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Decay resistance of modified wood

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DECAY RESISTANCE OF MODIFIED WOOD

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Abstract

Different modifications, namely hexanolylation, acetylation, thermal modification and silylation by trimethoxy vinyl silane (VTMS,) and by γ-methacryloxy propyl silane (TMPS) were applied to impart decay resistance to Corsican pine sapwood, which is a non-durable wood. The possible mechanisms by which the modifications impart decay resistance to the wood were also investigated. The silanes applied in this study showed completely different reactivity so that the vinyl group of VTMS remained un-reacted and the vinyl group of TMPS reacted (but its silanol was not very reactive). The decay resistance of the modified woods were assessed by soft rot, brown rot and white rot fungal tests. The decay resistance against basidiomycetes and soft rot fungi was improved by all the wood modifications applied in this study, but the wood treated with methanolic solutions of the silanes did not show complete decay resistance against brown rot fungi. The failure of the silanes to impart complete protection of wood against brown rot fungus (*C. puteana*) was attributed to the restriction of the silanes in penetrating into the cell wall. In the soft rot tests, VTMS modified stakes showed high decay resistance but TMPS modified wood showed a moderate decay resistance. This was attributed to the un-even distribution of TMPS in wood. An industrially acceptable treatment method (by using aqueous solutions of silane instead of methanolic solutions and pressure treatment instead of vacuum treatments was established). The performance of the silane treated wood was assessed by field tests. The method worked well with TMPS (the wood showed significant decay resistance in the test) but it didn not work with VTMS.

Since both anhydrides (hexanoic and acetic anhydride) used in this study, showed nearly the same performance against *C. puteana* and soft rot fungi, it was concluded that the improvement in decay resistance against the brown rot fungi and soft rot depends on the WPG only.

Heat treatment above 200°C was recognised to be an effective treatment in improving the decay resistance of wood. It was shown that heat treatment temperature plays a more important role in the improvement of decay resistance than the treatment time. Heat treatment at 250°C for 2 hours, imparted complete decay resistance to the wood against basidiomycetes and soft rot. No significant difference between decay resistance of heated

wood post-extracted and heated wood without any extraction against basidiomycet and soft rot fungi was obtained, suggesting that extractable fungicidal is not the reason for the improved decay resistance.

In addition to the decay tests, dimensional stability, pore cell wall pore accessibility and hygroscopicity of the modified wood were also studied to find the mechanism by which the modification imparts decay resistance to the wood. It was suggested that hexanoylation and acetylation reduces hygroscopicity so that not enough water is available for the diffusion of brown rot degrading agents into the cell wall, while lignin substitution might be the main reason for the improved decay resistance against white rot fungi. For heated wood, a good correlation between a reduction in FSP and WL due to decay was obtained. Thus, it was suggested that a reduction in the hygroscopicity of wood could be the main reason for the improved decay resistance. By using the Hailwood Horrobin model it was shown that a reduction in poly-molecular adsorption of heated wood is the main reason for the reduced hygroscopicity. Since good correlation between an increase in the lignin content and a reduction in the poly-molecular sorption was obtained, a reduction in the hygroscopicity of heated wood was suggested to be due to a reduction in the swelling of the wood cell wall in which microfibrils were placed in a matrix of condensed lignin and the hemicellulose residue, rather than a reduction in the hydroxyl groups of wood. Lignin modification is thought to be the main reason for the reduced hygroscopicity.

List of publications

Hill, CAS, Mastery Farahani, M.R. and Hale, M.D.H. (2003) The Use of Organo-Alkoxysilane Coupling Agents for Wood Preservation. *Holzforschung* (in press).

Conference proceeding

Mastery Farahani, M.R., Hill, C.A.S. and Hale, M.D. (2000) The effect of heat treatment on decay resistance of Corsican Pine sap wood. *Proceedings of the fifth European panel products symposium.* P. 303-308.

C.A.S. Hill[1], M.D. Hale, M.R. Farahani, S. Forster, E.D. Suttie, D. Jones, and A.N. Papadopoulos (2003) Decay resistance of Anhydride Modified Wood. European Conference on Wood Modification .

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Abbreviation

AIBN	Azo-isobutyronitrile
ASE	Anti shrinkage efficiency
CCA	Copper-chrome-arsenic
D	Density
DVS	Dynamic vapour sorption
EMC	Equilibrium Moisture content
FSP	Fibre saturation point
h	Relative vapour pressure
HFOETMOS	Heptadecafluorooctylethyl-trimethoxy-silane
H-H model	Hailwood-Horrobin Model
K1	Equilibrium constant of the hydrate water (in the Hailwood – Horrobin model)
K2	Equilibrium constant of the dissolved water (in the Hailwood –Horrobin model)
M	Total moisture content
MC	Moisture content
Mh	Water of hydration (in the Hailwood –Horrobin model)
MHP	Moisture/heat/pressure- treatment
Mo	Moisture content corresponding to complete polymer hydration (in the H-Horrobin model).
MOE	Module of elasticity
MOR	Module of rupture
Ms	Water of solution (in the Hailwood-Horrobin model)
MW	Molecular weight
PTMS	Propyltrimethoxysilane
RH	Relative humidity
S	Volumetric swelling
TEOS	tetraethoxysilanes
TMPS	γ-methacryloxypropyl trimethoxy silane
TMSAH	3 trimethoxysilyl)propyl (carboxymethyl) decylmethyl ammonium hydroxide salt and –
TMS-Cl	Trimethylsilyl chloride
UV	Ultraviolet
VC	Volume change
V_{rel}	Ratio of measured to theoretical volume
V_T	Theoretical volume
VTMS	Vinyl trimethoxy silane
WL	Weight loss
W_{mod}	Mass of treated sample
Wo	Molecular weight of sorbate per mole of sorption site (in the Hailwood-Horrobin model)
WPG	Weight percentage gain
W_{unmod}	Mass of unmodified sample

Chapter 1

Introduction

One of the main disadvantages of wood is that it is not generally durable against fungal attack. Thus, the preservation of wood against the fungal attack in order to the increase of wood life service, especially when wood is exposed to exterior conditions is a priority. Most present commercial methods for increasing of the decay resistance of wood involve impregnating it with toxic chemicals. The use of CCA have been restricted by the European commission because of risks included those to human health from the disposal of wood treated with wood preservatives CCA and in particular risks to childrens' health from the use of CCA treated wood in playground equipment, and a risk to the aquatic environment in certain marine. According to the legislation, CCA treated wood has been restricted in some applications such as any application where there is a risk of repeated skin contact, in residential or domestic constructions, whatever the purpose, in marine waters, in playground equipment. The commsion will apear in restricting or banning other metal containing biocides becouse of toxicity and thier probabl human resik. Thus, extensive effort has been made to find suitable alternatives to the protection of wood using toxic chemicals. Of the studied alternatives, chemical modification of wood, thermal modification of wood and impregnation of wood by resins deserve to be mentioned. These methods modify the wood in such way as to reduce the water absorbance and swelling significantly and to increase dimensional stabilisation of wood, as well as impart improved decay resistance to the wood (Stamm, 1964).

In general, non-toxic methods of wood preservation rely on the inhibition of the degrading organism by removing or restricting access to one or more of the various factors required by that organism for growth. The main factors required by wood decay fungi are listed below:

The substrate (*i.e.* wood) needs to be accessible to and digestible by the fungi and its enzymes. Decay fungi require other nutrients such as a source of nitrogen, and various metals, which are all available in the wood, but in low amounts.

Water is required by decay fungi for several reasons (Zabel and Morrel, 1992):

- As a reactant in the hydrolytic degradation of wood polymers.
- As a diffusion medium for extracellular degradative agents.
- As a constituent of fungal hyphae
- To swell the wood cell wall, allowing increased access of extra cellular degradative agents to cell wall polymers.

Wood which is kept dry is safe from microbial decay but as soon as a moisture content of 20% or more is attained it becomes susceptible to attack by fungi. The optimum moisture content range required by fungi depends on the density of the wood. The higher the density, the less the moisture required by fungi to degrade wood.

Decay fungi require oxygen for respiration and for oxidative degradation of wood polymers, this is particularly important when considering the moisture content of the wood, as the wood gets wetter less oxygen is available to decay fungi. The moisture content at which decay is pevetned depends on wood density effecting on wood prore structure. For emaple, for Picea with density of 0.34 gr/m^3 ' decay is prevented at moisture content range between 190 -200% (Parsa pajuh, 1994). Storing logs in water (pounding) is used to prevent decay, though in this case wood may still be susceptible to bacterial attack.

One other factor important to fungal growth is temperature. The temperature range required for the activity of most wood decay fungi is between 10 and 40°C, with optima between 20 – 30°C.

One the most widely studied non-biocidal methods of wood protection is thermal modification. When wood is heated, changes in the nature of cellulose, hemicelluloses, lignin and extractives can modify the hygroscopicity, stability, and permeability of the timber. The effect of heat treatment on the properties of the product (heated wood) depends on the time of treatment, the presence of a catalyst, atmosphere, wood species, dimension of wood, water content, and vessel or oven design (Fengel and Wegner , 1989,

Kosik *et al.*, 1969). Various processes have been developed in Europe, which rely upon heat treatment to improve the durability properties of wood *e.g.*, Retification (France), Plato (Netherlands) and Thermo-wood (Finland), which are discussed later. There has been much debate about the mechanism by which heat treatment imparts decay resistance to wood, but the precise mechanism has not been generally agreed upon. Some hypotheses are based on a reduction in the hygroscopicity of wood.

Depending on treatment temperature, the new product (heated wood) might contain furfural and some other potential toxic compounds (Kamdem *et al.* 1999). Kamdem (2000), reported that the amount of the toxicants produced in the retified wood were too little to contribute in the decay resistance. Since, the Retified wood is moderately resistant against basidomycetes and Retification is a heat treatment at high temperatures for short times, the question was made whether more decay resistance could be achieved by heat treatments with longer times without contribution from toxicants that might be produced as a result of heat treatment.

Esterification of wood is defined as a reaction between a hydroxyl group of a wood component and a carboxylic group of a carboxylic anhydride or carboxylic acid, with or without catalyst to form an ester bond between the two. It has been well established that chemical modification of wood through esterification is able to provide protection against fungal attack (Rowell, 1983).

Most esterification studies are restricted to the actetylation of wood. Various mechanisms have been postulated for explaining the protection of wood to decay by esterification. These can be summarised as:

- Modification of the wood cell wall polymers so that they can no longer be recognised by extracellular enzymes.
- Reduction in moisture content of the cell wall, preventing diffusion of degradative agents into the cell wall interior.
- Blocking of the cell wall micropores, preventing access to the cell wall interior.

Organo alkoxy silanes, are common coupling agents used on an industrial scale in the plastic and glass industries for various purposes, such as water repellence, improving mechanical properties, heat resistance *etc.* Silanes, with the general structure R-Si(OR')3 are the most technologically important adhesive promoters in use today (Pizzi and Mittal, 1994). These chemicals contain bi-functional, polar silanol groups and organofunctional groups, which are capable of reaction. Organo-functional silanes having vinyl groups as potential wood modifying agents have received a little attention and have been little studied for wood protection purposes.

The main purpose of this present study was to determine the mechanism(s) of protection of wood against decay fungi by using non-toxic modifications. In order to perform this study, three wood modification processes were investigated:

- Thermal treatment
- Esterificaton using two different anhydride reagents of different molecular size.
- Modification using two polymerisable silane reagents.

As a model study, Corsican pine sapwood was selected for this study.
The decay resistance of the modified wood was examined by exposing the modified wood to pure cultures white rot and brown rot fungi. The modified wood was also exposed in soft rot tests. These tests are reported in Chapters 4, 5 and 6.

The hydrolytic stability of the modified wood samples was also determined. The results of these studies are reported in Chapter 7.

Moisture uptake of the modified wood was examined. The results of these studies are reported in Chapters 8 and 9.

In Chapter 10, the cell wall micropore accessibility of modified wood was examined.

Chapter 11 brings together results from the studies, draws conclusions regarding this work and makes suggestions for future research.

Chapter 2

Literature review

2.1 Wood structure

The wood substance in softwoods is composed of two different cells: tracheids and ray cells. Tracheids are water transport cells of the wood and give soft wood the mechanical strength required. In addition to the ray parenchyma, some softwood has axial parenchyma as well. Parenchyma cells are the storage tissue of the wood.

Hardwood cells contain several types, specialized for different functions, which are fibres (the supporting tissue), vessels (the conducting tissue), ray and axial parenchyma cells (the storage tissue). In addition, hardwood contains hybrids of the above mentioned cells which are classified as fibre tracheids.

In both soft wood and hard wood, epithelial cells are found associated with the production of resins, gums, latex, etc.

Pits, which are found in both hardwoods and softwood, connect wood cells to each other and play important role in the permeability of wood to treating liquid and fungal hyphae. In addition to the pits, wood contains macro pores such as resin and gum ducts, intra cellular space and lumens (Tsoumis, 1991).

The wood cell wall is composed of several layers, namely the middle lamella (M), primary wall (P), the secondary cell (S) wall and warty layer (W). The secondary layer is explained later.

2.2 Chemical composition

The main chemical components in the cell wall are cellulose, hemicelluloses and lignin. The approximate wood composition (cellulose and hemicelluloses and lignin) for hard wood and soft wood are shown in Table 2.1. Hardwood and softwood are relatively uniform within their respective groups, but there are a few exceptions. For example, elm contains as much as 51% cellulose. Also, the majority of tropical hardwoods contain about 10% or more of lignin than do hardwoods grown in the temperate zone (Bodig and Jayne, 1982).

	Cellulose(%)	Hemicelluloses(%)	Lignin (%)
Sofwood	45	*30	28
Hardwood	41	*30	22

* The value is an approximate value

Table 2.1: The average percentage composition of wood (Bodig and Jayne, 1982).

2.3 Cellulose

Cellulose is the primary component of the cell wall. Cellulose in the cell wall, exits in the form of microfibrils which are generally thought to be more or less square in cross-section. The function of the cellulose content is to impart strength.

Cellulose is a crystalline linear polymer of cellobiose. The number of glucose units per cellulose molecule, (The degree of polymerisation, DP) is about 10000 in wood (Sjöström, 1981).

2.4 Hemicelluloses

Hemicelluloses are a diverse family of carbohydrate polymers containing a variety of sugar units. The hemicellulose substance in softwoods is quite different from those of the hardwoods. Mannose-containing hemicelluloses are more plentiful in softwoods. The most common of the hemicelluloses in softwoods are the galactoglucomannans. These consist of a backbone built up of mannose and glucose monomers, some which are acetylated. Xylose-containing hemicelluloses (xylans) are more plentiful in hardwood. The most common hemicellulose in hardwood is glucuronoxylan which is O-acetyl-4-O-methylglucurono-β-D-xylan.

Hemicelluloses are generally found in the amorphous state because of the presence of many side groups preventing the close association between molecules required for crystallinilty. This makes them more soluble and more susceptible to hydrolysis.

2.5 Lignin

Lignin is a polymeric material of phenylpropane structural units. The precursors of lignin biosynthesis of wood are p-coumaryl alcohol (which is minor precursor of soft wood and hardwood lignin), coniferyl alcohol (which is the pre-dominant precursor of softwood lignin) and sinapyl alcohol. Sinapyl alcohol , together with coniferyl alcohol are both precursors of hardwood wood lignin.

Several models have been put forward to explain the structure of lignin of hardwood and softwood. As an example, a model for the lignin of soft wood is shown in the Figure 2.1. A model for beech lignin is shown in Figure 2.2. There is thought to be a link between hemicellulose and lignin (Sjöström, 1993).

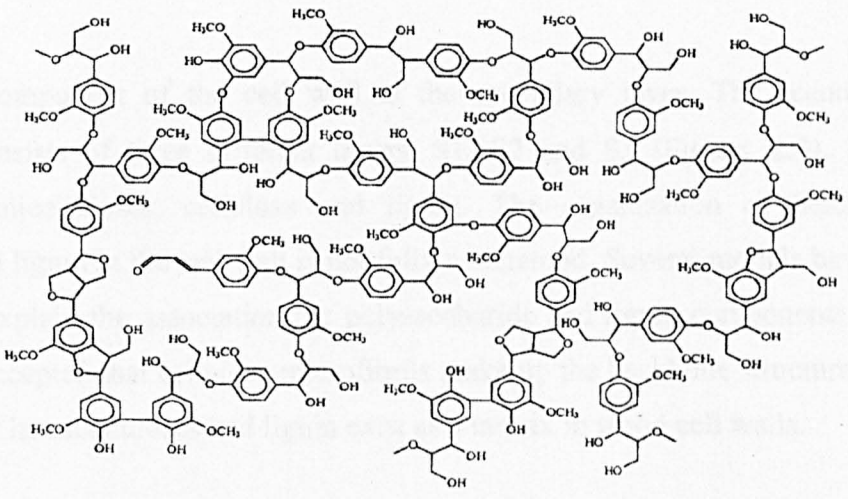


Figure 2.1: Lignin model of softwood (Reid 1996 in Simon 1998)

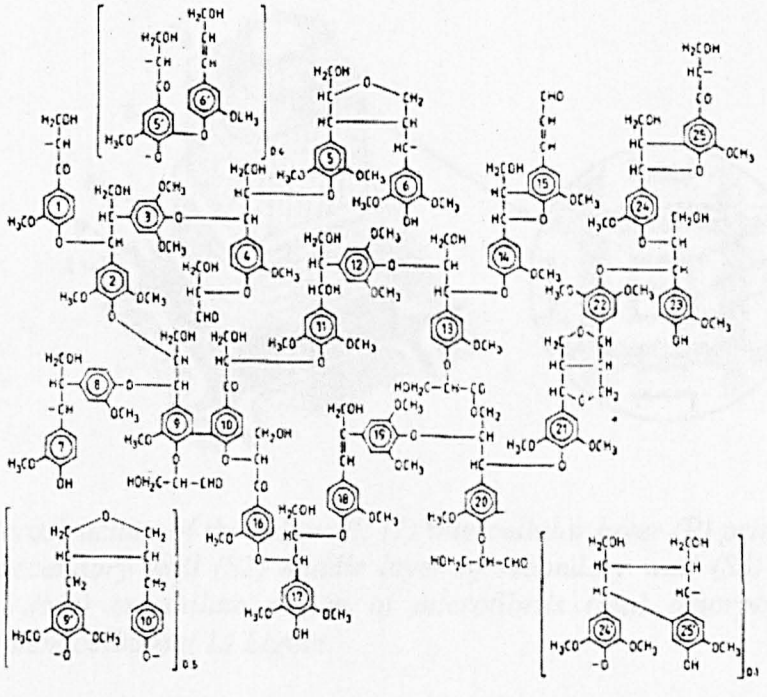


Figure 2.2: Lignin model of hard wood (Eaton and Hale, 1993).

2.6 The organisation of the cell wall

The main component of the cell wall is the secondary layer. The secondary layer normally consists of three different layers, S1, S2 and S3 (Figure, 2.3). Each layer contains hemicelluloses, cellulose and lignin. The organisation of hemicelluloses, cellulose and lignin in the cell wall is not fully understood. Several models have been put forward to explain the association the polysaccharide and lignin components in the cell walls. It is accepted that cellulose microfibrils make up the backbone structure of the cell wall and that hemicelluloses and lignin exist as a matrix in wood cell walls.

Figure 2.3 shows a model in which cellulose containing microfibrils are embedded in an amorphous matrix of lignin and hemicellulose molecules (Nakano and Miyazaki, 2003).

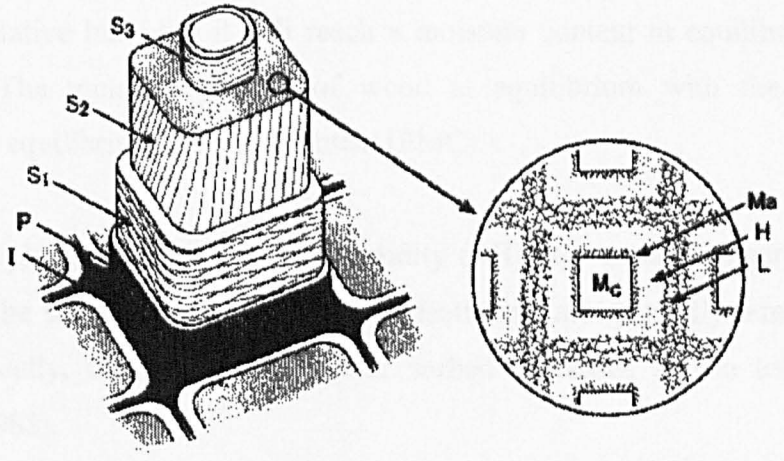


Figure 2.3: Microstructure of the cell wall: (1) intercellular layer (P) primary wall (S1) outer layer of secondary wall (S2) middle layer of secondary wall (S3) inner layer of secondary wall (Mc) crystalline region of microfibrils (Ma) amorphous region of microfibril. (H) hemicellulose(L) Lignin.

2.7 Water in wood

The presence of water in wood significantly modifies its physical and mechanical properties. Because of the hygroscopic nature of wood, the amount of water in wood changes, based on the amount of water in the atmosphere. As mentioned in Chapter 1, fungi need enough water to degrade wood. Since exposure of wood to outdoor conditions might provide enough water required by fungi, the ability of modification in reducing the water content of wood must be considered in order to understand the mechanism by which this imparts decay resistance to wood.

2.7.1: Sorption Isotherms

The mechanism by which water attaches to sites in the wood in response to changes in temperature or relative humidity is known as sorption. When wood is exposed to constant temperature and relative humidity it will reach a moisture content in equilibrium with these conditions. The moisture content of wood at equilibrium with the constant conditions is called equilibrium moisture content (EMC).

When the EMC is plotted against, relative humidity (RH) at constant temperature, the resulting curve is the sorption isotherm. Sorption isotherms are generally temperature–dependent. Specifically, the amount of vapour sorbed decreases as the temperature increases (Skaar, 1988).

Five different types of adsorption are recognised, cited by Stamm (1964). These are depicted in Figure 2.4.(b). Typical sorption isotherm of wood exhibit a sigmoid shape, known as type two which is shown in the Figure 2.4 (a and b) for adsorption and desorption.

Many theories have been proposed to explain the sorption of water by hygroscopic polymers such as wood. These sorption theories can be divided into two general categories. In one of these, sorption is treated as a surface phenomenon and in the others

as a solution phenomenon. Surface sorption theories can be represented by Brunauer *et al.* (1938), (BET) theory and solution theories by the Hailwood-Horrobin model (1946). Both of these theories consider bound water in the cell wall of wood to be held in two separate ways. mono-molecular (surface) and poly-molecular (capillary adsorption).

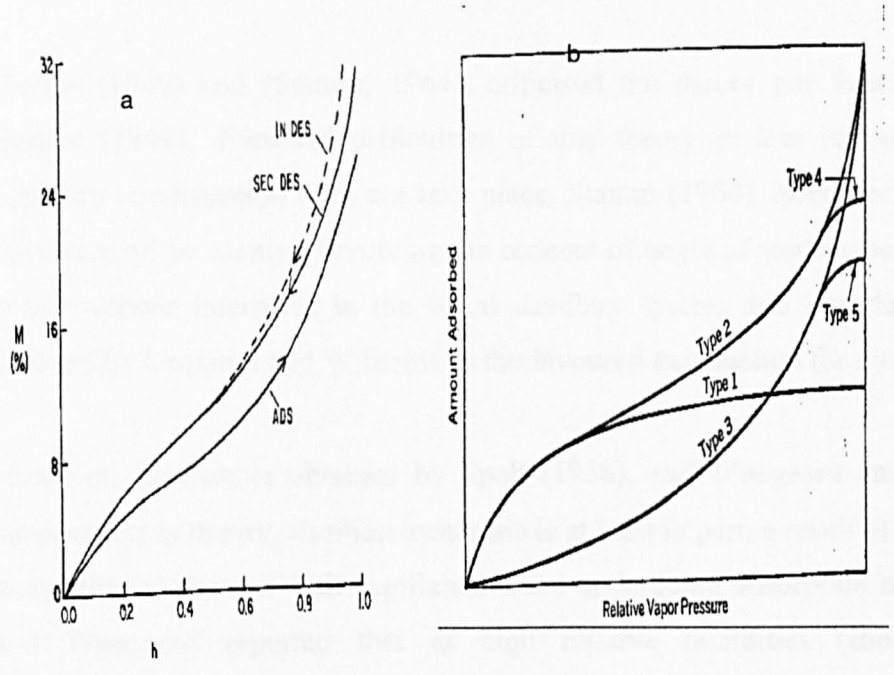


Figure 2.4 Sorption isotherm of Douglas fir in (Rowell 1984) (a) Different types of sorption isotherm (Stamm, 1960 (b))

2.7.2 Hysteresis

The EMC of wood depends on whether the wood is losing (de-sorption) or gaining (sorption) moisture in order to attain equilibrium. This phenomenon, known as sorption hystersis, has been studied extensively. Different explanations for the hystersis have been given by different authors. The most important theories which have been put forward are explained below:

A reduction in the number of surface sites due to lateral hydroxyl-to- hydroxyl bonding(Urquhart and Williams, 1924 and Urquhart 1960 in Stamm 1964).

Differences in the degree of aggregation or dispersion attained by the gel respectively in dry and saturated conditions (Baraks, 1949 and Spalt, 1958).

Differences between advancing and receding contact angles of water against the capillary walls producing higher wettability under de-sorption than under adsorption conditions (Zsigmondy *et al.* , 1912).

Baraks (1949) and (Stamm, 1964), criticised the theory put forward by Zsigmondy. Baraks (1949), discussed difficulties of this theory at low vapour pressures, where capillary condensation does not take place. Stamm (1964), questioned differences in the curvature of the menisci involving the concept of angle of wetting because of the lack of solid –vapour interfaces in the wood capillary system and introduced the theory put forward by Urquhart and Williams as the favoured explanation for hysteresis.

However, the results obtained by Spalt (1958), and Wangaard and Granados (1967), support that in theory, sorption hysteresis is at least in part, a result of the differenc in the wettability of the cell wall capillaries when undergoing adsorption or de-sorption. Chen and Wangaard reported that at high relative humdities (above 60-70 pecent), polymolecular and total hysteresis is positively correlated with wettabilty hysteresis. Spalt (1958), and Wangaard and Granados (1967), reported that the contribution of monomolecular sorption hysteresis to the total hysteresis is of minor importance in the range of relative humidities higher than 60%. Spalt concluded that the hystersis is primarily a capillary void-volume related phenomenon, although it's mechanism is most probably ascribed to lateral bonding theory.

2.7.3 Fibre saturation point (FSP)

Fibre saturation point is commonly defined as the amount of water required for saturation of the cell wall but with no free water present in the cell lumen. Absorbed moisture content is important, as it modifies the physical properties of wood, while free water (unless frozen) has no significant effect on physical properties. The presence of water in the cell wall swells the wood allowing fungal degrading agents access to wood cell wall materials (discussed later).

Different methods have been applied to measure the FSP of wood, which have been adequately explained in detail by Skaar (1988) and Siau (1996). Stone and Scallan (1968 a), measured the FSP of fresh cut black spruce (*Picea mariana* (Mill) F.S.P.) using a polymer exclusion technique and they and Griffin (1977), also used pressure plate method estimate FSP (also on *P.mariana*), both measurements FSP of approximately 40%. Siau (1996) argues that these figures are not consistent with shrinkage data and are probably due to the very thin microtome sections or pulp samples used, leading to higher swelling and higher FSP values than in solid wood, due to the lack of mechanical constraint. The existence of small permanent voids could also affect measurement using these methods.

It has been extensively discussed in all the literature that FSP is mainly a theoretical concept. The presence of solute in the parenchyma tissue cause an osmotic pressure that can lead to it to have higher moisture content and some free water before other cells have adsorbed water to F.S.P. In addition, at moisture contents close to FSP (and the corresponding atmospheric relative humidities), some condensation in the smaller permanent capillaries is unavoidable (Siau, 1996).

2.8 Cell wall micropores

In addition to the wood microvoids mentioned in Section 2.1, the cell wall of wood contains an extensive network of microvoids, which exist because of the incomplete filling of space by the cell wall polymers (Figure 2.5). In the model shown in Figure 2.5, just the cell wall microvoids have been shown and the other pores such as pits have been excluded.

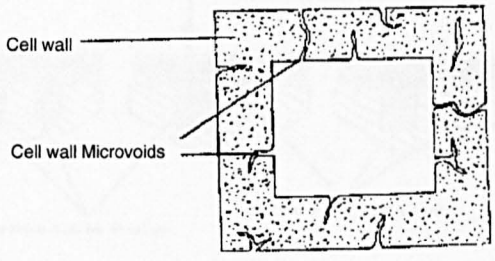


Figure 2.6: Microvoids in the cell wall (Tsoumis, 1991).

The network of wood microvoids is often referred to as transient, because these microvoids collapse when wood is dried. Swelling solvents are capable of swelling wood, thus opening up the cell wall microvoids. Of the most important swelling solvents, water is very important. Because it is very small (4 Å), and capable of penetrating into very small microvoids in the wood cell wall. Water is required by brown rot and white rot fungi to open up the cell wall and allow their degrading agents to get into the cell wall.

There are different methods to investigate microvoids within the wood cell wall. Some of them require the absence of water and others can be applied in the swollen state. The solute exclusion technique is a method for investigating wood in the swollen state and has been used to measure the accessibly of the wood degrading enzymes (Flournoy *et al.*, 1991 and Flournoy, 1993).

The solute exclusion technique is based on the measurement of the accessibility of water as function of the molecular size of a series of solutes (Figure 2.6). When a solute can penetrate into the cell wall, the water contained therein will contribute to its dilution. This moisture is logically called the accessible water. The measurement of the concentration changes of solute molecules of various sizes in the solution enables the accessible water to be determined for each solute molecule size. This determination in turn, permits the determination of the inaccessible water which corresponds to the cumulative microvoid volume.

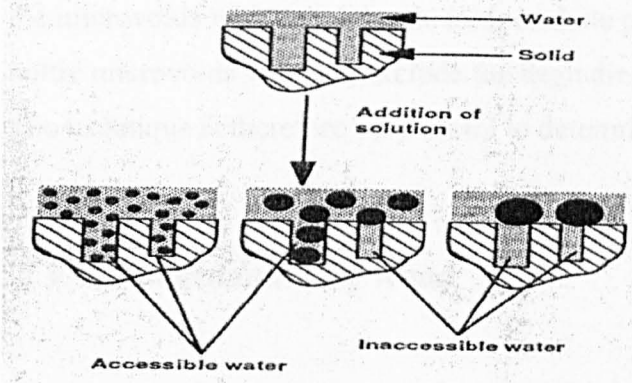


Figure 2.7: The principle of the solute exclusion technique

The apparent microvoid size distribution from this method reflects the shape as well as the size of the microvoids in wet cellulosic materials. A simple slit model, is considered to be appropriate for cellulosic materials (Stone and Scallan, 1968a). Whereas the larger microvoids (> 25 Å) are most probably slit like, as has been recognised in the general acceptance of the lamellar structure of the cell wall of pulp. The smaller (<25 Å) are of unknown configuration and have different properties (Stone and Scallan, 1968b).

By using the solute exclusion technique on fresh cut black spruce samples, Stone and Scallan (1965 a), found the maximum cell wall microvoid diameter to be 36 Å, although the median microvoid size (the size at which half the cell wall microvoid volume is made up from microvoids less than that size) was 12 Å. Using the same technique on previously dried Sweetgum, Flournoy *et al.* (1991), and Flournoy *et al.* (1993), estimated the maximum microvoid size to be just 20 Å.

The solute exclusion technique has been criticised by Alince (1991). Alince points to problems that could affect solute exclusion measurements such as osmotic pressures or the ink bottle effect where narrow microvoids could exclude probes from larger ones. Another point he argued that was the concentration of a probe within the microvoid could not be the same as that in bulk solution and that this condition will only be met if the probe molecule diameter infinitely is smaller. Walker (1993), suggested that solute exclusion may underestimate the actual of microvoid diameter because the initial hydrogen bonded mono-layer of water may not be accessible to probe molecule.

In the case of the study of the wood microvoid accessibility to fungal degrading agents by the solute exclusion technique, the ink bottle problem is not very important because, if

the microvoids with an ink bottle neck exclude probes from the larger microvoids, the ink bottle microvoids will also exclude the degrading agents of fungi from larger microvoids. The technique is therefore very useful to determine cell wall accessibility.

2.9. Biodegradation of wood

Wood decay fungi are classified into three main groups, depending on the way in which degrade wood.

Brown rot fungi degrade cellulose and hemicelluloses more rapidly lignin slowly. Lignin degradation in brown rot decay is limited to extensive demethoxylation of the aromatic portion (Eaton and Hale, 1993). Brown rot fungi are capable of degrading wood before causing a significant weight loss (Richard, 1954). This degradation is shown by a reduction of about 70% in toughness, for a weight loss of less than 1%.

White rot fungi have in common the capacity to degrade lignin as well as the other wood cell wall polymeric components. White rotted wood takes on a bleached appearance. Some white rot fungi have been shown to depolymerise lignin preferentially (Eaton and Hale, 1993). These fungi preferentially degrade large amounts of lignin in wood, with only slight or no loss or cellulose and moderate losses of hemicellulose. Other white rot fungi are not selective and remove all of the cell wall components simultaneously (Otjen and Blanchette, 1987). The categorization of white rot nto selective and simultaneous decay types is a generalisation, as most selective white rot fungi are able to cause a simultaneous decay in certain circumstances (Blanchette and Reid, 1986).

Soft rot fungi utilise carbohydrates but do not remove lignin as well as the white rot fungi. In fact, the type of lignin has an influence on the decay rate of wood by soft rot fungi (Eaton and Hale, 1991).

2.9.1 Brown rot decay mechanism

Brown rot fungi degrade wood with an unknown mechanism, but with some specific features which are mentioned below:

Brown rot fungi start decay from the S_2, leaving the S_3 unmodified (Green and Highley, 1997).

Most brown rot fungi cannot depolymerise pure cellulose unless it is located inside the wood (Eriksson *et al.*, 1990). However, it has been reported that coniophoroid brown rotters (Highley *et al.*, 1988) could degrade cellulose (over soil medium, agar medium and liquid culture) or dye cellulose microcrystalline (Highley, 1988). Highley (1988), also showed that *Postia placenta* is capable of degrading cellulose azure (which is a regenerated and noncrystalline cellulose) but it is not capable of degrading dye microcrystalline cellulose. He suggested that the fungus produced a deficient cellulolytic system. This conclusion was repeated by Highley *et al.*, 1988, where nonconiophoroid brown rotters were unable to degrade cellulose in a liquid culture while they degraded cellulose over soil and agar medium.

Different types of enzymes have been purified from brown rot fungi, which are capable of degrading cellulose. Brown rot fungi are capable of degrading the cell wall far from the hyphae. However, cellulose-degrading enzymes are too big to penetrate into the cell wall structure. For example, cellulases of brown rot have a typical dimension of *ca.* 5 nm if spherical and 3.3x20 nm if ellipsoidal, whereas the microvoids of the cell wall of sound wood have a microvoid diameter not greater than about 2 nm (Hill and Papadopoulos, 2002).

Flournoy *et al.* (1991), studied cell wall microvoid size and size distribution in sound wood and wood decayed by brown rot fungi. In their study, the cell wall microvoid volume at 35% weight loss was double that found in sound wood. They concluded that the cellulose-depolymerising agent of *P. placenta* must be between 12 Å and 38 Å in diameter and therefore the cell wall microvoids are too small to be penetrated by enzymes. In addition, Srebotnik and Messner, (1991), investigated the penetrability of degraded cell walls with two marker proteins (ovalbumin (45000D) and myoglobin

(16500D)) by immunoelectron microscopy. In their study, it was found that at 70 % weight loss due to decay , ovalbumin (with a molecular weight corresponding to that of some known wood degrading enzymes) did not penetrate the cell wall of pine wood (*Pinus sylvestris*).

Despite the fact that the studies by Flournoy *et al.* (1990) and Sterebotnik and Messner, (1991), suggested that non-enzymatic systems are only responsible for decay by brown rot at both stages of decay (initial and advance stages of decay), it is still probable that enzymatic systems of fungi are partially responsible for the degradation of wood at advanced stages of decay (Goodell *et al.*, 2003).

One of the non-enzymatic systems has been suggested to be responsible for the degradation of cellulose by brown rot fungi is a Fenton's reaction which was the first to be proposed as the possible non-enzymatic system involving peroxide and iron (Halliwell, 1965 in Koenig, 1974).

$^{H}{}_{2O2}{}^{+} Fe^{2+} + H+ \dashrightarrow H_{2O} + Fe^{3+} + .OH$

It has been suggested that the low molecular weight agents are Fenton reaction generated hydroxyl radicals, which diffuse into the cell wall (Hammel, 2002 and Goodell *et al.*, 2003). In a review of the literature, Goodell *et al.* (2003), challenges this suggestion because hydroxyl radicals must be generated in very close proximity to their reaction site to be effective and free ferric iron, is not found in oxygenated environments.

In the literature, cellobiose dehydrogenase, glycopeptides and hydroquninone have been mostly suggested to be low molecular agents that mediate Fenton reactions for white rot and brown rot fungi.

It has been suggested that glycopeptides are capable of reducing Fe^{+3} to Fe^{+2} and the production of the H_2O_2 but the diffusion of the glycopeptides into the cell wall is controversial. From a brown rot fungus *T. palustris*, glycopeptides with molecular weight of 7.2 -12KD have been extracted (Enoki 2003 in Goodell *et al.* 2003). Goodell *et al* (2003), states that compounds with molecular weights greater than 6000 D are excluded

from the cell wall thus glycopeptides should be excluded from the cell wall. But, some researchers have reported the diffusion of glycosylated effector from glycopeptides, capable of penetrating into the cell wall. It is also discussed that the shape of glycopeptides is elongated which might allow them to penetrate into the cell wall (Enoki 2003, in Goodell *et al.* 2003).

Cellobiose dehydrogenase (CDH) is an extra cellular enzyme produced by many white rot basidiomycetes, and by brown basidiomycetes in the family *Coniophoracaeae* and by some soft rot fungi. Using *C. puteana*, Hyde and Wood (1997), suggested that a pH gradient is set up within the wood cell wall due to the production of oxalic acid by the hyphae. Chelated Fe^{+3} (oxalate is assumed as the chelating species) is reduced to Fe^{+2} by cellobiose dehydrogenase which then diffuses into the cell wall. The higher pH within the cell wall enables the reduction of molecular oxygen by two Fe^{+2} complexes to form hydrogen peroxide, which can then react with a further Fe^{+2} present to form the hydroxyl radical. This system helps explain how hydroxyl radicals are formed at a safe distance from hyphae and why the S3 layer may seem resistant to attack early in the decay process). The authors admit that the theory is weak with regard to the reduction of Fe^{+2} to the Fe^{+3} required in the Fenton's reaction. Another issue is that auto-oxidation of iron to produce hydrogen peroxide at a specific pH may be problematic. Iron cannot be readily maintained in two different oxidation states in the same environment. If the pH is high enough for the Ferrous iron to auto-oxidize and form hydrogen peroxide, then this oxidant will diffuse and react with any ferrous iron in the immediate vicinity. It is unlikely given this scenario that significant amount of ferrous iron would then be available to diffuse into the wood cell wall.

Quinone redox cycling has long been known as a source of OH radicals and might provide a mechanism for an extra-cellular Fenton reaction. The principle of this mechanism is that the fungus reduces an extra-cellular quinone to its hydroquinone, which then reacts with Fe^{+3} to give Fe^{+2} and a semi-quinone radical. It has been suggested that hydroquininone compounds produced by some brown rot fungi can diffuse deep within the S2 layer of the wood cell wall to mediate Fenton reactions. By exploiting a pH gradient (as explained for cellobiose dehydrogenase) it has been suggested that

hydroquinone is capable of diffusing into the cell wall to mediate Fenton's reaction (Hammel *et al.*, 2002). Goodell *et al.* (2003), suggested that it is unlikely that the oxidised quinonic form would diffuse back repeatedly to the lumen to be reduced. The OH radical produced by the redox reaction can also attack the quinones and hydroquninones, in addition to the wood polymer. Thus, this model requires an adequate source of quinones. For the brown rot fungus *G. trabeaum,* this is fulfilled.

