln S	0.539	0.352	0.559	0.590	0.537	0.565	0.328		*	*
	Ln CA	0.522	0.594	0.575	0.420	0.601	0.412	0.181	0.451		**
	Ln CE	0.643	0.793	0.628	0.586	0.694	0.524	0.370	0.543	0.700	
Spruce	Ln MOR		**	**	**	**	**	**	**	**	**
	Ln MOE	0.964		**	**	**	**	*	**	**	**
	Ln R	0.765	0.656		**	**	**	**	**	*	**
	Ln WML	0.978	0.903	0.798		**	**	**	**	**	**
	Ln RLP	0.847	0.764	0.987	0.862		**	**	**	**	**
	Ln IS	0.968	0.897	0.838	0.973	0.892		**	**	**	**
	Ln H	0.656	0.533	0.750	0.696	0.743	0.733		**	*	**
	Ln S	0.856	0.738	0.674	0.906	0.716	0.850	0.567		*	**
	Ln CA	0.819	0.913	0.478	0.705	0.599	0.732	0.469	0.509		**
	Ln CE	0.839	0.828	0.616	0.780	0.699	0.834	0.597	0.580	0.764	

** Significant at $p< 0.01$
* Significant at $p< 0.05$
NS = not significant

All correlations between strength properties are positive and most of these are highly significant. The weakest correlations are between CA, CE and the rest of the properties and less so for H and S. Except for compression strengths, MOE has lower correlation with the properties than does MOR or IS, which have generally the strongest correlation with most of the remaining properties. However, the technical feasibility of determining non-destructively MOE makes the use of this parameter attractive for predicting other strength properties. For reasons of space it is not possible to present the models for all the possible combinations of strength parameters. The likely most useful models are given in Table 5.13; these models were computed using the average values per each treatment; values of CA from treatment 19 in pine were not included in the predictions for inconsistency.

Table 5.13 Models for predicting mechanical strength parameters of thermally modified beech, Scots pine and Norway spruce from MOE, MOR and IS (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, NS = not significant)

Species	Response	Predictor	R^2	F (sig)	b0	b1	SE	$n^{a)}$
Beech	Ln MOR	Ln MOE	0.717	45.55 ***	-21.54	2.782	0.195	20
		Ln IS	0.892	149.02 ***	3.47	0.457	0.120	20
	Ln MOE	LN MOR	0.717	45.55 ***	8.20	0.258	0.059	20
		Ln IS	0.489	17.24 ***	9.12	0.103	0.080	20
	Ln RLP	Ln MOE	0.723	47.02 ***	-11.91	1.719	0.118	20
		Ln IS	0.823	83.53 ***	3.57	0.270	0.095	20
		LN MOR	0.893	149.55 ***	1.57	0.581	0.074	20
	Ln R	Ln MOE	0.572	24.07 ***	-25.95	2.361	0.227	20
		Ln IS	0.829	87.12 ***	-4.80	0.418	0.144	20
		LN MOR	0.835	90.85 ***	-7.76	0.868	0.141	20
	Ln WML	Ln MOE	0.548	21.81 ***	-53.33	5.378	0.544	20
		Ln IS	0.956	394.49 ***	-5.36	1.046	0.169	20
		LN MOR	0.957	404.17 ***	-12.73	2.163	0.167	20
	Ln H	Ln MOE	0.562	23.10 ***	-8.92*	1.842	0.181	20
		Ln IS	0.819	81.41 ***	7.58	0.327	0.116	20
		LN MOR	0.924	219.22 ***	5.08	0.719	0.075	20
	Ln S	Ln MOE	0.681	38.45 ***	-9.45	1.252	0.095	20
		Ln IS	0.716	45.29 ***	1.84	0.189	0.090	20
		LN MOR	0.848	100.60 ***	0.36^{NS}	0.425	0.066	20
	Ln IS	Ln MOE	0.489	17.24 **	-42.23	4.752	0.540	20
		Ln MOR	0.892	149.02 ***	-6.53	1.953	0.248	20
	Ln CA	Ln MOE	0.370	10.56 **	-0.14^{NS}	0.458	0.067	20
		Ln IS		NS				20
		LN MOR	0.250	6.01 *	3.63	0.115*	0.073	20
	Ln CE	Ln MOE	0.588	25.67 ***	-6.45	0.912	0.085	20
		Ln IS	0.297	7.62 *	1.86	0.095*	0.111	20
		LN MOR	0.524	19.82 ***	0.90	0.262	0.091	20

The models are of the form: $y = b0 + b1 \cdot x$

a) Each element in n is the mean value of 4 to 10 replicates

All coefficient significant at $p < 0.01$ unless otherwise indicated

For units of variables, see Table 5.9

Abbreviations as in Tables 5.1, 5.3 and 5.5

Continued over...

Table 5.13 Models for predicting mechanical strength parameters of thermally modified beech, Scots pine and Norway spruce from MOE, MOR and IS (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; NS = not significant) (*Continued ...*)

Species	**Response**	**Predictor**	**R^2**	**F (sig)**	**b0**	**b1**	**SE**	**$n^{a)}$**
Pine	Ln MOR	Ln MOE	0.757	59.08 ***	-23.95	3.009	0.149	21
		Ln IS	0.926	239.39 ***	3.25	0.478	0.082	21
	Ln MOE	LN MOR	0.757	59.08 ***	8.33	0.252	0.043	21
		Ln IS	0.579	26.16 ***	9.17	0.109	0.057	21
	Ln RLP	Ln MOE	0.771	63.89 ***	-12.62	1.775	0.085	21
		Ln IS	0.741	54.49 ***	3.51	0.250	0.090	21
		LN MOR	0.880	138.69 ***	1.69	0.548	0.061	21
	Ln R	Ln MOE	0.631	32.44 ***	-27.77	2.515	0.169	21
		Ln IS	0.719	48.57 ***	-5.00	0.386	0.147	21
		LN MOR	0.830	92.75 ***	-7.74	0.834	0.114	21
	Ln WML	Ln MOE	0.623	31.35 ***	-59.06	5.918	0.404	21
		Ln IS	0.956	413.88 ***	-5.83	1.053	0.138	21
		LN MOR	0.965	530.51 ***	-12.67	2.131	0.122	21
	Ln H	Ln MOE	0.348	10.16 **	0.86^{NS}	0.692	0.083	21
		Ln IS	0.432	14.44 **	7.12	0.111	0.077	21
		LN MOR	0.423	13.90 **	6.41	0.220	0.078	21
	Ln S	Ln MOE		NS				21
		Ln IS	0.319	8.91 **	1.40	0.123	0.110	21
		LN MOR	0.291	7.80 *	0.65^{NS}	0.237*	0.112	21
	Ln IS	Ln MOE	0.579	26.16 ***	-47.51	5.300	0.396	21
		Ln MOR	0.926	239.39 ***	-6.11	1.938	0.165	21
	Ln CA	Ln MOE	0.352	9.78 **	-1.62^{NS}	0.567	0.051	20
		Ln IS		NS				20
		LN MOR	0.272	6.73 *	3.18	0.125*	0.054	20
	Ln CE	Ln MOE	0.630	32.30 ***	-6.71	0.868	0.058	21
		Ln IS	0.275	7.20 *	1.28	0.082*	0.082	21
		LN MOR	0.414	13.40 **	0.58*	0.203	0.073	21

The models are of the form: $y = b0 + b1 \cdot x$

a) Each element in n is the mean value of 4 to 10 replicates

All coefficient significant at $p < 0.01$ unless otherwise indicated

For units of variables, see Table 5.9

Abbreviations as in Tables 5.1, 5.3 and 5.5

Continued over...

Table 5.13 Models for predicting mechanical strength parameters of thermally modified beech, Scots pine and Norway spruce from MOE, MOR and IS (* $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, NS = not significant) (*Concluded*)

Species	Response	Predictor	R^2	F (sig)	b0	b1	SE	$n^{a)}$
Spruce	Ln MOR	Ln MOE	0.930	252.10 ***	-23.68	3.046	0.099	21
		Ln IS	0.936	278.84 ***	3.18	0.422	0.095	21
	Ln MOE	LN MOR	0.930	252.10 ***	7.87	0.305	0.031	21
		Ln IS	0.805	78.33 ***	8.85	0.124	0.052	21
	Ln RLP	Ln MOE	0.584	26.67 ***	-13.52	1.874	0.187	21
		Ln IS	0.795	73.87 ***	2.90	0.302	0.131	21
		LN MOR	0.718	48.43 ***	0.87*	0.658	0.154	21
	Ln R	Ln MOE	0.430	14.36 **	-29.25	2.677	0.365	21
		Ln IS	0.701	44.62 ***	-5.88	0.472	0.264	21
		LN MOR	0.585	26.78 ***	-8.89	0.988	0.311	21
	Ln WML	Ln MOE	0.815	83.96 ***	-57.85	5.961	0.336	21
		Ln IS	0.947	338.44 ***	-5.44	0.888	0.180	21
		LN MOR	0.957	425.91 ***	-11.88	2.045	0.162	21
	Ln H	Ln MOE	0.284	7.53 *	3.72*	0.402*	0.076	21
		Ln IS	0.537	22.06 ***	7.22	0.077	0.061	21
		LN MOR	0.418	13.64 **	6.75	0.155	0.068	21
	Ln S	Ln MOE	0.545	22.72 ***	-3.83	0.622	0.067	21
		Ln IS	0.720	48.94 ***	1.62	0.099	0.053	21
		LN MOR	0.731	51.69 ***	0.90	0.228	0.052	21
	Ln IS	Ln MOE	0.805	78.33 ***	-57.00	6.491	0.379	21
		Ln MOR	0.936	278.84 ***	-6.90	2.217	0.217	21
	Ln CA	Ln MOE	0.834	95.80 ***	-5.47	1.001	0.053	21
		Ln IS	0.537	22.03 ***	3.42	0.111	0.088	21
		LN MOR	0.671	38.79 ***	2.50	0.284	0.074	21
	Ln CE	Ln MOE	0.685	41.38 ***	-7.52	0.986	0.079	21
		Ln IS	0.696	43.41 ***	1.17	0.137	0.078	21
		LN MOR	0.705	45.34 ***	0.18^{NS}	0.317	0.077	21

The models are of the form: $y = b0 + b1 \cdot x$

a) Each element in n is the mean value of 4 to 10 replicates

All coefficient significant at $p < 0.01$ unless otherwise indicated

For units of variables, see Table 5.9

Abbreviations as in Tables 5.1, 5.3 and 5.5

All relationships between variables are of a linear nature in the log-log scale, which is common to the same relationship between mechanical properties in untreated wood (Green *et al.* 1999). MOR was consistently the best predictor of other forms of physical strength in all three species, although IS was better predictor of MOR than MOE in all the three species. In beech, IS also had comparable R^2 values to MOR; in spruce, IS was slightly better predictor than MOR for other three forms of mechanical strength. MOE had the lowest prediction ability in most forms of mechanical strength. Nevertheless, MOE was the best predictor for compression strength parallel and perpendicular to the axis except for CE in spruce, where it had comparable but smaller prediction ability than MOR and IS. Most models for the prediction of other forms of mechanical strength from MOE were highly significant though.

Multiple linear regression indicates than the addition of MOE to the model of IS (from Table 5.13) results in significant improvements for the prediction of some forms of wood strength (MOR in the three species, RLP in beech and pine; S in beech and CA in spruce). There were however, moderate signs of collinearity due to the inclusion of MOE and therefore the models are not completely warranted. Likewise, if EMC is included in the IS models[††], the significance of the predictions is improved for MOE and RLP in beech, MOE in pine, and MOE, S, CA and CE in spruce. In this occasion, no signs of collinearity were found, although the significant increment in R^2 was smaller than 10% in RLP in beech, MOE in pine and spruce, and S and CE in spruce. Important R^2 changes were found for the model of MOE in beech (R^2 from 0.489 to 0.735) and for the model of CA in spruce (R^2 from 0.537 to 0.818).

A remarkable finding for its potential practical utility is the result of multiple linear analyses adding EMC to the models of MOE. Without showing worrying signs of collinearity, these models resulted in significant increase in R^2 for most forms of mechanical strength tested except for CE. Improvements (in the order beech, pine and spruce) were found for MOR (R^2 from 0.717, 0.757 and 0.930, to R^2 = 0.922, 0.948 and 0.977), R (R^2 from 0.572, 0.631 and 0.430, to R^2 = 0.772, 0.776 and 0.617), RLP (R^2 from 0.723, 0.771 and 0.584, to R^2 = 0.856, 0.861 and 0.707), WML (R^2 from 0.548, 0.623 and 0.815, to R^2 = 0.912, 0.930 and 0.967) and IS (R^2 from 0.489, 0.579 and 0.805, to R^2 = 0.856, 0.866 and 0.928), respectively. Similarly, significantly improvements for H and S in beech (R^2 from 0.562 and 0.681, to R^2 = 0.850 and 0.788 respectively) as well as for S and CA in spruce (R^2 from 0.545 and 0.834, to R^2 = 0.826 and 0.922 respectively) were determined. These findings highlight the feasibility of predicting eight strength parameters by determining MOE and EMC in TMW using conventional non-destructive procedures, giving

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[††] Model of the form Ln (property) = Ln (IS) + Ln (EMC)

predictions at levels of significance comparable to, and in several instances greater than, any other predictor investigated in the present study. Furthermore, it has been shown that MOE is a fair predictor of MOR in modified large-sized specimens of spruce and pine wood (see below); the EMC in small- and large-sized specimens should not have large differences, so the approach investigated for the first time in this work may have potential commercial advantages for the strength characterization or classification of modified wood in usage dimension.

The high relationship between impact strength and other forms of wood strength point out the possibility of using a simple destructive test for the prediction of other forms of mechanical strength in TMW. The strong relationship between the resistance to multiple-impact milling and WL has been noted recently by Rapp *et al.* (2006). After ball-milling the sample, these authors predicted the WL from the weight of two opposite size fractions to form the index of resistance to impact milling. These authors hypothesize that it would then be possible to predict some mechanical properties from the estimated WL. Whereas this proposal is valuable, the additive effect of the error associated to the successive predictions may render the predictions of strength unreliable using this test; probably models for the prediction of mechanical strength directly from the mentioned index are needed. This possibility was explored in the present research, only for modified Norway spruce wood, based on an early finding of Cowling (1961) (he was dealing with decayed wood, though). The fraction of the < 60 mesh (0.250 mm aperture) fraction of cross-beater milled wood was weighted, and the >60 mesh fraction calculated by difference from the initial weight (see chapter 3. Methods). The relationship of the relative-to-control value of this fraction with strength parameters was examined by correlation and simple linear regression analyses. Treatment 20 (at 245 °C for 16 h, to WL = 26.3%) was not considered in the models for rendering the data not amenable to parametric analysis. The gravimetric determination had highly significant Pearson correlation with 7 strength parameters (MOR, MOE, RLP, S, Ln WML, Ln TW and Ln IS), very significant correlation with Ln R and weak -although significant, correlation with CE. No correlation with CA was found.

Equations for the prediction of mechanical properties from the relative-to-control >60 mesh fraction using linear regression are given in Table 5.14.

Table 5.14 Models for the prediction of strength parameters of thermally modified Norway spruce wood from the relative-to-control weight (in proportion) of the >60 mesh[a] fraction after cross-beater milling[b]

Response	R^2	F (sig)	b0	b1	SE	n[c]
MOR	0.883	135.3 ***	163.13	-74.599	4.850	21
MOE	0.681	38.4 ***	12,716.20	-2,551.600	311.690	21
RLP	0.531	20.4 ***	82.23	-34.420	5.770	21
Ln R	0.452	14.8 **	-2.71	-1.608	0.316	21
Ln WML	0.915	194.8 ***	0.65	-3.116	0.169	21
Ln TW	0.898	158.2 ***	0.94	-2.955	0.178	21
Ln IS	0.847	99.3 ***	6.22	-2.992	0.227	21
H	0.200	4.5 *	2,060.60	-327.969	117.140	21
S	0.831	88.4 ***	10.09	-2.872	0.231	21
CE	0.222	5.1 *	6.06	-1.199	0.400	21

The models are of the form: $y = b0 + b1\cdot(1/x)$

a) Reference > *60 mesh* fraction for control (untreated spruce) = 0.7447

b) For WL < 20%.

c) Each element in *n* is the mean value of 4 to 10 replicates

All coefficient significant at $p < 0.05$ unless otherwise indicated

For units of variables, see Table 5.8

Abbreviations as in Tables 5.1, 5.3 and 5.5

Based on the R^2 statistic, the best prediction was for WML followed by TW, although very good coefficients of determination were also found for MOR, IS and S. Models are somewhat less efficient for the prediction of MOE, RLP and R and just significant H and CE. The model was not significant for the predictions of CA. Except for the prediction of compression strength the coefficients of determination using this approach are comparable to the models for the strength predictions from WL[‡‡]. The inclusion of EMC in the model for the prediction of MOE added 14.8% to the already highly significant coefficient of determination ($R^2 = 0.681$) produced by the relative-to-control >*60-mesh* parameter. Thus, MOE can be more significantly predicted by using MOE = 16,974.4 – 4,573.60 · (1/relative-to-control>*60 mesh*) – 224.47 · EMC ($R^2 = 0.829$, F = 41.33, SE = 234.4).

Albeit of a destructive nature, the simple method described herein renders itself for automation. A conventional cross-beater or Wiley mill, coupled to an ultrasonic sifter can be used and the whole process performed in a few minutes per sample. Additionally, the sample required is very small (~ 20 g) with highly significant predictions for seven wood strength parameters.

[‡‡] Both model families are strictly not comparable, because models for the predictions using the >*60 mesh* fraction weight are based in average values for each treatment, whereas models for strength prediction from WL in spruce wood (Table 5.9) include all the observations in each treatment.

Two previous examples exists for the prediction of mechanical strength from other forms of strength in TMW. Bengtsson *et al.* (2002) pictured graphically the relationship of MOR in dependence of the MOE for heat-treated Norway spruce and Scots pine beams. They found a rectilinear relationship between these properties and, although models were not given, R^2 was 0.66 for spruce and 0.59 for pine. Similar results were found in the present study, with coefficients of determination being higher for spruce than for pine, although the R^2 values in both species were, as expected from testing small specimens, higher in the present study than in the cited reference. Another example is given by Widmann *et al.* (2007) in a recent study. This has been described in chapter 2 (p. 41).

5.10 Factor analysis for the development of a performance index of TMW

The discussions and arguments about the perspectives of a measure of TMW performance are ongoing and a few proposals continue being presented to assess it, despite the lack of a universally accepted model or scheme (*cf.* Syrjänen and Kangas 2000, Brischke and Rapp 2004, Homan and Tjeerdsma 2005). In order to apply strength and other measures of wood performance (*e.g.* ASE) to evaluate TMW more objectively and comprehensively, a better understanding of how factors influence the material's performance is needed. To date, little effort has been made to explore the complex interrelationships among the various factors with respect to the material's performance. This part of the study is motivated by the need of the development of a performance index; there is no attempt to address the research problem to integrate all the parameters of wood performance into one model. This study utilizes nine mechanical strength properties (MOR, MOE, RLP, LnR, LnWML, LnIS, CE, H and S) as well as the results from the dimensional stability test (ASE) for the analysis. It also integrates the inverse of a value of hygroscopicity (average relative-to-control hygroscopicity at 5 levels of RH at 20 °C, ARH, see chapter 6) as a surrogate measure of the potential increment in decay resistance of the modified material, PDR.

This study applies Factor Analysis (FA), which is a multivariate tool for identification of underlying variables, or factors, that explain the pattern of correlations within a set of observed variables. This tool was chosen as it is suitable for causal-predictive analysis in situations of high complexity but low theoretical information. Ideally, the FA will reduce the data from all the parameters (dimensional stability, hygroscopicity and strength) into one single value. This will be considered as an index of the overall performance of the material.

Initially, the mechanical strength parameters included the CA strength, but the inclusion of this in the analysis led in all models to the extraction of two factors, the second one being required to describe primarily the CA behaviour in the analysis. The foregoing and the impossibility of linearization of the CA response in relation to the score determined, and the very small extracted communality value for CA in beech (0.212), required the withdrawal of CA from the analysis.

Determination of the suitability of the data for factor analysis

For the analysis with eleven variables (9 mechanical properties plus ASE and PDR), the Kaiser-Meyer-Olkin measure of sampling adequacy statistic indicated that the proportion of variance in the variables which might be caused by underlying factors was high in the analysis for each of the three species (> 0.75). Additionally, Bartlett's test of sphericity statistic was significant at the $p < 0.001$ level in all analyses, indicating that the correlation matrix was not an identity matrix. This denotes that the variables are related and therefore the data was suitable for factor analysis (SPSS 2000). The Anti-image correlation matrix, which contains the negative partial correlations, had only small values off the main diagonal, signifying that the variables were relatively free of unexplained correlations. Each value on the main diagonal of this matrix also showed that the Measure of Sampling Adequacy for the respective item was always greater than 0.5 which indicated that all variables fit with the structure of the other variables. Finally, most of the residual of the reproduced correlations (with respect to the observed values) are small (< 0.1), indicating a good factor analysis solution.

Factor analysis solution

The initial communalities (the proportion of variance accounted for in each variable by the rest of the variables) were high for all variables in the three species. The extraction communalities (estimates of the variance in each variable accounted for by the factors) were also all high, which indicates that the extracted factors represent the variables well, although the extracted communality of CE in the three species, H in pine and spruce and S in pine were somewhat low (< 0.5 but > 0.35) and therefore not thoroughly explained by the extracted factor.

Table 5.15 Eigenvalues and variance explained for the factor solution in Thermally modified beech, pine and spruce woods. Extraction method: unweighted least-squares.

Species	Factor	Initial Eigenvalues			Extraction Sums of Squared Loadings		
		Total	% of Variance	% Cumulative	Total	% of Variance	% Cumulative
Beech	1	9.21	83.70	83.70	9.06	82.34	82.34
	2	0.79	7.16	90.86			
	3	0.53	4.84	95.69			
	4	0.26	2.37	98.06			
	5 - 11	0.21	1.94	100.00			
Pine	1	8.39	76.27	76.27	8.20	74.57	74.57
	2	0.91	8.26	84.53			
	3	0.72	6.52	91.04			
	4	0.53	4.85	95.89			
	5 - 11	0.45	4.11	100.00			
Spruce	1	8.87	80.65	80.65	8.69	79.02	79.02
	2	0.82	7.42	88.08			
	3	0.65	5.89	93.97			
	4	0.36	3.31	97.28			
	5 - 11	0.30	2.72	100.00			

The leftmost section of Table 5.15 shows the variance explained by the initial solution. Only one factor in the initial solution had eigenvalue greater than 1. This accounts for almost 83.7%, 76.3% and 80.7% of the variability in the original 11 variables for beech, pine and spruce, respectively. This suggests that there is a single latent influence associated with the material performance. The second section of Table 5.15 shows the variance explained by the extracted factors. The cumulative variability explained by this factor in the extracted solution is about 82.3%, 74.6% and 79.0% in the same order, a difference of 1.4% for beech and 1.7% for pine and spruce from the initial solution. The factor extraction method used in this work (unweighted least squares) adds the assumption that some of the variability in the data cannot be explained by the factor(s). As a result, the total variance explained by the solution is smaller, but the addition of this structure to the factor model makes this method ideal for examining relationships between the variables. Thus, less than 2% of the variation explained by the initial solution is lost due to latent factors unique to the original variables and variability that simply cannot be explained by the factors. However, as the single factor extracted explains about 83%, 75% and 79% of the variability in the original eleven variables in beech, pine and spruce, respectively, this considerably reduced the complexity of the data set by using only one factor, with only a 17.7%, 25.4% and 21% loss of information respectively.

The relationships in the unrotated factor matrix showed that the single factor extracted was positively correlated with all the parameters of mechanical performance, and negatively with dimensional stability and estimated decay resistance (Table 5.16). This is not surprising, because the mechanical strength and the hygroscopicity are two competing properties in the modified wood.

Table 5.16 Factor loadings for each variable on the unrotated factors for thermally modified beech, pine and spruce woods.

Property[a)]	Beech	Pine	Spruce
MOR	1.000	0.982	0.991
MOE	0.796	0.820	0.863
RLP	0.929	0.958	0.876
Ln R	0.900	0.952	0.838
Ln WML	0.987	0.986	0.999
Ln IS	0.947	0.942	0.984
H	0.967	0.650	0.702
S	0.906	0.598	0.872
CE	0.667	0.624	0.735
PDR	-0.863	-0.913	-0.929
ASE sqr	-0.967	-0.937	-0.934

[a)] Natural logarithm of R, WML and IS, and squared ASE were used in order to linearise the relationship between these and the scores

If two factors were extracted (the second being an artificial one, with eigenvalue < 1, but extracted just to be able to draw the loading plot) (Figure 5.35), it can be established that MOR, Ln IS, and other four strength properties are closely related with the first (significant) factor extracted, whereas CE and MOE are less related to this factor, and could be also explained by an hypothetical second factor accounting for 'stiffness and compressibility'. The first factor can be thought of as the 'overall performance'. The negative loading of the ASE and PDR are clearly in concordance of the physical data: the material becomes less strong as the hygroscopicity increases.

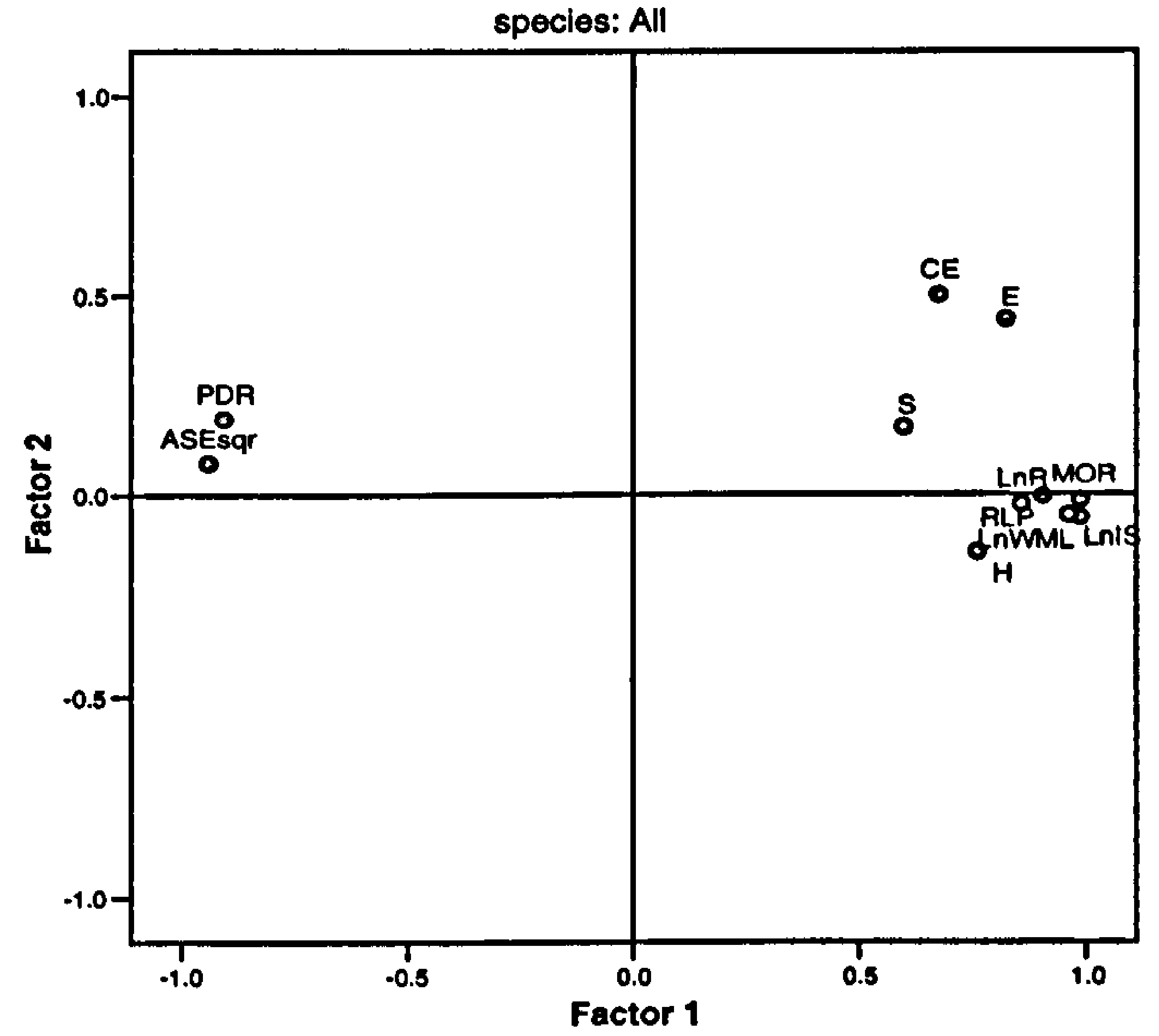


Figure 5.35 Factor plot in the rotated factor space (Quartimax rotation) for the factor analysis of the overall performance of TMW with a second (artificial) factor extracted. Data of the three species analysed together. Extraction method: unweighted least squares.

For the solution with only one factor extracted, the factor score for each case is computed by multiplying the case's standardized variable values[§§] by the component's score coefficients (coefficients not shown). The resulting factor score variable is representative of, and can be used in place of, the eleven original variables with only a 17.7%, 25.4% and 21% loss of information for beech, pine and spruce, respectively. The scores for the factor extracted could be considered therefore as an index of the overall performance of the material. In this study, an index value of zero would be considered as to *neutral*, a value where the mechanical performance is not outdone by a large ASE and PDR. Positive values are those were the mechanical performance is high compared to the reduced hygroscopicity, whereas a negative index value would be one where the ASE and PDR would be high at the expense of a larger reduction in mechanical performance.

[§§] Computed using list-wise deletion.

The overall performance index (OPI) was not the highest for the untreated control (Figure 5.36). In beech, treatments 1, 3 and 6 had higher OPI than treatment 0 (control), whereas treatment 7 in pine and treatment 1 in spruce had also higher OPI than control treatment; treatments 6 and 11 in pine and 3 and 6 in spruce had comparable OPI to the control one.

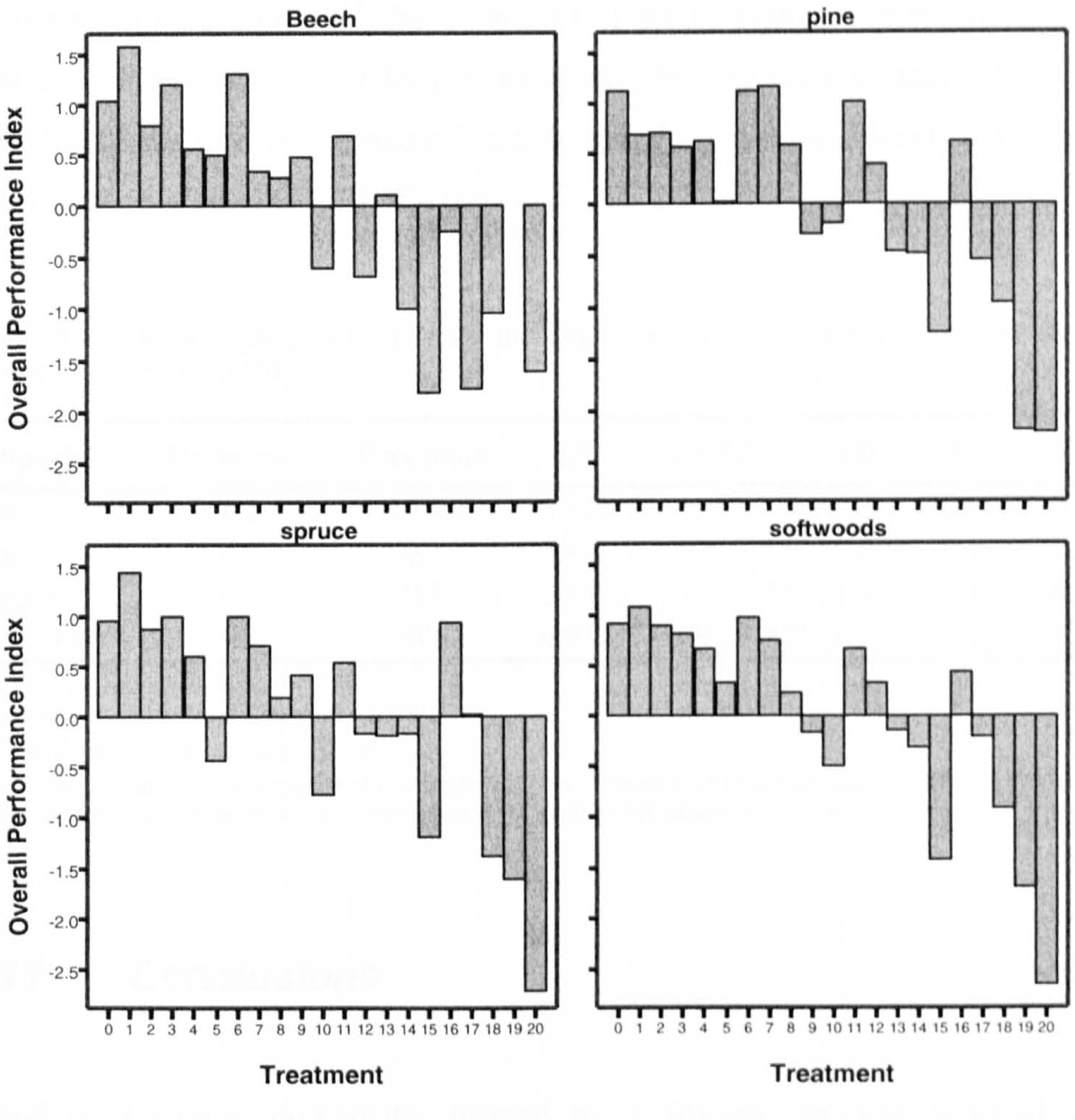


Figure 5.36 Bar plot for the Overall Performance Index of Thermally Modified beech, pine and spruce woods. For explanation on Treatment numbers, see Table 5.4.

A linear least-squares regression of the OPI on WL, gave that the neutral OPI value (OPI = 0) would be at a WL of 11.57%, 7.06% and 7.39% for beech, pine and spruce, respectively (Table 5.17). This level of modification would produce, for instance, an ASE of 49.8%, 36.6% and 36.9% respectively. Treatment at higher levels of WL would result, as indicated above, in a reduction in mechanical performance which would not be compensated for by the extra gain in ASE and PDR.

The optimum level of treatment is difficult of fix on, because this depends on the expected usage of the modified material and, as it has been found, on wood species. For instance, applications where relatively high mechanical integrity is desired, the maximum level of modification would be at the neutral index value, but the optimum would probably be at an OPI of 0.4 or higher. For applications where high dimensional stability or decay resistance is desired, the optimum value would be most likely the one at the neutral index, and the maximum level of modification would probably be at an OPI of – 0.3.

Table 5.17 Linear regression models for the estimation of the Overall Performance Index from Weight Loss (*** $p< 0.001$).

Species	Response	Predictor	R^2	F (sig)	b0	b1	SE	$n^{a)}$
Beech	OPI	WL	0.873	123.3 ***	1.226	-0.106	0.38	20
Pine	OPI	WL	0.921	222.2 ***	1.108	-0.157	0.29	21
Spruce	OPI	WL	0.857	113.9 ***	1.069	-0.145	0.41	21
Softwoods	OPI	WL	0.937	597.9 ***	1.094	-0.151	0.25	42

WL (%), Performance index (unitless)

The model is of the form: $OPI = b0 + b1 \cdot WL$

All coefficients significant at $p < 0.001$

$^{a)}$ Each element in *n* is the response of one treatment (a combination of time-temperature). Eleven properties were evaluated for each treatment, each property being the average between 4 and 10 replicates.

5.11 Conclusions

Wood is a natural composite, formed by a fibrous structure embedded in an amorphous matrix of hemicellulose and lignin. An inevitable consequence associated with any chemical transformation is the unavoidable related change in the mechanical properties of the composite system. Following thermal modification, all forms of mechanical strength changed, but the rate and magnitude of change differed between these (Figures 5.33 and 5.34). Evidently, different mechanisms, polymers or structures were involved in the degree of retention of each property. However, these factors appear to be unaffected by the species, because the relative-to-control behaviour was similar for most properties in the three species studied (except for hardness). This indicates that the underlying mechanisms for property change are in general the same regardless of initial density, thermal properties or chemical composition of the wood material.

Table 5.18 shows a summary of the findings for the mechanical testing as well as the most important factors thought to be involved in the changes in each mechanical strength parameter. The results show that some mechanical properties of the material are very sensitive to the thermal processing. At equivalent levels of WL, changes in the relative-to-control strength were in the order (from most to least): I ≥ MW ≥ TW > R ≥ SSML > MOR > SSLP > RLP > S > H > MOE > CE > CA in each species. No differences in the mechanical behaviour were found when comparing the three species at equivalent levels of WL, except for hardness in beech, which was more reduced than MOR. The rate of change in relative to control values was generally the same between softwoods and beech, beech performing somewhat better at WL > 8%.

Parameters less reduced by the modification were those related to compression strength and elasticity, which are proposed to be more related to changes in wood density and cellulose crystallinity. Conversely, the strength parameters more affected are those related with the energy required to cause failure or deformation, which are proposed to be more related to changes in the chemical composition, particularly to the increase in lignin at the expense of the reduction in hemicelluloses, and also due to physical changes in the cell wall material and residual stresses derived from the change in mass. The property most affect was IS in beech, most of the reduction occurring before the WL reached 4%.

At equivalent levels of WL, properties at maximum load in bending (MOR, WML and SSML) showed the smallest variability, whereas properties with the largest variability were generally those at limit of proportionality, particularly resilience (R). Shear strength also showed variability in softwoods, as did hardness in beech.

Table 5.18 Summary for the results of mechanical testing on heat-treated beech, Scots pine and Norway spruce woods. Properties are listed from the least to the most changed by the heat-treatment.

Property[a]	Species	Significant reduction at WL (%)	% Change at 8% WL[b]	% Change at 12% WL[b]	Factors involved with strength: Retention	Loss
CA	beech[c]	NR[d]	17.5	18.0	Reduced EMC	ND reduction
	pine	27.2	11.0	10.0		
	spruce[c]	30.6	11.7	10.9		
CE	beech	NR	12.2	10.6	Reduced EMC	ND reduction
	pine	NR	11.4	10.3		
	spruce	30.3	7.4	3.7		
MOE_{CE}	beech	25.0	-5.8	-8.2	Increase in cellulose crystallinity	ND reduction, cellulose DP reduction
	pine	NR	26.5	25.9		
	spruce	NR	3.5	0.9		
MOE_{CA}	beech	25.3	-1.0	-3.9	Increase in cellulose crystallinity	ND reduction, cellulose DP reduction
	pine	27.2	1.1	-1.9		
	spruce[c]	30.6	14.4	11.4		
MOE	beech	23.2	-5.2	-3.7	Increase in cellulose crystallinity	ND reduction, cellulose DP reduction
	pine	20.4	3.5	-0.7		
	spruce	15.3	1.1	-3.3		
H[e]	beech	5.5	-24.5	-34.4		ND reduction in all three species. GluXylan degradation in Beech
	pine	NR	-8.0	-12.7		
	spruce	17.5	-11.5	-16.3		
S	beech	20.1	-0.6	-7.3		ND and EMC reduction in all 3 woods. Differential chemical degradation at EW-LW interface in spruce
	pine	8.4	-14.1	-18.5		
	spruce	4.5	-16.7	-22.4		
RLP	beech	6.0	-13.3	-19.5		Increase in cellulose crystallinity; cross-linking in lignin
	pine	12.8	-8.3	-17.0		
	spruce	5.0	-11.3	-22.3		
SSLP	beech	3.8	-17.2	-24.4		Increase in cellulose crystallinity; cross-linking in lignin
	pine	10.6	-11.7	-21.3		
	spruce	5.0	-14.1	-25.8		
MOR	beech	3.8	-21.3	-30.7		Chemical degradation; densification of the cell wall; increase in cellulose crystalinity
	pine	3.8	-22.9	-35.3		
	spruce	8.7	-18.7	-31.4		
SSML	beech	3.8	-24.5	-34.6		Chemical degradation; densification of the cell wall
	pine	3.8	-25.5	-38.5		
	spruce	5.0	-21.1	-34.4		
R	beech	3.8	-34.2	-42.0		Increase in cellulose crystallinity; cross-linking in lignin
	pine	12.8	-19.6	-31.9		
	spruce	5.0	-32.4	-46.0		
TW	beech	3.8	-57.1	-70.6		Changes in WML
	pine	3.8	-59.3	-74.9		
	spruce	3.4	-56.1	-72.8		
WML	beech	2.8	-59.4	-70.9		Chemical degradation; densification of the cell wall; reduced EMC; increase in compression strength
	pine	2.7	-62.1	-74.9		
	spruce	3.4	-53.6	-70.6		
IS	beech	3.0	-65.4	-73.9		Residual thermal and mechanical stresses; differential chemical degradation; reduced EMC
	pine	2.2	-60.9	-72.5		
	spruce	4.0	-56.7	-71.7		

a) For abbreviations, see tables 5.1, 5.3 and 5.5

b) Calculated from models in Table 5.9

c) Significant increases were recorded for these parameters

d) NR = no significant reduction registered for any treatment

e) Different behavior was found in Beech and softwoods in this property

Two remarkable mechanical characteristics of TMW advantageous to construction and other housing application determined in this work were:

1. Modulus of elasticity is not affected. Irrespective of the temperature and length of treatment, MOE is equivalent to that of untreated wood of the same SG when the WL is smaller than 20%. Unchanged elasticity means that TMW is suitable for applications where high stiffness is required (*e.g.* flooring and decking).

2. Strength properties are less affected at limit of proportionality than at maximum load. This means that the performance of TMW would be somewhat better within the elasticity range than the expected performance calculated from values at maximum load. This behaviour was more noticeable in pine than in spruce or beech.

Reduction in some forms of wood strength caused by heat was highly influenced by the susceptibility of its chemical constituents. Degradation of chemical constituents followed the order GluMan ≥ GluXylan >> Cellulose >> Lignin. The relationship between chemical changes and property change was complex. Material loss was not the sole indication that chemical degradation has occurred and strong correlations between all polymers and most forms of wood strength were found (except for CA). It was difficult to separate the confounding effect of the increase in lignin derived from the breakdown of hemicelluloses in order to resolve the real effect of the change of each chemical constituent in property change. Results show that hemicelluloses, particularly GluXylan in beech and lignin in all three species are more correlated to property change, but these empirical determinations are also influenced by the underlying relationship between WL and the GluXylan in beech or the lignin in the three species. Strength properties at maximum load (MOR, SSML and WML) showed in general a slightly larger relationship to chemical changes, whilst CA, CE, H and MOE exhibited the least. It could be established that changes in the amount of cellulose play a minor role in the change of properties at WL up to 12% - 15% (the likely maximum of practical interest). Although not determined in this work, indirect evidence indicates that the crystallization of *para*-crystalline and amorphous cellulose have a negative effect in IS and also in the plastic deformation required for the viscous flow of polymers to give large energy areas in the strain-stress plot. Therefore, the increase in cellulose crystallinity probably causes significant reduction in various mechanical strength parameters such as MOR, WML, TW, SSML and IS, and in particular, this increase may be the major responsible for the reduction of properties at the limit of proportionality (R, SSLP and RLP). On the other hand, by limiting the handling over of the stress, hemicellulose degradation probably plays a significant role in the reduction of MOR, WML, SSML and TW. Polysaccharide crystallization and hemicelluloses degradation bear minor importance in the reduction in other properties such as stiffness in bending (MOE) and in compression (MOE_{CA} and MOE_{CE}), CA and CE; the increase in crystallinity and the relative increase is lignin probably have a positive effect in these properties.

Weight loss (WL) was found to be a good indicator of the extent of the modification: in most cases, the rate of property change in each species was the same at equivalent levels of WL irrespective of the temperature of treatment (Table 5.6). The rate of property change with respect to WL was also generally the same in pine and spruce independent of the temperature of treatment, but the one for beech was consistently different, in most cases smaller than in softwoods. Levels of WL that resulted in significant changes of mechanical properties varied slightly from temperature to temperature. In spite of this, in many cases the analysis of covariance of the property change at equivalent levels of WL showed that this was statistically the same regardless of temperature of exposure.

The prediction of mechanical strength parameters of TMW from gravimetric determination (WL, ND and SG_{OD}), and from chemical constituents are presented for the first time (Table 5.9 and Table 5.10). Linear-regression modelling was successfully accomplished; all regressions gave highly significant models, with R^2 statistics between 0.15 and 0.93. The best predictor of the gravimetric parameters was WL, but this varied slightly depending on the property. The best predictions using WL were for SSML, WML and MOR, and the less efficient for CE in beech and H in pine and spruce; ND gave the best predictions for CA, MOE and CE in beech and pine, and S and H in pine (Table 5.9). The best strength predictor among the chemical constituents was lignin in softwoods and hemicelluloses and GluXylan in beech (Table 5.10). It is concluded that WL is better predictor of modified wood strength because this reflects not only changes in density, but also changes in chemical composition.

A novel approach was offered for the prediction with a single model of property change from a range of process parameters (temperature and time of exposure). This was carried out by using the concept of severity factor (Table 5.11).

Predictions from treatment parameters using non-linear regression were also successfully accomplished, with R^2 values between 0.38 and 0.98. It was shown that a single model for each strength property could be used to predict the residual strength in the range of temperatures and times of treatment used in the present study.

The prediction of some mechanical properties from other properties of simpler or amenable to non destructive determination was also successfully accomplished (Table 5.13). R^2 ranged from 0.25 to 0.96. MOR was the best predictor for most mechanical properties, closely followed by IS whilst MOE was invariably the less effective predictor of other forms of mechanical strength, although a very significant one, except for S in pine and H in spruce. The best predictions from MOE are for MOR and RLP in beech and pine and for MOR in spruce. It is proposed that the non-destructive evaluation of MOE is feasible for the prediction of all the mechanical strength parameters studied, although this parameter is less effective than WL for the prediction of MOR. However, the inclusion of the EMC into the model for the prediction of wood strength from MOE, improved significantly the prediction of most strength parameters tested (except for CE). This result highlights the potential commercial advantage that would result from predicting strength by using MOE and EMC determined by conventional non-destructive procedures, giving predictions at levels of significance comparable to, and in several instances greater than, any other estimator explored in the present study (WL, ND, SG_{OD}, chemical constituents).

The prediction of strength properties from impact strength may be also feasible at least at the laboratory scale, due to the small specimen required and the high significance of the predictions. A simple, fast method to correlate the >60-mesh fraction of cross-beater milled TMW with wood strength was conceived. It was found that this method produced highly significant models for the prediction of seven forms of mechanical strength and has the potential to become automated. However, this method was only explored for spruce, and further research is required in this respect.

Finally, the analysis of the mechanical behaviour of TMW included the first effort in the public domain for the determination of the index of performance taking into account nine of the most important strength parameters, as well as the ASE and an indirect measure of the potential decay resistance (PDR = 1/ARH) of TMW. This was also effectively accomplished using an empirical approach. A single score was needed in place of the eleven original variables with only a 17.7%, 25.4% and 21% loss of information for beech, pine and spruce, respectively. The analysis indicate that a neutral overall performance index (OPI) is achieved when the extent of the treatment is at a WL of about 11.6% for beech, and about 7.2% for softwoods. At higher WL, the reduction in mechanical strength is not compensated for by an extra gain in ASE and PDR, and for modifications at lower WL, the mechanical strength is reduced at debatable gain levels in ASE and PDR.

The fibrous, composite structure and the failure character of TMW are little changed for WL up to about 12% - 14% in softwoods and up to 16% - 18% in beech, regardless of the processing conditions. Depending on the species in question, TMW possesses higher strength as compared to that of some common untreated timbers, except probably for impact strength. TMW members still have strength values that give them high strength to weight ratio. The reduction in mechanical performance by no means makes the material worthless: for instance, beech wood modified at neutral OPI (at a WL to about 11.6%), with an ASE of about 49.6%, still has the stiffness of untreated beech, comparable toughness (WML) of untreated binuang (*Octomeles sumatrana*, ND = 0.352 kg·m^{-3}), the hardness of untreated mahogany (*Khaya ivorensis*), and higher MOR than untreated Douglas-fir.

Chapter 6 Wood-moisture relationships in thermally-modified wood

6.1 Introduction

Generally, it is undesirable to have materials that respond readily to different moisture stresses; such susceptibility has a considerable negative effect on the mechanical and other physical properties in wooden building components. In normal, untreated wood, most mechanical properties, with the possible exception of toughness, decrease as the wood substance adsorbs moisture in the hygroscopic range. Moreover, the risk for the onset of biological colonization augments as the moisture content in any woody material approaches its fiber saturation point. The wider usage of TMW beyond its traditional role as cladding material requires a deeper knowledge on the hygroscopicity as other building elements are exposed to varying moisture conditions. This scientific understanding is particularly required now as the variety of wood species being thermally-modified is steadily growing.

Heating of wood at elevated temperatures leads to the reduction of its moisture uptake under changing moisture conditions, this is well known (Stamm and Hansen 1937, Seborg *et al.* 1953, Mitchell *et al.* 1953, Keith and Chang 1978, Burmester 1981, Mitchell 1988, Mouras *et al.* 2002, Gonzâlez-Peña *et al.* 2004). Reduced hygroscopicity of thermally-modified wood (TMW) has collateral benefits, since other undesirable characteristics of the material are also changed. Examples of these are the improved dimensional stability and smaller movement in service in heated wood materials. These properties are thought to originate from the smaller space that the decreasing amount of adsorbed water occupies between adjacent wood polymers in the cell wall, and/or due to an increasingly stiffer polymeric matrix restraining the expansion of wood polymers upon water adsorption.

An important advantage of the improved dimensional stability in heated wood is the better performance of fasteners, joints and finishes. The reduced hygroscopicity of heated wood is also involved in the enhancement of its decay resistance, which is particularly useful for treating non-durable but refractory woods which are difficult to impregnate with preservatives or reactants for chemical modification (Wang and Cooper 2005).

Thermal treatment also leads to the reduction of another undesirable material property in woody materials, the anisotropy in swelling or shrinking (Keith and Chang, 1978; Tjeerdsma *et al.* 1998b, Bekhta and Niemz 2003, Popper *et al.* 2005). Anisotropy is the response to moisture changes in wood that accounts for undesirable shape changes such as diamonding and couping. This behaviour could detract from the usefulness of a wood product. The decreased difference between swelling in the radial and tangential planes results in reduced stresses in the heated wood material when exposed to varying climatic conditions, with the consequent improvement in performance (Tjeerdsma *et al.* 1998b).

The reasons for the reduction of hygroscopicity in TMW is still matter of discussion. Hygroscopicity changes have been ascribed mainly to chemical changes, either the reduction of hydroxyl groups in the three polymers via the decomposition of hygroscopic constituents (mostly hemicelluloses), and/or the cross-linking of wood polymers, mainly within the lignin component. According to Rowell *et al.* (2002, cited by Garcia *et al.* 2006), the reduction in hygroscopicity in TMW is due to the partial degradation of the carbohydrate fraction of the cell wall to simple sugars and furans, which polymerize under heating, leading to cross-linking. These authors contend that reduction in water uptake in the solid residue is also due to the increase in cellulose crystallinity, and to the migration of wood extractives towards the surface of treated materials. The increasingly hydrophobic character of wood surfaces in heated materials has been confirmed by several authors, notably by Pétrissans *et al.* (2003) and Hakkou *et al.* (2005).

However, the relationship between gravimetric chemical changes and moisture related properties of TMW has not been explored so far. This work aims to contribute in this line of study. On the other hand, isotherm modelling for thermally modified wood has been reported scantly to date by Obataya and coworkers (Obataya *et al.* 2000, 2002) and by Popper *et al.* (2005). Only one communication is available in the public domain in English for isotherm fitting for heated woods within a small range of treatment (González-Peña *et al.* 2004). Furthermore, no generalized model for predicting hygroscopicity from more easily measured predictors (*e.g.* EMC) exists. This was also a general purpose of the second part of the present study.

Although a general relationship exists between total shrinkage and movement, individual untreated woods can behave differently over the reduced range of moisture content associated with movement (Dinwoodie 2000); in TMW this relationship is unknown. The present study intends also to add towards this subject of knowledge. A description of the properties to be modelled is also given in order to conceptualise the changes occurring on the wood substrate.

6.2 Anti-swelling efficiency (ASE)

The treatment average ASE of the treated samples ranged between -2.02% and 69.6% for beech, from 3.22% to 62.2% in pine, and from -1.8% to 61.3% in spruce wood. This stabilisation was achieved for weight losses between 0.39 and 26.0%, 0.75 and 21.2%, and 1.15 and 21.4% for beech, pine and spruce respectively. Improvements in dimensional stability varied with the temperature and time of treatment: higher temperatures or longer treatment times led to higher values of ASE. However, no clear difference in ASE could be observed at equivalent levels of WL, irrespectively of the heating schedule. In some instances, treatments at higher temperatures gave marginally better values of ASE, although in Norway spruce the treatment at 210 °C gave slightly better results than the one at 230 °C.

ASE improved rectilinearly with respect to the heat-induced WL in a normal-$\log_{10}$ plot (Figure 6.1). The similarity in the changing profile at equivalent levels of WL in the three species is really noticeable. If data for WL $\geq$ 2% is considered, analysis of covariance revealed that there is no significant difference for the regression lines of the ASE on Ln WL between species (Species, $p = < 0.165$; Species*LnWL, $p = 0.236$, Type I sum of squares), and therefore a single model could be used to describe the relationship between ASE and Ln WL for the three species together. This finding is remarkable, in view of the very different chemical composition and anatomical make up of beech wood compared to those of softwoods. However, the present study was limited to three woods with similar, very large dimensional instability (see Table 3.2, chapter 3 Methods). It would be too optimistic to hypothesise that this is a universal behaviour in most wood species, and further work in this area appears to be justified. Nevertheless, in very early research, three softwoods were also found to have comparable levels of ASE at equivalent levels of treatment (Stamm *et al.* 1946).

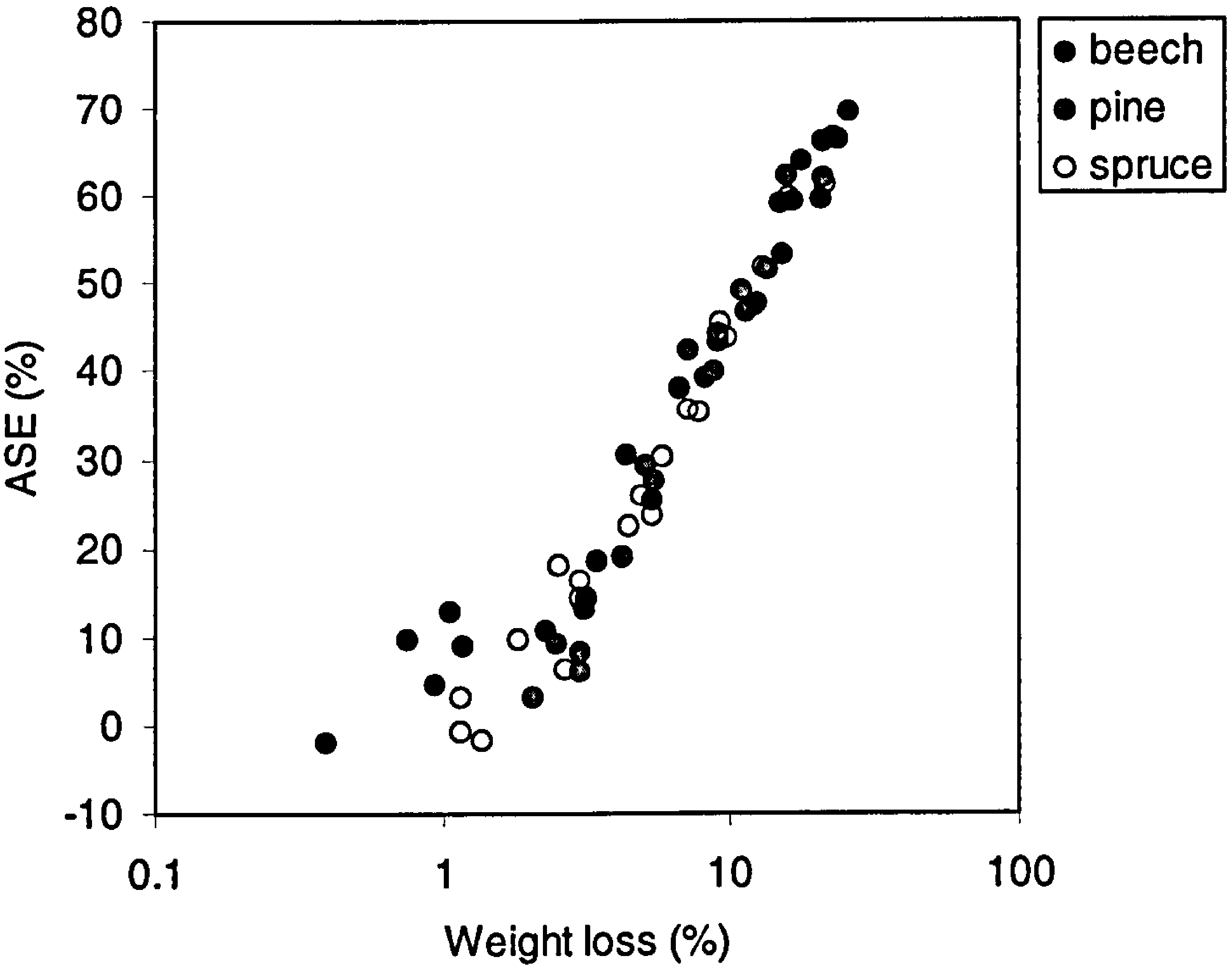


Figure 6.1 ASE of thermally-modified beech, Scots pine and Norway spruce woods in the range between 190 °C and 245 °C for up to 16 h. Average values per treatment are shown for clarity. Each symbol is the mean value of 10 replicate samples. Error bars omitted for clarity

At low levels of treatment, of WL from 0.4 to ~2%, little improvement in dimensional stability or even negative ASE was recorded (Figure 6.1). This could be explained by the release of growing and drying stresses and liberation of minute amounts of extractives and strongly sorbed water, which may cause a recordable WL which does not result in a decline in the swelling capacity of wood.

Above WL values of 1.5% – 2%, the rapid heat-induced degradation of the hemicelluloses and changes in less crystalline forms of cellulose leads to the substantial reduction of reactive hydroxyl groups, which in turn results in a less hygroscopic solid residue. This has been indirectly confirmed by the lower reactivity of heated wood towards esterification (Tjeerdsma and Militz 2005, Inari *et al.* 2007b). Moisture-induced changes in bond configuration of the non-crystalline regions of adjacent cellulose molecules and between cellulose microfibrils and polyoses decrease upon the absence of reactive hydroxyl sites, resulting in smaller amounts of swelling and shrinking of the cell wall material (Hillis 1984, González-

Peña and Hale 2007a). Other structural properties of the cell wall substance such as the increased stiffness of the material, reduced relaxation capability and lower accessible specific surface are probably implicated in the improved dimensional stability of TMW (González-Peña *et al.* 2005, Andersons *et al.* 2007). These properties likely reduce the ability of the cell wall to adapt to the strain caused by the expansion of the tissues in the course of the reaction of wood polymers with water: the resultant stiffer matrix limits the physical possibilities of wood polymers to expand. Even if it were possible for more water to be sorbed, no space is available for the water molecules to bind. This preposition is based on a similar phenomenon observed during wood esterification (Hill and Hillier 1999). Repellin and Guyonnet (2005) showed that the reduction of glucouranoxylan alone could not explain the reduction of FSP in heat-treated beech (the FSP was found to be strongly correlated with wood swelling). They argued that the removal of hemicelluloses upon heating probably disrupts the ultrastructural arrangement of the cell wall substance, reducing somehow the ability of the cell wall to adsorb moisture. Moreover, the major wood constituents differ in their shrinkage coefficients (Christensen and Kelsey 1958), and the resultant chemical make up of heated wood presumably also influences its total swelling and shrinkage capability.

The reason for an increasingly stiffer matrix has been ascribed to the presence of cross-linked substances in the solid residue, particularly arising from the lignin polymer (Tjeerdsma *et al.* 1998a). However, earlier research proved that the presence of ether bonds was unlikely the cause of the reduced swelling behaviour of heated wood, as this swelled to a comparable extent or more than untreated wood upon saturation with other liquids such as pyridine and NaOH (Seborg *et al.* 1953). But as noted elsewhere, the treatment schedules in that early research are severe compared to more recent treatment methods (Hill 2006c). Furthermore, other liquids may have access to cellulose fibrils with a higher degree of crystallinity; the pseudo-lignin resulting from wood heating is also readily soluble at room temperature in several solvents, so the increased swelling in other media does not necessarily demonstrate the absence of a cross-linked network within the lignin molecule. Thus, the cross-linkages in the lignin molecule upon repolymerisation cannot be excluded as at least a contributing factor to enhance the dimensional stability of heated wood. The appearance of these cross-linked structures arising from the isolated lignin polymer upon heating has however been challenged recently (Inari *et al.* 2007a).

6.3 *Hygroscopicity*

Wood is a hygroscopic porous material with a large amount of internal surface which contains sorption sites in the form of polar hydroxyl groups (Fan and Avramidis 1999). In the hygroscopic range, wood is capable of adsorbing and desorbing water molecules in response to changes in its surrounding atmospheric environment. The major factors influencing the moisture content of wood are temperature and relative humidity. Under normal service conditions, at temperatures below 50 °C, the sorption behaviour in wood is more affected by small changes in the surrounding relative humidity than by changes in temperature, particularly at the extremes of the hygroscopic range (Tsoumis 1991). Furthermore, differences exist between species, but they are revealed mainly at high relative humidity conditions. A review of the fundamentals of hygroscopicity is given by Tsoumis (1991). For hygroscopicity tests, samples were cut out from the same specimens for the ASE tests (see chapter 3 Methods.). This was to ensure that residual stresses from the treatment had largely disappeared because the first adsorption cycle from heat-treated wood always gives lower EMC than untreated material compared to subsequent sorption cycles (Keith and Chang 1978). Additionally, steps were taken to ensure that specimens for all the containers with saturated solutions were axially matched samples to eliminate bias due to within-sample variations.

6.3.1 *Sorption isotherms*

The sorption isotherm depicts the graphical representation of the moisture content as a function of relative humidity at a constant temperature (Skaar 1972, 1988). From the molecular point of view, untreated woods are characterised by the sigmoid shape of the type II sorption isotherms (Stamm 1964, Skaar 1988, Siau 1995, Sing 1998). The behaviour of the adsorption isotherms was alike for all the heat-treated species: this was sigmoid, type II in nature. This suggests that a similar sorption mechanism is involved in both untreated and modified woods. As an example, Figure 6.2 shows the adsorption isotherm for the three wood species treated at 210 °C. The desorption isotherm was also sigmoid, but this changed to a nearly rectilinear profile as the severity of the treatment increased (Figure 6.3).

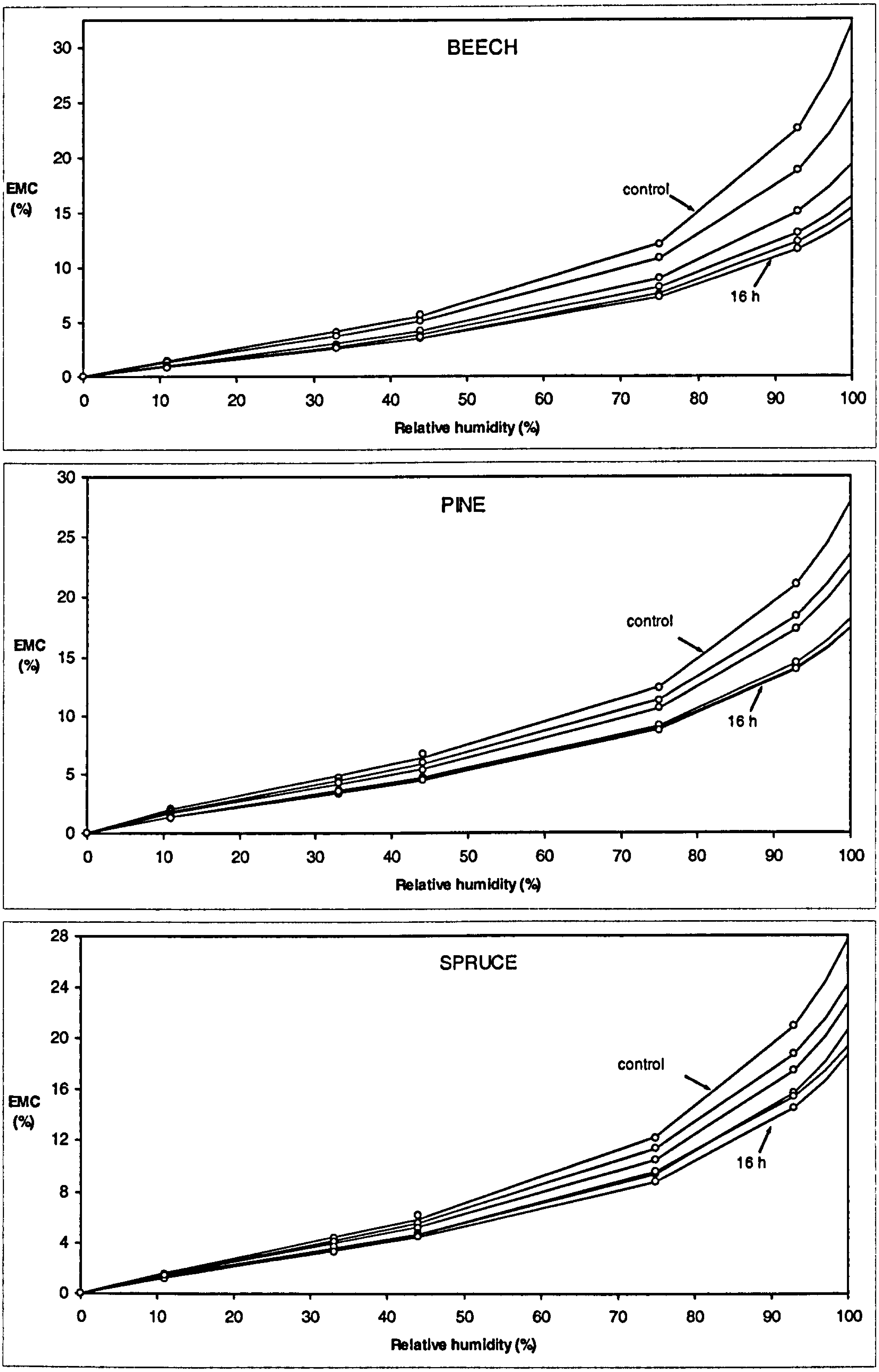


Figure 6.2 Modelled adsorption isotherms using a single-hydrate form of the Hailwood-Horrobin model for control and heat-treated specimens at 210 °C for 0.3, 1, 4 ,8 and 16 h of beech, Scots pine and Norway spruce woods. Symbols are for the experimental data; lines are for the modelled isotherms. Each symbol is the mean value of 4 replicates.

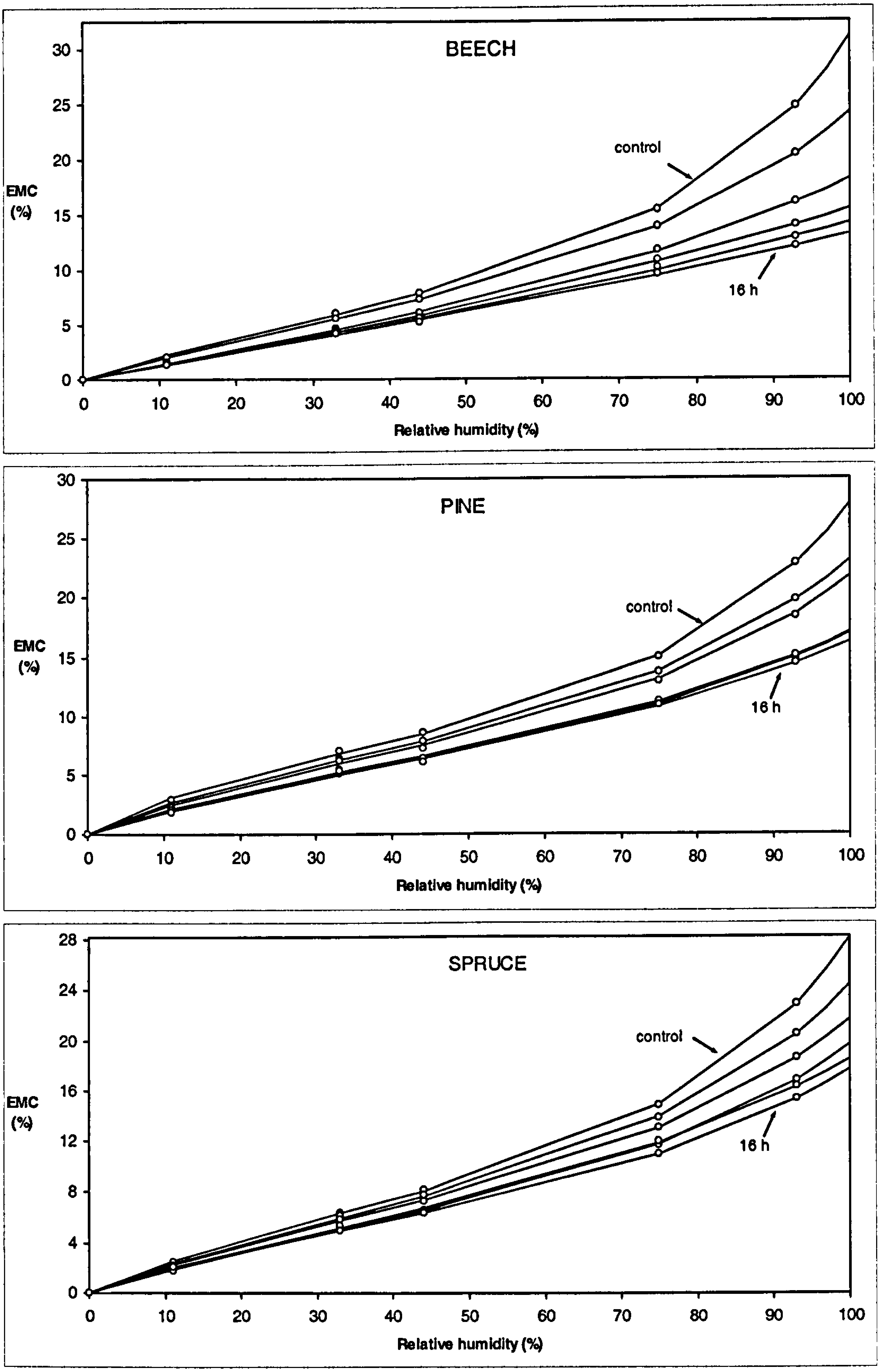


Figure 6.3 Modelled desorption isotherms using a single-hydrate form of the Hailwood-Horrobin model for control and heat-treated specimens at 210 °C for 0.3, 1, 4 ,8 and 16 h of beech, Scots pine and Norway spruce woods. Symbols are for the experimental data; lines are for the modelled isotherms. Each symbol is the mean value of 4 replicates.

The mean equilibrium moisture content (EMC) values (from four replicate samples) at each RH for twenty treatments plus control samples, for the three species studied are given in Table 6.1, for a full sorption-desorption cycle. The moisture uptake of heat-treated samples at various ambient humidity conditions, either in adsorption or desorption cycle, was smaller than untreated controls in all cases, attesting for the reduced affinity of heated woods towards water vapour. This concurs with findings from previous reports (Tjeerdsma *et al.* 1998 and references given therein).

The EMC reached during adsorption was smaller than for desorption at the same relative humidity, although this difference decreased towards both extremes of the isotherm irrespective of the treatment. In untreated beech wood, sorption hysteresis went from less than 0.6 % EMC at 11% RH to 3.2% at 75% RH, and then decreased to 2.2% at 92% RH (Table 6.1). A similar parabolic hysteresis profile was found for heated beech samples, and also for untreated and modified softwoods. The primary mechanisms for the occurrence of hysteresis appear not to be changed substantially by the chemical modification caused by wood heating. The main effect of the thermal treatment in this regard was the reduction of sorption hysteresis, although this differed according to the RH of exposure. In all cases, the hysteresis decreased along the heat-induced WL, but the reduction occurred at a faster rate at higher RH conditions. This trend was common to all the three species described. The steady reduction of hysteresis in line with the treatment was not unexpected, since it is believed that this phenomenon is closely related to the presence of free hydroxyls groups in the wood substance. These groups link between wood polymers when there is no moisture or very little moisture in wood, and that during the adsorption that follows, there is a smaller number of available hydroxyl groups for reaction with water vapour (Skaar 1979).

Table 6.1 Experimental EMC values (n=4) at five levels of relative humidity produced over saturated salt solutions for control (untreated) and heat treated beech, Scots pine and Norway spruce woods.

Temp (°C)	time (h)	EMC (%) at 20 °C at a relative humidity of															ARH	WL (%)	EMC (%)
		11%			33%			44%			75%			93%					
		Ads.	Des.	Hys.	Ads.	Des.	Hys.	Ads.	Des.	Hys.	Ads.	Des.	Hys.	Ads.	Des.	Hys.			
Beech																			
Control		1.49	2.06	0.58	4.12	6.01	1.88	5.65	7.89	2.24	12.09	15.31	3.22	22.52	24.69	2.17	1.00	0.00	10.15
190	0.3	1.50	2.10	0.60	4.13	6.00	1.86	5.70	7.79	2.09	11.66	14.95	3.30	20.89	22.77	1.88	0.98	0.39	9.22
	1.0	1.57	2.10	0.53	3.84	5.62	1.78	5.36	7.34	1.98	11.04	14.10	3.07	19.40	21.05	1.65	0.94	0.94	8.35
	4.0	1.19	1.78	0.59	3.47	5.29	1.81	4.97	7.01	2.03	10.15	13.00	2.85	17.21	18.53	1.32	0.84	2.29	6.86
	8.0	1.19	1.84	0.65	3.41	5.12	1.71	4.48	6.56	2.08	9.74	12.69	2.95	16.57	17.73	1.16	0.81	3.42	6.59
	16.0	1.23	1.82	0.59	3.28	4.93	1.65	4.22	6.23	2.01	9.27	11.99	2.72	15.07	15.91	0.84	0.77	5.40	5.92
210	0.3	1.38	2.00	0.62	3.74	5.59	1.85	5.08	7.30	2.22	10.76	13.86	3.09	18.77	20.39	1.62	0.90	1.06	8.11
	1.0	0.99	1.56	0.57	2.98	4.67	1.69	4.22	6.05	1.83	8.99	11.69	2.71	15.03	16.00	0.97	0.73	4.38	5.57
	4.0	0.91	1.49	0.58	2.83	4.48	1.65	3.72	5.57	1.84	8.15	10.76	2.60	13.10	13.93	0.83	0.67	9.08	5.34
	8.0	0.81	1.45	0.65	2.66	4.25	1.60	3.57	5.22	1.65	7.55	10.08	2.54	12.23	12.87	0.63	0.62	12.31	5.21
	16.0	0.76	1.37	0.60	2.60	4.16	1.55	3.69	5.26	1.58	7.23	9.55	2.31	11.64	12.08	0.43	0.60	15.27	5.41
230	0.3	1.00	1.63	0.63	3.40	5.03	1.63	4.53	6.46	1.93	9.71	12.49	2.77	16.77	19.32	2.54	0.79	3.19	6.01
	1.0	0.84	1.41	0.58	2.48	3.92	1.45	3.59	5.28	1.69	6.93	9.24	2.30	11.29	11.66	0.37	0.60	14.91	4.92
	4.0	0.81	1.41	0.60	2.55	4.03	1.48	3.33	4.96	1.62	7.12	9.34	2.22	11.07	11.47	0.40	0.59	16.73	5.17
	8.0	1.06	1.63	0.57	2.58	4.01	1.44	3.55	5.13	1.58	7.23	9.31	2.08	10.91	11.33	0.42	0.62	17.66	5.28
	16.0	1.05	1.65	0.60	2.87	4.32	1.45	3.78	5.42	1.64	7.19	9.11	1.92	10.58	11.06	0.48	0.64	23.00	5.80
245	0.3	1.05	1.66	0.61	2.76	4.42	1.67	3.80	5.83	2.03	8.26	10.82	2.56	13.21	13.81	0.60	0.69	8.30	5.11
	1.0	0.77	1.50	0.72	2.48	3.95	1.48	3.42	5.02	1.60	7.06	8.99	1.93	10.57	10.98	0.40	0.58	21.08	5.96
	4.0	0.92	1.62	0.71	2.59	3.94	1.35	3.49	4.98	1.50	6.82	8.72	1.90	10.00	10.58	0.58	0.59	23.83	5.78
	16.0	0.93	1.62	0.68	2.82	4.35	1.53	3.53	5.01	1.48	6.83	8.60	1.77	9.88	10.40	0.52	0.61	26.01	6.18
Pine																			
Control		2.01	2.84	0.83	4.67	6.96	2.29	6.66	8.59	1.93	12.29	14.92	2.63	20.98	22.81	1.84	1.00	0.00	10.34
190	0.3	2.01	2.72	0.71	4.54	6.92	2.37	6.08	8.06	1.98	11.72	14.23	2.51	19.87	21.22	1.35	0.96	0.75	9.79
	1.0	1.61	2.43	0.82	4.51	6.58	2.07	6.08	7.89	1.81	11.63	14.08	2.46	19.07	20.44	1.37	0.91	1.18	9.30
	4.0	1.78	2.45	0.67	4.43	6.54	2.12	6.01	7.84	1.83	10.98	13.40	2.42	17.54	19.13	1.59	0.89	2.48	8.66
	8.0	1.58	2.32	0.73	3.88	6.20	2.32	5.57	7.52	1.95	10.82	13.15	2.34	17.30	18.43	1.13	0.84	3.02	8.39
	16.0	1.60	2.33	0.73	3.97	5.92	1.95	5.28	7.06	1.78	10.35	12.58	2.24	16.40	17.28	0.88	0.82	4.26	7.95
210	0.3	1.83	2.47	0.64	4.36	6.40	2.04	5.94	7.84	1.90	11.26	13.70	2.44	18.38	19.70	1.32	0.90	2.08	8.54
	1.0	1.61	2.26	0.65	4.22	6.18	1.96	5.35	7.23	1.88	10.58	12.94	2.36	17.26	18.30	1.04	0.84	3.11	7.74
	4.0	1.52	2.25	0.74	3.34	5.13	1.79	4.66	6.33	1.68	9.00	11.24	2.24	14.01	14.85	0.84	0.72	6.74	6.40
	8.0	1.41	2.02	0.61	3.59	5.39	1.80	4.66	6.40	1.74	9.14	11.27	2.13	14.43	15.03	0.61	0.72	7.16	6.33
	16.0	1.22	1.77	0.55	3.55	5.32	1.77	4.48	6.09	1.61	8.72	10.92	2.20	13.87	14.43	0.56	0.69	8.83	6.09
230	0.3	1.57	2.20	0.63	3.98	6.02	2.04	5.36	7.16	1.80	10.54	12.83	2.29	17.37	18.38	1.01	0.83	3.02	7.68
	1.0	1.63	2.32	0.69	3.86	5.81	1.95	5.31	7.10	1.79	9.85	12.08	2.23	15.86	16.77	0.90	0.80	5.08	7.17
	4.0	1.45	2.08	0.63	3.34	5.07	1.74	4.43	6.13	1.69	8.73	10.77	2.04	13.34	14.07	0.73	0.70	9.19	5.95
	8.0	1.19	1.84	0.65	3.33	5.00	1.67	4.35	5.93	1.58	8.16	10.17	2.02	12.59	12.96	0.37	0.65	11.33	5.77
	16.0	1.15	1.72	0.57	3.29	4.90	1.61	4.33	5.88	1.55	8.04	10.02	1.98	12.00	12.34	0.34	0.64	13.46	5.67
245	0.3	1.29	1.97	0.68	3.82	5.80	1.98	4.76	6.52	1.77	9.81	12.13	2.32	15.54	17.03	1.49	0.76	5.43	6.75
	1.0	1.22	1.83	0.62	3.20	4.88	1.68	4.10	5.64	1.54	7.85	9.88	2.04	12.67	13.20	0.53	0.64	10.96	5.52
	4.0	1.15	1.72	0.57	2.88	4.50	1.62	4.12	5.53	1.40	7.29	9.05	1.76	10.96	11.22	0.26	0.59	15.75	5.32
	8.0	1.38	1.90	0.51	2.86	4.25	1.39	4.16	5.60	1.44	7.48	9.19	1.71	10.54	10.91	0.37	0.61	20.60	5.51
	16.0	0.94	1.53	0.59	2.89	4.36	1.48	3.77	5.13	1.35	6.82	8.32	1.50	9.90	10.52	0.62	0.55	21.22	5.55
Spruce																			
Control		1.59	2.49	0.90	4.45	6.38	1.92	6.16	8.16	2.00	12.14	14.82	2.69	20.91	22.87	1.97	1.00	0.00	11.43
190	0.3	1.49	2.37	0.88	4.42	6.28	1.85	6.05	7.99	1.95	11.69	14.34	2.66	20.63	22.46	1.83	0.97	1.15	10.50
	1.0	1.75	2.42	0.67	4.31	6.03	1.72	5.97	7.97	2.00	11.27	13.92	2.65	19.15	20.94	1.79	0.96	1.37	9.73
	4.0	1.42	2.14	0.72	4.11	5.82	1.71	5.40	7.46	2.05	11.11	13.66	2.55	18.81	20.30	1.49	0.90	1.83	9.19
	8.0	1.47	2.11	0.64	4.16	5.83	1.67	5.55	7.53	1.98	11.09	13.57	2.47	17.90	19.23	1.33	0.90	2.65	8.94
	16.0	1.21	1.95	0.74	3.91	5.55	1.64	5.30	7.30	2.01	10.45	12.74	2.29	17.20	18.47	1.27	0.84	3.00	8.35
210	0.3	1.44	2.22	0.79	4.40	6.15	1.75	5.65	7.74	2.09	11.29	13.76	2.47	18.74	20.45	1.72	0.93	1.15	9.03
	1.0	1.52	2.21	0.69	4.15	5.88	1.73	5.25	7.26	2.01	10.46	12.99	2.52	17.43	18.53	1.11	0.88	2.51	8.29
	4.0	1.46	1.95	0.49	3.70	5.27	1.57	4.82	6.55	1.73	9.32	11.66	2.34	15.69	16.78	1.09	0.80	4.42	7.29
	8.0	1.16	1.80	0.64	3.70	5.39	1.68	4.73	6.55	1.82	9.56	11.87	2.31	15.38	16.24	0.86	0.77	5.37	7.11
	16.0	1.50	2.06	0.56	3.37	4.96	1.59	4.53	6.37	1.84	8.81	10.96	2.15	14.47	15.29	0.82	0.76	7.13	6.40
230	0.3	1.34	1.94	0.60	3.80	5.42	1.62	5.12	7.07	1.95	10.14	12.58	2.44	16.71	18.02	1.31	0.83	3.00	7.60
	1.0	1.18	1.85	0.67	3.54	5.18	1.65	4.90	6.75	1.86	9.51	11.71	2.20	15.64	16.57	0.93	0.78	4.96	6.77
	4.0	1.20	1.73	0.54	3.42	5.00	1.58	4.37	6.15	1.78	8.32	10.42	2.10	14.25	14.94	0.69	0.72	7.86	6.26
	8.0	1.00	1.58	0.58	3.00	4.50	1.50	3.85	5.57	1.72	7.76	9.80	2.04	12.59	13.32	0.73	0.64	9.84	5.79
	16.0	0.90	1.63	0.72	3.14	4.54	1.40	3.63	5.36	1.73	7.45	9.44	1.98	12.26	12.52	0.26	0.63	12.38	5.73
245	0.3	1.32	1.92	0.60	3.14	4.70	1.56	4.60	6.45	1.85	8.66	11.04	2.39	14.33	15.36	1.02	0.74	5.83	6.20
	1.0	0.92	1.59	0.66	3.31	4.73	1.42	3.99	5.61	1.62	8.06	10.10	2.05	13.09	13.65	0.56	0.66	9.27	5.55
	4.0	0.96	1.41	0.45	2.73	4.04	1.31	3.63	5.18	1.55	7.01	8.95	1.93	11.39	11.70	0.31	0.59	13.03	5.37
	8.0	1.02	1.55	0.53	2.75	4.15	1.40	3.52	4.98	1.46	6.90	8.60	1.70	10.33	10.78	0.44	0.58	16.02	5.27
	16.0	0.70	1.38	0.68	2.53	3.86	1.33	3.48	4.93	1.44	6.53	8.26	1.73	10.54	11.11	0.57	0.54	21.43	5.53

Ads. = adsorption; Des. = desorption; Hys. = Hysteresis; WL = weight loss; EMC equilibrium moisture content.

ARH = Average relative-to-control hygroscopicity in adsorption and desorption at five RH of exposure

The remaining hygroscopicity (in percent to untreated control) as a function of WL was fairly similar for each the adsorption and desorption cycles, although a slightly larger reduction for adsorption was found at WL levels > 10%, particularly in beech. Differences between softwoods and beech probably arise from the different anatomical and chemical composition. In general, an average value of the EMC at the 5 RH condition tested was found accurate enough in practical terms as a measure of the treatment efficacy in the three species. This average relative-to-control hygroscopicity (ARH) in dependence of the WL was reduced at remarkably similar rates in the three woods (Figure 6.4), although the reduction was slightly larger in beech than in softwoods at equivalent levels of WL. In all cases, the maximum hygroscopicity reduction appears to be of around 45%, at WL levels ≥ 20%.

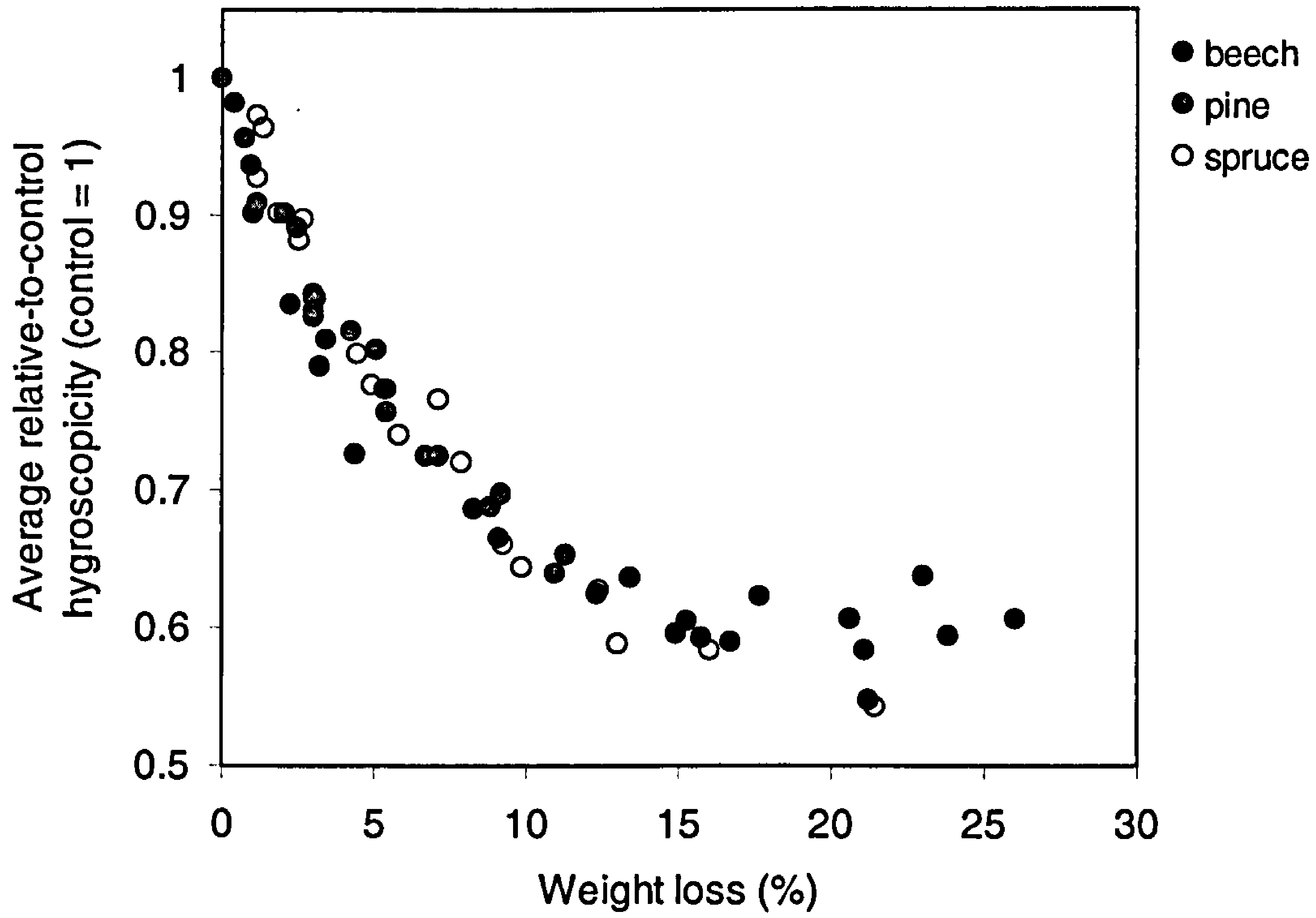


Figure 6.4 ARH in heat treated beech, Scots pine and Norway spruce woods. Each point is the mean value of four sample replicates

The relatively lower EMC values obtained from heated woods as compared to untreated samples may be accounted for by the heat-induced chemical changes in the wood substrate. The major constituents of wood have been listed in the following order of decreasing moisture adsorptivity (Christensen and Kelsey 1958): hemicelluloses, cellulose and lignin. The differences reflect the lower concentration of hydrophilic groups in lignin as opposite to carbohydrates, and the presence of non-reactive crystalline cellulose, compared to the amorphous nature of the hemicelluloses. Since moisture is adsorbed largely in the amorphous polymers that compose the cell wall, the moisture adsorbed is inversely related to the presence of these substances. Thus, the effect of the heat treatment on the hygroscopicity of wood is closely related to the heat stability of these polymers, and to the chemical composition of the resultant product. As seen in Table 6.1, the reduction of hygroscopicity was noticeable from the milder treatments, and at any RH. This indicates that the most hydrophilic substances, namely hemicelluloses, were rapidly modified or decomposed, even at the lowest temperature of treatment (190 °C). The increasingly larger differences are probably due to the continuous breakdown of the hemicelluloses, as denoted by the increasing WL, and also to an incipient modification of the amorphous regions of cellulose. A larger content of the less hydrophilic lignin as wood decomposed is probably also entailed in the lower hygroscopicity shown in wood treated to higher severity regimes. This was confirmed by wet-chemistry analyses of the solid residue (see section 6.6 below).

The relationship between EMC values at five RH conditions in the adsorption and desorption and the heat-induced weight loss is shown graphically in Figures 6.5 and 6.6 respectively. Clearly, the reduction rate is very similar for the different RH conditions in each species, more in the adsorption than in the desorption part of the loop. The hygroscopicity is reduced steadily for any RH condition of exposure for WL of about 20%. This suggests that the primary sorption events are not modified by the chemical changes in the substrate or the breakdown of cell wall polymers. An exemption to this general behaviour is found when the modified woods were exposed to very high RH surroundings. Here, the hygroscopicity reduction occurs at a faster rate than at lower RH conditions as the WL increases. This is probably caused by physical rather than by chemical changes in the wood substance. The presence of a stiffer wood matrix likely impedes mechanically the reconfiguration and expansion of adjacent wood molecules to accommodate increasingly higher amounts of water molecules in the cell wall material. However, there is a tendency for the EMC to re-increase if the treatment leads to WL levels higher than 20%. This is probably because the further evaporation of wood polymers upon heat-treatment leads to an increasingly revealed internal sorption surface.

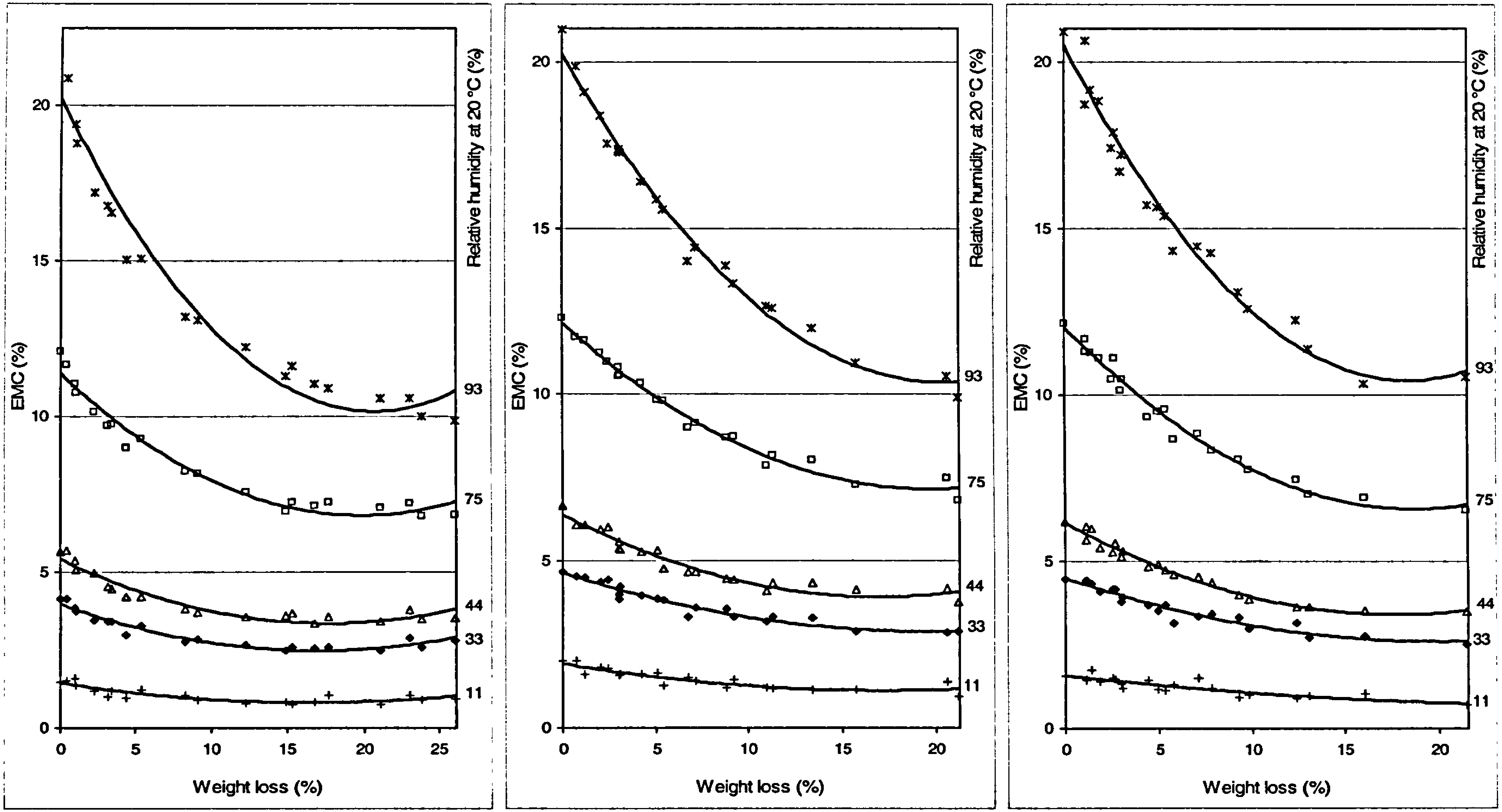


Figure 6.5. Equilibrium moisture content (EMC, %) of untreated and heat-treated beech, Scots pine and Norway spruce woods (from left to right) as a function of weight loss (WL, %) for five conditions of relative humidity in adsorption. Each symbol is the mean value of four replicates.

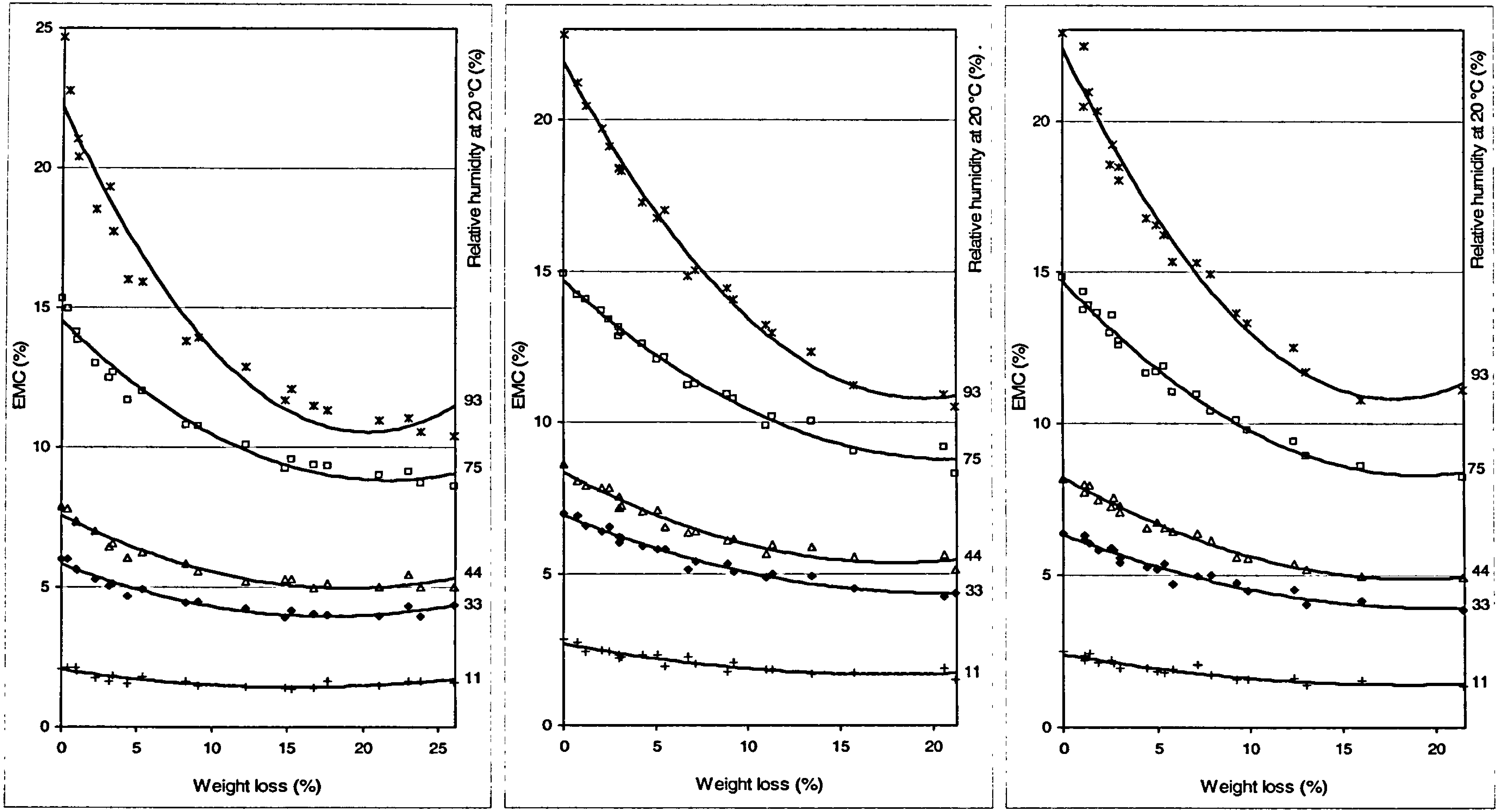


Figure 6.6 Equilibrium moisture content (EMC, %) of untreated and heat-treated beech, Scots pine and Norway spruce woods as a function of weight loss (WL, %) for five conditions of relative humidity in desorption. Each symbol is the mean value of four replicates.

Interestingly, untreated woods with lower hygroscopicity also exhibit its differences mainly at the upper extreme of the hygroscopic range. In a study of the hygroscopicity of 136 species at 30%, 60% and 90% RH at 25 °C, showed respective equilibrium differences between least and most hygroscopic woods of 3.3%, 5.4% and 11.5% (Tsoumis 1991). Thus, the increasingly hydrophobic TMW still possesses the sorption characteristics of untreated woods, although the underlying factors for these most likely differ between raw and heated woods.

According to Stamm (1964), the sorption surface area of wood is proportional to its moisture content at a RH of 30%. No salt solution employed in this work gave a RH of 30%, but if the data at 33% RH is used, it can be determined that the sorption surface is reduced to a similar extent in the three woods, curvilinearly to reach its minima at about 17% WL for beech wood and 20% for softwoods (Figure 6.7). According to this proposal the surface decreased roughly by 18% at 5% WL, and by 30% at a WL of 10%, yet the reason of this reduction is not completely clear at this time. A likely explanation is that the sorption surface was reduced due to heating because the porous matrix collapsed upon the volatilization of breakdown products, and/or due to the condensation and cross-liking of wood polymers leading to the irreversible densification of the cell wall substance.

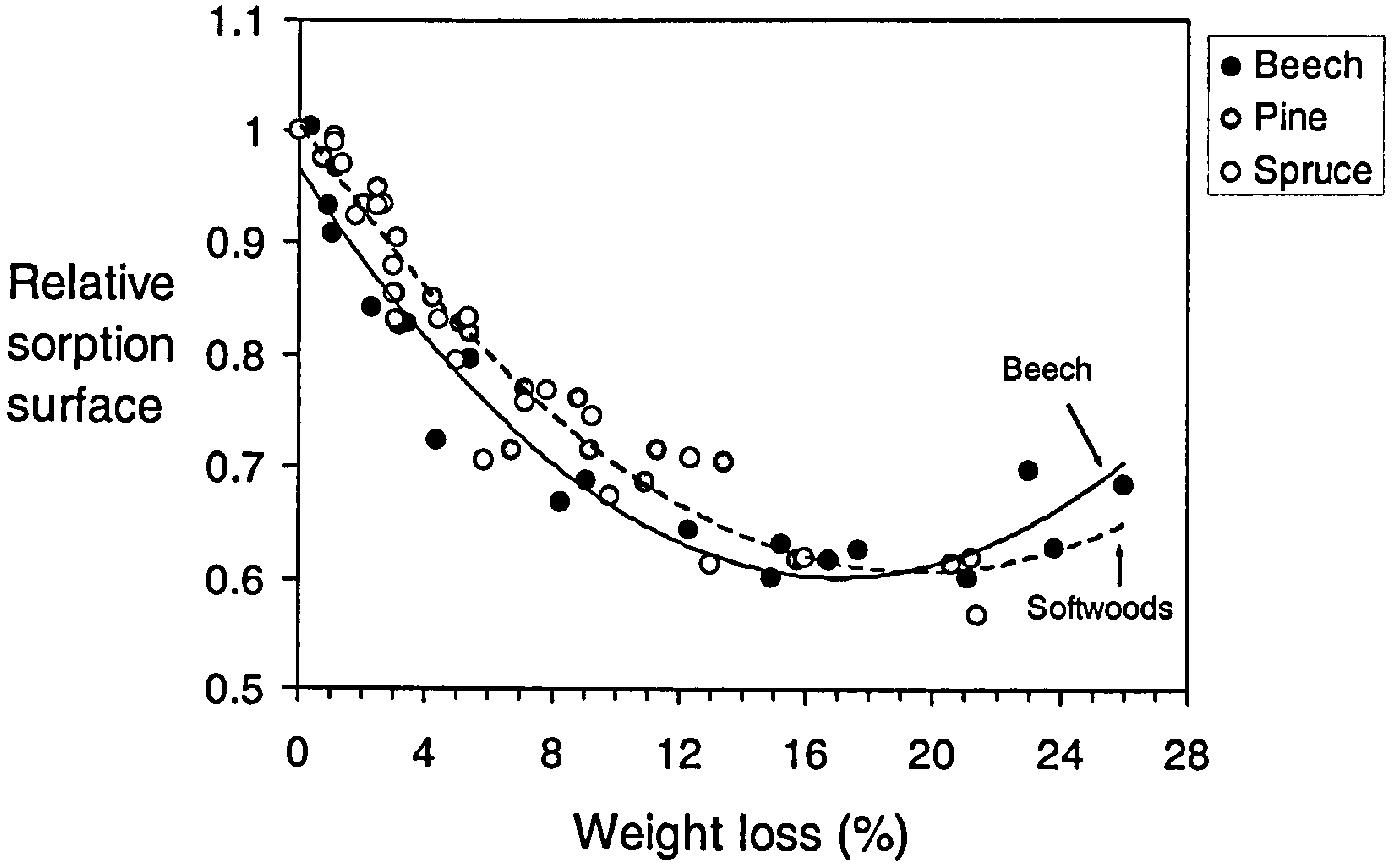


Figure 6.7 Relative sorption surface estimated from the an EMC of 33%.

Noteworthy is that the wood moisture uptake is related to the oven-dry mass of the treated specimen, but it would have been probably more rational to compare the hygroscopicity in terms of volume (considering water density ≈ 1 $\mathrm{kg{\cdot}m^{-3}}$) or in terms of the initial weight of the samples. This is because the heat-induced weight loss produces an apparent increase in EMC if the actual moisture uptake of the wood material were not changed. If the untreated weight were considered or the comparison were on a volumetric basis, the reduced hygroscopicity is still greater in the heated samples.

6.3.2 Isotherm fitting

In order to elucidate the possible differences in the sorption mechanism of untreated and heated samples, a single-hydrate model from the Hailwood-Horrobin (HH) theory of sorption was used to fit the adsorption isotherms. Among various models analyzed, the sorption behaviour of chemically modified wood has been found to be more appropriately described by the Hailwood-Horrobin theory (Papadopoulos *et al.* 2005). The HH theory assumes the water-polymer system to be a solution. Water adsorbed onto the polymer, M, at equilibrium with the relative pressure h, is assumed to exist in two states: water in solution with the polymer (dissolved water, M_s), and water combined with units of the polymer to form hydrates, M_h (Hailwood and Horrobin 1946). The theory is based on the equilibriums between polymer, hydrated polymer and the dissolved water, forming an ideal solid solution. There are two types of equilibria: one between the dissolved water and the water vapour of the surroundings, where K is the equilibrium constant, and n number of equilibria between the dissolved water and hydrates, designated with n equilibrium constants K_i ($i = 1...n$). A third fundamental constant, M_p, is defined as the molecular weight of the polymer unit that forms a hydrate. The model for the single-hydrate form is given by the equation 6.1:

$$M = \frac{1800}{\mathrm{M}_p}\left(\frac{Kh}{1-Kh} + \frac{K_1Kh}{1+K_1Kh}\right) \qquad \text{[Eq. 6.1]}$$

Where M, M_p, K, and h are as defined above, and K_1 is the equilibrium between the dissolved water and the first hydrate. The HH model for the relationship between M and h, was used to calculate the optimal values for the model parameters (M_p, K and K_1). These were obtained by minimizing the square deviations between experimental and model-predicted values using the non-linear iterative algorithm of Levenberg-Marquardt (SPSS 2002).

The fitting of the model worked quite well for adsorption and desorption isotherms of heat-treated woods (Figure 6.1, Table 6.2); all models have a coefficient of determination R^2 greater than 99.7%, confirming the sigmoid profile of the sorption isotherms. This suggests that the assumptions of the Hailwood-Horrobin theory of sorption still hold for modified wood materials; this also implies that the primary sorption mechanisms remain largely unchanged in heated woods compared to untreated controls. Calculations using the model parameters in Table 6.2 give a maximum M_h in adsorption of 3.53%, 4.22% and 3.94% for untreated beech, pine and spruce respectively. Papadopoulos and Hill (2003) have estimated that at least 8.6 mmol g^{-1} of OH groups per gram of dry wood exist in unmodified softwood. A moisture content of *ca.* 4% yields a value of 2.3 mmol g^{-1}, assuming that each molecule of hydrated water is associated with a primary sorption site in the polymer. It appears that the single-hydrate equation from the HH model underestimates the moisture content required for the complete combination of the polymer with water to form hydrates for both untreated and heat-treated wood.

However, the following deductions can be drawn from the results from the model: the constant K expresses the activity of dissolved water per unit relative vapour pressure, and its value should be unity if it has the same activity as liquid water (Okoh and Skaar 1980). The values for K vary between 0.66 and 0.85 in adsorption and from 0.24 to 0.73 in desorption, indicating that the dissolved water has lower activity than the liquid water in both untreated and heat-treated woods. This parameter generally decreases in line with the treatment severity. For heat-treated woods, the constant M_p, representing the molecular weight of the polymer substance necessary to associate with one molecular weight of water, exhibits a tendency to increase during adsorption as the temperature or the time of treatment increased. According to Spalt (1958), this effect implies that a lower proportion of sites are made available for water sorption. However, this trend was not as clear during desorption.

Table 6.2. Physical constants for the Hailwood-Horrobin model (K, K1 and M_p), maximum amounts of M_s and M_h (in % of the oven-dry weight), and fiber saturation point (FSP), for heat-treated beech, Scots pine and Norway spruce woods. Coefficients of determination (R^2) of the models are also given.

Temp.	time	Adsorption				Desorption				Maximum[a]		FSP[a]
(°C)	(h)	K	K1	Mp	R^2	K	K1	Mp	R^2	M_h	M_s	
Beech												
Control		0.8482	2.6304	352.48	0.999	0.7691	2.9100	232.57	0.999	3.53	28.53	32.1
190	0.3	0.8309	2.8817	352.72	0.999	0.7235	2.6466	213.34	0.999	3.60	25.08	28.7
	1.0	0.8242	2.8800	368.42	0.999	0.7085	2.5880	219.00	0.999	3.44	22.91	26.3
	4.0	0.7900	2.0000	352.03	0.999	0.6371	2.0500	194.65	0.999	3.13	19.24	22.4
	8.0	0.7980	2.0200	377.56	0.999	0.6187	1.8574	189.75	0.999	2.94	18.83	21.8
	16.0	0.7689	1.8410	367.32	0.999	0.5262	1.5422	156.59	0.999	2.87	16.30	19.2
210	0.3	0.8152	2.3790	362.21	0.999	0.6891	2.4394	211.34	0.999	3.28	21.92	25.2
	1.0	0.7737	1.5030	369.54	0.999	0.5539	1.3379	165.24	0.999	2.62	16.65	19.3
	4.0	0.7431	1.3408	373.40	0.999	0.4038	0.9632	111.70	0.999	2.41	13.94	16.3
	8.0	0.7516	1.5294	417.82	0.999	0.3671	0.9551	106.49	0.998	2.30	13.04	15.3
	16.0	0.7460	1.8143	437.14	0.999	0.3337	1.2262	107.98	0.999	2.37	12.09	14.5
230	0.3	0.8000	1.8638	374.48	0.999	0.7336	2.5940	259.84	0.999	2.88	19.23	22.1
	1.0	0.7623	2.1567	485.22	0.999	0.3193	1.2960	107.91	0.999	2.31	11.90	14.2
	4.0	0.7151	1.3492	399.63	0.999	NF[b]	NF	NF	NF	2.21	11.31	13.5
	8.0	0.7051	1.7503	401.91	0.999	0.2601	1.4536	91.46	0.999	2.47	10.71	13.2
	16.0	0.6886	2.3990	406.03	1.000	0.3385	2.6394	148.12	0.999	2.76	9.80	12.6
245	0.3	0.7425	1.3541	369.56	0.999	0.3586	1.0061	97.68	0.999	2.44	14.04	16.5
	1.0	0.6553	0.9865	329.60	0.999	0.2436	1.4684	88.53	0.999	2.14	10.38	12.5
	4.0	0.6687	1.7630	390.10	0.999	0.3607	2.3113	159.19	0.998	2.50	9.31	11.8
	16.0	0.6674	2.2092	403.31	0.999	0.4135	3.3787	204.79	0.997	2.66	8.96	11.6
Pine												
Control		0.8129	4.2673	330.80	0.999	0.7459	5.7494	242.31	0.999	4.22	23.64	27.9
190	0.3	0.8153	4.5260	354.31	0.999	0.7300	5.7920	247.41	0.999	4.00	22.43	26.4
	1.0	0.7814	3.1295	316.83	0.999	0.6974	4.2927	227.55	0.999	4.03	20.31	24.3
	4.0	0.7699	3.9067	334.81	0.999	0.6783	4.8097	232.09	0.999	4.03	17.99	22.0
	8.0	0.7615	2.5018	319.00	0.999	0.6588	4.0541	224.35	0.999	3.70	18.02	21.7
	16.0	0.7649	3.0390	345.39	0.999	0.6483	4.0940	232.05	0.999	3.64	16.96	20.6
210	0.3	0.7873	3.7639	339.74	0.999	0.6895	4.4880	231.38	0.999	3.96	19.61	23.6
	1.0	0.7877	3.5556	360.99	0.999	0.6797	4.2170	236.68	0.999	3.67	18.50	22.2
	4.0	0.7546	3.0294	389.28	0.999	0.6115	3.9150	242.51	0.999	3.22	14.22	17.4
	8.0	0.7639	3.1780	392.42	0.999	0.6015	3.6723	232.24	0.999	3.25	14.84	18.1
	16.0	0.7640	3.1500	408.51	0.999	0.5728	3.1756	220.36	0.998	3.11	14.26	17.4
230	0.3	0.7892	3.1651	358.43	0.999	0.6844	4.1182	242.50	0.999	3.59	18.80	22.4
	1.0	0.7785	3.8894	381.62	0.999	0.6553	4.7092	247.33	0.999	3.55	16.58	20.1
	4.0	0.7411	2.9100	388.72	0.999	0.5845	3.7529	237.46	0.999	3.16	13.26	16.4
	8.0	0.7381	3.0880	410.58	0.999	0.5158	3.3995	213.71	0.999	3.05	12.36	15.4
	16.0	0.7024	2.6837	378.29	0.999	0.3943	2.7368	157.10	0.999	3.11	11.23	14.3
245	0.3	0.7560	2.4070	346.98	0.999	0.6646	3.7045	244.56	0.998	3.35	16.07	19.4
	1.0	0.7798	3.7834	479.41	0.999	0.6112	4.1763	275.24	0.999	2.80	13.30	16.1
	4.0	0.7112	3.0411	431.09	0.999	0.4480	3.5338	209.77	0.999	2.86	10.28	13.1
	8.0	0.6575	2.7292	374.90	0.998	0.3271	3.0782	150.85	0.997	3.08	9.22	12.3
	16.0	0.6668	2.5858	409.40	0.999	0.4844	3.9566	250.23	0.999	2.78	8.80	11.6

[a] Calculated using the adsorption models

[b] NF = not fitted

Continued over...

Table 6.2 Physical constants for the Hailwood-Horrobin model (K, K1 and M_p), maximum amounts of M_s and M_h (in % of the oven-dry weight), and fiber saturation point (FSP), for heat-treated beech, Scots pine and Norway spruce woods. (*Concluded*).