Despite the fact that much effort has gone into explaining the cellulose degradation mechanism by the Fenton's reaction, Fenton reagent involvement has still not been proved. The Fenton's reagent doesn't seem to be an adequate model for all brown rot fungi. The effect of Fenton's reagent on wood components and model compounds are not duplicated by brown rot in many respects (Flournoy, 1994) and oxalic acid which is an important metabolite of brown rot fungi, might be produced at concentrations which have an inhibitory effect on the degradation of lignin by Fenton's reagent (Tanaka, 1994). For example, *Posita placenta* accumulate and lowers pH as low as inhibiting Fenton reactions (pH 4 is the most optimum pH for Fenton reaction) (Green *et al.* 1992).

Involvement of oxalic acid in the non-enzymatic degradation of hemicellulose and cellulose has also been proposed. It has been shown that oxalic acid takes part in either, directly depolymerising wood cellulose (Schmidt *et al.*, 1981) and hemicelluloses (Beck, 1987), or indirectly by donating an electron for oxidative cleavages of cellulose (Jordan *et al.*, 1996).

Similar to cellulose and hemicellulose degrading enzymes, lignin peroxidases which have dimensions of 4.7 nm (spherical) or 4.3 nm x 6.0 nm (ellipsoidal) (Flournoy *et al.*, 1993) are too big to penetrate into the cell wall. In addition to this, some brown rot fungi don't produce lignin peroxidase (Blanchette, 1988). Thus, lignin degradation or modification by brown fungi might be undertaken by non-enzymatic degrading agents having dimensions of 12-30 Å (Flournoy *et al.*, 1990). This has been verified by the work done by (Messner and Stachelberge 1982). They demonstrated that even after infiltrating of a wood specimen with the culture filtrates of *Fomitopsis pincola*, concentrated 300- fold, the peroxidase was not able to diffuse freely within to the cell wall even at 50% weight

loss due to decay. They concluded that most probably, all the other changes in the brown rotted cell wall, such as de-methylation of lignin are products of non-enzymatic reactions.

2.9.2 White rot decay mechanism

White rot fungi degrade cellulose largely through the synergistic action of three main types of enzymes namely, endo-1, 4-ß-glucanases, exo-1,4-ß-glucanase,1,4-ß-glucosidases. In addition to these hydrolytic enzymes, oxidative enzymes such as glucose oxidase, cellobiose dehydrogenase and cellobiose quinone oxidoreductase take part in cellulose degradation.

Extracellular enzymes, which are able to degrade hemicellulose have been isolated from fungi. The enzymes have not been investigated as extensively as cellulose degrading enzymes (Eaton and Hale, 1993).

Different enzymes have been purified from white rot fungi which are involved in lignin degradation. The most important enzymes which can be mentioned are Li–peroxidase, Peroxidases (lip) contain ferric haeme and operate *via* a typical peroxidase catalytic cycle. That is, lip is oxidised by H_2O_2 to a two-electron deficient intermediate, which returns to its resting state by performing two one-electron oxidations of donor substrate. Lips are more powerful oxidants than typical peroxidases are, and oxidize not only the usual peroxidase substrate such as phenols and anilines, but also a variety of non-phenolic lignin structures and other aromatic ethers that resemble the basic structural unit of lignin (Keresten *et al.*, 1990).

Mn- peroxidase is a haeme containing glycoprotein of 46 kD molecular size ,oxidising Mn^{+2} to Mn^{+3} which in turn oxidises phenols to form phenoxy radicals (Eaton and Hale, 1993).

Laccase is a phenoloxidase, oxidising lignin phenolics to phenoxy radicals, as in the case of Mn-p, though it is not hydrogen peroxide (or manganese) dependent. Of the fungi in which laccase has been recognised to be important factor in their lignin degradation mechanism is *Pycnoporus cinnabarinus* (Eggert, 1997). The role of laccase in lignin degradation is controversial, because not all fungi produce it and low activity of laccase is found in some fungi as well (Eaton and Hale, 1993).

Veratryl alcohol is a lignin degradation product produced by the most of white rot fungi (Balashin *et al.*, 2000). It has been suggested that Lignin peroxidases are capable of oxidising veratryl alcohol to a cation radical, which diffuses into the cell wall oxidising aromatic compounds of lignin. But the diffusion of the radical into the cell wall has been questioned because of the life-time of the radical which might not be long enough to remain active when diffusing into the cell wall. (Schick *et al.*, 1997).

By employing TEM studies, together with the immuno-labelling technique, it has been clearly shown that lignin degrading enzymes are not capable of penetrating the cell wall of sound wood (Daniel *et al.*, 1989, Srebotnik *et al.*, 1988, Blanchette *et al.*, 1989). In addition, not all fungi have the above-mentioned lignin degrading enzymes and in some fungi Mn and Li peroxidase are produced as a secondary metabolite of fungi (Eriksson *et al.*, 1990). Therefore, the activity of lignin degrading enzymes are restricted to the lumen surfaces, at least at early stage of decay. For selective white rot fungi, the penetration of lignin, hemicellulose and cellulose degrading enzymes into the cell wall after an initial degradation by a non-enzymatic system has been shown. The penetration could be the result of the removal of lignin which holds the wood microfibrils together. Srebotnik *et al.*, (1988), infiltrated decayed pine wood with the concentrated culture of *P. chrysosporium* (a selective white rot fungus) and then traced lignin peroxidase in the wood by immuno-gold labelling. Lignin peroxidase was found on the surface of the cell well within areas that were degraded extensively. Enzymes from the culture did not penetrate into the sound areas of the cell wall. Subsequently, Daniel *et al.* (1989), showed extracellular localization of lignin peroxidase in slime layers of the cell around fungal hyphae and along areas of cell wall erosion in decayed wood by using polyclonal antisera and immuno-gold labelling techniques. Blanchette and co-workers (1989), found the

same result with the simultaneous decay *C. versicolor* on birch, but a better penetrability of Lip peroxidases and Mn peroxidases throughout the degraded cell wall decayed by a selective white rot fungus was observed. Flournoy (1993), showed that simultaneous removal of the three main components through decay by the white rot fungi *P. chrysosporium* to 40% weight loss increased the microvoid volume of the wall only modestly and increased the median microvoid diameter only slightly. They concluded that lignin peroxidases are expected to penetrate only a small fraction of the sound cell wall microvoid volume, even after intensive decay. Blanchette *et al.* (1997), measured the ability of two proteins with different molecular weights to enter the cell wall of loblolly pine decayed by the selective white rot fungus, *Ceriporiipsis subvermispore*. The larger of the proteins (molecular weight 44287 D, approximately corresponding to the weight of lignin peroxidase) penetrated the cell wall after 8 weeks of incubation in wood with advanced stages of decay where extensive cell wall disruption was evident. Whereas another protein (Molecular weight 17600D, approximately corresponding xylanase or a small cellulase penetrated the cell wall after 4 weeks.

It's apparent that in simultaneous white rotted wood, lignin peroxidase cannot move within the degraded cell wall as freely as that in selective white rotted wood, thus a non-enzymatic system might be responsible for the lignin degradation throughout the decay (early stage of decay and advanced decay).

By examining the possible roles of one-electron oxidation activity by phenol oxidases and hydroxyl radicals in wood degradation by *P. chrysosporium*, Tanaka *et al.* (1999), reported that the generation of hydroxyl radicals in the redox reaction catalysed by low molecular substances secreted by the fungus was related to the rate of wood degradation, but the activity of phenol oxidases was not related. Thus, it was concluded that hydroxyl radicals in the redox reaction are important in the degradation of wood by white rot fungi. This is in the line with the conclusion made from the literature about the ability of white rot fungi to penetrate into the cell wall.

Recently, a new mechanism involving a powerful lignin degrading system based on coordinated Cu and peroxide, either hydrogen peroxide or organic peroxide has been

suggested to be the agent involved at least in the initial de-polymerisation and degradation of lignin by selective white rot (Messner *et al.* 2003).

2.9.3 Soft rot fungi

A variety of extra-cellular or cell –bound carbohydrate enzymes capable of degrading all of the wood carbohydrates such as cellulases, xylanases and manganese peroxidase have been shown for the soft rot fungi. Nilsson (1974), tested 33 fungi found to cause soft rot in birch, He found that not all of the soft rot fungi tested had each of these enzymes. Negative results were recorded for soft fungi which produced only one type. Nilsson suggested that the negative results were most likely due to imperfect test methods and not because of the incapability of the tested fungi to produce the enzymes.

Cellulases purified from soft rot are too big to penetrate into the cell wall. Since soft rot fungi cause erosion and cavities in the cell wall, it is generally thought that the decay is restricted to surfaces (Eaton and Hale, 1991).

Hale and Eaton (1988b), suggested that high proportion of the components at the tip of the cell wall penetration hyphae is an exoglucanase (with a lack of endoglucanase at this point), while cavity widening is largely due to the release of endoglucanase.

Haider and Trojanowski (1975), tested the ability of various soft rot fungi to degrade 14-C labelled lignin model compounds and dehydropolymers of coniferyl alcohol. They found these fungi were able to convert the propyl side chains, methoxy groups and aromatic rings to carbon dioxide.

Recently, similar to white rot and brown rot fungi, hydroxyl radicals produced by extra-cellular low molecular weight have been suggested to be degrading agent of decay by soft rot fungi. By correlating the phenoloxidase activity and one electron oxidation activity to the decay rate of wood due to six deuteromycete fungi, Tanka *et al.* (2000), reported that

the decay rate by soft rot fungi, is not correlated with phenol oxidase activity but is roughly correlated with one–electron oxidation activity in the cultures. In addition, there was no clear relationship between phenol oxidase activity and one electron oxidation activity. However, the role of phenol oxidase in wood degradation was found to be important, since the four deuteromycete fungi with significant level of phenol oxidase activity were capable of degrading wood but two of the deuteromycetes with no phenol oxidase activity did not significantly decay wood. In order to understand the mechanism by which soft rot fungi decay wood, the author suggest that isolation and identification of phenol oxidases from soft rot fungi and determination the agent responsible for one-electron oxidation in a culture of soft-rot fungi would be necessary.

2.10 Thermal decomposition of wood

All organic materials decompose when heated. In the case of wood, changes in composition begin to be perceptible at temperatures as low as 100°C, but more active decomposition occurs above 250°C. When wood is heated out of contact with air at temperatures between 100 and 250°C, it becomes darker in colourand suffers considerable loss in strength, but decomposition is very slow at these relatively lower temperatures. On further heating, an exothermic reaction begins at about 270°C, and extensive decomposition takes place without formation of the ordinary distillation products. Over 200 compounds have been found in the liquid products from the destructive distillation of wood, and are formed either as direct decomposition products of wood components, or as result of secondary reactions which occur during pyrolysis, or subsequently. It is clear that thermal degradation of wood is a highly complex process. Nevertheless, the major products can be largely accounted for in terms of the decomposition of the principle wood components, cellulose, hemicellulose and lignin. (Farmer, 1967).

2.10.1 Polyoses (hemicellulose)

The amount of hemicellulose in wood is usually between 20 and 30% of its weight. The first attempted thermal degradation of pentosans was carried out by Bergstrom (1913, cited by Niktin, 1966). The pyrolysis of pentosans, isolated from birch wood by alkaline extraction, yielded the following products: carbon 37.2%, aqueous distillate 33.6%, tars 11.1%, and gases 18.1% (of the oven dry weight). The water distillate contained only 0.29% acetic acid, 0.7% formic acid and about 9% furfural (Niktin, 1966).

The temperature at which hemicellulose decomposition begins depends on heating atmosphere, heating period and wood species and could be as low as 117°C (Fengel and Wegener. 1989) . The thermal stability of the pentosan portion of the hemicellulose is higher than the hexosan portion. Furan and its derivatives are the characteristic pyrolytic compounds relating to the pentosans of wood. However, dry distillation yields lower amounts of furfural compared with those that are released after the treatment of pentosans with hydrochloric acid solution. Pentosan molecules tend to breakdown into simpler compounds than furfural. The furan ring possibly is not formed or is not stable (Niktin, 1966).

The main source of acetic acid in the dry distillation of wood is the acetyl groups, which are mainly contained in hemicellulose (especially pentosans) (Niktin, 1966). A first - order reaction at 182-210°C, with an activation energy of 160 kJ /mole for the O-acetyl-compound was attributed to the hydrolysis of the acetyl group of glucomannans (Shimizu *et al.* 1972). Pentosans provide higher yields of acids of the acetic series than cellulose and lignin. This becomes obvious if the acid yields are compared between those of softwoods and hardwoods. Hardwoods provide more acid than softwoods due to a high of pentosan content, Since hardwood hemicelluloses contain higher amounts of acetyl groups than the softwoods. Pentosans are far less stable than cellulose. Thus, pyrolysis of pentosans occurs at relatively low temperatures. Decomposition of pentosans produces high yields of acids and acids require higher temperatures for the formation of formic or acetic acids. Therefore, if cellulose were decomposed first no acid yields would be observed and the reaction would be characterised by a high presence of charcoal, as happens at the later stages of carbonisation. (Niktin, 1966).

To determine the effect of thermal treatment on the hemicellulose, Fengel *et al.* (1970), extracted air heated spruce by cold and hot water. The quantity of hot water extract increased for wood heated above 100°C, whereas that of the cold water increased above 120°C., with largest increase in the both extracts occurring between 150 and 180°C, while the arabinose content decreased beyond 120°C. It was proposed that hemicellulose decomposition occurs in two stages. In the first stage there is a partial decomposition of macromolecules into fragments that are water soluble, and either a depolymerisation of short chains to monomer units and subsequent decomposition to volatiles or a rapid direct decomposition of the polymer chain to volatiles at such a high rate that detection of fragments is difficult.

In a study of the thermal degradation of wood components using the gas evaluation method, Ramiah and Goring (1967), found that birch xylan began degrading at 117°C with an energy activation of [46 Kcal / mole]. Pine glucomannan began degradation at 127°C, and was presumably more stable because of its crystallinity. The first order activation energy for de-composition was [249kJ/mole]. It was concluded that the hemicelluloses were the least stable of wood components.

2.10.2 Cellulose

The influence of heating on cellulose depends on the duration of heating, the temperature, the DP of the cellulose, the surrounding medium and ash content. When cellulose is heated above 120°C, depolymerisation occurs. When the depolymerisation of cellulose takes place, cellulose properties change. Cellulose viscosity decreases, (alpha-cellulose decreases), its mechanical properties are partially lost and its solubility in alkali and Kappa number increase. At higher temperatures (about 240°C) dehydration and alteration of the repeating unit of the macromolecular cellulose chain take place. When the duration of heating is short, these changes may the negligible. Heating cellulose at 275°C and higher, results in its extensive decomposition with the formation of liquids and gaseous products and evolution of heat. The evolution of liquid products is practically complete when the temperature is raised to 400-450°C, the residue is carbonised

cellulose. In general the main products of thermal decomposition are carbon, aqueous distillate, tar and gases (Niktin, 1966).

Farquhar and co-workers (1956) in Niktin (1966), heated raw cotton (a relatively pure source of cellulose) for 4 to 24 hr at temperatures of 75 to 220°C in air and nitrogen. This and another investigations (Major, 1958; Shafizadeh, 1968), show that oxygen and water have a profound effect in enhancing the deterioration and the thermal degradation of cellulosic materials. These reactions provide a type of oxycellulose, or by oxidation reactions, which on further heating decompose with evolution of H_20, $C0$,. $C0_2$. Under oxygen the degree of polymerisation rapidly decreases and then levels off at a value of 200, which corresponds to the size of the cellulose microcrystallines. In a nitrogen atmosphere, the degree of polymerisation decreases, but at a much slower rate. Carbonyl and carboxyl groups are also formed in the cellulose chain during heating under oxygen. Shaifizadeh (1984), studied the pyrolysis of cotton linter cellulose in the temperature range of 257-310°C in air and nitrogen atmosphere and estimated the activation energy of 71.4 kJ/mol for the weight loss due to the overall pyrolytic reaction of cellulose in air and 155.4 kJ/mol in a nitrogen atmosphere. The rate of pyrolysis determined by thermogravimetric analysis under isotherm conditions showed an initial rapid period of degradation that proceeds faster in air than in an inert atmosphere. As the extent of pyrolysis increased, the difference between pyrolysis under air and nitrogen gradually decreased and disappeared at 310°C.

As noted above, carbonyl and carboxyl groups are produced during heating under oxygen. The hydroxyl groups and the terminal-reducing group are the sites most susceptible to attack. Even in a nitrogen atmosphere, there is a possibility that oxidation reactions take place. Major (1958), studied the isothermal degradation of cellulose at 170°C and reported an increase in both atmospheres. Although carbonyl groups were formed in both atmospheres, only that of oxygen produced an increase in carboxyl groups. Some carbonyl groups must have formed along the cellulose chain because the number of end groups alone couldn't account for the high measured concentration. In the nitrogen atmosphere, the concentration of carbonyl groups reached a constant level after an initial rapid increase. This effect was unexplained, but it was speculated that the initial increase was caused by oxygen.

The thermal degradation of cellulose in air may involve a free radical mechanism. Shafizadeh monitored the formation of hydroperoxide groups on heating cellulose in air. The hydroperoxide functions are formed and decomposed simultaneously, and their concentration rapidly increase until a steady state is reached. The increase in the hydroxperoxide concentration appeared to follow first-order kinetics with a rate constant of $2.5x10^{-2}$ min^{-1} at 170°C (Shafizadeh, 1984).

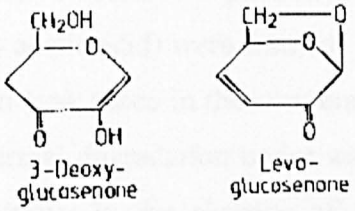
The products obtained from the vacuum decomposition of cellulose are different from those obtained under atmospheric pressure. The products mainly include β-levoglucosan, which distils over at 200-300°C. The aqueous distillate contained a small amount of other organic substances, mainly acetic acid and furfural (Niktin, 1996).

Heating cellulose up to a certain temperature, which may be as high as 200°C depending on the conditions involved, does not change its crystalline structure. The crystallinity of 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 (Fengel, 1967 in Fengel and Wegener ,1989). Roffael and Schaller (1971), observed an increase of crystallinity in thermally treated cellulose up to temperatures of 120-160°C. The temperature, at which the maximum value was reached, depended on the water content of the cellulose sample. During the heating of pinewood (*Pinus densiflora*). Taniguchgio and Nakata (1966) in Fengel and Wegener (1989), found no change of x-ray diffraction pattern up to 210°C. Above this temperature, the supramolecular structure is destroyed and a completely amorphous state was reached at about 270°C. A similar result was obtained with sulphite pulp from slash pine, at about 270°C. At 240°C the crystalline structure of cellulose obviously breaks down as the DP decreases within two hours below 200°C and 8 hours below 100°C.

Shafizadeh and DeGroot (1976), classified the reactions taking place during the thermal degradation of cellulose and other polysaccharides into the following categories:

1) De-polymerisation of the polysaccharides with transglycosylation, oligosaccharide synthesis at about 300°C to provide a mixture of levoglucosan, other monosaasccharide derivatives, and a variety of randomly linked oligosaccharides. This mixture is generally referred to as the tar fraction. The above reactions are accompanied by dehydration of

the sugar units in cellulose. These give unsaturated compounds, including 3-deoxyglucosenone, levoglucosenone, furfural, and a variety of furan derivatives which are found partly in the tar fraction and partly among the volatiles. As in aqueous reactions, the dehydration reactions are strongly catalysed by the presence of acidic reagents.



2) At somewhat higher temperatures, fission of sugar units provides a variety of carbonyl compounds, such as acetaldehyde, glyoxal and acrolein (toxic and flamable), which readily evaporate.

CH_2=CHCHO CHO-CHO CH_3CHO

Acetaldehy Acrolein glyoxal

3) Condensation of the unsaturated products and cleavage of the side chains by means of free radical mechanisms to leave a highly reactive carbonaceous residue containing trapped free radicals.

Ramiah and Goring (1967), used a sensitive method, based on gas evaluation, to determine initial decomposition temperatures of different forms of cellulose, and computed the first-order activation energy. The decomposition began at 164°C and gave a range of 514 to 522 kJ per mole. Cellulose was considered the most stable wood constituent.

2.10.3 Lignin

Although it is thought that lignin that is the most thermally stable component of wood, various changes have been observed even at temperatures below 200°C. It was shown that the non-hydrolysable residue of thermally treated wood was increased with increasing temperature up to 200°C (Fengel *et al.*, 1970). The yield of ethanolysis

products of spruce wood also increased, while the methoxyl content reduced after heating the wood at temperatures of 180°C and 200°C for 24 hours.

Mizina *et al.* (1967), studied the effect of water vapour on the thermal degradation of lignin. They found that the production of volatiles, began at 250°C and that at 350°C, 80% of volatile tar phenols, 90% of the non-volatile phenols and 80% of aliphatic acids (as acetic acid) were formed. Without water vapour, the decomposition started at 350°C, and took place in the temperature range 450-500°C. According to the investigations, the thermal degradation under water vapour led to the formation of polyhydric non-volatile phenols, In the absence of water vapour, thermal degradation led to a sticky mass, containing dimers and trimers of lignin, which resisted hydrolytic cracking, and which later condensed mutually or with lignin and formed a semi-coke.

It is thought that there is a linkage between hemicelluloses and lignin (Pearl, 1967) as mentioned earlier in Section 2.5. Kollman and Fengel (1967), investigated the thermal stability of probable linkages between lignin and polysaccharides. They heated model compounds (3-O-benzyl ethers of D-glucose and-O-benzyl ethers of methyl D-glucose) .The degradation of the ether linkages occurred at temperatures above 200°C, and was influenced by the methoxyl groups on aromatic rings, and by the hydroxyl ether bond, Both reduced the thermal stability of aryl ethers.

On studying HCl-lignin from aspen, Dumburg *et al.* (1966) in Fengel and Wegner 1989, showed aryl ether linkages are broken up at 270°C and in the range of 270 - 300 °C.

Segeeva and Miljutia (1960) in Fengel and Wegner 1989, found no change in lignin up to 155 °C. Heating at 175°C caused a lignin condensation, which increased with the heating temperature up to 240° C. At 260-280°C the lignin condensation was accompanied by other changes in the lignin molecules, which led to a reduction of hydrophilic capacity.

In an investigation of the thermal degradation of isolated wood components, Ramiah and Goring (1967) in Fengel and Wegener (1989), worked out decomposition activation of 217 kJ/mole for dioxane lignin and 435 kJ/mole for periodate lignin. Dioxane lignin

began decomposing at 130°C, whereas the periodated lignin degraded at 145°C. The thermal stability of lignin was considered greater than that of hemicellulose and less than that of cellulose.

2.10.4 Extractives

By analysis of extracted and un-extracted hardwoods and softwoods, Beal (1969), showed that extracted wood had more thermal stability than that without any extraction. Wettability of wood is reduced by heat treatment. Many studies have shown that wettability of wood remains unchanged when it is extracted by acetone or ether. To understand the role of acetone extractable components of wood on a reduction of wettability as result of heating, Hemingway (1969), examined fatty acids after air-heating at temperatures between 105°C-220°C. Heating wood in air at temperatures between 105° and 220°C didn't increase the concentration of fatty acids sufficiently to allow an explanation of the reduced surface wettability. The unsaturated fatty acids and esters undergo considerable oxidation under heat conditions was explained to be an explanation for the water repellancy (the reduction in wettability due to heat treatment).

2.11 Dimensional stability and decay resistance of thermally treated wood

Stamm and his workers were the first scientists who applied heat treatment of wood. Stamm *et al.* (1946), by heating white pine and Sitka spruce beneath the surface of molten metal, found that hygroscopicity deacresed when heating temperature rised, and the hygroscopicity reduction was accompanied by a reduction in mechanical properties (modulus of rupture, abrasion resistance, toughness). They also showed that the temperature of heat treatment is decreased linearly with an increase in the logarithm of time giving the same result.

Viitanen *et al.,* (1994), investigated the effect of high temperatutre heat treatment (above 150°C) on the properties of spruce. Samples were treated at temperatures within the range of 180-230□C for different periods. The decay resistance of spruce was improved 27-100% against the brown rot fungus *Coniophora puteana* and 42-82% against soft rot

micro - organisms. Mild heat treatment resulted in some improvement of decay resistance but not as much as observed with higher temperatures and longer time. Heat treatment of wood above 150°C changes the chemical composition of wood. Mailum and Arenas (1974), studied the effect of dry heat treatment at 90, 110, 130, 150 and 175¶°C for 240 hours on the quality of different Philippine wood species. Prolonged heat treatment at 130, 150 and 175°C resulted in increased decay resistance against the brown rot fungi species *Fomes lividus and Lenzitesa striate*. Kim *et al.* (1998), examined the effects of heat treatment on the decay resistance and the bending properties of wood. The air-dried and the green samples were heated in a convection oven at 120, 150, and 180°C for different times, (12, 24, 48, 72, or 96 hours, 6, 12, 24, 36, or 48 hours, and 4, 8, 12, 16, or 20 hours, respectively). Decay resistance of heated samples was compared with those that were impregnated with a 1% chromated copper arsenate (CCA) type B solution. Heat treatment decreased the bending properties by 30%. The reductions in mechanical properties were closely related to treatment time and temperature .The decay resistance of heat-treated wood was improved for all of the heat treatment regimes to some extent (*ca.* 35-65%) But the improvement (*ca.*77%) achieved by CCA was more than that achieved by the heat treatments. They suggested that more severe heating conditions should be applied to achieve a decay resistance comparable to that obtained by CCA treatment.

Keith and Change (1978), studied the hygroscopic properties of air-heated wood of four species (beech, maple, aspen, elm). Specimens were exposed to 180°C for 8, 16, and 32h, 200°C for 2, 4, and 8h, and 220°C for ½, 1, and 2h at atmospheric pressure in a forced-circulation laboratory oven. Heated samples showed lower EMC than control samples (un heated samples) at any given relative humidity (87, 84, and 97%). Drops in EMC due to heating were generally proportional to treatment temperature and arrived at a maximum of more or less one-half in samples heated for 2 h at 220°C. The heat -treated specimens were exposed to moisture cycling (humidification--dehumidification). The EMC for the first adsorption were below those for subsequent cycles over most of the hygroscopic range. This inconsistency was not observed after the first cycle and the following EMC's remained quite constant and lower than those of control samples. Edvardsen and Sandland and (1999), studied the influence of increasing temperature on the dimensional stability of wood. Specimens were heated in an oven at 110°C and 50°C for 48h and then exposed to five cyclic climate changes. This method of exposing samples at high levels of relative humidity recorded the dimensional stability for samples that are not intended

to be exposed in ground contact. After five drying cycles, samples heat-treated at 110°C, showed considerably lower MC and higher dimensional stability than those treated at 50°C. The reduction in the hygroscopicity and the dimensional stability improvement due to the high temperature treatment was permanent and it didn't change even after five cycles.

In Finland, heat treatment as an alternative for preservation toxicants has been extensively studied. These studies led to the establishment of an air-heat treatment process used for the treating of Finish species .The treatment process can be divided into three different stages:

1-temperature rise period (preliminary warm up (100°C) + kiln dry at hot temperatures if needed (100-150°C), + temperature rise period (150°C), 4...40 hours
2-actual heat treatment (constant temperature of between 150-240°C), 0.5...4 hours
3-cooling + stabilizing, 5...15 hours more easy to (Syrjämn, T. and Kangas, 2001).

Decay resistance of the heat-treated wood is improved, but its strength properties (especially tensile strength) are noticeably reduced. Depending on the treatment conditions and species, the cleavage strength may be reduced by 50%, making the heat-treated timber split easily (Syjanen and Kallgas, 2000).

The authors of the above-mentioned works investigated the upgrading of wood by air - heat treatment. Thermal degradation of wood in air or oxygen is accompanied by oxidation, which may decrease the mechanical properties of wood more than heating in an inert atmosphere (Stamm, 1964). The greater reduction of mechanical properties in an air atmosphere may be caused by the rapid oxidation of the whole of amorphous cellulose, even at rather low temperatures such as 170°C and the reduction of crystalline cellulose content. Thus, most studies of dry-heat treatment have been concentrated on heating wood in an inert atmosphere (normally nitrogen).

The rate of the thermal degradation that occurs in both wood and paper to give dimensional stabilisation can be greatly increased by introducing various mineral acids or salts (as a catalyst in thermal degradation) into the wood or paper prior to heating (Stamm 1964). Stamm (1959) examined the effect on the dimensional stability of paper by

catalysed heat treatment, and showed that unbleached Kraft paper containing 1.25% of zinc chloride developed dimensional stability, when heated at a fixed temperature, about 46 times as fast as when no catalyst was present. Stamm and Baechler (1960), studied the decay resistance of heat-treated and heat -catalysed treated wood. Two sets of samples were separately impregnated with zinc chloride (0.5%) and sodium chloride (0.5%) with the purpose of catalysing the thermal degradation of wood. The samples, together with controls (unheated) were treated in an oven between brass plates at 180°C for 0.5 to 46 hours. However, Weight loss is greater when zinc chloride is used as a catalyst, lower when sodium chloride is used, and least in the absence of a catalyst. After leaching, all samples were subjected to a soil block test for three months. Decay resistance of wood both for free-catalyst and for catalysed heated wood significantly increased. Thermal reaction with zinc chloride catalyst present seemed to be slightly more effective than with those that were heated without catalyst. Decay was practically eliminated when reductions in swelling of about 40% were obtained.

The presence of water affects thermal degradation by means of reducing the activation energy and promoting hydrolysis. Wood degrades much faster when heated in steam or water, rather than when heated in the dry condition (Stamm, 1964). Heating wood in the presence of water or steam causes the formation of organic acids, mainly acetic acid, which catalyses the hydrolysis of hemicellulose to soluble sugars, thus speeding the degradation of the hemicellulose (McGinnis *et al.*, 1984). The effects on wood components caused by this hydrothermal treatment include hemicellulose depolymerisation, cellulose alteration (mainly in connection with its physicochemical features) and chemical alteration of lignin (which facilities further delignification with organic solvent and /or alkaline solution) and the effect of hydrothermal treatment on hardwood, owing to the their higher contents in acetyl groups, which results in higher concentrations of acetic acid during treatment with softwood. Garrotte *et al.* (1999) and Zaman *et al.* (2000), studied the chemical composition of steamed pine and birch wood. Pine and birch feed stocks were heated at 200-230°C for 3-4 h in a steam atmosphere to stabilise the material against fungal attack. The lignin, the extractives (extraction was performed by acetone and dichloromethane), oxygen, the carbon, the hydrogen and the nitrogen content of the treated wood were determined. As temperature and duration of the treatment decreased. Oxygen and hydrogen ratio decreased while carbon ratio increased and nitrogen ratios remained unchanged. Decrease in oxygen showed a decrease in

carbohydrate content, which is rich in oxygen, and an increase in carbon ratio showing that lignin content remained unchanged. Little difference between the two species in wood composition was observed, the difference mostly might result from the differences in the chemical structure and the content of the hemicellulose in soft wood (pine) and hard wood (birch). The pentosans of hardwoods are more susceptible to thermal degradation than the hexosans of hardwoods. In the case of birch, the mass proportion of extractives increased in heated wood so that the extractives amount after heating at 220°C was more or less tree times as great as in the unheated wood. Such an increase wasn't observed with pine.

In the Netherlands, a heat treatment based on the combination of dry heating and hydro-thermal treatment with the purpose of upgrading wood (Plato process) has been developed. This treatment principally consisted of two steps with an intermediate drying operation. In the first step (hydrothermolysis) of the process, green or air dried wood is treated at typically between 160°C -190°C under increased pressure. A conventional wood drying process is than used to dry the treated wood to low moisture content (*ca.* 10%). In the second step (curing), the dry intermediate product is heated to temperatures typically between 170°C - 190°C. Boonstra *et al.* 1998, and Tjeerdsma *et al.* (2000), studied the effect of the treatment conditions on increasing the decay resistance of wood Plato treated for 1-16 hours against soft rot, white rot (*Coriolus versicolor*) and brown rot (*Coniophora puteana*) and compared the effectiveness of the Plato-process with a dry heat treatment process for 1-16 hours. The Plato treatment was found to be more effective, compared to a dry heat treatment, in improving the decay resistance. Using UV-spectroscopy, Sander *et al.* (2001), studied the effect of a two-stage treatment on the lignin of Norway spruce wood. Significant changes in the absorption spectra of the treated wood lignin were observed. De-masking reactions within the S2 layer resulting from hydrolysis of carbohydrates and side chain reactions were explained to be the probable reason for the spectral changes. A severe reduction in absorption at the lower end of the spectra towards 250 nm was observed. The reduction was attributed to changes or even splitting of biphenyl structures of lignin.

Since the cleavage of C-C bonds takes place at higher temperatures than those used in Plato treatment, more accurate studies by NMR are required to confirm their interpretation of the lignin spectra.

Kamdem *et al.* (1999), investigated the decay resistance of heated wood, treated at a range of temperatures from 200 to 260°C in a nitrogen atmosphere for 1 to 24 hours against white rot and brown rot fungi. Two hardwoods (poplar and beech) and two softwoods (pine and spruce) were used. Heated and unheated samples were tested for decay using an agar block test and a soil block test for 6, 8, or 12 weeks respectively. Significant weight losses due to decay were observed. Bending strength and lignin content (insoluble lignin), acid number and were also determined. Heat-treated samples showed a higher lignin content and a lower acid number, compared to untreated control, indicating the degradation of some hemicellulose and extractive compounds. The data from the bending test showed that the heat treatment might result in a 10% to 50% reduction in MOR. Swelling of heated wood were measured by immersion in water and in an alkali solution containing 18% sodium hydroxide for 24 hours. The lack of reduction in swelling of heated wood in the solution indicated that the dimensional stability of thermally treated wood could not be totally caused by the formation of ether cross-links but that other causes need to be studied.

Retification, which is a dry thermal treatment of wood at temperatures typically between 200 and 270°C in an inert atmosphere, has been developed and is applied on an industrial scale in France. Retification is claimed to improve the resistance properties of wood to decay agents and improve dimensional stability, while preserving its physico-mechanical properties (Gohar and Rene *et al.*, 1998). By using a small retification reactor equipped with a spectrophotometer and weighing device, and Rajohnson *et al.* (1994), investigated the effect of main treatment parameters (time and temperature of treatment, initial moisture content, pressure, wood species) on the kinetics of weight loss of wood and the evolution of temperature. The kinetics of gas production (CO, CO_2, CH_3COOH) which result from the degradation of wood component, was correlated with weight loss.

Troya and Navarrete (1994), studied the degradation of retified wood through ultrasonic and gravimetric techniques. The samples were submitted to a thermal treatment of 220 to 260°C at four time periods (5,10,15 and 20 hours). Heat- treated samples were exposed to *Serpula lachrymans* for a five-month period. The optimum result was obtained at 240°C and 5 hours of treatment, however the results obtained from 220°C during 15 hours were also satisfactory. In an effort to indicate the inhibiting effect of retification on wood of

susceptible species mainly spruce, fir and poplar, to destroying fungi, Dirol and Guyonnet (1993), exposed wood to conditions of light pyrolysis (250°C) under a dry nitrogen flow (1 atm) for 10 or 20 min (in the case of poplar only 20 min). The decay resistance of the treated wood was studied against a white rot fungi, *Coriolus versicolor*, two brown rot (*Coniophora puteana* and *Gloeophylum trabeum*) and soft rot fungi only for poplar. The wood species, especially poplar, showed very good resistance against the fungi. The products, mainly a mixture of non-condensable gases, retified wood and a yellowish liquid were also chemically analysed. Analysis of the incondensable phase indicated that carbon monoxide evolves instantaneously, carbon dioxide was subsequently detected. Analysis of effluent products were carried out by chromatography and showed that the liquid was composed of water (21%), acetic acid, formic acid (5%) and methanol (3.5%). Analysis of retified wood indicated that hydrogen and oxygen ratios decreased considerably when compared with that of carbon. Analysis of retified wood showed that the reduction of weight after the treatment resulted in loss of water of constitution together with pentosans (hemicellulose) is accompanied by dimensional stabilisation. Bourgois *et al.* (1989), analysed torrefied pine wood (sawdust) which was heated for 30 minutes at temperatures of 240 to 290°C under an atmosphere of nitrogen (1 atm). The analysis showed that lignin and carbon content of the treated wood increased with increasing temperature and time of treatment, whilst oxygen and hemicellulose and content decreased. Temperature of the treatment had the most effect on the nature of the obtained products.

Increase in the pressure of heat treatment accentuates thermal degradation, Burmester (1974), tried to optimise the heat stabilisation process by treating moist wood specimens under pressure in an inert atmosphere. He called this process Feuchte/ Waerme/ Druk-Behadulng''(FWD): translated in English, Moisture/heat/pressure- treatment (MHP). Burmester achieved stabilisation effects up to 50% and found only small losses of wood strength. He also exposed particleboards made with MHP- treated chips and isocyanate binder to decay tests against *Coiniophora puteana* and *Poria vaillantii.* All boards made from MHP-treated chips showed improved decay resistance. In boards made from chips treated for 5 hours, the weight losses after four months were not significant. Moisture content remained lower than the 16% necessary for fungal growth. Geibeler (1983), studied dimensional stabilisation of solid wood and wood composites (ply wood and particle wood) produced by MHP treatment. The treatment was carried out in 1.8 m^3

reactor at temperatures of 180-200°C under a nitrogen pressure (8-10 bar). The treatment resulted in reduction in swelling and shrinkages of 50 to 80% and improvement in resistance against fungi and insects as well as a 10% loss of strength. Feist (1987), tried to improve weathering behaviour of beech and spruce by reducing their hygroscopicity. using the procedure described by Geibeler (1983). The samples were treated under nitrogen pressure (10 bar) at 175 and 185 °C for 2 and 3h respectively. Contrary to the recommendation of Burmester, wood moisture content was kept low (8-10%) to avoid drying damage. The treated and untreated specimens were subjected to artificial and natural weathering. Beech had a significantly lower hygroscopicity and improved dimensional stability after treatment and was more resistant against weathering than the unheated samples. Although the hygroscopicity of spruce was also significantly reduced by heat treatment, weathering resistance was decreased.

One of the heat treatment methods of wood that have been studied in order to increase dimensional stability and decay resistance is oil heat treatment. In this method, wood is heated at an oil bath with high temperature. Because of the absence of oxygen and water in oil heat treatment, which causes oxidation and hydrolysis respectively, mechanical properties are reduced less than when heating in the presence of air or steam (Troughton and Rozon, 1974). Sailor *et al.* (2000), examined the effect of oil-heat treatment on the dimensional stability of pine and spruce wood and their resistance against *Coniophora puteana.* Specimens with a moisture content of 6% were heated at three temperatures (180°C, 200°C and 220°C) at ambient pressure and in the absence of oxygen in an oil bath of refined linseed oil for 15 minutes. In order to load the desired oil, the specimens were cooled off in the oil bath for 15 minutes. Heat treatment in an air atmosphere for 4.5 hours at the corresponding temperature was also performed for comparison. Specimens for the examination of swell and shrink improvement (ASE) were exposed to a temperature of 20°C and a relative humidity of 35%, 65% and 85% after the oil-heat treatment. In addition, the MOE and impact bending were determined. The improvement in the ASE of the specimens that were treated at 220°C was similar for both types of treatment, (about 40%). When the humidity was increased, the ASE became lower. Untreated spruce controls showed a 48% loss of mass and pine controls a 40% loss of mass. The decay resistance of the heat-treated wood was improved with increasing temperature. The combination of plant oils and heat treatment led to a greater improvement in the resistance of wood to *C. puteana.* A loss of mass of less than 2% was

found in the case of pine sapwood heated in oil at 200°C. With spruce, on the other hand, a notable increase in decay resistance was only obtained at 220°C. There was no reduction in the values for the modulus of elasticity of untreated coniferous wood with either heat treatment process. On the other hand, the impact bending strength was noticeably reduced. Oil-treated wood showed a reduction of 49% in the impact bending strength and air heat-treated wood a reduction of 53% in the impact bending strength as the treatment temperature increased. Leithoff and Peek (2001), studied the effect of oil heat treatment on the decay resistance of bamboo against basidomycetes and soft rot, and on its mechanical properties. The specimens were treated at 180°C, 200°C and 220°C for 30 min, 60 min and 120 min (real treatment time at nominal temperature) in hot hemp seed oil. Oil heat treatment above 200°C significantly increased the decay resistance of bamboo against basidiomycetes, as well as soft rot but the shock resistance was considerably reduced. Oil treatment caused no changes or only a slight increase in MOE.

2.12 Mechanisms by which heat treatment reduces the hygroscopicity of wood

Despite some studies on the reasons for a reduction in the hygroscopicity of wood by heat treatment, the precise mechanism by which this occurs is not understood.