Temp. (°C)	time (h)	Adsorption				Desorption				Maximum[a]		FSP[a]
		K	K1	Mp	R^2	K	K1	Mp	R^2	M_h	M_s	
Spruce												
Control		0.8093	2.9410	321.52	0.999	0.7486	4.2210	239.33	0.999	3.94	23.76	27.7
190	0.3	0.8225	3.3548	347.17	0.999	0.7570	4.4620	251.87	0.999	3.81	24.03	27.8
	1.0	0.8087	3.9199	355.71	0.999	0.7248	4.2130	241.71	0.999	3.85	21.39	25.2
	4.0	0.8000	2.6278	341.56	0.999	0.7100	3.3315	233.46	0.999	3.57	21.08	24.7
	8.0	0.7667	2.4687	314.13	0.999	0.6523	2.8339	203.68	0.999	3.75	18.83	22.6
	16.0	0.7735	2.3477	334.41	0.999	0.6724	3.1632	228.00	0.999	3.47	18.38	21.9
210	0.3	0.7879	2.8664	328.81	0.999	0.7106	3.8768	235.24	0.999	3.79	20.34	24.1
	1.0	0.7980	3.4835	371.91	0.999	0.6770	3.7362	233.42	0.999	3.56	19.12	22.7
	4.0	0.8066	4.0599	431.17	0.999	0.6826	3.7340	262.23	0.999	3.20	17.41	20.6
	8.0	0.7622	2.3774	358.65	0.999	0.6071	2.7273	210.93	0.999	3.23	16.09	19.3
	16.0	0.7960	3.9075	446.80	0.999	0.6579	4.0911	269.68	0.999	3.05	15.72	18.8
230	0.3	0.7821	2.6761	358.68	0.999	0.6627	2.9664	225.31	0.999	3.40	18.01	21.4
	1.0	0.7719	2.5129	371.95	0.999	0.6477	3.1517	236.15	0.999	3.19	16.38	19.6
	4.0	0.8116	4.1632	485.51	0.999	0.6686	4.1543	286.06	0.999	2.86	15.97	18.8
	8.0	0.7720	2.6065	457.27	0.999	0.6006	3.0137	255.89	0.999	2.63	13.33	16.0
	16.0	0.7855	3.0958	500.28	0.998	0.5844	3.4287	264.57	0.999	2.55	13.18	15.7
245	0.3	0.7889	3.1860	434.27	0.999	0.6325	3.1243	243.51	0.998	2.97	15.49	18.5
	1.0	0.7715	2.7160	440.47	0.999	0.5975	2.9744	246.97	0.999	2.77	13.80	16.6
	4.0	0.7744	2.9934	515.24	0.999	0.5099	2.3761	220.26	0.999	2.44	11.99	14.4
	8.0	0.7130	2.5445	452.00	0.999	0.4768	3.0674	228.58	0.999	2.57	9.89	12.5
	16.0	0.7522	2.3512	505.09	0.999	0.5777	3.2210	291.34	0.999	2.28	10.82	13.1

[a] Calculated using the adsorption models

The trend observed for the physical constants K, K_1, and M_p obtained in this study were found to be in line and of the same order of magnitude with those previously reported by Spalt (1958) and by Papadopoulos and Hill (2003) for esterified wood, and for González-Peña *et al.* (2004) for heat-treated woods.

TMW always gave lower M_h and M_s in adsorption than untreated wood, when it was calculated using the parameters of Table 1 (Figure 6.8).

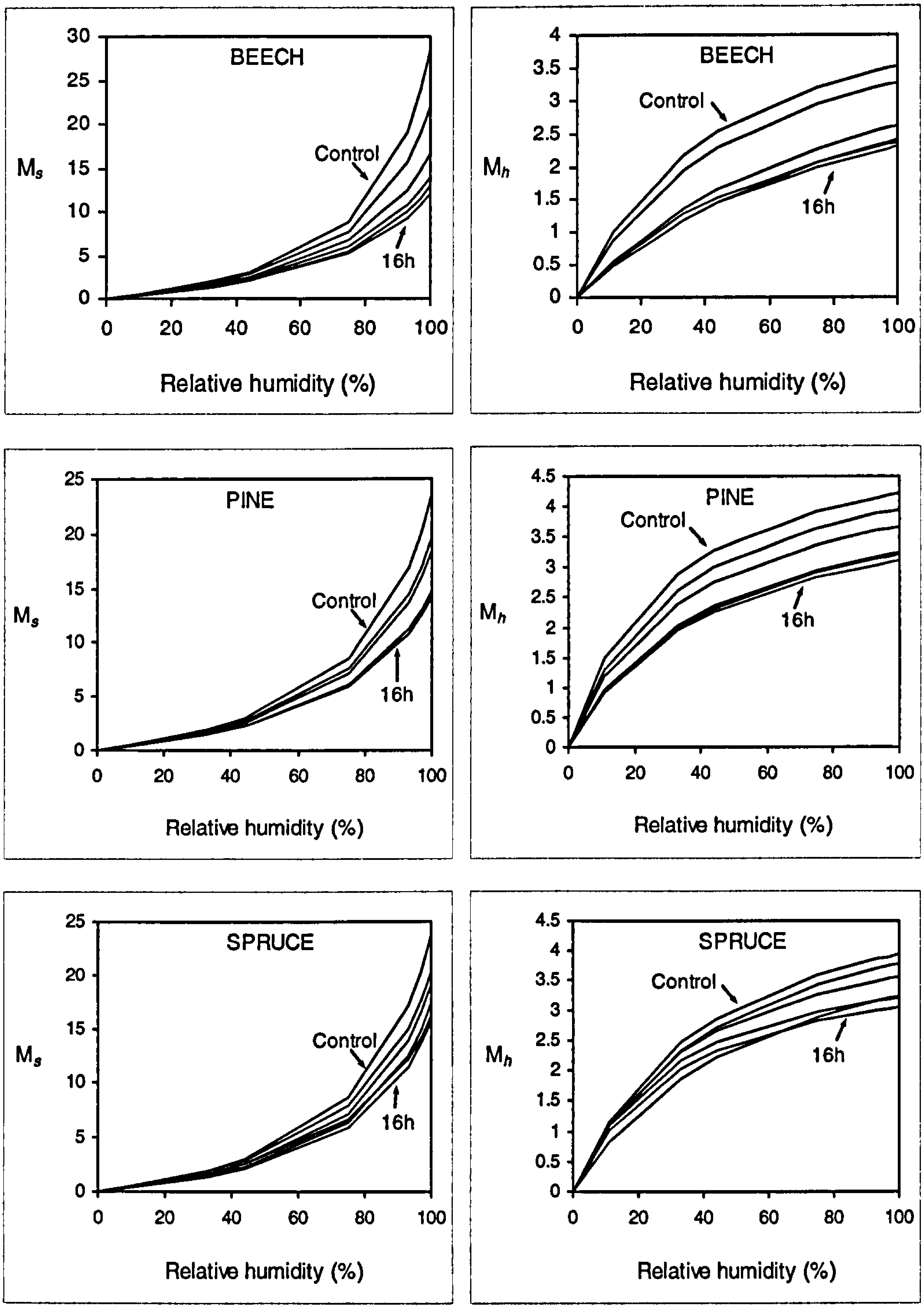


Figure 6.8 Dissolved water M_s and water forming hydrates M_h in % of the oven-dry weight, in the cell wall of heat-treated beech, Scots pine and Norway spruce woods (from top to bottom). Untreated samples and wood treated at 210 °C for 0.3, 1, 4, 8 and 16 h are shown

An analysis of the sorbed water in dependence of the WL shows that water forming hydrates calculated from the HH model, M_h, experienced a fast reduction irrespective of the species, and remained somewhat constant at values around 60% of untreated samples at any exposure humidity for WL above 4% (Figure 6.9). This suggests that the more readily accessible OH groups were rapidly reduced, and that the further chemical breakdown had little influence on the more strongly chemisorbed water. In contrast, the dissolved water, M_s, was steadily reduced in line with the heat-induced weight loss, and the reduction was greater at higher RH exposure conditions. Thus, the difference in the way water was adsorbed in the untreated and heated samples was dictated by the amount of dissolved water held.

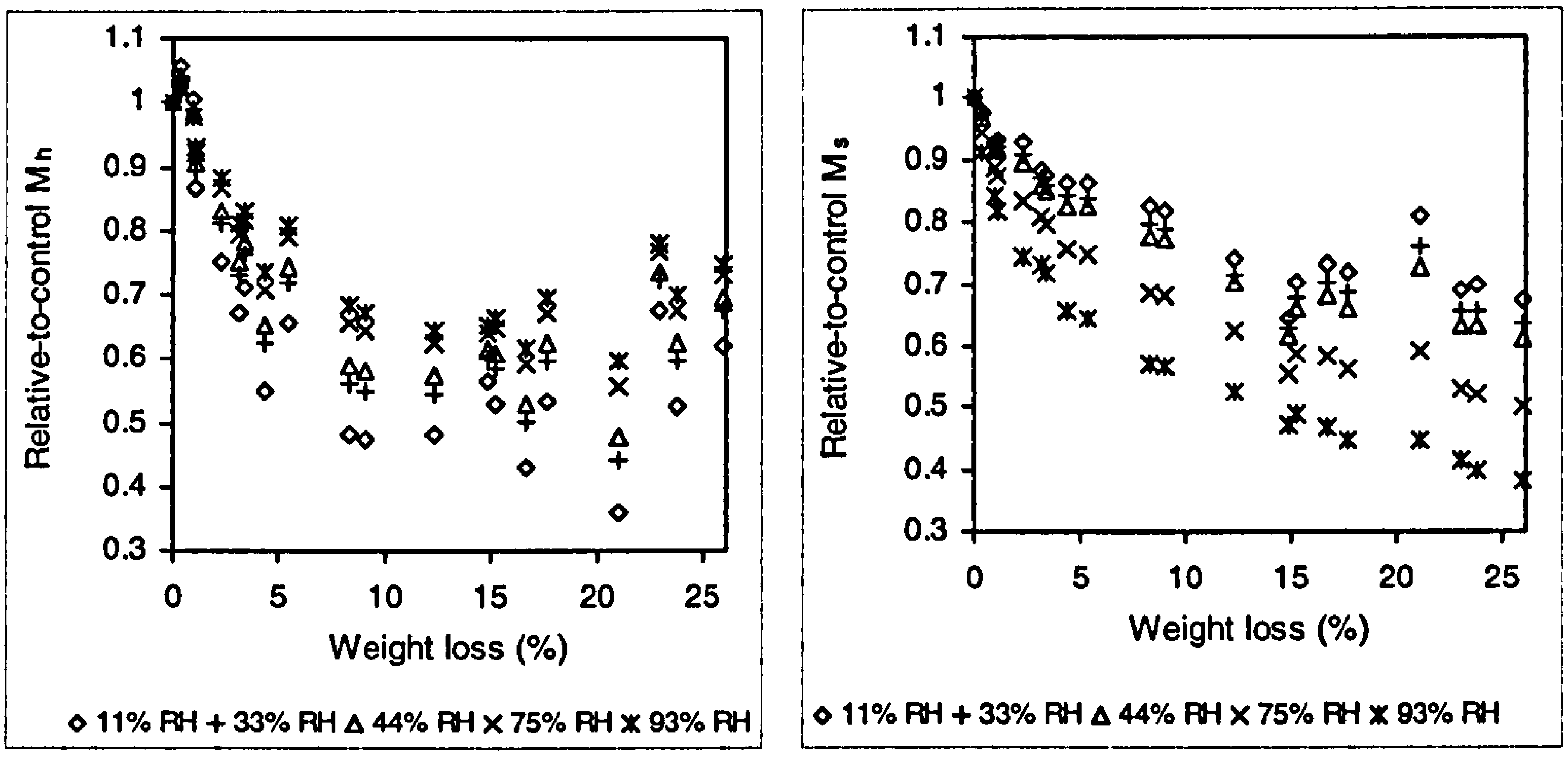


Figure 6.9. Relative-to-control M_h and M_s *vs*. WL at five levels of RH in heated beech wood

The fiber saturation point included in Table 6.2 was calculated from the HH model for a *h* value of 1. As anticipated, the FSP decreases with the extent of the treatment. The reduction (in relative-to-control values) in dependence of the WL, was faster in beech than in softwoods for WL up to about 15%. In pine and spruce the rate of reduction was nearly identical. The decrease in FSP is also related to the chemical breakdown of wood polymers in the cell wall material. If the lower resultant density in heated material is considered, it is concluded that the reduction in FSP is greater than the calculated by simply calculating the EMC at 100% RH. This is because the FSP in untreated woods decreases *per se* as the density increases (Walker *et al.* 1993).

6.4 Movement

Dimensional changes occur to a smaller extent than from the saturation to the oven-dry condition in TMW in service at moisture contents below the FSP when the humidity of the surroundings varies. These changes occur seasonally and frequently also on a daily basis, and are commonly referred as to movement (Dinwoodie 2000). Movement in heat-treated wood is considerably smaller than the dimensional variation measured in the ASE test. However, these changes can result in micro-checking, loosening of furniture parts and gaps in strip linings. As indicated above, movement in service is also in great part responsible for the performance of wood finishes. Although a general relationship exists between total shrinkage and movement, individual untreated woods can behave differently over the reduced range of moisture content associated with movement (Dinwoodie 2000); in TMW this relationship has not yet been described.

Movement in untreated wood is customarily measured as the dimensional change (in %) between wood conditioned at 90% RH and at 60% RH at 20 °C (Dinwoodie 2000). However, in this work this was measured almost all along the hygroscopic range (*i.e.* from 0% to 93% RH at 20 °C) (see chapter 3, Methods). In relatively large wood members, where reaching the EMC is practically difficult, swelling and shrinking take place about simultaneously in different depths of the wood. Thus, it is perhaps impractical to define movement in both directions of the hygroscopic cycle. Movement in this work was measured only for samples at the end of the desorption process (see chapter 3, Methods); therefore these determinations are likely to be the maximum movement that could be expected in the TMW. Table 6.3 shows the result of the volumetric movement measurement in three heated woods, from the volume attained at five relative humidity conditions at 20 °C to the oven-dry condition. Movement from the volume at 93% RH to that at 44% RH is also given. Movement between all other RH environments can be computed by simple difference. The results for movement at each transversal direction (radial and tangential) for the same exposure conditions are given in Appendix 3.

Table 6.3. Volumetric movement in small samples of thermally modified beech, Scots pine and Norway spruce woods.

Temp. (°C)	time (h)	Volume increase in terms of the oven-dry volume (%) at 20 °C at RH					Volumetric movement between 93% and 44% RH
		11%	33%	44%	75%	93%	
Beech							
Control		1.77	4.30	5.60	10.40	16.82	11.22
190	0.3	1.94	4.28	5.51	10.52	16.46	10.95
	1.0	1.72	3.76	5.23	9.45	14.59	9.36
	4.0	1.31	3.58	4.91	8.93	14.09	9.18
	8.0	1.35	3.54	4.80	8.91	12.81	8.01
	16.0	1.74	3.55	4.38	8.14	13.36	8.98
210	0.3	1.55	3.77	4.97	9.03	13.42	8.45
	1.0	1.33	3.12	4.66	7.60	11.13	6.47
	4.0	1.24	2.97	3.67	6.92	9.32	5.65
	8.0	0.92	2.58	3.70	6.45	8.71	5.01
	16.0	1.09	2.90	3.18	6.49	8.86	5.68
230	0.3	1.63	3.71	4.75	8.93	14.24	9.49
	1.0	0.66	2.56	3.39	5.72	8.27	4.88
	4.0	1.06	2.41	3.56	6.00	8.38	4.82
	8.0	1.13	2.14	3.38	5.80	7.95	4.57
	16.0	0.95	2.49	3.18	6.38	7.57	4.39
245	0.3	1.12	2.64	3.77	7.59	9.81	6.04
	1.0	1.12	2.18	3.35	6.03	7.86	4.51
	4.0	0.48	2.10	3.38	5.82	6.71	3.33
	16.0	0.80	2.06	3.14	4.85	6.17	3.03
Pine							
Control		1.58	3.10	4.29	7.69	11.92	7.62
190	0.3	1.33	3.34	3.67	7.17	10.50	6.83
	1.0	1.40	4.06	4.04	7.47	11.10	7.05
	4.0	1.60	3.46	4.34	7.27	9.90	5.56
	8.0	1.58	3.39	4.21	7.55	11.43	7.22
	16.0	1.07	2.68	3.60	5.99	8.84	5.23
210	0.3	1.23	3.14	4.18	7.13	10.69	6.50
	1.0	1.25	3.04	3.27	7.26	10.19	6.92
	4.0	0.87	2.79	3.23	5.05	7.52	4.30
	8.0	0.89	2.41	2.93	5.53	7.28	4.35
	16.0	0.96	2.30	2.87	5.26	7.16	4.29
230	0.3	1.20	3.33	4.43	6.62	10.34	5.91
	1.0	1.10	2.66	3.27	5.42	7.73	4.46
	4.0	0.83	2.45	3.07	4.76	6.75	3.68
	8.0	0.76	2.09	2.59	4.81	6.06	3.47
	16.0	0.92	2.22	2.72	4.68	6.40	3.68
245	0.3	1.23	2.77	3.15	6.23	8.92	5.77
	1.0	0.76	2.16	2.49	4.69	6.43	3.95
	4.0	0.58	1.59	2.13	3.99	4.71	2.58
	8.0	0.69	1.77	2.73	4.62	5.48	2.76
	16.0	0.66	1.93	2.15	3.81	5.42	3.27

Continued over...

Table 6.3 Volumetric movement in small samples of thermally modified beech, Scots pine and Norway spruce woods (*concluded*).

Temp. (°C)	time (h)	Volume increase in terms of the oven-dry volume (%) at 20 °C at RH					Volumetric movement between 93% and 44% RH
		11%	33%	44%	75%	93%	
Spruce							
Control		2.10	4.50	5.78	9.95	15.14	9.37
190	0.3	1.69	4.46	5.63	9.70	13.87	8.24
	1.0	2.23	4.15	5.12	9.84	14.02	8.90
	4.0	1.98	4.04	4.62	8.33	12.38	7.75
	8.0	1.69	3.68	4.90	8.76	11.77	6.87
	16.0	1.69	3.76	4.76	8.25	11.71	6.95
210	0.3	2.14	4.18	5.27	8.80	13.43	8.16
	1.0	1.62	4.37	5.05	8.04	12.21	7.16
	4.0	1.55	3.61	4.44	7.01	10.93	6.49
	8.0	1.44	3.39	4.20	7.77	10.81	6.62
	16.0	1.29	3.62	3.93	6.84	9.69	5.76
230	0.3	1.24	3.43	4.80	8.02	11.79	7.00
	1.0	1.42	3.38	4.73	7.68	10.49	5.76
	4.0	0.91	2.98	4.09	6.78	9.92	5.83
	8.0	1.10	2.70	3.16	5.87	8.10	4.93
	16.0	0.94	2.06	3.19	6.21	8.37	5.17
245	0.3	1.14	3.06	4.19	6.92	9.42	5.23
	1.0	0.87	2.65	3.57	5.98	8.85	5.27
	4.0	1.05	2.44	3.03	5.70	6.85	3.81
	8.0	0.84	2.01	2.55	4.70	6.37	3.82
	16.0	0.96	2.31	2.96	5.20	7.35	4.39

From data in Table 6.3, it is noticeable that the volumetric movement at any given relative humidity is smaller in the heated material than in untreated wood. Movement is reduced steadily in line with heat-induced WL at any temperature of treatment. Despite the large differences in absolute movement between species, the reduction in volumetric movement in relative to control volume was very similar between the three woods at equivalent levels of WL (Figure 6.10). At a WL of say 8%, volumetric movement for wood conditioned at 93% RH and at 44% RH, is reduced by about 40% in beech, and by 43% in softwoods. The relative reduction in volumetric swelling is nearly rectilinear for values of about 10% and tends to level off thereafter, for a maximum reduction of about 64% at a WL of around 20%.

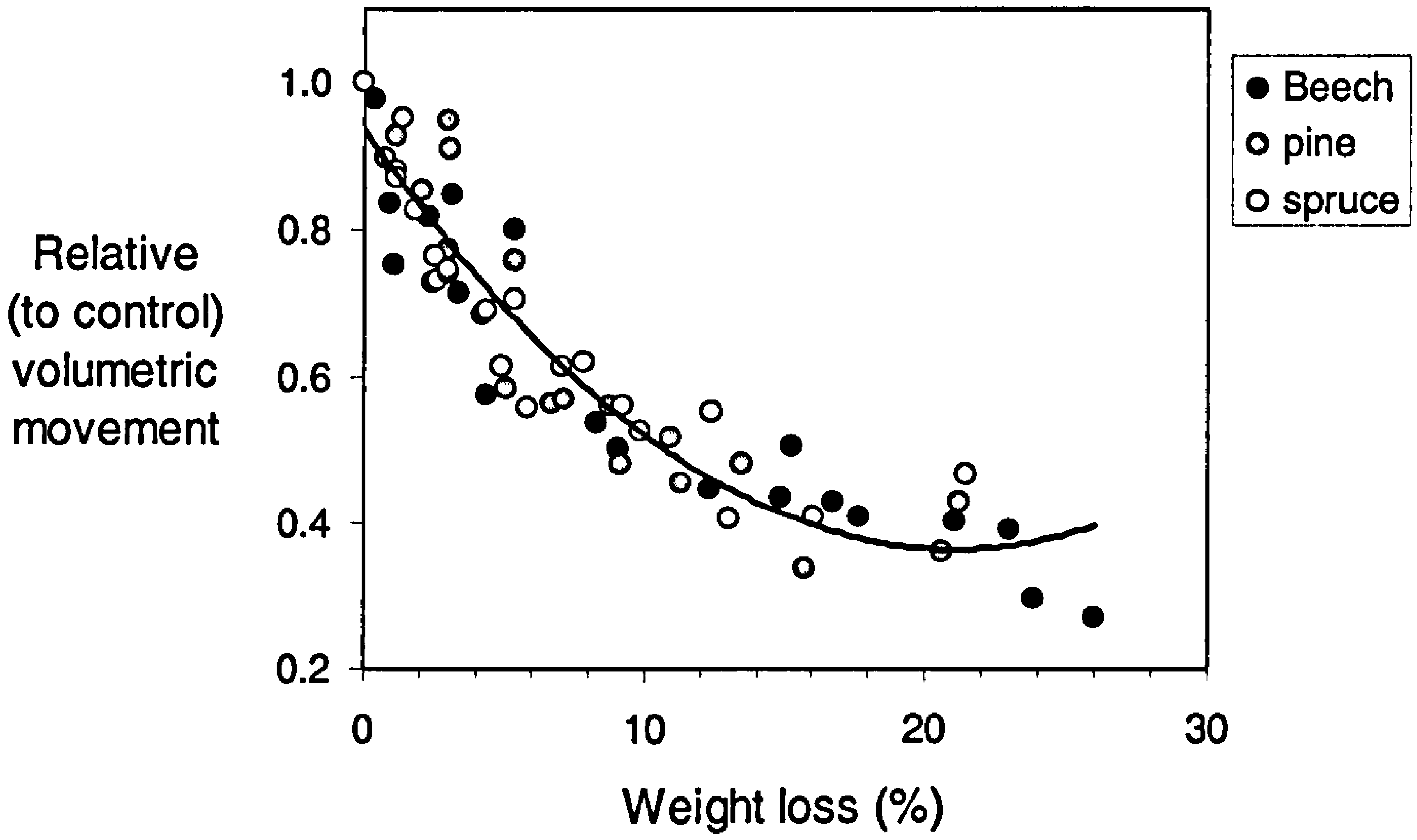


Figure 6.10 Relative-to-control volumetric movement between 93% and 44% relative humidity for heat-treated beech, Scots pine and Norway spruce woods (untreated woods = 1). Each symbol is the mean value of four sample replicates

Figure 6.11 shows the volumetric movement isotherm (between 93% and 0% RH) for the three woods heated for temperatures of 210 °C for 0.3, 1, 4,8 and 16 h, as an example of the behaviour encountered in modified woods. The sigmoid profile in movement in untreated wood is well established (Rijsdijk and Laming 1994). The volumetric movement isotherms also have a sigmoid profile in heated woods although these tend to become less curved for higher treatment regimes. However, this trend was not observed for the movement in either the tangential or radial planes. Apparently, the primary movement mechanism is not modified by the treatment. The flatter appearance of the volumetric movement isotherm is probably influenced by the differential reduction in the swelling in the tangential and radial directions.

The effect of the treatment in reducing the volumetric expansion was most pronounced at the upper extreme of the hygroscopic range (at 93% RH), whilst at the other three environment moisture conditions (11, 33, 44 and 75% RH) this was very similar (Figure 6.12). This is probably caused by the faster reduction of hygroscopicity at higher RH conditions in heated materials (section 6.3.1).

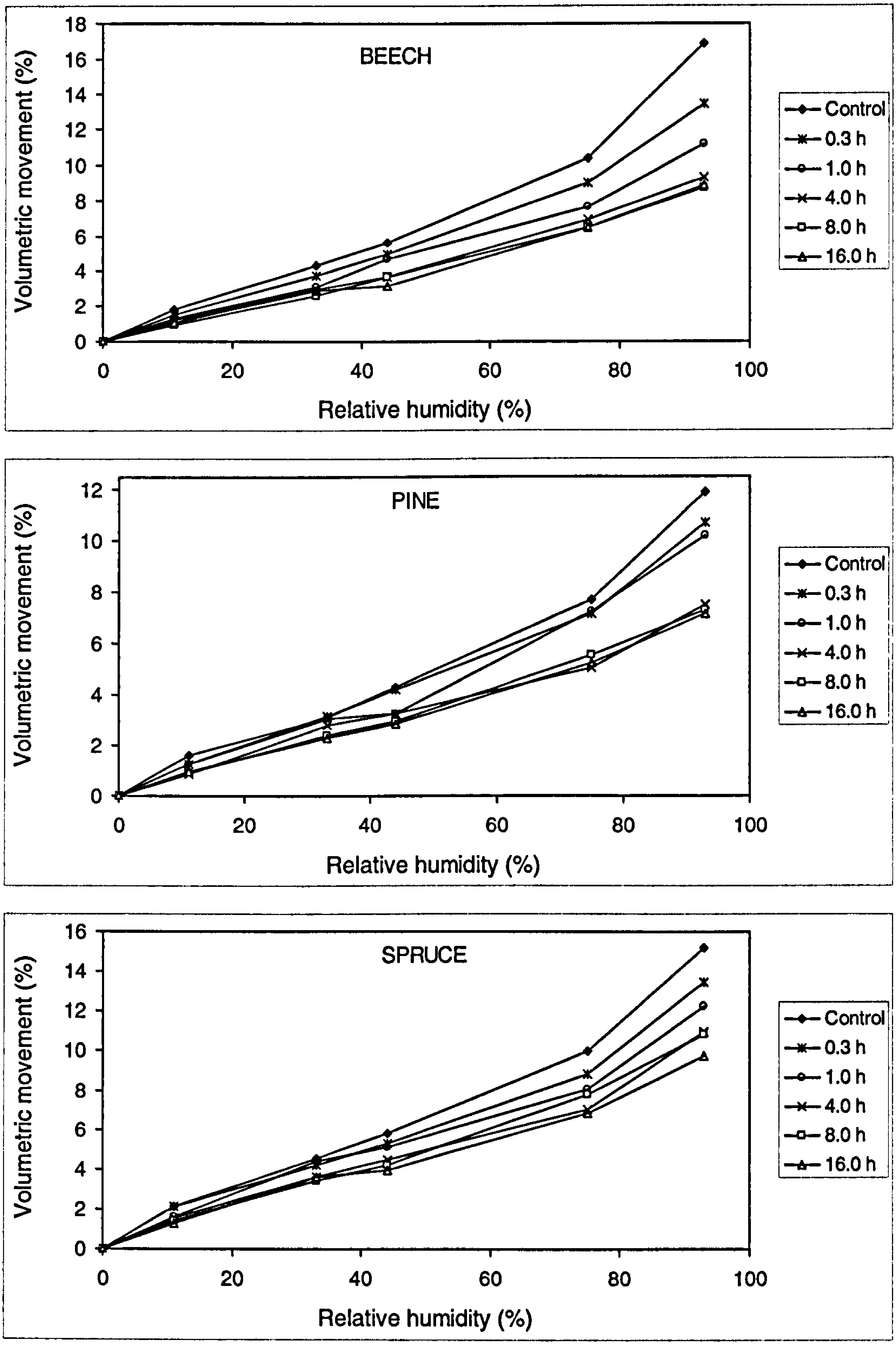


Figure 6.11 Volumetric movement (between 93% and 0% RH at 20 °C) isotherms for beech, Scots pine and Norway spruce woods heat-treated at 210 °C for 0.3, 1, 4, 8 and 16 h. Each symbol is the mean value of four replicates

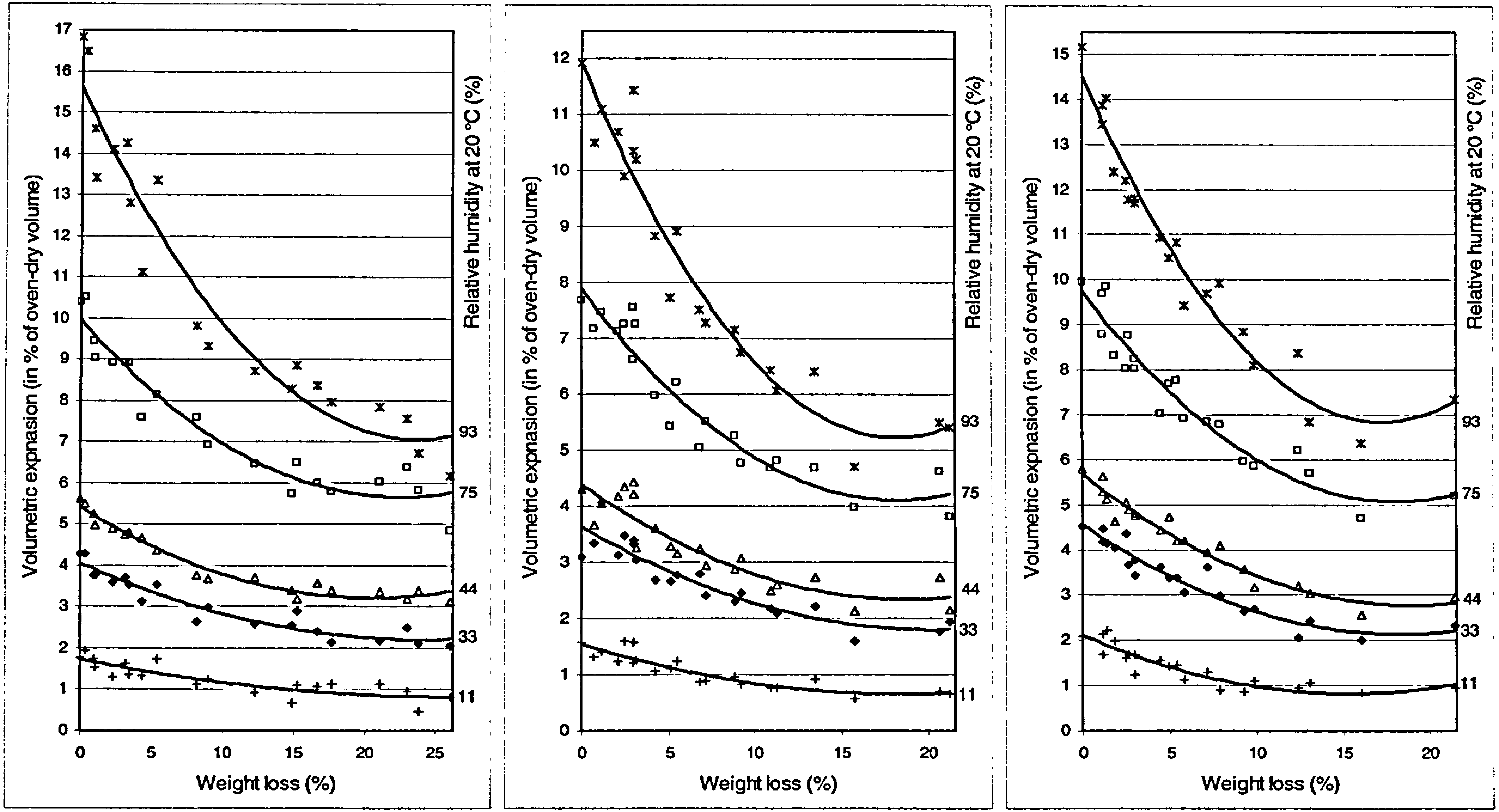


Figure 6.12. Volumetric movement of heat-treated beech, Scots pine and Norway spruce woods (from left to right) in dependence of the weight loss (WL, %) for five conditions of relative humidity. Volumetric movement is in % of the volume at the oven-dry condition. Each symbol is the average value of 4 samples.

6.5 Anisotropy in swelling and total water absorption

Changes in anisotropy in wood swelling in the plane perpendicular to the axis have been previously reported on heat-treated woods (Keith and Chang, 1978; Tjeerdsma *et al.* 1998b, Bekhta and Niemz 2003, Popper *et al.* 2005). However, the reason of this is not completely clear at present. In the transverse direction, the cellular organisation and cross-sectional shape of the cells play an important role in swelling and shrinkage (Schniewind and Berndt 1991). Radial expansion upon adsorption closely depends on anatomic factors beyond individual cell structure and composition. Among these, a major feature affecting swelling in the radial plane is the restraint caused by rays because of its low shrinkage potential and high stiffness as compared to tissues of longitudinally aligned sclerenchyma cells. Radial swelling is therefore probably more dependent on the cellular organisation, and the potential reduction in the swelling capacity upon heat degradation is not as obvious as that on the tangential plane. This would be if the chemical composition at both planes were the same, which is apparently not the case. Based on measurements of differentiating tracheids of eastern hemlock, Boyd (1972) showed that the cells expanded more than 20% in the radial plane, and this was proposed as an indication of higher lignin content in the radial walls (Boyd 1982). According to this proposal, the lignin acts as a bulking agent in the cell wall, and tends to resists dimensional changes in the cell wall, thereby resulting in smaller movement in the radial direction.

The ratio between tangential and radial swelling was in the order Scots pine > beech > Norway spruce. Tangential swelling was more susceptible to thermal treatment than the radial swelling. Figure 6.13 shows that the rate of reduction in swelling in dependence of the WL is greater in the tangential than in the radial plane in all the three species, the former being reduced some 53%, 27% and 20% faster than the one in the radial plane for beech, pine and spruce, respectively.

However, the swelling anisotropy is reduced only moderately. Anisotropy is reduced in a stepwise manner along the extent of the treatment (Figure 6.14). In beech, the anisotropy ratio tangential-radial is reduced at low treatment levels from 2.5:1 in control samples to about 2:1 at WL of 1%. This ratio remains fairly constant at about 2 for WL of up to 15%, and then decreases suddenly again to reach a ratio of 1.4:1 to remain there for WL of up to 26%. Softwoods follow a similar pattern: in pine, the anisotropy ratio decreases from 3.2:1 to about 2.5:1 at low levels of the treatment (WL 2-3%), and then changes again at WL of about 15% to reach ratios of 2:1. Similarly, in spruce wood the anisotropy ratio decreases at low WL levels, from 2.2:1 to 1.8:1 and remains around this value for WL up to 15%, where a further reduction results in a ratio of 1.5:1.

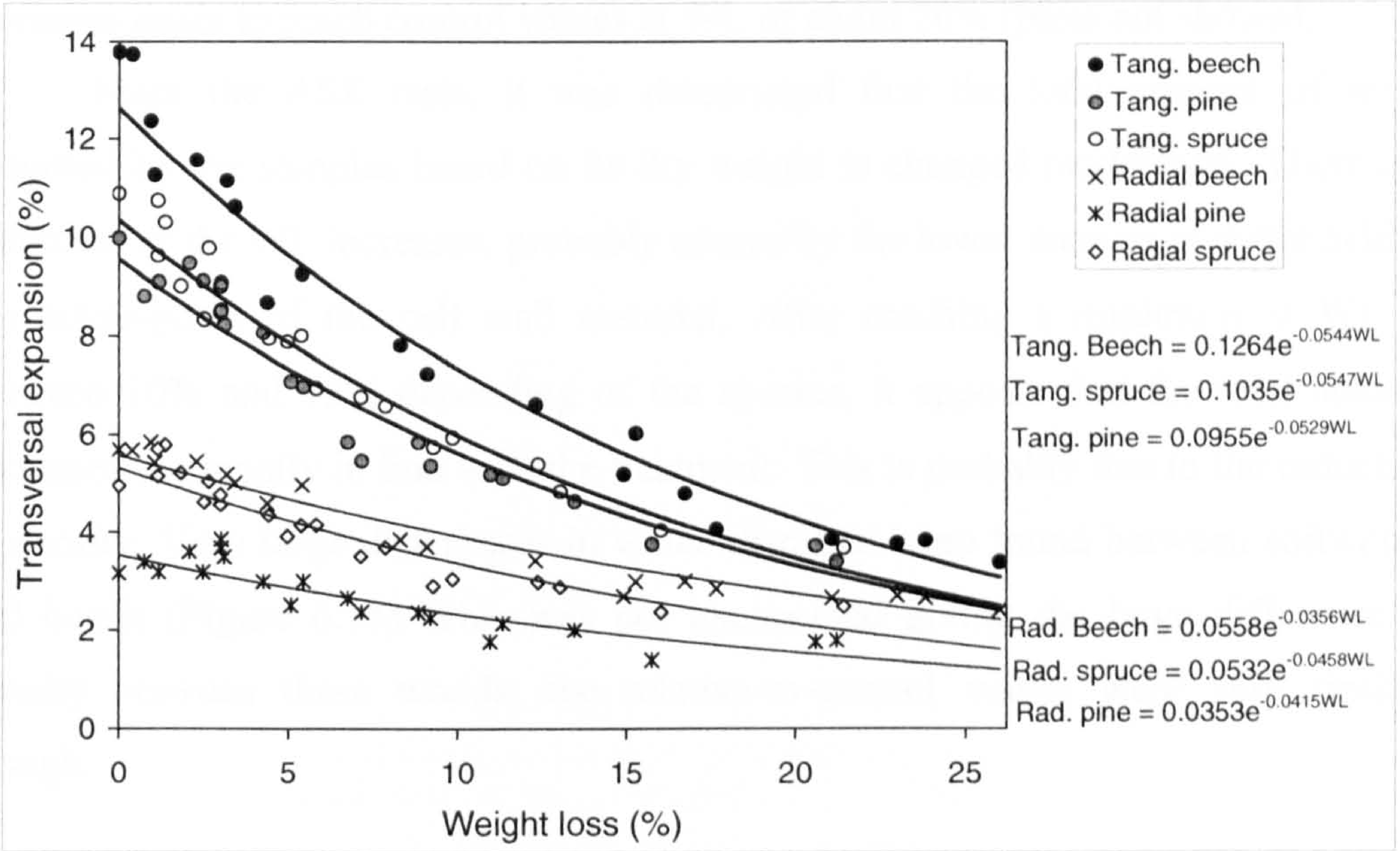


Figure 6.13. Total expansion upon soaking in the tangential and radial directions (in % of the oven-dry dimension) for thermally treated woods *vs.* weight loss. Each symbol is the mean value of ten measurements. Thicker line, transversal direction; thinner line, radial direction

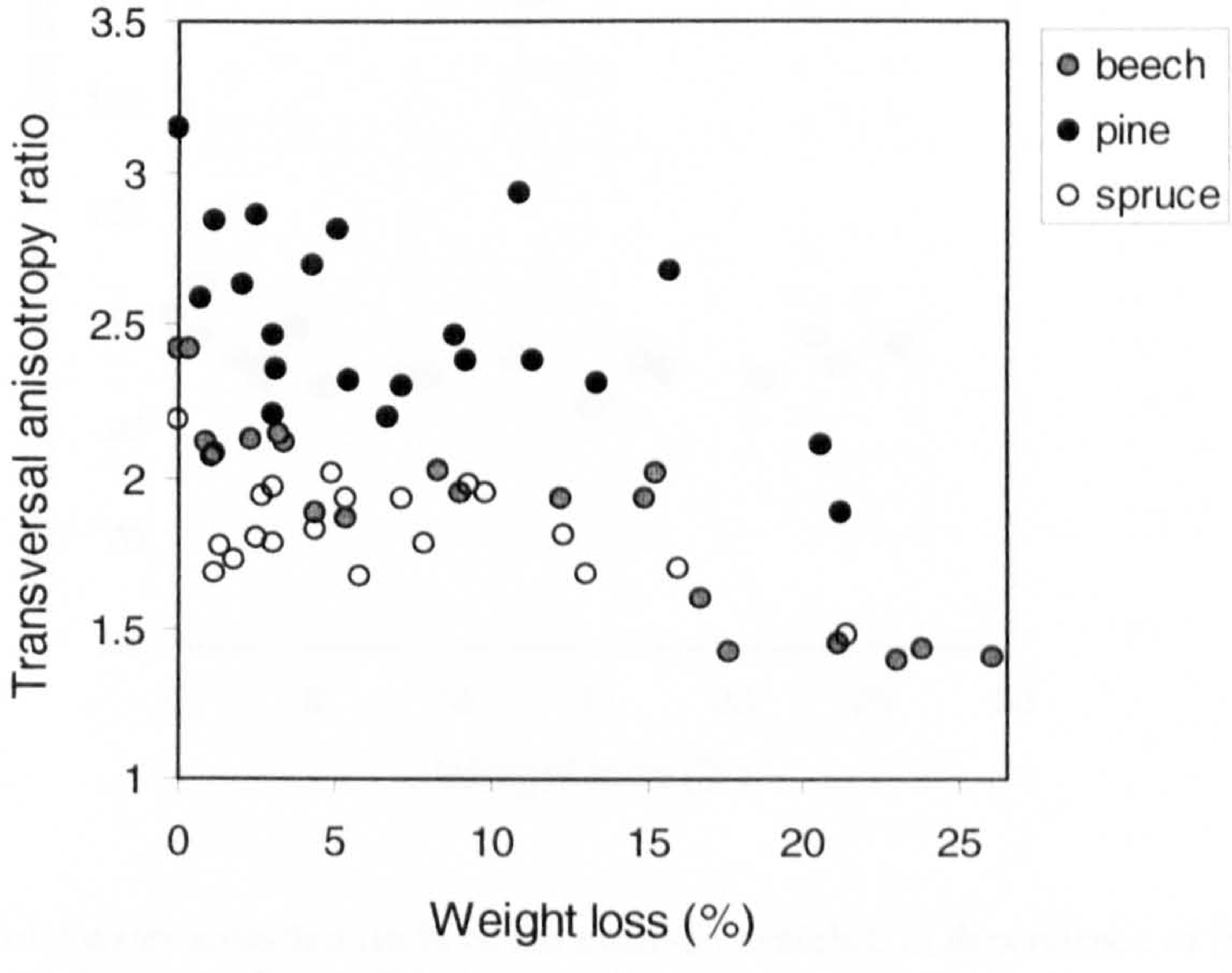


Figure 6.14 Anisotropy changes in relation to WL in heated woods

In respect of the longitudinal expansion upon water soaking, there is no change in this value for beech and spruce, and it remains fairly constant regardless of the WL at about 0.16% and 0.13% respectively. In pine there is a parabolic profile in the linear expansion in dependence of the WL. This starts at 0.2% for control samples, and decreases to reach values of 0.11% at approximately 13% WL, and then increases again to reach control values at WL of about 26% (plots not shown).

From the ASE tests, it was determined that the total amount of water absorbed by the samples based on its dry weight is changed moderately. There is a reduction as the WL increases, probably caused by the lower amount of water held in the micro-pores of the cell wall material. After reaching a minimum at WL of between 10% and 15% depending of the species, it appears that the total amount increases marginally in line with the treatment. This is probably due to the reduction in density. Very large differences in water absorbed were found between softwoods and beech (Figure 6.15). This was not unexpected giving the large difference in density between these woods; the relative-to-control values were very similar, though.

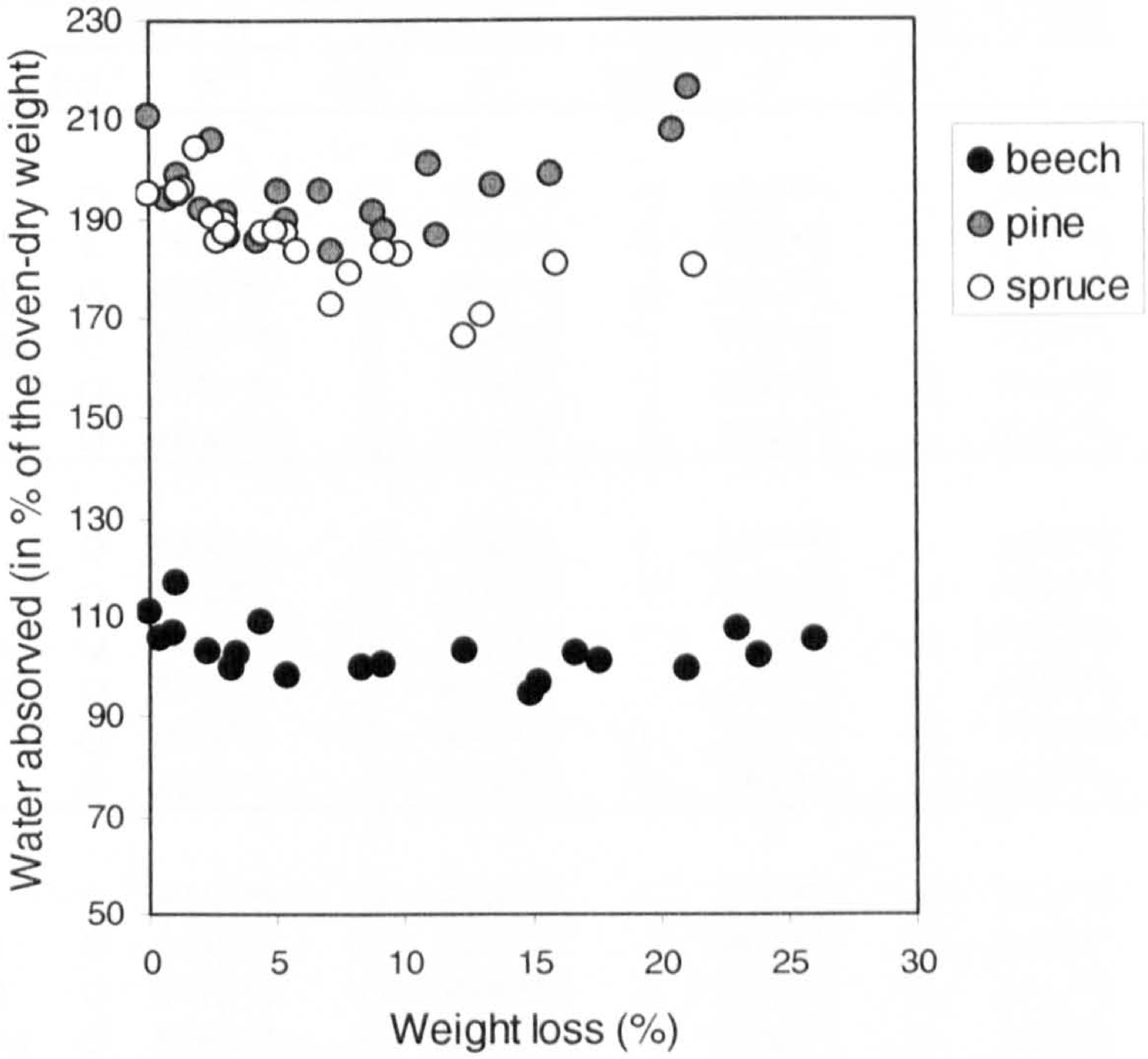


Figure 6.15 Total water absorbed (in % of the oven-dry weight), in dependence of the heat-induced weight loss (in%) for thermally modified beech, Scots pine and Norway spruce woods. Each symbol is the mean value of ten sample replicates.

6.6 Relationship between chemical changes and moisture-related properties

The analysis of the relationship between chemical changes and moisture-related properties was carried out by simple regression analysis, because in several instances the relationship between these characteristics was too curved to be amenable to correlation analysis. The results for regression analysis show that most properties are strongly correlated with changes in each of the chemical constituents (Table 6.4) (measured in terms of the R^2 statistic). In several instances, the relationship between chemical constituents and moisture properties was not rectilinear. The relationship of most moisture parameters with lignin was almost invariably curved, as was the relationship between the major contributor of hemicelluloses in each species (GluXylan in beech, GluMan in softwoods).

Table 6.4 Linear regression analysis to determine the relationship between moisture-related properties with gravimetric determination of chemical constituents (**, $p < 0.01$, NS = not significant).

Property	Lignin (%)		GluMan (%)		GluXyl (%)		Hemicell. (%)		Cellulose (%)	
	Rel.[a]	R^2	Rel.[a]	R^2	Rel.[a]	R^2	Rel.[a]	R^2	Rel.[a]	R^2
Beech										
ASE (%)	Q	.910(**)	L	.783(**)	Q	.965(**)	L	.956(**)	Q	.638(**)
Movement (%)	L	.756(**)	L	.772(**)	Q	.884(**)	L	.882(**)	Q	.473(**)
Tang Swell (%)	Q	.895(**)	Q	.856(**)	Q	.961(**)	L	.957(**)	Q	.531(**)
Radial Swell (%)	Q	.891(**)	Q	.828(**)	Q	.970(**)	L	.951(**)	Q	.529(**)
ARH	Q	.780(**)	L	.771(**)	Q	.939(**)	Q	.933(**)	Q	.308(**)
EMC (%)	Q	.494(**)	Q	.666(**)	Q	.832(**)	Q	.874(**)		NS
Pine										
ASE (%)	Q	.929(**)	Q	.776(**)	L	.625(**)	L	.705(**)	L	.498(**)
Movement (%)	Q	.873(**)	Q	.758(**)	L	.633(**)	Q	.704(**)	L	.365(**)
Tang Swell (%)	Q	.929(**)	Q	.768(**)	L	.613(**)	L	.701(**)	L	.530(**)
Radial Swell (%)	Q	.817(**)	Q	.686(**)	L	.555(**)	L	.628(**)	L	.425(**)
ARH	Q	.958(**)	Q	.831(**)	L	.706(**)	Q	.771(**)	L	.422(**)
EMC (%)	Q	.919(**)	Q	.715(**)	Q	.578(**)	Q	.675(**)	L	.393(**)
Spruce										
ASE (%)	Q	.924(**)	Q	.921(**)	L	.924(**)	Q	.937(**)	Q	.578(**)
Movement (%)	Q	.816(**)	Q	.823(**)	Q	.841(**)	Q	.869(**)	Q	.507(**)
Tang Swell (%)	Q	.891(**)	Q	.899(**)	L	.887(**)	L	.917(**)	L	.547(**)
Radial Swell (%)	Q	.929(**)	Q	.898(**)	L	.928(**)	Q	.909(**)	Q	.592(**)
ARH	Q	.900(**)	Q	.912(**)	L	.935(**)	Q	.938(**)	Q	.547(**)
EMC (%)	Q	.757(**)	Q	.782(**)	Q	.882(**)	Q	.874(**)	Q	.429(**)

[a] Rel. = Relationship between variables; Q, quadratic; L, linear

Regardless of the species, the weakest correlation between moisture parameters and chemical changes was with the cellulose fraction; in beech the EMC was found not to be related with this component. In beech and spruce woods, the strongest correlation was with GluXylan closely followed by hemicelluloses for all moisture parameters but for radial swelling in spruce, where lignin ranked first. In spruce wood, changes in the lignin component had also comparable levels of correlation to that of hemicelluloses and GluXylan. In pine, the strongest correlation was for lignin, followed by GluMan.

In general, it is held that the strong correlation between moisture-related properties and chemical changes reflect the contribution of all chemical constituents towards the reduction of hygroscopicity -with the consequent reduction in swelling and movement.

In untreated softwoods, the *in situ* relative sorption capacity is 1.56 for hemicellulose, 0.6 for lignin and approximately 0.94 for cellulose (Schniewind and Berndt 1991). From these figures, the total adsorbed water in untreated wood, 47% is held by cellulose, 37% by hemicellulose, and 16% by lignin, albeit these fractions represent 50, 24 and 26% of total wood respectively. Following this reasoning and assuming that the hygroscopic capacity of the polymers in the solid residue remains unchanged, it is possible to calculate the theoretical relative-to-control hygroscopicity of the heated materials from its chemical constitution.

The actually measured reduction in hygroscopicity was found greater than the calculated from individual polymer coefficients at equivalent levels of WL (Figure 6.16). Thus, two probably complementary causes subsist to explain this difference between theoretical and measured hygroscopicity. One is that the sorption capability of the individual polymers is also reduced by the treatment, and the next is that structural changes hinder the reaction of wood polymers with water. Repellin and Guyonnet (2005) reported that the hygroscopicity at 70% RH of isolated lignin from heated beech wood (at 260°C for 5 minutes) was reduced by about 48% compared to that of untreated controls. Such a large reduction was not found here, but the analysis of the hygroscopicity of the isolated acid insoluble lignin showed that the sorption of this fraction was significantly reduced by the treatment when exposed at RH higher than about 60% (Figure 6.17). The effect of a higher moisture surroundings was an increasingly larger hygroscopicity reduction. Thus, the sorption capacity of lignin is reduced with the heat-induced weight loss. This factor is probably linked to the differences determined between theoretical and actual sorption reductions in the modified substrates.

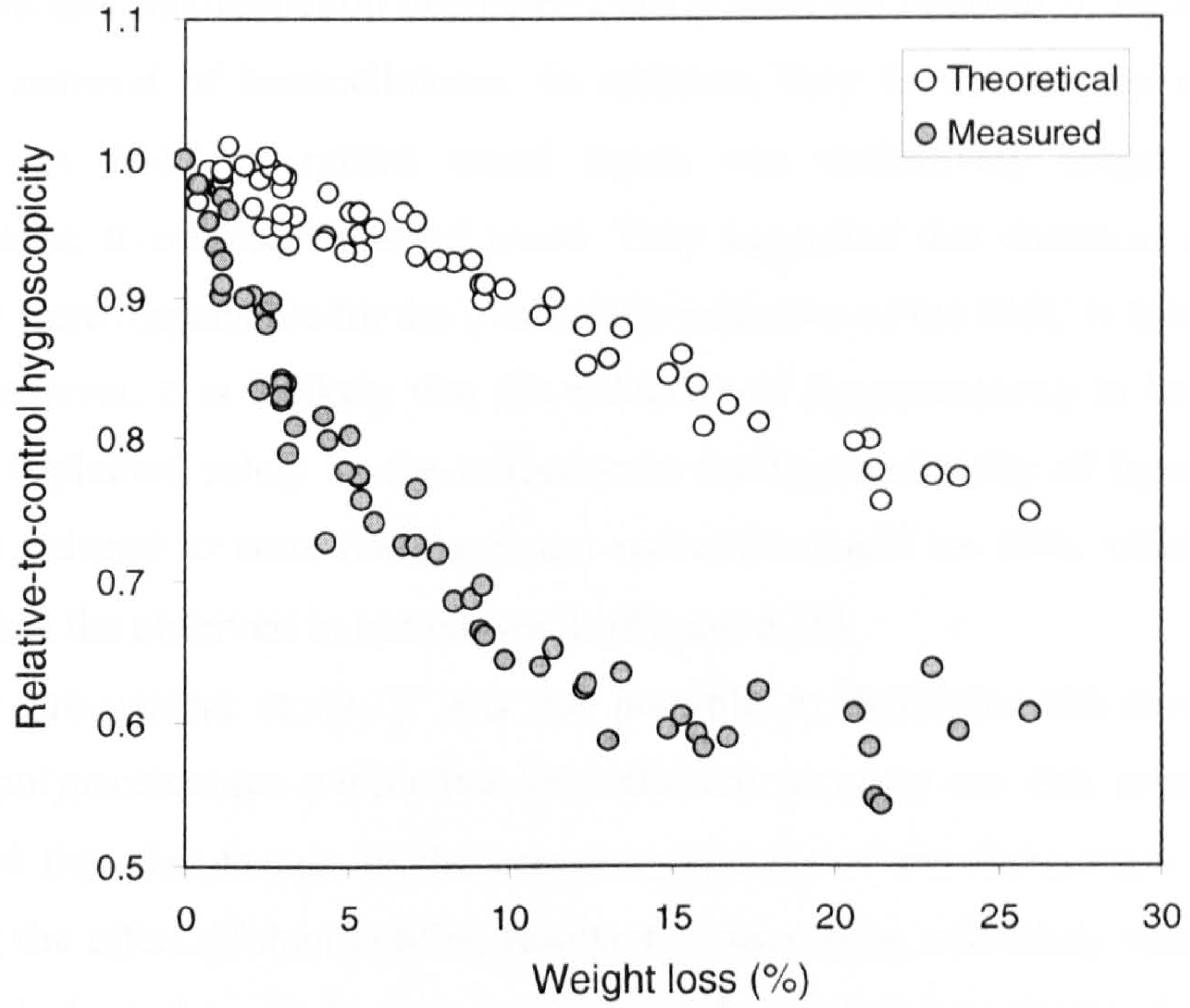


Figure 6.16 Average relative-to-control hygroscopicity (measured) in heated woods and theoretical hygroscopicity calculated from the resultant final chemical composition of heated woods. Data for all the three species is included in the plot. Each symbol is the mean value of 4 replicates

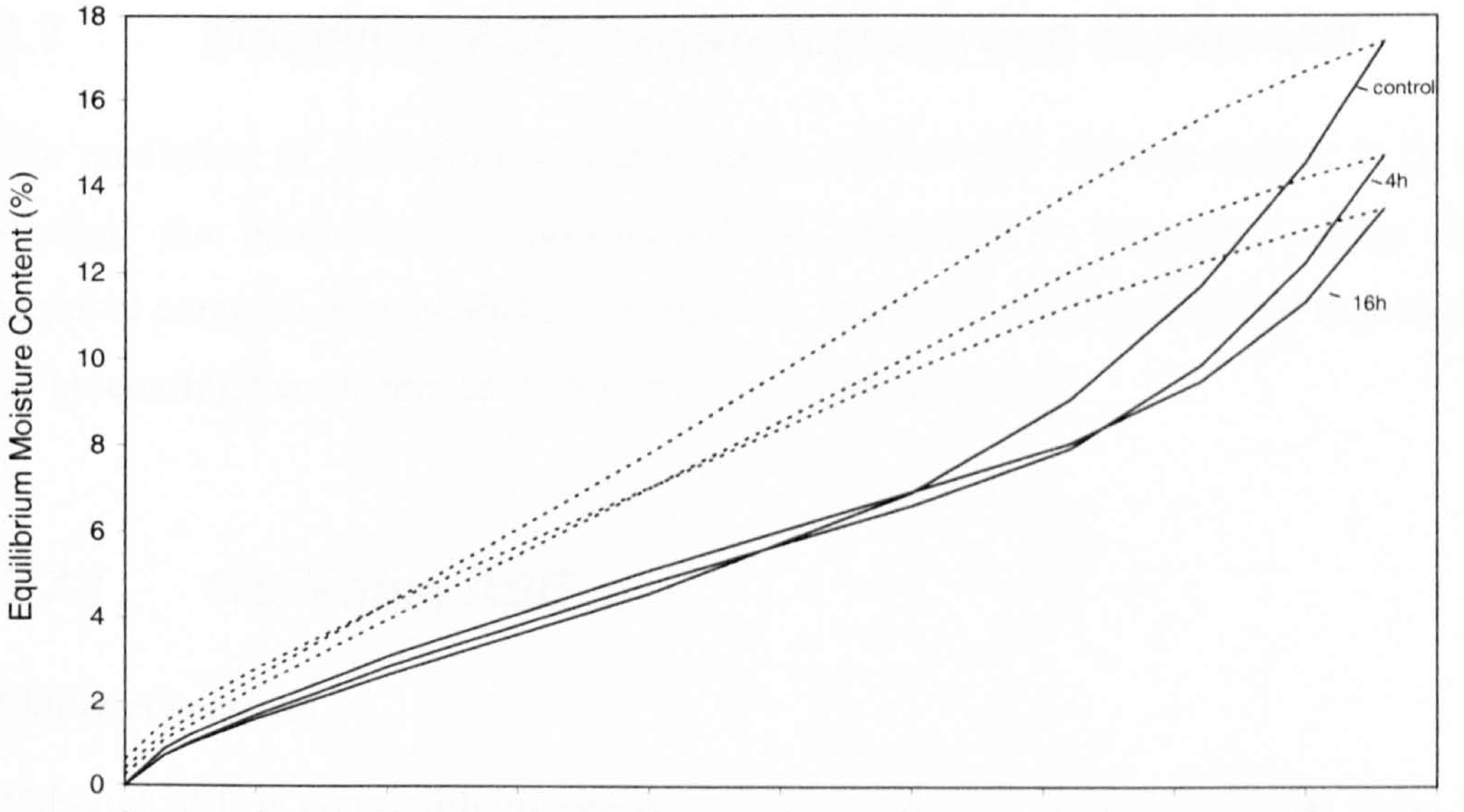


Figure 6.17 Sorption isotherms of Klason lignin for untreated and heat-treated Norway spruce wood at 210 °C as determined in the DVS instrument. Solid lines: adsorption; broken line, desorption

Obataya and Tomita (2002) found that heating spruce wood at temperatures higher than 140 °C lead to a permanent reduction in the EMC of the samples. They determined that this reduction decreased clearly with the removal of lignin, but not with the removal of hemicelluloses. In addition, they found that the irreversible reduction in EMC of milled wood lignin was definitively larger than that holocellulose, α-cellulose or solid wood. They suggested that chemical changes in the lignin were responsible for the irreversible reduction of the EMC in heated wood.

However, it is unlikely that the reduction of hygroscopicity in heated wood could be explained solely by the reduction in the hygroscopicity of lignin. Even if this were reduced to zero, the maximum reduction would be 16%, which is much smaller than the observed in heated woods (Figure 6.16).

In the present study, it was not possible to determine the isotherms for isolated polysaccharides within the time allowed to carry out this research. It is speculated that the change in the sorption capacity of the three main polymers, including the effect of the modified resultant composition, will likely sum up to the reduction in heated wood, because as it was elaborated above, chemical changes in the nature of each polymer of the cell wall are proposed to be the major contributors of the increasing hydrophobic character of heated materials.

6.7 Modelling ASE, hygroscopicity and movement

The prediction of ASE from colour changes will be deal with in chapter 7. In this section, the prediction of moisture-related properties is attempted using other physical parameters as predictor, namely WL and EMC. Lastly, the ASE is predicted by processing parameters using the severity factor approach.

6.7.1 Modelling ASE

Linear regression

Although WL is not readily measured on a hygroscopic material as TMW, there is a good relationship between ASE and WL and makes it appealing to predict ASE from the mass change parameter. On the other hand, although it takes a long time to reach an EMC in TMW, the EMC is more easily measured industrially than the ASE.

Therefore the moisture content of wood is also a suitable candidate for predicting the dimensional stability.

As a graphic example of the dependence of ASE on EMC, Figure 6.18 shows this relationship for heated Norway spruce wood. Similarly, Figure 6.19 shows the close relationship between ASE and WL also in spruce in a log-normal plot. Table 6.5 shows the results from the prediction of ASE using WL and EMC as predictors.

For regression of ASE on EMC, only samples treated to WL ≤ 20% in each species were included in the model. Above this WL threshold, the relationship between ASE and EMC becomes too curved to be handled with a curvilinear relationship. This is because there is a positive effect of the treatment on ASE for WL > 20%, whilst no further reduction in EMC (at 65% RH at 20 °C) is attained when WL is greater than about 20%. On the other hand, the modelling of ASE in dependence of WL was carried out taking into consideration the ASE data for WL ≥ 2%. As pointed out before, at lower levels of modification the relationship is rather erratic due to the effect of extractives, residual stresses and possibly some strongly adsorbed moisture remaining in the sample before thermal-processing (regarded as oven-dried before the treatment).

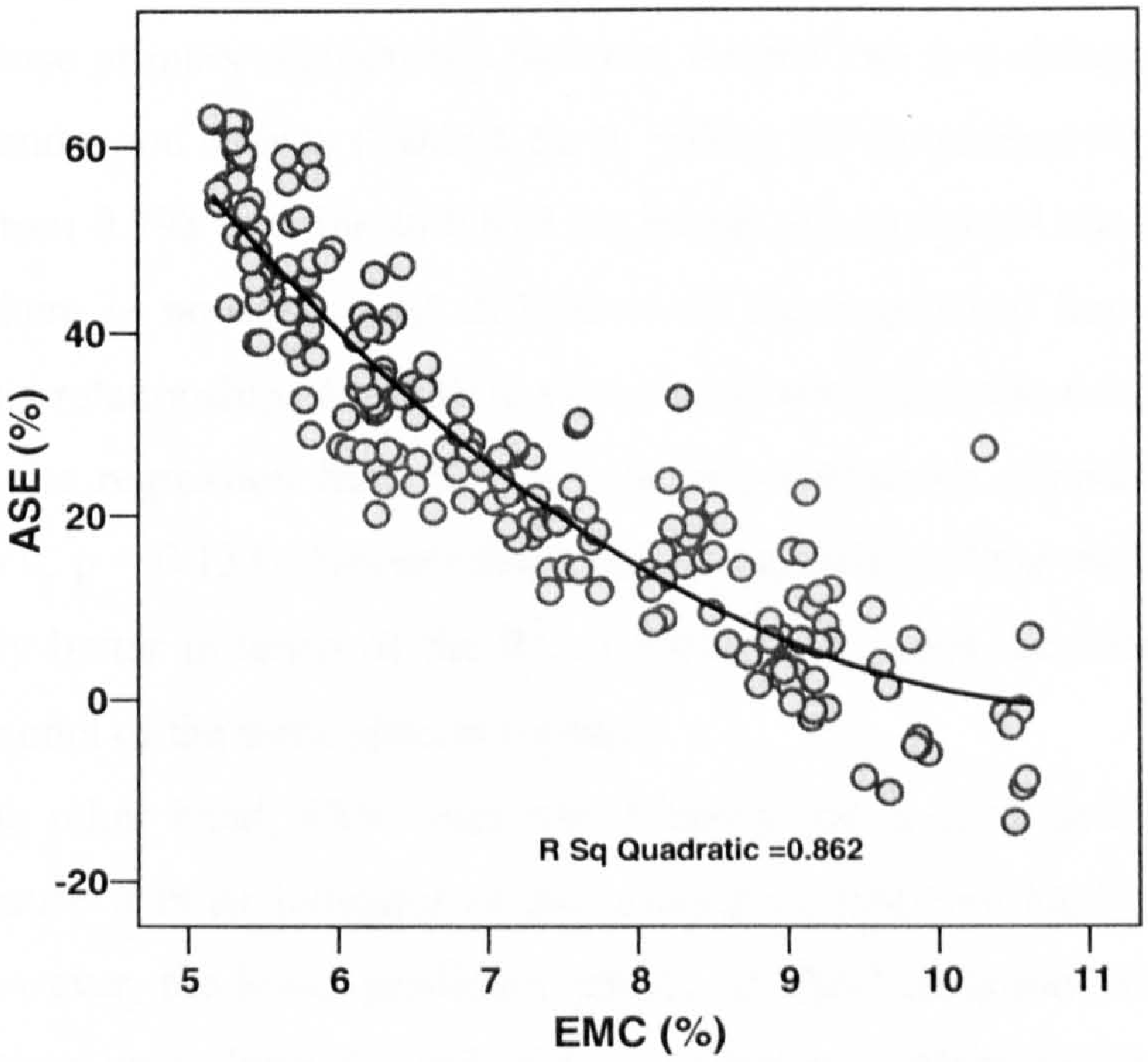


Figure 6.18 Relationship between anti-swelling efficiency (ASE, %) and equilibrium moisture content at 65% RH at 20 °C (EMC, %) in thermally-modified Norway spruce wood, for WL ≤ 20%. *n* = 190

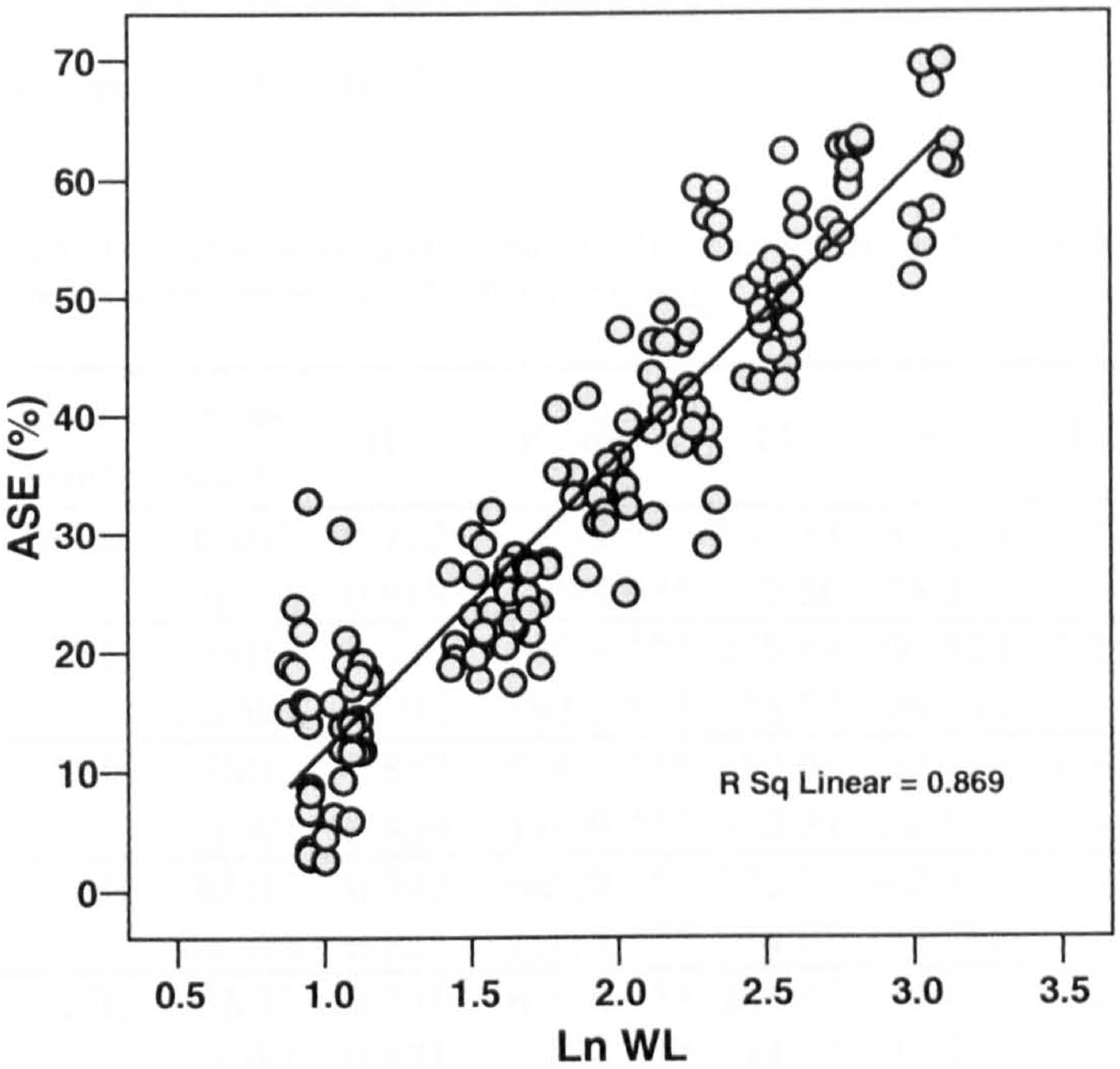


Figure 6.19 Relationship between anti-swelling efficiency (ASE, %) and weight loss (WL, %) in thermally-modified Norway spruce wood, for WL ≥ 2%. $n = 160$

Invariably, WL was a better predictor of ASE than EMC; this probably reflects the close primary relationship between weight loss and changes in chemical composition and wood density (Table 6.5). R^2 values for the predictions of ASE from WL ranged from 0.798 for pine to 0.919 for beech. As explained above, ANCOVA shows that there is no significant difference in the regression line for the three species for this relationship. ANCOVA also demonstrates that there is no significant difference in the regression lines between the two softwoods (Species, $p = 0.889$; Species*LnWL, $p = 0.133$). Nevertheless, the fitting ability of the model of ASE on WL is slightly better in terms of the R^2 coefficient for beech modelled on its own than for the model of the three species together.

On the other hand, EMC was also found to be a good predictor of ASE, probably because it is an indicator of the amount of moisture held between wood polymers. However, the lower prediction ability of EMC compared to WL suggests that other factors apart from the reduction in moisture content are involved in the improvement of dimensional stability in heated wood. The best prediction using EMC in the model was for spruce wood ($R^2 = 0.862$), although all models were highly significant, with R^2 values from 0.722 to 0.862. The addition of EMC to the regression model of ASE on WL gave marginally better predictions only for Norway spruce wood (R^2 from 0.869 to 0.871).

Table 6.5 Regression of the anti-swelling efficiency (ASE, %) on EMC or WL for thermally modified beech, Scots pine and Norway spruce woods (*** $p < 0.001$)

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	n
Beech	ASE	EMC	0.722	193.9 ***	297.33	-68.220	3.938	11.73	152
		Ln WL	0.919	1,792 ***	-12.50	25.270	-----	5.87	160
Pine	ASE	EMC	0.736	219.3 ***	288.84	-60.520	3.254	10.52	160
		Ln WL	0.798	592.3 ***	-16.74	26.680	-----	9.37	152
Spruce	ASE	EMC	0.862	584.1 ***	192.95	-34.790	1.561	7.07	190
		Ln WL	0.869	1,049 ***	-12.81	24.661	-----	6.22	160
Softwoods	ASE	EMC	0.792	660.9 ***	221.93	-42.350	2.045	8.96	350
		Ln WL	0.826	1,475 ***	-14.85	25.716	-----	7.92	312
All 3 species	ASE	EMC	0.731	678.0 ***	205.55	-39.430	1.913	10.68	502
		Ln WL	0.871	3,179 ***	-14.53	25.777	-----	7.31	472

Units: ASE, %, EMC, %; WL, %.
Models for ASE *vs.* EMC, for WL ≤ 20%. Model of the form $ASE = b0 + b1 \cdot EMC + b2 \cdot EMC^2$
Models for ASE *vs.* WL, for WL ≥ 2%. Model of the form $ASE = b0 + b1 \cdot LnWL$
All coefficients significant at $p < 0.05$

Severity Factor

It has been shown that a single model could be used for the prediction of mechanical properties in heated wood modified in the 190 – 245°C temperature range for up to 16 h using the severity factor approach (section 5.8.3). Now, this approach is used for estimating the ASE at any given condition within these ranges of time and temperature of treatment.

It was found that the severity factor was an effective parameter for predicting ASE in all three species, although the prediction was slightly better in both softwoods based in the coefficient of determination (R^2) statistic. The relationship between the dimensional stabilisation and the severity of the treatment was found to be curvilinear in each species. Using Norway spruce wood as an example, Figure 6.20 shows the relationship between the ASE and the severity factor R_O in the customary normal-$\log_{10}$ plot.

Table 6.6 Model parameters for predicting ASE in thermally modified beech, Scots pine and Norway spruce woods from the severity factor R_O, and the optimal ω parameter for computing R_O

Property	Species	b0	b1	b2	ω	R^2
ASE (%)	Beech	-438.96	53.86	-1.4235	10.870	0.867
	Pine	-208.25	23.61	-0.4737	11.469	0.915
	Spruce	-55.65	2.284	0.1436	8.6403	0.966
	Softwoods	-147.81	14.19	-0.1720	10.252	0.912

The model is of the form: ASE = b0 + b1Ln R_O + b2 $(\text{Ln}R_O)^2$, where R_O is the severity factor

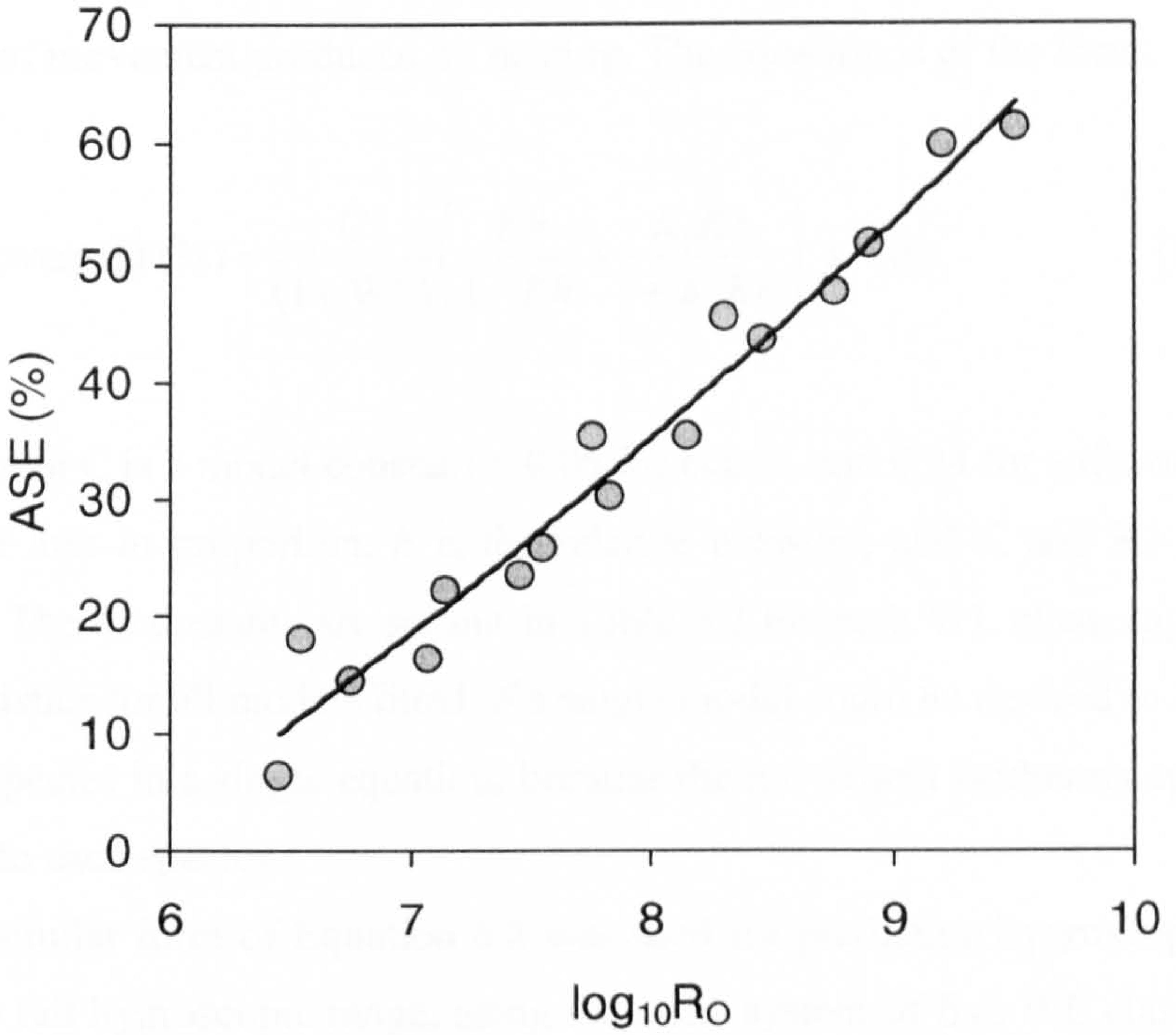


Figure 6.20 ASE *vs.* $\text{Log}_{10}R_O$ for TM Norway spruce wood. Each symbol is the mean value of ten sample replicates

6.7.2 *Modelling hygroscopicity and movement*

From Figure 6.12 it is obvious that WL is a good descriptor of the movement in a range of relative humidity conditions. The same is true for hygroscopicity (Figures 6.6 and 6.7). Furthermore, it is also appreciated that WL could be used to determine the average relative-to-control hygroscopicity or the movement expected in heated woods at any given level of WL (Figures 6.5 and 6.11, respectively). However, it is useful to have a single model for the prediction of movement in the full hygroscopic range, because the service environmental conditions will vary according to the final application of TMW.

In section 6.3.2 it was shown that for the fitting of the isotherms using the HH model, the constant M_p (the molecular weight of the polymer substance necessary to associate with one molecular weight of water), exhibits a tendency to increase in adsorption as the temperature or the time of treatment increased. This is convenient because the HH model affords for the prediction of movement using the WL instead of the M_p parameter. Therefore, a single equation (Equation 6.2) from a modified form of the HH model can be used for a five-class system of WL levels to cover the full range of movement produced by heating. The equation is of the form:

$$\text{Movement}\,(\%) = \frac{\mathrm{C}}{(1+\mathrm{WL})}\left(\frac{Kh}{1-Kh}+\frac{K_1Kh}{1+K_1Kh}\right) \times 100 \qquad \text{[Eq. 6.2]}$$

Where C is a model constant = 0.05 for beech, and 0.04 for softwoods, WL is the weight loss in proportion, *h* is the relative pressure, and K and K1 are model constants. These constants are set out in Table 6.7 for each WL class, together with the R^2 statistics for all models fitted. No single model could be devised to encompass the three species in a single equation, because the movement isotherms appear to be particular to each species.

A similar form of Equation 6.2 was used for predicting hygroscopicity from WL in the full hygroscopic range, using the same system of five WL classes. In this case, the parameter C was = 0.05 for adsorption isotherms in the three species, and 0.1 and 0.08 for beech and softwoods respectively for the desorption model.

Models for predicting movement or hygroscopicity isotherms from WL showed a remarkably good prediction ability each WL class, with R^2 statistics from 94.3 to 99.9% and from 98.6 to 99.9% respectively. Figure 6.21 shows graphically an example of the fitting ability of the models for movement in the full hygroscopic range at various levels of thermal modification of beech wood.

Table 6.7. Model parameters for predicting the movement and hygroscopicity isotherms in heated beech, Scots pine and Norway spruce woods according to Equation 6.2. Fitting efficiency of the model in terms of the R^2 is also included.

WL class	WL range (%)	Movement			Hygroscopicity					
					Adsorption			Desorption		
		K	K1	R^2	K	K1	R^2	K	K1	R^2
Beech										
0	0	0.7772	4.1280	0.999	0.8520	2.8246	0.999	0.7099	1.5446	0.998
1	0.1 - 4.0	0.7391	3.5010	0.986	0.8120	2.3526	0.987	0.6485	1.6994	0.986
2	4.1 - 8.0	0.7017	2.9832	0.975	0.7764	1.7800	0.999	0.5829	1.8281	0.999
3	8.1 - 12.0	0.6426	2.7798	0.992	0.7538	1.5410	0.999	0.5419	2.0370	0.998
4	12.1 - 16.0	0.6226	2.5202	0.993	0.7355	1.4800	0.998	0.5097	2.1535	0.996
5	>16.0	0.5916	2.8629	0.975	0.7130	2.1608	0.997	0.4733	2.8977	0.995
Pine										
0	0	0.7426	4.0398	0.998	0.8305	5.6462	0.999	0.7254	4.7119	0.999
1	0.1 - 4.0	0.7097	4.7623	0.989	0.8030	4.3460	0.994	0.6826	4.2989	0.993
2	4.1 - 8.0	0.6369	3.3082	0.979	0.7704	3.3069	0.993	0.6352	3.9264	0.990
3	8.1 - 12.0	0.5869	2.9002	0.989	0.7419	2.7589	0.997	0.5884	3.8597	0.994
4	12.1 - 16.0	0.5433	2.7674	0.943	0.7127	3.0014	0.995	0.5418	4.4672	0.992
5	>16.0	0.5535	2.8790	0.983	0.6914	3.3071	0.994	0.5221	4.6577	0.993
Spruce										
0	0	0.8014	12.0703	0.996	5.6462	4.1743	0.999	0.7326	3.6012	0.999
1	0.1 - 4.0	0.7589	8.7315	0.980	4.3460	3.5409	0.992	0.6957	3.4285	0.989
2	4.1 - 8.0	0.7075	5.7592	0.988	3.3069	2.5062	0.996	0.6355	3.1309	0.996
3	8.1 - 12.0	0.6666	3.4986	0.994	2.7589	1.9135	0.998	0.5931	2.9019	0.999
4	12.1 - 16.0	0.6485	3.3803	0.971	3.0014	1.7100	0.995	0.5622	3.0235	0.996
5	>16.0	0.6264	2.9542	0.971	3.3071	1.8983	0.997	0.5389	3.2445	0.996

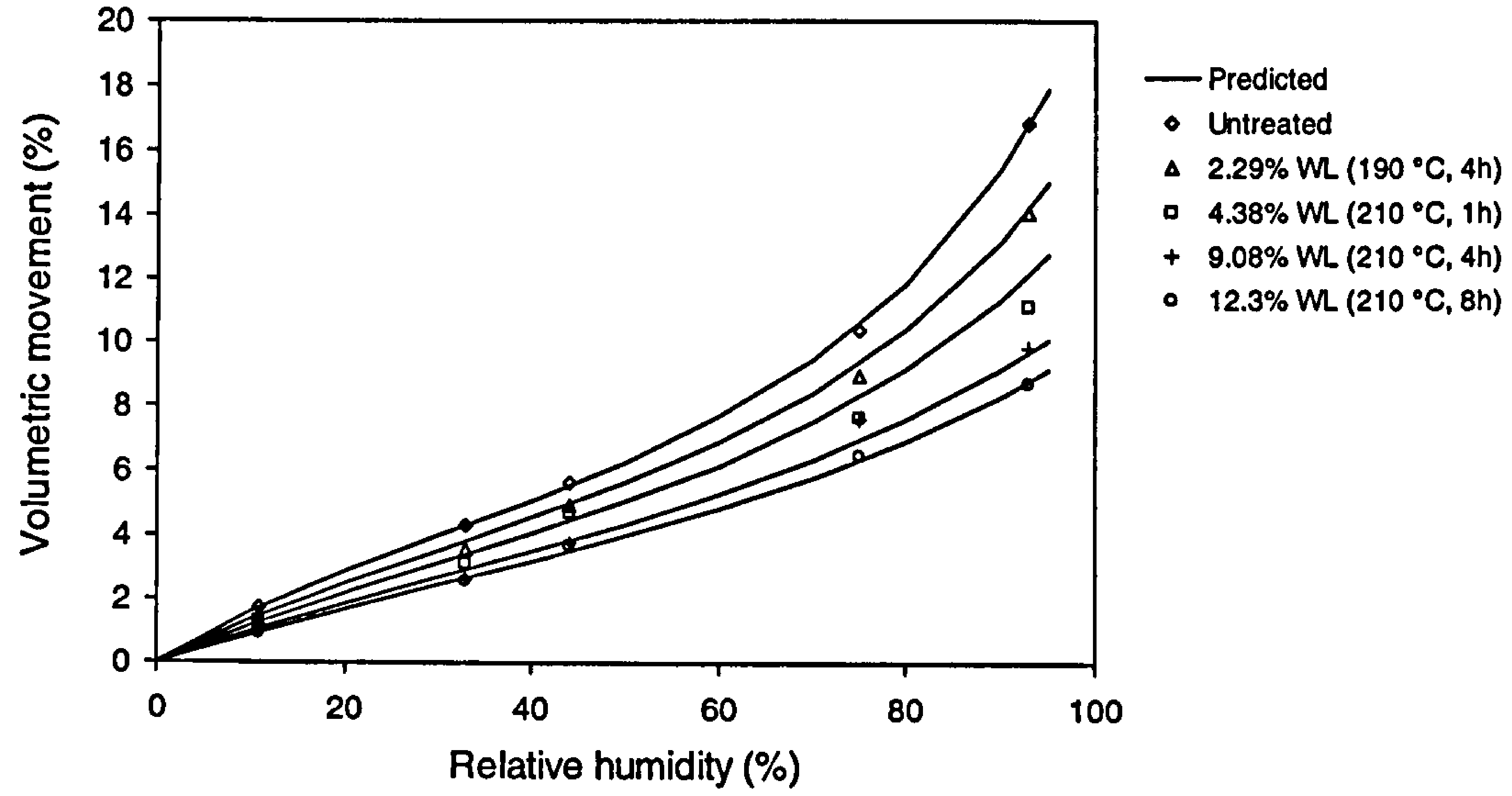


Figure 6.21. Observed volumetric movement (symbols) and predicted movement (lines) using a modified form of the Hailwood-Horrobin model in heated beech wood.

6.7.3 Relationship between moisture-related properties

It was shown in section 6.71 that the EMC is a fair descriptor of ASE. However, it is also interesting to explore the relationship between other moisture-related parameters and EMC. This is because the EMC is measured simply in woody materials. Similarly, we have seen that the ASE is closely related to the heat-induced weight loss, and this relationship makes appealing the prediction of finer moisture-related characteristics form the ASE.

The relationship between average relative-to-control hygroscopicity (ARH), movement and tangential swelling in both the radial and tangential directions with the ASE parameter is shown in Figures 6.22 and 6.23 for the three species. There is a clear, strong relationship between these properties. The relationships are rectilinear in all cases. Similarly, it can be observed in Figures 6.24 and 6.25 that several moisture-related properties could be estimated from the EMC. In this case, the relationship between the EMC and all moisture parameters is curved; at low levels of EMC this is probably too curved as to be fitted with a curvilinear model. As explained above for the ASE, the prediction of other moisture-related parameters could be improved if values at the higher end of WL are excluded from the analysis. This is not explored further here for a matter of space.

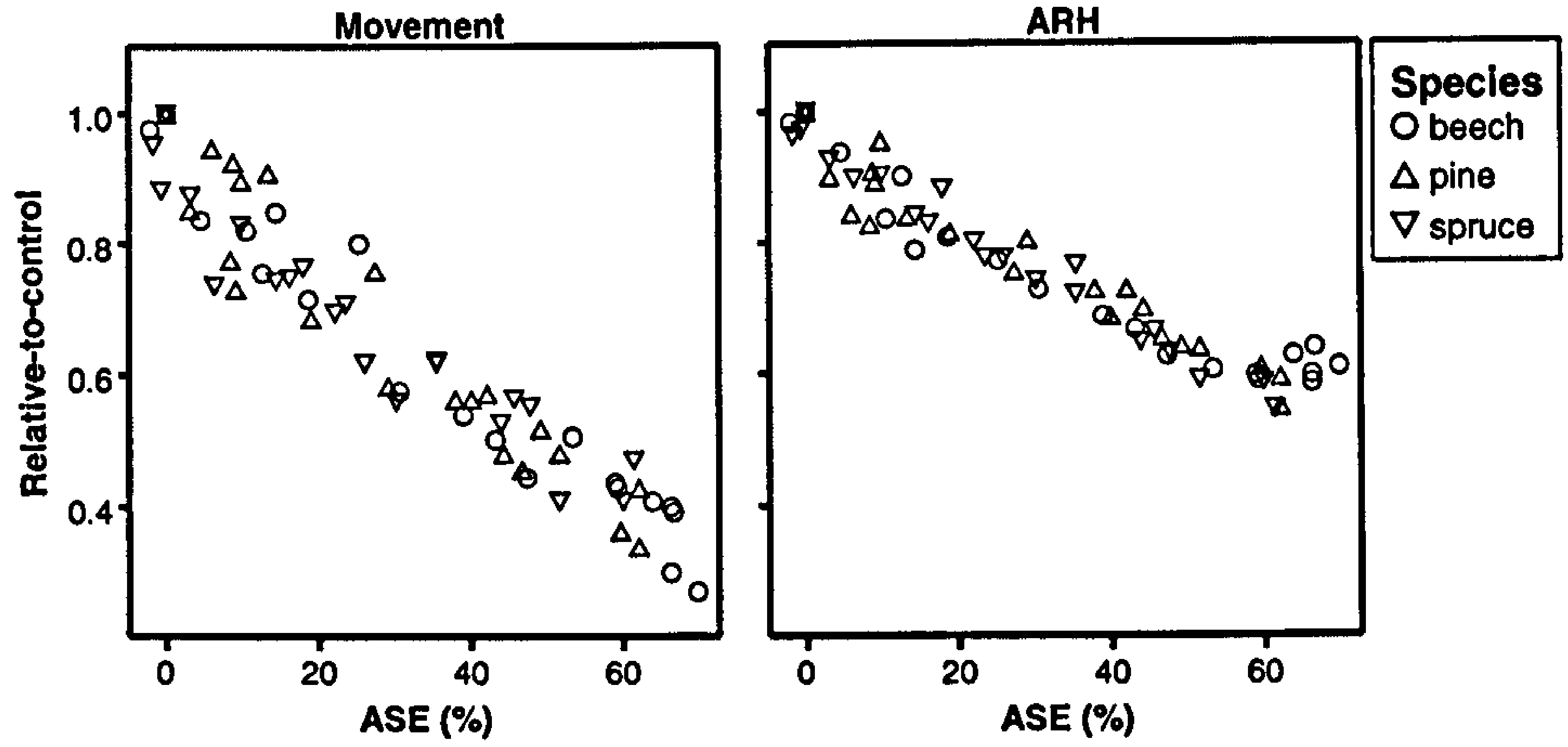


Figure 6.22. The relationship between relative-to-control total volumetric movement and average relative-to-control hygroscopicity (ARH) with the anti-swelling efficiency (ASE, %) in three thermally- modified woods

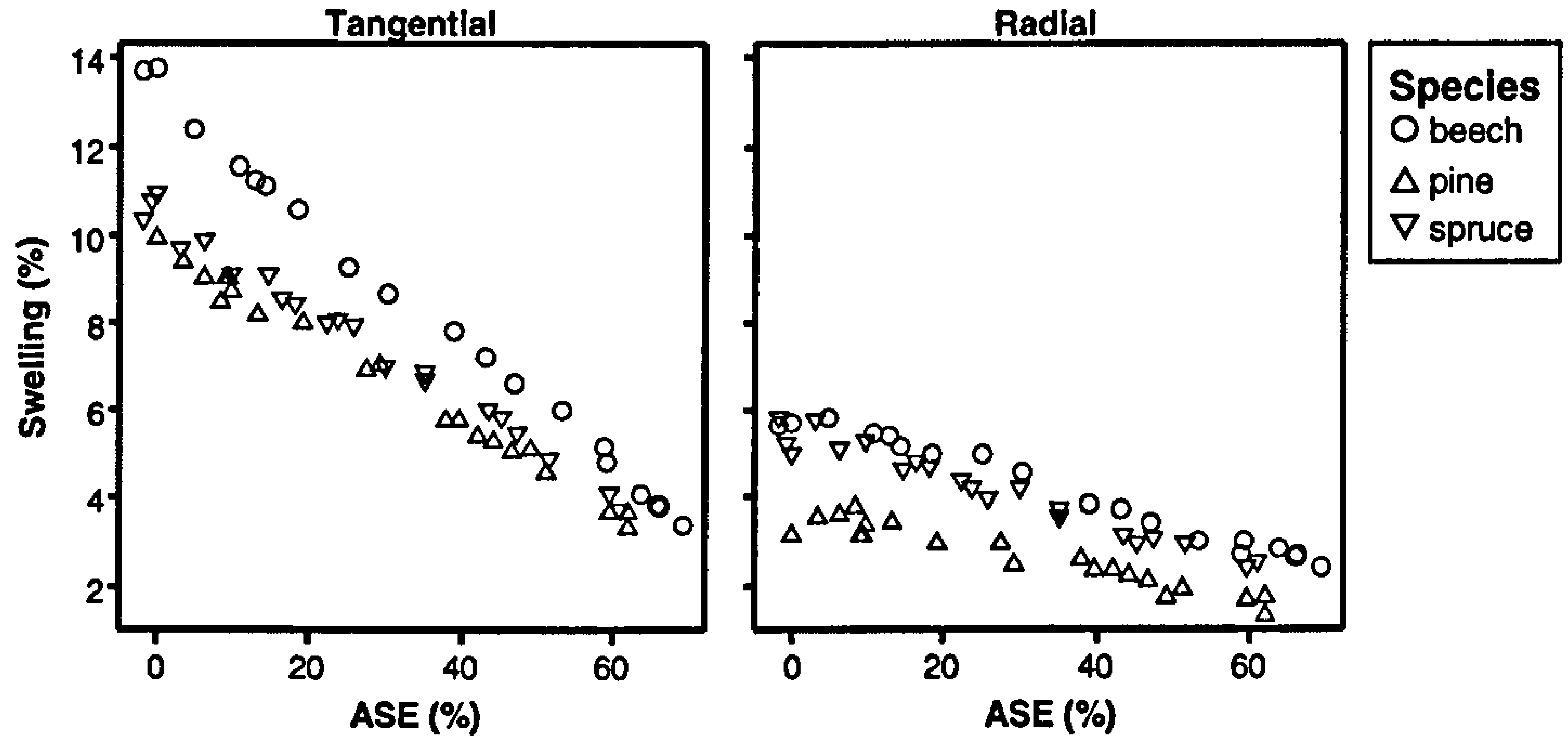


Figure 6.23. The relationship between swelling in the tangential and radial directions with the anti-swelling efficiency (ASE) in three thermally- modified woods

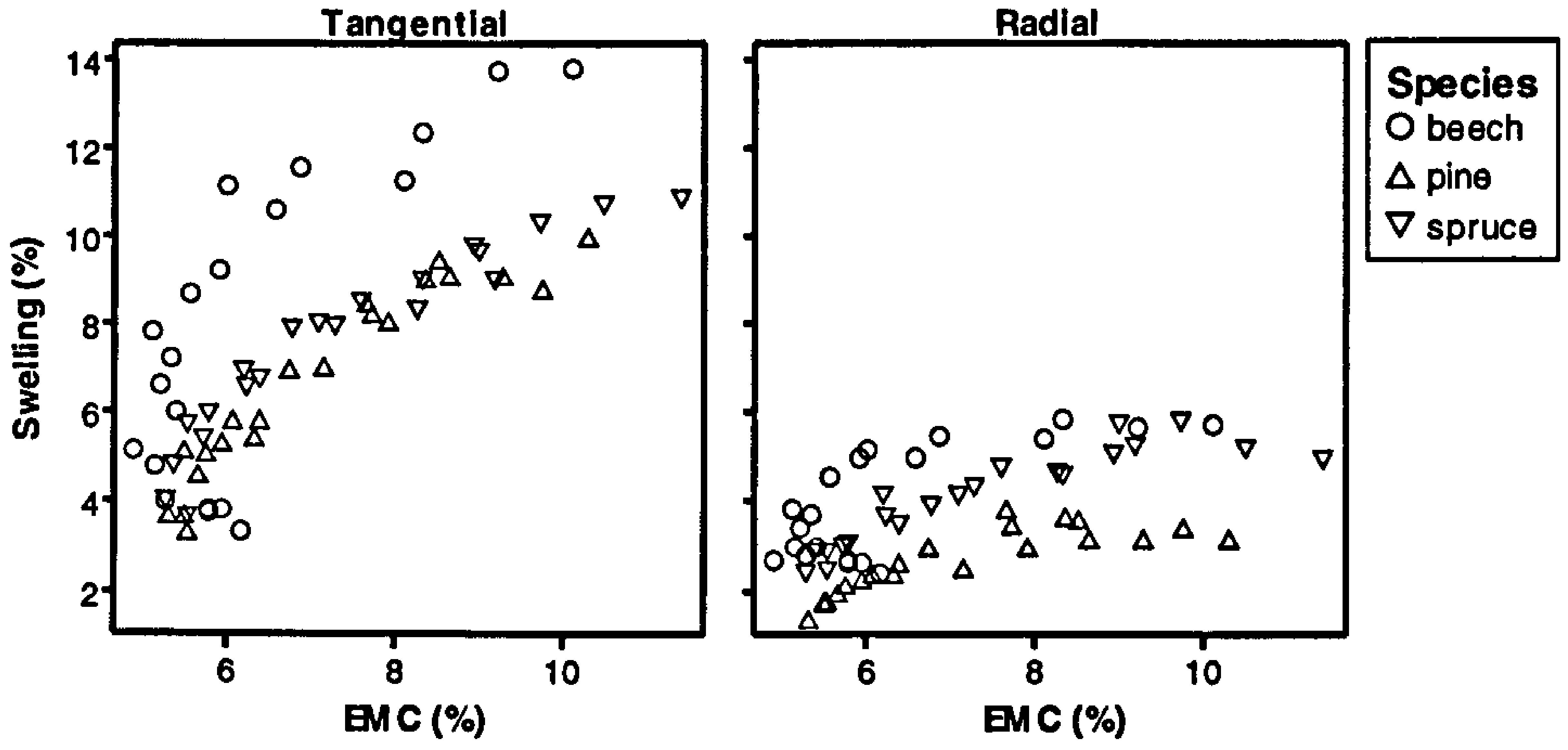


Figure 6.24. The relationship between swelling in the tangential and radial directions with the equilibrium moisture content (EMC) in three thermally- modified woods

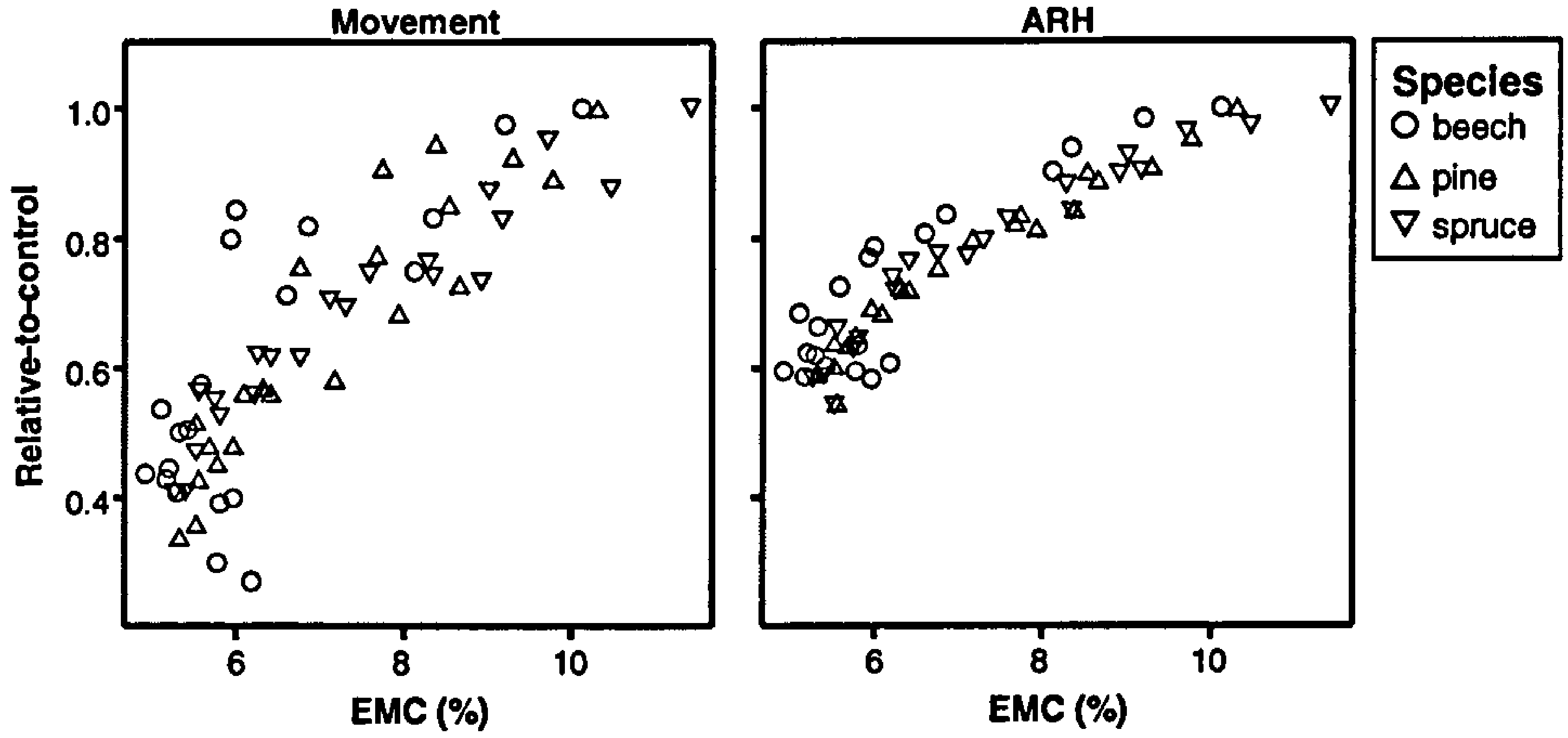


Figure 6.25. The relationship between relative-to-control total volumetric movement and the average relative-to-control hygroscopicity (ARH) with the equilibrium moisture content (EMC) in three thermally- modified woods

6.8 Conclusions

In addition to improvements in the dimensional stability of heat-treated woods, measured as in increase of the ASE along with the heat-induced weight loss, the reduced hygroscopicity of the material resulted in a significant reduction of movement in the modified wood (from 93% RH to 44% RH conditions). Moreover, the decreased affinity towards water led to the reduction of the anisotropy in swelling in the modified substrate, although this effect was moderate.

Numerous studies exist on the wood-moisture relation in heated woods, but little has been done in order to arrive to comprehensive models to characterise the behaviour of modified wood materials. This study shows that in principle it is possible to arrive at generalisations in some of the wood-moisture interactions in thermally-modified woods. ASE was found to change linearly with the weight loss, for WL > 2% up to the maximum WL value registered in this study (26%). The ASE appears to be the same at equivalent levels of WL regardless of species concerned. From this finding, it can be proposed that it is possible to use the ASE for the comparison of treatment efficiency, particularly if the modification has been carried out in different heating media or using different commercial thermal processes.

The increase in dimensional stability (ASE) was proposed to occur by the conjunction of chemical and physical changes in the cell wall material resulting in a more hydrophobic and rigid substance. Chemical changes include the degradation of moisture-reactive hemicelluloses and the reduction of reactive hydroxyl groups in the remaining polymers of the cell wall substance. These chemical changes are proposed to be the main contributing factors for the reduction in wood hygroscopicity. The reduction of the water affinity of isolated lignin from modified woods was demonstrated.

Both movement (from 93% to 44% RH conditions) and average relative hygroscopicity (in relative-to-control values) behaved very similarly in the three wood species at equivalent levels of WL, despite the large differences in the individual sorption isotherms and swelling in the transverse direction in the three species.

Movement, sorption and desorption changed following a similar profile in line with the weight loss at any given RH exposure condition. The Hailwood-Horrobin theory of sorption was found apt for the description in the sorption behaviour of modified woods.

Finally, the modelling of the ASE was successfully accomplished. Highly significant models were found when the WL or the EMC were used as predictors of the dimensional stability. For the prediction of hygroscopicity and movement in the full hygroscopic range, an equation based in a modified form of the Hailwood-Horrobin model was proposed, using a system of five-class levels of WL. It is shown that this approach is an efficient way to predict either movement or hygroscopicity isotherms at any level of WL in thermally modified woods.

Further work is currently under way to study in detail the hygroscopic behaviour of TMW at a range of temperature conditions, as well as the absolute contribution of the polysaccharide fraction in the reduction of the hygroscopicity in the solid residue.

Chapter 7 Colour changes in heated wood and prediction of its physical properties from ΔE* and ΔL* using image analysis

7.1 Introduction

Wood colour is one of the most important anatomical characteristics for its use as a material, it is a component of the aesthetic (Usta 2007). There is also an emotional dimension of colour, which plays an important role in the selection of wood species for the work, due to the significant contribution that colour makes to the professed warmth and beauty of the material (Moslemi 1969, Hon and Minemura 2001). Together with figure, grain and lustre, colour in wood is an essential quality-related property for joinery; these determine wood's value and suitability in the woodworking industry.

One form of changing wood colour, mainly towards darker shades, without using stains or other chemicals is by means of the thermal modification of wood. Already in 1920, when Thiemann was investigating the effect of high-temperature drying of wood, he contended that the colouring of wood would be potentially valuable for the use of thermally-treated timber in wood trim. From that early research, colouring of wood due to thermal processing has been repeatedly signalled as an advantage and also as an alternative to conventional staining of light coloured species (Chang and Keith 1978, Johansson and Morén 2006). This is because the colour of the modified wood is fairly homogeneous throughout its thickness, which is helpful when further machining is required; the darker colour can also camouflage many blemishes and discolorations. Colouring of wood by heat exposure has aroused renewed interest derived from the fact that several consumers confer greater value to tanned shades of wood than to natural light colours in applications like cladding, decking and flooring purposes (Syrjänen 2001). Currently, colouring of wood as a sequel of the thermal modification is gaining more relevance because of the global tendency for reducing the use of solvent-borne finishes mainly in furniture processing (Fonseca 2004).

Another proposal for the use of colour changes in thermally modified wood is for monitoring its thermal conversion, either for chemical changes (Bourgois *et al.* 1991, Esteves *et al.* 2007) or for changes in physical properties such as wood strength (Bekhta and Niemz 2003, Johansson and Morén 2006), heat-induced weight loss (Patzelt *et al.* 2003, Brischke *et al.* 2007), EMC and shrinking (Patzelt *et al.* 2003) and wood density (Bourgois *et al.* 1991).

The relationship between colour changes and wood strength has not been reported exhaustively so far. Changes in colour in TMW have been studied to assess the possibility of predicting some mechanical parameters in bending and impact strength tests, but the results are inconclusive. Moreover, only two species have been studied. Bekhta and Niemz (2003) found a strong, linear relationship ($R^2 = 0.99$) between total colour difference (ΔE^*) and MOR in bending for spruce wood pre-conditioned at three atmospheres (35%, 65% and 95% relative humidity) and then modified at 200 °C. However, only three levels of modification were reported. In a more recent study, Johansson and Morén (2006) studied the relationship between colour and strength changes in birch wood treated at 175 °C and 200 °C for up to 10 h. Static bending strength and impact bending strength were investigated, but the approach followed by these authors to build the models was unfortunate. To construct the partial least squares (PLS) regression models, they used colour changes, EMC and other unrelated parameters such as position in the board, and dimension of the samples, in clear violation of the assumptions for the use of the PLS technique: independent variables must be highly collinear (Miller and Miller 2005). They arrived at the conclusion that colour changes were not useful for the prediction of mechanical strength in modified birch, but the validity of this remains in doubt.

Investigations in order to correlate colour change and predict from this other forms of wood strength plus other important physical properties of TMW such as ND and ASE are unknown.

Quality assessment of TMW for different applications is one of the major challenges in the field of wood modification; this is currently the matter of initiatives of regulatory bodies within the EU (Homan and Tjeerdsma 2005). On the other hand, characterisation and quality control and assurance by non destructive methods are desirable. The steady change in lightness and colour of modified wood in line with the severity of the treatment should allow for the prediction of some physical characteristics, several of them also changing linearly with the modification. At the industrial environment, at least one major producer in Finland is currently using colorimetry for the non-destructive assessment of the thermal treatment of wood using the ThermoWood® process (Anon. 2005).

In the present study, it is described how colour modification in three wood species, analysed by image analysis, could be used to predict the changes in several physical properties of TMW. A description of the effect of the modification on colour parameters as well as the relationship between chemical composition and colour changes is given initially.

7.2 Modification of wood colour parameters upon heat-treatment

Effect of time and temperature in colour parameters

Figures 7.1, and 7.2 show the evolution in lightness (L*) and in the chromatic coordinates a* and b* respectively, of the different woods with respect to exposure time at each temperature of treatment. Heating of beech, pine and spruce woods induced noticeable modifications in colour parameters, mainly a decrease in lightness L* (darkening), irrespective of the temperature of treatment. Whatever the species, wood darkening increased as the time of exposure increased. In beech L* decreased slowly only for the treatment at 190 °C; colour conversion was fast for the treatment at 210 °C, and almost instantaneous at 230 °C or 245 °C, to reach a minimum of about L* = 35. Evolution of L* in pine and spruce was gradual for treatments at 190 °C and 210 °C, following a decaying pattern, and fast for treatments at 230 °C and 245 °C (Figure 7.1). Minimum at 16 h in pine and spruce varied with temperature of exposure, from L* = 70 and 75 at 190 °C, to L* = 28 and 34 at 245 °C, for pine and spruce respectively. Apparently, the heating temperature was more important than the duration of the treatment in changing the colour of beech, whilst both factors have somewhat different but significant contribution in modifying the colour of softwoods.

The evolution in a* (redness) and b* (yellowness) showed somewhat a more complex profile with respect to the processing time and temperature compared to L* (Figure 7.2).