Reduction in hygroscopicity with heat was at first believed to result from a cross linking reaction, in which water is eliminated between hydroxyl groups on two adjacent cellulose chains, with the formation of ether linkages. This has been extensively disproved by Seborg (1957), who disproved this by showing that swelling in pyridine and in an 18 percent aqueous solution of sodium hydroxide is not decreased (unlike the swelling in water) by the heat treatment. If ether linkages had been formed, swelling should have been reduced in all three solution. Subsequently, Stamm and Baechler (1960), suggested that the thermal treatment of wood result in furfural polymers of breakdown sugars, which are less hygroscopic towards than the hemicellulose from which they are formed.

Tjeerdsma (1998), Sivonen *et al.*(2002), proposed that cross linking of wood due to heat treatment is the most important reason of the reduction in the hygroscopicity of heated wood.

Kamdem *et al.* (1999), suggested that stress relaxation stored between wood microfibrils and the wood matrix following the removal of hemicelluloses could be one of the probable reasons for the reduction in the hygroscopicity of wood due to heat treatment and criticized the theory put forwarded by Tjeerdsma. Kamdem (1999), showed that heated wood soaked in NaOH swelled as much as that for untreated wood, thus, he argued that if there was any ether cross linking as suggested by Tjeerdsma,(1998) and Sivonen *et al.* (1999), the heated wood should have shown a reduction in swelling compared to untreated wood as it showed in water.

By FTIR spectroscopy of heated wood, Nakano and (2003), proposed chemical changes (a reduction in hydrophilic sites) in wood as results of heat treatments at temperatures below 250°C could be the main reason for the reduction in the hygroscopicity of wood.

2.13 Pore structure of heated wood

By using liquid state NMR spectroscopy technique, Hietala *et al.* (2002), studied cell wall microvoid size and distribution heated wood and reported heat treatment increased pore and distribution of pore size with diameter but didn't change the cell wall size of wood.

2.14 The mechanism by which heat treatment imparts decay resistance to the wood

Several mechanisms have been proposed to explain why heat treatment imparts decay resistance to wood:

Some toxic material produced as result of heat treatment could participate in the decay resistance afforded

The moisture content of heated wood is below the limit required by fungi. Some researchers support theory that heat treatment reduces moisture content below the limit require by fungi (Stamm *et al* , 1960, Tjeerdsma, 1998 and 2000).

Wood modification changes the cell wall polymers in such a way that fungi can not recognise the wood. This has mostly been attributed to the removal/modification of hemicelluloses.

Tjeerdsma (2000), observed that decay by white rot fungus was found to be less dependent on the process conditions in the curing step of Plato treatment. The increased resistance by white rot already was achieved after the hydrothermal step of the process, demonstrated by the strong initial decrease in weight loss. They suggested that the reduction of hygroscopicity as a result of heat treatment might increase decay resistance of wood and reduction of hemicelluloses might be the main cause of the increased resistance against white rot fungi which depend upon hemicelluloses to degrade the cellulose.

Dirol and Guyonnet, (1993), and Kim *et al.* (1998), suggest that degradation of hemicelluloses (which is normally an easily digestible substrate, especially during the early stages of decay) by heat treatment is the main reason for the increased decay resistance.

Kamdem and co-workers (2000), investigated the presence of potentially toxic compounds in pine and poplar wood heated at temperatures varying from 200 to 250°C depending on species for 6h. The heated samples were extracted by organic solvents (acetone and dichloromethane). The extractives were then analysed by GC/MS and NMR. The formation of some toxic polynuclear aromatic hydrocarbons compounds such as derivatives of phenanterene, as well as other classes of polyaromatic compounds in very low amounts, were detected. They suggested that the presence of all such compounds contributes, perhaps to a substantial extent, to the reported resistance of heat-treated timber to fungal and other biological attack. Subsequently, by studying the decay resistance of heated wood extracted by acetone, water and chloroform separately, Kamdem *et al.* (1999), refuted the possibility of contribution of any toxic material which might be produced as result of heat treatment in the decay resistance.

Weiland and Guyonnet, (2003), discussed that hemicellulose removal cannot be the possible reason for the improved decay resistance. They suggested that lignin modification due to heating in a way that degrading enzymes of fungi can not recognise wood can be the main reason for the improved decay resistance.

2.15 Chemical Modification of wood

The chemical modification of wood is a process where wood is treated with a chemical that produces some change within the cellular structure. These changes can be as a result of the chemical bonding within the cellular structure such as esterification or through of blocking of chemical and physical processes by a non-bonded material such as grafting wood with MMA and other monomers.

2.15.1 Chemical modification of wood through coupling agent

2.15.1.1 Coupling agent

A typical silane coupling agent may be simplified to the general form of X- Si-OR where X is an organofunctional group, and OR is a hydrolysable group (*e.g.* methoxy). Both ends of the silane molecule may undergo chemical reaction, ether separately or simultaneously. The OR group can be changed or hydrolysed without altering the X group, or the X group may be modified without changing while retaining the X group. Chemical modification of X may precede application to the surface or take place after silylation.

2.15.1.2 Coupling agents and solid wood

The issue of whether a particular coupling agent is actually chemically bonded to the wood components or other organic surfaces is still a debatable issue. Other types of

interactions, such as physisorption or hydrogen bonding probably play a significant role too. The Si-O-C bond is unstable to hydrolysis (unlike the Si-O-Si), especially in an acidic environment.

The most common type of coupling agents used industrially are alkoxysilanes (Pluddemann , 1982). Of the alkoxysilanes, γ-methacryloxypropyl trimethoxysilane (TMPS), and vinyl trimethoxy-silane (VTMS) were used to treat solid wood (Ogiso *et al.*, 1994). Ogiso *et al.* (1994), treated wood with a methanolic solution with a concentration of 50% in the presence of a free-radical catalyst (benzoyl peroxide) at a curing temperature of 80°C for six hours. A weight gain of 8% was obtained. But, the chemical was mostly extracted when the treated wood was water extracted for 10hr. In the contrast with VTMS, with TMPS at the same treatment conditions, a higher WPG about 40% was gained. Rozman *et al.* (1997), treated rubber wood with methanolic solutions of γ-methacryloxypropyl trimethoxysilane, followed by curing at 110°C. The WPG of TMPS was increased when the moisture content increased. But, the WPG was was reduced when satutaed wood was used. Miyasita (1999), impregnated wood with, γ-methacryloxypropyl trimethoxysilane (TMPS) in solution of methanol and water and then heated at 80°C in the presence of 1% benzoyl peroxide. A weight gain of 38% and a volume increase (VC) of 2.5% was obtained.

In addition to the coupling agents containing vinyl groups mentioned above which are capable of free radical polymerisation, solid wood has been treated with some other organo-functional silanes (sol-gel process) which don't have the vinyl group such as Propyl trimethoxy silane (PTMS), 3-(trimethoxysilyl)propyl (carboxymethyl) decylmethyl ammonium hydroxide salt (TMSAH) and –heptadecafluorooctylethyl-trimethoxy-silane (HFOETMOS), 3,3-trifluoropropyl-trimethoxysilane (TFPTMOS) and IPTEOS, β-(3,4-epoxycyclohexyl) ethyl trimethoxysilane (EETMOS). Goethals (1994), treated wood with an aqueous solution of PTMS at 100 °C for 48 hr.

Wood has also been treated with tetramethoxysilanes (TMOS) tetraethoxysilanes (TEOS) and tetrapropoxysilanes (TPOS) which don't have any organofunctional group and produce inorganic glasses consisting of pure polymeric SiO_2 (Saka *et al.*,1992). Saka mostly used TEOS to prepare a sol gel for his studies. Saka *et al.* (1992), treated wood,

which either had been pre-conditioned at different relative humidities or water impregnated, at a temperature of 105°C for 48 hr. The WPG's increased with the increasing wood MC.

Chlorosilanes have also been used for the treatment of solid wood. Cholorosilanes react with wood very rapidly, but the main disadvantages of this reaction are the formation of hydrochloric acid (Stevens, 1985). Stevens used the same curing temperature and time as those used for the treatment at solid wood with alkoxysilanes but Zollfrank (2001), treated wood with a cholorosilane TMS-Cl at room temperature. Pyridine was used as a catalyst and solvent for the reaction. SEM-EDAX analysis showed that reaction with the wood interior had occurred. The formation of a covalent bond Si-O-C was shown by FTIR. Increase at the intensities of bands at 1125, 883 and 840 cm^{-1} were observed and attributed to Si-O-C bond.

In another attempt, Zollfrank *et al.* (2002), used (Trimethylsilyl)imidazole and Trimethylsilyacetamide to treat soft wood and hard wood. Successful silylation of softwood and hardwood were confirmed by EDAX, and FTIR studies. By means of an SEM study, the reaction site was determined to be on the lumen-faced side of the cell wall. Half of the S_2 wall appeared to be silylated.

2.15.1.3 Dimensional stability of silane treated wood

Silane treatments have been reported to improve dimensional stability of the wood. Increases in dimensional stability of wood, depend strongly on the location of the silane coupling agent in the wood (Saka, 1992). The more the chemicals deposit within cell wall, the greater improvement in ASE that is obtained. If the chemicals don't penetrate into the cell wall, no improvement in ASE is obtained by the treatment, even at very high WPG's . An ASE of about 30% was reported for a weight gain of 10% of TEOS after 1 cycle. The lowest improvement in dimensional stability was obtained when water used as a solvent (Goethals, 1994). Stevens reported a maximum ASE of 24.5% for a WPG of 24.4% when PTMS treated pine wood was exposed to five water soaking /drying cycles. Since the authors didn't use any alcohol or acid to stabilise the silane in water, the oligomerisation of the silane in the water could have reduced the penetration of the

chemical into the cell wall. The highest ASE obtained was found by using IPTEOS compounds (about 60% at 20% WPG) (Saka and Yakake, 1993).

For the coupling agent TMPS, the highest ASE was reported by Schneider and Brebner (1985) which was about 70% for TMPS treated pine wood with a WPG of 32%. But the ASE was reduced to about 40% after 4 cycles. An ASE of 42% was obtained when a solution of methanol and water was used as the solvent for the TMPS treatment with Sugi wood (Miyashita, 1999).

2.15.1.4 The hygroscopicity of silane treated wood.

TMPS modified wood was reported to reduce the moisture content of wood but not as effectively as it improved the dimensional stability of wood (Schneider *et al.* 1985). Goethals and Steven (1994), reported that PTMS treatment hardly reduced EMC.

2.15.1.5 Decay resistance of silane treated wood

The biological effectiveness of silanes, bulking the cell wall (Rozman, 1997), is an interesting area for research, which hasn't been studied extensively. Decay resistance of solid wood treated by silane coupling agents having vinyl groups has not been studied, although decay resistance of organo-silanes and pure sol gel modified wood has been studied.

The decay resistance of propyl trimethoxy silane treated wood was studied by Goethals and Goethals (1994). They reported that the treated wood showed poor decay resistance against basidomycetes. According to the data obtained by Tanno *et al.*(1998), wood composites based on polysiloxane bonds of TEOS (sol gel composites) at a WPG of about 6% didn't impart decay resistance to wood. Using silanes such as the amphoteric quaternary ammonium compound 3-(trimethoxysilyl)propyl (carboxymethyl) decylmethyl ammonium hydroxide salt (TMSAH) and –heptadecafluorooctylethyl-trimethoxy-silane (HFOETMOS) containing NH_4 and fluorine respectively, have been found to improve the decay resistance of treated wood against fungal attack. The

chemicals lost some of their activity against brown rot fungi. In order to improve the resistance of the chemical to leaching, they fixed the chemicals with TEOS with the SiO_2-TMSAH and especially the SiO_2-TMSAH-(HFOETMOS) composite at low Wag's showing high resistance against brown rot and white rot. The composite, especially SiO_2-TMSAH-(HFOETMOS) composites showed high decay resistance when they were exposed to an un-sterile soil test.

The decay resistance of chlorosilane treated wood was examined against *Coriolus versicolor* (white-rot) and five brown-rotters (Owens *et al.*, 1980). All treated samples showed significantly lower weight loss than untreated controls. Tetrachlorosilane ($SiCl_4$), methyltrichloro silane (CH_3SiCl_3), dimethyldichloro silane ($(CH_3)_2SiCl_2$), methyldichlorohydrogen silane (CH_3SiHCl_2) and trimethylsilyl chloride $(CH_3)_3SiCl$ were tested, applying basic hydrochloric acid acceptors (triethylamine, formamide, dimethylformamide) as well as hexane as solvent (Stevens, 1981 and 1985). The decay resistance of wood treated with $SiCl_4$, $(CH_3)_3SiCl$ and CH_3SiCl_3 was very low, while CH_3SiHCl_2 and $(CH_3)_2SiCl_2$ showed a considerable reduction of weight loss (5-10% compared to 25-34% in the controls). The efficacy of chlorosilanes against blue stain fungi and moulds was low.

Of the other silicon compounds, Furuno *et al.*, (1991), studied the decay resistance of sodium silicate impregnated wood follow by precipitation using aluminium sulphate or calcium silicate. The composite formed by using sodium silicate showed relatively poor decay resistance, while the composite formed with calcium chloride didn't impart any decay resistance to the wood and was leached out.

2.15.1.6 Mechanical properties of silane modified wood

Cross linking of wood by TMPS caused an improvement in mechanical properties of wood (Rozman, 1997). This increase could be because of the filling of wood cavities with the cross linked polymers. Reduction in hygroscocipity of silane modified wood could be another reason for the improved mechanical properties.

2.15.1.7 Heat resistance of silane treated wood

One of the properties of siloxane linkage is good stability of the link against high temperatures in the absence of oxygen. Thus, it's expected that polysiloxanes show high temperature stability in an nitrogen environment (Brodson, 1977). The heat resistance of silane modified wood in air, nitrogen, and oxygen have been studied extensively by Saka, (1992, 1993, and 2001). The heat resistance of wood was increased when a silane treatment was applied. According to Saka's work, a better protection to wood is obtained when the silane is located in the cell wall.

2.15.2 The esterification of wood and decay resistance

Decay resistance of wood esterified by acetic anhydride has been studied extensively. It has been accepted that the chemical modification of wood through esterification is able to provide protection against fungal attack. It is generally reported that acetylation to a weight percentage gain of *ca.* 20% is required before complete protection is achieved.

Goldestein *et al.* (1961), studied the decay resistance of acetylated Ponderosa pine using acetic anhydride in xylene (non swelling solvent) against six basidiomycete fungi, five brown rot and one white rot. A WPG of 17% was reported to be sufficient to provide decay resistance.

Takhashi, *et al.* (1989), studied the decay resistance of Japanese red pine, cedar, and beech which were acetylated with undiluted acetic anhydride to different WPG's. They exposed the acetylated wood to brown fungi *T. palustris, Serpula lacrymans* and the white rot fungus *C. versicolor* and to soft rot fungi in an un-sterile soil test. Weight loss to *T. palustris,* in all wood species was almost zero at 20% WPG. For *C. versicolor*, 6% WPG was sufficient to protect softwood while hardwoods required 12-15% WPG. In the cases of *S. lachrymans* the soft rot, the effect of acetylation was found to be intermediate between that for T. *palusteris* and *C. versicolor.*

Beckers *et al.* (1994) exposed Scots pine acetylated with undiluted acetic anhydride to brown rot fungi (*C. puteana, G. trabeum and P. placenta*), a white rot fugus (C. *versicolor*) and soft rot fungi (un-sterile soil test with 12 months exposure time). They found WPG's of 18% (*C. puteana, G. trabeum*) and over 20% (*P. placenta*) and 12.5% (*C. versicolor*) were required to prevent decay in pure culture tests, and 11% was required for full protection of in the soft rot test.

Using low and high moisture content soil block tests, Forster (1998), found that acetylation to a WPG of 17%, provided full protection against the white rot fungi *T. versicolor* and *P sanguineus*, and a WPG of 24% for the brown rot fungi *C. puteana,* and *G . trabeum,.* Insignificant difference were found between the thresholds for the low and high moisture tests.

Suttie *et al.*, (1999), exposed Scots pine sapwood modified by acetic, butyric, or hexanoic to decay tests with a high moisture content environment against a white rot fungus *T. versicolor*, and three brown rot fungi (*C. puteana, G. trabeum* and *P. placenta*). Resistance against soft rot fungi was also assessed using a modified ENV 807 stake test in un-sterile soil. In this, it was found that a threshold of *ca* 23% was required to ensure protection, regardless of the anhydride used.

Papadopoulos *et al.* (2002), studied the decay resistance of wood modified with linear chain carboxylic acid anhydrides namely, acetic, propionic, butric, valeric and hexanoic anhydride against a brown rot fungus *(C. puteana)* and reported that with all anhydrides a WPG of 18% following reaction ensured complete protection.

Using a field test on acetylated samples, Larsson Brelid *et al.* (2000), found that an acetyl content of 20 % prevented attack by brown, white and soft rot fungi. In the laboratory un-sterile soil tests on acetylated ministakes, with a slightly lower acetyl content (18.5 %) was required to provide full protection against fungal attack by brown, white and soft rot fungi.

For acetylated wood, a lower WPG was required for the full protection of wood against white rot reported. Beckers *et al.* (1994) and Ohkoshi *et al* (1999) studied the decay

resistance of acetylated wood against *C. versicolor*. They reported a WPG of 12% with the white rot fungus as the threshold level of protection for wood modified with acetic anhydride.

2.15.2.1 The reason for the decay resistance of the esterified wood through esterification

The mechanism by which modification imparts decay resistance has not been fully explained. Several mechanisms have been put forward to the protection afforded by wood modification:

- The fungi are not able to recognise the substrate because the hydroxyl groups have been substituted.

- The moisture content of the cell wall is below the limit required by the fungi.

- Blocking of the cell wall micropores by bonded adduct prevents access of the degrading agents to the cell wall interior.

Rowell (1982), emphasised the importance of hydroxyl substitution over that of suppression of cell wall moisture content and criticised the importance of lignin substitution in the protection of wood from decay.

Takahashi (1989), proposed that preferential substitution of lignin during the acetylation of wood could be the cause of the higher resistance of acetylated wood to white rot fungi. Rowell (1996) has argued that although brown rot decay cannot proceed when the hemicellulose component is protected, it is the moisture of the wood cell wall that is the critical factor in protecting wood against decay fungi. He suggested that protection is due to water not being able to get close to the glycosidic bonds in wood, and that these bonds in their dry state cannot be broken by fungal action (Rowell, 1996: cited by Suttie, 1997).

Cardias (1992), criticised the theories of Rowell and co-workers, and proposed that that the extent of protection against decay imparted by modification depends upon the

reduction of the absorbed water in the modified wood, and by the physiological capacity of the decay fungi to tolerate water stress.

By correlating volumetric swelling due to water soaking and FSP of modified wood the decay weight loss of modified due to white rot and brown rot fungi at different WPG's Forster (1998), reported that in most cases , a good correlation between the weight losses and the volumetric swelling due to water soaking were obtained. In addition to this, good agreement between the curve for different modification was obtained but this was not observed when FSP was plotted against weight loss due to decay. Thus, he concluded that a blockage in the cell wall transient micro-pores could be the main reason for the decay resistance of the modified wood against white and brown rot fungi.

Ibach and Rowell (2000), proposed two main mechanisms by which decay resistance afforded to wood which are: substrate modification in such a way that specific enzyme reactions cannot take place and a reduction in cell wall moisture content below the limit required by fungi. Ibach and Rowell (2000), studied the decay resistance and hygroscopicity of propylene oxide, butylene oxide and acetic anhydride modified wood, and found a positive correlation between a reduction in the moisture content of wood and weight loss due to decay for acetylated and butylene oxide modified wood. Thus, they proposed moisture exclusion as the mechanism for the decay resistance of modified woods. But, propylene oxide imparted decay resistance to wood without reducing hygroscopicity. Thus, they proposed that the substrate modification in such a way that specific enzyme reactions cannot take place could be the mechanism for the decay resistance. In another work in studying the decay resistance of epichlorohydrin modified wood, Ibach *and et al.* (2000), suggested substrate modification could be the reason for the decay resistance imparted by the modification because the modification didn't reduce the hygroscopicity of wood.

2.15.2.2 Esterification and hygroscopicity

The hygroscopicity of wood modified with anhydrides has been extensively been studied.

Stamm and Tarkow (1954), reported that acetylated wood with an acetyl group content of 30% (W/W) showed a 67% reduction in hygroscopicity compared to unmodified wood when it was exposed to 95% relative humidity.

Using the Hailwood-Horrobin model to fit isotherms to sorption data, Spalt (1958) studied the sorption behaviour of sixteen unmodified wood species and for modified white spruce acetylated to a 32% acetyl content. The acetylated sample showed a reduction by 63% in EMC at saturation. By separating isotherms into the two components (monolayer and multilayer), he found that when 60% of the hydroxyl groups of wood were acetylated, a 62% reduction in surface sorption and 67% reduction in the capillary condensation took place. However, he calculated that 76% of the reduction in the total water sorbed was due to blocking of the wood cell wall micro-capillaries .

Popper and Bariska (1972), measured the sorption properties of white fir modified with acetic and phthalic anhydride. Both the anhydrides reduced the hygroscopicity (the total water in wood) of the wood but, monolayer sorption isotherms of phthalic anhydride modified wood were similar to untreated wood. This was attributed to the hydrophilic groups introduced during reaction with phthalic anhydride. Reduction in sorption due to phthalic anhydride modified wood was attributed to bulking the cell wall due to the adduct, thus causing a reduction in the poly-molecular adsorption.

The sorption properties of Corsican pine and beech modified with mono- and difunctional isocyanates were measured by fitting isotherms using the Hailwood-Horrobin model (Martains,1992). He proposed three mechanism by which the modification reduced the hygroscopicity:

- Blocking hydroxyl groups due to the modification affecting monolayerr sorption.
- Bulking of the cell wall due to the adducts affecting poly-molecular sorption
- Cross-linking limiting swelling of wood (in the case of difunctional isocyanates)

Papadopoulos (2001), measured the sorption characteristics of Corsican pine and Scots pine modified with linear carboxylic anhydrides with different sizes (the smallest was acetic anhydride and the biggest was hexanoic anhydride). Increasing WPG caused a reduction in the sorption. He attributed this mostly to the bulking of the cell wall due to the adducts. No difference between the anhydrides having different sizes in reducing the hygroscopicity was observed. Monolayer sorption isotherms were very similar for all anhydride modifications, despite the significantly lower number of hydroxyls blocked, especially with the biggest anhydride (hexanoic) studied. This was attributed to the site shielding by the large hydrophobic chain introduced into the wood cell wall. This had been reported by Martins (1992) who studied the sorption behaviour of Corsican pine and beech modified with butyl (molecular weight 99.13) and octadecyl isocyantes (molecular weight 295.1). However, the monlayer de-sorption isotherms were found to differ slightly, with octadecyl isocyanate modified wood sorbing more water at the monolayer. It was concluded that at saturation, the ocadecyl chain may move slightly away from the sorption sites within the cell wall, making some extra sites available for sorption.

2.15.2.2 Esterification and dimensional stability

Many studies have studied the dimensional stability of esterified wood, especially with acetic anhydride. In all cases, improvements in dimension stability proportional to an increase in WPG or acetyl content have been reported.

Hill and Jones (1996), found that the ASE of wood modified with a variety of linear carboxylic anhydrides was governed by the WPG of the modifying chemical, regardless the length chain of the anhydride involved. They achieved ASE's approaching 90% for wood modified with linear anhydrides to 30% WPG. A dimensional stability of 100% was reported by Risi and Arseneau (1958), for a WPG of 60%, although the ASE (%) fell when the modified wood was exposed to subsequent water soak/ oven-dry cycles.

Many researchers have agreed that bulking of wood due to esterifcation is the primary reason for the improvement achieved by the modification (Stamm and Tarkow, 1947, Hill and Jones, 1996, Cetin, 1999, Papadopoulos, 2001). This was concluded because for all the cases, the same ASE at a comparable WPG was obtained with the acetic anhydride

modified wood and for wood modified with anhydrides having higher chain lengths such as butyric (Stamm and Tarkow (1947), Hill and Jones (1996) and heptanoic anhydride (Hill and Jones (1999).

The interesting point is that bulking of wood might be related to a decrease in the cell wall micropore structure of modified wood. This would result in a decrease in the accessibility of the cell wall to fungal degrading agents and also reduce the hygroscopicity of wood because of a reduction the cell wall space required for capillary sorption (see Section 2.7.3.) and increases in dimensional stability. Thus, some connections between an improvement in dimensional stability and decay resistance must exist. Stamm (1960), correlated dimensional stability to decay resistance and reported when an ASE of 70% is achieved by acetylating, decay is completely prevented. Foster (1998), obtained nearly the same results as obtained by Stamm for acetylated wood.

Chapter 3

Modification of wood

3.1 Wood samples

Corsican pine sapwood, which is classified as non-durable, was used for these studies. Kiln dried boards were cut to samples of two sizes depending on the fungal test design.

For the pure culture tests, blocks of dimensions 5mm (longitudinal) x 20mm (radial) x 20mm (tangential) were used. This size was chosen in order to make sure that even penetration and distribution of the chemical in wood blocks occurred. Effective penetration and distribution of treatment chemicals is necessary studying the mechanism by which chemical modification imparts decay resistance to wood (Forster, 1998). In addition, samples with a longitudinal thickness of 5mm have been frequently used for the study of the decay resistance of wood treated with methanolic solutions of silanes (Tanno *et al.*, 1997 and 1998) and with aqueous solutions (Goethtals and Stevens, 1994).

For the soft rot test samples of dimensions 100mm (long.) x 5mm (rad.) 15mm (tang.) were used.

For the field test samples of dimension 200mm x 40mm x 40mm (long. x rad. x tang.) were used.

3.2 Chemicals

3.2.1 Silane coupling agents

γ-methacryloxypropyl trimethoxy silane (TMPS) and vinyl trimethoxy silane (VTMS) were chosen for these studies (Table 3.1 and Figure 3.1). These chemicals were supplied from Aldrich and Fluorochem, respectively.

Table 3.1 Physical properties of the silanes used in this study

Silane	Boiling point (°C)	Density (g cm^{-3})	Molecular weight	Molar volume (cm^3 mol^{-1})
TMPS	190	1.045	248.35	238
VTMS	123	0.980	136.25	139

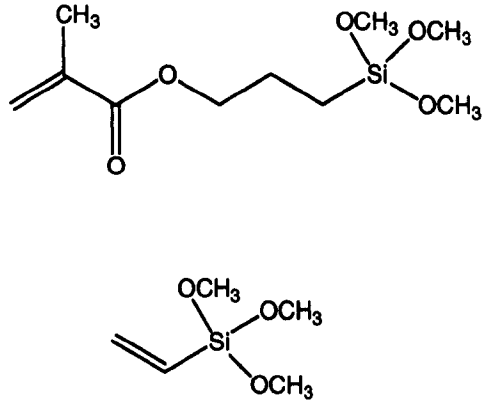


Figure 3.1: The structures of the silanes used in this study, (a) TMPS and (b) VTMS

As explained in Chapter 2, silane-coupling agents are capable of polymerising *via* their hydrolysed silanol groups and their organofunctional group. Trialkoxysilane in the presence of moisture hydrolyses to give the corresponding silanol (Figure 3.2). Different models in the literature have been suggested for the reaction of lignocellulosic materials with silanol, which are shown in Figures 3.2-3.5.

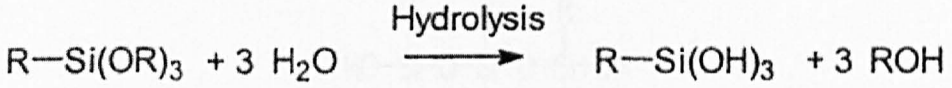


Figure 3.2: Hydrolysis of alkoxysilane to silanol

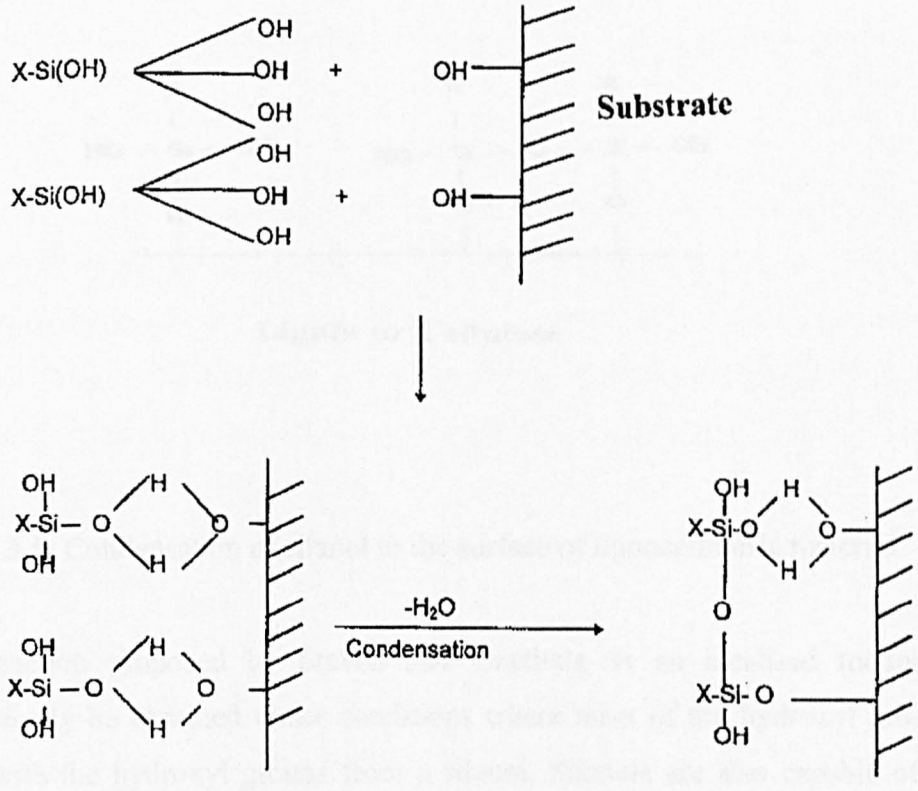


Figure 3.3: Proposed silane bonding mechanism: Silane to fibre surface (Ahmad Fuad et al., 1994 in Abdul Khalil, 1999).

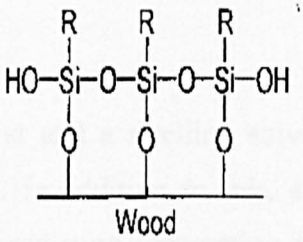


Figure 3.4: A model for the condensation of silanol to wood (Goethtals and Stevens, 1994)

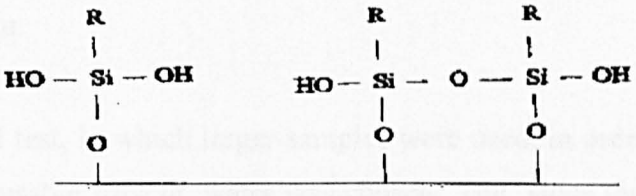


Figure 3.5: Condensation of silanol to the surface of lignocellulosic material

The reaction proposed by Steven and Goethals, is an idealised model that could theoretically be obtained under conditions where most of the hydroxyl groups of wood react with the hydroxyl groups from a silanol. Silanols are also capable of condensing with other free silanols to form polysiloxanes. In the silylation of wood, the use of high temperatures (above 100°C) or acidic catalysts should be avoided because of the potential degradation of the wood. Even with the same treatment conditions such as curing temperature, the reaction of silanols depends on the hydrolysis and condensation rate of the silane, which varies according to the type of silane. For these reasons, different models for the reaction of silanol groups with lignucellulosic materials have been suggested.

The Si-O-C bond is very susceptible to hydrolysis (particularly under acidic conditions). As a consequence, the covalent bonding of silanes to the wood cell wall polymers is unlikely to be of importance.

Methanol was used as a carrier and a swelling solvent to swell the wood to allow the silanes to enter the cell wall. In addition to this, since the coupling agent undergoes hydrolysis in the presence of moisture (generating methanol and eventually condensed polysiloxane), dissolving the chemical in this solvent presumably increases its longer-term stability. The presence of methanol suppresses both the free radical reaction of the functional group, and hydrolysis of the hydrolysable group (Liyden and Collins, 1978). Thus, the removal of methanol is necessary for the polymerisation and hydrolysis of the silanes in situ.

For the field test, in which larger samples were used, in order to treat wood with a more industrially usable solvent, water was chosen. But, since the silanes (especially VTMS) could oligmerise in the presence of water at room temperature before penetrating into the cell wall, stabilising the silane in methanol was necessary. According to a trial based on the clarity of the solution, a solution of methanol and water (40% water, 60% methanol) was used as a solvent for treatment.

3.2.2 Anhydrides

Two modifying linear anhydrides (acetic and hexanoic anhydride) were used in this study (Table 3.2). These chemicals have been used and reported previously for the chemical modification of wood. Of these two anhydrides, the most commonly used and reported is acetic anhydride. The reaction between wood and linear carboxylic anhydrides is a single site reaction as depicted in Figure 3.6, all anhydrides yield the corresponding carboxylic acid as by product of their reaction with the wood.

Since hexanoic anhydride is too big to penetrate into the cell wall, a swelling solvent was required. Thus, pyridine solvent was used for the reaction. Pyridine was used for the following reasons:

1. Hexanoic anhydride is highly soluble in pyridine.

2. Pyridine swells wood to a greater extent than water (approximately 25% greater: Stamm and Tarkow, 1947; Risi and Arseneau, 1957), allowing even non-swelling modifying chemicals access to the cell wall polymers.

3. Pyridine is catalyst of wood modification reactions with anhydrides.

4. The disadvantage of using pyridine in these experiments was its toxicity. Extreme caution was exercised when handling this solvent.

Chemical Name	Formula	Boiling point °C	Density gr/cm3
Acetic anhydride	CH_3COOH	138-140	1.082
Hexanoic anhydride	$C_5H_{11}COOH$	246-248	0.926

Table 3. 2: Physical properties of the linear carboxylic anhydrides used in this study

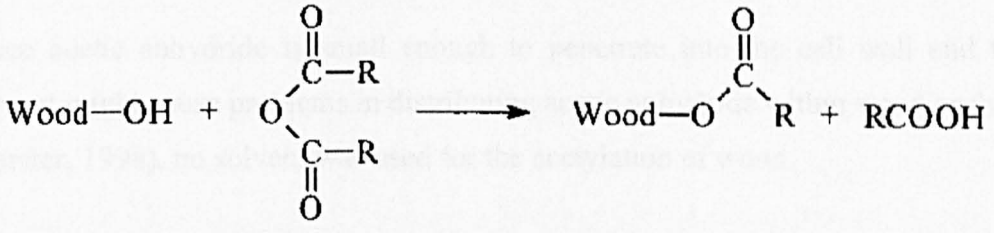


Figure 3.6 Anhydride modification scheme, where R=CH_3 (acetic anhydride), R=C_5H_{11} (hexanoic anhydride). (Rowell, 1988 in Papadopoulos, 2003)

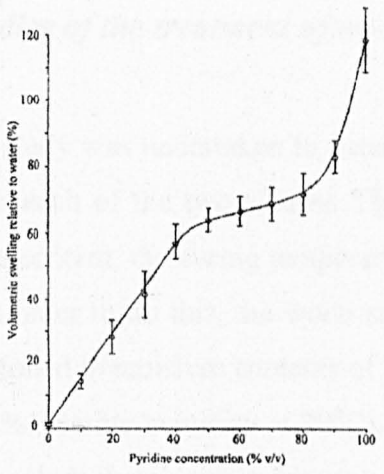


Figure 3.7: Graph of volumetric swelling relative to water with solution of pyridine in toluene of varying concentration (West, 1988).

Regarding the swelling capacity of pyridine (point 2 above) it should be noted that the formation of a solution with the modifying chemicals would have affected the ability of pyridine to swell the wood. Wood swelling tests by West (1988) in varying ratios of pyridine to toluene showed the relationship of volumetric swelling to concentration of pyridine to give a sigmoid shape graph (Figure 3.7).

Since acetic anhydride is small enough to penetrate into the cell wall and the use of solvent might cause problems in distributing acetic anhydride within wood or the cell wall (Forster, 1998), no solvent was used for the acetylation of wood.

3.3 Reaction procedure

3.3.1 Sample preparation

Prior to the reaction, wood blocks were carefully sanded to remove loosely adhering fibres. Sanded blocks and wood strips, except for the blocks put aside as a controls for thermally modified wood, were placed in a Soxhlet extractor for solvent extraction using toluene /methanol /acetone (4:1:1 by volume) for 8 hours. Extracted blocks were then oven dried and weighed using a four-figure balance. Non-extracted wood were used for the field test.

3.3.2 Preliminary studies of the treatment of wood with silanes

Initially, a preliminary study was undertaken to determine the optimal conditions for the treatment of wood with each of the two silanes. Three variables were investigated, the effect of wood moisture content, the curing temperature and the absence or presence of a free-radical initiator. In order to do this, the wood samples were either used in an oven-dry condition, or conditioned to moisture contents of 12% (by equilibrating for two weeks in an atmosphere of 65% relative humidity at 20°C), or 33%, (by placing samples above deionised water in a sealed chamber for two weeks at 20°C). Silane impregnation solutions were made up to 25% of the silane in methanol (v/v), in some cases with the addition of the free-radical initiator, azo-isobutyronitrile (AIBN) at 1% (v/v). Dry or conditioned wood samples were placed in a beaker containing the silane treatment solution, which was located in a vacuum desiccator. The lid was placed on the desiccator and a vacuum applied using a rotary pump for 1 hour, to remove trapped air from the wood. Air was admitted into the desiccator and the samples left in the impregnating solution for 24 hours at ambient temperature to allow for diffusion of the silane into the cell wall. Impregnated samples were then removed from the solution and left in a fume cupboard for 8 hours to allow the methanol to evaporate. Samples were then transferred to an oven and cured at either 50°C or 100°C for 48 hours. Upon removal, the samples were weighed (four-figure balance), transferred to a Soxhlet apparatus and solvent extracted, oven-dried, re-weighed and dimensions determined as detailed above.

3.2.2.1 The result of preliminary treatment studies

The results obtained in the preliminary silane treatment studies are shown in Appendix A.1.a and Figures 3.8 and 3.9 In most cases, the weight percentage gain (WPG) after treatment followed by solvent extraction was not significant. Treatment with TMPS, followed by curing at 50°C, resulted in WPG's in excess of 20%, but these values decreased to 2%, or less, when the treated wood samples were subjected to solvent extraction. This indicates that little polymerisation of the silane occurred at this temperature. Rather higher WPG values were found after solvent extraction when the curing temperature was 100°C, particularly when the free-radical initiator (AIBN) was present. In the case of treatment with TMPS in the presence of AIBN with a curing

temperature of 100°C, WPG's in the region of 19 - 20% were found after solvent extraction at 12 and 0% MC. The wood moisture content (MC) influenced the results, with a decrease in WPG (8.4%) recorded when the wood moisture content was 33%. In the case of VTMS treatment, wood moisture content was found to be a significant factor influencing the results, with the highest WPG's recorded when the wood MC was 33%. In the case of VTMS, the presence of AIBN did not have significant influence on the results. Ogiso and Saka (1994) treated oven-dry wood samples with 50% methanolic solutions of VTMS or TMPS with 1% benzoyl peroxide and reported WPG's (after water extraction) of 2.3% and 43.0%, respectively. These results, are similar to those reported herein and illustrate the low level of reactivity of the organic functional group of VTMS in free-radical polymerisation.