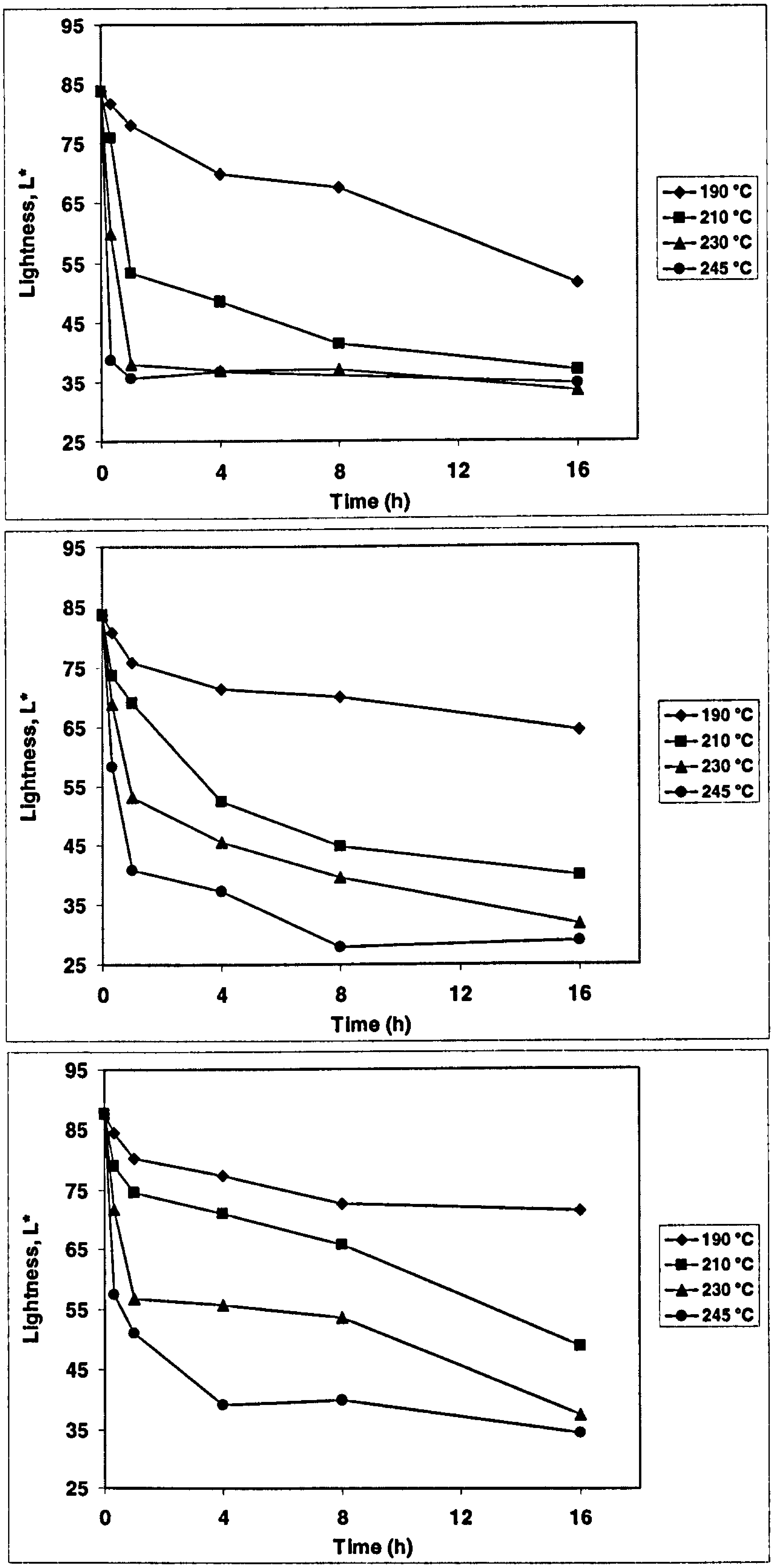


Figure 7.1 Evolution of lightness L* in the CIE L*a*b colour space for beech (above), Scots pine (middle) and Norway spruce (below) woods (on radial plane) as a function of time and temperature of heat-treatment. Each symbol represents the mean value of ten replicates

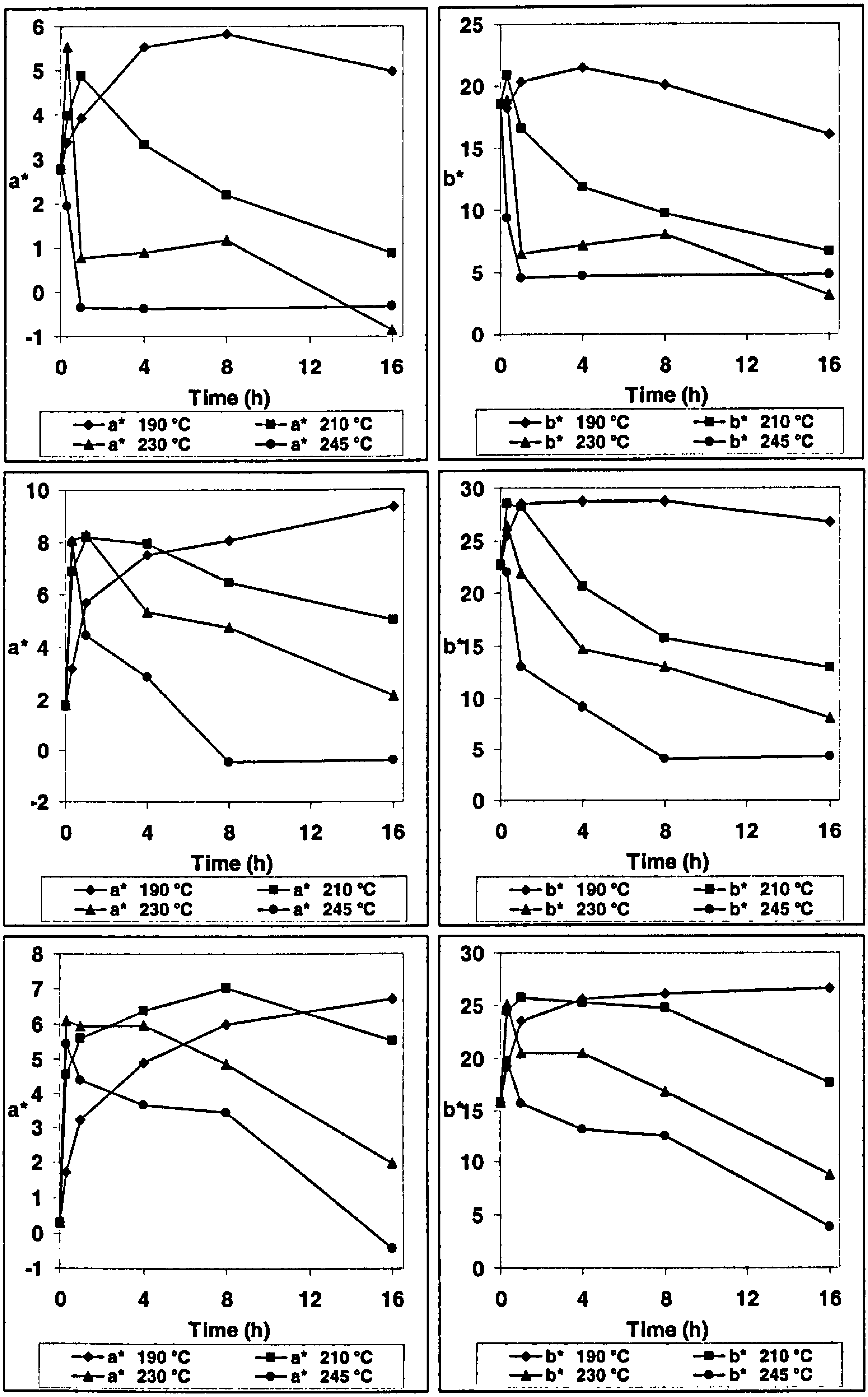


Figure 7.2 Evolution of the a* and b* chromatic coordinates in the CIE L*a*b* colour space for beech (above), Scots pine (middle) and Norway spruce (below) woods (on radial plane) as a function of time and temperature of heat-treatment. Each symbol represents the mean value of ten replicates

In all the three species, a* and b* increased at the beginning of the treatment, regardless of the processing temperature, except for beech treated at 245 °C (Figure 7.2). After reaching a maximum, both a* and b* declined at longer times of exposure. An increase in the temperature resulted in an acceleration of this increase-decrease cycle. Maxima in a* and b* varied according to species concerned. Maximum in a* was about 5 to 6 for beech, from 8 to 9.5 in pine and between 6 and 7 in spruce. The a* coordinate has a small contribution for the initial colour in the three woods, particularly in spruce, which was almost grey along this axis (control a* = 0.32). In b*, maxima reached between 18 - 22, 26 - 28 and 25-26 for beech, pine and spruce respectively. The b* coordinate has a larger contribution towards colour in the three species, again control spruce showing the smallest b* value.

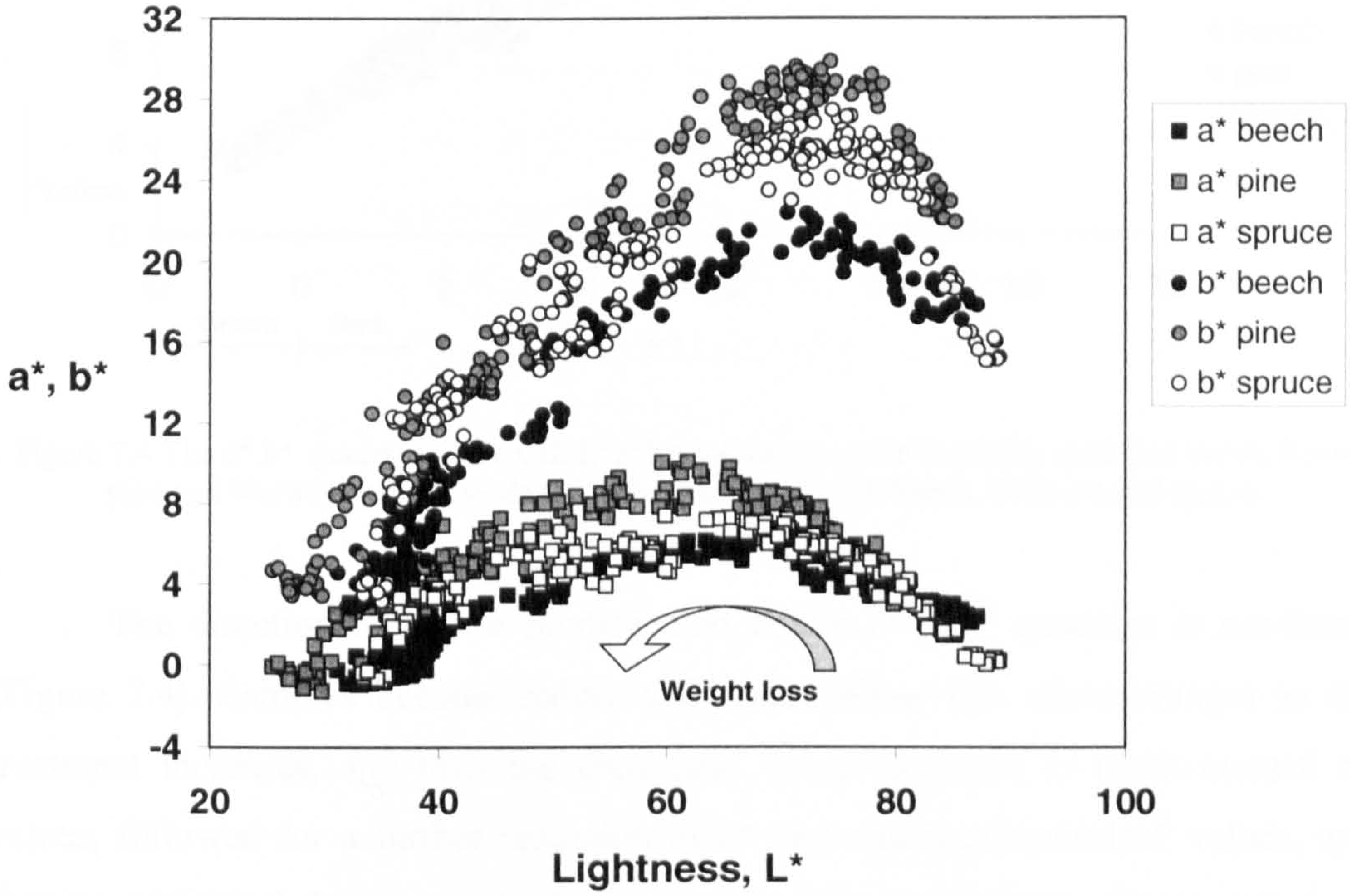


Figure 7.3 Relationship between the a* and b* chromatic coordinates and lightness L* in the CIE L*a*b* colour space in thermally modified beech, Scots pine and Norway spruce woods (on radial plane). All data plotted irrespective of exposure conditions. *n* = 200 beech, 220 pine and spruce

From the L*a*, L*b* plot (Figure 7.3), it is derived that both b* and a* varied in a similar parabolic pattern with the decrease in lightness. Regardless of the species, the coordinates reach a maxima at L* = 60 for a* and at L* = 72 for b*. Modification of the a* and b* coordinates in beech are smaller than softwoods at equivalent values of L*. Pine shows larger variation than spruce. At equivalent values of L*, the modification in b* is larger than in a*; b* increases more as L* decreases, but the reduction in b* is also larger after reaching its maxima, attaining values of nearly zero at L* values < 30. Both a* and b* coordinates remain positive for most of the treatments, although a* becomes negative for L* values > 30 - 40.

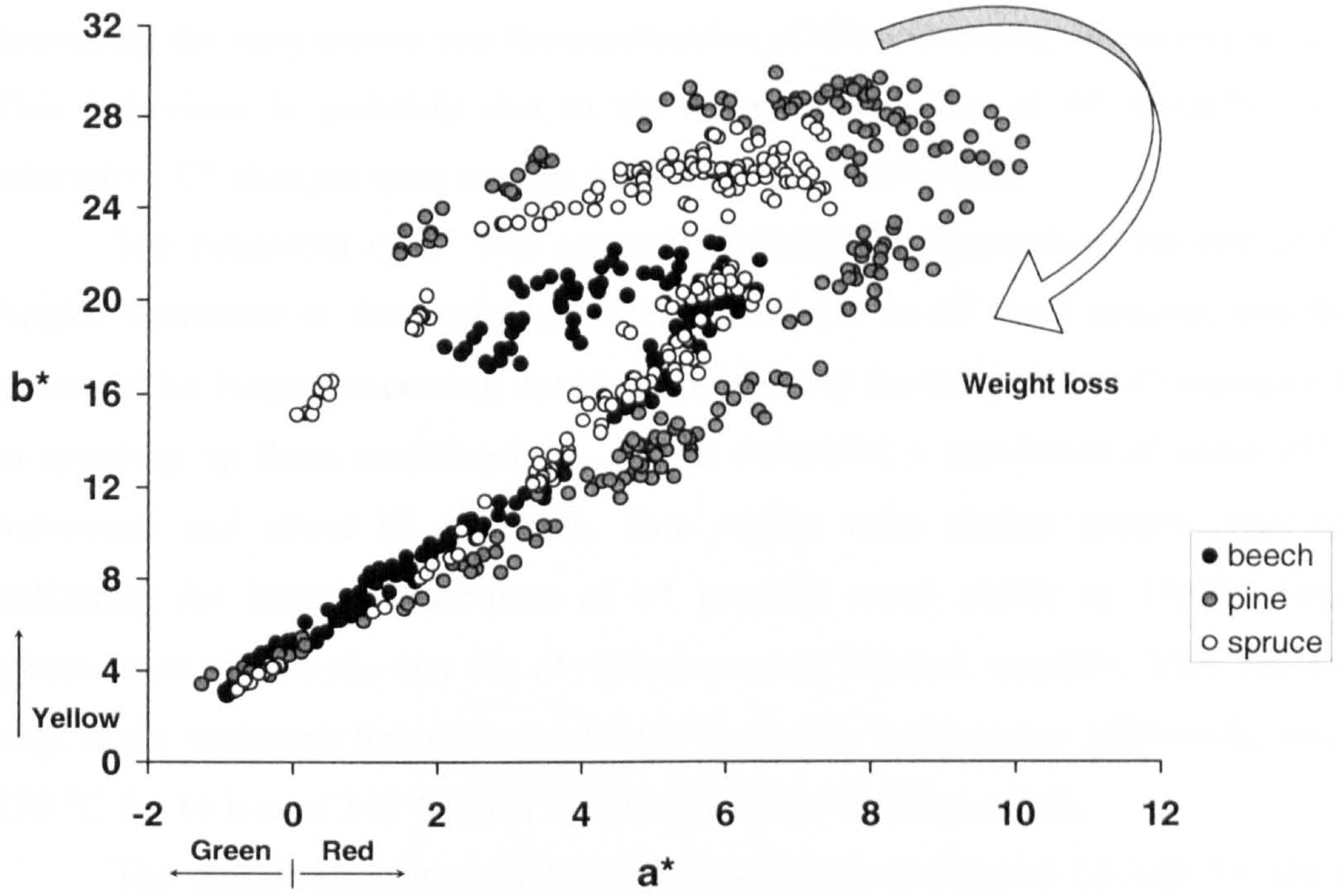


Figure 7.4 The a*,b* quadrant in the CIE L*a*b* colour space for thermally modified beech, Scots pine and Norway spruce woods (on radial plane). $n = 200$ beech, 220 pine and spruce

The direction of colour modification in the a* - b* quadrant is not-linear (Figure 7.4). Samples become redder and more yellow (*i.e.* more orange) as the treatment increases, and then the chromatic values decrease to reach control b* values, followed for a further reduction of b* and reaching control a* values, and then an additional decrease in both coordinates. All modifications always remained in the positive quadrant of the a*, b* coordinate system except at the very high levels of treatment, where both coordinates reached almost zero (the samples became essentially hueless); the a* coordinate even reaches small negative values (appears green). The description of the colour changes is better explained as an orange darkening towards dark grey in the three wood species. Acceptable colour changes would depend on the application, but the optimum probably lies above the stage where the b* coordinate reaches control values after reaching its maxima, at L* values of around 43-50.

The evolution of colour saturation, C*, and hue angle, h*, upon heating also follow complex behaviour (Figure 7.5). C* varied differently according to the treatment temperature, in a similar way as described for the b* coordinate above, *i.e.* C* values increased at the beginning of the treatment, and then decreased at lengthier exposure periods irrespective of species or temperature of treatment. The effect of increasing the temperature was the acceleration of this increasing-decreasing process. This behaviour is probably due to the large contribution of b* towards colour saturation. C* changes were smaller in beech than in softwoods.

The behaviour of h* was somewhat similar but opposite to the one of C*. Angles decreased at the beginning of the treatment in all three species, and then increased for longer processing times; the increase in the temperature of exposure led to speeding up these modifications. Angles decreased a maximum of some 15° in softwoods and about 9° in beech. Hue angles were always greater than 65°, indicating the larger contribution of b* towards wood colour in TMW. Angles greater than 90° imply that the a* coordinate has became negative. This occurred only at the treatment temperature of 245 °C for 8 h or longer in softwoods, and at 230 °C for 16 h or at 245 °C for 1 h or longer in beech (Figure 7.5).

The modification in colour components given in Figures 7.3 and 7.4 are for all the samples plotted together (treated from 0.3 to 16 h at temperatures of 190 - 245 °C). Apparently, the modification in lightness and chromatic coordinates are the same at equivalent levels of treatment, regardless of the processing time or temperature, which may be useful to monitor the reaction irrespective of the heating schedule. However, colour homogeneity in each coordinate within individual samples differed at equivalent levels of treatment. Variability in colour is undesirable, because it might be considered to be a processing defect. The largest variation was in the L* coordinate. The SD of the L* values increased rapidly for WL up to 4%, and then decreased slowly whatever the species. However, as average L* values were also declining, the coefficient of variation actually increased, somehow fast for WL up to 2% and 6-8% in beech and softwoods respectively, and then continued rising at a much smaller rate. The consequence of this is that treatment should probably to be carried out preferably at WL > 4% in order to get the most acceptable results in terms of colour homogeneity.

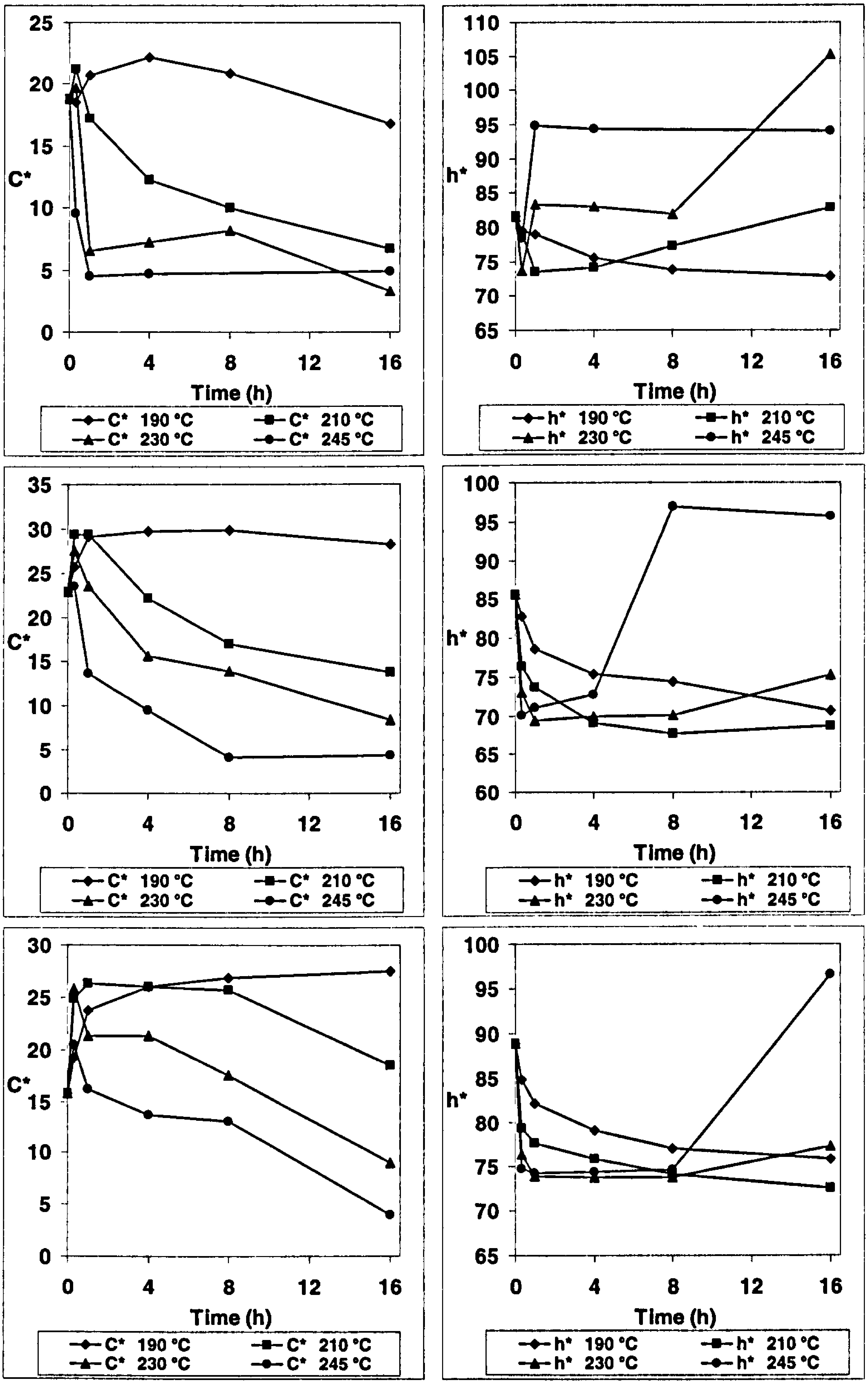


Figure 7.5 Evolution of the saturation C* and hue angle h* (in °) in the L*C*h* colour space for beech (above), Scots pine (middle) and Norway spruce (below) woods (on radial plane) as a function of time and temperature of heat-treatment. Each symbol represents the mean value of ten replicates

A few cross-cut beech samples were scanned transversally and no colouring gradient was detected across the thickness (difference in L* between edge and central zones < 1%). However, samples for this study were small (initial thickness = 10 mm), and these were treated in a very accurate heating chamber. As it was described in chapter 3 (Methods), samples treated at temperatures ≥ 210 °C virtually reached the same temperature at the centre and on the surface of the specimens for heating times > 2 h. Thus, although the appearance of colour gradients on larger wood members is possible, characterising the surfaces may give a satisfactory account of the colour changes, especially if the material were to be treated at nearly usage dimensions.

Findings from the present study confirm previous reports, where L* has been found to decrease at any given time or temperature of treatment (Unsal *et al.* 2003); the small increase in the a* and b* coordinates before decreasing as the treatment continues has also been document (Bekhta and Niemz 2003, Brischke *et al.* 2007).

Finally, a short note on the changes in colour parameters in softwoods, regarding the differences in early- and late-wood is necessary. As it is explained in chapter 3 (Methods), samples were scanned on the radial face, where the annual rings are clearly visible. For colour analyses, average L*, a* and b* values where used for each specimen. However, the frequency histogram for L* for individual samples was left-skewed; if a sharp colour difference between tissues exists, two modes appeared in the histogram (mainly in pine), one from each EW and LW. The highest mode, comprising some 60 percentile, at higher L* values, was for EW. The mean L* was up to 2.4 units smaller than the median (hardly noticeable to the human eye); the bimodal distribution impacted more the SD than the mean sample value, though. L* values tend to converge as the treatment proceeds. This implies that EW darkened faster than LW, probably due to differences in their chemical make up. In treatments at 210 °C for > 8 h, at 230 °C for > 4 h and at 245 °C for 1 h or longer (leading to WL >10%), the histogram for the L* distribution already appears nearly symmetric.

The colour distribution in individual softwood samples along the a* and b* coordinates was more complex. In untreated samples, the histogram also showed two modes, LW being redder and more yellow than EW. As the treatment proceeds, colour in EW and LW in the a* coordinate tend to converge; at WL of around 6%, the histogram appears almost symmetric. However, changes in LW were slower and an asymmetric histogram appears again at a WL of 11%, now EW being redder than

LW. After this level of modification, a* in EW and LW tend to converge again, both approaching zero at WL > 20%. In the b* coordinate, the behaviour was similar. b* values in LW decreased at a faster rate than in EW after a small increase in each tissue. At a WL of about 5%, b* values tend to converge, but at higher levels of WL, LW became less yellow than EW. After reaching a maxima difference at a WL of about 7%, b* in both tissues tend to slowly converge again, approaching zero at WL > 20%.

Change in colour parameters as a function of the WL

The severity of treatment, R_O, resulting from the combination of the processing time and temperature, is closely related to the heat-induced weight loss (WL) (chapter 5). Therefore WL is an ideal surrogate measurement of the severity of the treatment. WL is mainly due to the evaporation of carbohydrates form the wood substance (chapter 4). Differences in colour parameters are presented in the following section in function of WL, in order to make comparisons between species.

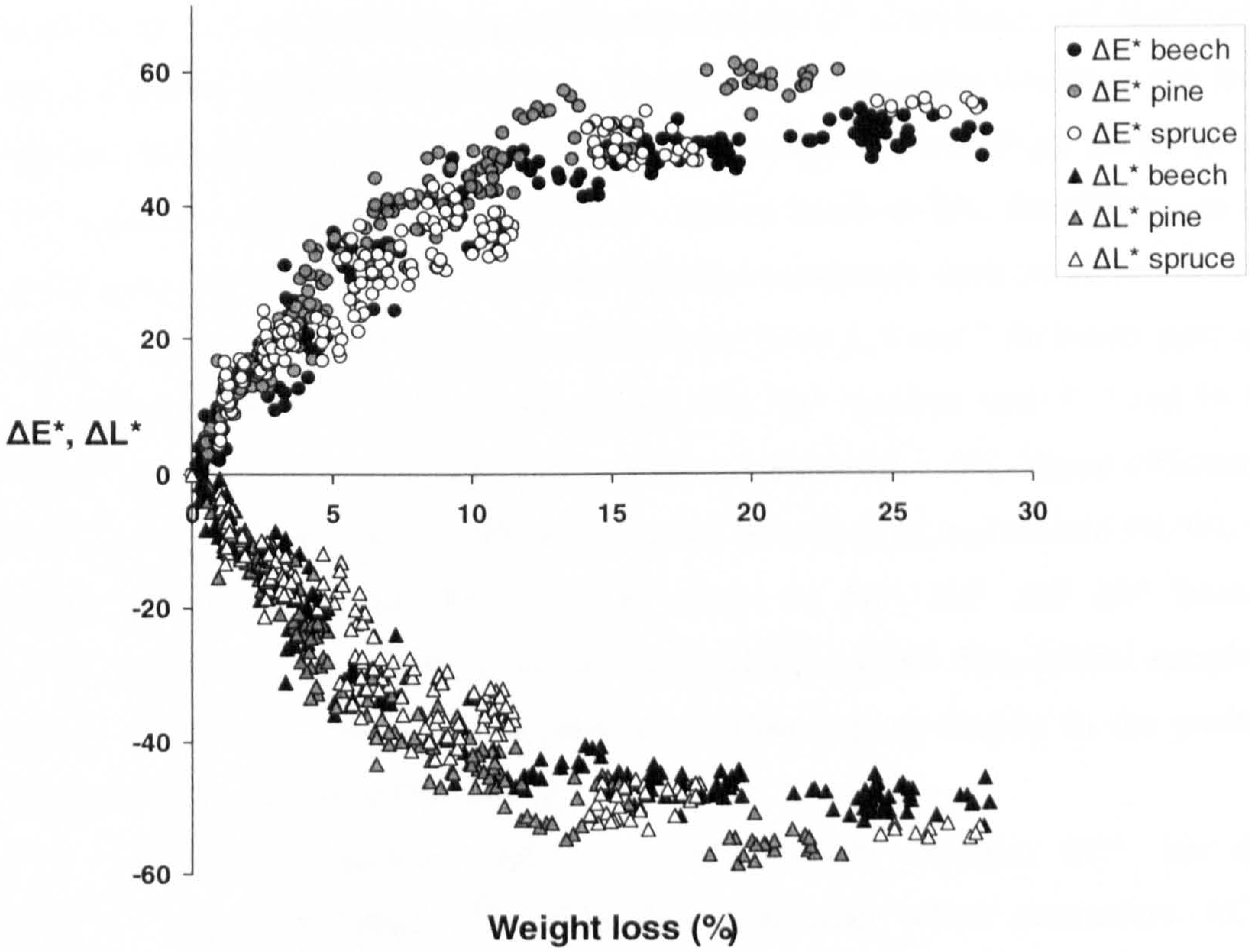
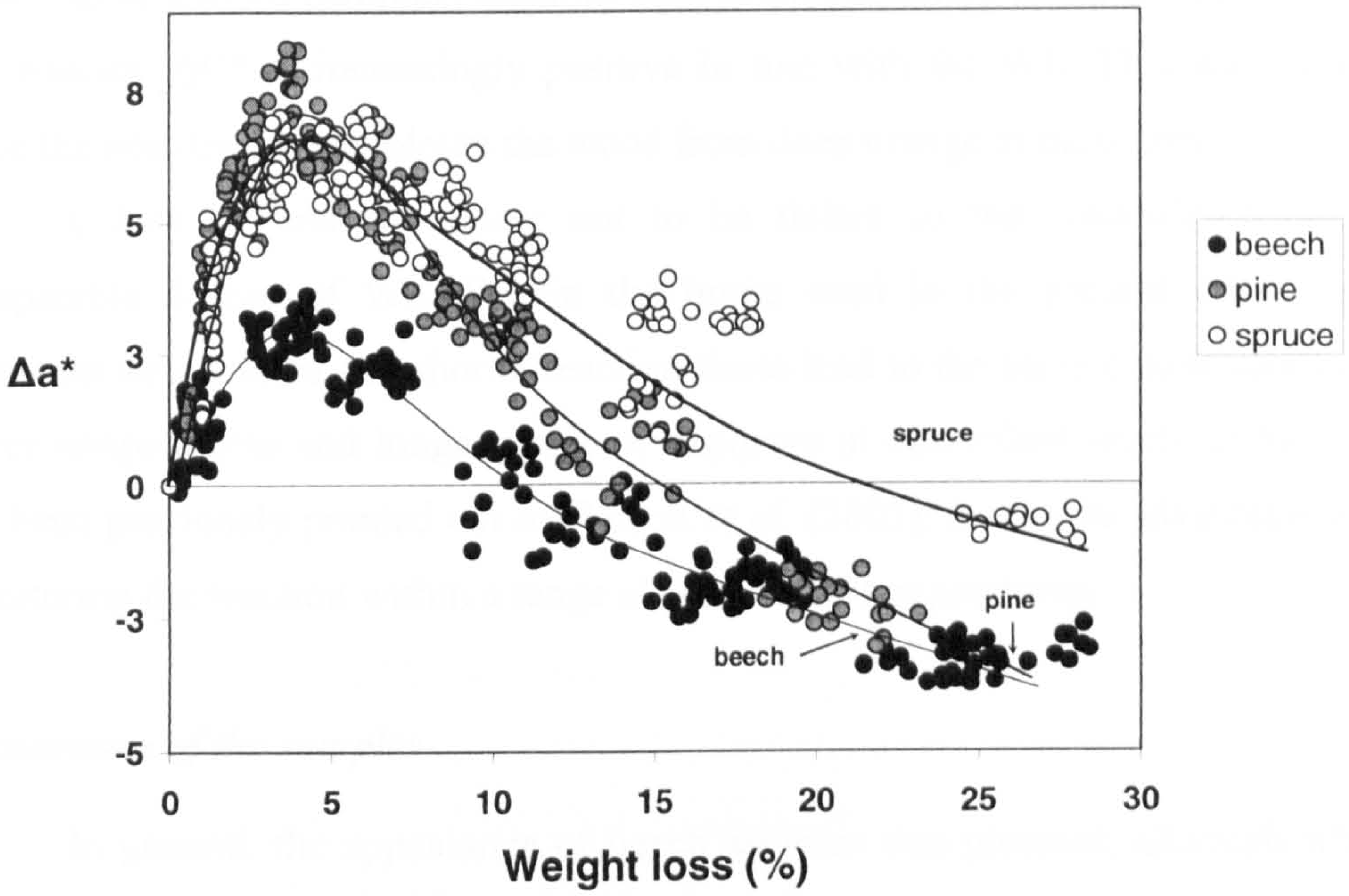


Figure 7.6 Total colour difference, ΔE*, and Lightness difference, ΔL* in the CIEL*a*b* colour space for heat-treated beech, Scots pine and Norway spruce woods as a function of the heat-induced weight loss. *n* = 200 beech, 220 pine and spruce. On radial plane.

An obvious, negative curvilinear relationship exists between ΔL^* and WL in the three woods (Figure 7.6). Moreover, ΔL^* at equivalent levels of WL is very similar in the three species, despite the initial different colour and chemical make up between coniferous samples and beech wood; the differences in lightness in pine wood increased at a slightly higher rate than in the other two species, though. The profile of ΔL^* follows a decaying pattern in line with the WL. On the other hand, a strong, curvilinear positive relationship exists between the WL and total colour change, ΔE^*, in the three species (Figure 7.6). Then again, ΔE^* is very similar in the three woods at equivalent levels of treatment, although pine samples show a slightly larger changing rate than the other two species. Beech specimens also had somewhat smaller ΔE^* than softwoods at WL > 20%. Obviously, the total colour differences were highly influenced by the difference in lightness. The smallest colour difference in treated wood was visually rated at $\Delta E = 2.5$. As the ΔE^* value increased, colour differences were more conspicuous, being moderate at $\Delta E^* = 2.5 - 17$, large at 17 – 40 or very large at ΔE^* values greater than 40.

Colour differences in the chromic characters a* and b* are smaller at equivalent levels of treatment than differences in the L* coordinate, and displayed a more complex behaviour (Figure 7.7). The behaviour was quite similar in the three species, though. Both Δa^* and Δb^* follow a quasi-sigmoid, non-linear profile as the WL increases; Δb^* being greater than Δa^*. At low levels of WL, the differences are positive and increase sharply. After reaching their maximum, each coordinate decline as the treatment proceeds. Maximal values in Δa^* were 3, 8 and 7 for beech, pine and spruce, respectively, at a WL of around 4%. For Δb^* maxima were 4, 7 and 10 for beech, pine and spruce, respectively, at a WL of about 2% – 3%. These differences reach control values at WL > 10% in Δa^* in the three species, and around 5% WL for beech and pine, and at 10% WL for spruce in Δb^*. Δa^* and Δb^* became subsequently negative (samples are less red and less yellow than control samples), but as it has been shown above, both coordinates remain largely in the positive quadrant (they are approaching grey).

Saturation differences ΔC^*_{ab} and chromaticity changes, ΔC^*, are also complex and the pattern is less clear than with other colour parameters. ΔC^*_{ab} follows a similar pattern than Δb^*, increasing sharply at the beginning of the treatment, and then decreasing before becoming negative at around 5% WL in beech and pine, and at 10% WL in spruce. This means that samples are more coloured than untreated controls at early levels of treatment, and then tend to become hueless.



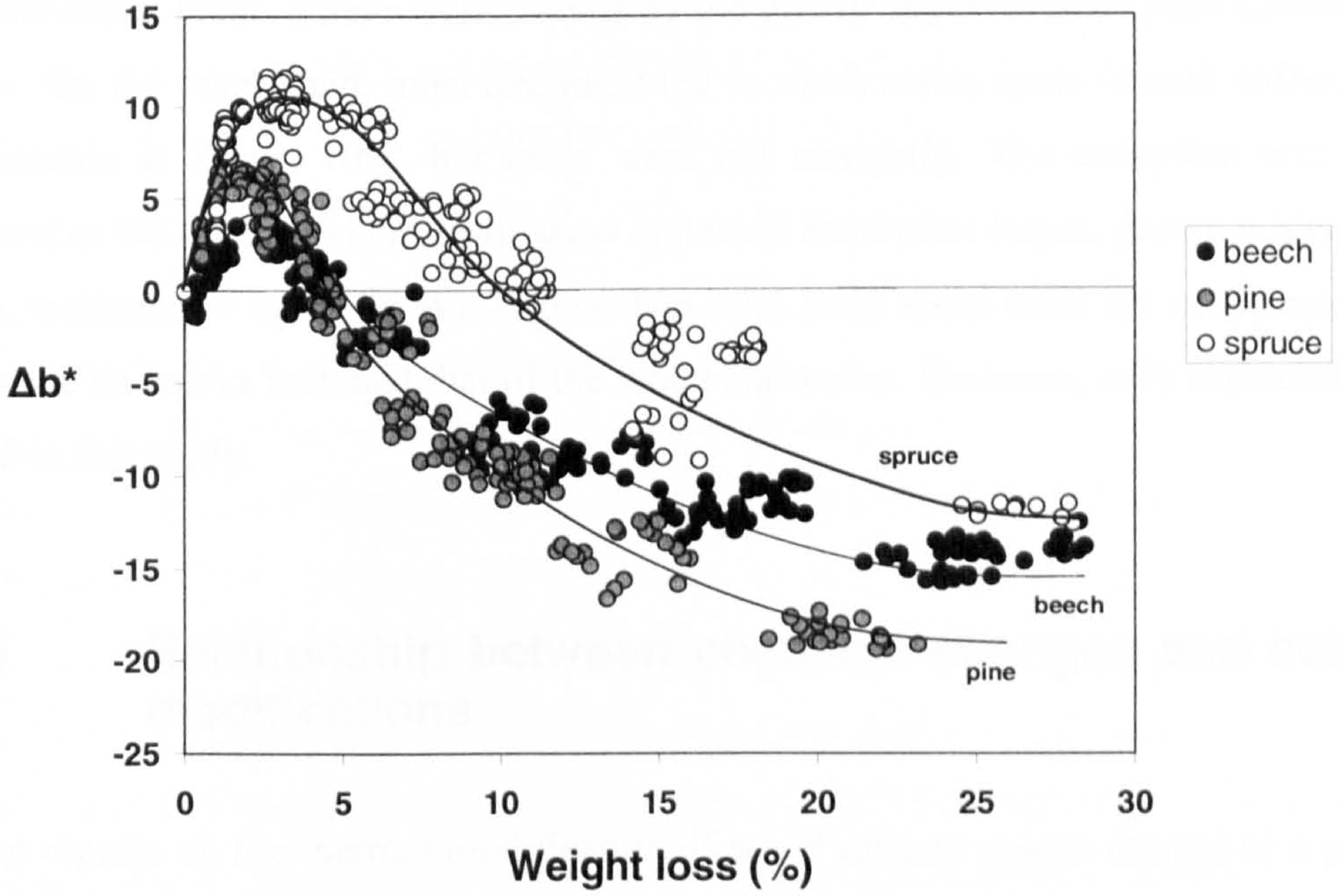


Figure 7.7 Colour differences along the a* coordinate, Δa* (above) and along the b* coordinate, Δb* (below) in the CIEL*a*b* colour space for heat-treated beech, Scots pine and Norway spruce woods as a function of the heat-induced weight loss. $n = 200$ beech, 220 pine and spruce. On radial plane.

Negative values in ΔL* and positive values in ΔC^*_{ab} leads to the opacity of the material, while increasingly negative values in both ΔL* and ΔC^*_{ab} results in the blackening of the wood substance (Bourgois *et al.* 1991). Chromaticity changes ΔC^* are composite: in beech and pine these are almost linear at WL > 5% and in spruce these follow a more complex, sigmoid behaviour, becoming linear at WL > 10%. In any species, ΔC^* is increasingly positive in line with the WL. This was expected since the heat-treatment colours the wood from deep orange to deep grey.

Colour differences appear not to be linked to the schedules leading to comparable degree of WL. Within the limits used in the present study, higher treatment temperature and shorter reaction times lead to the same colour variation as lower temperatures and longer times of exposure at equivalent levels of WL. This has been previously pointed out by Patzelt *et al.* (2003); it may be advantageous for monitoring the reaction within a range of processing temperatures.

Appearance of the samples

In general, the appearance of beech samples was pleasant, although whitish spots were observed at low (WL < 2%) or very high (WL > 15%) levels of treatment on the radial plane. These were caused by the glossy appearance of parenchyma ray cells. On the other hand, most treatment led to small resins spots in both softwoods, noticeable at WL < 10%, but these were not unsightly. The exception was pine treated at WL < 2%, where resin areas appeared somewhat larger, giving a blemish-like, unattractive view. At WL higher than 10% resin spots were not easily noticed, because its colour matched that of the wood substance. However, only sapwood was used in this study.

7.3 Relationship between chemical changes and colour modifications

Most reports on the thermal modification of wood refer to colour change as a prime characteristic of this practice, but very little has been done to unveil the origin of the heat-developed colour in the wood material.

The identification of the components responsible for colour in untreated wood is far from complete, and heat-induced changes in colour are not completely understood. In untreated wood, the α-carbonyl conjugated carbon-carbon double bond and phenolic hydroxyl groups are the principal chromophoric groups in the material (Hon and Minemura 2001). Polysaccharides (cellulose and hemicelluloses) do not absorb visible light, whilst lignin isolated with minimal physical or chemical degradation is pale yellow (*Idem.*). In raw softwoods, phenyl-substituted benzoquinone and coniferaldehyde groups are major contributors to the colour of lignin (Pew and Connors 1971). Colour in untreated coniferous wood beyond 500 nm is caused by the absorption of phenolic substances present in extractives, particularly in heartwood (Hon and Minemura 2001, Kondo and Imamura 1985).

It is well known that wood discolors when it is subject to high temperatures. If heated for short periods, wood colour changes to yellow, brown, red, grey, etc. In other practices in the woodworking industry involving heating (*e.g.* wood drying), these colour changes are associated to superficial staining of the material, as a result of enzyme-mediated (Maillard) reactions between sugars, phenolic compounds and amino acids, or to the oxidative reactions between extractives and the atmosphere (Keey 2005, Thompson *et al.* 2005). Kiln stains are also thought to develop due to the migration of darkened coloured compounds to the surface of boards as free water is removed upon drying. However, extractives rapidly disappear from heat-treated Scots pine wood at early stages of modification (Nuopponen *et al.* 2003). In the present study, only oven-dry sapwood was used and colour changes were not only large ($\Delta E^* > 17$), but also fairly even and throughout the sample. Therefore, extractive-induced or enzyme-mediated discolorations are unlikely to be major factors in the colour changes noted here.

In heated wood, chromatic coordinates a* and b* behaved in a similar manner between themselves, but differently to L* in the rate and magnitude of change at equivalent levels of WL (section 7.2). Evidently different mechanisms are involved in the change of chromatic coordinates and lightness. Lightness is reduced steadily from the beginning of the treatment, whilst the chromatic characters increase at low levels of modification and then decrease gradually. The behaviour of lightness is similar to that of hemicelluloses upon heat-treatment, where these decrease from the beginning of the treatment (chapter 4). However, lignin also increases gradually in line with the severity of the treatment, so it is difficult to deconvolute the effect of each individual polymer on lightness change. The decrease in lightness is probably due to concurrent events: proportionally higher lignin content (itself tan coloured) and development of colouring compounds in all the three main components, although the presence of potential chromophoric groups is more abundant in lignin than in polysaccharides. The evolution profile in a* and b* is more complex, and hence more difficult to assign to chemical changes. These may be because of the production and subsequent destruction of chromophoric species, probably originated from extractives, or due to the lignin condensation and re-polymerisation, which may cause a paraboloid profile in these coordinates.

Correlation between gravimetric changes in chemical composition and colour change

When wood is left at high temperatures for long periods, it usually becomes brown. The formation of coloured substances from a phenolic compound oxidized with air and the formation of dark materials from hydrolysis of hemicelluloses have been considered the cause of discoloration (Hon and Minemura 2001). In TMW, colour changes have been vaguely assigned to the formation of oxidation products such as quinones (Tjeerdsma *et al.* 1998). In earlier research, the difference in intensity of colour of the surface before and after heat-treatment was closely correlated with the decreases in X-ray crystallinity, degree of polymerisation of cellulose, and hydroxyl content at the wood surfaces (Chow and Mukai 1972). In subsequent studies on colour change, the decrease in lightness and the increase in colour difference resulting from thermal modification of Scots pine wood at 100 °C and at 210-310 °C were found to result from the degradation of pentosan and increase of lignin (Bourgois *et al.* 1991); a better relationship was found between the latter and colour parameters, though. In a subsequent study, a strong relationship between lightness reduction and several chemical components was determined for Pitch pine (*Pinus pinaster* Aiton.) (Esteves *et al.* 2007). The strongest association using linear regression was for glucose (R^2 = 0.96) closely followed by hemicelluloses (R^2 = 0.92). The coefficient of determination for lignin and extractives was smaller, R^2 = 0.86 and 0.62, respectively.

Table 7.1 shows the correlation between colour differences and lignin, cellulose, total hemicellulose and the two main hemicellulose types, glucouronoxylan (GluXylan) and galactoglucomannan (GluMan) in heated woods. In general, strong correlations are found between all chemical components and ΔL*, Δb* and ΔE*. Δa* normally had the lowest correlation with any chemical constituent; in spruce, this has significant correlation only with lignin. In pine and beech, the strongest correlation for Δa* was also with the lignin content. ΔE* was positively related to lignin, and negatively related to the other chemical components, whilst the opposite was true for the other colour parameters (ΔL^*, Δa^* and Δb^*). Regardless of the species, the smallest correlation between colour differences and chemical changes was with cellulose. The relationship between ΔL^*, Δb^* and ΔE^* and chemical content was mixed. ΔL^* has the strongest correlation with hemicelluloses in beech, with lignin in pine and with GluXylan in spruce. On the other hand, Δb^* was more strongly correlated with GluXylan, lignin and GluMan in beech, pine and spruce, respectively. In beech, total colour difference had the largest correlation with hemicelluloses, followed by GluXylan; in pine the largest correlation was with lignin followed by GluMan, and in spruce with GluXylan followed by hemicelluloses.

Table 7.1 Pearson correlation between chemical constituents and colour parameters in thermally modified beech, Scots pine and Norway spruce woods.

Species		Lignin (%)	GluXylan (%)	GluMan (%)	Hemicelluloses (%)	Celullose (%)
Beech	ΔL^*	-.809(***)	.913(***)	.882(***)	.930(***)	.595(**)
	Δa^*	-.879(***)	.871(***)	.623(**)	.841(***)	.825(***)
	Δb^*	-.899(***)	.962(***)	.795(***)	.952(***)	.751(***)
	ΔE^*	.821(***)	-.921(***)	-.884(***)	-.937(***)	-.610(**)
Pine	ΔL^*	-.926(***)	.802(***)	.849(***)	.839(***)	.705(***)
	Δa^*	-.661(**)	.481(*)	.661(**)	.593(**)	.575(**)
	Δb^*	-.937(***)	.752(***)	.866(***)	.829(***)	.776(***)
	ΔE^*	.934(***)	-.819(***)	-.864(***)	-.855(***)	-.694(***)
Spruce	ΔL^*	-.874(***)	.966(***)	.943(***)	.959(***)	.751(***)
	Δa^*	-.472(*)	NS	NS	NS	NS
	Δb^*	-.863(***)	.752(***)	.874(***)	.851(***)	.555(*)
	ΔE^*	.874(***)	-.955(***)	-.931(***)	-.948(***)	-.758(***)

*** significant at $p< 0.001$ level (2-tailed).
** significant at $p< 0.01$ level (2-tailed).
* significant at $p< 0.05$ level (2-tailed).
NS not significant

Results from the correlation analysis probably reflect the contribution that all components make to colour change. However, changes in the three main polymers are strongly correlated between themselves and the real contribution of each component on colour changes is difficult to resolve. Furthermore, analysis like this on the empirical correlation between chemical degradation and colour changes is of questionable utility, because the gravimetric determinations do not reflect the qualitative changes undergone in the each polymer (*e.g.* colour change).

Changes in lignin and its relationship with colour change: changes in lignin colour

An investigation between total colour changes in lignin and in the wood substance gave that total colour difference in lignin is closely, though non-linearly associated to total colour change in treated softwood, which suggests a strong correlation between the underlying colouring events (Figure 7.8). In beech this relationship was almost linear, but with a larger scatter in the data.

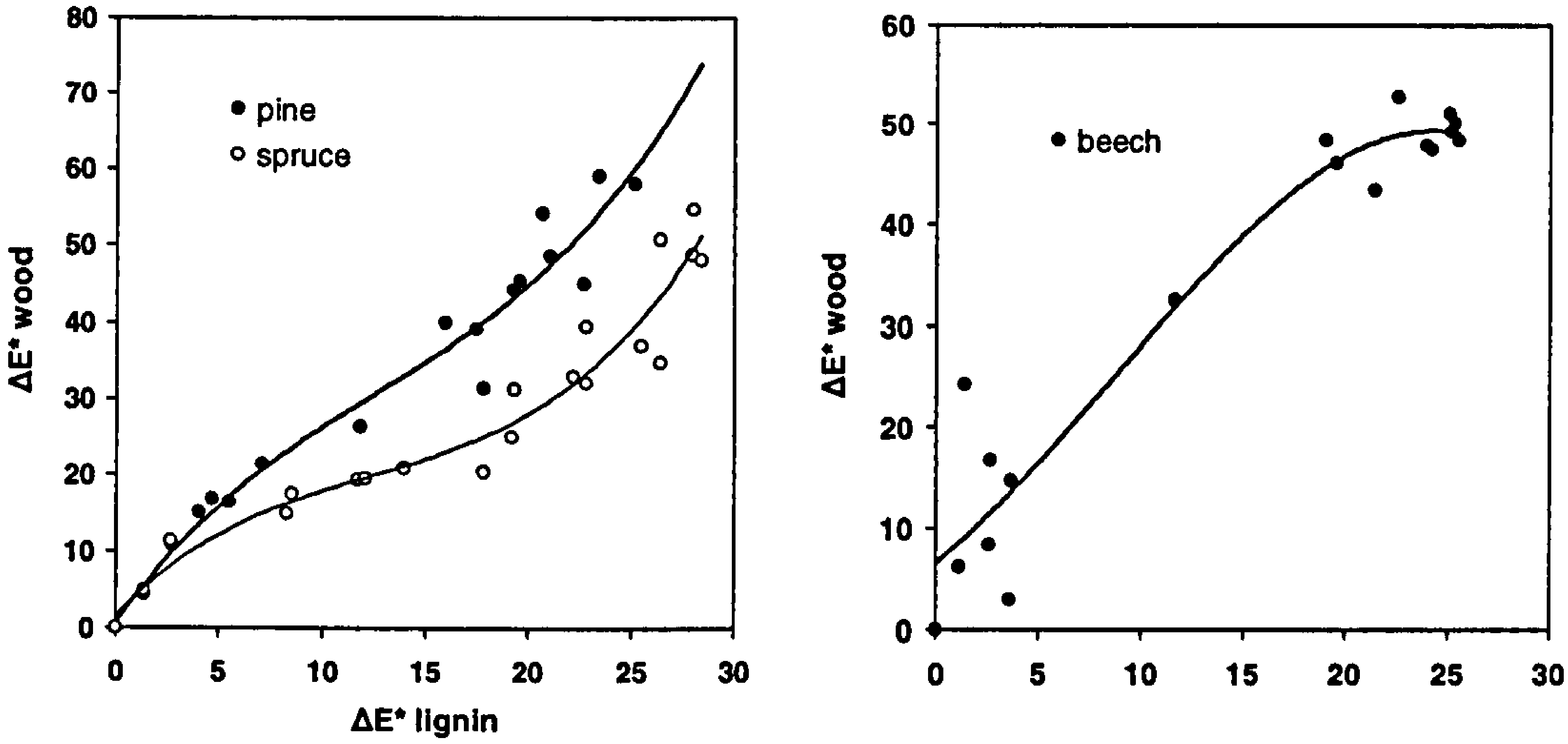


Figure 7.8 Relationship between total colour difference in heated softwoods (left) and beech wood (right) and total colour difference in Klason lignin.

Irrespectively of the species, colour differences in lignin accounted for 40% or more of the colour differences in wood at WL > 7 – 8%. At earlier levels of WL, the remnant chemical constituents (including extractives) possibly have a larger involvement in the colour modification of wood. Colour changes in isolated cellulose and hemicelluloses were only quantified in a few samples in spruce wood. Although the extraction procedure doubtless changes the nature of the isolated polysaccharides, these also changed in colour, but to a much smaller degree than lignin. For instance, cellulose from wood heated at 210 °C for 16 h (to a WL of 8.7 %), has a total colour difference of 10.2 units, whilst in hemicelluloses this was 3.2 units. For comparison, ΔE* in lignin was 22.8 units. Apparently the rule of mixtures does not apply; the difference in wood colour does not reflect the simple accumulative difference in colour of individual chemical components, because at this level of treatment ΔE* in wood was 39.4 units. Probably the absorption in the visible range of chromophoric groups in lignin is amplified by integrating these into a polysaccharide medium. This remark is sustained on the finding that colour of coniferaldehyde in solution is considerable enhanced by its incorporation into a cellulosic matrix, whilst on its own it extends just up to the green-yellow range of the visible spectrum (Pew and Connors 1971). The data analysed for carbohydrates was limited, though.

Although development of colouring compounds is possible in all the three main components, lignin is richer than carbohydrates in latent chromophoric groups. Additionally, the available evidence indicates that modifications in wood colour are dominated by differences in lignin colour, and the chemical changes undergone in lignin largely dictate the overall colour transformation in the solid residue. Therefore a closer examination of chemical changes by the analysis of the infrared spectra is limited to the lignin macromolecule. Modifications to the infrared spectra of wood resulting from heating are described in detail in chapter 8.

Chemical changes in lignin monitored by IR spectroscopy and its relationship to colour changes

The difference spectra of lignin for Norway spruce, for treatments resulting in WL between 1 and 15%, reveal an absorbance increment at several wavenumbers in the carbonyl region (Figure 7.9). Several positive peaks appear in this region markedly at 1708, 1637, 1630 and 1600 cm^{-1}. The band at 1708 cm^{-1} is for the CO stretching of various functional groups (unconjugated ketones, carbonyl and ester groups, Faix 1992) and tends to dominate the spectra. Although the difference spectra are for isolated Klason lignin, the large peak in this region may also contain the vibration from CO groups derived from the oxidative carboxylation of polysaccharides (Chow 1971). These groups possibly percolated and remain trapped within the lignin network even after the acidic removal of carbohydrates. This observation is substantiated in the increase of acid insoluble lignin at the expense of the carbohydrate fraction following the thermal exposure of wood, the so called pseudo-lignin, which is well established (Nikitin 1966, Garrote *et al.* 1999, Inari *et al.* 2007a, b). The rising peak at 1600 cm^{-1} is probably due to the increasing C=O stretch vibration, rather than from aromatic skeletal vibration (Baeza and Freer 2001).

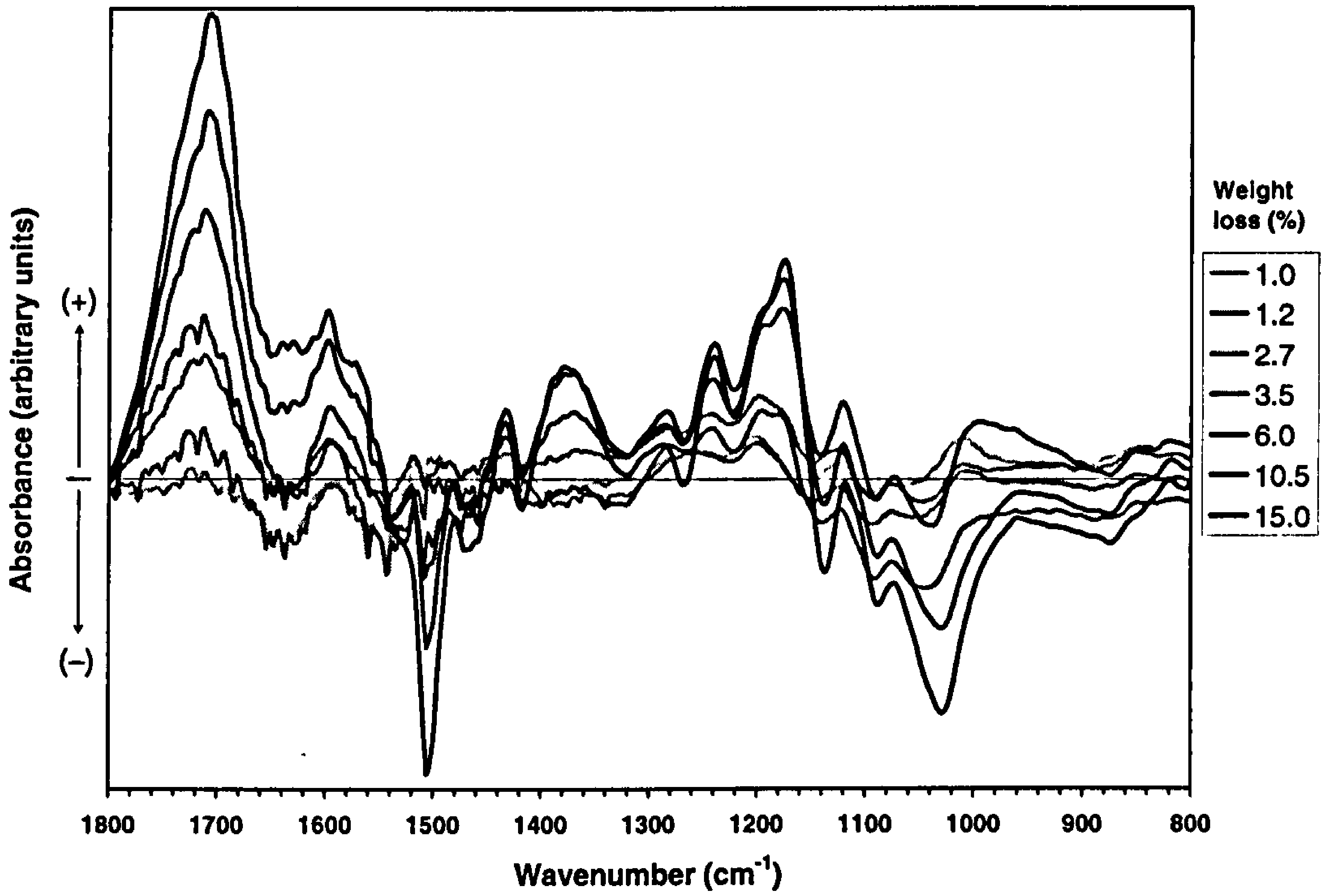


Figure 7.9 Difference spectra of Klason lignin for seven levels of thermal modification in Norway spruce wood (treated sample minus control spectra)

The sharp decreasing band for pure aromatic skeletal vibrations at 1506 cm^{-1} has previously been reported in heated wood (Grandmaison *et al.* 1987, González-Peña and Hale 2007c). However, the reason for this decline in materials with increased lignin content is not completely understood. Degradation of aromatic structures involving the opening of the aromatic ring leading to the formation of muconic acids rich in carbonyl structures are common results of wood bleaching proceedings (Mononen *et al.* 2005). Similarly, the opening of aromatic rings via the muconic acid splitting mechanism results in the formation of carboxyl acids and/or their lactones in light-irradiated wood; these give rise to the CO vibration above 1700 cm^{-1} (Tolvaj and Faix 1995). Moreover, the intensities of carbonyl bands at 1700-1763 cm^{-1} and the aromatic skeletal vibrations at 1505-1510 cm^{-1} show characteristic patterns when plotted as a function of the irradiation time. The two curves act as mirror images: the CO band increases to a comparable extent as the aromatic band decreases; this indicates that a strong correlation between the underlying photochemical changes exists (*Idem.*). In lignin from heat-treated wood, a similar phenomenon is verified if the result for the difference spectra at 1708 and 1506 cm^{-1} is plotted against the WL (Figure 7.10); the reduction of the latter is some 30 – 50%

smaller than the increase at 1708 cm^{-1}, though. However other vibrations arising from the aromatic skeletal in lignin (*e.g.* at 1140 cm^{-1}) are also declining with the severity of the treatment, and probably contribute towards the increase of the CO expression at 1708 cm^{-1}.

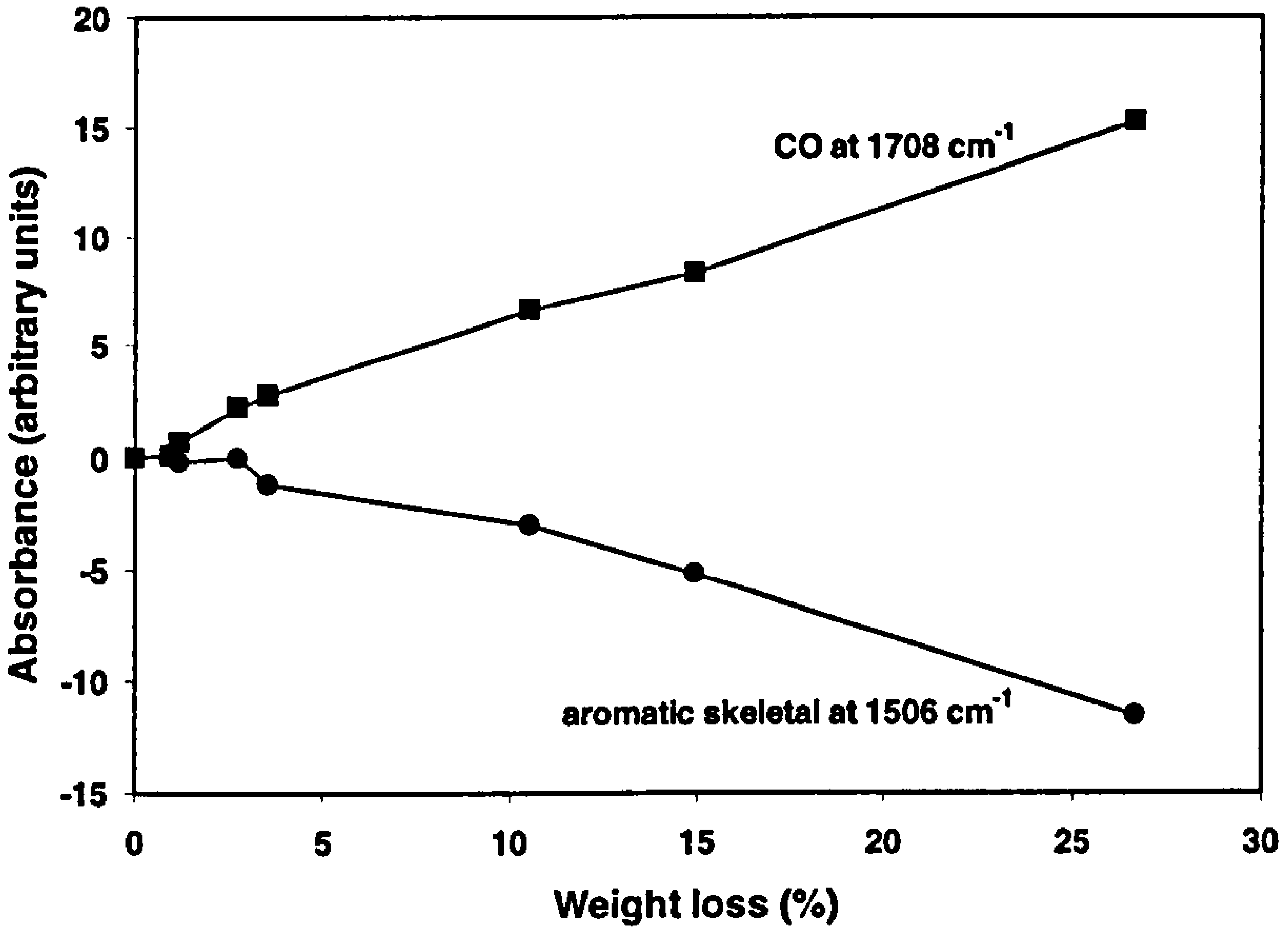


Figure 7.10 Absorbance *vs.* heat-induced weight loss for the bands at 1708 cm^{-1} and 1506 cm^{-1} in Klason lignin of Norway spruce wood (difference spectra of treated sample minus control spectrum)

The results obtained by FTIR spectroscopy indicate that the reaction products formed during heating of wood are likely of the muconic acid type. These acids have a characteristic FTIR band at 1430 cm^{-1} (Anon. 2006) which was likely responsible for the appearing peak at this wavenumber in the difference spectra of heated wood lignin. Some evidence of the opening of the aromatic ring in lignin of heat-treated Norway spruce wood has also been detected by UV spectroscopy (Boonstra and Tjeerdsma 2006).

Changes in most other lignin bands come from the condensation and demethoxylation of lignin substance and probably due to the char formation from polysaccharides. Increasing bands appear at 1370, 1278, 1236 and 1172 cm^{-1}, whilst minima were found at 1465, 1086 and 1030 cm^{-1} (Figure 7.9). The band at 1370 cm^{-1} arises from the aliphatic C-H stretch deformation (symmetric) in CH_3, but not in methoxyl groups. G ring plus C=O stretch is the responsible for the vibration at 1278 cm^{-1}, whilst C-C plus C-O plus C=O stretch vibrate at 1236 cm^{-1}. C=O in ester groups (conjugated) is accountable for the vibration at 1172 cm^{-1}. On the other hand, the reduction at 1465 cm^{-1} is given by the declining manifestation of C-H deformation (asymmetric) in CH_3 and $-CH_2-$. The decreasing band at 1086 cm^{-1} is for the C-O deformation in secondary alcohols and aliphatic ethers, whereas the band at 1030 cm^{-1} is for C-H in plane deformation, plus C-O deformation in primary alcohols plus C=O stretch (unconjugated) (Faix 1992). Changes in some of these bands agree with those listed for lignin from a smaller experiment of powdered maritime pine heat-treated at 260 °C (Bourgois and Guyonnet 1988).

For the matter at hand, peaks at 1637 and 1630 cm^{-1} most likely arise from quinone carbonyl groups, since these are expected at 1690-1600 cm^{-1} (Kemp 1991). Quinone structures absorb in the visible region and are probably the main reason for colour changes in heated wood. Although peaks indicating its presence are not very pronounced, quinones can cause an intense colour at very low concentrations (Tolvaj and Faix 1995). Condensation reactions of lignin led to the production of these coloured compounds. Sudo *et al.* (1985) showed that lignin was broken down by extensive cleavage of β-aryl ether linkages during steaming of wood below 215 °C and that wood lignin steamed at 230 °C consisted of heavily condensed types of structures. Condensation reactions of lignin model compounds subject to pyrolysis conditions at 250 °C for 2 h have also shown that vinyl condensation and quinone methide mechanisms are important condensation pathways for these compounds (Nakamura *et al.* 2007). Lignin modification upon heat exposure is mainly a diphenylmethane (DPM) type condensation; up to 75% of non condensed units in protolignin were converted to DPM type units following heat exposure of milled wet wood up to 220 °C (Funaoka *et al.* 1990). The most reactive sites of lignin side chains (α-positions) are attacked rapidly by adjacent phenyl nuclei regardless the pH conditions to form C_α-aryl linkages (DPM type structures). These units are readily oxidized to give coloured mesomeric quinone-methides, which form strong hydrogen bonds with hydroquinones or phenols. DPM type structures appearing in the lignin substance greatly influence the colour of this macromolecule (*Idem.*).

7.4 Prediction of physical properties from colour parameters

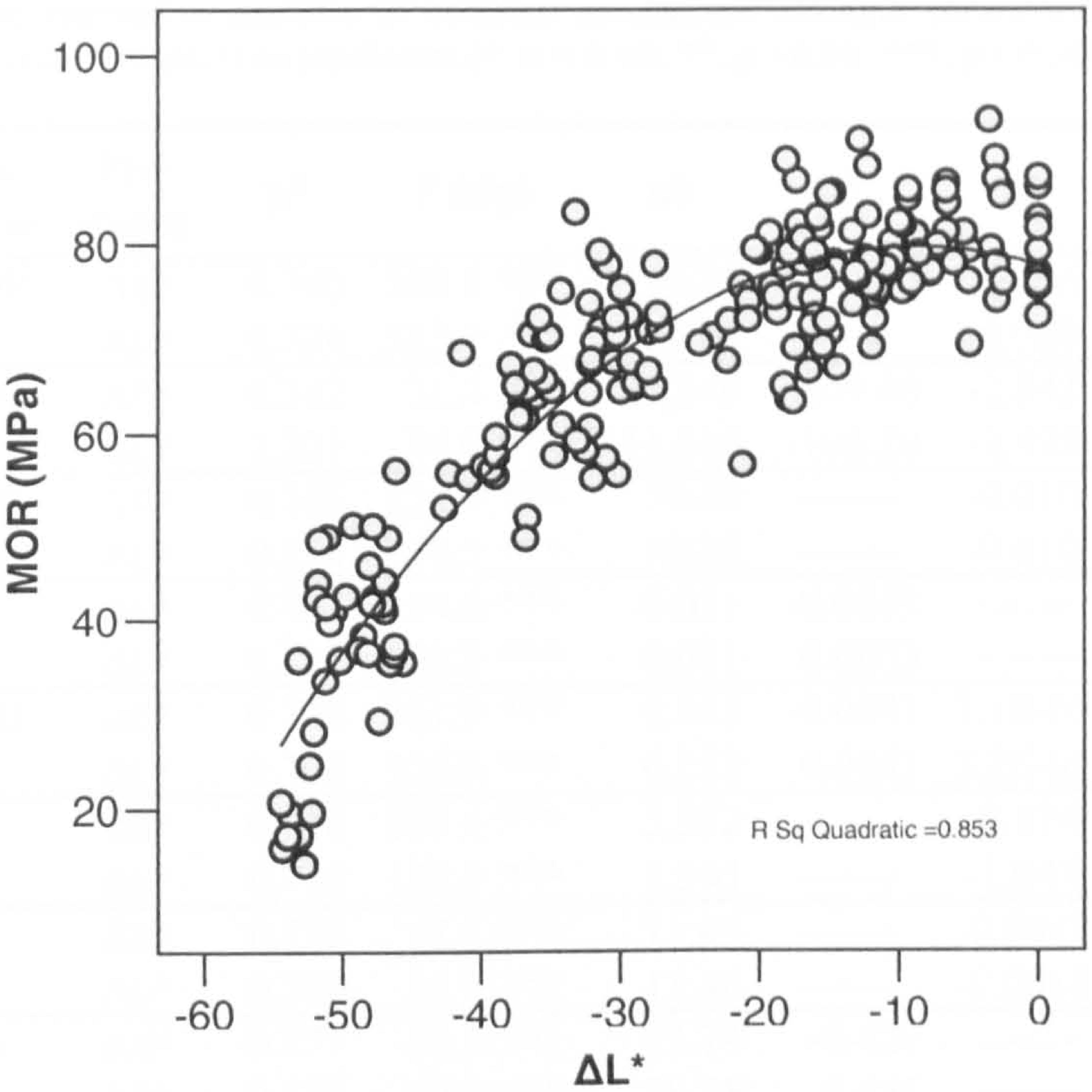
Colour inspection is critical in many wood processes, either as an aesthetic attribute or as indicator of product quality. In other woodworking industries (*e.g.* panel products) image analysis is routinely used for quality control and for matching and classification in various processes. An extension of these machine-vision systems for the prediction of physical properties of TMW from colour changes is enticing, because to date there is no established procedure for the quality assurance of TMW. In this section, the feasibility of predicting strength from colour changes is evaluated, namely for MOR, MOE, RLP, R, WML, IS, CA, CE, H and S. Additionally, the prediction of ASE is attempted, as well as the prediction of after-treatment nominal density (ND) and heat-induced weight loss (WL).

Prediction of mechanical properties by linear regression

Figure 7.11 represents the MOR of Norway spruce wood plotted against ΔE^* or ΔL^*, as an example of the nature of the relationship borne between mechanical strength and colour parameters. Table 7.2 presents the results of the simple linear regression to estimate ten mechanical strength parameters using ΔE^* or ΔL^* as predictors. Previously to the modelling, diagnostic checks were carried out to verify that the data conformed to the primary assumptions of the analysis of variance.

An examination of Table 7.2 shows that all models were at least very significant. Both ΔE^* and ΔL^* have similar prediction ability based in the coefficient of determination (R^2) statistic. However ΔE^* was better predictor for all the properties, but for R and H in spruce. The significance of the models was similar for the three species, although the predictions were slightly better for softwoods.

Most properties in the three species have a curvilinear relationship with ΔE^* or ΔL^*; most equations were parabolic, except for IS in the three species, WML in softwoods, and R in beech and spruce, where the models were rectilinear. Properties at the limit of proportionality (RLP, R) gave less efficient predictions than those properties at maximum load (MOR, WML). This observation may be associated with the larger inherent variability of strength parameters at the limit of proportionality.



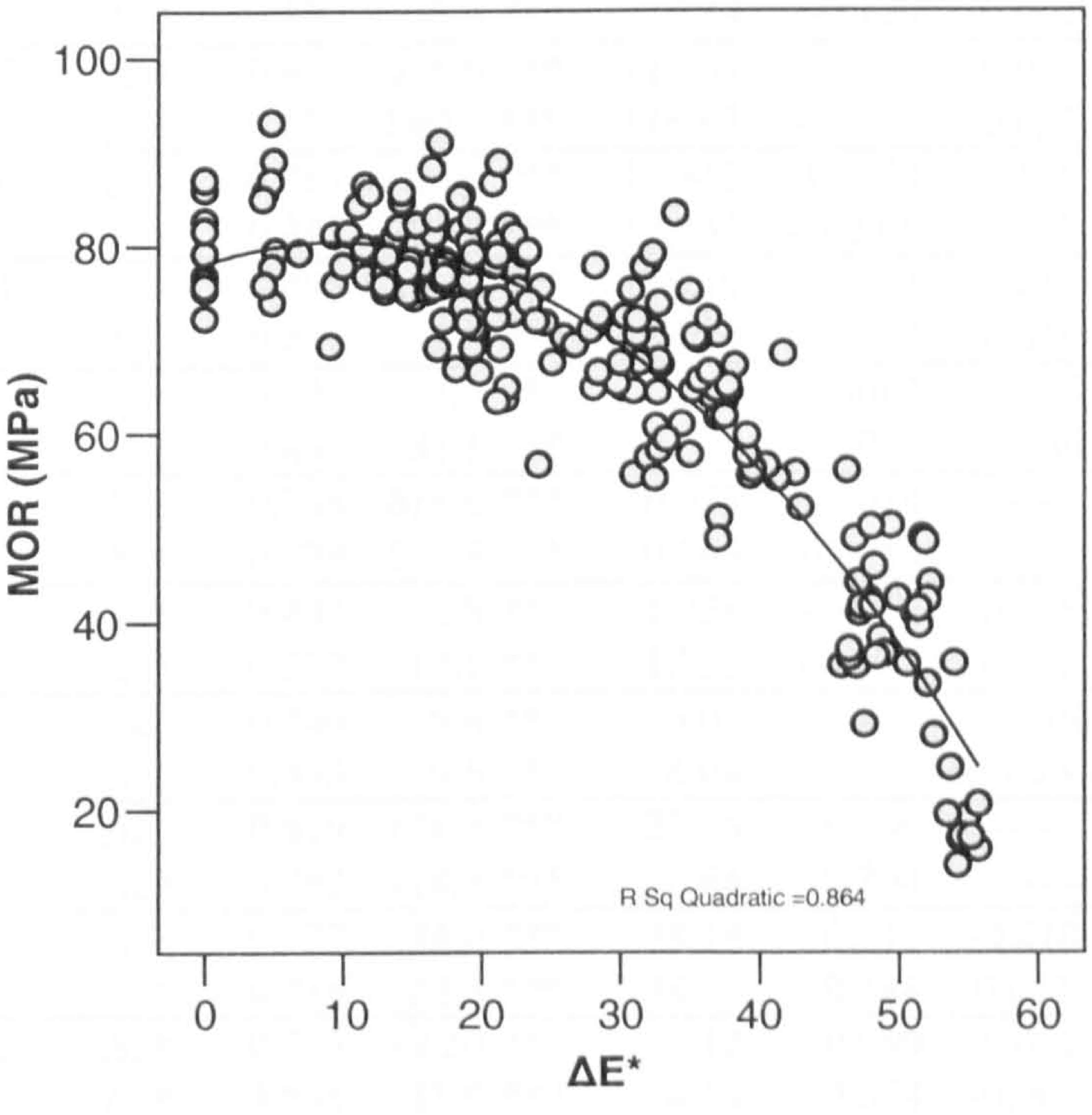


Figure 7.11 The nature of the relationship between MOR in bending and ΔL* (above) or ΔE* (below) in thermally modified Norway spruce wood

Table 7.2 Linear regression analysis to estimate mechanical strength parameters of TMW using colour parameters (ΔE* or ΔL*) as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$).

Species	Res-ponse	Pre-dictor	R^2	F (sig)	b0	b1	b2	SE	n
Beech	MOR	ΔE*	0.740	562.7 ***	129.75	------	-0.026	16.0	200
		ΔL*	0.726	523.7 ***	129.90	------	-0.028	16.4	200
	MOE	ΔE*	0.242	31.4 ***	11,549	109.40	-2.542	1,434	200
		ΔL*	0.221	27.9 ***	11,616	-106.20	-2.595	1,454	200
	RLP	ΔE*	0.386	125.9 ***	79.45	------	-0.010	12.40	200
		ΔL*	0.374	118.5 ***	79.38	------	-0.010	12.50	200
	R	ΔE*	0.405	134.6 ***	0.031	-0.0003	------	0.006	200
		ΔL*	0.397	130.2 ***	0.031	0.0003	------	0.006	200
	WML	ΔE*	0.766	321.9 ***	0.153	-0.0041	3.1E-05	0.024	200
		ΔL*	0.765	320.6 ***	0.152	0.0041	3.2E-05	0.024	200
	H	ΔE*	0.918	201.4 ***	5,532	------	-0.974	314.0	20
		ΔL*	0.910	182.9 ***	5,545	------	-1.047	328.0	20
	S	ΔE*	0.728	48.2 ***	11.46	------	-0.0012	0.810	20
		ΔL*	0.709	43.9 ***	11.46	------	-0.0013	0.84	20
	IS	ΔE*	0.777	62.7 ***	25.74	-0.427	------	4.340	20
		ΔL*	0.777	62.7 ***	25.75	0.441	------	4.340	20
	CA	ΔE*	0.631	14.5 ***	57.42	0.937	-0.018	3.27	20
		ΔL*	0.611	13.4 ***	57.58	-0.968	-0.019	3.36	20
	CE	ΔE*	0.568	11.20 **	7.72	0.123	-0.003	0.71	20
		ΔL*	0.550	10.4 **	7.74	-0.128	-0.003	0.72	20
Pine	MOR	ΔE*	0.822	958.6 ***	117.07	------	-0.019	10.2	210
		ΔL*	0.810	889.4 ***	116.63	------	-0.021	10.5	210
	MOE	ΔE*	0.367	60.0 ***	12,443	101.30	-2.180	1,103	210
		ΔL*	0.347	55.1 ***	12,535	-103.00	-2.350	1,120	210
	RLP	ΔE*	0.495	101.3 ***	68.19	0.543	-0.016	9.2	210
		ΔL*	0.489	99.0 ***	68.30	-0.587	-0.018	9.3	210
	R	ΔE*	0.439	81.0 ***	0.021	0.0002	-6E-06	0.005	210
		ΔL*	0.439	81.1 ***	0.023	-0.0002	-7E-06	0.005	210
	WML	ΔE*	0.748	618.6 ***	0.097	-0.0014	------	0.015	210
		ΔL*	0.739	588.8 ***	0.095	0.0014	------	0.015	210
	H	ΔE*	0.403	12.8 **	1,758	------	-0.088	125	21
		ΔL*	0.389	12.1 **	1,755	------	-0.093	126	21
	S	ΔE*	0.340	9.8 **	6.05	------	-0.0004	0.58	21
		ΔL*	0.333	9.5 **	6.04	------	-0.0004	0.58	21
	IS	ΔE*	0.879	138.4 ***	27.56	-0.396	------	2.70	21
		ΔL*	0.862	118.6 ***	26.84	-0.394	------	2.89	21
	CA	ΔE*	0.727	24.0 ***	38.19	0.519	-0.010	2.04	21
		ΔL*	0.715	22.5 ***	38.56	-0.544	0.011	2.08	21
	CE	ΔE*	0.555	11.20 **	4.12	0.050	-0.001	0.28	20
		ΔL*	0.551	11.0 **	4.14	-0.054	-0.001	0.28	20

For abbreviations, see footnote at the end of the table.

Continued over...

Table 7.2 Linear regression analysis to estimate mechanical strength parameters of TMW using colour parameters (ΔE* or ΔL*) as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$) (*Continued ...*)

Species	Res-ponse	Pre-dictor	R^2	F (sig)	b0	b1	b2	SE	n
Spruce	MOR	ΔE*	0.864	658.1 ***	78.16	0.492	-0.026	6.546	210
		ΔL*	0.853	600.6 ***	77.69	-0.455	-0.026	6.8	210
	MOE	ΔE*	0.515	109.8 ***	9,208	78.82	-2.098	783	210
		ΔL*	0.504	105.1 ***	9,266	-78.11	-2.136	792	210
	RLP	ΔE*	0.561	265.7 ***	45.49	-------	0.008	6.5	210
		ΔL*	0.550	254.6 ***	44.72	-------	-0.008	6.6	210
	R	ΔE*	0.525	230.3 ***	0.014	-0.0002	-------	0.003	210
		ΔL*	0.533	237.1 ***	0.013	0.0002	-------	0.003	210
	WML	ΔE*	0.834	1,046 ***	0.075	-0.0013	-------	0.009	210
		ΔL*	0.830	1,017 ***	0.070	0.0012	-------	0.009	210
	H	ΔE*	0.429	14.3 **	1,795	-6.02	-------	110	21
		ΔL*	0.437	14.7 **	1,774	5.68	-------	109	21
	S	ΔE*	0.807	79.5 ***	6.96	-------	-0.0006	0.27	21
		ΔL*	0.795	73.6 ***	6.91	-------	-0.0006	0.28	21
	IS	ΔE*	0.937	283.9 ***	23.57	-0.413	-------	1.69	21
		ΔL*	0.921	221.4 ***	21.97	0.383	-------	1.89	21
	CA	ΔE*	0.687	19.7 ***	35.03	0.624	-0.013	2.45	21
		ΔL*	0.680	19.2 ***	35.84	-0.619	-0.013	2.47	21
	CE	ΔE*	0.644	16.30 ***	4.37	0.046	-0.001	0.35	21
		ΔL*	0.618	14.6 ***	4.45	-0.042	-0.001	0.36	21

Units: MOR, MOE, RLP, CA, CE, S = MPa. R, WML = mmN/mm^3.
IS = kJ/m^2. H = N.
The model is of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$
All coefficients significant at $p < 0.05$
Abbreviations as in Tables 5.1, 5.3 and 5.5

In beech, coefficients of determination (R^2) for the best predictor ranged from 0.918 for H to 0.242 for MOE[1]. The best predictions in beech were for H, IS and WML, whilst the less efficient models were for MOE, RLP and R. On the other hand, in both softwoods the best predictions were for IS and MOR, whereas the less efficient predictions were for H, MOE and R in both pine and spruce, and for S in pine. In pine, R^2 values for the best predictor ranged from 0.879 for IS, to 0.340 for S. In Norway spruce these varied from 0.937 for IS, to 0.429 for H.

The strength parameters more efficiently predicted are those with largest relationship with chemical changes (chapter 5). This probably reflects the underlying relationship between colour changes and strength changes with the chemical

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[1] Coefficients of determination for models calculated using all the observations per treatment (MOR, MOE, RLP, R and WML) are strictly not comparable to those calculated using the average values per treatment (H, S, IS, CA and CE). See Theorem of Central Limit.

conversion, rather than a direct relationship between colour changes and mechanical properties. ΔE* was consistently better predictor than ΔL*, but the determination of the former requires the determination of the three colour coordinates (L*, a* and b*). These three components are also required for the multivariate prediction of physical parameters (see below). As modern industrial scanners can acquire the three colour parameters readily, the use of ΔE* should probably be preferred.

Prediction of ND, WL and ASE by linear regression

The prediction of other physical properties in TMW is central to product characterisation and for comparisons between treatments. For instance, according to Eurocode 5 on timber structures, a certain characteristic density should be guaranteed for visually graded timber (Hoffmeyer and Pedersen 1995). On the other hand, WL is closely related to other properties not included in the present study (*e.g.* decay resistance) and therefore its prediction is greatly desirable. ASE is itself a valuable property in TMW, and could serve as an indicator of the general hygroscopicity reduction in heated wood.

Similarly for the results for mechanical properties, both ΔE* and ΔL* have similar prediction ability of ND, WL and ASE, although ΔE* was generally the best predictor except for dimensional stability in coniferous woods (Table 7.3). The relationship between both ΔE* and ΔL* and ND or WL was curvilinear, meanwhile this was linear for ASE. According to the R^2 statistic, the best prediction was for ASE, although in softwoods comparable prediction ability was found for WL. In all the three species, the less efficient model was for ND, though all models were highly significant. The reason for this may be in part due to the small changes in ND due to heating, because of the shrinkage of the wood material compensates somewhat the loss in mass. Even if changes in ND are quantifiable, it would be hard to detect chemically against the background of the similar specific gravity of the three main polymers of the cell wall substance (Kellogg 1979). In contrast, the higher prediction ability for WL and ASE may be exposing the underlying relationship of colour and physical changes with the large chemical modification undergone in the substrate.

Table 7.3 Linear regression analysis to estimate physical parameters of TMW using colour parameters (ΔE* or ΔL*) as predictors (*, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$, NS = not significant)

Species	Response	Predictor	R^2	F (sig)	b0	b1	b2	SE	n
Beech	ND	ΔE*	0.367	57.0 ***	635.5	2.177	-0.061	34.20	200
		ΔL*	0.357	54.7 ***	636.0	-2.265	-0.066	34.40	200
	WL	ΔE*	0.989	870 ***	1.438	-0.173	0.0112	2.88	200
		ΔL*	0.884	747 ***	1.465	0.196	0.0123	3.09	200
	ASE	ΔE*	0.925	220 ***	-5.608	1.310	-----	7.10	20
		ΔL*	0.915	193 ***	-5.415	-1.346	-----	7.55	20
Pine	ND	ΔE*	0.277	39.6 ***	513.0	1.156	-0.029	21.90	210
		ΔL*	0.266	37.5 ***	513.5	-1.211	-0.032	22.00	210
	WL	ΔE*	0.932	2,854 ***	0.640	-----	0.0052	1.59	210
		ΔL*	0.919	1,177 ***	1.370	0.060	0.0066	1.73	210
	ASE	ΔE*	0.936	279 ***	-4.444	1.136	-----	5.47	21
		ΔL*	0.944	318 ***	-2.829	-1.147	-----	5.14	21
Spruce	ND	ΔE*	0.309	93.1 ***	371.5	-----	-0.012	15.80	210
		ΔL*	0.307	92.0 ***	370.4	-----	-0.011	15.80	210
	WL	ΔE*	0.910	2,097 ***	0.580	-----	0.0070	1.97	210
		ΔL*	0.899	1,847 ***	1.221	-----	0.0068	2.09	210
	ASE	ΔE*	0.921	223 ***	-8.228	1.251	-----	5.77	21
		ΔL*	0.935	271 ***	-3.839	-1.179	-----	5.26	21

Units: ND, kg m^{-3}; WL, %; ASE, %.
The model is of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$
All coefficients significant at $p < 0.05$

Prediction of physical properties by multivariate regression

Multiple stepwise regression using all the eleven colour parameters (ΔE*, ΔL*, L*, a*, b*, h*, C*, Δa*, Δb*, ΔC* or ΔC^*_{ab}) as independent variables, improved the prediction of several properties. Models which led to R^2 increments larger than 2.5% compared to linear regression, without conducing to worrying collinearity problems, were for MOR, MOE, RLP, R, S, IS and ASE in beech, for MOE, S, IS, ND and WL in pine, and for MOE, RLP, CA, and WL in spruce (Table 7.4). Marginal gains in the coefficient of determination were also found for WML, CE and ND in beech, for MOR, RLP, R and WML in pine, and for MOR, CE and ND in spruce.

Multivariate analysis by principal-component regression using all the eleven colour parameters reduced the data to only two dimensions in each species. R^2 improvements larger than 2.5%, compared to simple linear regression, were only found for MOE and S in beech ($R^2 = 0.338$ and 0.811 respectively), and for H in pine

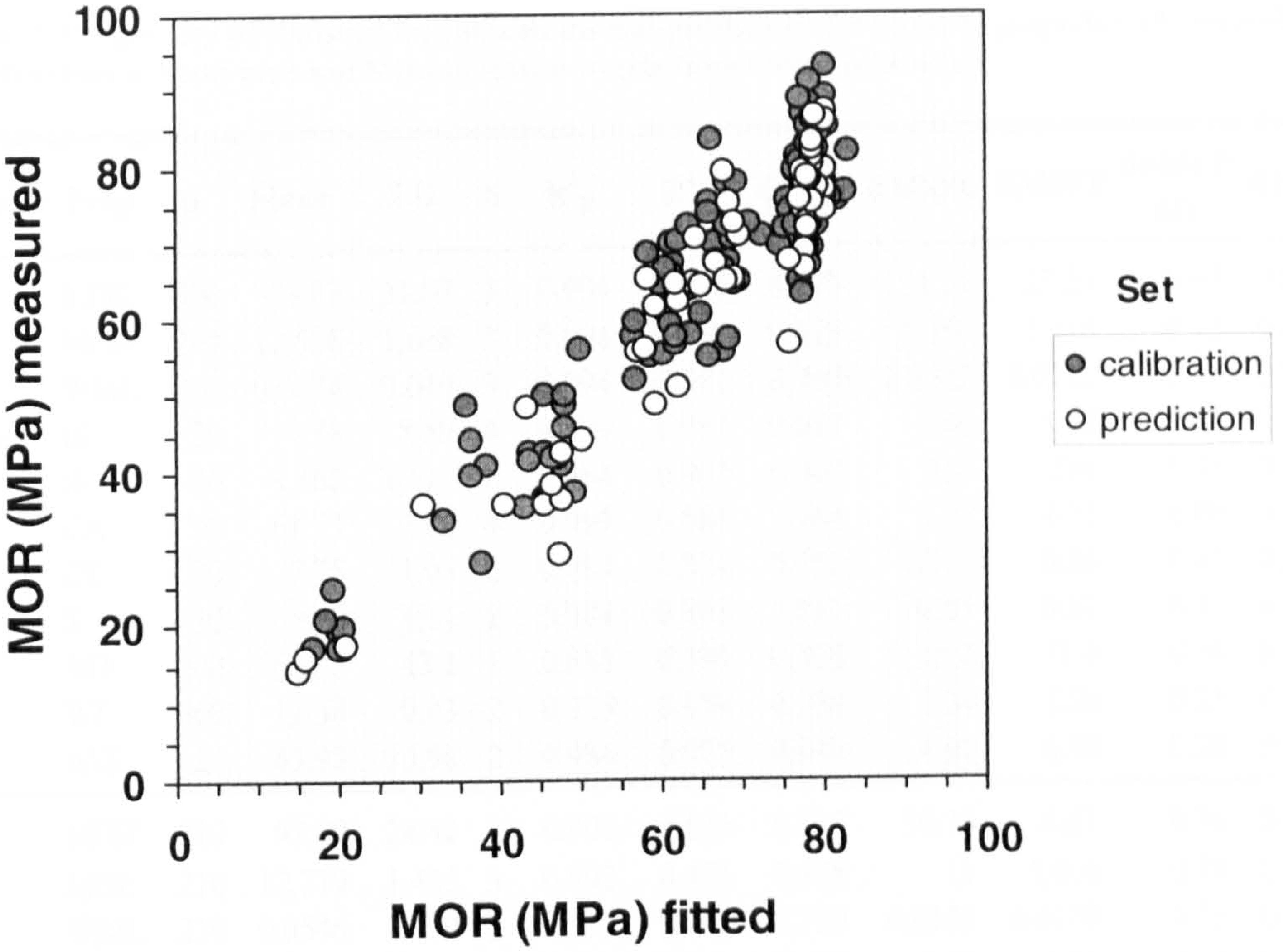
($R^2 = 0.467$). Marginally larger R^2 coefficients were also found for MOR, RLP, H and ND in beech, for MOR, RLP, R, ND, WL and ASE in pine, and for ASE in spruce.

Table 7.4 Colour parameters significantly included in the models as predictors, to estimate physical parameters of thermally modified beech, Scots pine and Norway spruce woods using multiple stepwise regression. Included models are only those with larger R^2 than in simple linear regression

Species	Response	Predictors included in the model	R^2	n
Beech	MOR	ΔE*, h*	0.799	200
	MOE	h*	0.374	200
	RLP	h*, a*, L*	0.558	200
	R	ΔE*, h*, a*	0.555	200
	S	C*, h*	0.839	20
	IS	ΔE*, C*, ΔC*	0.947	20
	ASE	ΔE*, ΔC*	0.962	20
Pine	MOE	ΔC*, h*, a*	0.432	210
	S	ΔC*	0.383	21
	IS	ΔE*, b*, ΔC*	0.948	21
	ND	ΔC*, a*	0.318	21
	WL	Δb*, ΔC*, h*	0.968	21
Spruce	MOE	ΔC^*_{ab}, ΔC*	0.606	210
	RLP	a*, Δb*, ΔC*, ΔE*	0.640	210
	CA	ΔE*, h*	0.950	21
	WL	ΔL*, h*	0.950	21

The model is of the form: $y = b0 + \Sigma bi \cdot xi$

On the other hand, PLS regression improved significantly the estimation of most physical properties (Table 7.5). The largest improvements compared to linear regression according to the R^2_Y statistic, with gains in R^2 from 6.8% to 26.6%, were for MOE and CA in the three species, IS, CE and S in beech and pine, and ND in pine. Moreover, all predictions using samples not used for building the calibration PLS models were excellent irrespective of the species in concern. The best predictions according to the RPE statistic (RPE > 0.90) were for ASE and WL in the three species, for IS in softwoods, and for CA and S in spruce. The less efficient predictions, though still very good ones (0.11 < RPE < 0.50) were for MOE and ND in beech and pine, CA and CE in beech and S in pine. Figure 7.12 gives a graphic example of the fitting ability of colour parameters for MOR and WL in pine.



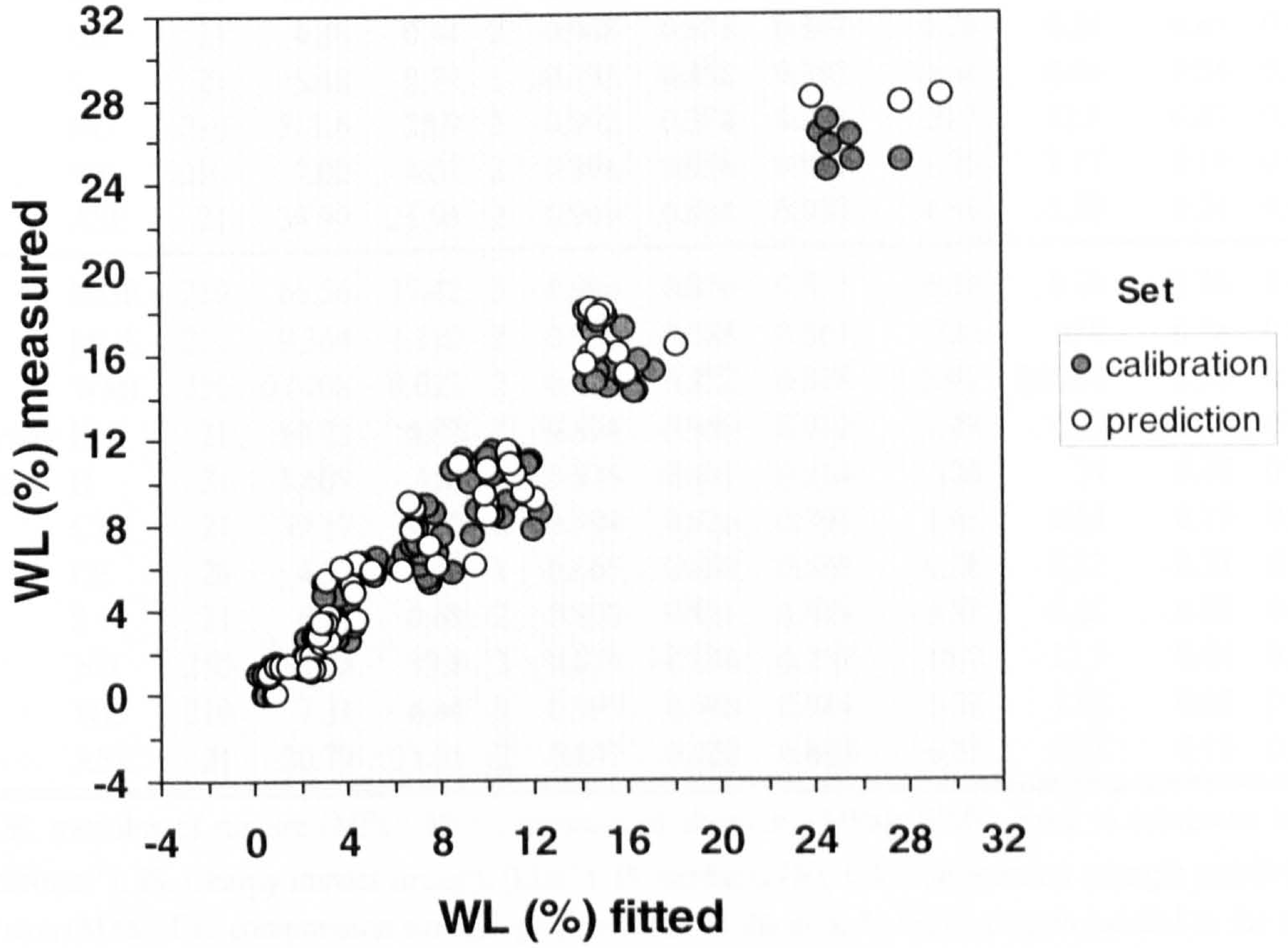


Figure 7.12 Calibration plots for MOR (above) and WL (below) for thermally-modified Scots pine wood using PLS regression using eleven colour parameters

Table 7.5. Summary of statistics for calibrations and predictions for physical properties of thermally-modified beech, Scots pine and Norway spruce woods from colour parameters.

Species	Prop.	n	Mean	S.D.	A	R^2_X	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	$\frac{RMSEP}{SD}$	RPE
Beech	MOR	200	93.03	31.07	3	0.994	0.795	0.773	14.24	13.29	0.43	0.82
	MOE	200	11,526	1,668	3	0.994	0.359	0.325	1,350	1,214	0.73	0.47
	WML	200	0.0624	0.049	3	0.994	0.781	0.769	0.0232	0.0215	0.44	0.81
	IS	20	9.88	8.59	4	0.999	0.982	0.947	1.40	3.71	0.43	0.81
	H	20	3,862	1,110	2	0.984	0.962	0.949	238	384	0.35	0.88
	CA	20	61.73	4.86	4	0.999	0.885	0.764	2.02	4.32	0.89	0.21
	CE	20	7.75	1.03	2	0.984	0.834	0.752	0.46	0.86	0.83	0.30
	S	20	9.30	1.61	2	0.984	0.863	0.811	0.65	0.67	0.42	0.83
	ND	200	621.3	43.2	1	0.888	0.339	0.325	35.2	31.8	0.74	0.46
	WL	200	11.58	9.03	2	0.925	0.939	0.939	2.24	2.06	0.23	0.95
	ASE	20	43.92	25.08	2	0.984	0.973	0.949	4.49	6.98	0.28	0.92
Scots pine	MOR	210	92.99	24.42	2	0.901	0.823	0.817	10.34	8.81	0.36	0.87
	MOE	210	12,779	1,435	3	0.992	0.475	0.438	11	1,066	0.74	0.45
	WML	210	0.0546	0.030	3	0.992	0.741	0.729	0.0156	0.0109	0.36	0.87
	IS	21	13.96	8.30	3	0.994	0.970	0.940	1.65	1.91	0.23	0.95
	H	21	1,639	183	1	0.796	0.489	0.375	136	100	0.55	0.70
	CA	21	41.18	4.20	2	0.948	0.795	0.717	2.07	2.17	0.52	0.73
	CE	21	4.38	0.44	2	0.948	0.635	0.507	0.29	0.27	0.61	0.62
	S	21	5.48	0.70	1	0.793	0.458	0.397	0.54	0.66	0.94	0.11
	ND	210	511.6	25.9	3	0.992	0.374	0.323	20.7	22.6	0.87	0.24
	WL	210	7.02	6.02	2	0.896	0.958	0.957	1.25	1.17	0.19	0.96
	ASE	21	34.99	21.94	2	0.949	0.964	0.937	4.53	5.30	0.24	0.94
Norway spruce	MOR	210	66.56	17.42	3	0.993	0.876	0.873	6.19	6.30	0.36	0.87
	MOE	210	9,364	1,110	2	0.731	0.585	0.561	720	638	0.58	0.67
	WML	210	0.0408	0.021	2	0.904	0.822	0.818	0.0091	0.0080	0.37	0.86
	IS	21	10.73	6.82	2	0.894	0.959	0.932	1.49	1.77	0.26	0.93
	H	21	1,607	156	2	0.875	0.431	0.214	128	74	0.48	0.77
	CA	21	39.17	4.92	3	0.994	0.936	0.791	1.43	0.84	0.17	0.97
	CE	20	4.33	0.60	1	0.665	0.630	0.528	0.38	0.32	0.53	0.72
	S	21	6.27	0.68	2	0.890	0.821	0.679	0.32	0.22	0.32	0.90
	ND	210	361.3	19.8	2	0.879	0.274	0.257	16.9	12.7	0.64	0.59
	WL	210	7.31	6.44	3	0.993	0.946	0.944	1.52	1.58	0.25	0.94
	ASE	21	30.79	21.51	2	0.897	0.928	0.882	6.27	3.81	0.18	0.97

MOR, modulus of rupture (MPa); MOE, modulus of elasticity (MPa); WML, work to maximum load ($mmNmm^{-3}$); IS, Charpy impact strength (kJm^{-2}); H, hardness (N); CA, compression strength parallel to the axis (MPa); CE, compression strength perpendicular to the axis; S, shear strength parallel to the axis (MPa); ND, nominal density (kgm^{-3}); WL, weight loss (%); ASE, antiswelling efficiency (%). n: total samples tested: 2/3 calibration set, 1/3 prediction set. Samples with n = 20, 21 are for average values per treatment. A, dimension of the calibration model. For statistics abbreviations, see chapter 3. Methods.

Kotilainen *et al.* (2001) have earlier applied PLS regression to UV/Vis spectroscopy data for the prediction of WL in samples of two hardwoods (*Alnus glutinosa* and *Populus tremula*) heated for 180 minutes between 150 °C and 220 °C. They found that WL could be predicted using filtered reflectance data, with Q^2_{CUM} statistics of 0.94 and 0.93 for alder and aspen samples, respectively. Results from the present research verify the previous outcome, and highlight the feasibility of predicting several physical properties of TMW using data from the visible range.

7.5 Prediction of total colour difference ΔE* from treatment parameters

No reference exists for the prediction of colour change by using a single model that includes simultaneously a range of temperatures and times of exposure, in spite of the prediction of colour changes *per se* is an important subject of study. This is because natural dyeing is the main aim of thermal modification of some light-coloured species in Scandinavia (Syrjänen 2001).

In chapter 5, the severity factor approach was used for the prediction of the residual oven-dry weight and 10 mechanical properties in heated woods (for details see section 5.9.3). In this section, the same approach is chosen because total colour differences in each species are generally the same at equivalent levels of WL regardless of the temperature of treatment (Figure 7.6), and therefore candidates for the analysis using this phenomenological approach.

The general profile of the relationship between Ln R_O and ΔE* was sigmoid, so the equation proposed for modelling was:

$$\Delta E^* = \frac{1}{\frac{1}{u} + b0 * b1^{LnR_O}}$$

where u, b0 and b1 are model coefficients, and R_O is the severity factor = $t * \exp(\frac{T_{(t)} - T_{(ref)}}{\omega})$, where t is the reaction time in minutes, $T_{(t)}$ is the reaction temperature in °C which may vary with time (t) in non-isothermal conditions, $T_{(ref)}$ is the reference temperature (the temperature at which not significant reaction occurs, in this work set at 115 °C) and ω is a parameter expressing the importance of temperature in the specific reaction considered.

The expression of the severity factor R_O and the suitable model for the relationship between Ln R_O and ΔE^* were used to calculate the optimal values for the model parameters (ω, b0, b1, u). These were obtained by minimizing the square deviations between experimental and model-predicted values using the non-linear regression algorithm of Levenberg-Marquardt (SPSS 2002). The graphic relationship between both the experimental and model-predicted values of ΔE^* in dependence of R_O is shown in Figure 7.13 for beech wood; both values are plotted as customary in dependence of the $\log_{10} R_O$.

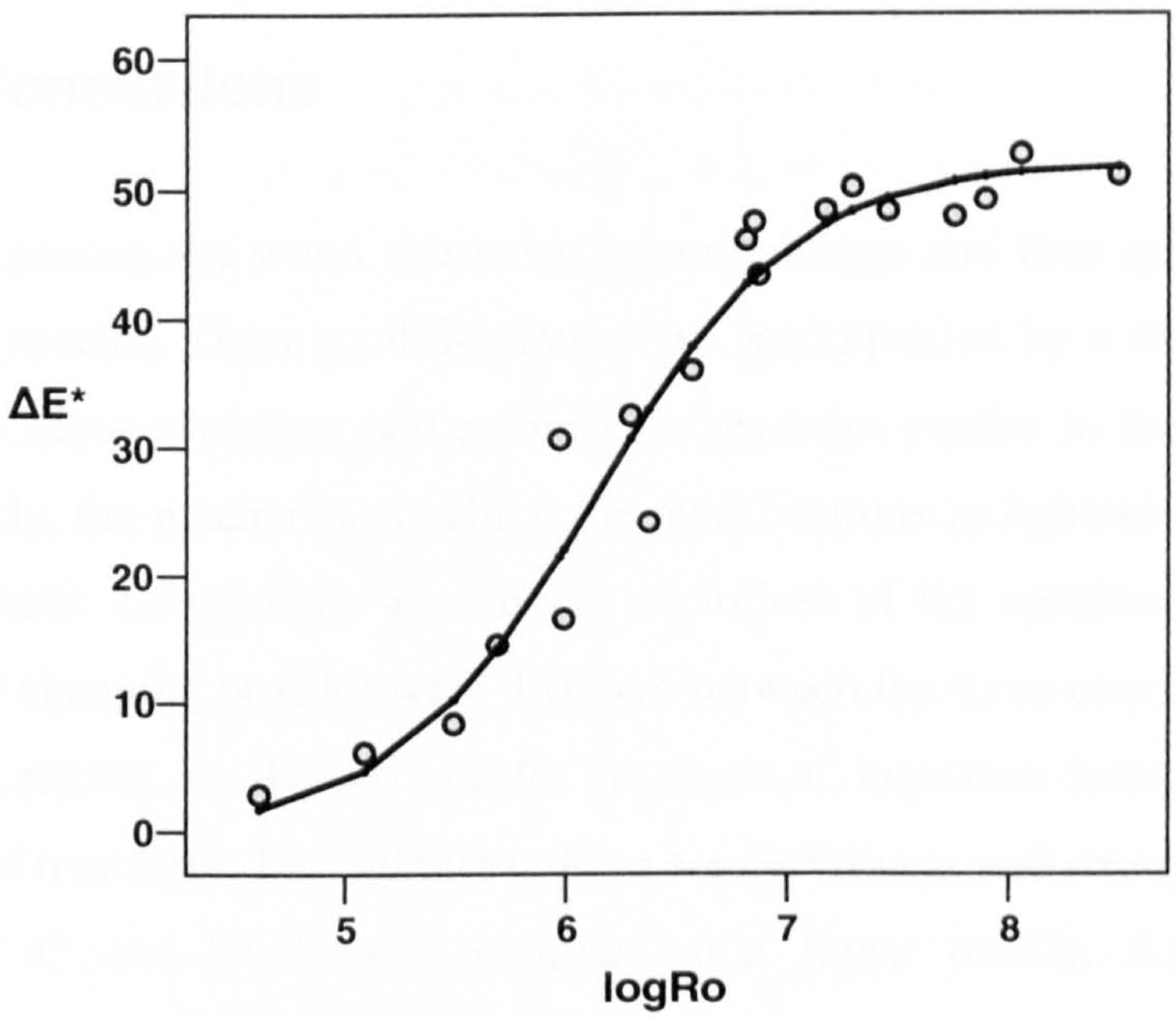


Figure 7.13 Total colour difference ΔE^* *versus* $\log_{10} R_O$ (R_O = severity factor) in modified beech. The line represents the fitted model. Each point represents the mean experimental value of 10 samples.

The relationship between total colour difference in beech and $\log_{10} R_O$ have a sigmoid shape, although in pine and spruce this profile was less curved than in beech, close to rectilinear. The modelling was successful, with R^2 values of 0.953, 0.961, 0.942 and 0.931 for beech, pine, spruce and softwoods, respectively (Table 7.6). From figure 7.13 it is noticeable that the fitting ability of the model is remarkably good for beech wood, but the prediction at moderate severity regimes, at about $\log_{10} R_O$ of 6.20 – 6.65, the scatter in the data is somewhat large. A similar account is given for softwoods. Therefore a single model could be employed for the prediction of ΔE^* for these woods modified in the range of temperatures and heating times used in this work, but the best predictions would be for ΔE* values smaller than 25 or greater than 40 units.

Table 7.6 Model parameters for predicting ΔE* in thermally modified beech, Scots pine and Norway spruce woods from the severity factor R_O, and the optimal ω parameter for computing R_O

Property	Species	*u*	b0	b1	ω	R^2
ΔE*	Beech	51.95	15255	0.3819	9.8420	0.953
	Pine	67.44	42.04	0.5650	12.055	0.961
	Spruce	88.15	4.084	0.7279	9.4908	0.942
	Softwoods	72.69	12.27	0.6446	10.913	0.931

7.6 Conclusions

Upon heat exposure, the wood substance became orange and then approached gray whatever the species. These modifications were accompanied by a steady reduction in lightness. Colour evolution and colour changes were similar in the three species studied. Clearly, the mechanisms behind the modifications in lightness and in the a* and b* chromatic components are similar regardless of the species. However, the evolution and changing profiles were different between the three coordinates in each species with respect to the WL or to the time of exposure irrespective of the temperature of treatment. For lightness, these are curvilinear and steady, whilst these variations in a* and b* have a complex, non linear profile. Apparently, the underlying causes leading to the modification in each of the three chromatic characters upon heating are different, although the subject was complex and not amenable to simple interpretations.

In principle, it can be proposed that colour modification in thermally treated wood results from chemical changes leading to the production and/or destruction of chromophoric groups. Unlike in untreated wood, these chromophoric species are proposed to originate from main structural components in TMW rather than upon minor wood components. Colour changes were found to be more linked to changes in the lignin substance than in the polysaccharide component, not only because of the highest lignin proportion in the solid residue, but also for the darkening of the lignin itself. Darkening of lignin was associated to the production of chromophoric groups, mainly the increase in carbonyl groups appearing in the infrared spectra of lignin between 1710 and 1600 cm^{-1}, particularly the appearance of quinone species.

Finally, total colour differences in TMW (to untreated controls), ΔE*, were highly influenced by differences in lightness, ΔL*. Differences in the chromatic coordinates, Δa* and Δb*, have a smaller, though significant, contribution to ΔE*.

On the other hand, it is demonstrated that colour modifications measured using an image analysis system can efficiently be used to predict several physical properties in small samples of heated wood. Ten mechanical strength parameters plus ASE, ND and WL were successfully predicted from ΔE* or ΔL* using simple linear regression. ΔE* was found to be a better predictor than ΔL* for all properties but for resilience and hardness in spruce. The addition of other colour parameters into the models significantly improved the predictions for several properties in the three species. However, the best fitting ability for most properties, based in the R^2 ($=R^2_Y$) statistic, was for the models of the multivariate analysis using PLS regression. The consequence of these findings is that several properties can be efficiently predicted with only one after-treatment measuring of colour in the CIEL*a*b* space. Optimistically, colour differences will be ordinarily utilized for the mechanical and physical characterization of thermally-modified wood at the industrial stage in the foreseeable future.

Lastly, colour modifications could also be anticipated from processing parameters using a single model for woods treated within the range of temperatures (190 °C – 245 °C) and heating periods (0.3 – 16 h) used in this work. The severity factor R_O approach was efficiently employed to predict total colour difference in each species, with highly significant predictions.

Colour measurements should ideally be taken as soon as possible after the treatment, because the colouring in heated wood is permanent but not stable upon light irradiation. In some instances, colour on heated wood surfaces has shown significant improved performance compared to surfaces of untreated woods at the laboratory scale, mainly in regards to the smaller colour change and faster colour stabilisation upon exposure to UV-light (Ayadi *et al.* 2003, Letourneau *et al.* 2005). However, these changes seem to be more noticeable in heated than in raw wood, due to the higher contrast between the initial and altered appearances (Junghans and Niemz 2005). Colour instability and ways to reduce this is currently matter of active research, because rapid colour fading has caused disappointment to some final users opting for TMW because of its darker shade.

Chapter 8 Rapid assessment of physical properties and chemical composition of TMW using infrared spectroscopy*

8.1 Introduction

The improvement of the dimensional stability and biological resistance of wood has been the object of study for many years. One way to accomplish this is by modifying the polymers of the cell wall, with the overriding aim of reducing the reactivity of hemicelluloses, cellulose and lignin towards water, and hence the hygroscopicity in the wood substance. In the last fifteen years, considerable research has been conducted on the thermal modification of wood with this purpose in mind. Results from most investigations on the thermal modification of wood have shown improved dimensional stability and fungal decay resistance of various timber species (Tjeerdsma *et al.* 2000, Farahani *et al.* 2001, Welzbacher and Rapp 2002, González-Peña *et al.* 2004). These investigations have ultimately been realized in several commercial developments mainly in Europe, but with increasing industrial activity in Oceania and North America (Militz 2002, Christmas *et al.* 2005, Shi *et al.* 2007).

The extent of the thermal modification of wood has generally been determined by gravimetric methods in small samples at the laboratory scale, but for larger samples, where the simple task of measuring weight change on a hygroscopic material is not readily achievable industrially, other methods for determination of the extent of the conversion and the associated changes in physical properties in TMW are required. Likewise, thermal modification carried out in other heating media (*e.g.* oil) is not readily monitored by gravimetry.

The most common technique so far proposed to predict mechanical strength changes in thermally modified wood (TMW) rely on colour changes, but results from this estimation are scant, inconclusive, and in some cases apparently contradictory

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* Some results from this chapter have been presented at the IRG-WP 38th meeting (González-Peña and Hale 2007a). This communication constitutes the first reference in the world for the prediction of mechanical properties and dimensional stability of TMW using MIR spectroscopy. MMGP was granted the Ron Cockcroft Award in order to attend the Conference to present his results.

(*cf.* Bekhta and Niemz 2003, Johansson and Morén 2006). Another approach would be the non-destructive prediction of the ultimate strength in bending from the direct or indirect measurement of wood stiffness (Santos 2000, Repellin and Guyonnet 2003). However, this has the drawback that the correlation between the MOR and the MOE decreases with increasing thermal treatment (Chang and Keith 1978, Bengtsson *et al.* 2002). MOE is generally not negatively influenced until weight losses exceed 10%, as opposite to the MOR, which is reduced at early stages of the thermal conversion of wood (Schneider 1971, Rusche 1973, Mouras *et al.* 2002, Bekhta and Niemz 2003, González-Peña and Hale 2007b).

The major constituents of wood comprise carbohydrates (cellulose and hemicelluloses) and lignin, together with small amounts of extractives and inorganic materials (Sjöström and Westermark 1999). When wood is exposed to heat, within the range of the commonly used temperatures for thermal modification, multiple chemical reactions in the individual wood components take place. Chemical conversion is complex, but it is generally acknowledged that it occurs in the order hemicelluloses >> amorphous cellulose > lignin ≥ cellulose (Fengel and Wegener 1984, Bourgois and Guyonnet 1988, Kotilainen *et al.* 2001, Alén *et al.* 2002). Correlation between property changes and easily detectable chemical changes in thermally modified wood shows a potential possibility to develop proper quality control methods for physical changes.