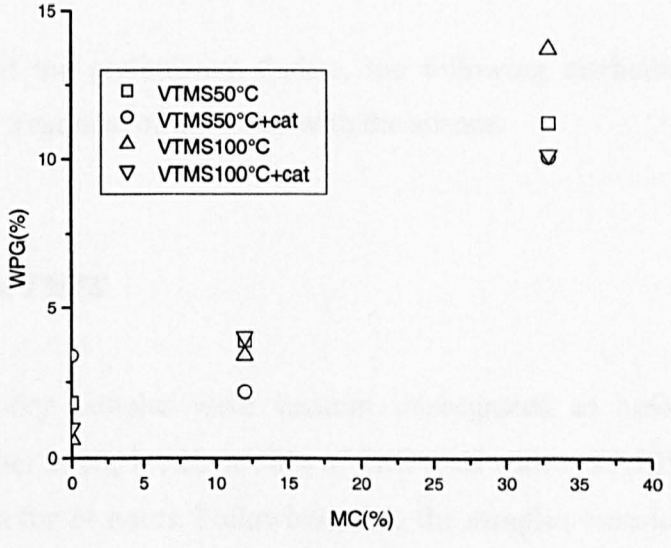


Figure 3.8: Relationships between MC and WPG of VTMS treated wood following extraction

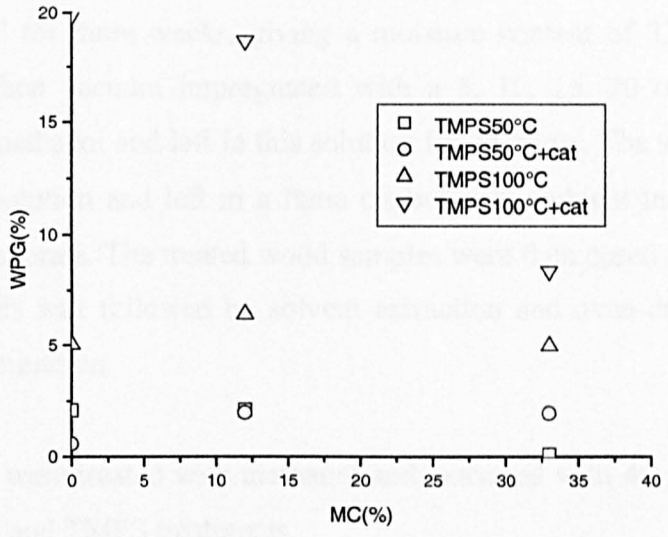


Figure 3.9: Relationships between MC and WPG of TMPS treated wood following extraction

Based upon the results of the preliminary studies, the following methods were then adopted for all subsequent treatment of the wood with the silanes.

3.3.2.1 Treatment protocol TMPS

Extractive-free and oven-dry samples were vacuum impregnated as before with a methanolic solution of either 5, 10, 15, 20 or 50% of TMPS all with 1% AIBN (v/v), and left to stand in the solution for 24 hours. Followin9g that, the samples were left in a fume cupboard overnight to allow the methanol to evaporate and subsequently cured at 100°C for 24 hours. The samples were then vacuum impregnated with water for 30 min to hydrolyse any residual methoxy groups. The water-saturated samples were then air-dried for 24 hours followed by oven-drying at 100°C for 48hr. Treated samples were Soxhlet extracted and oven-dried as detailed previously. Weight gain and dimensional change due to treatment were then measured as detailed above.

3.3.2.2 Treatment protocol VTMS

Extracted and weighed oven-dry samples were subsequently conditioned over deionised water at a constant 20°C for three weeks, giving a moisture content of 33%, the thus conditioned wood was then vacuum impregnated with a 5, 10, 15, 20 or 50% (v/v) solution of the silane in methanol and left in this solution for 24 hours. The samples were then removed from the solution and left in a fume cupboard at ambient temperature to allow the methanol to evaporate. The treated wood samples were then cured in an oven at 100°C for 48 hours. This was followed by solvent extraction and oven-drying, before weight and volume determination.

In addition, some blocks were treated with methanol and extracted with 4:1:1 to be used as controls for the VTMS and TMPS treatments.

3.3.2.3 Pressure treatment

Pressure treatment was applied to treat the larger samples used for the field test. The procedure was carried out in a Parr pressure reactor according to the following:

Filling of pressure vessel with an aqueous solution of VTMS or PTMS with a concentration of 25% W/V (In the case of TMPS, 1% AIBN was added to the solution).
Soaking of the wood with the solution under vacuum for 30min.
Removing vacuum and increasing pressure up to 12 bars and keeping the pressure for 15 minutes to ensure lateral penetration of the chemicals into the wood.
Removing pressure and unloading the pressure reactor.
Drying the impregnated wood for three days in a fume cupboard (in the case of VTMS treated wood 2 days).
Curing the impregnated wood for 5 days at 70°C for VTMS, treated wood.
In the case of TMPS, a higher curing temperature in two stages (50°C for one day and 80°C for 4 days were used to prevent the wood from cracking during curing.
The chemical uptake of the samples were calculated according to the below mention formula which are given in the Appendix A.1.C.
U= (W2-W1)/V
Where:
U= Uptake (Kg/m^3)

W_1= Weight befor pressure impregnation (Kg)

W_2= Weight after pressure impregnation (Kg)

V= Volume of the sample (m^3)

3.3.3 Anhydride modification

3.3.3.1 Acetic anhydride

Acetylation was performed without catalyst by vacuum impregnation of weighed, oven-dry wood samples with acetic anhydride. The impregnated samples were then added to a pre-heated flask containing acetic anhydride for between 1 and 72 h (to give different degrees of reaction expressed as weight per cent gain, WPG) set in an oil bath at 100°C. The hot reagent was decanted off and ice-cold acetone was added to the flask to quench the reaction. The samples were then removed from the acetone and were cleaned according to the procedure explained in Section 3.3. In addition, the extracted samples were used as controls for the acetylation of the samples.

3.3.3.2 Hexanoic anhydride

Since hexanoic anhydride is too big to enter the cell wall without the presence of any swelling solvent, pyridine was used as solvent and a catalyst for the reaction. For this reaction, the oven-dry, weighed wood samples were vacuum impregnated with pyridine at ambient temperature overnight and then added to the flask containing hot pyridine plus 1 M anhydride. Reaction was done at 100°C for a specified time to obtain the required level of reaction.

Wood 1, 2, 4, 6 hours

Stakes 1, 2, 4, and 18 hours

Ater finishing the reation time, the reaction was quienched by ice cold acetone and samples solvent extracted as detailed above. For the modification of stakes with hexanoic anhydrides, longer treatment time (over night) was chosen to get at least a 20% WPG.

After the cleaning up procedure explained above, samples were oven dried at 105°C for 18 hours and weighed. The weight gain due to reaction was then calculated.

In addition, some blocks were treated with pyridine as just described and extracted with 4:1:1 as controls.

It should be mentioned that in the case of decay tests, isotherm sorption and cell wall micropore accessibility studies, since no difference was found between methanol, pyridine and extracted wood, For a better comparison between the performances of the chemicals, extracted wood was used as a control for all of the modifications.

3.4 Heat treatment

The samples were heated in at different temperatures for different times in a 0.044m^3 vacuum oven. Heat treatments were conducted in a nitrogen atmosphere. A vacuum was drawn on the wood for 10 min for two stages (two 5 minutes, one in desiccator and another one in the oven, prior to the second vacuum stage, vacuum removed by introducing nitrogen into the desiccator), prior to flushing the vessel with nitrogen. Nitrogen was slowly fed through the vessel throughout the treatment process to remove pyroligneous gaseous products liberated during heating. This was because such products may have an adverse effect on the wood by acid hydrolysis at temperatures above 200°C. After heat treatment, samples were cooled to room temperature before exposure to air. A high purity nitrogen (with just 5 ppm oxygen) was used for this treatment. Temperature strips supplied by Thermographic Measurements CO LTD with 1% accuracy, were stuck on the block surfaces to check the temperature of the oven and the surfaces of the samples. Temperatures of the sample surfaces after all of the treatments were identical with the adjusted oven temperatures. In addition to the samples exposed to heat treatments, some un-extracted and unheated samples were used as control samples.

3.5 Confirmation of the wood reaction with the chemicals

In this chapter only WPG, OH substitution level and volume increase due to the modifications are discussed. In Chapter 7, FTIR and NMR studies of silane treated samples are presented.

3.5.1 Weight gain (WPG)

Weight gain was calculated according to the equation below:

$$WPG\ (\%) = [(W_{mod} - W_{unmod}) / W_{unmod}] \times 100 \qquad 3.1$$

Where: W_{mod} is the mass of the treated wood sample and W_{unmod} is the mass of the untreated sample.

3.5.2 Volume increase percentage

Of 50 blocks (20 x 20 x 5mm) reacted, 40 blocks were chosen and their dimensions were measured. Block volume and volume increase due to modification were calculated.

Volume change (*VC*) due to the modification was calculated according to:

$$VC\ (\%) = [(V_{mod} - V_{unmod}) / V_{unmod}] \times 100 \qquad 3.2$$

Where V_{mod} is the volume of the oven-dry wood sample after modification and V_{unmod} is the volume of the oven-dry wood sample prior to treatment.

Theoretical volume (V_T) of reagents located in the wood was calculated thus:

$$V_T\ (cm^3\ mol^{-1}) = Weight\ gain\ of\ wood\ due\ to\ modification\ / D \qquad 3.3$$

Where *MW* is the molecular weight in grams and *D* is the density in g cm^{-3}.

3.6 Ratio of theoretical and measured volume increase V(rel)

For understanding how much silane has gone into the cell wall, $V_{(rel)}$ the ratio of theoretical and measured volume increase was calculated according to formula 3.4.

$$V_{(rel)} = (V_T / V_C) \qquad 3.4$$

3.7.1 Silane modified wood

A good range of weight gains was obtained. The WPG of the samples which were used for the isotherm studies are shown in Appendix 1.3.

Although the extent of polymerisation of the silane can be determined from the permanence of the WPG after solvent extraction, it is also important to determine the location of the silane in the wood. For the purposes of an effective preservative treatment, it is necessary that the silane is located inside the cell wall. This was determined by measuring the volume change of the wood after treatment and extraction (Table 3.3, and Figure 3.10) a non-linear relationship was found between the volume change and WPG due to treatment. This indicates that as the WPG increases, a lower proportion of the silane is located in the cell wall. Furthermore, it can be seen that the change in volume is no greater than *ca.* 7%, even at WPG levels of the order of 50%. Since the sapwood samples of Corsican pine used in this study exhibited a maximum (*i.e.* water-saturated) swelling of the order of 15%, it follows that there remains a significant portion of the cell wall where no penetration of the silane occurs. The data for the ratio between the measured and theoretical volume change ($V_{(rel)}$) also indicates that a lower proportion of the reagent is located in the cell wall as the WPG increases. If all of the silane was located within the cell wall at all levels of treatment, then a value of unity would be found for $V_{(rel)}$, which would not change with WPG. The $V_{(rel)}$ values are larger than unity above a WPG value in excess of *ca.* 10% (TMPS) and ca. 20% for VTMS, indicating that the measured increase in volume is less than that theoretically predicted. This shows that at these levels of chemical add-on, a proportion of the silane is not located within the cell wall, but is located in the lumen. At low levels of weight gain, the values of $V_{(rel)}$ are less than unity, showing that the wood has swollen to a greater amount than accounted for

solely by the presence of the silane in the cell wall. This was also found in a previous study of the treatment of wood with TMPS (Schneider and Brebner, 1985), attributed to the wood being left in a partially swollen condition after silane treatment. Using an EDX a study of TMPS modified wood with a WPG of 45%, Oisgo (1994), also showed that TMPS is located mostly inside the lumen.

The ability of the silane to penetrate the cell wall is governed by the accessibility of these molecules to the cell wall interior, which is in turn dependent upon a number of factors. The silane in question must be small enough so that it can enter the micropore network of the cell wall. It has been shown from studies of the penetration of organic liquids into the cell wall of oven-dried wood, that liquids with molar volumes of larger than 100 cm^3 mol^{-1} are not able to penetrate the cell wall to any appreciable extent (Mantanis *et al.* 1994). However, if a penetrant molecule possesses more than one H-bonding site per molecule, then 100 cm^3 mol^{-1} is not an upper limit (Ishimaru and Maruta 1996). In the case of both the silanes in this study, the molar volumes are both greater than this limit (TMPS, 238 cm^3 mol^{-1}; VTMS, 139 cm^3 mol^{-1}), but both have more than one H-bonding site per molecule, provided that hydrolysis of the methoxy groups attached to the silicon atom has occurred. Bearing in the mind that moisture conditioned blocks were used for the treatment with VTMS. This would allow for hydrolysis of this silane. Hydrolysis of TMPS would presumably not occur during treatment.

Some parts of the cell wall micropore network may simply be inaccessible to the silanes, due to their size. This will be influenced by the extent of swelling of the cell wall by the solvent.

Full penetration of the cell wall will only occur if the pathways within the micropore network are not blocked. Such blocking can occur if some pre-curing polymerisation takes place during the initial 24 hour diffusion stage of the treatment. If this polymerisation occurs *via* the silanol bonds, then the presence of water within the cell wall will hydrolyse the silanes and may promote such polymerisation. However, since the hydrolysis of the methoxy groups will result in the generation of methanol, the use of methanol as a solvent will tend to inhibit such a process. If polymerisation occurs via a free-radical mechanism, then any micropore blocking at the diffusion stage will depend upon the rate of free-radical generation at ambient temperature.

Table 3.3: Effect of silane solution concentration upon weight percent gain (WPG), volume change (VC) and ratio of measured to theoretical volume (V_{rel})

	Concentration (v/v)	WPG* (%)	VC (%)	V_{rel}
TMPS	5%	6.1	1.80	0.91
	10%	11.0	3.60	1.79
	15%	20.8	4.91	1.88
	20%	27.6	4.96	2.16
	50%	52.0	7.38	3.08
VTMS	5%	2.7	2.06	0.67
	10%	6.2	3.99	0.88
	15%	16.5	5.18	1.51
	20%	18.7	5.48	1.43
	50%	48.0	6.20	3.19

* The WPG are the average of 40 samples.

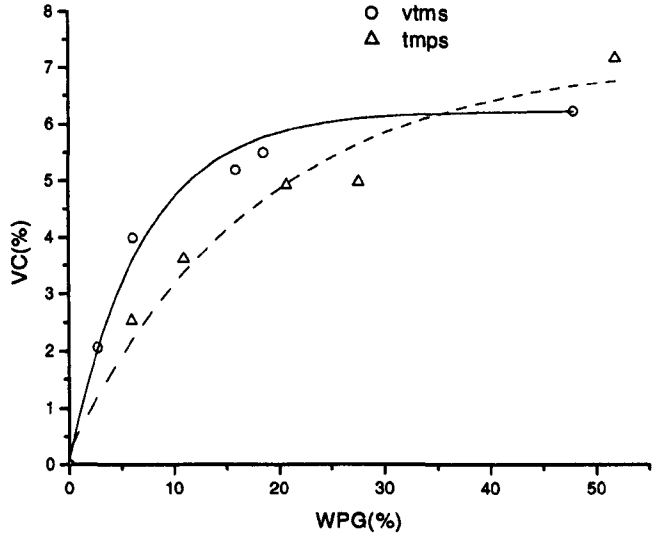


Figure 3.10: Relationship between percentage volume increase and WPG of Corsican pine sapwood modified with VTMS and TMPS.

3.7.2 WPG and VC of carboxylic modified wood

A good range of WPG's was obtained for the anhydride modification reactions. As stated in Chapter 2, a WPG of about 20% is required for the full protection of wood against brown rot and soft rot (Sutttie *et al.*, 1999 and Papadopoulos and Hill, 2002),

Figure 3.11 illustrates the relationship between percentage volume increase, due to modification with linear chain anhydrides and WPG for Corsican pine sapwood at 100°C. It can be seen that there is a linear relationship between percentages volume increase and WPG. This behaviour is commonly found (Stamm and Takow, 1947; Cetin *et al.* 1999, Papadopoulos, 2001). The constant relationship between volumetric increase with increasing WPG for samples reacted with acetic anhydride for rather long reaction time (three days) suggests that no substrate degradation has occurred at extended reaction times.

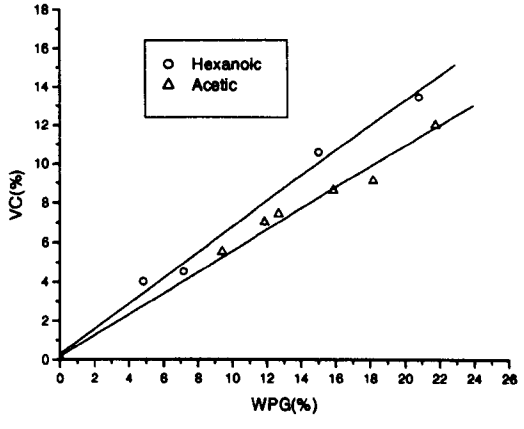


Figure 3.11: Relationship between percentage volume increase and WPG of Corsican pine sapwood modified with hexanoic and acetylated wood.

3.7.3 OH Substitution level

The OH substitution level (mMoles/g) was calculated as follow:

$$OH(\text{ mMoles/g}) = [(W_{mod} - W_{umod})/(W_{umod} \times MW)]$$

The equation assumes that one mole of wood hydroxyl groups is reacted for every mole of modifying chemical (*ie.* no cross-linking or polymerisation reactions). Thus, this equation was not used for the calculation of hydroxyl group substitution with silane coupling agents, which are able to polymerise with the hydroxyl groups of another silane or polymerise *via* free radical reaction of their organo functional group. By FTIR spectroscopy on extensively leached silane modified wood, a qualitative estimation of hydroxyl groups of wood blocked by silane coupling was made, which will be discussed in Chapter 7. Figure 3.12 shows the extent of the hydroxyl substitution versus WPG of hexanoic and acetyl modified wood. As can be seen, at the same WPG, hexanoic anhydride (having a higher molecular weight) reacts with fewer hydroxyl groups than acetic anhydride.

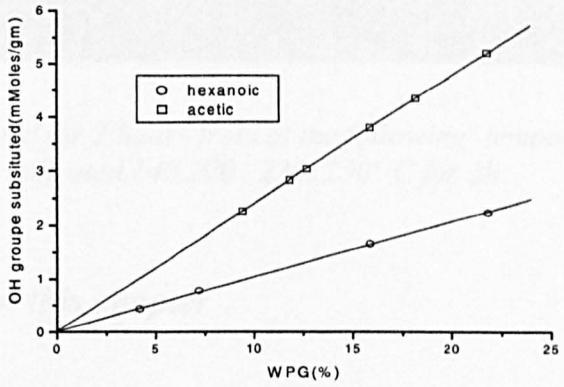
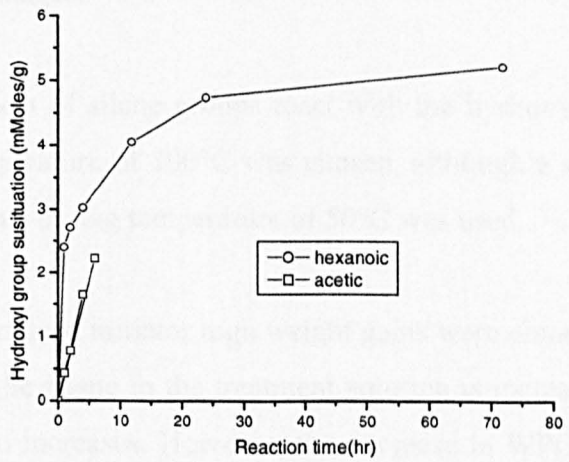


Figure 3.12: The substitution level of wood modified with varying reaction times



3.13: Reaction profiles of carboxylic acid anhydrides with wood cell wall polymers

3.7.4 The surface of heat treated wood

No cracks as a result of heat treatment were observed on the surface of heat-treated wood (3.15). The colour of the wood was changed as result of heat treatment. The effect of heat treatment on the colour depends on the treatment temperature and the time. For the treatment with short times and low temperatures, no significant colour change was observed while the wood became dark brown when it was heated at temperatures as high as 255°C for at least 90 min. The significant changes in the colour (Figure 3.14) suggest significant changes in wood structure.

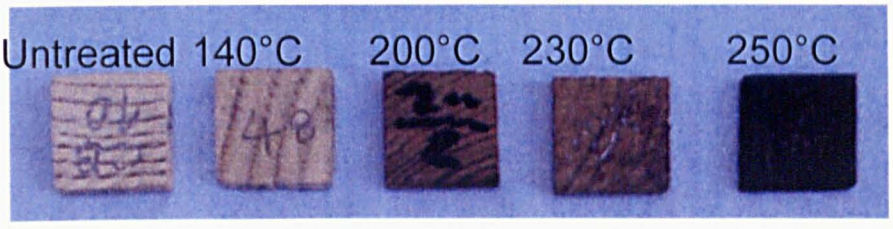


Figure3.14: Wood heated for 2 hours from at the following temperatures left to right unheated,140,200 , 230, 250° C for 2h.

3.8 Points raised from this chapter

At temperatures of 100°C and lower, even in the presence of AIBN as a free radical initiator, the vinyl group of VTMS remains mostly un-reacted, with polymerisation occurring via siloxane linkages.

In order to make sure most of silane groups react with the hydroxyl groups of wood or each other, a curing temperature of 100°C was chosen, although a significant WPG was obtained for VTMS when a curing temperature of 50°C was used.

In the presence of a free radical initiator high weight gains were obtained for TMPS.
As the concentration of the silane in the treatment solution is increased, the WPG of the wood after treatment also increases. However, this increase in WPG is not accompanied by a proportional increase in the volume of the wood after treatment. The volume increase due to treatment was no greater than 7%, with the green volume of the wood being of the order of 15%.

Corsican pine samples were satisfactory reacted with acetic anhydrides and hexanoic anhydride at 100°C without presence of any catalyst and under pyridine catalyst respectively. A constant relationship between the WPG and VC of acetic and hexanoic anhydrides suggested that no degradation of wood took place during the reaction.

The colour of heat-treated wood significantly changed when the wood was heated above 200°C. This shows that significant changes in chemical structure of wood as a result of the heat treatments.

Chapter 4

Pure culture test of heat treated wood against white rot and brown rot fungi

4.1 Introduction

The aim of this part of the study was to give an indication of the ability of heat treatments with different times and temperatures to protect wood against white rot and brown rot and establish the optimal conditions for heat treatment of wood to impart complete decay resistance against different fungi with various decay mechanisms.

4.2 Materials and Methods

4.2.1 Samples

Kiln-dried Corsican pine sapwood samples measuring 20x20x5 mm at 8% moisture content were heated as explained in Chapter 3.

4.2.2 Test Fungi

Three fungi were used, the brown rot fungus *Coniophora puteana* (strain number FPRL 11E.) Karst. and the white rot fungi *Trametes versicolor* (strain number CTB 863A) and *Phanerochaete chrysosporium* (strain number FPRL S179) (Table 4-1). Two of them are commonly used, but the third one (*P. chrysosporium)* was chosen in order to investigate the inhibiting effect of heat treatment on decay by a selective white rot fungus which preferentially attacks lignin.

Table 3.2: decay fungi and test conditions

Fungus	Strain number	Decay type	Sample position
Coniophora puteana	FPRL 11E	Brown rot	Over support
Trametes versicolor	CTB 863A	Simultaneous white rot	Direct contact with agar
Phanerochaete chrysosporium	EH(SS)	Selective with rot	Direct contact with agar

4.2.3. Decay test

Prior to exposure, oven dried and weighed heat-treated samples were conditioned at 20°C and 60% RH for 2 weeks, packed in a nitrogen atmosphere and sterilised by gamma irradiation (2.5 Mrad).

For each fungus, nine replicates of each treatment were exposed to decay by two white rot fungi. Additional sets of sterile controls were exposed as below but without fungal inoculation. The blocks were exposed using the EN113 test with the following modifications:

- 500 ml squat jars were used
- The incubation period was 8 weeks and *P. chrysosporium* was incubated at 28°C.
- Smaller than standard block sizes were used.
- For the white rot fungi, wood blocks were exposed directly on the agar in accordance with the recommendations of Kleist *et al.* (1998).

The modifications in the size of samples and the incubation time was chosen based on a decay test had been done on Corsican pine sapwood. In the decay test, high weight losses due to decay were obtained by *C. puteana* for shorter incubation times than recommended in the standard EN 113 (Table 4.2). In addition to relying on the results shown in Table 4.2, some untreated blocks used as virulence controls showed that the fungi achieved high weight loss in two months, thus, after two months of incubation, weight loss due to decay

for all treated and untreated samples was assessed. Following 8 weeks incubation in a conditioning room (22°C and 70%) or in an incubator in the case of *P. chrysosporium* conditioned as mentioned above, the blocks were removed, weighed, oven dried, and reweighed. Moisture contents and weight losses were calculated. Blocks heated at 255°C and exposed to the fungi were used for the microscopic study. For each fungus, one sample was studied. The blocks were then softened by impregnating with water. The water impregnated blocks were splitd by a blade and then were sliced by a microtome. The inner sections were used for the study. The sections were transferred to a slid with few drops of water and then were examined by a light microscope for evidence of fungal decay. The rays, tracheids, and pits of the samples at different area of the wood slices were carefully looked at finding out whether the samples are completely sound or not. SEM was carried out on the sample in which the sign of decay could be observed. SEM was carried out according to the method explained in Cardias, 1992.

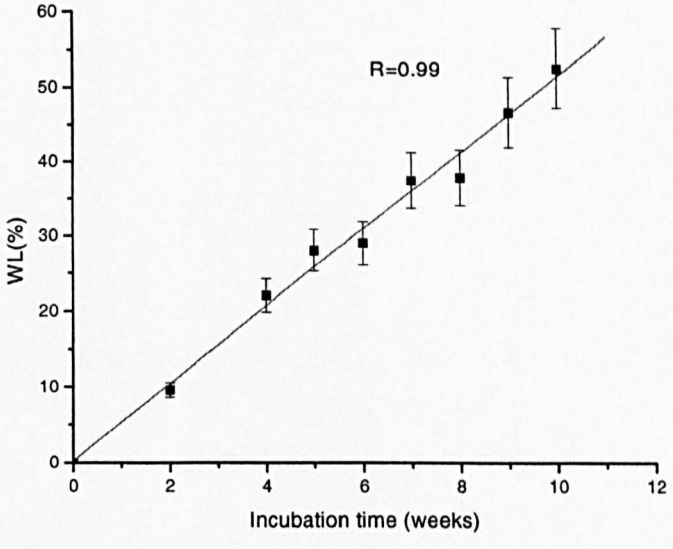


Figure 4.1: The average of weight loss of Corsican pine sapwood exposed to C. puteana after different incubation time

4.3 Results and Discussion

4.3.1 Decay resistance of heated wood

The weight loss and final moisture content of the heated and unheated Corsican pine sapwood after two months incubation (Table 4-2, Figures 4.2-4.4) shows that the heat treatment below 200 °C imparted little decay resistance.

Table 4.2 The average of weight loss percentage (WL) and moisture content (MC) of heated and unheated wood due to decay

Treatment Temp. (°C)	Treatment Time (h)	*T. versicolor*		*P. chrysosporium*		*C. puteana*		*Control*	
		WL (%)	MC (%)	WL (%)	MC (%)	WL (%)	MC (%)	WL (%)	MC (%)
Untreated	0	27.5	179	30	207	31.9	75	0.9	33
140	2	23.6	147	28.7	207	43.1	77	0.9	33
	4	26.7	160	27.7	181	33.5	79	0.3	32
	6	21.9	152	24.1	168	30.6	71	1.6	32
	8	18.7	133	25.6	169	22.1	67	0.8	30
	12	22.3	148	20.9	169	37.3	78	0.5	30
	18	20.9	137	23.2	182	34.7	63	0.1	29
	24	19.7	134	23.5	175	24	72	0.9	32
170	2	25.4	150	21	140	32.3	76	1.4	30
	4	16.4	106	20.4	123.2	35.4	79	0.9	29
	6	21.	132	16.5	122.0	26.9	69	1.1	28
	8	16	125	12.6	130	34.6	71	1	29
	12	18.4	142	20.2	154	35.8	72	0.9	30
	18	17.9	150	17.5	135	27	68	0.7	30
200	2	12.2	105	6.2	102	12.3	56	0.8	27
	4	10.6	86	7.2	120	12.4	65	0.9	27
	6	9.5	117	3.3	82	11.4	41	0.3	26
	8	3.7	99	3.7	112	7.1	44	0.5	27
	12	6.1	89	5.6	123	10.9	44	0.5	26
230	2	5.9	94	8	110	6.9	46	0.6	26
	4	7.0	76	3	59	1.5	39	0.3	23
	6	5.4	90	0.2	93	0.1	39	0.8	24
	8	1.5	73	-0.2	116	-2.6	36	-0.1	22
255	2	1.0	53	-0.8	87	-2.5	46	-0.5	17
	4	0.1	55	-1.0	98	-3.9	37	-0.4	17
	6	-0.1	42	-2	69	-3.7	40	-0.7	13

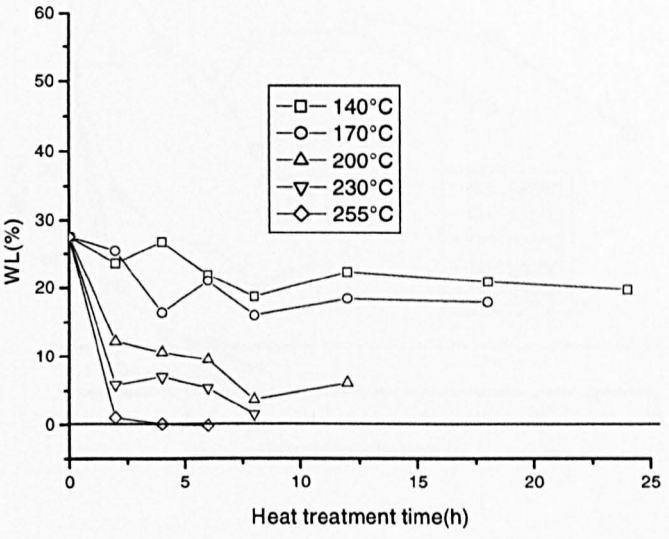


Figure 4.2: Average of weight loss (WL) of heat treated wood exposed to Trametes versicolor

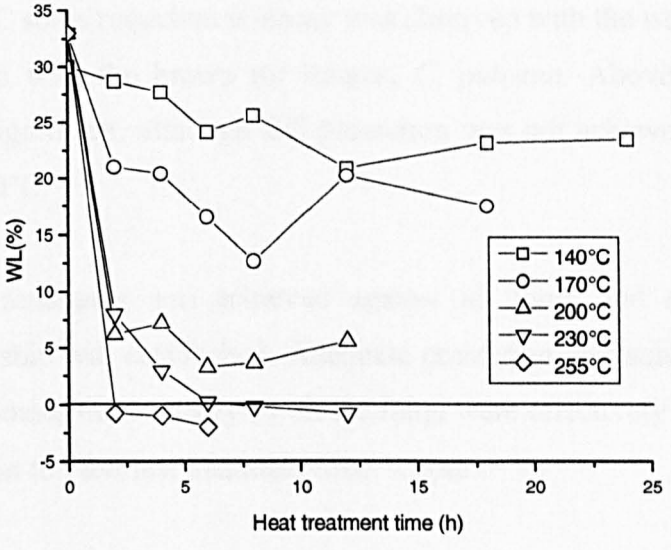


Figure 4.3: Average of weight loss (WL) of heat-treated wood exposed to P. chrysosporium

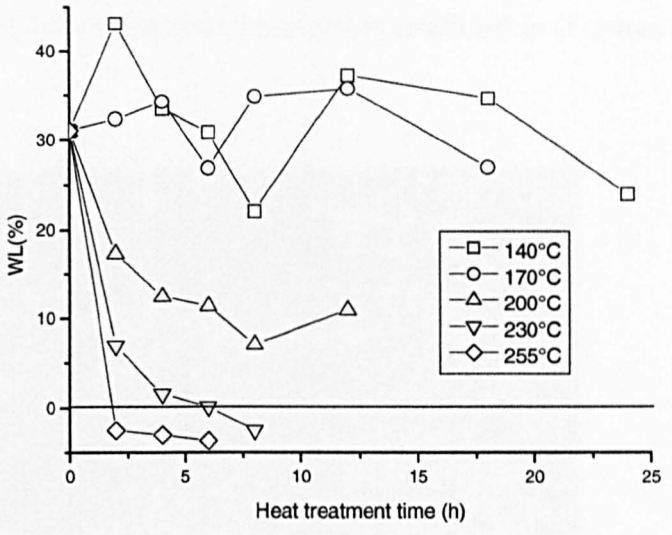


Figure 4.4: Average of weight loss (WL) of heat-treated wood exposed to C. Puteana

With all of the fungi tested, little difference was noted between untreated wood and wood heated at 140°C. At 170°C some reduction in decay was observed with the white rot fungi but no effects were seen with the brown rot fungus, *C. puteana.* Above 200°C, the protection effects were significant, although full protection was not achieved even after 12 hours of heating at 200°C.

At 230°C good decay resistance was achieved against all fungi and a reasonable time/temperature relationship was established. Adequate protection was achieved after 4 treatment hours. Weight losses due to decay by all the fungi were effectively repressed by the 255°C treatment within the shortest treatment time, 2 hours.

Above 200°C the protection effects were significant for the white rot fungus, *P. chrysosporium* and with extended treatment time the effects with *T. versicolor* improved.

The results suggest that the treatment temperature played a more important role in the improvement of decay resistance than the treatment time. These results are in the agreement with the results of Guyonet *et al.* (1988), who reported the temperature of heat treatment (Torrefication) played the most important role in changing chemical structure of wood. At the intermediate temperature, 200°C, the time temperature relationships were

visible. However, short treatment times (i.e. less than 2 hours) at the higher temperatures (255°C, would probably give a similar time / protection relationship (Figures 4.2-4.4).

Figure 5.5: The performance of heat treatment with different temperatures for two hours against C. puteana (The shrinkage of untreated and low temperature heated samples exposed to decay is due to decay by C. puteana)

It is clear that a dry heat treatment with temperatures less than 200°C for relatively short times (for example, 140°C for 24h) is not effective to protect Corsican sapwood wood against basidiomycetes, especially against *C. puteana*. Heating at above 200°C, even for the shortest treatment time (2h) significantly changed the colour of wood. This suggests a significant modification in its chemical composition evident from the substantially improved decay resistance (Figure 4.5P) shows an example of the performance of heat treatment).

Wood retification processes (dry heat & nitrogen atmosphere) at temperatures of 200-260°C are used to treat woody species industrially (Gohar and Guyonnet, 1998). Significant improvement of bamboo decay resistance using heat treatment at temperatures above 200°C have also been reported (**Liethoff**, and Peek, 2001).

4.3.2 Relationship between moisture and decay resistance of heated wood

Little can be gained from a direct comparison of end of test moisture content and weight loss as increasing levels of decay lead to increasing moisture content. Reasons for this include:

- A reduction in the dry weight of wood (the denominator in the moisture content calculation.
- The production of water through metabolism of wood polymers.
- The creation of additional void space in which water can condense or sorb.
- An increasing quantity of fungal hyphae within the wood, which themselves contain a high proportion of water.

However, there is still value in comparing end of test moisture contents between heat treaments and also in examining the moisture content of blocks after exposure in sterile conditions, which give an indication of moisture available to decay fungi before decay occurs (Figure 4.9).

All heat treatments had a noticeable effect on the moisture content of the blocks but this reduction only became pronounced at treatment temperatures above 200°C. Heat treatment that imparted high decay resistance brought down the moisture content of wood below the levels to theoretically support decay (i.e. less than 20%). For example, the moisture content of the sample heated at 250 °C was 17%. In Chapter 8, it will be shown that FSP of Corsican pine sapwood is reduced by extensive heat treatments to below the limitation required by wet rot fungi. These results are in contrast with the results obtained by Kamdem (1999) who reported that retified wood heated blocks incubated over sterile agar showed enough moisture content (70%) for fungal activity.

Given that the blocks for the white rot tests were exposed directly on the agar, the reductions in moisture content recorded (Table 4.1) are remarkable. However, these reductions alone are insufficient to inhibit fungal activity, i.e. the moisture contents of all the blocks were high enough for the growth and activity of the fungi. For example, the moisture content of the samples treated at 255°C for 2 hours that showed complete decay resistance after exposure to *T. versicolor, P. chrysosporium, C. puteana* were 53%, 87%, 45% respectively. These results are in agreement with the result of Dirol and Guymont *(1993).* They reported that heat treated wood had enough moisture content for fungal activity after exposure to fungi. Between the two white rot fungi that were studied, *P. chrysosporium* increased moisture contents of heated and unheated wood more than those increased by *T. versicolor.* This suggests that the moisture content of heated wood after

decay is dependent on the type of fungus. In addition, in contrast with *T. versicolor* for *P. chrysosporium,* a poor relationship between weight loss reduction and moisture content of heated wood was obtained. For *C. puteana*, there is a big difference between the moisture content of wood heated above and below 200°C (Figure 4.8).

Regarding the moisture content of blocks after exposure to fungi, it is hard to judge whether low water absorption of heated wood is the certain reason for the increased decay resistance. In order to assess the effect of the cell wall moisture content on decay resistance, a comparison of weight loss with FSP is required. This is further discussed in Chapter 11

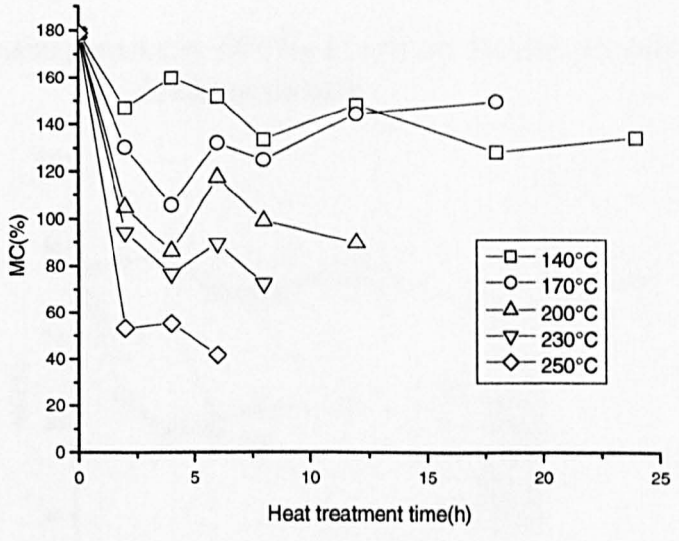


Figure 4.6: Moisture content percentage (%) at the end of test of wood exposed to T. versicolor

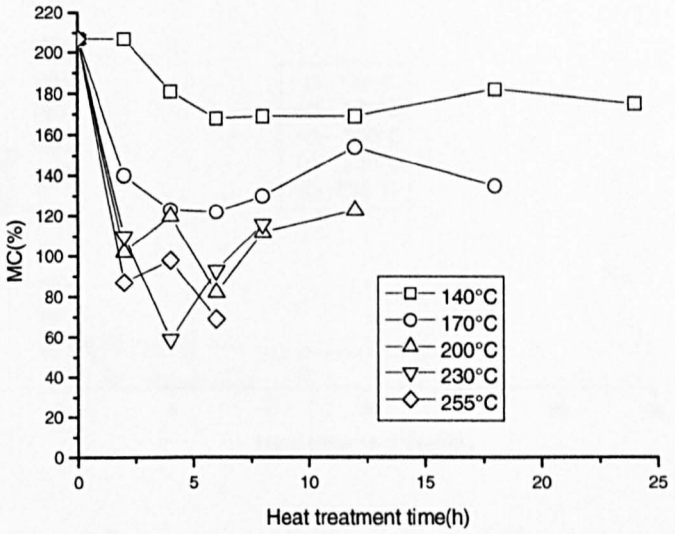


Figure 4.7: Moisture content percentage (MC%) of wood at the end of wood exposed to P. chrysosporium

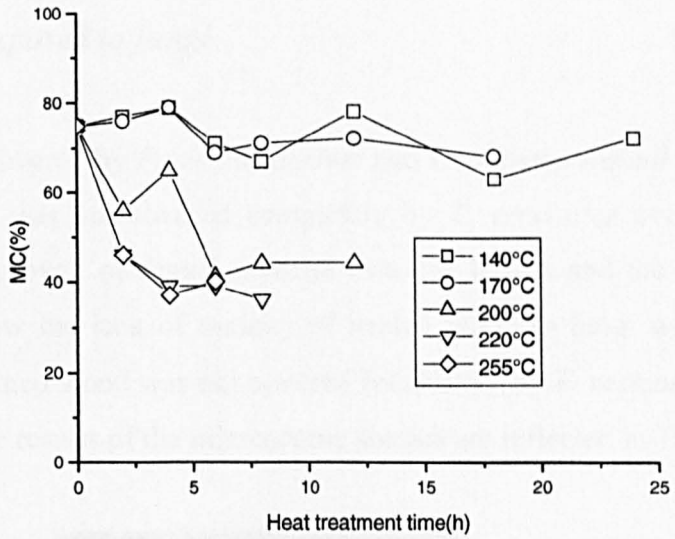


Figure 4.8: Moisture content percentage (MC%) of the wood at the end of test exposed to C. puteana

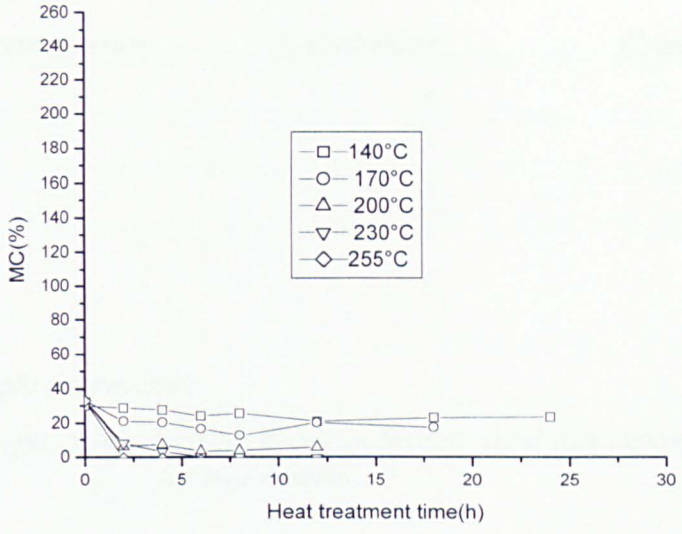


Figure 4.9: Moisture content Percentage (MC%) at the end of test of sterile wood (Controls)

4.3.4 Covering of heat-treated wood by the mycelia of the fungi and microscopic study of heated wood exposed to fungi

Heat -treated wood was covered by *P. chrysosporium* and *C. puteana hyphal mats* after a month of incubation but was not covered completely by *T. versicolor* even after two months incubation. The growth of fungal mycelia over the blocks and the presence of mycelia in the wood show the lack of toxicity of heated wood to fungi with different mechanisms, although heated wood was not covered completely by *T. vesicolor* after two months of incubation. The results of the microscopic studies are reflected in Table 4.3.

Unheated wood  Heated wood

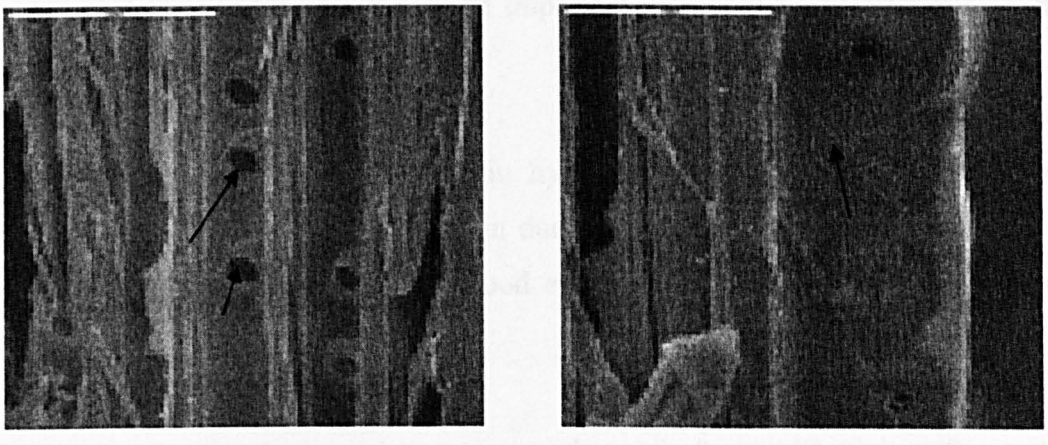
Figure 4.10: Covering of Corsican pine sapwood unheated and heat treated at 255°C for 2 hours by T. versicolor mycelia after 2 months exposure.

	P. chrysosporium	*T. versicolor*	*C. puteana*
Mycelia	-	+	+
Bore hole	-	-	-
Cell wall thinning	-	-	-
Erosion	-	-	-
Cell wall opening	-	-	**

***Notobserverd using light microscopy*

Table 4.3: The microscopic characteristics decay in heated wood was exposed to fungi for two months.

Although, no obvious signs of decay were observed by light microscopy in the extensively heated wood, extensive pit damage was seen. Even extensively heated samples marginally decayed.



(a) *(b)*

Figure 4.11: SEM of heated wood exposed to brown rot (a) Extensive pit damage (b) mycelia C. puteana.

4.3.4 Direct contact samples with mycelia

In this work the white rot fungi were incubated in direct contrast with the agar medium. Other workers often avoid this practice, as test blocks are prone to waterlogging.

However, this study suggests that the support may have an inhibiting effect on decay against these white rot fungi. Control weight losses of the untreated pinewood directly exposed to white rot fungi are higher than reported in many previous studies, e.g. Highley (1978) and in this case were similar to those recorded for the brown rot fungus, *C. puteana*, 31.5%. This level of ability to decay softwoods is unusual with these white rot fungi.

4.4 Points raised in this chapter

Intensive heat treatments with temperatures above 200°C are required to improve decay resistance of Corsican pine sapwood against fungi.

Heat treatment temperature plays a more important role in the improvement of decay resistance than the treatment time.

Good relationship between a reduction in hygroscopicity as result of heat treatment temperature was observerd and increase in durability, except for *P. chrysosporium* was observed, although extensively heated wood exposed to fungi showed a high moisture content.

Heat treatment imparts decay resistance to wood against fungi with three different decay mechanisms but significant decay resistance of wood against all different of fungi is achieved with very intensive heat treatments (255°C) above 2 hours.

No sign of decay was found by light microscopy, but by SEM microscopy, extensive pit damage was spotted in wood heated at 255°C for two hours which didn't show any positive weight loss in decay test.

Heated wood was covered by the mycelia of all fungi and mycelia of *T. versicolor* and *C. puteana* were observed in the heated samples at 255°C by light microscopy. These suggest the lack of toxicity of heated wood to fungi.

Chapter 5

Pure culture tests of modified wood

5.1 Introduction

This Chapter describes assessments of the ability of different chemical modifications (anhydride, or silane) and heat treatments to impart decay resistance against basidiomycetes. In the previous chapter, an assessment was made of the most suitable heat treatment regime for providing protection against decay. Based upon these results, heat treated samples heated at 250°C for 2 hours were also tested. In addition, the possible role of toxicants that might be produced as a result of intensive heat treatments in imparting decay resistance were also investigated.

5.2 Materials and methods

5.2.1 Modified wood

Chemically modified wood (silane treatments, linear carboxylic modification) was produced according to the methods described in Chapter 3 and leached in distilled water for three days.

Corsican pine sapwood was heated at 250°C for different treatment times (0.5, 1, 1.5 and 2 h) according to the procedures explained in Chapter 3.

5.2.2 Decay tests

The same decay tests and fungi as those reported in Chapter 4 were used to assess the decay resistance of the modified wood, but the wood samples were incubated for 4 months over malt agar in the work described in this chapter.

Thershold was calcuated dased on the intercept of the linear part of corrolation between WL and WG with fiting line of the WPG s at which WL was around zero and constant. (Figure 5.1).

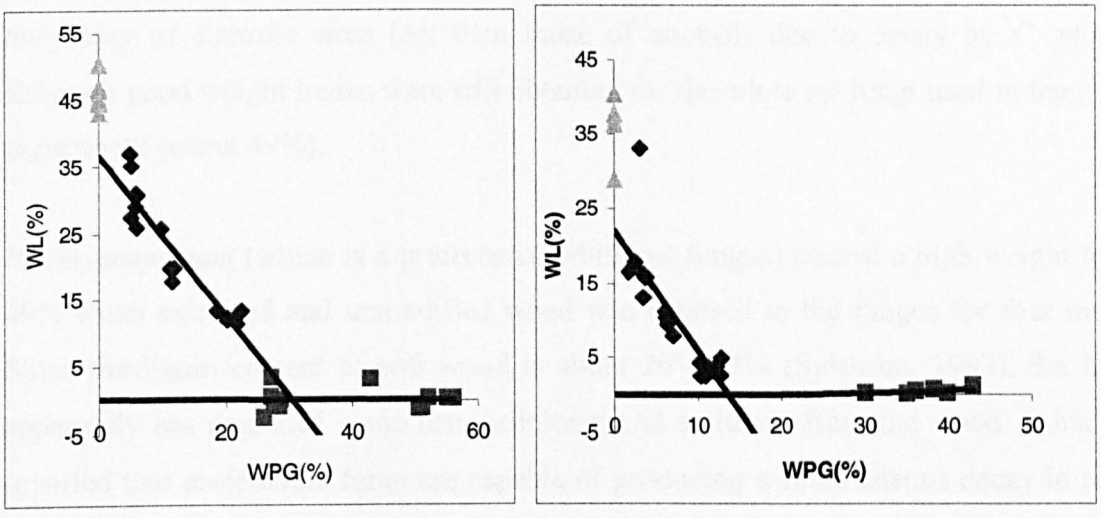


Figure 5.1: The determination of the thetshold of modyfying chemicals measuring % weight loss of treated test blocks threshold ?

5.3 Results and discussion

5.3.1 Chemically modified wood

The performance of chemically modified wood against three fungi with different degradative mechanisms is depicted in Figures 5.2 to 5.4. In these figures each data point represents mean weight loss and mean WPG data for 6 stakes. In some cases, the mean significantly varied in WPG and weight loss so the data should only be used for comparative purposes. The performance of each type of the chemical modifications studied is discussed in the next sections.

A high weight loss of about 65% due to decay by *C. puteana* was obtained when unmodified and extracted wood was exposed to the fungus for four months. No significant difference in the weight loss due to decay by the fungus with extracted wood and pyridine treated wood (used as controls for the modifications) was obtained thus the

weight loss due to the decay of extracted wood was used as a decay rate control for all types of chemical modification studied.

In this chapter, for the white rot fungi, in contrast with Chapter 5, the weight losses due to the decay of controls were less than those of controls due to decay by *C. puteana*, although good weight losses were still obtained for the white rot fungi used in the current experiment (about 49%).

P. chrysosporium (which is a preferential white rot fungus) caused a high weight loss of 49% when extracted and unmodified wood was exposed to the fungus for four months. Since the lignin content of soft wood is about 26%-32% (Sjöström, 1993), the fungus apparently has degraded some hemicelluloses and cellulose from the wood. It has been reported that preferential fungi are capable of producing a simultaneous decay in certain circumstances, such as an increase in the nitrogen content of wood or increase in incubation time (Leatham and Kirk,1983, Buswell et al. 1984, Shimada and Haraguchi, 1991). In this study, an increase in the incubation time might have been the main reason for the high weight loss, since the fungus caused a weight loss of only *ca.* 30% for a two month incubation.

For all the modifications applied in this study, the weight loss was lower than that for untreated wood. The details of the effect of each type of the modifications on the decay resistance of Corsican pine sapwood are discussed in the next sections. All chemically modified wood incubated over malt showed moisture contents less than that for unmodified wood, although the ability of the treatments in reducing the moisture content and weight loss due decay was different (Figures 5.2 to 5.5).

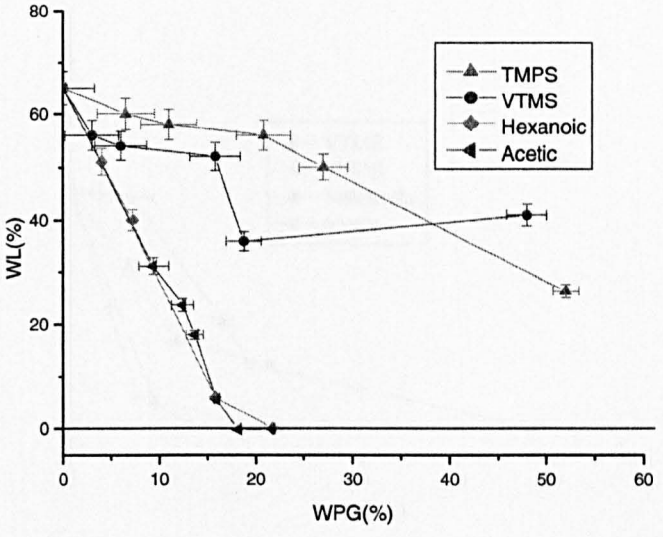


Figure 5.2: Corrected weight loss of chemically modified wood exposed to C puteana for four months as a function of WPG

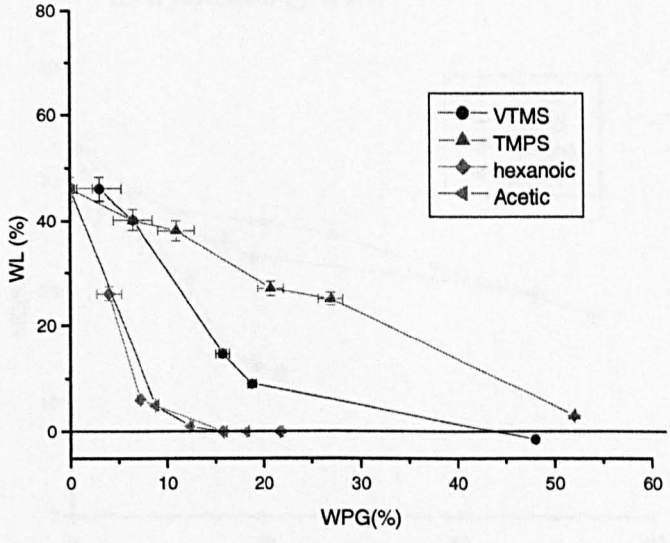


Figure 5.3: Corrected weight loss of chemically modified wood exposed to P. chrysosporium for 4 months as a function of WPG

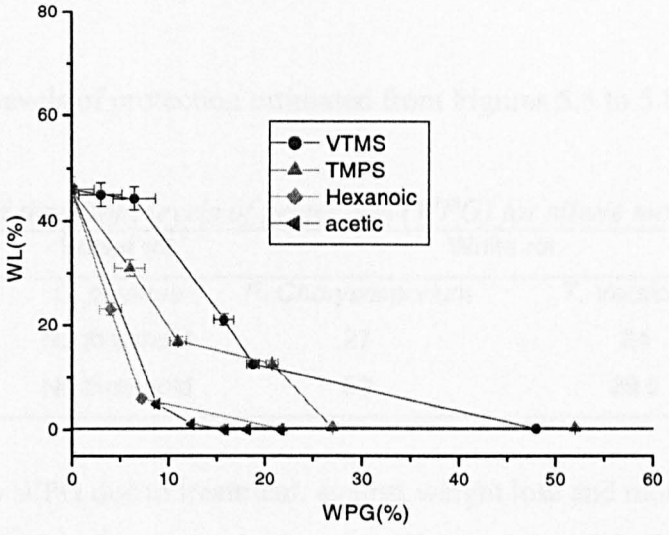


Figure 5.4: Corrected weight loss of modified wood exposed to T. versicolor for 4 months as a function of WPG

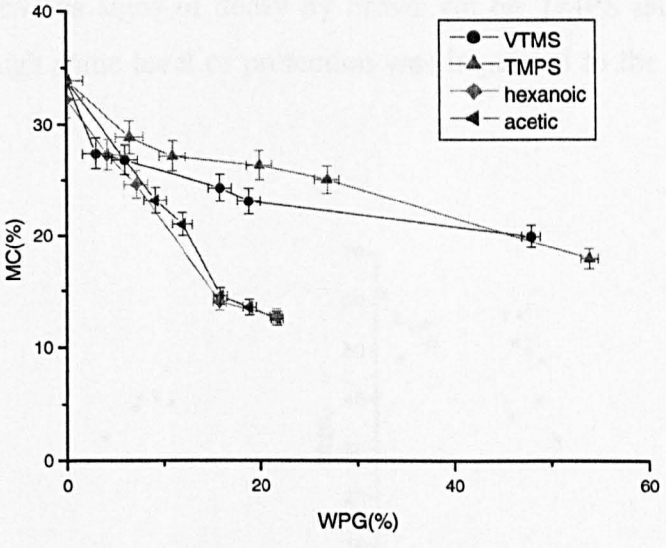


Figure 5.5: The end moisture content of sterile controls incubated over malt agar for four months as a function of WPG

5.3.2 Silane modified wood

Table 5.1 lists threshold levels of protection estimated from Figures 5.5 to 5.8.

Table 5.1: Estimated threshold levels of protection (WPG) for silane modified wood

	Brown rot	White rot	
	C. puteana	*P. Chorysosporium*	*T. Versicolor*
VTMS	No threshold	27	24
TMPS	No threshold	59	29.5

The relationship between WPG due to treatment, against weight loss and moisture content of wood following exposure to *C. puteana* is shown in Figures 5.6 to 5.7. Treatment with either silane results in a similar relationship between WPG and weight loss. It is clear that neither treatment is capable of providing full protection against decay, even at WPG's in excess of 50%, although as WPG increases, there is a slight increase in decay resistance (Figures 5.6 and 5.7). Obvious signs of decay by brown rot on TMPS modified wood could be observed, although some level of protection was impa`rted to the wood by the treatment (Figure 5.8).

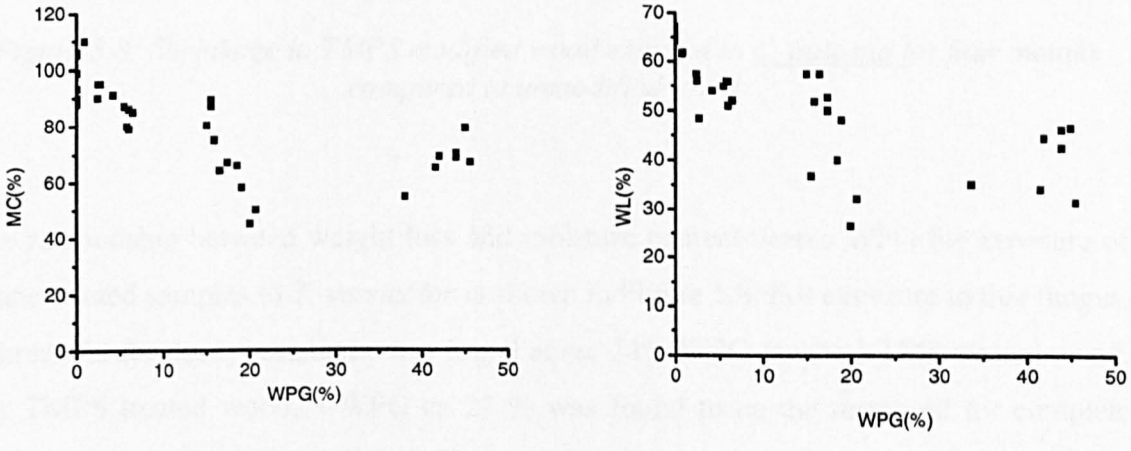


Figure 5.6:% WL due to decay and the end % moisture content of VTMS modified exposed to C. puteana for four months

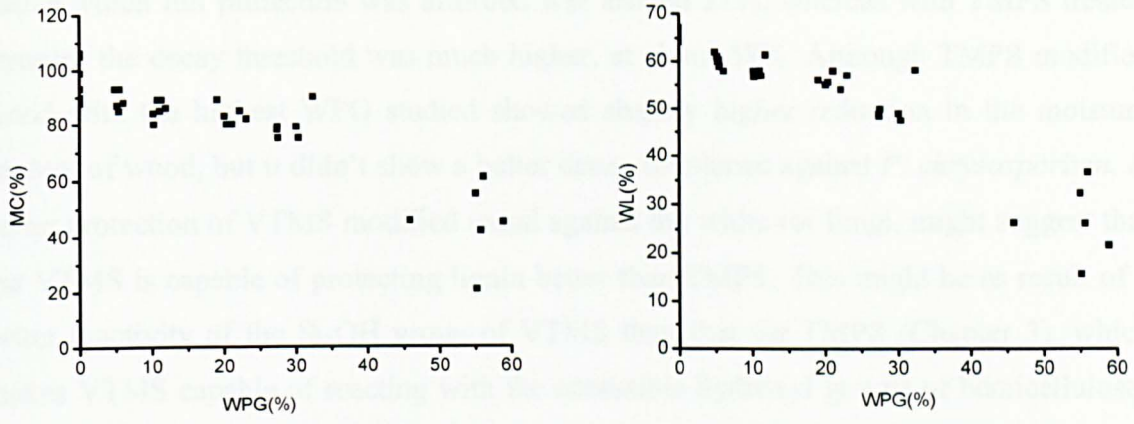


Figure 5.7:% WL and end MC due to decay and the end % moisture content of TMPS modified wood exposed to C. puteana for four months

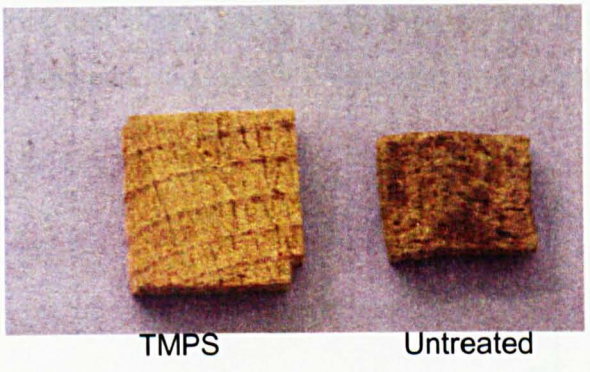


Figure 5.8: Shrinkage in TMPS modified wood exposed to C. puteana for four months compared to unmodified wood.

The relationship between weight loss and moisture content versus WPG for exposure of silane treated samples to *T. versicolor* is shown in Figure 5.8. For exposure to this fungus, a threshold for decay resistance was found at *ca.* 24% WPG for the VTMS treated wood. For TMPS treated wood, a WPG ca 27 % was found to be the threshold for complete protection against white rot fungus (Figure 5.10).

The relationship between WPG due to treatment with the two silanes and weight loss and moisture content due to exposure of treated samples to *P. chrysosporium* is shown in Figures 5.10 and 5.12. Distinctly different behaviour was found for wood samples treated with the two silanes. In the case of VTMS treated samples, the WPG threshold

above which full protection was afforded was around 27%, whereas with TMPS treated samples the decay threshold was much higher, at about 58%. Although TMPS modified wood with the highest WPG studied showed slightly higher reduction in the moisture content of wood, but it didn't show a better decay resistance against *P. chrysosporium.* A better protection of VTMS modified wood against the white rot fungi, might suggest that the VTMS is capable of protecting lignin better than TMPS. This might be as result of a better reactivity of the Si-OH group of VTMS than that for TMPS (Chapter 3), which makes VTMS capable of reacting with the accessible hydroxyl groups of hemicelluloses covering lignin or with lignin itself. It should be mentioned that although, Si-O-C is easily hydrolysable in acidic conditions, it could be fairly resistant against hydrolysis dependent on its substituent group. No work has clearly investigated the resistance of the bond between cellulose and silanol group to hydrolysis. Since white rot fungi do not acidify wood, the bond between wood and VTMS might be resistant to hydrolysis.

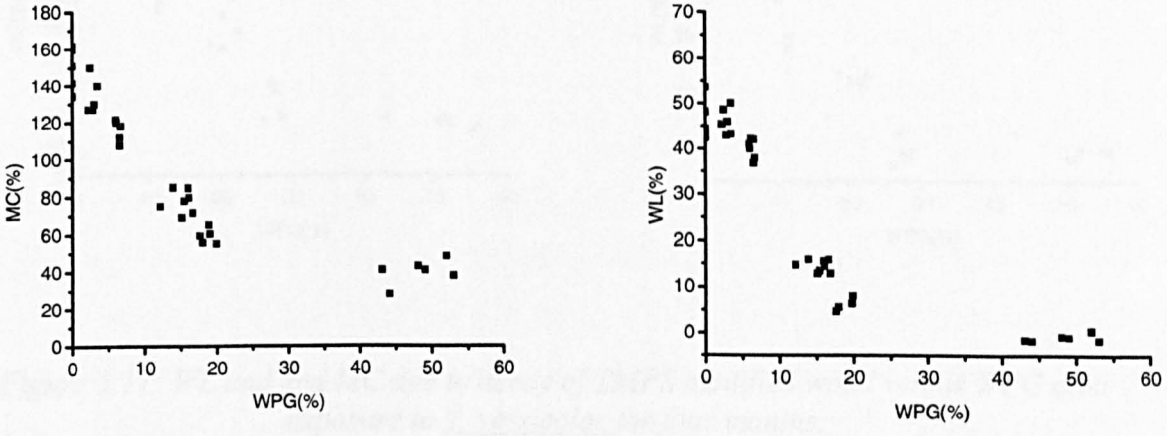


Figure 5.9:% WL due to decay and the end % moisture content of VTMS modified exposed to T. versicolor for four months.

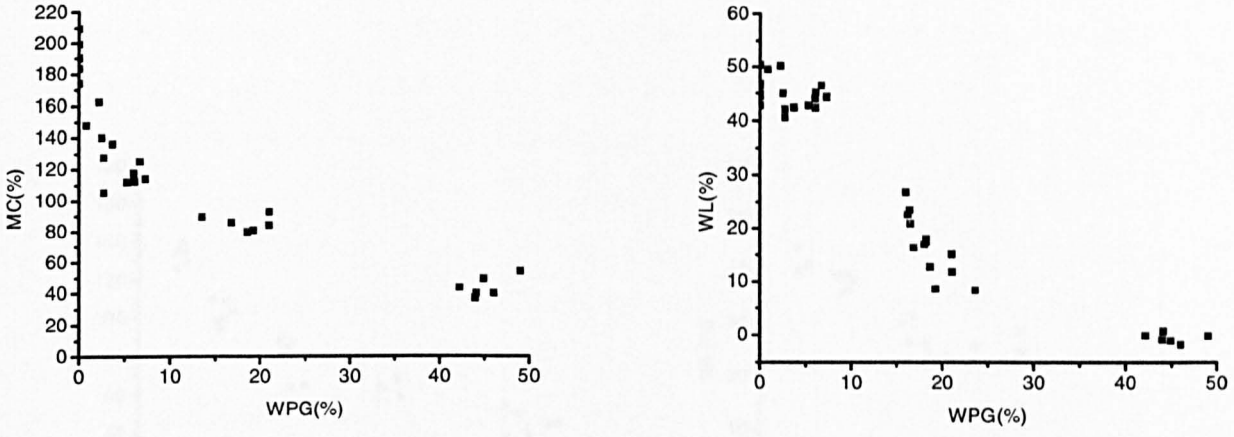


Figure 5.10: % WL and end MC due to decay of VTMS modified wood versus WPG after exposure to P. chrysosporium for four month

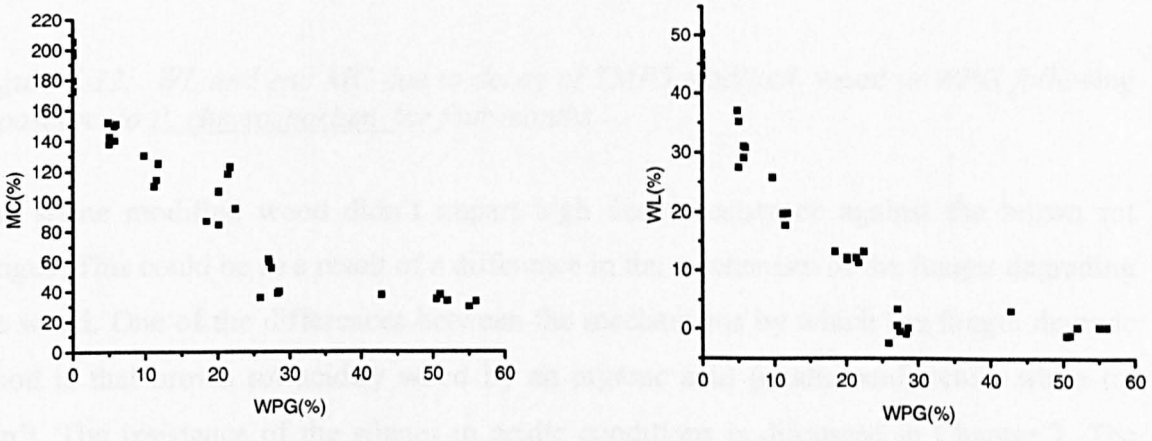


Figure 5.11: WL and end MC due to decay of TMPS modified wood versus WPG after exposure to T. versicolor for four months.

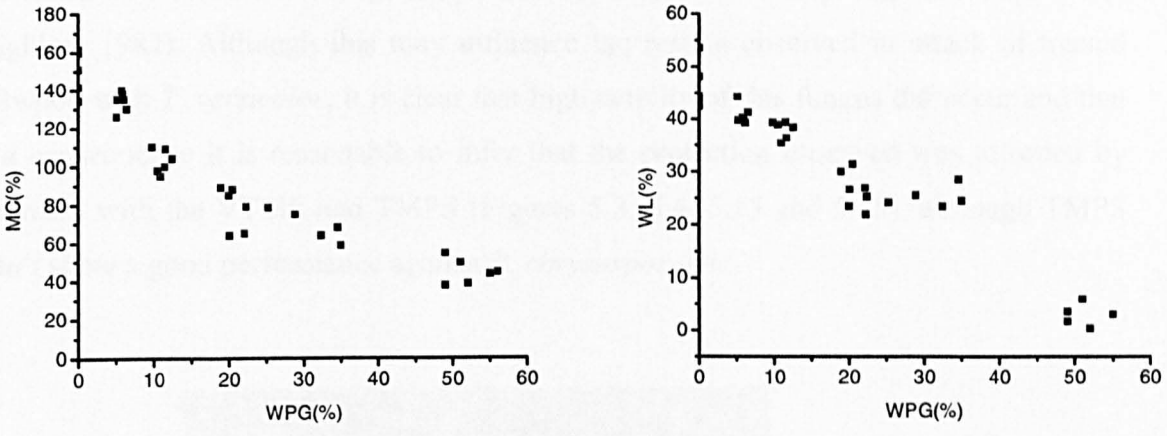


Figure 5.12: WL and end MC due to decay of TMPS modified wood vs WPG following exposeure to P. chrysosporium for four months

The silane modified wood didn't impart high decay resistance against the brown rot fungus. This could be as a result of a difference in the mechanism of the fungus degrading the wood. One of the differences between the mechanisms by which the fungui degrade wood is that brown rot acidify wood by an organic acid (oxalic acid) while white rot don't. The resistance of the silanes to acidic conditions is discussed in Chapter 7. The moisture data suggest that the silanes are not capable of reducing moisture content as much as that by anhydride modification. This might suggest that a moderate reduction in the moisture content of the modified wood causes a moderate reduction in the weight loss due to decay. The correlation between moisture and weight loss due to decay is discussed in the next section.

The results of fungal decay tests of PTMS treated wood have been reported by Goethals and Steven (1994), where PTMS treated beech with maximum WPG of **20%** was tested against *T. (Coriolus) versicolor* and PTMS treated pine against *C. puteana*. It was reported that PTMS treated pine did not show any significant protection against *C. puteana*, in agreement with the results reported here. Poor protection was also reported for PTMS treated beech against *T. versicolor*, whereas with the present study decay

protection was found at a WPG of 27% for VTMS treated Corsican pine. Treatment with VTMS was also able to provide protection against *P. chrysosporium* with both tests achieving high decay levels in the untreated wood. The ability of *T. versicolor* to decay wood is influenced by the type of lignin present, with guaiacyl-rich species of softwoods and some hardwoods exhibiting a higher decay resistance than syringyl-rich hardwoods (Highley, 1982). Although this may influence the results observed in attack of treated softwood with *T. versicolor*, it is clear that high activity of this fungus did occur and that as a consequence it is reasonable to infer that the protection observed was afforded by treatment with the VTMS and TMPS (Figures 5.3, 5.4, 5.13 and 5.15), although TMPS didn't show a good performance against *P. chrysosporium*.

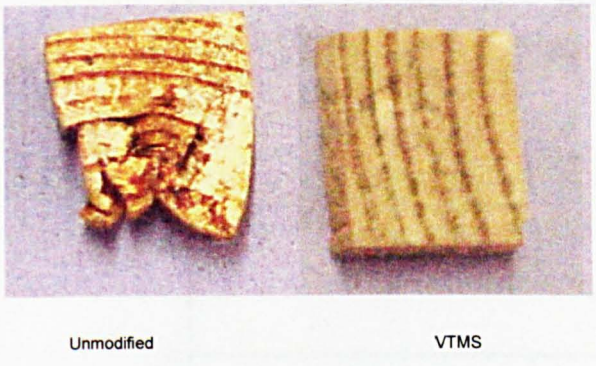


Figure 5.13: VTMS modified wood with the WPG of 48% after exposure to T. versicolor for four months compared to unmodified wood.

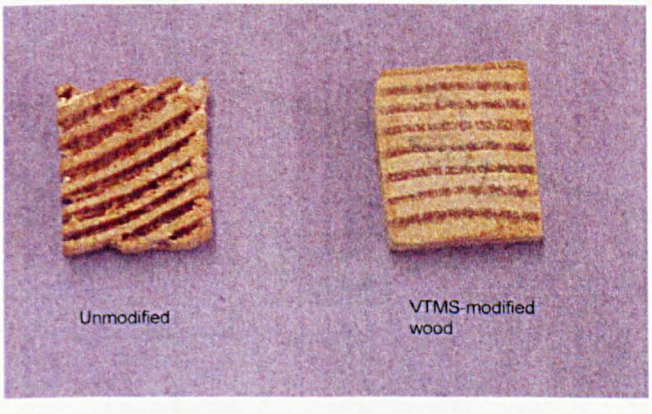


Figure 5.14: VTMS modified wood with the WPG of 48% exposed to P. chrysosporium for four months compared to unmodified wood.

As can be observed in Figure 5.15, there is a correlation between WPG and a reduction in the moisture content of the modified wood incubated over malt agar. The pattern of the variation in the moisture content and WPG is very close to the pattern of variation in the relationship between WPG and volume change due to modification showing how much of the chemicals penetrate into the cell wall. In Figure 5.16, MC has been plotted against VC due to modification. A good correlation was found (high R-value, 96%) between the end moisture content and volume change due to modification.

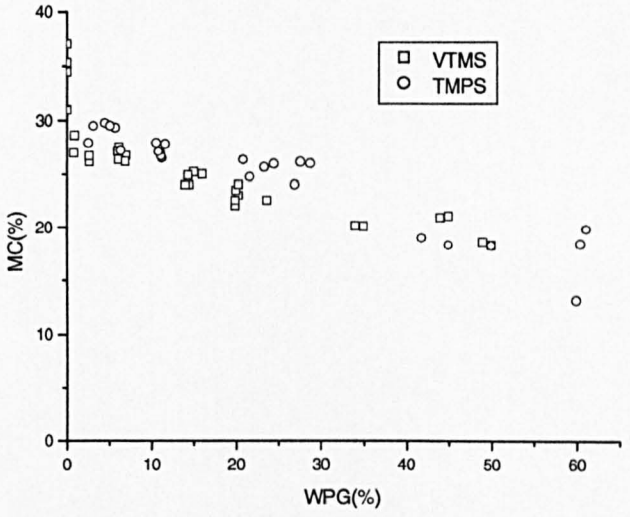


Figure 5.15: End moisture content of silane modified wood incubated over sterile malt agar for four months.

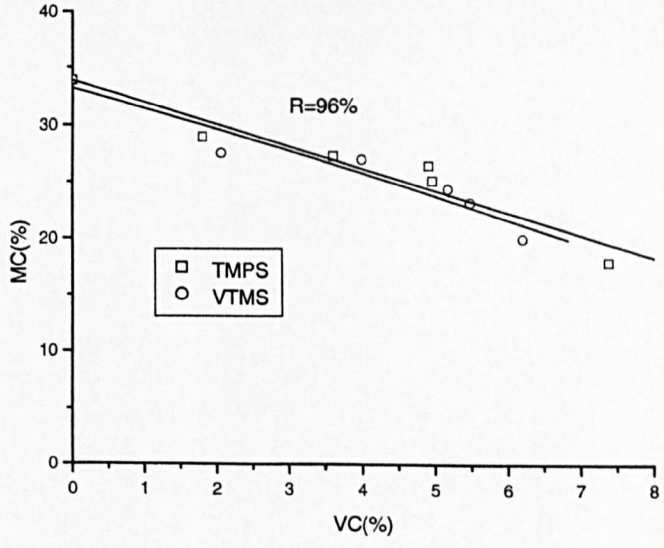


Figure 5.16: Relation between end moisture content of silane modified wood used as a sterile control and volume increases due to the silane treatments

5.3.3 Decay resistance of linear carboxylic anhydride modified wood.

Table 5.2 lists the threshold levels of protection estimated from Figures 8.13 to 8.16.

Table 5.2: Estimated threshold level of protection (WPG %)

	Brown rot	White rot	
	C. puteana	*P. chrysosporium*	*T. versicolor*
Acetic anhydride	17.7	12.5	*Below 9 AA
Hexanoic anhydride	17	11.4	**8 .HEX

* The lowest WPG (9.4)of acetylated wood used in the decay test showed complete protection

**Not enough data points

As can be observed in Figures 5.17 to 5.22, WL's due to decay by all the fungi decrease when weight gains of linear carboxylic anhydride increase. Moisture content of the modified samples also decreased with increasing WPG (Figure 5.23). The level of protection against brown rot fungus which was found in this study is in the line with the level of protection reported by the other workers. For acetylation, Goldstein *et al.* (1961), reported a general protection level against basidiomycete fungi (brown and white rot) of 18%. Beckers *et al.* (1994), also found that 18% WPG due to acetylation protected against *G. trabeum* and *C. puteana*, but found *P. placenta* required over 20% WPG. They found wood acetylated to 12% to be protected against *Coriolus (Trametes) versicolor.*

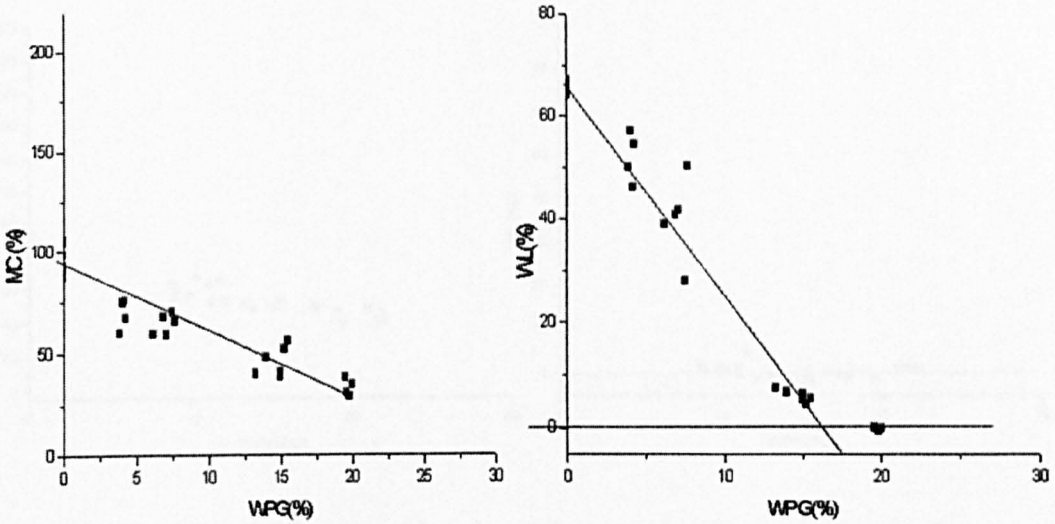


Figure 5.17: MC and WL of hexanoylated wood exposed to C. puteana for four months.

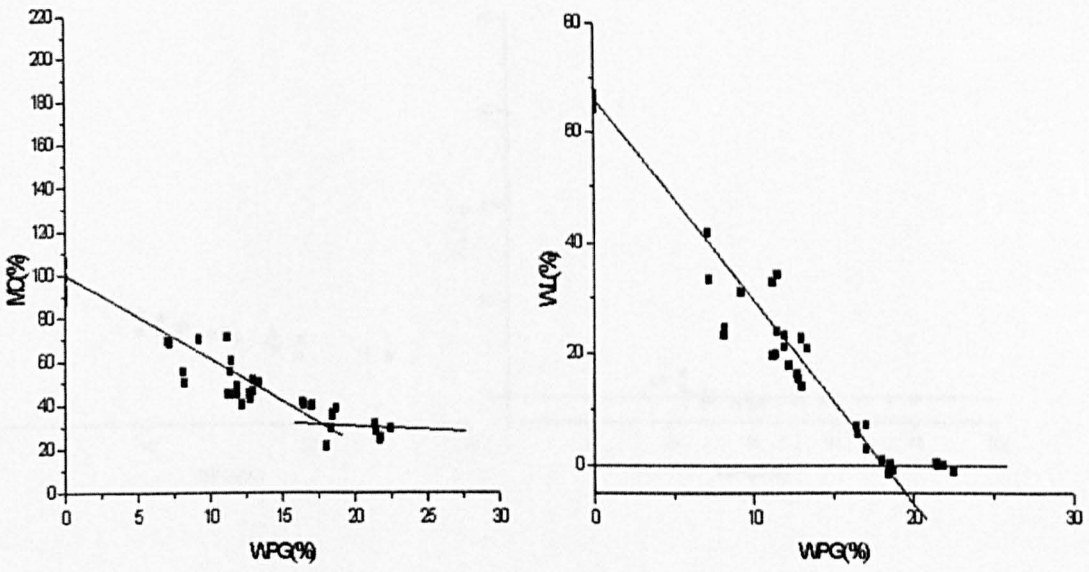


Figure 5.18: MC and WL of acetylated wood exposed to C. puteana for four months.