Vibrational spectroscopy is a fast method for detecting chemical bonds and thus examining different functional organic groups and changes in their presence and amount. On the basis of this premise, wood has been subject to several studies using vibrational spectroscopy in the near-infrared (NIR) and mid infrared (MIR) regions of the spectrum. These methods provide information on the molecular structures of diverse woods and, in many instances, wood specimens have been examined directly without further preparation. Thus, it is possible to obtain information at the molecular level on the interaction between wood polymers in their native solid state. In addition of being inexpensive, a distinct advantage of these methods is that they are both fast and non-destructive. A potential shortcoming is that the signals from the three main wood polymer constituents partly overlap in the spectra due to the similar structural characteristics of wood polymer's moieties. By using multivariate techniques to analyse the spectra, it is possible to largely overcome this limitation. Besides being able to deconvolute information out of the highly correlated, strongly overlapping bands, modern multivariate methods such as partial least squares (PLS) regression have the advantage of being able to handle cases in which the number of samples is small in comparison to the large number of predictor variables used for building the models (Miller and Miller 2005).

Multivariate analysis of wood spectra for the prediction of mechanical properties started in Denmark in 1995; this technique has been rapidly adopted ever since for the non-destructive strength evaluation of wood in several applications. The most common spectroscopic method for the multivariate assessment of mechanical properties of untreated solid wood has been near-infrared spectroscopy (Hoffmeyer and Pedersen 1995, Gindl *et al.* 2001, Schimleck *et al.* 2001, Thumm and Meder 2001, Schimleck *et al.* 2002, Kelley 2003, Meglen and Kelley 2003, Kelley *et al.* 2004a, b). Most of these reports have shown that multivariate analysis of spectral data is a powerful tool to extract, often complex, chemical and physical information of wood in the laboratory environment. An extension of this to the rapid assessment of physical properties in TMW would be of great benefit for the generalised use of this new material, and for the prospective adoption of thermally modified wood in load-bearing applications. Additionally, the eventual implementation of this technique for the prediction of valuable TMW properties such as decay resistance and dimensional stability would be appealing. Initial proposals for the multivariate analysis of infrared spectra in TMW include the classification of heated beech or Norway spruce woods by cluster or principal component analyses of NIR data (Hinterstoisser *et al.* 2003, Schwanninger *et al.* 2004, Bächle 2007).

No studies have been conducted for the mechanical evaluation of wood using MIR spectroscopy. A few reports exist on the multivariate estimation of density and chemical composition of untreated wood, though (Rodrigues *et al.* 1998, Costa e Silva *et al.* 1999, Meder *et al.* 1999, Rodrigues *et al.* 2001, Nuopponen *et al.* 2006). In TMW, a multivariate prediction of the thermal degradation by measuring weight loss in thermally-treated spruce and pine woods has been attempted using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (Kotilainen *et al.* 2000); multivariate analysis of FTIR spectra has also been applied for the study of the chemical degradation in decayed heat-treated pine wood (Sivonen *et al.* 2003).

Lately, Inagaki *et al.* (2007) estimated the cellulose content and crystallinity of heat-treated Hinoki cypress (*Chamaecyparis obtuse*) wood from its NIR spectra, but the prediction of the chemical composition of TMW has not been attempted in the MIR range. On the other hand, no reference exists for the indirect estimation of dimensional stability using any form of vibrational spectroscopy.

In chapter 5, the prediction of mechanical strength from process parameters, gravimetric determinations and chemical constituents was described in detail. In this part of the study, the prediction of the mechanical performance of TMW is investigated by using the multivariate analysis of Fourier transform MIR spectra. Defect-free, small specimens of Norway spruce, Scots pine and beech wood were thermally modified to WL between 0.2% and 34.4% and thence subjected to bending and Charpy impact strength tests (see section 3.3.4). The FTIR spectra of representative milled samples were obtained and the spectral data analysed using PLS regression to predict the mechanical performance of these wood species. The prediction of chemical constituents was also examined to gain a deeper understanding of changes in wood polymers associated with changes in physical properties. In a further study, another set of treated samples was used to investigate the predictability of ASE of spruce wood only. DRIFT spectra were acquired from these samples without further preparation, and the multivariate prediction of the dimensional stability of treated wood carried out.

8.2 Model calibration and prediction of mechanical properties

The statistics in Table 8.1 reveal that excellent calibrations can be obtained for each mechanical strength parameter based on the analysis of mid-infrared spectra of heated wood. The calibrations developed for all eight strength parameters in bending and for impact strength were in all cases excellent, with goodness of fit R^2_Y coefficients > 0.99 and goodness of prediction Q^2_{CUM} values ≥ 0.97, irrespective of the species studied. For the predicted values, the modelling is also very good, with ratios of RMSEP/SD < 0.9 and RPE values > 0 in most cases. In terms of the relative prediction error (RPE), the best prediction in bending for the three species was for SSML followed by MOR, although the best strength prediction in pine was for impact strength, IS (Q^2_{CUM} = 0.998, RPE = 0.85). Also in terms of the RPE, the lowest prediction ability in beech was for the models of MOE, WML and R, although these still were within acceptable ranges.

Table 8.1 Summary of statistics for calibrations and predictions for mechanical properties of thermally-modified beech, Scots pine and Norway spruce woods from FTIR spectra.

Species	Property	Mean	S.D.	A	R^2_X	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	$\frac{RMSEP}{SD}$	$\frac{RMSEP}{Mean}$	RPE
Beech	MOE	11,840	1,122	2	0.623	0.996	0.985	88.40	935.32	0.83	0.08	0.31
	MOR	96.64	33.76	1	0.591	0.999	0.993	0.86	14.45	0.43	0.15	0.82
	RLP	67.30	16.66	1	0.540	0.997	0.976	0.91	12.13	0.73	0.18	0.47
	R	0.0223	0.0080	1	0.534	0.997	0.987	0.0004	0.0064	0.79	0.29	0.37
	WML	0.0687	0.0560	1	0.631	0.997	0.971	0.0032	0.0451	0.81	0.66	0.35
	TW	0.1222	0.0952	1	0.626	1.000	0.982	0.0015	0.0691	0.73	0.57	0.47
	SSML	3.270	1.289	1	0.605	1.000	0.993	0.029	0.518	0.40	0.16	0.84
	SSLP	2.303	0.656	1	0.572	0.998	0.983	0.028	0.436	0.66	0.19	0.56
Scots pine	MOE	12,812	1,180	1	0.553	0.996	0.994	73.71	901.27	0.76	0.07	0.42
	MOR	94.11	27.51	1	0.690	0.999	0.999	0.68	13.22	0.48	0.14	0.77
	RLP	64.92	12.99	1	0.591	0.994	0.990	1.06	12.55	0.97	0.19	0.07
	R	0.0195	0.0057	1	0.581	0.996	0.991	0.0004	0.0058	1.02	0.30	-0.04
	WML	0.0565	0.0320	1	0.739	0.998	0.996	0.0013	0.0192	0.60	0.34	0.64
	TW	0.1107	0.0619	1	0.729	0.994	0.992	0.0050	0.0428	0.69	0.39	0.52
	SSML	3.22	1.00	1	0.698	0.999	0.999	0.03	0.45	0.45	0.14	0.80
	SSLP	2.21	0.48	1	0.613	0.996	0.993	0.03	0.42	0.88	0.19	0.22
	IS	17.63	8.87	1	0.734	0.999	0.998	0.33	3.45	0.39	0.20	0.85
Norway spruce	MOE	9,254	1,311	1	0.664	0.999	0.970	46.98	786.07	0.60	0.08	0.64
	MOR	64.80	22.02	1	0.687	1.000	0.988	0.38	6.04	0.27	0.09	0.92
	RLP	36.75	11.58	1	0.629	0.997	0.993	0.71	7.43	0.64	0.20	0.59
	R	0.0087	0.0041	1	0.624	0.994	0.989	0.0003	0.0024	0.59	0.28	0.66
	WML	0.0416	0.0260	1	0.655	0.998	0.993	0.0011	0.0071	0.27	0.17	0.93
	TW	0.0677	0.0437	1	0.651	0.998	0.994	0.0018	0.0171	0.39	0.25	0.85
	SSML	2.23	0.79	1	0.689	1.000	0.989	0.01	0.21	0.26	0.09	0.93
	SSLP	1.26	0.42	1	0.644	0.998	0.994	0.02	0.26	0.62	0.21	0.61
	IS	12.27	7.57	1	0.716	0.999	0.995	0.31	3.62	0.48	0.29	0.77

MOE, modulus of elasticity (MPa); MOR, modulus of rupture (MPa); RLP, fibre stress at the limit of proportionality (MPa); R, resilience (mmNmm^{-3}); WML, work to maximum load (mmNmm^{-3}); TW, total work (mmNmm^{-3}); SSML, horizontal shear stress at neutral plane at maximum load (MPa); SSLP, horizontal shear stress at neutral plane at limit of proportionality (MPa); Charpy IS, impact strength (kJm^{-2}). A, dimension of the calibration model. For statistics abbreviations, see chapter 3. Methods.

Apparently, the prediction of resilience, R, in pine was not acceptable, probably influenced by the large inherent variability of this mechanical parameter. Spruce gave slightly overall better predictions than pine and beech, with no major differences between these last two species; in spruce all the models for the mechanical strength parameters had very good prediction ability.

Except for MOE in beech, all the models for mechanical strength parameters gave only one dimension after extraction of two OSC components (A=1). It appears that OSC-filtering reduced model dimensional complexity to only one significant component (2 for beech MOE), making it easier to interpret the model compared to the one of the raw data. For the latter, model dimensionality were generally higher (between 2 and 4 dimensions, data not shown). Whilst PLS can manage to include the unwanted variation of the raw data in the model at the expense of more factors without seriously affecting the prediction of new samples, it is always preferred to have the smallest number of dimensions to reduce the risk of model over-fitting (Martens and Næs 1989).

Although the RMSEC values for the calibration of each strength property were up to one order of magnitude smaller than the RMSEP results (Table 8.1), the former values were very small, in some cases almost zero. RMSEP values were well below one SD for each property in question, indicating that calibrations based in FTIR spectroscopy can be effectively used to predict most of the strength properties from samples not included in the calibration model. Calibration models for energy-associated properties (R, WML, and TW) gave smaller prediction abilities for samples not included in the calibration set. This was in part caused by the inherently larger variation of these properties, and in part probably by a smaller correlation of these properties with the chemical information in the spectra of TMW. Similarly, calibration models for properties up to the maximum load (MOR, SSML, WML), had somewhat better predictive ability than the correspondent models for the properties up to the limit of proportionality (RLP, SSLP, R).

In order to illustrate graphically the estimation and prediction abilities of the models, plots of the experimentally-fitted versus FTIR-fitted individual strength properties are shown in Figure 8.1 for MOR, MOE, RLP, SSML, SSLP and IS. Predicted values for each property are plotted in the same charts as well. Excellent fit can be observed for the calibration model of each property, all the filled symbols for the calibration set being nearly along a 45° line in the measured *vs.* fitted plot. For the predictions (open symbols), the model for MOR in beech and spruce was excellent, whereas the predictive ability of the pine model was slightly poorer. MOE was confidently predicted with the calibration model up to around 12,000 MPa. At higher values, one predicted value for pine was slightly under-estimated, whilst for beech one value was just over-estimated. RLP, SSML and SSLP showed some degree of under- and over-estimation in the three species, but the general model prediction ability was acceptable. The prediction of IS was also very good for pine and spruce; in the latter most predicted values were slightly under-estimated, though.

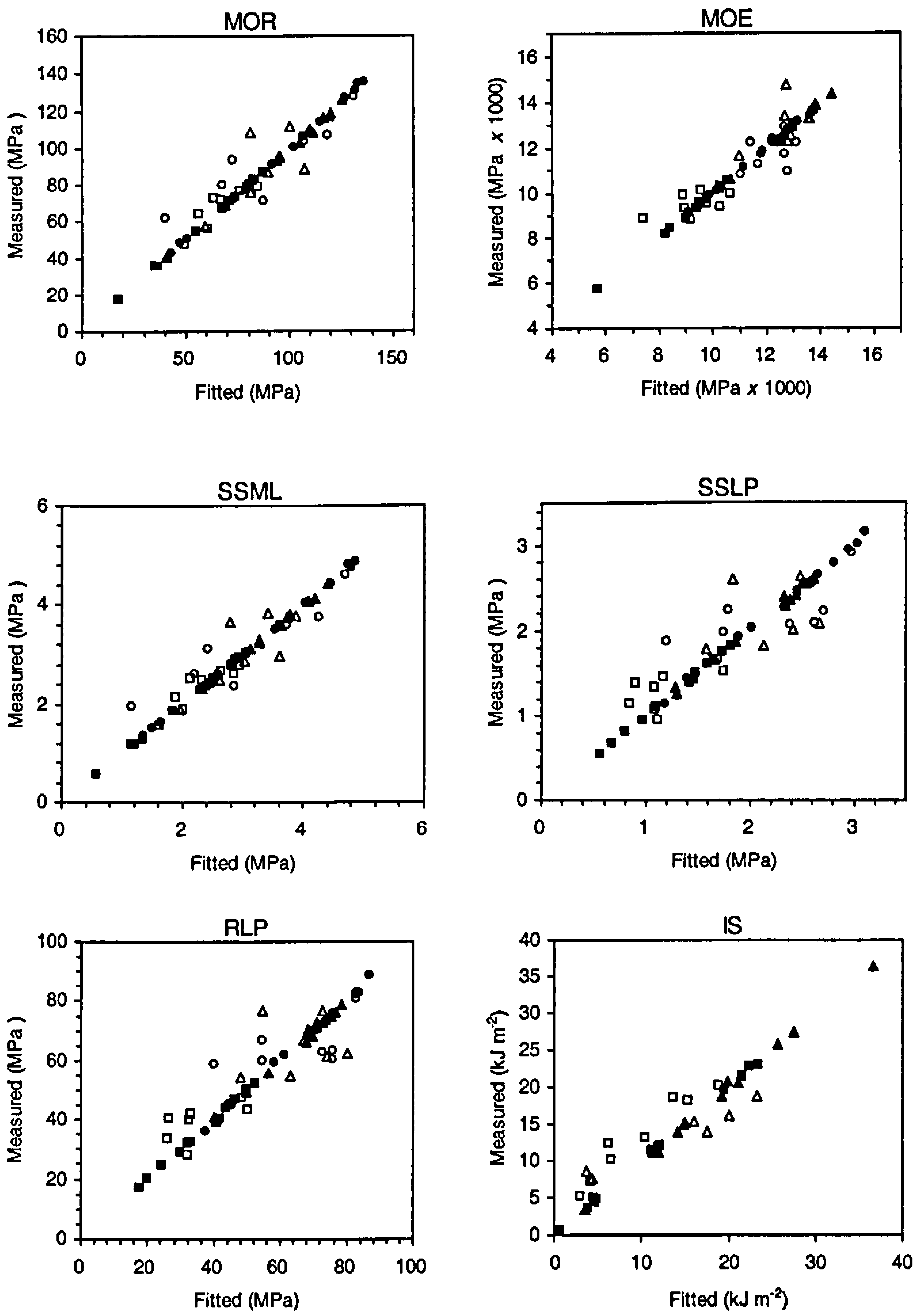

Figure 8.1 Calibration plots for MOR, MOE, SSML, SSLP, RLP and IS for heat-treated woods. Predicted values for each property are also included. Filled symbol, calibration set; open symbol, prediction set; beech, circles; Scots pine, triangles; Norway spruce, squares

As it was pointed out above, no reference exists for the prediction of strength properties using FTIR spectra in either treated or untreated wood. Studies based on other forms of vibrational spectroscopy, mostly in the NIR region of the spectrum, have shown the potential for using spectral information to predict the chemical and physical properties of untreated wood. Hoffmeyer and Pedersen (1995) studied the prediction of compression strength of Norway spruce of small samples, and the bending strength of structural-sized specimens using NIR spectroscopy. Excellent calibrations were obtained using 14 dimensions for compression strength, with RMSEC of 1.0 MPa, RMSEP of 2.8 MPa and r^2 ($\equiv R^2_Y$) of 0.97. Values of RMSEP for bending strength were also remarkably low (3.8 MPa) for the 3-dimension model, but the prediction power of the model was poor ($r^2 = 0.29$). The authors declared that the last results were expected, since the strength in structural sized members is affected by other factors such as knots, grain angle and other wood artefacts. They claimed however that this approach was at least as powerful as the annual-ring-width ($r^2 = 0.20 – 0.27$) or knot size ($r^2 = 0.16 – 0.20$) as predictor of strength, at the time used in some locations for the visual strength-grading of structural timber.

Similarly, Kelly *et al.* (2004a) reported the results for their investigation on chemical composition, microfibril angle and MOR and MOE in bending of 72 untreated samples of loblolly pine also using NIR spectroscopy. These authors found RMSEP of about 10.4 MPa and 1,490 MPa for MOR and MOE, respectively. The first value is similar to the one reported here for the softwoods MOR, but the one reported for MOE is significantly higher to that obtained in the present study. These authors used no signal correction prior to the PLS analysis, and consequently model complexity was high (5 dimensions for each property).

There are a few other studies mainly on the prediction of MOE and MOR for cored samples, directly on standing trees, and on clear or decayed small samples in bending, all of them using NIR spectroscopy; the interested reader is referred to recent reviews (So *et al.* 2004, Tsuchikawa 2007).

Changes in the FTIR spectra and its relationship with property change and loadings of the PLS modelling

The FTIR spectra of both modified and untreated wood samples show the same general features, despite several modifications that appeared after thermal modification (Figure 4.4, chapter 4). Common to all spectra was a strong OH stretching band centered at around 3550 cm^{-1}, a prominent C-H stretching absorption at about 2900 cm^{-1}, and a strong, broad packet in the region from 1750 to 1000 cm^{-1}, upon which several discrete, sharp or broad absorptions could be discerned. The qualitative monitoring of the chemical degradation of wood during heat treatment using its infrared spectra was a challenging task due to the difficulty of defining a reference band which remains unchanged during the thermal conversion. Nevertheless, steady changes in several bands became increasingly evident among spectra representing successively more severe treatment conditions. Figure 8.2 shows the difference spectra, for control spectra minus the spectra of the treated samples, for 10 levels of modification of Norway spruce samples. Evidently, the mid-infrared region was effective in detecting gradual changes in wood polymers. Several bands can be identified where the changes are occurring during the thermal conversion. For instance, at around 1712 cm^{-1} an increasing absorption can be clearly noticed as the weight loss increases (Figure 8.2). Several other varying bands can be discerned as the thermal modification proceeds (*e.g.* at 1290 cm^{-1} or 1057 cm^{-1}).

Even small variations in the infrared spectra such as relative heights of neighbouring bands or the presence of weak shoulders are of considerable significance for detecting changes in chemical composition (Hergert 1971). While FTIR spectroscopy is highly sensitive and sufficiently detects subtle absorption differences, multivariate analysis is a powerful technique to extract such information from the spectra, unlike univariate analysis.

Within the mid-infrared spectral regions chosen for this study (3500 - 2800 cm^{-1}, 1800-550 cm^{-1}), the plot of the PLS loadings for the MOR in spruce wood showed an analogous profile with the difference spectrum obtained by subtracting the spectrum of the treated samples from that of untreated wood (Figure 8.2). Wood samples were separated by PLS regression according to their strength in the direction of the single factor extracted. The largest loadings in the loading plot match somewhat the bands with the largest changes in the difference spectra. The band with the largest negative loading in the loading plot is the one with maxima at 1712 cm^{-1}, and therefore has the largest importance for the calibration. Other major loadings that accounted negatively for the estimation of MOR, also appearing in the difference spectra as absorption maxima, were at 1600, 1290, 1200, 1057 and 1031 cm^{-1}, while absorption minima at 3500, 3220, 2920, 2850, 1508, 700, 670 and 625 cm^{-1} had the largest positive influence on the single factor extracted for MOR.

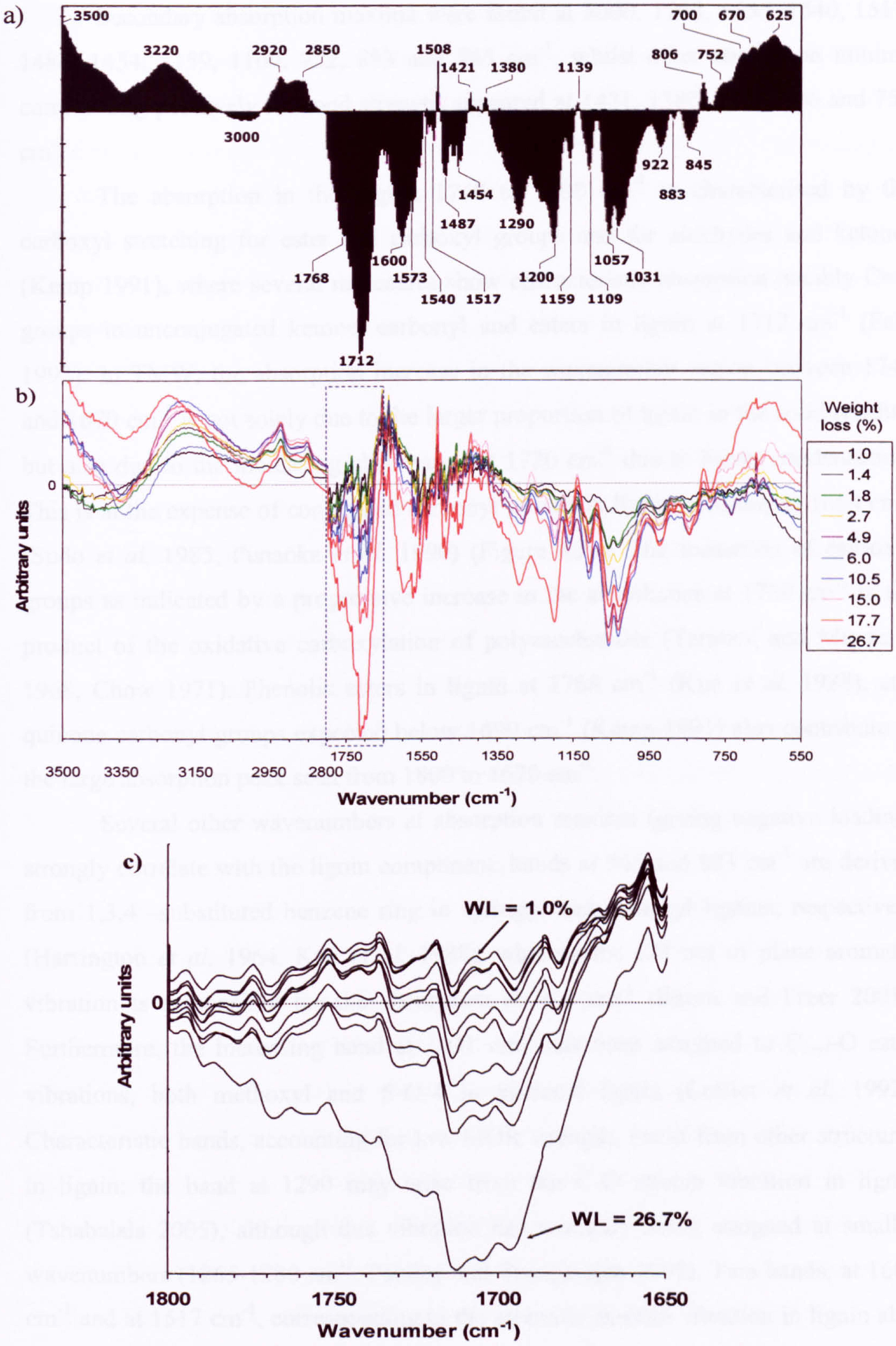

Figure 8.2 a) Loading plot for the PLS model of MOR in thermally modified Norway spruce wood. b) Difference spectra for control treatment minus treated wood at ten levels of modification (expressed as weight loss). c) Enlarged view for the spectral region marked in b; spectra are for increasing levels of weight loss in the same order as in the legend in b.

Secondary absorption maxima were found at 3000, 1768, 1556, 1540, 1517, 1487, 1454, 1159, 1109, 922, 883 and 845 cm^{-1}, whilst other absorption minima contributing positively to wood strength appeared at 1421, 1380, 1139, 806 and 752 cm^{-1}.

The absorption in the region 1740 to 1600 cm^{-1} is characterised by the carboxyl stretching for ester and carboxyl groups and for aldehydes and ketones (Kemp 1991), where several molecules show characteristic absorption notably C=O groups in unconjugated ketone, carbonyl and esters in lignin at 1712 cm^{-1} (Faix 1992). In TMW, the absorption increase in the wavenumber region between 1740 and 1670 cm^{-1} is not solely due to the larger proportion of lignin in the solid residue, but also due to the increasing absorbance at 1720 cm^{-1} due to lignin condensation. This is at the expense of conjugated carbonyl groups in lignin vibrating at 1654 cm^{-1} (Sudo *et al.* 1985, Funaoka *et al.* 1990) (Figure 8.2c). The formation of carboxyl groups as indicated by a progressive increase in the absorbance at 1730 cm^{-1} is the product of the oxidative carboxylation of polysaccharides (Teratani and Miyazaki 1968, Chow 1971). Phenolic esters in lignin at 1768 cm^{-1} (Kuo *et al.* 1988), and quinone carbonyl groups expected below 1690 cm^{-1} (Kemp 1991) also contribute to the large absorption peak seen from 1800 to 1670 cm^{-1}.

Several other wavenumbers at absorption maxima (giving negative loading) strongly correlate with the lignin component: bands at 845 and 883 cm^{-1} are derived from 1,3,4 –substituted benzene ring in syringyl and guaiacyl lignins, respectively (Harrington *et al.* 1964, Kuo *et al.* 1988), whereas the CH out of plane aromatic vibration is responsible for the absorption at 922 cm^{-1} (Baeza and Freer 2001). Furthermore, the increasing band at 1031 cm^{-1} has been assigned to C_{aryl}-O ester vibrations, both methoxyl and β-O-4 in guaiacyl lignin (Collier *et al.* 1992). Characteristic bands, accounting for low MOR strength, result from other structures in lignin: the band at 1290 may arise from the C-O stretch vibration in lignin (Tshabalala 2005), although this vibration has normally being assigned at smaller wavenumbers (1265-1280 cm^{-1}, Pandey and Theagarajan 1997). Two bands, at 1600 cm^{-1} and at 1517 cm^{-1}, corresponding to the aromatic skeletal vibration in lignin also showed increased absorbance, although in the difference spectra the band at 1600 cm^{-1} had lower absorbance than untreated wood for WL up to about 10%. The absorption increase at this band could be enhanced by the presence of chelated conjugated carbonyl structures or methylene or ether linkages (Grandmaison *et al.*

1987), probably developing upon lignin repolymerisation. Lastly, the observed broad increasing absorption peaking at 3000 cm^{-1} corresponds to the CH stretch in CH_3 and CH_2 groups in lignin (Baeza and Freer 2001). The band at 1508 cm^{-1}, reported to originate from aromatic skeletal vibrations (Hergert 1971), showed a clear decrease with the treatment. Although this has been previously reported (Grandmaison *et al.* 1987), no direct explanation can be offered for this effect at this time, although it could be related to the decreasing 'true' lignin remaining in the solid residue (Windeisen *et al.* 2007).

On the other hand, bands with decreasing absorbance (giving positive loading) were mostly related to the polysaccharide portion of the wood material. The band centered at the 2900 cm^{-1} region, which was broad in the initial wood sample, was progressively resolved into two separate bands at 2850 cm^{-1} and 2920 cm^{-1} as the heat-induced WL increased. These two bands have been assigned to CH_2 symmetric and anti-symmetric stretching in cellulose, respectively (Baeza and Freer 2001). Similarly, the broad band for the OH stretching vibration due to intermolecular hydrogen bonding in cellulose, encompassing from 3100 to 3500 cm^{-1} (the largest wavenumber analysed), was also gradually resolved into two broad peaks as the severity of the treatment increased. One broad peak appeared between 3500-3420 cm^{-1}, with minima at 3500 cm^{-1}; the other peak was at 3270-3100 cm^{-1}, with minima at 3176 but shifting to higher frequencies (at ~ 3220 cm^{-1}). This doublet could be due to the conversion from amorphous to a more crystalline form of cellulose. The general reduction in OH bands may be the manifestation of the loss of OH groups following dehydration upon heating, in the course of which double bonds, responsible for coloured compounds, are formed (Tolvaj and Faix 1995). In the region of the pyran ring vibration, at the other extreme of the spectra, the broad peak between 730 and 550 cm^{-1} showed two minima at 700 and 670 cm^{-1}, both arising form the C-O-H out of plane bending mode in cellulose (Kuo *et al.* 1988, Baeza and Freer 2001). Similarly, the decreasing band at 806 cm^{-1}, has been assigned mainly to vibration of mannan and C-H out of plane deformation vibration in guaiacyl lignin, which may reflect hemicellulose degradation (Harrington 1964, Kuo *et al.* 1988), although this signal has also been found to arise from ring breathing (β) in cellulose (Baeza and Freer 2001).

In addition, decreasing bands to a smaller degree belong all to the cellulose and hemicellulose constituents, which in turn are the components most degraded during the modification. The observed absorption peaks with minimum at 752 cm^{-1}, has been assigned to CH_2 rocking in cellulose while the 1139 cm^{-1} wavenumber is due to anti-symmetric bridge oxygen in cellulose (Baeza and Freer 2001). Several studies have shown that the absorption in the band 1430 – 1380 cm^{-1} strongly correlates with the polysaccharide component in various woods. The absorbance at 1380 cm^{-1} is due to CH bending vibration in cellulose and hemicellulose (Baeza and Freer 2001, Harrington 1964), while the band at 1421 cm^{-1} expresses the absorbance due to CH_2 scissors vibration in cellulose (Harrington 1964, Faix and Böttcher 1992, Baeza and Freer 2001). The reduction in the band at 1380 cm^{-1} in TMW has been corroborated by the decrease of the C4 signal of crystalline cellulose at 89 ppm observed by NMR, indicating a conformational modification of wood polysaccharides (Hakkou *et al.* 2005).

A few bands (*viz.* 1200, 1159, 1109 and 1057 cm^{-1}) arising from the frequencies in the cellulose environment and from the hydrogen bonding system do not appear to agree well with the reduction in absorbance found in other bands largely originated from the polysaccharide component. As noted elsewhere, the hydrogen bonding array appears to be disrupted at elevated temperatures. Increasing bands appeared at 1200 cm^{-1} and 1109 cm^{-1} both known to arise from O-H groups linked to polysaccharides. The one at 1200 cm^{-1} has been assigned to O-H in plane bending vibration in cellulose and hemicellulose (Harrington 1964), whereas the shortest frequency has been assigned to an O-H association band in cellulose and hemicelluloses (*Idem.*). Additionally, the observed absorption maxima at 1057 cm^{-1} has been associated to xylan (Harrington 1964), though more frequently is quoted as arising from the C-O stretching vibration in cellulose and hemicellulose (Kuo *et al.* 1988, Faix and Böttcher 1992, Pandey and Theagarajan 1997, Tshabalala 2005). The increase in absorption at this wavenumber may indicate the formation of aliphatic alcohols during heating (Faix 1992) rather than the proportionally higher occurrence of this function in the original polysaccharide system. Likewise, the increasing absorbing band at 1159 cm^{-1} comes up from the C-O-C asymmetric bridge stretching vibration in cellulose and hemicellulose (Harrington 1964, Faix and Böttcher 1992, Tshabalala 2005), but the increase in these linkages may also be due to condensation reactions (Weiland and Guyonnet 2003). Absorption bands reported here mostly agree with those determined by Grandmaison *et al.* (1987), Bourgois and Guyonnet (1988), Kotilainen *et al.* (2000), Weiland and Guyonnet (2003), Nuopponen *et al.*

(2004b) and Hakkou *et al.* (2005) for heat-treated lignocellulosics. Qualitative results are also consistent with analytical determinations previously reported (chapter 4).

Evidently, the success in predicting bending strength in the mid-infrared region could be attributed to divergence in lignin and polysaccharide contents, whereby the lignin content had a negative influence on wood strength, whilst the signals arising from the carbohydrate component are linked to strength retention. This is further corroborated by an earlier study that documented the decrease in hemicellulose contents in longleaf pine, Douglas-fir, and southern red oak with the severity of the heating exposure, along with reductions in wood toughness (Davis and Thompson 1964). Furthermore, an increase in lignin (or pseudo-lignin) upon heating and reduction in hemicellulose content in several woods has been reported, especially xylan and other pentosans in hardwoods (Bourgois *et al.* 1989, Garrote *et al.* 1999, Zaman *et al.* 2000, Kotilainen *et al.* 2001, Alén *et al.* 2002, Boonstra and Tjeerdsma 2006), while reductions in mechanical strength had typically been ascribed to these modifications (*e.g.* Mouras *et al.* 2002).

The observations made for the difference spectra and loading plot of Norway spruce still hold for Scots pine: the degradation and dehydration of polysaccharides as well as the increase of lignin and its condensation are noticed. Peaks in the difference spectra of pine wood and the loading plot for MOR are similar to that of spruce wood, with three small variations: the decreasing peak at 1380 cm^{-1} is not observed in pine. Similarly, the broad peak observed in spruce from 2950 to about 2840 cm^{-1} with minima at 2850 cm^{-1} and at 2920 cm^{-1} are unimportant in pine wood for the calibration model. On the other hand, the signal responsible for the peak at 700 cm^{-1}, is clearly more conspicuous in the pine spectrum compared to the one in spruce.

The findings made for softwoods for the difference spectra and loading plot are still valid for beech, but noticeable changes in the latter species are seen in the magnitude of the loadings and intensities of the peaks. Additionally, several bands appeared at slightly lower or higher wavenumbers compared to the difference spectra in softwoods, but this was not unexpected. Significant changes in four bands should be noted for beech: unlike in softwoods, important absorption increases (giving negative loading) were determined at 670 cm^{-1} and 788 cm^{-1}. Furthermore, the broad peak observed in softwoods between 3270-3100 cm^{-1}, with minima at 3176-3220 cm^{-1} no longer appears in beech. However, the largest change in the loading plot of beech compared to the one in softwoods is the decrease at 1747 cm^{-1}, assigned to C=O stretch in carboxyl groups from xylan (Owen and Thomas 1989, Tolvaj and Faix 1995), indicating hemicellulose degradation. Earlier reports have shown a decrease in this band at incipient levels of heat-treatment (Chow 1971), indicating the dehydration reaction of wood polysaccharides had taken place. Although in the plot for the difference spectra in softwoods a decrease for this group at 1736 cm^{-1} was observed at WL smaller than 6.0%, in the loading plot no decreasing peak appears at this band. In softwoods, the OSC-filtering algorithm probably superimposes the large increase in other bands in the spectral range between 1740 and 1700 cm^{-1} derived from the carboxylation of polysaccharides and lignin condensation over the initial decrease at 1736 cm^{-1} due to the initial loss of esters and carboxyl groups particularly in xylan, and assigns a negative loading to this band. In contrast, a sharp peak develops in the difference spectra of beech at 1747 cm^{-1} and a large positive loading also appears in its loading plot. This is probably due to the larger proportion of xylan in untreated beech, accounting for 23.04% of its dry weight, and also to the large, fast degradation of xylan upon heating. The positive loading may reflect the dependability of wood strength on this component.

In the remaining strength parameters in bending and in impact strength, the loading plot showed similar profile for the MOR loading plot but for small changes in the loadings. For chemical constituents increasing in line with the thermal modification (*e.g.* lignin content), the profile in the loading plot was also analogous but the loadings had opposite sign to the ones in the plot for MOR. For most other chemical polymers or monomers and physical properties (WL, ND, SG_{OD}), the profile of the loading plot was also alike to the one of MOR. The only noticeable difference was the loading plot for the prediction of EMC, where most of the loadings dominated by the carbohydrate component in the region 1290-550 cm^{-1} had negative values. The profile of the loading plot for the prediction of ASE was significantly different from the previous description, but for reasons of space this will not be explained here.

Findings from the present research accord with previous studies that have demonstrated the efficacy of the multivariate analysis of infrared spectra to predict mechanical strength not only in solid wood, but also in reconstituted wood products (*cf.* Tsuchikawa 2007 and references given therein).

8.3 Model calibration and prediction of WL, ND, EMC and SG_{OD}

In addition to chemical information, the infrared spectrum contains physical information that can be used to determine inherent physical properties in the wood material. Density, microfibril angle and specific gravity of the cell wall can all be derived from the spectra with the appropriate treatment of the data. This capability has been attributed to interaction between atoms in different molecules (such as H-bonds and the dipole moment) that perturb vibrational energy states, thereby shifting the existent absorption bands and creating new ones through variations in crystal structure (Blanco and Villarroya 2002). In TMW for instance, dehydration of the cell wall substance following heat exposure can be directly related to changes in crystallinity of amorphous cellulose. Since amorphous and crystalline cellulose have identical bonds, the IR spectra of these two types of cellulose are essentially the same. However, the sharpness of certain IR peaks is directly related to cellulose crystallinity (Schultz *et al.* 1985). Crystalline samples would have bonds of identical strengths and orientations. In contrast, in the amorphous form the physical environment is different, and a given bond would have a broader range of strengths and orientation environments, thereby given spectra with broader peaks. Analysis of the spectra in turn allows crystal forms to be identified and physical properties determined.

Excellent calibrations were obtained for each physical property studied based on the analysis of mid-infrared spectra of wood (Table 8.2). The calibrations developed for WL, ND, MC and SG_{OD} were in all cases excellent, with coefficients of the goodness of fit $R^2_Y > 0.98$ and goodness of prediction $Q^2_{CUM} > 0.96$, irrespective of the species studied.

Table 8.2 Summary of statistics for calibrations and predictions for physical properties of thermally modified beech, Scots pine and Norway spruce woods using FTIR spectra.

Species	Property	Mean	S.D.	A	R^2_X	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	$\frac{RMSEP}{SD}$	$\frac{RMSEP}{Mean}$	RPE
Beech	WL	11.06	9.87	1	0.635	1.000	0.995	0.18	1.27	0.13	0.11	0.98
	EMC	6.53	1.60	1	0.653	1.000	0.992	0.03	1.07	0.67	0.16	0.55
	ND	618.72	39.00	1	0.462	0.992	0.961	3.55	27.48	0.70	0.04	0.50
	SG_{OD}	0.6425	0.0433	1	0.514	0.997	0.983	0.0024	0.0336	0.78	0.05	0.40
Scots pine	WL	7.01	6.88	1	0.713	1.000	0.999	0.09	0.99	0.14	0.14	0.98
	EMC	7.48	1.63	1	0.705	0.984	0.981	0.21	0.56	0.34	0.07	0.88
	ND	514.40	19.05	1	0.534	0.987	0.980	2.24	19.82	1.04	0.04	-0.08
	SG_{OD}	0.5373	0.0233	1	0.618	0.995	0.991	0.0018	0.0201	0.86	0.04	0.26
Norway spruce	WL	7.75	7.94	1	0.723	1.000	0.984	0.10	1.09	0.14	0.14	0.98
	EMC	7.63	1.99	1	0.732	0.999	0.997	0.07	0.31	0.16	0.04	0.98
	ND	357.98	17.99	1	0.616	0.998	0.986	0.76	11.19	0.62	0.03	0.61
	SG_{OD}	0.3751	0.0224	1	0.686	1.000	0.994	0.0004	0.0122	0.54	0.03	0.70

WL, weight loss (%); EMC, equilibrium moisture content at 65% relative humidity at 20°C (%); ND, nominal density = oven-dry weight/volume at 65% relative humidity at 20 °C (kg m^{-3}); SG_{OD}, oven-dry after-treatment specific gravity (unitless). A, dimension of the calibration model. For statistics abbreviations, see chapter 3. Methods.

For the predicted values, the fit was also very good, with ratios of RMSEP/SD < 0.9 and RPE values > 0.2 in most cases. Based on the ratio RPE, the best predictions using FTIR spectra were for WL and EMC in the three species. Apparently, the prediction of ND in pine was not completely acceptable according to the REP or RMSEP/SD indicators, although from the scatter in the plot of measured *vs.* fitted values, this is not evident (Figure 8.3). Figure 8.3 also includes the plots for other individual physical properties for the experimentally-fitted versus FTIR-fitted, namely for WL, SG_{OD} and EMC. Predicted values for each property are plotted in the same charts as well.

From plots in Figure 8.3, it can be seen that excellent fits for the calibration model were obtained for each property (solid symbols). Also from the plots, remarkably good predictions were found for WL, ND, SG_{OD} and EMC, except for one specimen in beech in the latter parameter, which was over-estimated by about 2%.

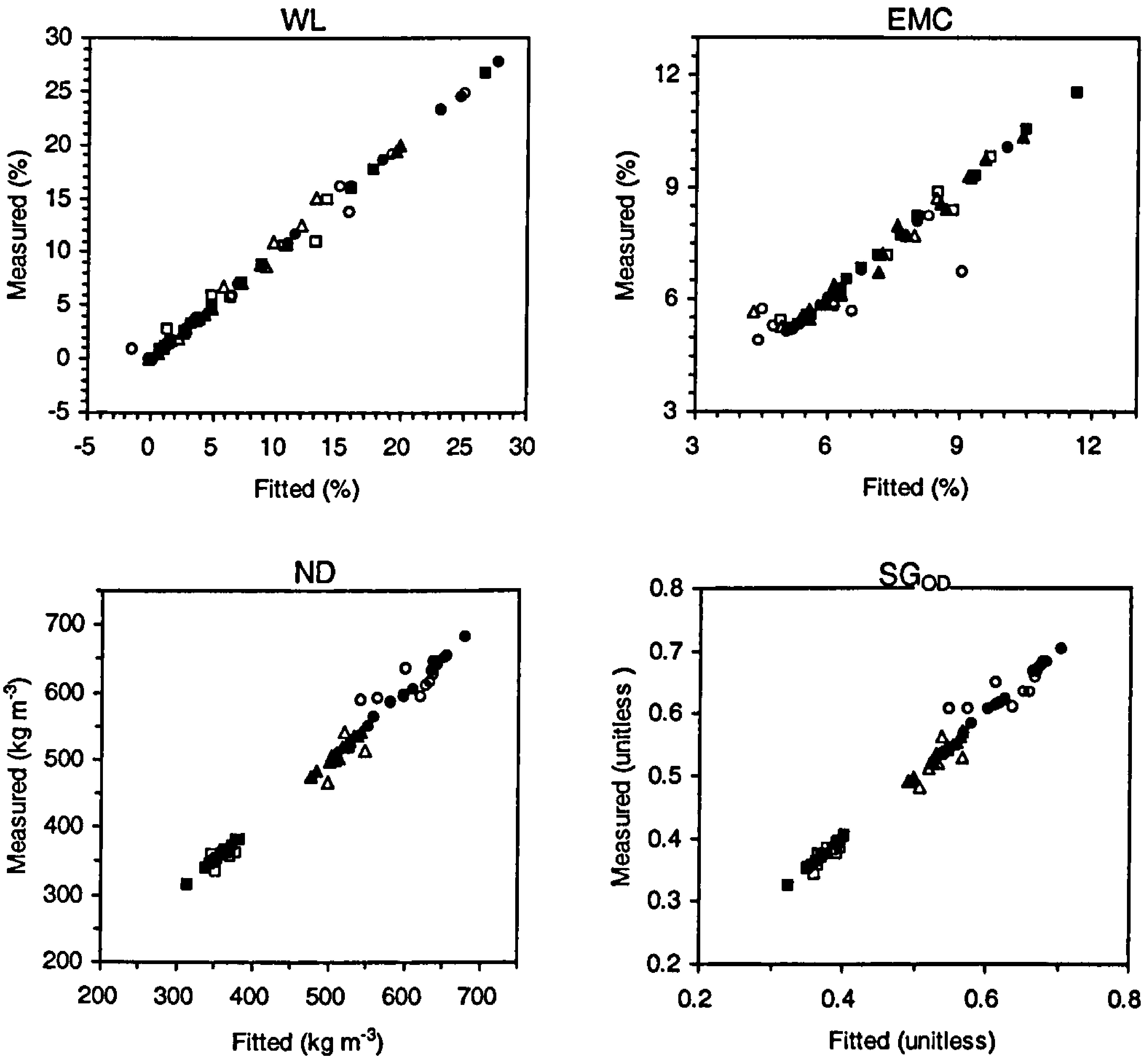

Figure 8.3 Calibration plots for WL, EMC, ND and SG_{OD}. Filled symbol, calibration set; open symbol, prediction set; beech, circles; Scots pine, triangles; Norway spruce, squares. Calibration models and subsequent predictions were calculated for each species separately.

Values of RMSEP in this work are similar but compare favourably with other studies on the prediction of wood density using FTIR spectroscopy. In their study for the rapid determination of basic density of *Pinus radiata* (mean 371 kg m^{-3}, S.D. 51 kg m^{-3}), Meder *et al.* (1999) found RMSEP's of 25.5 and 36.9 kg·m^{-3} for calibration models built with transmission FTIR and DRIFT spectra, respectively. In both cases, the number of factors (dimensions) determined by the authors was four. In a similar study, Nuopponen *et al.* (2006) used OSC-filtered DRIFT spectra to estimate wood basic density of cores of 50 different 15-year-old clones of Sitka spruce (*Picca sitchensis*, mean 344 kg m^{-3}, SD 43.3 kg m^{-3}) and also to estimate the density of a mixture of samples containing cored samples of Sitka spruce and Scots pine and blocks of 24 tropical Ghanaian hardwood species (pooled mean ~367 kg·m^{-3}, pooled SD ~49 kg·m^{-3}). Despite having very good levels of goodness of prediction for the model with all the woods together (Q^2_{CUM} = 0.88), and only one dimension in the calibration, they found low predictive ability of the model for samples not included in the calibration set, with values of RMSEP of 56 kg·m^{-3}, and negative values of RPE (-0.32). These authors emphasised that the model was still functional for separating between very high- and low-density wood samples. The model for the Sitka spruce samples alone was still inferior to that constructed from all three groups of samples, with a value of Q^2_{CUM} of 0.65, whereas the RMSEP was 55 kg·m^{-3}, the RPE working out to be -0.63.

Using another form of vibrational spectroscopy, Hoffmeyer and Pedersen (1995) assessed the predictability of ND in small- and structural-sized specimens of untreated Norway spruce wood using NIR region of the spectrum. These authors found that most statistics were clearly in favour of the large-sized specimens, with RMSEP = 37 kg·m^{-3} and 11 kg·m^{-3} for small- and large-sized specimens respectively.

No previous references exist for the estimation of this ND, SG_{OD} or EMC in thermally modified wood in the MIR range. In the case of the prediction of WL, in their study of DRIFT spectra of thermally-modified Norway spruce and Scots pine powdered woods, Kotilainen *et al.* (2000) evaluated the prediction on WL using PLS regression; they found a so-called correlation coefficient R^2 for the validation set of 0.894, with six dimensions in their model. No further statistics were given, though.

The present work includes the study of a property that is independent of the moisture content of the samples, after-treatment specific gravity, SG_{OD}. This is because it is feasible that the analysis is evaluating the possible dependence of wood properties on its moisture content, rather than the dependence of these on chemical composition. As it can be appreciated in Table 8.2, statistics for SG_{OD} give slightly better results than those for ND in softwoods, and almost equivalent results for beech. Although this does not prove that the direct assessment of strength with FTIR spectroscopy is possible, it highlights the moisture-independence of this important property, and could probably be extended to the prediction of mechanical strength properties independently of the EMC of the specimens.

8.4 Prediction of physical properties using selected IR bands

It was shown in Figure 8.2 that the loading plot for the calibration model of MOR had several distinctive bands changing noticeably in line with the severity of the treatment, so it was found expedient to assess the possibility of making predictions with a smaller number of bands. Calibrations containing from 8 to 10 wavenumbers instead of spectral ranges 3500-2800 and 1800-550 cm^{-1} were thus attempted with FTIR spectra for the evaluation of MOE, MOR, WL and ND in spruce wood only (Table 8.3).

Table 8.3 Summary of statistics for calibrations and predictions for physical properties of thermally modified Norway spruce wood using selected bands of FTIR spectra, DRIFT spectra and low-resolution DRIFT spectra.

Spectra	Property	Mean	S.D.	A	R^2_X	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	$\frac{RMSEP}{SD}$	$\frac{RMSEP}{Mean}$	RPE
	MOE[a]	9,254	1,311	1	0.892	0.963	0.959	263.61	751.76	0.57	0.08	0.67
$FTIR_{few}$	MOR[b]	64.80	22.02	1	0.908	0.992	0.990	2.07	7.89	0.36	0.12	0.87
	WL[b]	7.75	7.94	1	0.913	0.992	0.991	0.75	0.58	0.07	0.07	0.99
	ND[a]	358.0	17.99	1	0.865	0.923	0.920	5.22	14.07	0.78	0.04	0.39
DRIFT	WL	4.59	3.47	1	0.968	1.000	1.000	0.00	1.66	0.48	0.36	0.77
	ASE	21.30	16.32	1	0.963	1.000	1.000	0.00	5.96	0.37	0.28	0.87
$DRIFT_{low}$	WL	3.13	3.13	1	0.888	1.000	0.999	0.00	1.29	0.41	0.41	0.83
	ASE	15.16	16.20	1	0.863	1.000	0.998	0.02	4.86	0.30	0.32	0.91

$FTIR_{few}$, FTIR selected wavenumbers ([a] = 3500, 1712, 1600, 1290, 1200, 1057, 1031 and 620 cm-1; [b] = 3220, 1712, 1600, 1508, 1290, 1200, 1159, 1107, 1057 and 1031 cm^{-1}). $DRIFT_{low}$, DRIFT low resolution (24 scans at 8 cm^{-1} resolution); MOE, modulus of elasticity (MPa); MOR, modulus of rupture (MPa); WL, weight loss (%); ND, nominal density = oven-dry weight/volume at 65% relative humidity at 20 °C (kg m^{-3}); ASE, anti-swelling efficiency (%). A, dimension of the calibration model. For statistics abbreviations, see chapter 3. Methods.

The reduction of predictors from 492 to the 8 to 10 more significant ones led in most cases, to small increases in the RMSEP for all four properties studied. This highlights the possibility of using a simple, hand-held device for the prediction of mechanical and other physical properties of modified wood at a larger scale. Portable IR instruments reading a small number of wavelengths have been used for many years in other industries, primarily for kinetics studies in processes concerning either gaseous or liquid materials (Rouessac and Rouessac 2000); several prototypes have also been developed in recent times for the measurement of selected mid-infrared bands in solid materials with hand-held devices (Workman 1999).

The proposal of using specific bands of FTIR spectra for monitoring the degree of thermal modification was suggested in a related earlier study by Bourgois and Guyonnet (1988). Working with powdered heat-treated maritime pine, these authors found that the most significant changes of wood spectra were in the carbonyl (at 1742 cm^{-1}) and ethylenic (at 1644 cm^{-1}) functions. Together with an increase in intensity, they noted what they believed was a shift of these bands towards smaller wavenumber, to 1712 cm^{-1} and 1602 cm^{-1} respectively. Intensity changes were linear with time, and thus proposed to be of interest to monitor the extent of treatment of modified woods. Nevertheless, it is not always possible to use the absorbance at a single wavenumber to predict the concentration of one of the absorbers due to the overlapping nature of spectral peaks, the so called selectivity problem. Results from the present study confirm that it is not only possible to monitor the chemical conversion of TMW, but also to confidently estimate several complex strength properties using multivariate analysis of a few selected OSC-filtered bands.

8.5 Model calibration and prediction of chemical constituents

In general, the modelling of chemical constituents was superior in both the calibration and prediction ability to all other models, except for the models for galactan in beech and pine, which gave unacceptable predictions (Table 8.4).

Excellent calibrations were obtained for the remaining monosaccharides and polymers based on the analysis of mid-infrared spectra of wood (Table 8.4). The calibrations developed for wood polymers [lignin, glucomannan (GluMan), glucuronoxylan (GluXylan), hemicellulose and cellulose] had all goodness of fit R^2_Y and goodness of prediction Q^2_{CUM} statistics ≥ 0.975, irrespective of the species studied. For the predicted values, the fit was also very good, with ratios of RMSEP/SD < 0.8 and RPE values ≥ 0.55 in most cases. Model complexity for all polymers was also low (A=1).

Table 8.4 Summary of statistics for calibrations and predictions for chemical composition of thermally-modified beech, Scots pine and Norway spruce woods using FTIR spectra.

Species	Constituent (%)[a)]	Mean	S.D.	A	R^2_X	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	$\frac{RMSEP}{SD}$	$\frac{RMSEP}{Mean}$	RPE
Beech	Lignin	28.62	4.97	1	0.625	1.000	0.995	0.098	2.322	0.47	0.08	0.78
	GluXylan	12.65	8.26	1	0.646	1.000	0.995	0.133	2.185	0.26	0.17	0.93
	GluMan	1.42	1.58	1	0.677	1.000	0.998	0.019	0.653	0.41	0.46	0.83
	Hemicellulose	14.07	9.46	1	0.670	1.000	0.997	0.120	2.033	0.21	0.14	0.95
	Cellulose	42.90	5.06	1	0.480	0.995	0.975	0.377	2.998	0.59	0.07	0.65
	Arabinan	0.202	0.229	1	0.677	1.000	0.993	0.002	0.135	0.59	0.67	0.65
	Galactan	0.505	0.508	1	0.477	0.994	0.938	0.041	0.515	1.01	1.02	-0.03
	Glucan	44.990	5.695	1	0.544	0.999	0.983	0.194	3.075	0.54	0.07	0.71
	Xylan	12.395	8.227	1	0.652	1.000	0.996	0.120	1.951	0.24	0.16	0.94
	Mannan	0.792	0.892	1	0.678	1.000	0.998	0.011	0.367	0.41	0.46	0.83
Scots pine	Lignin	31.87	3.32	1	0.703	1.000	0.998	0.071	0.956	0.29	0.03	0.92
	GluXylan	5.58	2.97	1	0.663	0.996	0.989	0.206	1.413	0.48	0.25	0.77
	GluMan	10.37	4.37	1	0.682	0.999	0.996	0.143	1.208	0.28	0.12	0.92
	Hemicellulose	15.95	7.24	1	0.680	0.997	0.991	0.420	2.460	0.34	0.15	0.88
	Cellulose	43.01	3.62	1	0.613	0.989	0.983	0.388	2.440	0.67	0.06	0.55
	Arabinan	0.590	0.487	2	0.803	0.995	0.988	0.038	0.399	0.82	0.68	0.33
	Galactan	1.231	0.644	1	0.654	0.892	0.873	0.220	0.850	1.32	0.69	-0.74
	Glucan	46.467	4.210	1	0.651	0.992	0.988	0.381	2.543	0.60	0.05	0.64
	Xylan	4.026	2.150	1	0.663	0.995	0.989	0.150	1.024	0.48	0.25	0.77
	Mannan	7.998	3.373	1	0.682	0.999	0.996	0.107	0.906	0.27	0.11	0.93
Norway spruce	Lignin	32.06	4.92	1	0.714	1.000	0.975	0.067	1.332	0.27	0.04	0.93
	GluXylan	4.74	2.63	1	0.716	0.999	0.991	0.061	0.971	0.37	0.20	0.86
	GluMan	10.15	4.81	1	0.682	1.000	0.986	0.096	1.749	0.36	0.17	0.87
	Hemicellulose	14.89	7.40	1	0.695	1.000	0.988	0.172	2.554	0.35	0.17	0.88
	Cellulose	42.96	5.51	1	0.724	1.000	0.998	0.105	4.321	0.78	0.10	0.39
	Arabinan	0.458	0.368	1	0.737	1.000	0.995	0.008	0.143	0.39	0.31	0.85
	Galactan	0.905	0.463	1	0.670	0.997	0.993	0.025	0.166	0.36	0.18	0.87
	Glucan	45.726	6.338	1	0.734	1.000	0.993	0.076	4.062	0.64	0.09	0.59
	Xylan	3.473	1.945	1	0.719	0.999	0.992	0.055	0.691	0.36	0.20	0.87
	Mannan	7.947	3.784	1	0.686	1.000	0.987	0.076	1.367	0.36	0.17	0.87

[a)] % content of the before-treatment oven-dry weight

For statistics abbreviations, see chapter 3. Methods.

Based on the ratio RPE, the best predictions using FTIR spectra differed between softwoods and beech. For the latter, the best prediction was for hemicellulose, followed by GluXylan, whilst for gymnosperms the best prediction was for lignin, followed by GluMan and hemicelluloses. In all three species, the less efficient prediction -although a very good one, was for cellulose. This may be because significant changes in cellulose were not reflected by mass change only, but also by structural modifications (*e.g.* increased crystallinity), which are not expressed in the gravimetric determinations.

For the calibrations for wood monosaccharides (converted to individual polysaccharides), arabinan, galactan, glucan (including glucose in cellulose), xylan and mannan, the R^2_Y and Q^2_{CUM} statistics were > 0.99 and > 0.98 respectively, regardless of the species in concern, except for galactan in beech and pine. Predictions were also very good, with ratios of RMSEP/SD < 0.8 and RPE values ≥ 0.55 in most cases. Based on the ratio RPE, the best predictions were for xylan in beech, and for mannan in softwoods.

The poor fitting ability for galactan, the constituent with the second lowest contribution in the chemical composition, may be influenced by the close elution of galactan with glucose as seen in the chromatogram, making the quantification less exact for this monosaccharide. This can easily seen in the rather large scatter in the contents of this component against WL (chapter 4). Subtle differences in chemical composition and chemical changes are likely to be detected by the spectra. Indeed, IR spectra has a very high resolution, and can detect components present in the analyte in very small quantities, in the order of ppm. However, the quality of the spectral-based predictions is a different matter, because these rely upon the accuracy of the wet chemistry quantifications. Components comprising small quantities in wood, tend to have larger errors of determination during the wet chemistry measurement, and this may be one of the reasons why IR spectra is not as useful for the calibration of components in small quantities as is for the quantification of major, predominant wood constituents.