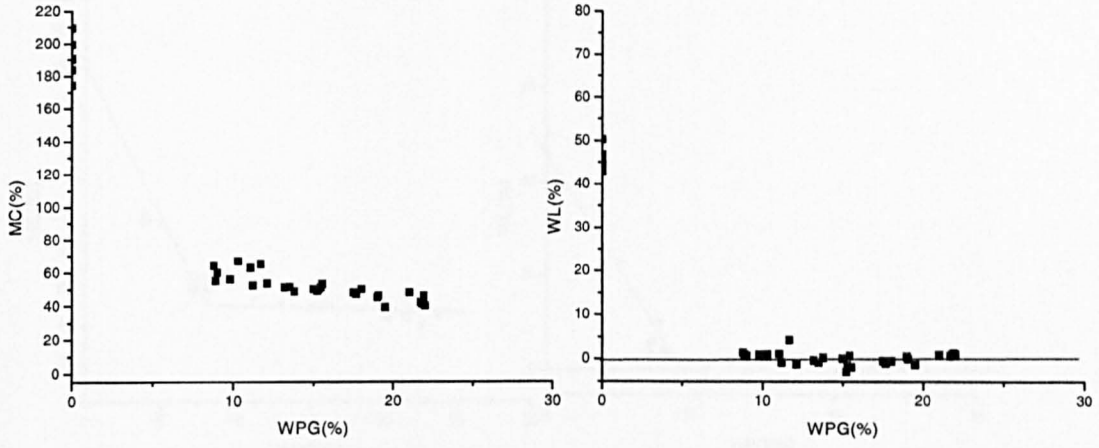


Figure 5.19: MC and WL of acetylated wood exposed to T. versicolor for four months.

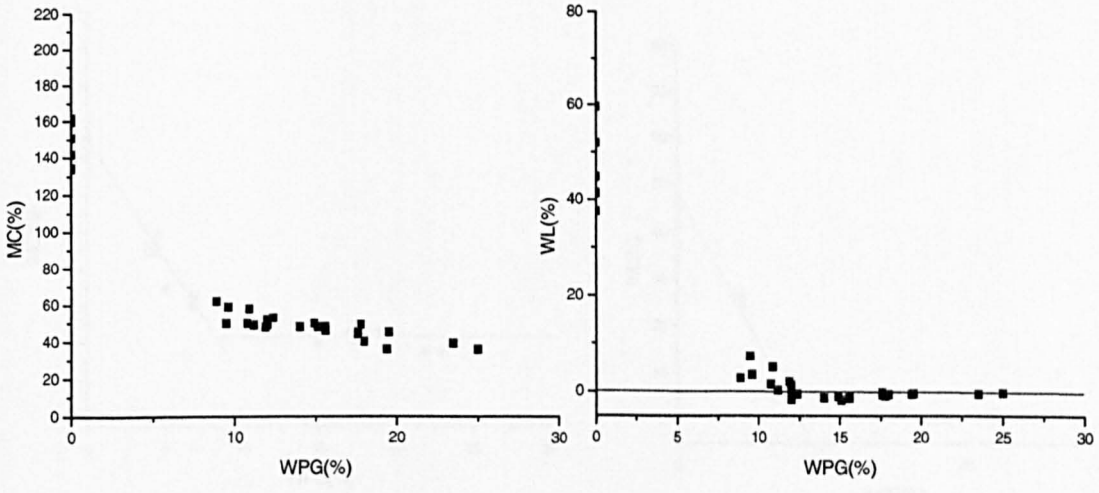


Figure 5.20: MC and WL of acetylated wood exposed to P. chrysosporium for four months

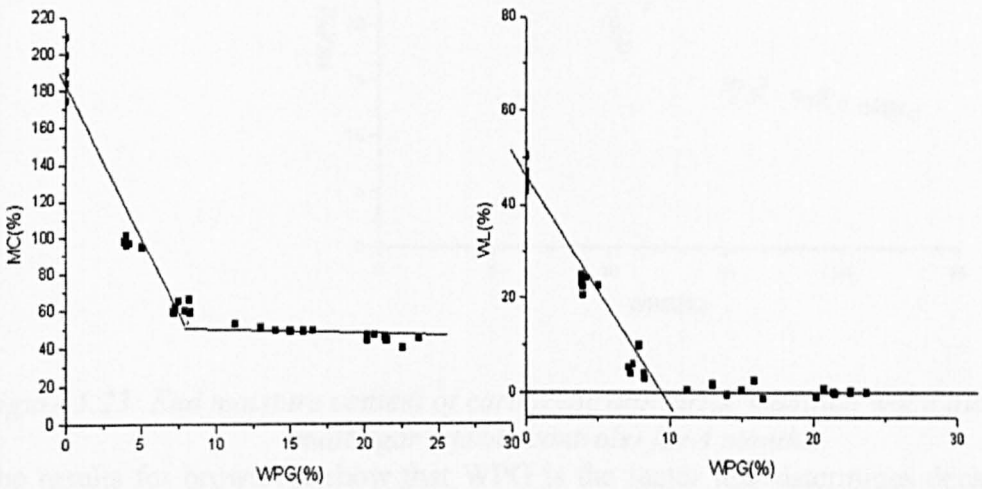


Figure 5.21: MC and WL of hexanoylated wood exposed to T. versicolor for four months.

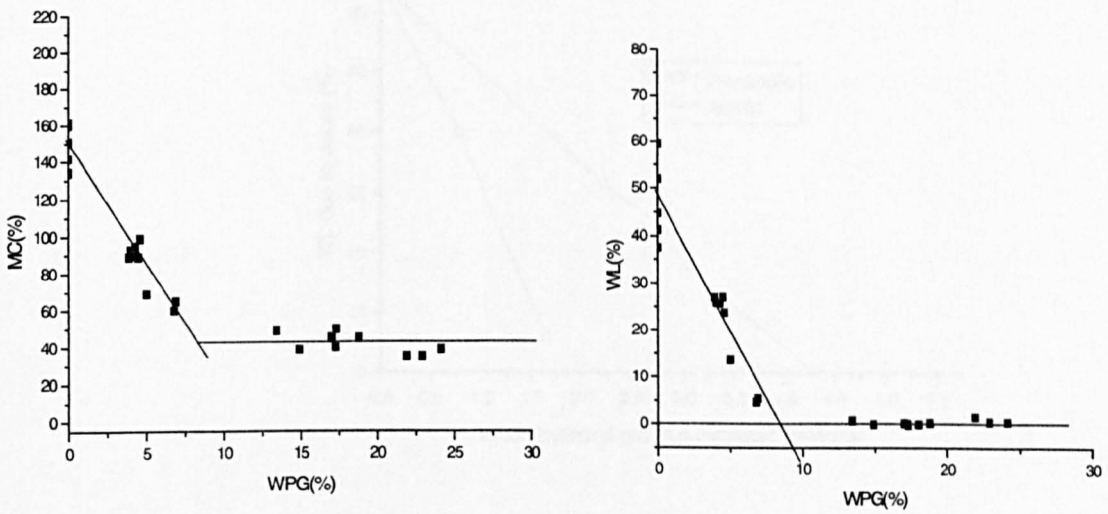


Figure 5.22: MC and WL of acetylated wood exposed to P. chrysosporium for four months.

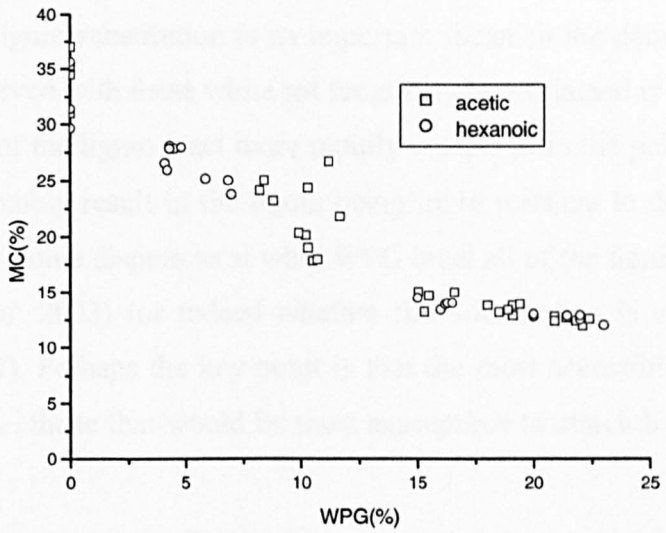


Figure 5.23: End moisture content of carboxylic anhydride modified wood incubated over malt agar (sterile controls) for 4 months.

The results for brown rot show that WPG is the factor that determines decay resistance and not extent of OH substitution (Figure 5.24).

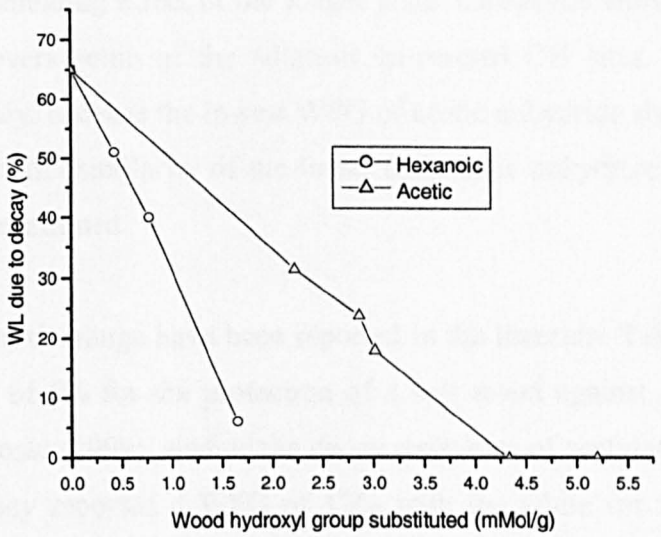


Figure 5.24: Corrected weight loss in blocks exposed to C. puteana as a function of wood hydroxyl groups reacted.

The results from white rot decay experiments with Corsican pine sapwood modified with acetic or hexanoic anhydrides are shown in Figures 5.17-5.22. With both the simultaneous white rot fungus *(T. versicolor)* and the preferential white rot fungus (*P. chrysosporium*), the results show that the decay protection is achieved at WPG's far lower than the thresholds for *C. puteana*. When lignin is preferentially degraded by

the selective white rot fungus, higher thresholds were required to fully protect the wood. This might suggest that lignin substitution is an important factor in the decay resistance. The lower threshold observed with these white rot fungi may be explained if it is assumed that the phenolic groups of the lignin react more rapidly compared to the polysaccharides OH's. This would presumably result in the lignin being more resistant to degradation at low WPG levels. There is some dispute as at what WPG level all of the lignin OH groups are substituted (Hill *et al.* 2003) (or indeed whether full substitution is ever achieved (Ohkoshi and Kato, 1997). Perhaps the key point is that the most accessible OH groups are substituted rapidly, *i.e.* those that would be most susceptible to attack by degradative agents.

Hexanoic anhydride has a higher molecular weight than acetic anhydride, thus at the same weight gain, hexanoic anhydride reacts with less hydroxyl groups of wood than acetic anhydride. Since both chemicals showed nearly the same efficacy in the protection of wood against white rot fungi, partial blocking of accessible hydroxyl group of lignin to the fungi might be by a shielding effect of the longer chain carboxylic anhydrides where the adduct physically covers some of the adjacent un-reacted OH sites. It should be mentioned that in this study, because the lowest WPG of acetic anhydride showed little or no decay, judgment about the similarity of the linear carboxylic anhydride performance couldn't be completely determined.

The protection level are in the range have been reported in the literature Takahashi, *et al.* (1989), reported a WPG of 6% for the protection of a soft wood against *T. versicolor.* Beckers (1994), and Ohkoshi (1999), studied the decay resistance of acetylated Scots pine against *T. versicolor.* They reported a WPG of 12% with the white rot fungus as the threshold level of protection for using acetic anhydride.

In this study, the threshold levels of acetylated wood against *T. versicolor* was not estimated because the lowest WPG of acetic anhydride (9%) used, showed complete protection against this fungus.

5.3.4 Decay resistance of heat treated wood.

The relationships between the moisture content and weight loss of the wood heated at 250°C as a function of time are depicted in Figures 5.26 to 5.28. As can be seen in Figures 5.26-5.28, for *C. puteana* and *P. chrysosporium*, the wood heated at 250°C for 90 min showed a weight loss close to 0% while for *T. versicolor* a longer treatment time is required to reduce the decay weight loss to zero. Since intensive changes in the chemical structure of wood due to heat treatment at 250°C for 2 hours takes place (Chapter 8), it could be concluded that a significant reduction in the weight loss of heated wood due to exposure to *T. versicolor* is achieved when hemicelluloses are significantly removed by the treatments. The removal of hemicellulose causes a significant reduction in the moisture content of wood (Figure 5.29), which are important in determining the hygroscopicity of wood. These results support the results obtained in Chapter 4, in which the wood heated at 250°C for two hours showed significant decay resistance against the three fungi. Weight loss due to brown rot which is capable of degradation of hemicelluloses without causing any significant weight loss (Highley 1988) wouldn't be a good decay measuring parameter for heated wood (Chapter 4), although zero weight loss shows that significant decay resistance imparted to the wood (Figure 5.26).

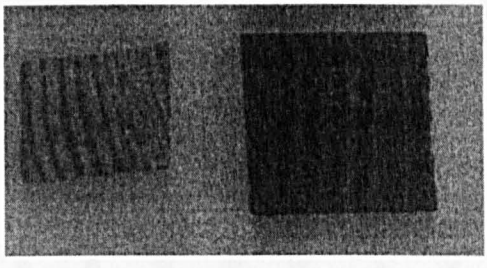


Figure 5.25: Picture of heated wood exposed to C. puteana for 4 months compared to untreated wood.

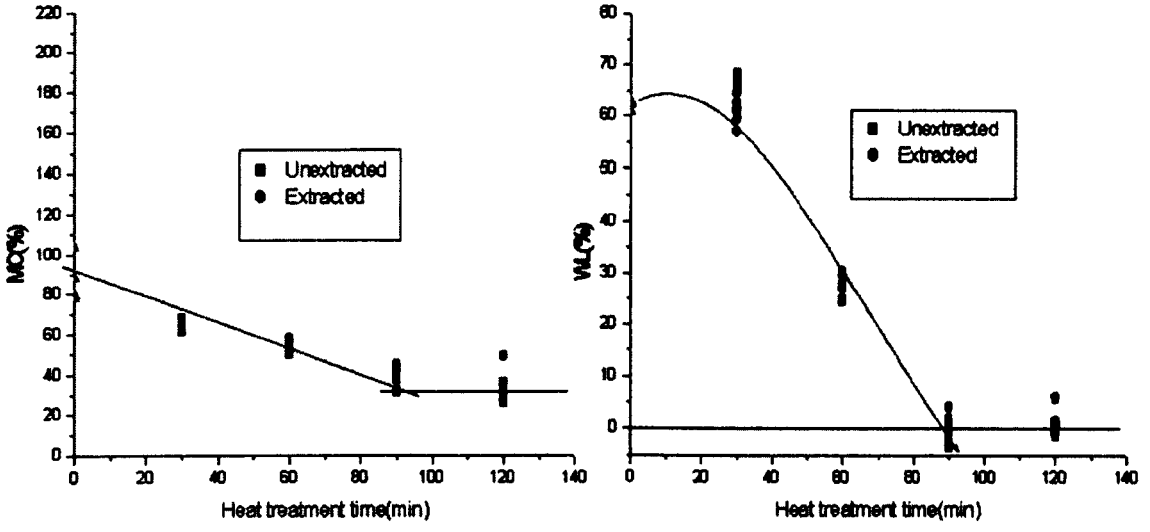


Figure 5.26: End moisture content and weight loss of heated wood exposed to C. puteana for four months

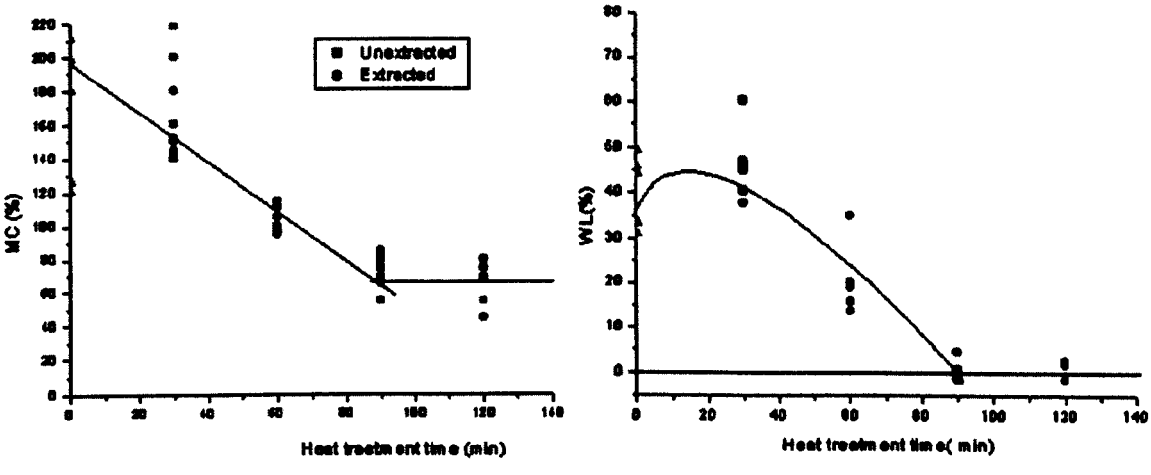


Figure 5.27: End moisture content and decay weight loss of heated wood exposed to P. chrysosporium for four months

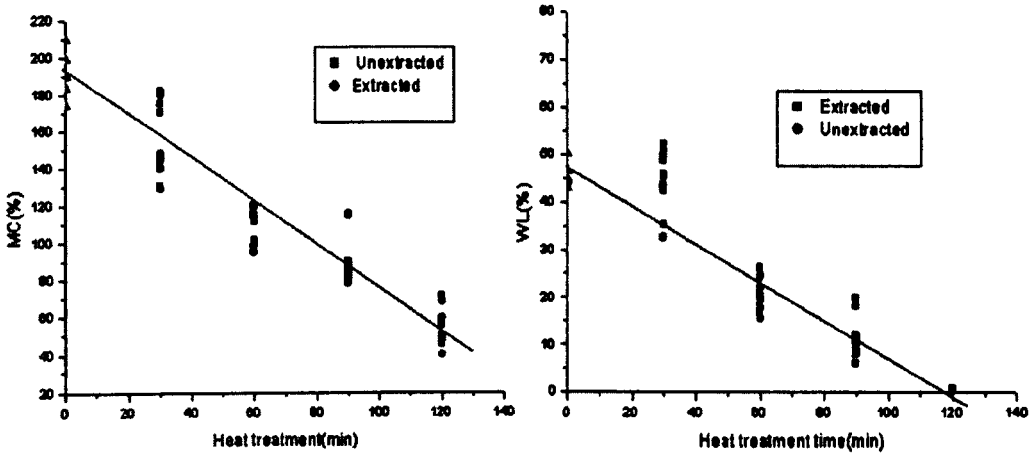


Figure 5.28: End moisture content and decay weight loss of heated wood exposed to T. versicolor for four months.

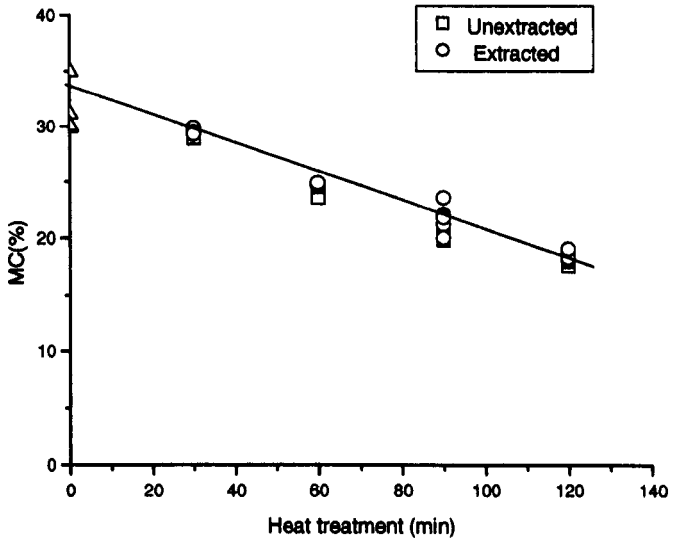


Figure 5.29: End moisture content of heated wood (sterile control) incubated over malt agar for four months

As can be observed in Figures 5.26 to 5.28, no significant difference between extracted and un-extracted heat treated wood was observed. This shows that even at these high temperatures toxic materials are not responsible for the observed decay resistance.

Kamdem *et al.* (2002), studied the decay resistance of Retified wood (Retification is a heat treatment at high temperatures for short times) and reported that incomplete protection by the treatment was obtained. The Retified wood showed just 63% and 54 % improvement in the resistance against *G. trabeum* (brown rot) *and L. lacteus* (white rot fungus), respectively.

5.3.6: The relationship between moisture content and decay

The end moisture content of the silane or anhydride modified wood after decay was reduced when WPG increased (Figures 5.30 to 5.32). For the brown rot test, where the chemically modified blocks were incubated over a support, the final moisture content reduced to about 20-35% when WL was reduced to zero. For white rot fungi, in which the samples were incubated directly over malt agar, the end moisture content of the modified wood was higher than that obtained for the brown rot fungus (30-60%). From a comparison of the end moisture content of un-decayed modified wood exposed to fungi with those for sterile modified wood incubated over malt agar, it was thought that the extra water could be as result of an increase in the free water in the lumens instead of the cell wall bound water (Figures 5.16 and 5.22). The moisture content of chemically modified wood exposed to fungi (especially white rot fungi) were higher than the limit required for fungal attack, although the moisture content of carboxylic anhydride modified wood that remained un-decayed and exposed to brown rot fungus was close to 20%.

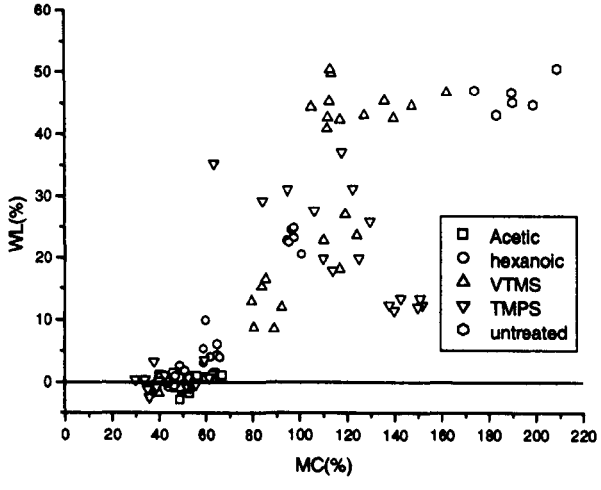


Figure 5.30: Moisture content/ weight loss relationship of chemically modified wood after 4 months exposure to T. versicolor

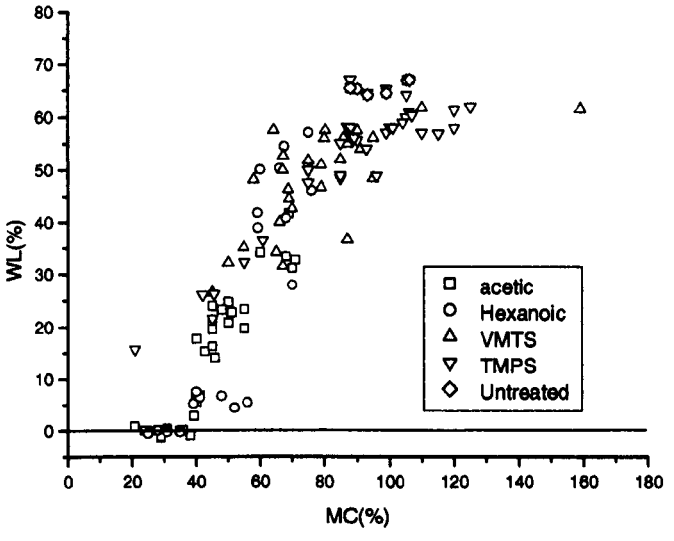


Figure 5.31: Moisture content/ weight loss relationship of chemically modified wood after 4 months exposure to C. puteana

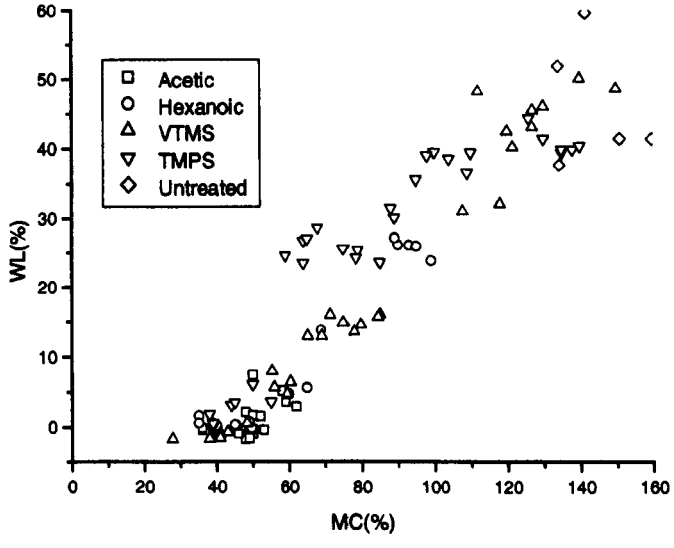


Figure 5.32: Moisture content/ weight loss relationship of chemically modified wood after 4 months exposure to P. chrysosporium

Thermally modified wood showed the same behaviour as that observed for chemically modified wood, but the modified blocks which remained un-decayed showed slightly higher moisture contents than those for unmodified wood (Figs. 6.33-6.36).

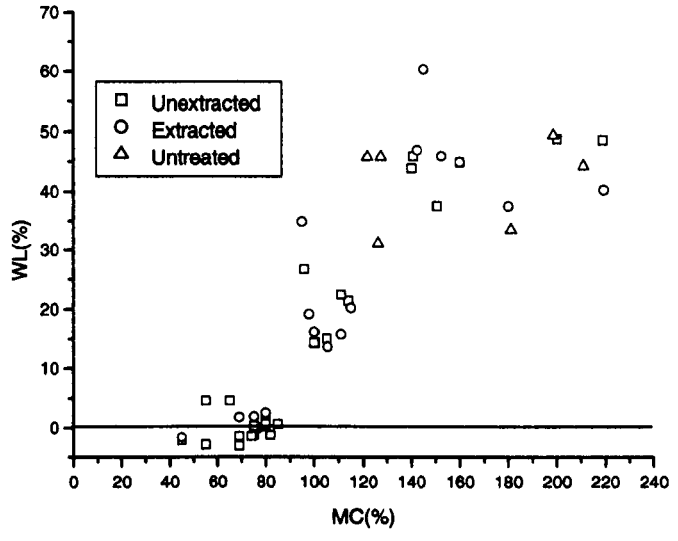


Figure 5.33. Moisture content/ weight loss relationship of thermally treated and untreated wood after 4 months exposure to P. chrysosporium

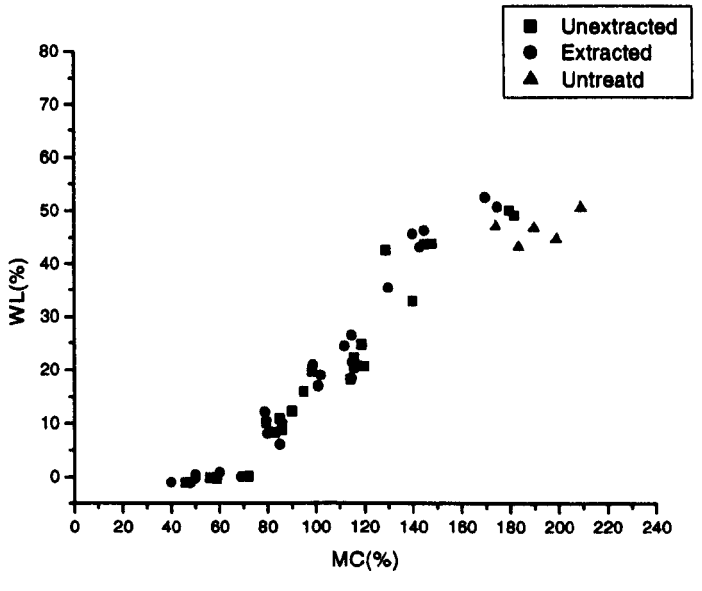


Figure 5.34: Moisture content/ weight loss relationship of thermally treated and untreated wood after 4 months exposure to T. versicolor

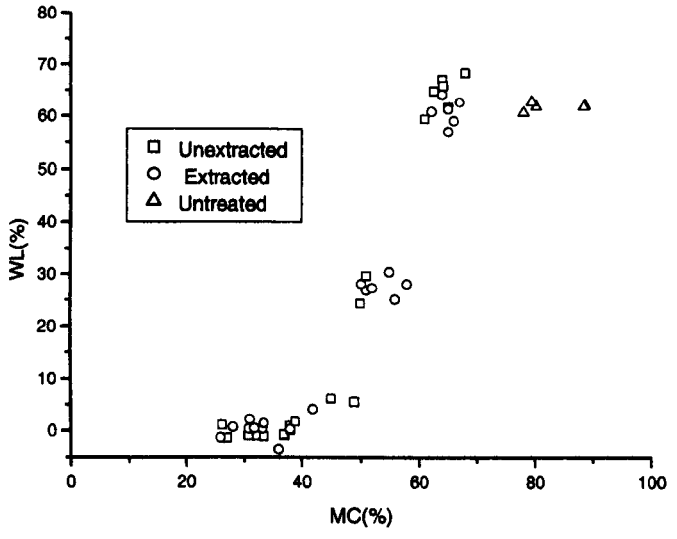


Figure 5.35: Moisture content/ weight loss relationship of thermally treated and untreated wood after 4 months exposure to C. puteana

5.3.7 The relationship between moisture content of sterile control and weight loss due to decay

As was mentioned earlier, the modifications reduced the end of the test moisture content of the wood as the level of modification increased (WPG, in the case of chemically modified and treatment time in the case of heat treated wood) and increased the durability of the wood. Regression analysis was used to investigate whether there was a significant correlation. According to the regression analysis, all the correlations are significant at the levels of confidence between 1-10%. This suggests that a reduction in the moisture content by the modifications could be an important factor in the reduction of weight loss due to decay.

In the case of acetylated and hexanoylated wood, the correlation between a reduction in the moisture content of the modified wood and weight loss due to decay by white rot fungi were not investigated because of complete protection was achieved by the modification at very low WPG's

	C. puteana		*T. versicolor*		*P. chrysosporium*	
	F	K	F	K	F	K
VTMS	5.15**	63.2	136	97.85	32	91.47
TMPS	9.98	76	75.37	97.41	67	95.7
Heated	154	99.7	116	98.3	98.8	98.8
Heated (extracted)	162	99.38	1656*	99.8	85.5	99.38
Acetic	432*	99.081				
Hexanoic	1324*	99.84				

* Significant at 1%

**Significant at 10%

The other results are significant at 5%

Table 5.3: regression analysis of the correlation between moisture content and weight loss due to decay by different organisms.

Between the modifications, the lowest F value was obtained for the relationship between weight loss due to decay by brown rot and a reduction in the moisture content. This was because the silane improved the decay resistance only slightly against brown rot fungi. However, the relationships were significant at level of 5% and 10%, this might suggest that one of the reasons that the silanes couldn't achieve complete decay resistance to the wood is that the silane's reduce the moisture content only moderately.

5.4 Points raised from this chapter

High weight losses in unmodified controls were achieved for all three fungi in this test; although the weight loss of the white rot decayed controls were lower than those for the brown rot decayed wood.

Both silanes used in this study were not effective in protecting wood against brown rot while VTMS imparted better protection against white rot fungi than that was achieved by TMPS. It was assumed that the difference could be result of a better reactivity of Si-OH from VTMS blocking hydroxyl groups of lignin and hemicelluloses which cover lignin. Although, the smaller VTMS molecule may be able to penetrate the cell wall more effectively.

For carboxylic anhydride modified wood, decay by white rot fungi was more easily controlled than decay by brown rot fungi. The threshold levels of protection for the two white rot fungi with different mechanisms were very close to one another as were the thresholds for the two adducts hexanoic and acetic anhydrides. It was assumed that phenolic groups of the lignin react more rapidly compared to the polysaccharides. Since both chemicals showed nearly the same efficacy in the protection of wood against white rot fungi, it was assumed that blocking of accessible hydroxyl group of lignin to the fungi partially is due to a shielding effect of the longer carboxylic anhydrides where the adduct physically covers some of the adjacent un-reacted sorption sites.

No difference was observed in the performance of hexanoylated and acetylated wood against brown rot fungus, thus it was concluded that WPG is the factor that determines decay resistance and not extent of OH substitution.

All the modifications applied in this study reduced the moisture content of the un-decayed wood. Silane modified wood didn't reduce this as much as compared with carboxylic anhydride modified wood. Since the different sized anhydride molecules exhibit the same level of bulking at comparable WPG's, it is reasonable to infer that bulking is the main mechanism which determines decay resistance.

A longer heat treatment at 250°C was required to impart significant decay resistance to the wood against *T. versicolor* than that against *C. puteana* and *P. chryosporium.*

No significant difference was seen between the performance of extracted heated wood and the heated wood without any extraction against all of the fungi. It was concluded that the decay resistance of extensively heated wood is not due to any extractable toxicants which might be produced as result of heat treatments.

A significant correlation between a reduction in the moisture content of the modified wood and a reduction in the weight loss due to decay was obtained. The correlation between a reduction in the moisture content of carboxylic anhydride modified wood and weight loss due to decay by white rot fungi were not investigated because complete

protection was achieved by the modification at very low WPG's with anhydride modified wood.

The modified samples exposed to the brown rot fungus showed a moisture content around 20% when weight loss was reduced to zero while the moisture content of the modified wood which showed complete decay resistance against white rot was higher than the limit required by fungi. From comparison between the moisture content of the modified wood incubated over malt agar and modified wood exposed to fungi, it is evident that the extra water will largely be in the form of free water within the cell lumen.

Chapter 6

Exposure of modified wood to un-sterile soil

6.1 Introduction

In this chapter, an attempt was made to assess the decay resistance of modified wood, establish the threshold levels of protection for the treatment chemicals and establish the heat treatment time required for preventing attack by soft rot fungi. To assess the possible toxicity of heated wood to soft rot fungi, heated wood extracted by a solvent system of toluene/acetone/methanol (4:1:1, by volume) was also exposed to soft rot test.

In addition to the soft rot test, the decay resistance of the samples which were treated with silanes in a more industrially acceptable way were assessed by a field test.

6.2 Modified wood samples

6.2.1 Un-sterile soil test

Corsican pine sapwood stakes measuring 5mm x 15mm x 100mm (radial x tangential x longitudinal) were modified as described in chapter3 (Sections 3.3.2.1, 3.3.2.2.and 3.3.3). Pyridine treated, extracted and un-extracted controls were also exposed.

6.2.2 Field test

6.3 Test conditions

6.3.1 Unsterile soil test

The modified and control stakes were exposed to a soft rot test according to modified European pre-standard ENV807. The number of unexposed stakes varied from that stated

in ENV807. All modified stakes were exposed to a leaching test according EN 84 before being exposed to the soft rot test. The weight lost of the modified and unmodified wood due to the leaching test are shown in Table 6.1. Stakes were planted to a depth of 80mm in a plastic bin of dimension 100 x 60 x 55 (deep) cm containing John innes No.2 with compost wetted to 95% of its water holding capacity. The average of pH of the aqueous soil extract (10 g of soil in 25 ml of distilled water) was 5.7. All replicates for each treatment were distributed throughout the bin. A lid was placed over the bin with gap being created between lid and the bin for ventilation purposes. The bin was stored in a conditioning room at 27° C for 34 weeks. Some sets of untreated Scot pine and beech as virulence controls were planted and removed after 8, 16, 24, 32 and 34 weeks. Corsican pine stakes were planted and removed after 16 weeks and 34 weeks. Shirley cotton strips were used to determine the biological activity of the soil. Soil moisture content was monitored and maintained throughout the duration of the test by some Corsican pine sap stakes used as moisture content controls. The experiment was run in a conditioning room with lower relative humidity (about 40%) than that recommended (70 ±5%) in the standard. This was because of a non-functionality room ventilation pump.

The modified and solvent control stakes were exposed to the test for slightly longer than the 32 weeks recommended in the ENV807 standard (34 weeks). Weight loss and end of test moisture content for these sets of stakes were calculated after oven drying (105 °C) to constant weight.

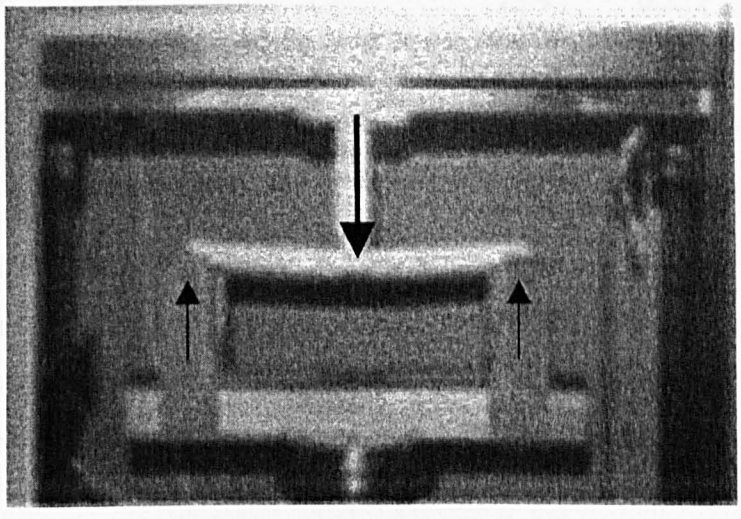
Strength parameters have been reported to be more sensitive indicators of decay (Hale and Eaton, 1993). Thus, MOR of all the stakes including stakes exposed to the soil test and unexposed stakes were tested to assess the efficiency of the treatments.

After measuring weight loss, MOR of the exposed and unexposed stakes placed in desiccators to maintain dryness condition were measured by universal instron testing machine on a three point test (Figure 6.1). The tangential face of each sample was loaded. A cross head speed of 5 m/min and a span of 8 cm were chosen for the test.

Strength loss due to the soft rot test was calculated according a formula mentioned in below:

Percent strength loss or MOR change = [(MOR of unexposed sample – MOR of exposed sample) x 100]/ (MOR of unexposed sample).

Light microscopy was used to confirm the presence of soft rot decay. Soft rot cavity attack of the cell wall was taken as evidence of soft rot. The same method explained in Section 4.2.3 was used for the light microscopic study. In this section of the study, stakes was not split up by a blade as it was explained in Chapter 5 but the inner sections were used.



Figure, Three-point static bending test (Eaton and Hale, 1993).

Table 6.1: Weight loss of chemically modified wood due to exposure to a leaching procedure according to EN 84.

VTMS		TMPS		Acetic		Hexanoic	
WPG(%)	WL(%)	WPG(%)	WL(%)	WPG(%)	WL(%)	WPG(%)	WL(%)
0	0.54	0	0.54	0	0.54	0	0.7
3.05	1.3	8	0.7	2.5	0.54	6	0.66
6.4	2.1	17.34	1.1	14.5	0.5	10	0.8
11.35	1.81	27	1.1	16.5	0.50	15	0.66
11.4	1.79	65	4	20.33	0.16	28	0.68
36.9	1.03			23.9	0.225		

6.3.2 Field test of silane modified wood

The treated samples were exposed to three different field tests (out of ground, ground contact and soil burial test) for one year. The field tests were performed in Llandegfan, Anglesey. For each chemical, one sample was used, plus control (three samples in all per test). In the burial test, the samples were planted to the depth of the 150mm in a soil with no chemical fertilizers. In the out of ground contact, the samples were stacked on conceret wall with the angel of 45°C with no shelter in order to maximase the photochemical effect of icident sunlight on the treatment as well as chemical or wood degrdadtion product leaching due to • oisoned. In the ground contact test, the samples were • oisoned on soil so that just one their surfaces had direct contact with soil. After finishing the incubation time, all samples were assessed visually.

6.4 Results and discussion

6.4.1 Un-sterile soil test

6.4.1.1 Virulence controls

Virulence controls of beech and Scots Pine revealed the fungal activity within the bin. The weight loss by Scots pine and beech controls were typical for the ENV 807 test. For beech, fungal control stakes were covered by moulds and showed higher moisture content (152 %), and weight loss due to decay (50%), than those for Scots pine (MC, 86%) and (WL, 36%) respectively.

The difference between beech and Scots pine controls (Fig. 6.2) might be result of the qualitative and quantitative difference in the lignin. Wood cell walls containing syringyl-rich lignins are more readily degraded by soft rot fungi than are cells walls containing guaiacyl-rich lignin (Eaton and Hale, 1993). Cell wall soft rot cavity chains were observed in the light microscopy images of the soft rotted Scots pine used as a virulence control, which confirms that the wood was heavily soft rotted (Figure 6.3).

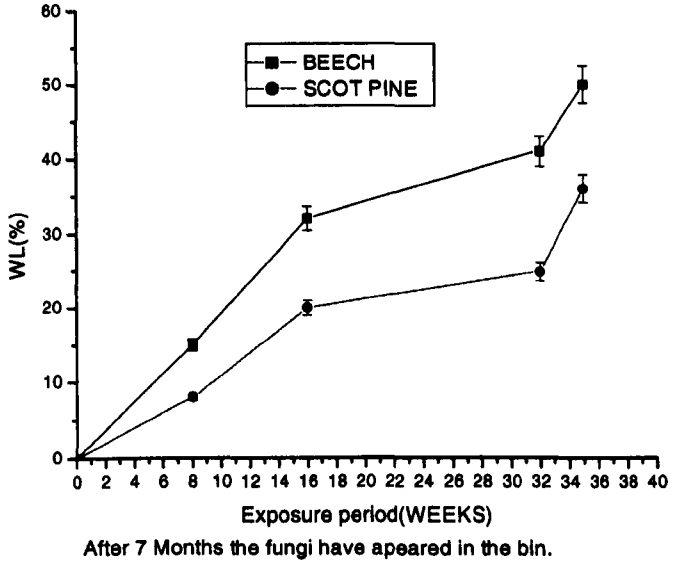


Figure 6.2: Weight loss (WL%) due to soft rot versus incubation time (weeks) for Scots pine and beech controls.

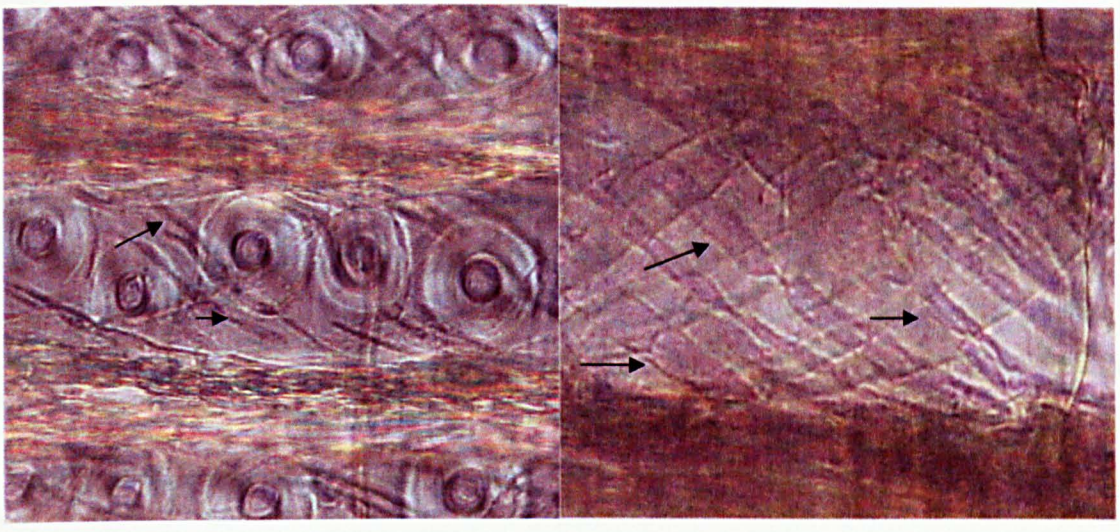


Figure 6.3: Soft rot cavities (cavity chains), observed in Scots pine sap wood tracheids oriented at an angle to the longitudinal axis of the cell (Radial longitudinal section, x 40, polarized light microscopy, ¼ wave plate)

6.4.1.2 Performance of chemically modified wood in un-sterile soil

The performance of silane treated and chemically modified wood is depicted in Figure.6.3 In this Figure each data point represents mean weight lost and mean WPG data for 6 stakes. In some cases the mean significantly varied in WPG and weight loss so the figure should only be used for comparative study.

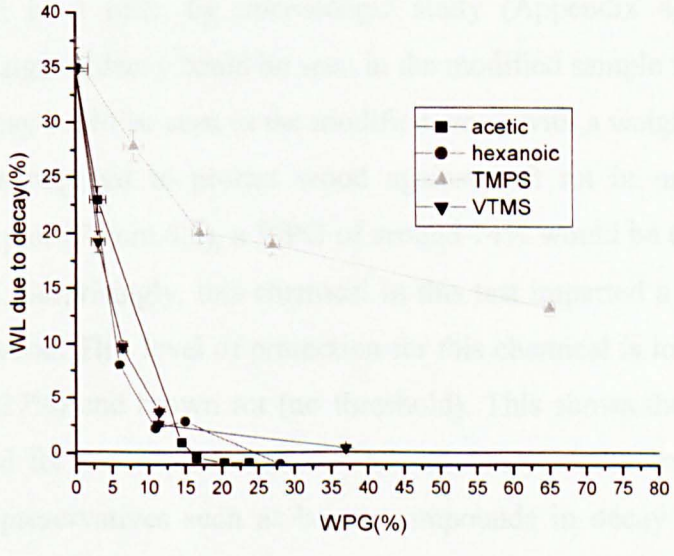


Figure 6.4: Weight loss percentage (WL %) of chemically modified wood versus WPG

Figure 6.4 shows scatter plots of weight loss and moisture content data of all individual stakes modified with VTMS and TMPS after 34 weeks exposure.

Figure 6.4 shows scatter plots of weight loss and moisture content data of all individual stakes modified with VTMS and TMPS, after 34 weeks exposure. As can be seen in Figure 6.4, for VTMS, WL due to decay was reduced when WPG increased. The data was analysed by an Anova one way test. The analysis showed that at least one of treatments was different from the others. Tukey pair- wise comparison was used to find out which treatments were different (Table 6.2.).

Table 6.2. Tukey's pair-wise comparisons test between weight loss of VTMS modified sapwood at different WPG's (NS: not significant, S: significant)

%	0.0	3.0	6.0	11.3	11.4	36
0		S	S	S	S	S
3	S		S	S	S	S
6	S	S		S	S	S
36	S	S	S	NS	NS	

Treatment with VTMS at all WPG's reduced the WL due to decay significantly. Although the difference between WPG's 36 and 11% is not significant (they are different when they are assessed by t test), by microscopic study (Appendix 4) and visual examination no obvious sign of decay could be seen in the modified sample while a slight colour change due to decay could be seen in the modified wood with a weight gain of 11. Thus, a higher WPG is required to protect wood against soft rot in un-sterile soil. According to the scatter plot (Figure 6.5), a WPG of around 14% would be the protection threshold for the VTMS. Surprisingly, this chemical in this test imparted a great deal of decay resistance to the wood. This level of protection for this chemical is lower than that required against white (27%) and brown rot (no threshold). This shows the potential of this chemical to be used for wood preservation. The efficiency of the combination of VTMS with less toxic preservatives such as boron compounds in decay resistance of wood would be worth studying in the future.

In contrast with VTMS, TMPS modified wood even with high WPG's showed some decay and its end of test EMC were always higher than the limit required by fungi. There are several possible reasons to explain the poor performance of TMPS: As was shown in Chapter 3, the larger size of the TMPS molecule may preclude effective penetration of the cell wall. Cross linking of such a large molecule within the cell wall might open up slightly the cell wall micropores when the WPG increases and the chemical fail to impart more decay resistance. The distribution of the chemical within the annual ring could be one the reason. Microscopic work showed that some parts of the modified decayed more than the other parts. TMPS has been reported to impart significant decay resistance to oil reinforced polyetster palm composite (Hill and Khalil, 2000) when the composites were exposed to a soil test with high moisture, suitable for soft rot fungi. But in this study, it was shown that no threshold protection level appears against soft rot fungi using TMPS modified wood.

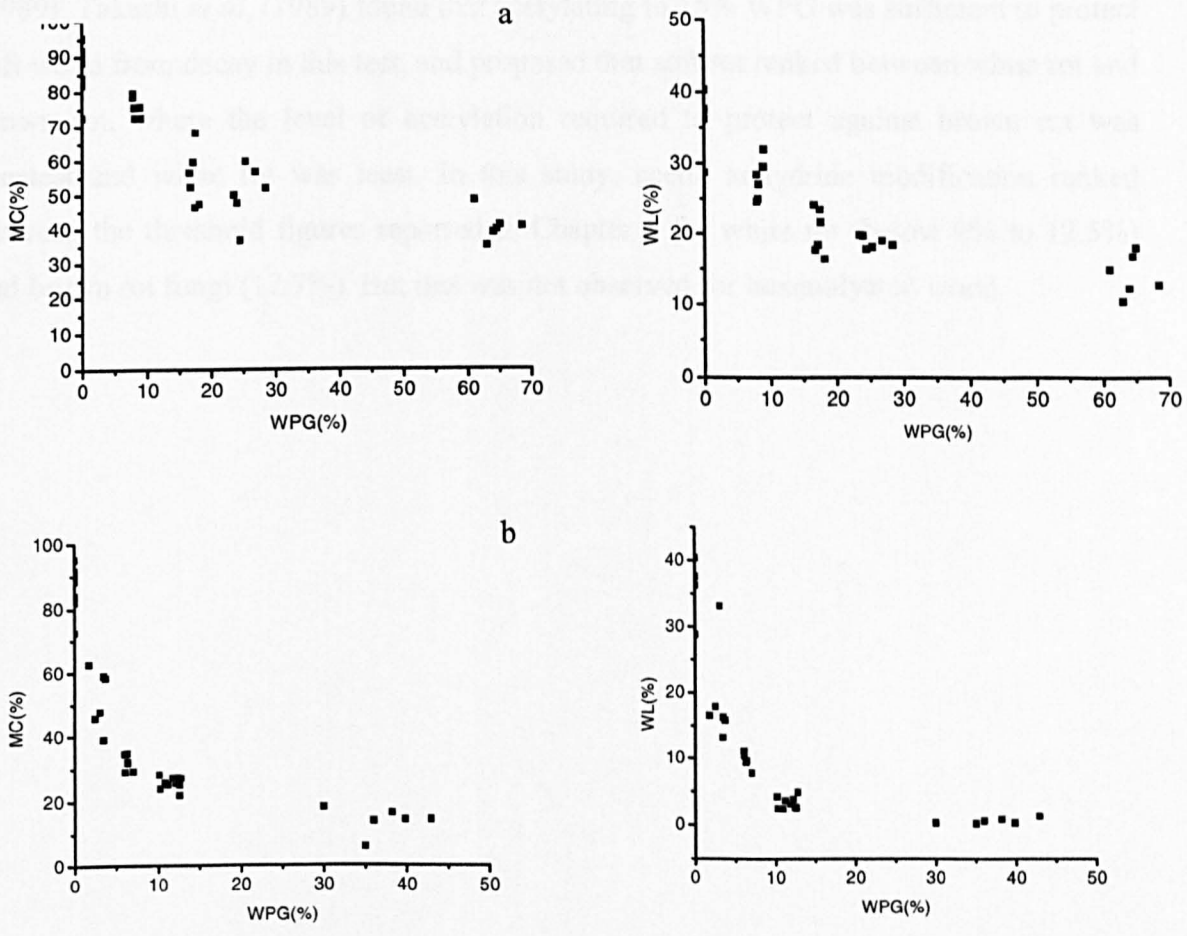


Figure 6.5: Weight loss percentage (WL %) and Moisture content percentage (MC %) in Silane modified wood, (a) TMPS modified wood, (b) VTMS modified wood.

Figure 6.6 shows scatter plots of weight loss and moisture content data of all individual staks modified with acetic anhydride, or hexanoic anhydride, after 34 weeks exposure. Threshold of about 16 and 17(%) were estimated for acetylated and hexanoylated wood. The data were analysed by one way Anova. The difference between the treatments was significant. The results of Tukey's pair-wise tests are shown in Tables 6.3 and 6.4. As can be seen, the differences between WPG's of 15, 16%, 21 and 23 were not significant. A weight gain of 16% should be the threshold level for the chemical. All samples visually were sound. A sample with a WPG of 15% was examined. No cell wall cavities were found in the sample. As can be seen in Figure 6.5, moisture content of the modified wood is lower than the other modifications applied in this and below the limit fungi required for growth.

The result for acetylated wood is in agreement with the results obtained by Takashi (1989). Takashi *et al*, (1989) found that acetylating to 15% WPG was sufficient to protect soft wood from decay in this test, and proposed that soft rot ranked between white rot and brown rot, where the level of acetylation required to protect against brown rot was greatest and white rot was least. In this study, acetic anhydride modification ranked between the threshold figures reported in Chapter 5 for white rot (below 9% to 12.5%) and brown rot fungi (17.7%). But this was not observed for hexanolyated wood.

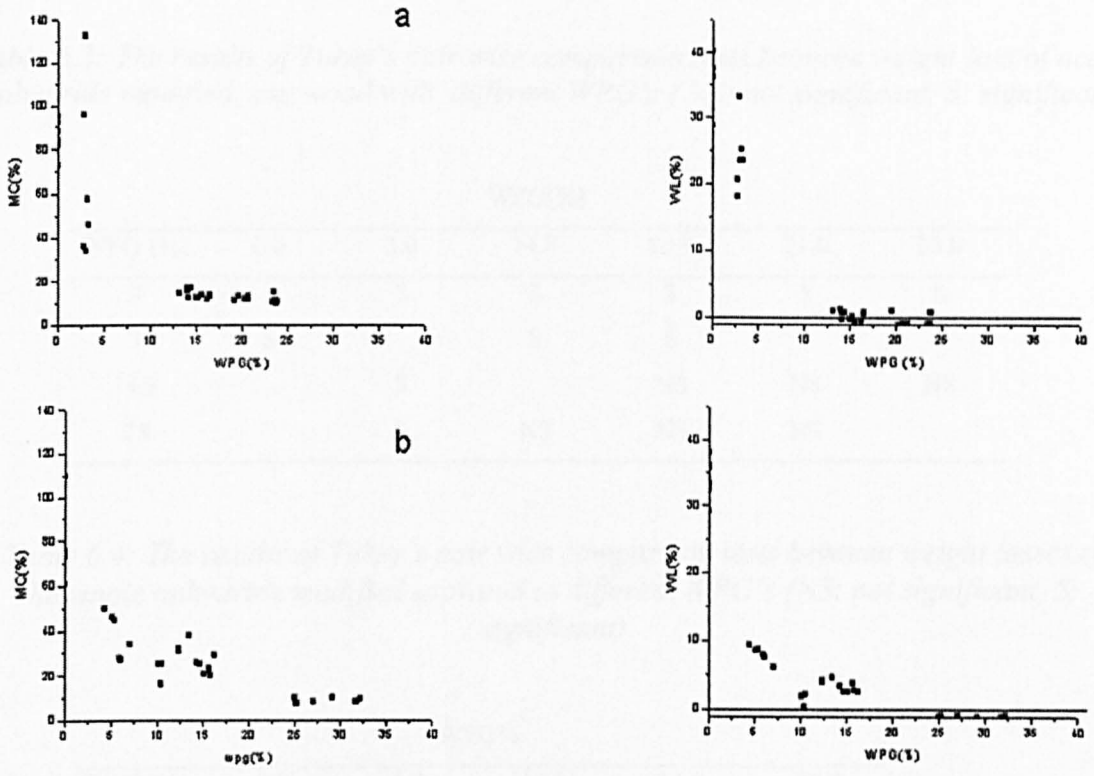


Figure 6.6: Weight loss (WL%) and moisture content (MC %) of acetylated and hexanoylated wood (a) acetic anhydride modified wood (b) hexanoic anhydride modified wood in unsterile soil tests.

Table 6.3: The results of Tukey's pair wise comparison tests between weight loss of acetic anhydride modified sap wood with different WPG's (NS: not significant, S: significant)

	WPG(%)					
WPG (%)	0.0	3.0	14.8	15.9	21.0	23.0
0		S	S	S	S	S
3	S		S	S	S	S
14.8		S		NS	NS	NS
23		S	NS	NS	NS	

Table 6.4: The results of Tukey's pair wise comparison tests between weight losses of hexanoic anhydride modified sapwood at different WPG's (NS: not significant, S: significant)

	WPG%				
WPG(%)	0.0	3.0	10.0	14.8	28.0
0.0	S				
5.0	NS	S	S	S	S
14.8	S	S	S		S
28.0	S	S	S	S	

6.4.1.3 Performance of heat-treated wood in the un-sterile soil test

The performance of thermally modified wood is depicted in Figure 6.7. In this figure, each data point represents mean weight loss and mean WPG data for 6 stakes.

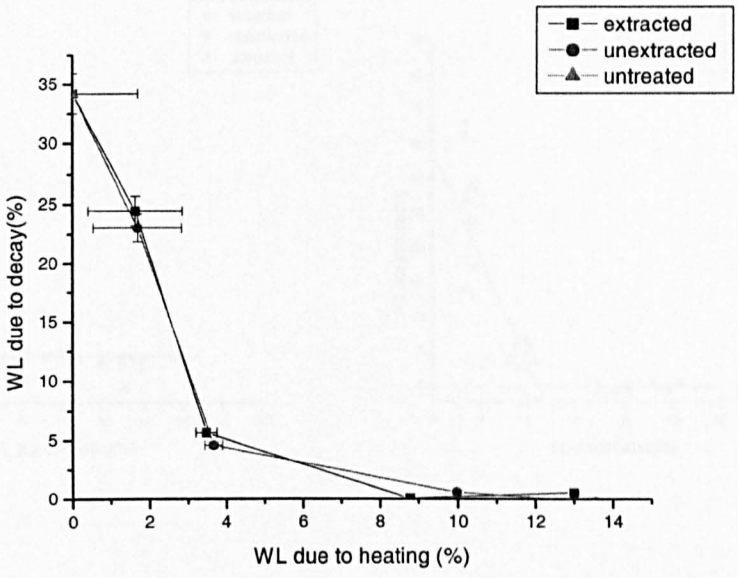


Figure 6.7: weight loss percentage (WL %) of thermally modified wood versus WL due to heating

Similar to the data for chemically modified wood, in some cases the mean varied in WL (%) due to heating and

WL due to decay so the figures should be only used for comparative studies.

Figure 6.8 shows the scatter plots of weight loss and moisture content data of individual heated samples with or without post-extraction after 34 weeks exposure. As can be seen in Figure 6.8, by increasing WL (%) due to heating, the decay resistance of the wood was increased. However, high decay resistance is imparted to the wood by heat treatment when the intensive changes in the wood take place. Intensive changes in the wood took place when the wood was heated at 250°C. The changes were monitored by a reduction in strength of about 41 % (Section 6.5.5.) and a weight loss due to heating of 8%. The reduction in strength (Section 6.5.5) and weight loss show that some degradation of cellulose occurred due to the treatment. A weight loss of about 8% was required to significantly prevent soft rot attack.

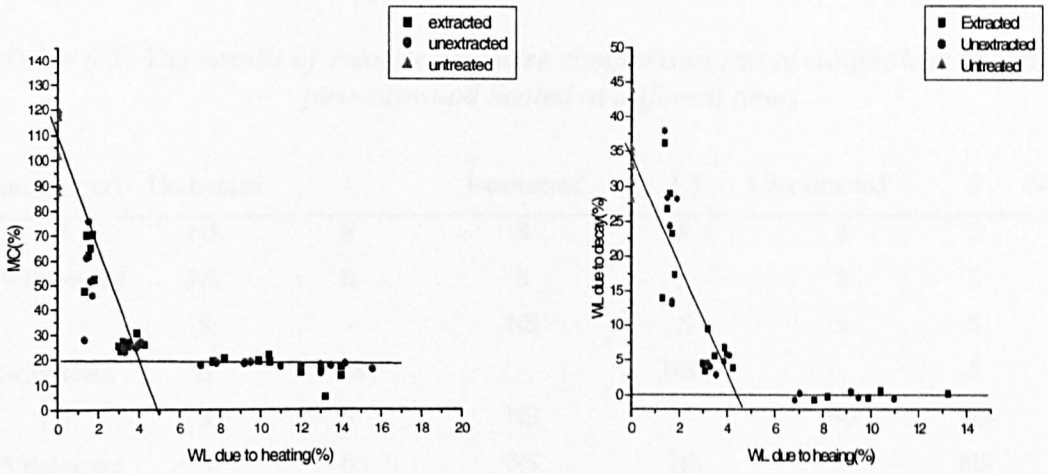


Figure 6.8: Weight loss percent (WL %) and moisture of heated wood after 34 weeks exposure to un-sterile soil.

Kamdem (2000), reported that no significant difference was observed between heated wood extracted by organic solvents and water, and heated wood without any extraction. Since in their study, the heated wood didn't show high decay resistance and the heated wood showed high weight loss due to decay, this work was under taken to show whether high decay resistance could be achieved by heat treatment without any contribution of any toxic material.

Since in some cases, some difference was seen between weight loss in heated wood due to decay which was extracted by 4:1:1 and heated wood without any extraction, the data was statistically analysed by two way ANOVA to find out whether the difference are statistically significant and to find whether the interaction between treatment time and post-extraction is significant. The difference between WL of heated wood and heated wood extracted by 4:1:1 was not significant at the level of 95% when the data were analysed by two way Anova. The interaction between the heat treatment time and the post-extraction was also not significant at the level of 95%. But the difference between treatments with different times was significant. These shows the lack of the toxicity of heated wood to the fungi attacked wood in the un-sterile soil test.

Table 6.5: The results of Tukey's pair wise comparison test of weight loss of Corsican pine sapwood heated at different times.

Time (Hour)	Un-treated	1	1-extracted	1.5	1.5-extracted	2	2-extracted
0.5	NS	S	S	S	S	S	S
0.5-Extracted	NS	S	S	S	S	S	S
1	S	-	NS	S	S	S	S
1-extracted	S	NS	-	NS*	-	S	S
1.5	S	S	NS	-	NS	NS	NS
1.5 Extracted	S	S	NS	NS	-	NS	NS
2extracted	S	S	NS	NS	NS	NS	-
2	S	S	NS	NS	NS	-	NS

The difference between treatments was investigated by Tukey pair-wise. The results are shown in Table 6.5. The difference in WL due to decay between heated and unheated wood, except for heating at half an hour hours is significant. Thus, In this study, it was clearly shown that significant decay resistance can be achieved by heat treatment of wood without any contribution of extractable toxic material, which might be produced in heat treated wood as result of heating of wood at high temperatures.

6.4.1.4 The relationship between moisture content and decay

Figure 6.9 shows a plot of moisture content of the wood at the end of the test against weight loss for chemically modified wood, irrespective of weight percent gain. Wood modified with silanes, or carboxylic acid anhydrides each gave a very similar moisture content-weight loss relationship.

In contrast with unmodified wood which showed high moisture content of 150% for beech and 86% for Scot pine, the moisture content of the modified wood with a weight loss of 0% were around or lower than the theoretical point (20%) required for fungi to degrade wood. Of course, this is in contrast with the results obtained for brown rot and white rot test in chapters 4 and 5. Foster (1998), reported that highly modified wood

exposed to any fungal test (brown rot, white rot, soft rot) had higher moisture contents than that required by fungi.

A reduction in the final moisture content of wood after decay as a result of the protection of wood by modification and even toxic preservatives (Foster1998) is expected because of the reasons mentioned in Chapter 4. But the lack of presence of significant decay in the modified samples with the final moisture content below the theoretical limit required by fungi might suggest that a reduction in moisture content due to the modification plays an important role in imparting decay resistance against soft rot fungi to the wood.

Although the moisture content of linear carboxylic acid modified wood after exposure was less than the limit required for fungi to degrade wood, the substitution of hydroxyl groups cannot be judged to be the most important reason for the improved decay resistance. Because, the bulking of wood, as result of the presence of a chemical (Spalt, 1958, Martins, 1992 and Papadopoulos 2002) or extractives (Wangaard, 1967), within the cell wall, reduces poly-molecular adsorption and total adsorption significantly.

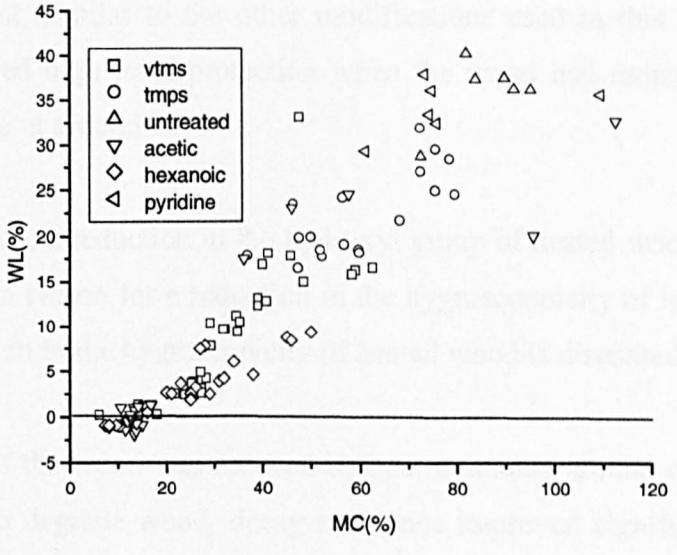


Figure 6.9: Moisture content/ weight loss relationship of chemically modified wood after 34 weeks exposure in un-sterile soil

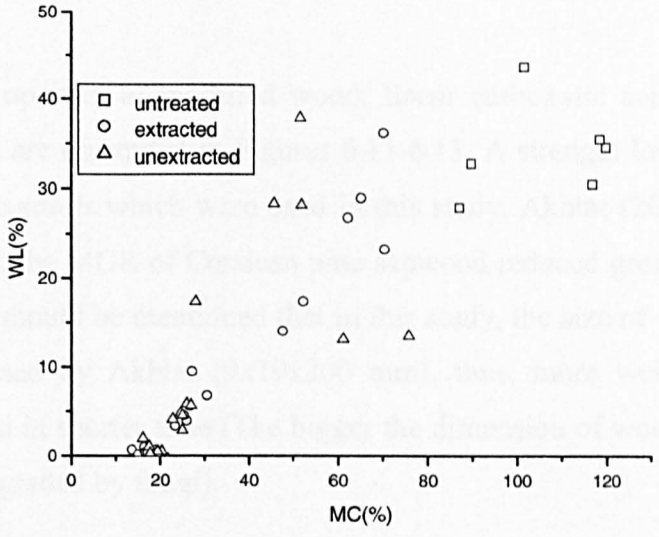


Figure 6.10: Moisture content/ weight lost relationship of heated wood after 34 weeks exposure in un-sterile soil

As it can be seen in Figure 6.10, the relationship between the moisture content and weight loss for heated wood, shows much more scatter than the data in Figure 6.10. In the case of heat treatment, similar to the other modifications used in this study, the heated wood when showed high level protection when the wood had moisture lower than that required by fungi at around 20%.

In the case of heated wood, a reduction in the hydroxyl group of heated wood cannot be also judged to be the main reason for a reduction in the hygroscopoicity of heated wood. The reason for the reduction in the hygroscopicity of heated wood is discussed latter.

When moisture content of the wood was reduced by heat treatment around or below the limit required by fungi to degrade wood, decay resistance improved significantly. This shows that moisture content could be one the important reason for the improved decay resistance of the wood against soft rot. More accurate judgment about the role of moisture content in imparting decay resistance to the wood can be made by correlating the weight loss due to decay to the FSP of modified wood as it was discussed in chapter 4.

6.4.1.5 Flexural properties:

The losses in flexural properties of modified wood, linear carboxylic acid, silane and thermally modified wood are illustrated in Figures 6.11-6.13. A strength loss about 90% was obtained for all the controls which were used in this study. Akhtar (2002), reported after 12 months exposure, the MOR of Corsican pine sapwood reduced greater than 45% at a weight loss 5-6%. It should be mentioned that in this study, the size of samples were smaller than that was used by Akhtar (9x19x200 mm), thus, more weight loss and strength loss was obtained in shorter time (The bigger the dimension of wood, the longer it takes the wood to be degraded by fungi).

Similar to weight loss, differences between MOR of heated wood and heated wood extracted by 4:1:1 were not significant at the level 95% when the data were analysed by two ways ANOVA. The interaction between the heat treatment time and the extraction was also not significant at the level of 95%. The difference between treatments with different times was significant. Turkey's pair-wise was used to show difference between the treatments (Table 6.7).

Table 6.7: The results of Tukey's pair wise comparisons test between strength of Corsican pine sap wood heated at different times.

Time (hour)	Un-treated	1	1-extracted	1.5	1.5-extracted	2	2-extracted
0.5	NS	S	S	S	S	S	S
0.5	NS	S	S	S	S	S	S
1	S	-	NS	S	S	S	S
1-extracted	S	NS	-	NS*	-	S	S
1.5	S	S	S	-	NS	NS	NS
1.5	S	S	S	NS	NS	NS	NS
2extracted	S	S	S	NS	NS	NS	-
2	S	S	S	NS	NS	-	NS

NS*= Not Significant

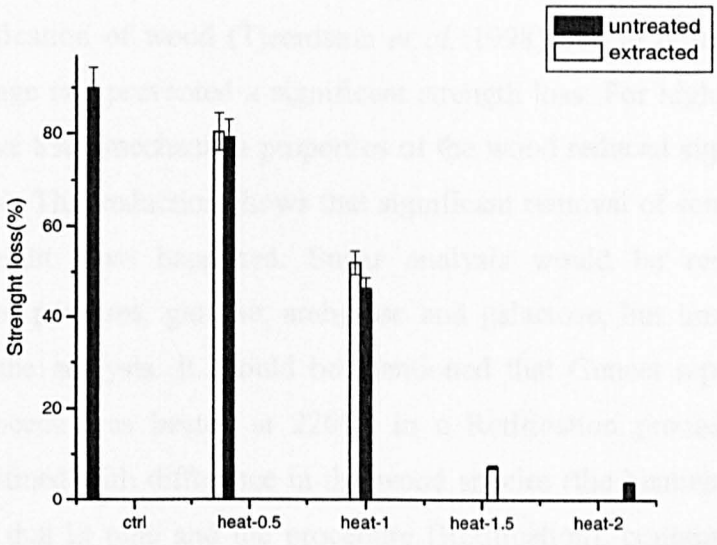


Figure 6.11: Loss of flexural properties of heated wood after 34 weeks exposure to un-sterile soil

In heated wood, even small weight loss due to decay shows high reduction in strength of the wood. As a result of the sensitivity of MOR to decay, the difference of the wood heated for 1 hours and the wood heated for 1.5 and 2 hours was significant while the difference was not significant when weight loss due to decay was used as a decay measuring parameter. For the same reason, the difference of the untreated and wood heated for 0.5 hour in strength loss was not significant while the difference was significant when weight loss due to decay was used as decay measuring parameter. However, the correlation coefficient and P value between strength loss and WL were 0.82, 0.000 respectively. This shows that there is an acceptable correlation between WL and strength loss results. Thus, the strength loss data also shows the lack of toxicity of the heated wood.

At low weight losses due to heating (1.7, 3.5%), no significant reduction in the MOR of the wood was obtained. These results are in agreement with the results obtained by Guneet (2003), who reported for a weight loss of around 3% no significant decrease in the mechanical properties of the heated beech was observed. The side groups of the two major softwood hemicelluloses is more susceptible to heating than hemicellulose backbone and even as result of their degradation due to heating, a MOR loss might be expected (Levan *et al.* 1990). Although the dried weight loss of the wood shows that at

least some degradation in hemicelluloses must have happened as result of heating but the cross linking and resinification of wood (Tjeerdsma *et al.* 1998) due to heating might have recovered the damage and prevented a significant strength loss. For higher weight loss due to heating (above 8%), mechanical properties of the wood reduced significantly (41% for 8% weight loss). This reduction shows that significant removal of some part of amorphous cellulose might have happened. Sugar analysis would be required to investigate the amount of pentoses, glucose, arabinose and galactose, but limitation in time did not allow for the analysis. It should be mentioned that Guneet reported 3% weight loss when the beech was heated at 220°C in a Retification procedure. The difference could be explained with difference in the wood species (the hemicellulose in beech is more sensitive that in pine and the procedure (Retification), containing some primary heating procedures.

The correlation of strength and weight loss for the different treatments is reflected in Table 6.7 For all chemically modified wood, correlation between weight loss and trength loss were significant. This shows that strength loss could be used as a parameter for evaluating decay in chemically modified wood (in this case, mostly soft rot). These are in the contrast with the results obtained by Foster (1998), who reported that deflection tests couldn't be used to measure the decay of modified wood.

Table 6.7: Correlation of strength loss and weight loss for chemically modified wood.

	P-value	Pearson correlation
Hexanoic	0.000	0.72
Acetic	0.000	0.86
VTMS	0.000	0.83
TMPS	0.04	0.4

However, in some cases, because of high strength variations in unexposed samples and the low numbers of samples (4), strength loss was underestimated. For example, the strength of acetylated wood at a WPG of 20%, which was not exposed to the soil test, was 79.8 KPa while for the exposed sample (with 6 replicate) was 102 KPa. Thus, a negative strength loss of 24% was calculated. This caused the difference between acetylated at 15.5 and higher WPG became significant while it was not significant for their weight loss.

This problem in the case of hexanyolated wood with a WPG 15% and 28% was also observed. Regardless of the problems mentioned in above, the calculated threshold for by strength loss for acetylated and hexanyolated wood were nearly the same (20%). These are higher than those were calculated by the weight loss. Acetylated wood with WPG of 14% and 16% showing weight loss 1% and 0.1 showed strength loss about 12% and 10%. No obvious sign of decay was also by microscopic studies in the samples with 16% while decay signs could be observed in the weight loss of 14%. Thus, theses different threshold don't invalidate the data obtained by weight loss.

In the case of VTMS modified wood, the statistical results of the strength loss data was completely in line with the statistical results of weight losses when they were used as a measuring parameter for decay (Table 6. 8). Although a negative strength loss was obtained for the modified wood with WPG 36%, the difference between strength loss of the modified wood with WPG 11 and 36% was not significant. For TMPS, high strength loss even for TMPS with the highest WPG was obtained showing high levels of decay (Figure 6.13.). However, the differences of all treatments were significant when they were compared to untreated samples. By strength loss data, a threshold of 13% was calculated for the fully protection of wood against soft rot attack. This value is in the line with thresholds calculated by weight loss data (14%).

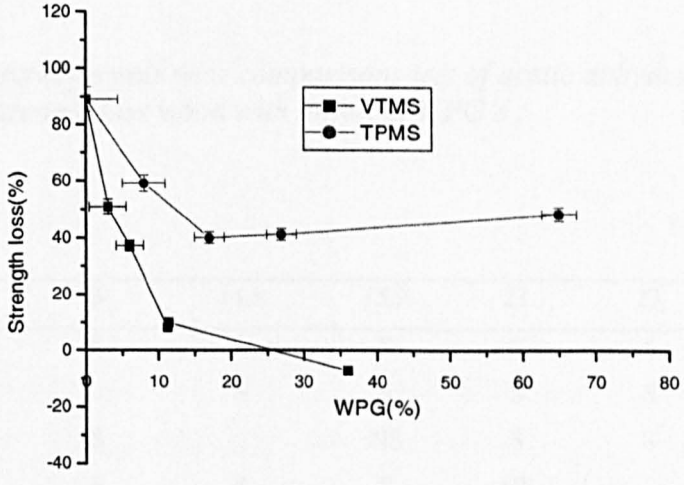


Figure 6.12: Strength loss of silane-modified wood after exposure to an un-sterile soil test for 34 weeks.

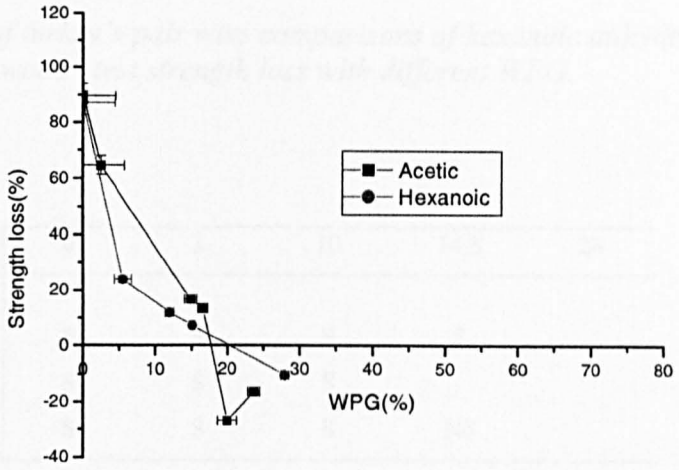


Figure 6.13: Strength loss of linear carboxylic anhydride modified wood after exposure to an un-sterile soil test for 34 weeks.

Table 6.8: The results of Tukey's and Fisher's pair wise comparisons test between strength loss due to decay of VTMS modified wood at different WPG's .

%	0	3	6	11.3	11.4	36
0		S	S	S	S	S
3	S		S	S	S	S
6	S	S		NS/S	NS/S	S
36	S	S	S	NS	NS	

Table 6.9: The results of turkey's pair wise comparisons test of acetic anhydride modified strength loss wood with different WPG's .

%	0	3	14.8	15.9	21	23
0	S	S	S	S	S	S
3	S		S	S	S	S
14.8	S	S		NS	S	S
23	S	S	S	S	NS	

Table 6.10: The results of turkey's pair wise comparisons of hexanoic anhydride modified sap wood test strength loss with different WPG.

%	0	3	10	14.8	28
0					
5	S	S	S	S	
14.8	S	S	S		
28	S	S	S	NS	

NS: not significant, S: significant

Table 6.11: The results of Tukey's pair wise comparisons of TMPS modified sap wood test strength loss with different WPG.

%	0	8	17	27	65
0		S	S	S	S
5	S	NS	NS	NS	NS
14.8	S	NS	NS	Ns	NS
28	S	NS	NS	NS	NS

NS: not significant, S: significant

6.5 Points raised from this section:

In general, when the modifications reduced the end of test moisture content below and around 20%, a high level of decay resistance against soft rot was imparted to the wood. TMPS modification didn't reduce moisture content below the limit required by fungi and didn't impart high decay resistance to the wood. Old cell wall cavities could be seen in the light microscopy of TMPS modified wood. While no cell wall cavities were found in the VTMS modified wood with a corrected weight loss of 0.6%.

Although VTMS treatment with a WPG of 11.4% imparted good decay resistance (a weight loss lower than 3%) its data was not statically different compared with the data for

VTMS with a WPG 36% (a weight loss of 0.6%), visual signs of decay (slight colour change due to decay) could be seen in the wood but no obvious sign of decay could be seen in the wood with a WPG 36%. This shows that higher WPG is required to impart significant decay resistance to the wood. A weight gain of about 14% was calculated as the threshold level for VTMS treatment.

Significant correlation between weight loss and strength loss was obtained. Thus in this, it was shown that strength loss could be used as parameter for evaluation of decay level of modified wood. However, in some cases, the low number of samples for unexposed samples and a high standard deviation in the strength loss of the unexposed samples caused an under-estimation of strength loss.

For acetylated and hexanoylated wood, higher threshold levels were calculated by strength loss than those calculated by weight loss while for VTMS, nearly the same threshold as that was calculated by weight loss was calculated.

The difference between decay measuring parameters (weight loss and strength loss) of unmodified wood and of the chemically modified at the lowest weight gains studied was statistically significant when they were analysed by a Tukey comparison pair wise test. This shows the efficiency of the chemicals studied in imparting decay resistance to the wood. However, TMPS failed to impart significant decay resistance to the wood even at high WPG levels.