The connotation of the results from the present study is substantiated by the results of a similar study to predict lignin and cellulose contents of untreated cored samples of two softwoods and blocks of 24 tropical hardwoods, by using OSC-filtered DRIFT spectra (Nuopponen *et al.* 2006). Despite having good levels of goodness of prediction for the lignin and cellulose models for spruce and for all the woods together (Q^2_{CUM} between 0.66 and 0.77), these authors found low predictive ability of the model for samples not included in the calibration set. RMSEP values were 1.6 – 1.8 and 3.3 – 3.7, for lignin and cellulose, respectively, with RPE values between -0.02 and -0.44 and -0.45 to -0.88 in the same order. RMSEP values are similar to the ones in the present study, 0.96 – 2.32 for lignin, 2.44 – 4.32 for cellulose. However, the RPE values in the present study are significantly larger and in no case smaller than 0 (between 0.39 and 0.65 for cellulose and from 0.78 to 0.93 for lignin). Nuopponen *et al.* (2006) contend that their model for lignin predictions was still useful in applications where a 'few percent' precision sufficed.

8.6 Model calibration and prediction of the ASE

The plot for the experimentally-determined versus DRIFT-fitted ASE in spruce wood is given in Figure 8.4. Predicted values are included in the same chart as well. An excellent fit can be seen for the calibration model. Additionally, excellent predictions were obtained for ASE for samples from the prediction set. Calibrations and predictions of WL were also successfully accomplished with DRIFT-spectra data (Table 8.3).

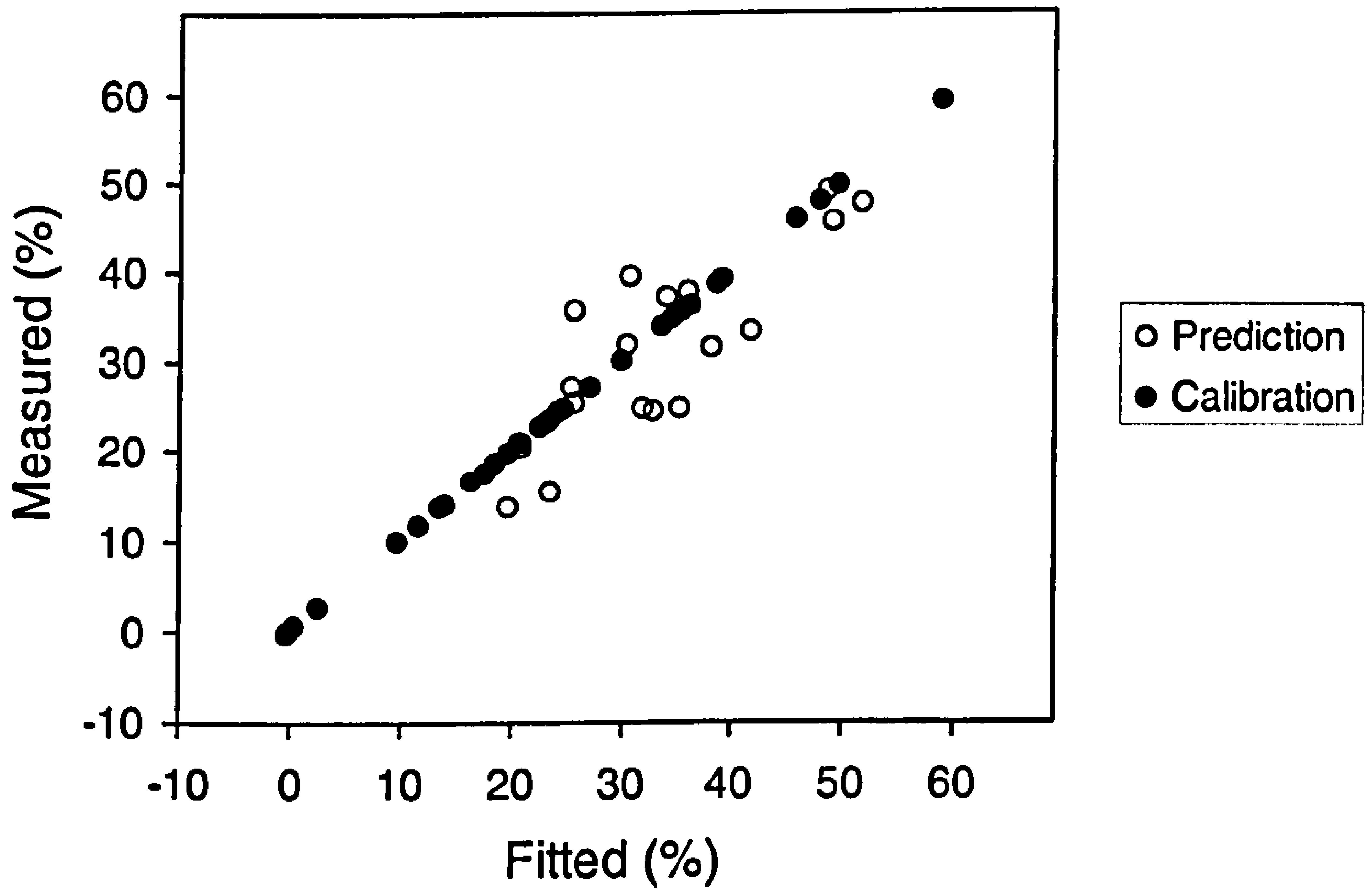

Figure 8.4 Calibration plot for ASE of heat-treated Norway spruce wood. Predicted values are also included.

The results show that the calibration model derived from the OSC-corrected spectra was excellent in terms of model complexity (A = 1 for WL and ASE) and predictive power (Q^2_{CUM} = 1.000 in WL and ASE) compared with raw spectra (A= 2 and Q^2_{CUM} = 0.986 and 0.925 for WL and ASE respectively). The possible sources of systematic variation could be light scattering due to the rough surface of the wood samples, and path length differences arising from the positioning of the individual samples during scanning: samples with increasingly higher levels of treatment had slightly smaller depth, and the elevation of the holding plate was not adjusted for each sample, but used in the same position for scanning all specimens. The OSC filtering has traditionally been used in NIR spectra, although there is not theoretical limitation for using this tool in mid-infrared spectra (Fearn 2000) and, as it has been shown, it improves the model in terms of complexity using MIR spectroscopy.

For comparison, least squares linear regression of ASE on WL was computed with a random selection of 70% of the observations, the remnant 30% of the cases being left apart for the prediction of the ASE with the model computed with the first lot of samples. This procedure was done 5 times for the same Norway spruce samples treated at 210 °C and 230 °C used for the PLS modelling. The RMSEP calculated for the 30% of the samples, varied from 5.02% to 7.57% (mean = 6.18%), which is very similar to the RMSEP of the model obtained using the DRIFT spectral data (5.96%, Table 8.2), emphasizing the robustness of the PLS model. Clearly, the disadvantage of using the WL over the DRIFT spectra for predicting ASE is that the former should be measured in a hygroscopic material. This requires laborious weighing of wood and determination of the moisture content of the material prior and after modification to calculate the effective WL on the wood material due to the treatment. On the contrary, having established a calibration model, using the DRIFT spectra requires a single after-treatment measurement, making it possible the correctly predict the ASE on a specimen-by-specimen basis.

The diffuse reflectance spectra was collected without any further sample preparation, a condition probably required if this approach would have any practical relevance. However, the collection of each spectra took *ca.* 10 minutes, so another set of measurements was taken with fewer scans (24) at reduced resolution (8 cm^{-1}), $DRIFT_{low}$ (see chapter 3, Methods). In this way, the collection of the spectra for each sample took 39 seconds. In the low resolution spectra (Figure 8.5), the absorbance intensity is reduced, and the spectra also appears noisy.

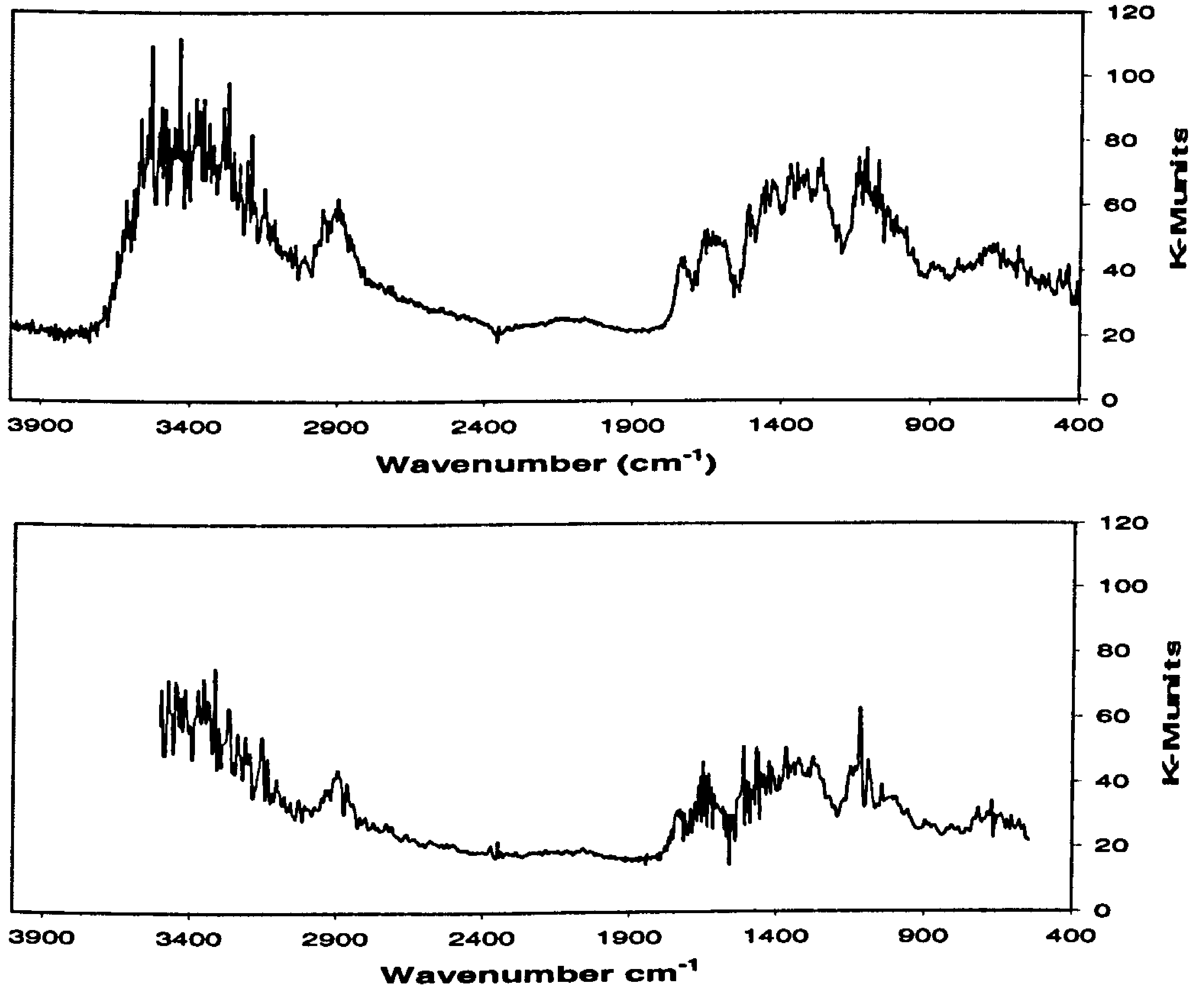

Figure 8.5 Diffuse reflectance spectra for heat-treated Norway spruce wood. Above: 200 spectra acquired at 4 cm^{-1} resolution. Below: 24 spectra acquired at 8 cm^{-1} resolution

Nevertheless, results confirm that predictions of ASE and WL from the low resolution DRIFT spectra data are still excellent (Table 8.3, DRIFT$_{low}$), with values of RMSEE and RMSEP similar to the calibration using the higher resolution spectra. This result is encouraging, since it substantiates the possibility of using a system for the prediction of the ASE of modified wood in a continuous process environment. In a recent study, DRIFT spectroscopy was successfully explored at a laboratory scale for the determination of chemical composition of wood chips in motion using PLS regression of wood spectra collected with a BOMEM MB100 spectrophotometer similar to the one used in the present study (Jones *et al.* 2002).

Whilst the properties of small-sized specimens of TMW appear to be confidently detected by FTIR and DRIFT spectroscopy, the potential of this technique for the evaluation of properties of large-sized specimens remains to be assessed. Although no reference is available, common knowledge indicates that the ASE of long-sized specimens would be little influenced by the presence of knots or other wood defects, rendering this approach viable for the study of larger specimens. On the other hand, it should also be possible to evaluate WL in large members, irrespective of the defects present in the material. This latter estimation could then be incorporated into the X-matrix (along with other process parameters such as time and temperature of exposure or IR-determined before-treatment chemical composition and density) in order to produce more robust models for the prediction of strength properties in larger timber members.

8.7 Conclusions

A systematic study has been conducted to characterize the mechanical performance and chemical composition of TMW. The results reported in this research demonstrate the capability of the mid-infrared Fourier transform spectroscopy combined with multivariate analysis, as a powerful tool for the rapid and non-destructive prediction of several properties of modified wood.

Characteristics of the analysis of infrared spectra for the prediction of the mechanical performance and other physical properties advantageous to the quality management and process control of modified wood can be summarised as follows:

1) By characterising the material with training sets including untreated samples, and using the appropriate statistical handling techniques, it is possible to predict mechanical properties in bending and impact strength, heat-induced weight loss, density, EMC, ASE and chemical make up of TMW by collecting uncomplicated spectra measurements;

2) All properties are estimated with only one after-treatment measurement of the spectra. This measurement could be obtained in less than one minute to arrive to predictions with low margin of error, at the laboratory scale; and

3) The method itself is inexpensive, and has the potential to be incorporated into online process control.

In the foreseeable future, the use of biocides for wood protection will reduce worldwide and continuous emphasis should be given towards developing simple, cost-effective and potentially automated systems for the non-destructive evaluation of properties of new material alternatives, such as thermally modified wood.

Following the recent developments in other forest products industries, such as pulp and paper and OSB, where multivariate analysis of spectral data is routinely used for quality control and assurance, it is imminent that this technology will be made available to other processes, including the thermal modification of wood.

Several recent technological advancements will soon make an impact in the way the quality management in a range of forest products is to be carried out. Portable devices in the mid and near infrared region and near-infrared cameras for the prediction of physical properties are actively being tested in a range of forest products at the industrial scale -and in due course will do so in the TMW industry. Hence, spectroscopy-based methods are prime candidates to play a pivotal role in the quality control and assurance of TMW. This may eventually result in a more generalised use of this new material, and would also facilitate, perhaps initially at the laboratory scale, the prospective evaluation and ultimate adoption of TMW for structural applications.

This technique could be examined for use with other forms of chemical modification, in order to compute for instance, values of ASE or weight gain in esterified wood, or for the prediction of biological performance in TMW and other modification processes.

Chapter 9 General conclusions and recommendations for further work

9.1 General overview

To fulfil the objectives set out at the beginning of this study, the work described herein allowed generally:

1. To further the current understanding of the effect of heating on the physical properties and chemical composition in small samples of wood, using three representative species.
2. To devise forms of predicting the resultant physical properties of the treated material using non-destructive methods, as well as envisaging methods for the overall appraisal of the heated material.

A study was planned and carried out to realise the primary objectives of this research, whereby nearly three thousand matched samples of wood were modified following twenty treatment schedules (five residence times at four temperatures of exposure). Three commercially important European wood species, representing hardwoods (beech) and softwoods (Scots pine and Norway spruce) were included in the study. Following treatment, all the samples were studied for dimensional and density changes (chapter 4). Modified and control (untreated) samples were further processed for most studies to standardised dimensions for each programmed test. One part of the treated samples was tested mechanically in six main forms of stress (chapter 5). Prior to mechanical tests, samples from the bending test had been used for the study of colour changes in heated woods (chapter 7). After mechanical testing, selected test samples from the bending test were used for chemical studies (chapter 4). Another part of the modified stock was allotted for the study of wood-water relationships in the modified material (chapter 6). Results from most of the referred studies were used for building multivariate models for property prediction (chapter 8). In chapters 4, 5, 6 and 7 analyses of the data included comparisons of means (ANOVA) and comparison of regression lines (ANCOVA). Modelling of the properties is also included. Techniques used in these chapters include univariate methods (least-squares linear and multiple regression, and correlation and path analyses), and multivariate methods by principal component and partial-least squares (PLS) regressions, and cluster and factor analyses.

At the beginning of this research it was held that the thermal deterioration of wood is conveniently measured by its declining weight, since some evidence existed in this respect. Thus, a distinctive approach of most studies described in the present document is that most of the comparisons between wood species and within wood species (treatments) were performed in dependence of the heat-induced weight loss.

This study is probably the most detailed program carried out ever on the major physical properties on matched small specimens of heated wood, modified under the same conditions. This affords for a more ample judgments on the findings.

9.2 Principal findings

The studies presented in the preceding chapters have centered on the relationship between the combination of time and temperature and the initial chemical composition of three wood species and on the physical performance of the material.

Chapter 4 studies the thermal-induced changes in the three main polymers of wood, as well as dimensional and other gravimetric changes in solid wood blocks and in the cell wall substance. Following thermal modification, wet chemistry analyses were carried out for all the treatment schedules (20 + control per each species). These included the gravimetric determination of extractive content, Klason lignin, acid soluble lignin, and monosaccharide composition. From the results of the monosaccharide composition, an algorithm (Janson 1970) was used to determine the cellulose content and the quantities of the two main hemicelluloses in the wood substance (glucuronoxylan and glucomannan). Results show that the hemicellulose is the most labile component of all the constituents of the wood substance. The differences in the rate of decomposition between hemicellulose types were found to be species-dependent. In beech, glucomannan was degraded at an appreciably similar but faster rate than glucuronoxylan, whilst in both softwoods the opposite was found. Cellulose remained gravimetrically unchanged up to very high levels of the treatment (to WL > 15%) in all three species. Differences between cellulose and hemicelluloses were endorsed to their differences in molecular weights and polymer crystallinity.

Conversely, the total lignin content increased with the extent of the treatment (WL) in the three species. This was credited to the percolation of carbohydrate by-products in the lignin network which remain trapped upon condensation reactions of the lignin substance.

On the other hand, the oven-dry weight decreased for all the schedules tested in this work. This reduction was accelerated by increasing the temperature of exposure, although in all cases, the exposure for longer times lead to the decline in the rate of weight loss. Invariably, WL in beech was higher than in softwoods for any combination of time and temperature of exposure. It was shown that this was because the higher glucuronoxylan content in beech.

In chapter 5, fifteen mechanical strength parameters are qualitatively and quantitatively analysed after testing wood samples in six forms of stress (Tables 5.1, 5.3 and 5.5). In general, relative (to control) property changes were shown to slightly vary between species, for samples treated in the 190 – 245 °C temperature range, with no clearly identifiable temperature or initial density effect at equivalent levels of WL.

Prior to this thesis, changes in wood strength had been often credited to the chemical degradation of wood upon heating. In this study, it has been shown that properties behaved differently in the rate and magnitude of change at equivalent levels of weight loss. Different polymers, mechanisms or structures were proposed to be involved in the degree of retention of each property. However, the primary factors behind each strength parameter were found to be the same regardless the species concerned, except for hardness. In terms of the property change at a given level of WL, and by correlation and path analyses, it was determined that some properties were very sensitive to chemical degradation and also to other changes in the cell wall substance upon wood heating (*e.g.* thermal stresses). The most susceptible property to heat exposure was impact strength; properties related to the energy required to cause failure were also found to be readily reduced (WML, TW). On the other hand, other properties were found to be fairly resistant to the heat-induced chemical changes, particularly compression strength and the MOE in bending. Significant changes were found in these properties only at WL levels much higher than those likely to be industrially targeted. This behaviour was attributed to the close relationship between these strength parameters and density, cellulose crystallinity and microfibril angle, all of these little changed by the thermal processing. Overall, the deconvolution of the real effects of the gravimetric chemical change in wood polymers on the changes in mechanical properties was complex.

Mechanical characteristics of TMW advantageous to construction and other such applications can be summarised as follow:

a. TMW still have characteristic values that give wood a high strength/weight ratio;
b. The fibrous, composite structure of TMW and its mode of failure is little changed macroscopically for WL as high as 14%, irrespective of the time and temperature of treatment. Depending on the species in question and the level of WL, TMW possesses comparable strength in several forms of stress to that of some common untreated timbers, with the possible exception of toughness.
c. Despite the often negative perception for the use of heated materials for non-critical load-bearing applications (*e.g.* not load-bearing walls), TMW is likely to pose little structural risk assuming that this material is used in a technical compliant manner, in situations where no unpredictable sudden critical loads may occur.

Chapter 6 describes the response of wood to moisture at a much larger scale than ever carried out before for heat-treated wood materials. The interest was to depict not only the behaviour of the product, but also the underlying changes for the characteristics of the modified substance. The responses analysed included hygroscopicity, dimensional stability, movement and anisotropy changes. The Hailwood-Horrobin (HH) theory of sorption was used to investigate the underlying causes of hygroscopicity reduction. A singly-hydrate form of the HH model was found appropriate to describe empirically the sorption isotherms; the differences in hygroscopicity was found to be related more to the reduction in the dissolved water than to the water forming hydrates. Evidence of the contribution of the lignin component in the overall hygroscopicity of solid wood was clearly demonstrated. On the other hand, the analysis of the ASE show that the dimensional stabilisation is caused by other reasons beyond the hygroscopicity reduction of the material. The existence of a stiffer matrix was proposed as a contributory reason for the increased dimensional stability of TMW. ASE was found to be the same at equivalent levels of WL between species. Hygroscopicity, movement and anisotropy changes were also found to have close similarities between species, but the reduction of these undesirable material characteristics was found to be species specific.

Colour changes and their relationship with chemical changes and qualitative changes in the acid-insoluble lignin by difference analysis of the FTIR spectra were described at length in chapter 7. Evolution of lightness (L*) of the CIEL*a*b* colour space was gradual. Conversely, evolution of the a* and b* colour coordinates was complex, but these followed the same changing profile in the three species analysed. Then again, changes in the main colour parameters were found to be comparable in the magnitude and rate of change between species. Total colour change, ΔE*, was dictated more by changes in wood lightness, ΔL*, than for changes in the chromatic coordinates Δa* and Δb* in the green-red and blue-yellow directions, respectively. The presence of a lignin substance richer in C=O groups and the presence of quinone carbonyl groups was demonstrated. Therefore, changes in wood colour were attributed mostly to changes in the acid insoluble lignin.

Having succeeded with the description of the material, empirical models were used to describe the relationship between gravimetric measurements (WL, ND, and chemical constituents) or dimensional changes, and the properties described in chapter 4, 5 and 6. In chapter 7, several relationships between changes in colour parameters and physical changes were investigated statistically. Results for the statistical modelling are tabulated in each chapter. All in all, most properties of interest were found amenable to prediction, usually giving highly significant models. Density, all parameters for the wood-moisture interaction, and mechanical strength properties of TMW can be efficiently predicted by using either WL, or colour parameters as predictors.

The analysis of solid state FTIR and DRIFT spectra for the prediction of mechanical properties, physical properties (ND, ASE, WL) and chemical components is presented in chapter 8. This approach was established as a powerful tool for the fast and non-destructive evaluation of several properties of modified wood. Calibration models were successfully developed for all characteristics using PLS regression of OSC-filtered data. Furthermore, the prediction ability for the properties of samples not included in the calibration models was remarkably good for most properties in terms of the RPE. Chapter 8 also included a detailed qualitative analysis of chemical changes in heated materials by analyzing the difference FTIR spectra of modified woods, and the relationship of this with property change. It was found that bands assigned to the lignin substance were negatively related to mechanical strength, whilst several bands arising from the carbohydrate environment were found to correlate positively with strength retention in TMW.

In chapters 5, 6 and 7 it was found that it is difficult to correlate gravimetric changes in the three main polymers of the wood substance with changes in most physical properties. This was because the sole mass modification of these fractions did not reflect the structural and chemical changes undergone in each wood constituent. However, the qualitative study of the FTIR spectra of solid wood and Klason lignin, was shown to be very useful to unveil some of the primary causes behind both the chemical changes and changes in other wood properties, such as colour and some mechanical properties.

9.3 Contribution to the understanding and characterisation of TMW

In the course of this research and in writing this report, thermally-modified wood has been unveiled as a complex material with a lot of personality. Despite the natural variability of the untreated material, amplified by the physicochemical changes introduced by the thermal conversion, it was a fascinating subject of study. Overall, the behaviour of the material was found to be readily predictable. In pursuing the objectives set out at the beginning of this work, several ideas have been considered in the course of this research to further the frontiers in the field of wood modification. Some of the major contributions realizing the aims of the study are:

Chemical characterisation and other gravimetric changes

The study of the heat-induced chemical degradation is a general contribution to the field of study. However, the description of the heat-induced changes in individual hemicelluloses (even if these were estimated from monosaccharides), in similar conditions as those used for thermal modification industrially has not been reported before. Also, no previous work has been published on the changes in the specific gravity of the cell wall substance in heated woods. To the knowledge of the author, previous to this research, there was only one systematic study dealing with macroscopic dimensional changes in solid wood samples (Chang and Keith 1978), but this included four hardwoods only. Thus, the results form this thesis constitute the first effort in the public domain to establish the relationship of WL with dimensional changes in softwoods. In general, these comprehensive studies give us an overall understanding of the behaviour of TMW.

Mechanical properties

In the past, several investigations have dealt with the changes in mechanical properties in wood due to the thermal exposure. In all cases, these studies have been limited to the description of either one species or few mechanical parameters. Alternatively, independent studies have been constrained to a very limited range of modification, frequently at low levels of conversion. The use of matched small samples encompassing a wide range of WL and a large number of properties was until now absent. The wide range of treatment levels used here demonstrated its value during the development of an overall performance index of TMW (see below). An ample spectrum of modification was also very useful for studying tendencies not readily apparent from studies carried out on a small range of WL.

The fact that property change is usually the same at equivalent levels of weight loss regardless of the temperature of treatment was statistically established. The consequences of this result may be potentially useful in an industrial setting, since it substantiates the possibility of establishing a process control method of TMW based on WL irrespective of the treatment temperature (within the 190 – 245 °C temperature range). Finally, to the extent of the writer's knowledge, there is only one previous report on the relationship between one mechanical property and thermal-induced changes in chemical composition. Hence, the description of the relationship between chemical changes and property change in this work is unprecedented. This information as well as information described in chapter 4 was used to elaborate the primary mechanisms for property modification. This is opposed to previous studies, which often focus on the extent of property change, but pay little attention to the fundamental causes behind property transformation.

Wood-water relationships

Many reports exist of the description of the reduced hygroscopicity of TMW, yet studies on the modelling of this behaviour are rather scant. Only two workers have applied a given theory of sorption for describing the behaviour of heated materials[a]. Thus, the report in this thesis is a genuine contribution for the understanding of the heat-induced changes in the reaction of wood with water vapour. Similarly, the prediction of the FSP in a wide range of WL has not been published before. The FSP is an important parameter since the standpoint of the increased risk at very high RH conditions for the potential of biological colonisation and decay of wood, and therefore is a valuable input to the field of study.

Colour studies

As stated in the introduction of chapter 7, there are few published studies touching the subject of colour changes in modified woods. Often, these include only one species or the evaluation of a few colour parameters (ΔE*, ΔL* or L*). The most comprehensive scientific report was given previously by Bourgois *et al.* (1991)[b], but these authors analysed pine wood only. The present research probably constitutes the first methodical study for the comparative behaviour of colour changes in both softwoods and a hardwood. Similarly, no precedent exists for the correlation of colour changes in solid wood with colour and qualitative chemical changes in the lignin substance, the latter largely accountable for colour changes in the substrate.

Non-destructive characterisation and prediction of wood properties

The thermal modification of wood is a relatively new process to provide the material with enhanced desirable characteristics. This material is currently being used as a environmentally less aggressive alternative than conventional treatment technologies of wood in conditions of moderate risk of biological degradation (*e.g.* European use classes 3 and less). The treatment leads, however, to the reduction of several mechanical properties, which is of some concern depending on the application.

Several thousands of m^3 of TMW are being produced and commercialised in Europe at present. This activity is carried out currently without any CE-marking, yet some voluntary industrial standards exist. Considering the tendency for widening the range of species used for thermal modification, quality control and assurance is essential. This coupled with increased interest to expand the uses of TMW for load-

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[a] In German and Japanese [from the abstracts in English]
[b] In French

bearing applications, made clear that studies on the characterisation towards material standardisation were needed.

Before this study, the status of the knowledge in the subject of the prediction of the properties of TMW was fairly basic, as it has been explained in the respective chapters. A substantial effort in the present research was undertaken to develop novel methods for the characterisation of the material using non-destructive or cost-effective techniques. The studies were successful inasmuch as the properties in small samples of wood were effectively predicted, and models gave usually highly significant statistics. The most important inputs to this field of work was the prediction of the following properties:

- Weight loss: This parameter was predicted in discrete steps with a model derived from the Arrhenius equation. Somewhat similar work was carried out in earlier research (Stamm *et al.* 1946, Millet and Gerhards 1972), so these predictions were only a general input to this sphere of knowledge;
- Weight loss, mechanical properties, ASE: Original contributions were the prediction of these characteristics (and ΔE^*) from treatment parameters using a newly developed method for solid wood, the severity factor approach. Moreover, several strength parameters, ASE and WL (and nominal density) were also predicted from colour parameters by using several forms of data handling, notably PLS regression. Additionally, these parameters were predicted for the first time by advanced chemometric techniques using data from the mid-infrared spectra;
- Mechanical properties: These were also predicted from chemical changes, density parameters, or from interrelationship between mechanical properties. One of the potentially most important findings in this regard is that models including both MOE and EMC were highly efficient for the prediction of several forms of wood strength. For the prediction of several mechanical parameters an innovative, fast test was also envisaged. This was a gravimetric milling procedure requiring a very small sample; it was found that models derived from this system were able to predict seven mechanical properties of TMW with highly significant statistics; and
- Hygroscopicity and movement: Seminal work has been presented for the development of a new model, based on the a single-hydrate form of the sorption model of the Hailwood-Horrobin theory. A single model using WL as the

independent variable, is used for the prediction of adsorption, desorption and movement isotherms in the full hygroscopic range, using a five-class system of WL.

Finally, the analysis of the data included the first documented effort in the public domain for the determination of an overall performance index (OPI) of TMW. This was developed by taking into account nine of the most important strength parameters in TMW, as well as the ASE and an indirect measure of the potential decay resistance (PDR = 1/ARH). This effort was also effectively accomplished using factor analysis. The results indicate that a neutral (OPI) is achieved when the extent of the treatment is at a WL of about 11.6% for beech, and about 7.2% for softwoods. At higher WL, the reduction in mechanical strength is not compensated for by the extra gain in ASE and PDR, whilst modifications at lower WL, the mechanical strength is reduced at debatable gain levels in ASE and PDR.

Applications of the study

The use of TMW relies on its resultant physical properties, such as mechanical strength and reduced hygroscopicity. A fast but effective characterisation of the material is required in a rapidly developing environment where several species on various applications are being tested.

Arguably, the single most important physical property in TMW was found to be the heat-induced weight loss (WL). This was the physical property most strongly correlated with the severity factor R_O for any given combination of time and temperature (section 5.8.3). By including in these studies three wood species, it has been revealed that several fundamental thermal properties of wood have limited importance in its behaviour during thermal conversion at the scale used in this work. This suggest that the heat-induced WL is largely insensitive to other characteristics in the material (*e.g.* wood density, thermal conductivity); WL is predominantly related only to the time and temperature of treatment. WL is therefore proposed as the best surrogate measurement of the severity of the treatment.

It has been demonstrated that the WL is a very efficient predictor of most mechanical properties and of most other properties of interest in TMW. If standardisation were to be introduced, this undoubtedly should include the WL as an indication of the degree of the modification.

However, the seemingly simple task of determining the WL in an hygroscopic material is not readily accomplished industrially in larger wood members. In this scenario, non-destructive characterisations, amenable for continuous processing operations, could be achieved by analysing total colour change (ΔE^*) or by the multivariate analysis of the infrared spectra. These techniques are considered not to be particularly capital-intensive or requiring complex multi-step procedures; similar techniques are already used routinely in other forest products processes such as panel products and the paper industry.

Attempts described in this document will hopefully provide the starting ground for other workers interested in the physical characterisation and property prediction of TMW. Moreover, by describing the physical characteristics and behaviour of thermally modified wood, users would be able to understand the potential of the material, and find alternatives to deal with the limitations before TMW could be used widely as a building material.

9.4 Recommendations from this study for the thermal modification of wood

In general, it has been determined that properties in the material are in practical terms the same regardless the temperature of treatment (in N_2 atmosphere). However, it was found that an exothermic reaction occurs at higher temperatures of exposure ($\geq$ 230 °C), particularly in beech. This situation could represent a small risk of fire if the treatment is carried out in the presence of air in a fan-assisted kiln. On the other hand, it was shown in the experimental section that samples treated at the lowest temperature (190 °C) did not reach that temperature at the surface of the sample. This could lead to cross-wise unevenness in the extent of the treatment, whereby the material closer to the surface is treated at a different extent than the substance in the interior of the sample. Therefore, temperatures between 200 °C and 225 °C would be the recommended range for the heat-treatment of wood.

As is was pointed out in section 7.2 (chapter 7), variability in lightness (L^*) evolution is somewhat higher for WL < 4%. Treatments should probably be carried out at WL above this threshold to get the best results regarding colour homogeneity.

Facing the scant information on the behaviour of large-sized specimens, a general recommendation would be to use the timber of the highest possible quality for thermal modification in a commercial setting, thus avoiding the possible reduction of the positive influence on some forms of strength of a lower EMC in TMW due to defects in the original material.

Where timber is to be aimed at applications with wide fluctuations in relative humidity, care must be exercised to select a treatment level that results in low movement values. As indicated in section 5.20 (chapter 5), the treatment selection leading to a required level of WL should also consider the concomitant reduction in mechanical performance at that level, and the end-user of TMW should be prepared to compromise.

9.5 Limitations of this study and recommendations for further research

Suitability and limitations of the methodology

A general goal in this work was to make a comparison of the behaviour of the two major groups of wood, hardwoods and softwoods. This aim has been addressed by studying and comparing the behaviour in one hardwood and two softwoods. The study could have probably benefited if it had included at least another hardwood species. However, this was not possible due to logistic and financial constrains.

The experimental part of this work was conceived to determine the changes in a substantial range of WL levels, up to the limit where the transformations in the wood material reached the point that the resultant product no longer could be considered 'wood' and needed to be treated as a charred residue. The upper extreme of the treatments used in this work is doubtless of minimal practical importance. However, this proved to be a very pertinent approach for the study of heated woods, because in this form it was possible to detect changes with a more panoramic overview.

The most obvious limitation of a study of this type is that findings from testing small samples are not always valid to larger wood members. In the latter, naturally occurring defects can have a significant influence in several characteristics of the treated material, especially in some mechanical properties. However, as indicated elsewhere in this text, this concession was done in the belief that this was the most cost-effective way to treat samples at a larger range of modification levels.

Samples slightly shrank due to the treatment and, in few cases, treated beech samples at high WL regimes appeared slightly distorted. Treatment of boards of larger dimensions could have been prescribed, to cut up from these all the replicates of the same size and to avoid the issue of sample distortion. However, no equipment was available locally for treating samples longer than 0.50 m.

As samples were conditioned at 65 RH at 20 °C prior to testing, the strength values were probably influenced by the sample EMC at test. Nevertheless, this condition was regarded as the most likely scenario of service for TMW and no correction was performed to the values determined. Except for the energy-related strength parameters, most properties are though to be favourably affected by the reduced EMC at test. The role of this effect was probably dependent on the extent of the treatment, the positive influence on strength upon a reduced EMC being greater for milder treated wood than for highly modified material.

Recommendations for further work

1. The proposal of classifying TMW on the basis of the temperature of treatment has no technical justification, because as it has been shown throughout this study, most of the properties are dependent primarily on the heat-induced weight loss, regardless of the temperature of treatment. Modification of other species is probably needed to confirm this finding.
2. Further work is needed to resolve the effect of sample sizes in the WL and its homogeneity across the sample. This could also help to fine-tune model parameters based in the severity factor R_O approach.
3. Similarly, validation of the results on the prediction of mechanical properties on larger timber members is a subject that requires immediate attention. Ideally, samples should be treated at a single processing temperature but in a wide range of WL levels. A mechanistic modelling approach could be used to consider the rate of thermal diffusion into the wood and to consider the duration of the core at a modifying temperature. It should also be borne in mind however that the core will cool down more slowly than the surfaces and so continue to modify when the periphery has stabilised.
4. The most sorely neglected subject in this work is obviously the study on the biological performance of TMW. It was very unfortunate not to be able to

include decay studies in this research, because the treated material is too valuable to be disposed of. To further evaluate the role of the chemical changes and the reduced hygroscopicity in the heated wood substrate, systematic decay studies are required. Furthermore, as pointed out during the development of the OPI, a surrogate measure of the potential decay resistance was used for computing this index. The results in this study therefore assume that the decay resistance is only increased by changes in the hygroscopicity of the substrate, an assertion which may not be completely comprehensive. It would therefore be highly desirable to have an actual measure of the biological performance for the computation of this index.

5. Complementary to point 4, the possibility of forecasting the decay resistance of TMW is technically and economically important. This could be done on the basis of the WL, but probably more conveniently from colour determinations or infrared spectroscopy.
6. The effect of fungal decay or other forms of biological degradation on the strength of thermally modified wood is unknown. Following decay tests, testing for strength loss is a field that requires urgent attention. According to EN113 (BSI 1997) 3% weight loss in test samples after basidiomycetes decay tests is considered to be a safe threshold as far as material performance is concerned. However, whether this level of degradation is too large for TMW, because the material has already suffered a significant strength reduction and a further decrease would be unacceptable for many purposes is unknown.
7. One of the most obvious subjects requiring attention is on methods for limiting the toughness reduction issue. It may be of interest to test whether the material performance can be enhanced by a secondary -or concurrent, treatment, *e.g.* acetylation or polymer impregnation, but not by densification as pointed out by others (*e.g.* Welzbacher *et al.* 2005).
8. By studying the properties of TMW after heating in other media it should be possible to produce more universal results regarding the dependence of property changes on WL and also to evaluate the suitability of the R_O approach. Before this, ways to determine WL in oil media (as a means of heat transfer) are needed. As it was explained in chapter 3, initial trials with a limited set of specimens were carried out using synthetic oil as the heating medium. The treatment was

very successful in terms of ASE, but the association of this to easily measured parameters was complex.

9. Mechanical strength tests should be carried out to compare strength losses (and costs) due to heat-treatment to those strength changes caused by other treatments aimed at increasing the decay resistance of wood (*e.g.* CCA impregnation, furfurylation).
10. Methodical studies on surface changes in TMW following weathering and accelerated UV surface degradation tests, and ways to predict these changes are also required.

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Appendices

Appendix 1. The effect of thermal modification on the chemical composition of beech, Scots pine and Norway spruce woods.

Temp.	time	WL	Extractives	Total lignin	Arabinan	Galactan	Glucan	Xylan	Mannan	Rhamnan	Total
(°C)	(h)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Beech											
Control		0.00	0.00	24.49	0.65	0.81	47.64	23.04	2.92	0.39	99.95
190	0.3	0.33	-0.28	22.86	0.56	1.28	53.18	20.08	1.53	0.49	99.71
	1.0	0.98	0.34	25.79	0.68	0.88	48.44	21.00	2.05	0.00	99.17
	4.0	2.84	1.09	24.95	0.30	0.64	47.64	20.63	1.85	0.24	97.34
	8.0	4.03	0.72	24.22	0.25	0.82	50.91	18.14	0.91	0.18	96.15
	16.0	6.74	2.33	26.08	0.14	0.36	47.32	16.25	0.77	0.16	93.41
210	0.3	1.31	0.27	24.27	0.44	0.78	50.29	21.83	0.93	0.26	99.07
	1.0	6.32	2.06	24.27	0.10	0.54	51.18	15.33	0.67	0.11	94.25
	4.0	9.95	1.87	28.38	0.00	0.41	46.51	11.30	1.22	0.00	89.69
	8.0	13.13	1.82	28.79	0.00	0.26	46.35	9.07	0.33	0.00	86.62
	16.0	16.17	2.11	30.32	0.00	0.16	43.60	6.91	0.53	0.00	83.64
230	0.3	3.84	1.26	24.78	0.29	1.64	50.66	17.91	0.00	0.00	96.55
	1.0	16.36	3.38	31.63	0.00	0.00	42.59	6.05	0.15	0.00	83.81
	4.0	18.01	1.67	31.65	0.00	0.12	43.77	4.36	0.00	0.00	81.57
	8.0	18.88	1.02	33.91	0.00	0.38	41.80	4.01	0.27	0.00	81.39
	16.0	24.47	0.59	36.48	0.00	0.00	36.80	1.68	0.17	0.00	75.72
245	0.3	12.21	3.93	26.65	0.14	0.26	44.37	13.51	0.38	0.00	89.24
	1.0	22.84	1.31	32.49	0.09	0.12	40.20	2.72	0.00	0.00	76.93
	4.0	24.89	0.96	34.92	0.00	0.00	38.18	1.10	0.00	0.00	75.16
	16.0	27.01	0.43	38.62	0.00	0.00	32.89	0.91	0.00	0.00	72.85
Pine											
Control		0.00	-0.14	28.75	1.55	2.19	46.24	7.61	11.69	0.00	97.90
190	0.3	0.61	-0.02	28.79	0.61	1.18	50.56	5.95	10.54	0.00	97.62
	1.0	1.26	-0.02	29.03	0.94	1.57	48.96	5.67	10.82	0.00	96.97
	4.0	2.31	-0.09	29.84	0.38	0.81	53.38	3.70	8.51	0.00	96.53
	8.0	3.00	-0.20	30.18	0.03	0.83	52.97	3.60	8.46	0.00	95.86
	16.0	4.48	0.00	31.27	0.21	0.82	50.80	3.05	8.54	0.00	94.68
210	0.3	2.30	-0.19	29.10	1.32	1.73	49.25	5.24	9.90	0.00	96.35
	1.0	3.12	-0.03	29.68	0.91	1.45	46.58	6.10	10.72	0.00	95.41
	4.0	7.20	0.12	31.36	0.88	1.49	42.88	5.55	9.36	0.00	91.64
	8.0	7.95	-0.07	32.06	0.88	1.39	42.77	5.45	9.06	0.00	91.53
	16.0	10.01	0.17	32.75	0.63	1.54	42.31	4.06	7.89	0.00	89.35
230	0.3	2.99	-0.08	30.10	0.82	2.02	47.95	4.95	9.92	0.00	95.68
	1.0	5.15	0.01	30.73	0.64	1.31	46.91	4.72	9.55	0.00	93.87
	4.0	9.39	0.01	33.36	0.22	0.91	47.08	2.35	6.21	0.00	90.13
	8.0	11.40	0.21	34.73	0.17	0.58	43.63	2.63	6.29	0.00	88.24
	16.0	13.95	0.03	35.23	0.23	0.62	42.75	2.01	5.38	0.00	86.24
245	0.3	5.59	-0.02	31.94	0.49	1.73	47.76	3.92	8.22	0.00	94.03
	1.0	11.50	0.26	34.41	0.15	0.63	45.42	1.87	5.73	0.00	88.47
	4.0	16.06	0.12	36.57	0.00	0.30	43.77	0.91	2.93	0.00	84.60
	8.0	21.80	0.18	37.94	0.00	0.29	39.43	0.28	1.33	0.00	79.44
	16.0	21.53	0.09	39.43	0.00	0.00	39.21	0.00	0.33	0.00	79.05

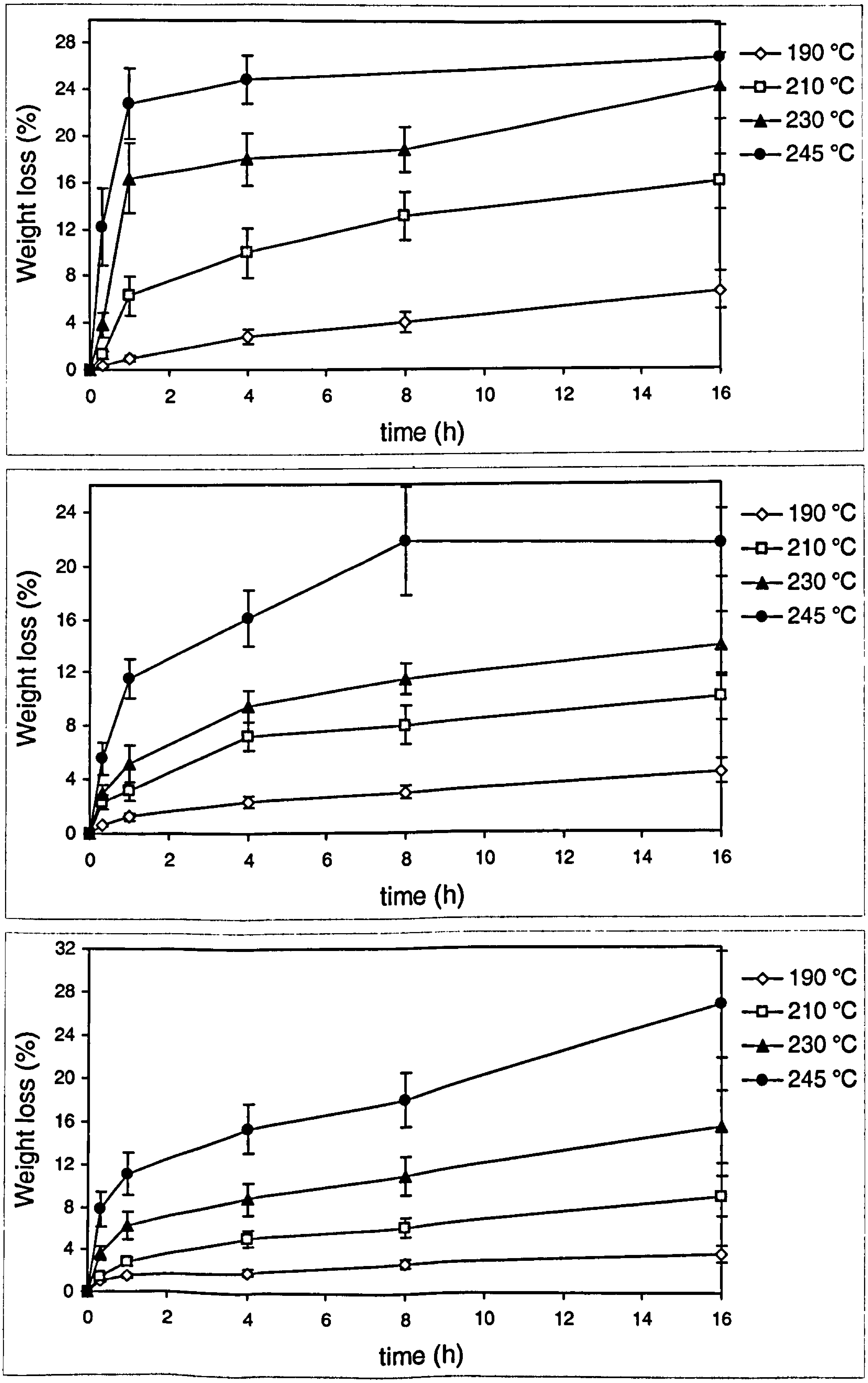
Continued over...

Appendix 1. The effect of thermal modification on the chemical composition of beech, Scots pine and Norway spruce woods (*concluded*).

Temp. (°C)	time (h)	WL (%)	Extractives (%)	Total lignin (%)	Arabinan (%)	Galactan (%)	Glucan (%)	Xylan (%)	Mannan (%)	Rhamnan (%)	Total (%)
Spruce											
Control		0.00	-0.67	29.06	1.07	1.53	49.22	6.08	11.65	0.00	97.94
190	0.3	1.05	-0.30	27.69	0.93	1.36	51.71	5.23	10.54	0.00	97.16
	1.0	1.50	-0.50	27.52	0.87	1.26	50.19	6.29	11.12	0.00	96.74
	4.0	1.99	-0.60	28.40	0.67	1.11	50.59	4.97	11.12	0.00	96.26
	8.0	2.87	0.25	29.26	0.76	1.27	47.52	5.08	11.21	0.00	95.34
	16.0	3.64	0.26	30.34	0.78	1.28	46.67	4.70	10.66	0.00	94.69
210	0.3	1.39	-0.30	28.32	0.91	1.28	50.61	5.10	10.90	0.00	96.83
	1.0	2.85	0.18	29.11	0.72	1.08	47.42	5.43	11.35	0.00	95.28
	4.0	5.21	0.58	30.38	0.48	1.08	46.46	4.50	9.84	0.00	93.32
	8.0	6.24	0.45	30.81	0.37	0.93	46.91	3.75	9.14	0.00	92.36
	16.0	9.02	0.96	32.02	0.26	0.57	46.39	2.65	7.18	0.00	90.03
230	0.3	3.59	0.72	28.35	0.55	1.01	49.37	4.42	10.41	0.00	94.81
	1.0	6.27	0.76	30.45	0.28	2.94	46.15	3.71	8.14	0.00	92.43
	4.0	8.93	1.15	32.01	0.28	0.66	46.18	2.56	7.15	0.00	89.99
	8.0	11.05	1.12	33.21	0.15	0.41	45.35	2.18	5.76	0.00	88.19
	16.0	15.42	0.47	37.16	0.00	0.18	41.91	1.05	3.41	0.00	84.19
245	0.3	7.74	1.09	30.66	0.35	0.70	47.14	3.23	8.23	0.00	91.38
	1.0	11.08	1.36	32.84	0.00	0.39	45.81	2.04	5.89	0.00	88.33
	4.0	15.54	1.17	35.15	0.00	0.22	43.73	0.85	3.26	0.00	84.38
	8.0	18.12	0.75	38.05	0.00	0.75	40.60	0.44	1.48	0.00	82.07
	16.0	26.68	0.52	44.38	0.00	0.10	27.60	0.23	0.74	0.00	73.56

Lignin and carbohydrates represent the content (in %) with respect to the initial oven-dry
Total carbohydrate content was computed from lignin by difference. Beech wood not tested
Weight loss (WL) is the mean values of 44 replicates. The other values are a single
Sugars represent monosaccharides converted to individual oligosaccharides, corrected by

Appendix 2. The effect of heating on the oven-dry weight loss (WL) of small samples of beech, Scots pine and Norway spruce wood (from top to bottom) treated at 190 °C, 210 °C, 230 °C and 245 °C in N_2. Each symbol is the mean value of 44 replicates. Error bars represent ± 1 SD.



Appendix 3. Movement in the radial and tangential directions of small samples of thermally-modified beech, Scots pine and Norway spruce woods.

		Expansion in terms of the oven-dry volume (%) at 20 °C at RH									
Temp.	time	Radial					Tangential				
(°C)	(h)	11%	33%	44%	75%	93%	11%	33%	44%	75%	93%
Beech Control		0.64	1.60	1.97	3.66	5.16	1.12	2.66	3.57	6.49	11.08
190	0.3	0.82	1.67	1.85	3.43	5.04	1.11	2.57	3.59	6.85	10.87
	1.0	0.66	1.37	1.96	3.44	4.78	1.06	2.36	3.21	5.82	9.37
	4.0	0.52	1.30	1.78	3.27	4.78	0.79	2.25	3.08	5.48	8.88
	8.0	0.41	1.28	1.66	2.90	4.11	0.93	2.23	3.09	5.83	8.35
	16.0	0.61	1.27	1.68	2.79	4.11	1.12	2.25	2.65	5.20	8.88
210	0.3	0.45	1.28	1.63	3.04	4.71	1.17	2.40	3.07	5.71	9.10
	1.0	0.34	0.91	1.15	1.92	2.81	0.32	1.63	2.21	3.73	5.32
	4.0	0.42	0.96	1.48	2.12	3.03	0.64	1.43	2.05	3.79	5.19
	8.0	0.49	0.81	1.22	1.96	2.58	0.64	1.32	2.14	3.76	5.24
	16.0	0.24	0.87	1.25	2.11	2.61	0.71	1.60	1.91	4.18	4.84
230	0.3	0.60	1.31	1.80	3.25	4.55	0.94	2.44	3.12	5.60	8.48
	1.0	0.49	1.11	1.62	2.76	3.66	0.84	1.98	3.00	4.71	7.20
	4.0	0.39	1.05	1.24	2.32	3.08	0.84	1.90	2.40	4.50	6.05
	8.0	0.34	0.98	1.25	2.39	2.98	0.58	1.59	2.42	3.96	5.56
	16.0	0.28	1.24	1.02	2.21	3.09	0.81	1.64	2.15	4.18	5.60
245	0.3	0.33	0.89	1.21	2.27	2.73	0.79	1.28	2.11	3.68	4.99
	1.0	0.39	0.92	1.20	1.87	2.35	0.41	1.13	1.92	2.92	3.74
	4.0	0.41	0.91	1.11	1.92	2.40	0.07	1.18	2.24	3.82	4.21
	16.0	0.42	1.04	1.37	2.55	3.24	0.70	1.58	2.37	4.91	6.36
Pine Control		0.51	0.91	1.32	2.21	3.29	1.06	2.17	2.93	5.36	8.35
190	0.3	0.49	1.04	1.19	2.14	3.07	0.83	2.28	2.45	4.93	7.20
	1.0	0.40	1.28	1.22	2.23	3.24	1.00	2.74	2.79	5.13	7.61
	4.0	0.49	0.95	1.26	2.18	2.82	1.09	2.49	3.04	4.98	6.89
	8.0	0.43	0.96	1.33	2.63	3.74	1.14	2.41	2.84	4.80	7.41
	16.0	0.25	0.79	0.86	1.57	2.17	0.67	1.42	1.84	3.06	4.14
210	0.3	0.30	0.93	1.42	2.16	3.24	0.93	2.19	2.73	4.86	7.21
	1.0	0.48	1.03	1.00	2.36	3.10	0.77	2.00	2.24	4.78	6.88
	4.0	0.29	0.66	0.86	1.57	2.23	0.67	1.63	1.99	3.64	4.82
	8.0	0.40	0.85	1.12	1.65	2.38	0.47	1.92	2.08	3.35	5.02
	16.0	0.37	0.73	0.88	1.80	2.33	0.51	1.67	2.04	3.65	4.84
230	0.3	0.43	0.94	1.53	2.26	3.48	0.77	2.37	2.86	4.26	6.63
	1.0	0.24	0.60	0.70	1.17	1.74	0.42	1.33	1.43	2.61	3.61
	4.0	0.31	0.68	0.91	1.42	2.01	0.52	1.76	2.14	3.29	4.65
	8.0	0.27	0.62	0.82	1.46	1.89	0.49	1.47	1.76	3.30	4.09
	16.0	0.31	0.76	1.04	1.57	2.22	0.79	1.88	2.21	3.79	5.39
245	0.3	0.41	0.87	0.97	2.12	2.68	0.82	1.88	2.15	4.02	6.08
	1.0	0.24	0.61	0.75	1.29	1.82	0.51	1.54	1.72	3.36	4.53
	4.0	0.19	0.56	0.65	1.18	1.44	0.39	1.02	1.48	2.78	3.23
	8.0	0.26	0.56	0.88	1.50	1.82	0.43	1.20	1.83	3.07	3.60
	16.0	0.37	0.90	1.14	1.86	2.63	0.69	1.76	2.44	4.05	6.04

Continued over...

Appendix 3. Movement in the radial and tangential directions of small samples of thermally-modified beech, Scots pine and Norway spruce woods (*concluded*).

		Expansion in terms of the oven-dry volume (%) at 20 °C at RH									
Temp.	time	Radial					Tangential				
(°C)	(h)	11%	33%	44%	75%	93%	11%	33%	44%	75%	93%
Spruce											
Control		0.73	1.58	2.00	3.42	5.24	1.36	2.87	3.71	6.32	9.41
190	0.3	0.22	1.49	1.98	3.20	4.37	1.47	2.93	3.58	6.30	9.10
	1.0	1.11	1.46	1.97	3.61	5.01	1.10	2.65	3.08	6.01	8.58
	4.0	0.81	1.52	1.52	3.00	4.20	1.16	2.49	3.05	5.17	7.85
	8.0	0.52	1.45	1.79	2.82	4.04	1.16	2.19	3.06	5.78	7.42
	16.0	0.52	1.35	1.63	2.72	3.72	1.16	2.38	3.08	5.38	7.70
210	0.3	0.82	1.60	2.00	3.22	4.68	1.31	2.55	3.20	5.41	8.36
	1.0	0.60	1.86	1.73	2.79	4.09	1.02	2.46	3.27	5.11	7.80
	4.0	0.47	1.40	1.54	2.73	3.57	1.07	2.18	2.86	4.17	7.11
	8.0	0.49	0.92	1.44	2.70	3.37	0.95	2.45	2.71	4.94	7.20
	16.0	0.42	1.28	1.33	2.26	3.46	0.87	2.31	2.57	4.48	6.02
230	0.3	0.42	1.10	1.80	2.69	3.86	0.82	2.31	2.94	5.19	7.64
	1.0	0.43	1.16	1.56	2.55	3.37	0.99	2.19	3.13	5.00	6.89
	4.0	0.47	1.00	1.43	2.29	3.33	0.44	1.96	2.63	4.39	6.38
	8.0	0.30	0.94	1.11	1.93	2.62	0.80	1.74	2.03	3.87	5.34
	16.0	0.34	0.57	1.12	2.29	2.96	0.60	1.48	2.05	3.84	5.26
245	0.3	0.42	1.28	1.52	2.44	3.08	0.72	1.76	2.64	4.38	6.15
	1.0	0.13	1.08	1.33	2.13	2.87	0.75	1.55	2.21	3.77	5.81
	4.0	0.41	0.95	1.12	2.03	2.32	0.64	1.48	1.90	3.60	4.43
	8.0	0.28	1.11	0.90	1.78	2.20	0.57	0.89	1.64	2.86	4.08
	16.0	0.42	0.92	1.21	2.08	3.06	0.53	1.38	1.72	3.06	4.16