In this study, acetic anhydride modification ranked between the threshold figures reported in chapter for white rot (below 9%) and brown rot fungi (around 17.7). But for hexanoylated wood, a WPG (17%) threshold nearly the same as that for the brown fungi was obtained.

The presence of toxic extractable materials as a result of heat treatment did not have any significant effect on the decay resistance of heated wood against soft rot fungi.

Some decay resistance by heat treatment can be achieved without strength losses due to heating. But, intensive heat treatment is required to impart significant decay resistance to wood in un-sterile soil. Significant the decay resistance is accompanied with significant strength loss (41%).

A good relationship between a reduction in weight loss and end of test MC for chemically modified wood was obtained. The relationship for the heated wood was not as good as that observed for chemically modified wood.

6.6 Field test of silane treated wood

6.6.1 Results and Discussion

6.6.1.1 The decay resistance

The modified sample exposed to the tests were visually assessed. In the burial test, VTMS imparted some decay resistance to the wood while significant decay resistance was imparted by TMPS (no obvious sign of decay was observed on the modified wood, Figure 6.16). In this section of study, aqueous solutions of VTMS and TMPS was used while in the other parts of studies the methanolic solutions of silanes were used. These results suggest that under the present treatment conditions, not enough VTMS could have penetrated in to the cell wall because of oligomerisation of the VTMS (which has a very reactive Si-OH group) (Chapter 3) after removing the sample from the treating vessels. Trials showed that aqueous solutions of VTMS bulked wood blocks with dimensions of 20x20x5mm just 1% when a vacuum desiccators method was used. This bulking is at least five times smaller than that was obtained when methanolic solution were used (Chapter 3).

In the contrast with VTMS, the Si-OH from the TMPS is not very reactive and even at high temperatures, no significant polymerisation *via* siloxanes takes place (Chapter 3). Thus, the silane oligermerisation doesn't take place extensively at room temperature. As was discussed in Chapter 3, hydrolysed silane might accesse to more cell wall micropores (provided that it doesn't oligomerise or polymerise). Thus, the hydrolysed silane could

have penetrated in the cell wall sufficiently to protect wood against fungal attack. In conclusion, the treatment method was found to be a proper method to treat wood with TMPS.

6.6.1.2 Weathering resistance

In the out of ground contact and soil contact tests, none of the samples showed obvious sign of decay while distinctive signs of weathering could be seen on the untreated sample (Figures 6.14 and 6.15). Both silanes imparted some weathering resistance to the wood but TMPS imparted slightly higher weathering resistance to the wood.

Pizzi and Mittal, (1994), stated that the saturated backbone and high Si-O bond energy results in products that perform very well in applications involving exposure to sunlight. They also suggest that the poly-siloxane polymer doesn't absorb energy in the ultraviolet (UV) region of the light spectrum, UV light can pass through clear silicones to the surface below the sealant. Thus clear silicone doesn't protect the substrate. As can be seen, VTMS treatment doesn't colour the wood but TMPS slightly colours wood. In addition, it is shown in Chapter 7, that the double bound of TMPS reacts while the double bound of VTMS modified wood remains untreated. These could be the possible reasons for a slight better weathering resistance of silane modified wood with TMPS.

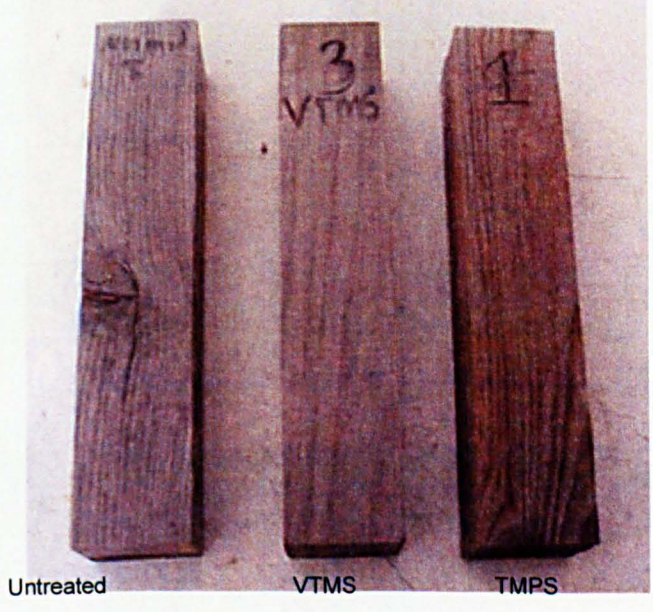


Figure 6.14: Out of ground contact test of silane modified wood.

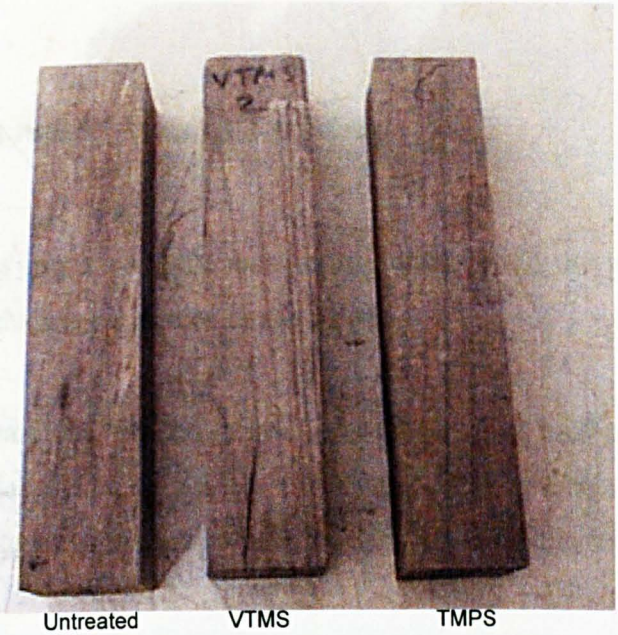


Figure 6.15: Ground contact test of silane modified wood

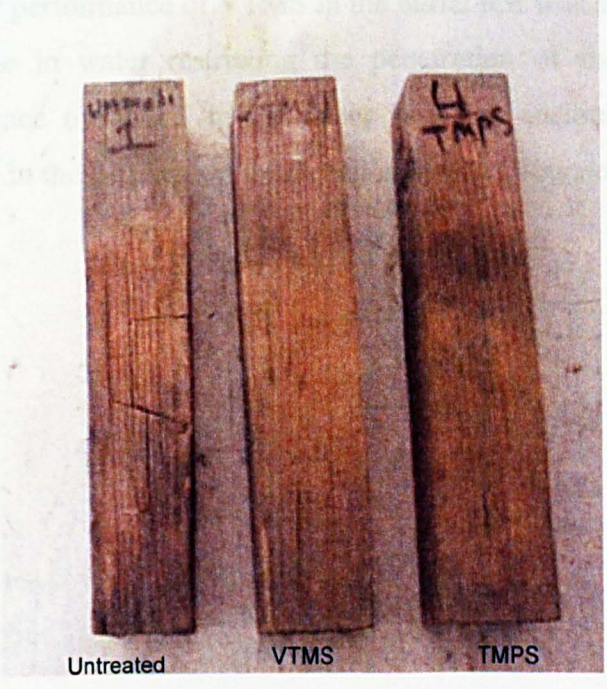


Figure 6.16: Silane modified wood compared to unmodified wood which were buried in soil for 12 months.

6.7 Points raised from this section

Both silanes imparted some weathering resistance to the wood. TMPS imparted slightly higher weathering resistance to the wood

Pressure treatment was recognised to be an effective method in treating wood with TMPS when the wood is used in contact the with soil. A solution of alcohol and water was also recognised to be a suitable solvent for using the silane in industrial purposes.

In the burial test, VTMS imparted some decay resistance to the wood while significant decay resistance was imparted by TMPS.

The poor performance of VTMS in the burial test was attributed to the oligomerisation of the silane in water restricting the penetration of the silane in the cell wall. Good performance of TMPS in the decay test was attributed to a better capability of the chemical in the penetration to the cell wall when aqueous solution of the silane was used.

Chapter 7

The physical properties of modified wood

7.1 Introduction

Wood in exterior conditions can be exposed to high moisture levels. In addition, fungi transfer water in to the wood to open up the cell wall pore structures. Thus, the stability to hydrolysis of any modification, either through the formation of chemical bonds to the cell wall or by a polymer matrix filling the cell wall micropore structure, is important in imparting decay resistance or dimensional stability to wood. Thus, it was necessary to assess the stability of silane modification or the ester bonds of anhydride modified wood to hydrolysis. In order to determine the stability of the ester bond, Si-O bond and polymer matrix to hydrolysis, the modified wood was subjected to a series of five water soak/oven-dry cycling tests. In addition, since the ability of water to swell wood cell wall might influence the accessibility of wall polymers to fungal degradative agents, the capability of the treatment in reducing the wood swelling due to water soaking might give important information about the mechanism by which the modifications impart decay resistance to the wood.

Many brown rot fungi have a tendency to be potent acid producers and can cause a drop in pH of the growth medium. The acids produced are a variety of organic acids, notably oxalic acid. The Si-O bond is not stable against concentrated base or acid. Thus, the determination of the stability of silanes to acidic conditions was important for assessing their ability to impart decay resistance to wood against the fungi.

The ability of intensive heat treatment at a temperature of 255°C used in the chapter 4 in imparting permanent dimensional stability to Corsican pine sapwood was also assessed.

7.2 Experiment

7.2.1 Chemically modified wood

Corsican pine sapwood blocks measuring 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were chemically modified as described in Chapter 3.

7.2.2 Thermally modified wood

Corsican pine sapwood blocks measuring 20 mm x 20 mm x 5 mm were thermally modified at 250°C for different times (0.5, 1, 1.5 and 2 hour) according to the procedure explained in the previous Chapter.

7.2.3 Dimensional stability

The dimensions of the oven-dried modified samples (five replicates) were measured by using a digital caliper accurate to +/- 0.1 mm and weight determined to 0.1 mg. Following measurement, blocks were then vacuum impregnated with deionised water for the water-soak test. Samples were soaked for five days at 22°C. Following measurement, blocks were oven dried first at 60°C for 24 hr and then at 100°C for 48 hr, in order to ensure dryness to constant weight. Once fully dry, samples were again measured and reweighed. This procedure was repeated for a total of 5 oven-dry (OD) water soak (WS) cycles.

The volumetric swelling coefficients (S) were calculated according to:

$$S(\%) = (V_w - V_d) * 100 / V_d \qquad (1)$$

Where: V_w = volume of water saturated wood and V_d = volume of oven dry wood.

The anti shrinkage efficiency (ASE) was calculated according to:

$$ASE(\%) = (S_c - S_m)*100/S_c \quad (2)$$

Where: S_c = volumetric swelling coefficient of control (Unmodified sample) and S_m = volumetric swelling coefficient of modified sample

7.2.4 Infrared spectroscopy of silane treated wood

Fourier transform infrared spectroscopy (FTIR) was performed using a (Nicolet 750-2) spectrophotometer. The unmodified and modified samples with four different WPG's used for the dimensional stability measurement were milled to a fine mesh, and oven dried at 100°C overnight, mixed with KBr in a ratio of 1:100 mg (wood :KBr) and pressed under a vacuum to form pellets.

7.2.5 Nuclear magnetic resonance spectroscopy

Solution ^{13}C NMR spectra of VTMS and TMPS were run on a Bruker Avant 500, 500 MHz nmr spectrometer, using $CDCl_3$ as the solvent, using a 5 mm broad band observation (BBO) probe. The acquisition time was 1 second, and the number of transients was 1000. Solid-state cross-polarised magic angle spinning 13-C NMR spectra were run on the same instrument on powdered wood samples, using a 4 mm BBO probe. The acquisition time was 0.035 seconds and the number of transients was 1000.

7.2.6 Resistance to Oxalic acid

In order to assess the acidic hydrolytic stability of VTMS and TMPS, Two samples of VTMS and TMPS modified wood with the highest WPG were vacuum impregnated with a solution of oxalic acid with a pH of 1.7 and then were shaken slowly in the solution for two weeks. After each week of the incubation, the acidic solution was changed to leach degradation products. In addition to this, at the end of incubation, the oxalic treated wood

was leached by distilled water for three days. FTIR was used to confirm the stability of the modified wood against oxalic acid with a pH similar that observed in decayed wood.

7.7 Results and discussion:

7.7.1 Leaching of chemically modified wood:

For chemically modified wood, most of leaching takes place in the first cycle of leaching. Between different chemical modifications used in this study, the highest and the lowest WL due to leaching were obtained for TMPS and acetylated wood respectively (Table's 7.2 and 7.3).

For acetylated and hexanoylated wood, lower WL's due to leaching than those found for untreated wood were obtained (Table 7.2). These are in the agreement with the results were obtained by Cetin, 1999.

For VTMS treated wood, a WL of about 3% due to leaching was obtained which was nearly the same as that found for the untreated wood (Table 7.1). After cycles 2 (for most WPG's) and 3 for the lowest WPG's of VTMS and TMPS, leaching was not accompanied with a reduction in the dimensional stability of the wood (see Section 5.7.3). Thus, the WL's obtained in cycles 3, 4, and 5 might be because of the degradation of hemicellulose rather than the chemicals. In addition to the dimensional stability test, nearly the same data weight loss due to water leaching was obtained when the modified wood was incubated in water for 9 months at a temperature of 20°C (the detail of the exposure was given in Chapter 6 which is related to the solute exclusion technique). The similarity between weight loss due to leaching after exposure of the modified wood to 9 months soaking in water and exposure the modified wood to five cycles of water soaking drying shows that the polymer matrix from both chemicals are fairly resistant to water soaking at a neutral pH (Table 7.1).

Table 7.1: Weight losses (%) of modified wood samples determined after 9 months soaking in water

VTMS	
WPG(%)	WL(%)
48	3.9
18.9	4
TMPS	
60	4.9
27	7
Unmodified	
0	2.7

Pluddemann (1982), states three conditions for maintaining Si-O-Si linkages in the presence of water.

- A maximum initial formation of Si-O-Si bonds.
- A minimum penetration of water to the interface.
- A polymer structure, that holds silanols at interface.

In this study, VTMS was polymerised in wood using the bound water of the wood at 100°C for 48 hr (Chapter 3). This study shows that a polymer matrix of VTMS with a multilayer based on poly-siloxane bonds in wood is fairly stable to hydrolysis at neutral pH. This could be explained by the sufficient formation of Si-O–Si bonds under these treatment conditions. The proof of formation of siloxane bonds for VTMS will be confirmed in Sections 7.8.6 and 7.8.7 using FTIR and NMR.

In Chapter 3, it was shown that a free radical reaction of the TMPS organofunctional group under the treatment conditions takes place. This will be confirmed by FTIR and NMR, in Sections 7.8.6 and 7.8.7. The organic linkages are not hydrolysable, and so this could be the reason for the hydrothermal stability of the modified wood. Leaching of some TMPS occurs after the first cycle, might be the result of loss of some monomeric or oligomeric silane from in the cell wall.

Table 7.2: Weight losses (%) of modified wood samples determined during the dimensional stabilisation test

WPG(%)	Cycle					Total
	1	2	3	4	5	
TMPS						
52.0	5.1	0.5	0.9	0.1	0.1	6.7
27.6	5.6	0.5	0.3	0.5	0.3	7.2
20.8	5.6	0.3	0.0	2.6	0.0	8.5
11.0	3.9	0.0	0.1	0.1	0.0	4.1
6.1	2.0	0.1	0.6	0.1	0.1	2.9
VTMS						
48.0	2.4	0.0	0.2	0.0	0.2	2.8
18.7	1.1	1.8	0.1	1.1	0.6	4.7
16.5	2.3	0.6	0.1	0.1	1.0	4.1
6.2	1.3	1.0	0.0	0.0	0.9	3.2
2.7	1.1	0.6	0.5	0.4	0.6	3.2
Unmodified						
0	1.0	0.4	0.6	0.6	0.7	3.3

Table7.3: Weight losses (%) of linear carboxylic modified wood samples determined during the dimensional stabilisation test

WPG(%)	cycle 1	2	3	4	5	
			Hexanoylated			
21.8	0.6	0.02	0.04	0.03	0.01	0.7
15.7	0.57	0.3	0.02	0.2	0.01	1.1
7.2	1.01	0.27	0.02	0.05	0.01	1.36
4.2	1.6	0.27	0.1	0.03	0.04	2.04
			Pyridine			
0	1.9	0.29	0.4	0.6	0.31	3.5
			Acetylated			
23	0.4	0.02	0.02	0.03	0.02	0.49
18	0.22	0.02	0.25	0.2	0.02	0.71
16	0.39	0.06	0.27	0.01	0.01	0.74
13.7	0.23	0.08	0.04	0.051	0.2	0.601
12	0.36	0.2	0.16	0.06	0.05	0.83
8.8	0.78	0.06	0.16	0.07	0.04	1.11
			Extracted			
0	1.055	0.5	0.6	0.4	0.49	3.045

7.7.3 Volumeteric swelling coefficient values (S%)

Changes in the swelling coefficient (S%) of modified wood for each cycle of the dimensional stabilisation test are shown in Table's 7. 4 and 7.5. For the chemically modified wood, at the most cases, it was noted that S% values obtained in the water soak /oven dry cycle 1 were un-representative of results obtained in following cycles.

In the case of silane treated wood, total weight losses of the modified samples were higher than recorded for the unmodified samples at all but the lowest weight gains, but in no case was there a major loss of the silane. Changes in the swelling coefficient (S%) for each cycle of the dimensional stabilisation tests are shown in Table 7.4. In all cases (including the unmodified control samples) there was an increase in S% from cycle 1 to cycle 2. This initial increase is attributed to loss of non-bonded silane leached out from the cell wall in cycle 1 of the test in the case of treated samples as well a loss of water soluble fragments of hemicelluloses. Thereafter, the increase in S% was more gradual, indicating that there was some slight loss of material from the cell wall. Thus, for silanes, the average of swelling of the three cycles that showed more consistency was calculated and plotted against WPG (Figure 7.1).

Table 7.4: Variation in swelling coefficient S (%) determined during the dimensional stabilisation test.

WPG(%)	Cycle					Average
	1	2	3	4	5	
			S(%)			
			TMPS			
52.0	7.37	8.37	8.15	9.56	9.70	8.95
27.6	8.02	9.38	9.27	8.82	9.60	9.27
20.8	8.34	10.05	10.60	10.04	10.52	10.30
11.0	10.01	10.69	10.60	10.30	10.90	10.62
6.1	10.75	11.56	13.20	13.60	13.50	12.97
			VTMS			
48.0	7.50	9.25	9.56	9.60	9.30	9.43
18.7	7.70	9.52	9.92	9.96	9.98	9.85
16.5	8.59	9.60	9.66	10.43	11.31	10.25
6.2	8.90	10.69	11.16	11.20	11.61	11.17
2.7	10.90	11.85	13.20	13.12	13.20	12.84
			Unmodified			
0.0	15.01	15.50	15.80	15.80	15.90	15.75

Table 7.5: Variation in swelling coefficient S (%) determined during the dimensional stabilisation test

Cycle					
	1	2	3	4	5
Hexanoic					
21.8	4.3	4.5	4.06	4.42	4.33
15.7	6.31	6.6	6.9	6.7	6.75
7.2	10.77	11.52	11.12	11.15	10.93
4.2	12.69	12.89	12.9	12.7	12.9
Extracted					
0	15.07	15.32	15.08	15.04	15.23
Acetic					
23	4.4	3.9	3.94	3.9	3.87
18	5.1	5.37	5.42	5.1	5.2
16	6.39	6.6	6.5	6.43	6.57
13.7	7.8	7.9	7.95	8.09	7.95
12	8.66	8.7	8.84	8.8	8.7
8.8	9.2	9.7	9.92	9.93	9.98
Pyridine					
0	15.07	15.32	15.08	15.04	15.23

A nonlinear relationship between reduction of wood swelling and the silanes WPG's was observed, which could be related to the location of the silanes in the wood. The ratio calculated showed that for VTMS and TMPS modified wood with high WPG, some chemical was situated in the lumen. Dimensional stability of modified wood arises from two factors. One is the replacing of the hydrophilic hydroxyl groups of wood components with more hydrophobic moieties and the resulting reduction in hygroscopicity of wood. The second is the bulking effect of modifying reagents which holds the wood structure in a swollen state; therefore little additional swelling can take place. Thus, when the silanes are not situated in the cell wall, neither swelling of cell wall nor hydroxyl substitution can take place.

For acetylated and hexanoylated wood, in most cases, S(%) increased just slightly after the first cycle (less leaching) and became nearly constant. Thus, the average of the five cycles was taken and plotted against WPG to show the effect of the modification on the swelling of the wood. It was assumed that the leaching of the modified wood was as result of losing the wood materials rather than the adduct.

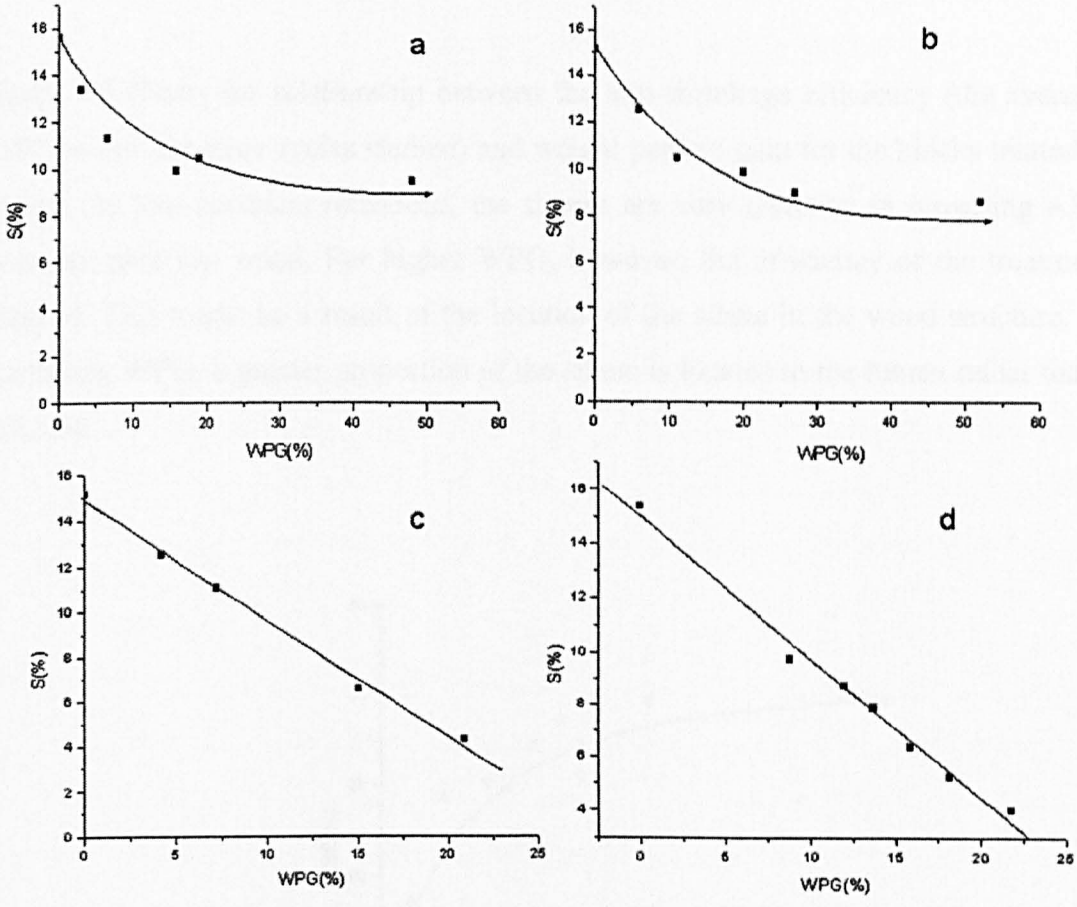
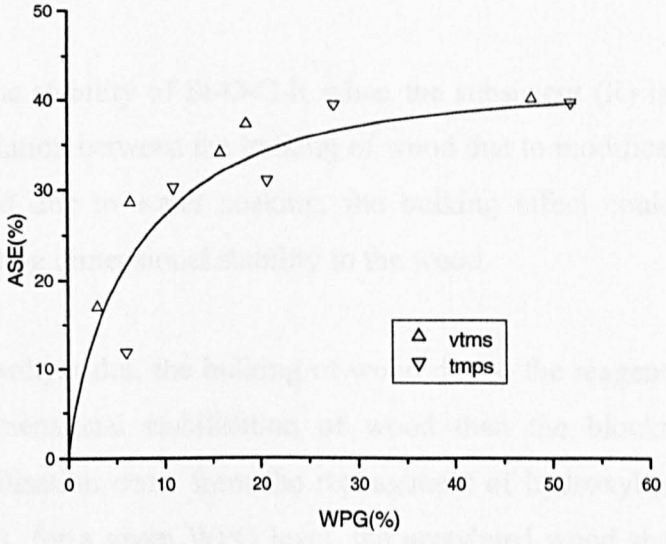


Figure 7.1: Average of swelling coefficient (S%) of VTMS (a), TMPS, (b), acetic (c) and hexanoic anhydride modified wood, versus weight percent gain(WPG).

7.8.4. Anti-shrinkage efficiency (ASE%) results:

Figure 7.2 shows the relationship between the anti-shrinkage efficiency (the average of ASE for the last three cycles studied) and weight percent gain for the blocks treated with silanes. At low chemical retentions, the silanes are very effective in imparting ASE to Corsican pine sap wood. For higher WPG, however, the efficiency of the treatment is reduced. This might be a result of the location of the silane in the wood structure. With increasing WPG, a greater proportion of the silane is located in the lumen rather than the cell wall.



7.2: Comparison of average ASE of TMPS and VTMS modified wood versus WPG

In a study of the treatment of white birch, trembling aspen and white pine with TMPS, ASE's of the order of 60-70% were reported when the modified wood was exposed to water in a single cycle of water soaking and drying (Schneider and Brebner, 1985). The ASE value reduced to about 39% when the wood was exposed to three more water soaking and drying cycles. In a study of the treatment of beech and Scots pine with propyl trimethoxy silane (PTMS), Goethals and Steven (1994) reported ASE values of between 21-35% after five water-soak / oven-dry cycles.

In this study nearly the same ASE as reported by Schneider and Brebner (1987), was obtained when the wood was exposed to five water soaking drying cycles, although the ASE for the first cycle (about 50% for a WPG of 38%) was lower than the value reported by them (60-70%).

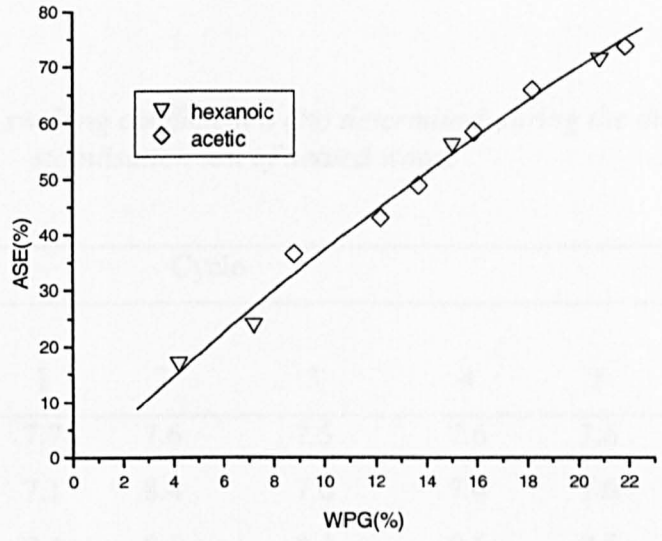
In the case of hexanoylated and acetylated wood the ASE average of the last five cycles of water soaking and drying was fairly constant when plotted against WPG.

As Figure 7.3 shows in contrast with silane treated wood, for hexanoylated and acetylated wood a near linear relationship between ASE and WPG was obtained. These results are in agreement were obtained by (Li *et al.*, 2000). They reported a linear relationship between WPG and ASE for *linear carboxylic* modified wood with the WPG less than 30%.

There is no data about the stability of Si-O-C-R when the subsistent (R) is cellulose or lignin. Since there is a relation between the bulking of wood due to modification (chapter 3) and swelling of wood due to water soaking, the bulking effect could be a more important factor in imparting dimensional stability to the wood.

For hexanoic and acetic anhydrides, the bulking of wood due to the reagents has a more significant effect on dimensional stabilisation of wood than the blocking of wood hydroxyls. Since, if stabilisation came from the replacement of hydroxyl groups by the more hydrophobic groups, for a given WPG level, the acetylated wood should have the greater anti-shrinkage efficiency, than that for hexanoylated wood.

At a given WPG, a decreasing molecular weight of the reagent means that there is an increase in the level of hydroxyl group substitution. The extent of substitution level of hexanoylated wood is one third of the level of hydroxyl group substitution for acetylation. Acetylated and hexanoylated wood exhibited similar anti-shrinkage at similar WPG. For example, acetylated and hexanoylated wood showed ca 70% ASE at 20% WPG.



7.3. Comparison of average ASE of acetic and hexanoic anhydride modified wood at different WPG's.

7.8.5. Thermal modification

Variation in the swelling coefficient S (%) determined during the dimensional stabilisation tests of heated wood is depicted in Table 5.7. Little change was observed when the treated wood was exposed to 5 successive cycles of water soaking and drying. This shows that the dimensional stability of heated wood is permanent.

Figure 7.4 (b) shows that the maximum dimensional stability imparted by the heat treatment of Corsican pine sapwood is about 50%. Dimensional stability increased when the heat treatment time increased to 90 min and then reached a constant value when wood was heated for longer periods. These results are in agreement with the results obtained by Seborge *et al.* (1953). Seborge *et al.*, reported that heat treatment of wood in an open system under a nitrogen atmosphere improves dimension stability of wood to a maximum of 50% and longer treatment doesn't impart more stability. In an open system, with the control of nitrogen flow it might be possible to impart higher dimensional stability wood. But, it must be mentioned that a slower nitrogen flow imparts more dimensional stability to wood but it causes more damage to wood due to acidic degradation. The dimensional stability of unheated wood was increased slightly, especially after the first cycle, which

could be a result of extracting water soluble materials which might have been within the cell wall.

Table 7.7: *Variation in swelling coefficient S (%) determined during the dimensional stabilisation test of heated wood.*

Heating time (min)	Cycle				
	1	2	3	4	5
120	7.7	7.6	7.5	7.6	7.6
90	7.1	8.4	7.6	7.4	7.6
60	9.4	9.5	9.4	9.6	9.5
30	11.2	11.2	11.2	11.2	11.19
Unheated	14.6	15.1	15.2	15.3	15.1

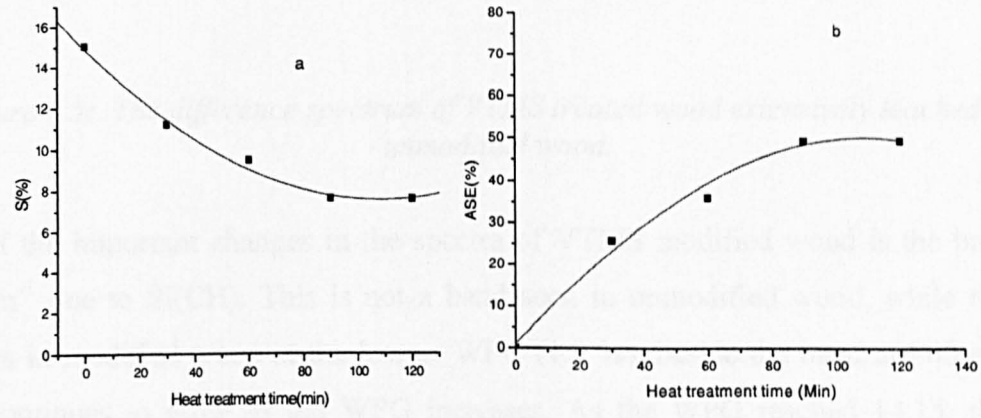


Figure 7.4: (a) S (%) and(b) ASE (%) averages of heated Corsican pine sap wood

7.8.6. FTIR spectroscopy of silane modified wood

7.8.6.1. Vinyl trimethoxy silane

The FTIR spectra of unmodified wood, VTMS and TMPS modified wood are shown in Appendix 3 In order to monitor the exact differences between modified and unmodified wood, the spectra of the modified wood were subtracted from unmodified wood. The difference spectra are shown in Figures 7.5 and 7.6. The most important bands which are observed in the difference spectrum are explained in Table 5.9.

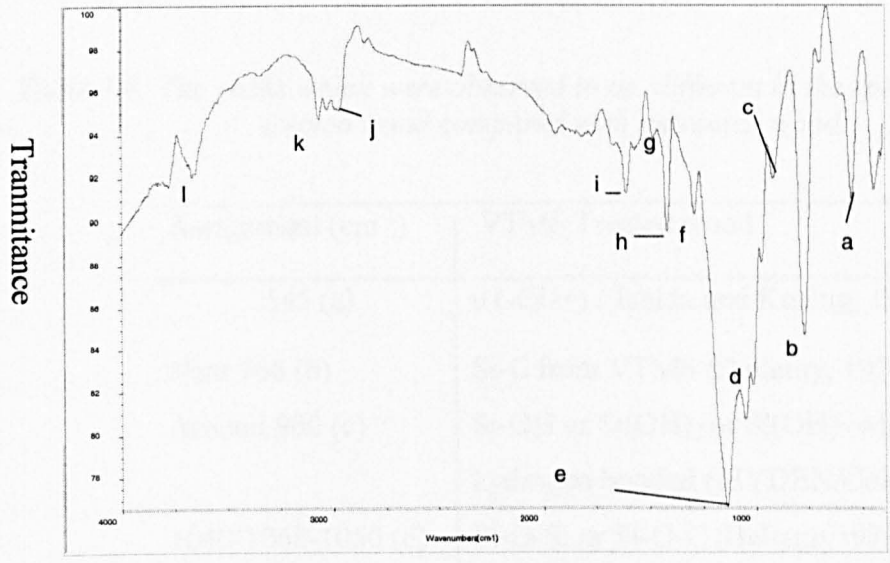


Figure 7.5: The difference spectrum of VTMS treated wood extensively leached from unmodified wood.

One of the important changes in the spectra of VTMS modified wood is the band near 765 cm^{-1} due to Si(CH). This is not a band seen in unmodified wood, while the band appears in modified wood at the lowest WPG (1.8 %), beside the band at 800 cm^{-1} and then continues to grow as the WPG increases. As the WPG reached 14.15, the band covers up completely its adjacent band for a band at 800 cm^{-1} (Appendix A.2). Denes *et al.* (1999), found evidence for a band at 780-720 cm^{-1} in hexamethyldisiloxane-plasma coated wood and attributed this to $SiCH_3$ and CH_3 end group. Sebe and Brook (2001), observed the band at 740 cm^{-1} and attributed to Si- CH_3. The same band was reported by Zolfrank (2002) at TMSIM treated wood.

A small band at 900 cm^{-1} due to hydrogen bonded silanol groups of VTMS, which can be observed in the spectrum confirms that the most of Si-OH group have reacted and formed

Si-O-Si bonds, and just a few hydroxyl groups which are strongly hydrogen bonded. Both the presence of a strong band at 1160 cm $^{-1}$,due to Si-O-Si after the extensive leaching procedure and the presence of the VTMS double bond confirm the stability of the polymer matrix based on polysiloxane bonds to water and organic solvent leaching.

The ratio of the band at 766 cm $^{-1}$ due to the Si-C to the carbonyl band, increased when the WPG increased (Figure 7.6). This confirms the stability of the silane to leaching at a neutral pH hydrolysis.

Table 7.8: The peaks which were observed to be different in the spectrum of VTMS treated wood compared with untreated wood.

Assignment (cm^{-1})	VTMS Treated wood
545 (a)	υ (-CH=) (Ishida and Koeing, 1977).
Near 766 (b)	Si-C from VTMS (Bellamy, 1975)
Around 900 (c)	Si-OH or $Si(OH)_2$ or $Si(OH)_3$ which strongly hydrogen bonded (lEYDEN/Collins 1980).
1040-1068-1050 (d)	Si-O-Si or Si-O-C (Bellamy1975)
1161(e)	Si-O-Si
1290 (f)	Si-C
1414-1419 (g)	Vinyl group (Meloan, 1963)
1471(h)	Stretch CH from VTMS
1600-1650 (i)	*υ(C=C)*
3029(j)	C-H stretch from the double bond of the VTMS
3058 (k)	Symmetrical stretch from the double bond of VTMs (Meloan, 1963)
3600 (l)	A negative band showing a reduction in the hydroxyl group of wood.

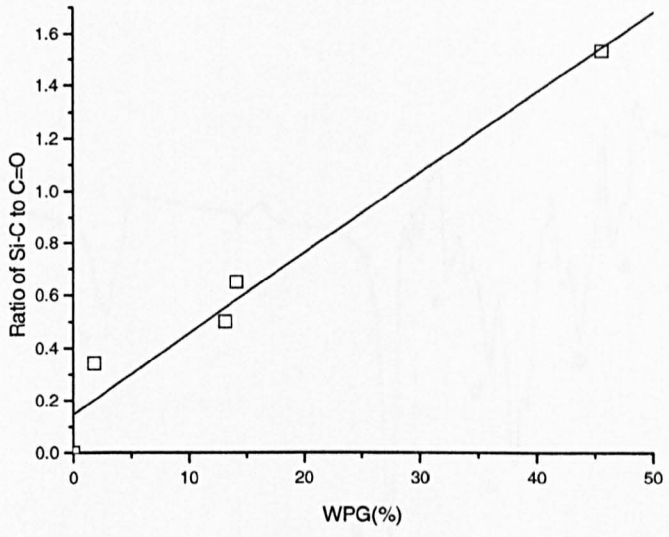


Figure 7.6: The correlation between the ratio of the band 766 cm^{-1} due to the Si-C band (1736 cm^{-1}) due to carbonyl group versus WPG after leaching of VTMS treated wood.

7.8.6.2. TMPS

The bands which are observed to be in the different in the spectrum of the TMPS modified compared withthe unmodified wood (Figure 7.7) are explained in Table 7.9.

As it can be seen in Figure 7.7 and Appendix A.3, the major difference between the spectra obtained for TMPS modified and unmodified wood is a significant increase in the intensity peak due to the carbonyl group. The intensity of the band increased in TMPS modified wood as the WPG increased. The ratio of the spectra the band of 1736 cm^{-1} due to carbonyl to the internal bond at 1510 cm^{-1} was calculated and is shown in. Figure 7.10.

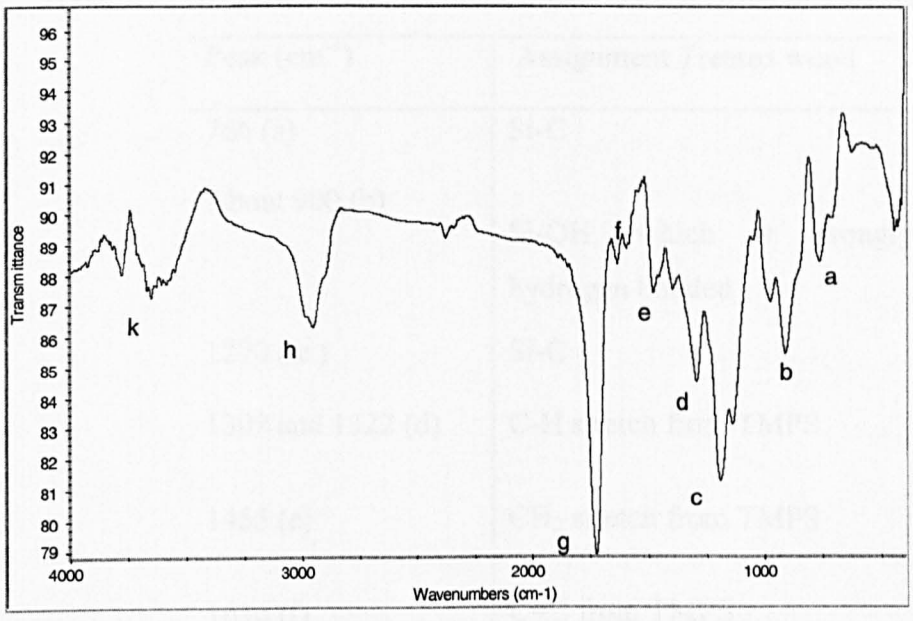


Figure 7.7: The difference spectrum of TMPS treated wood compared with unmodified wood

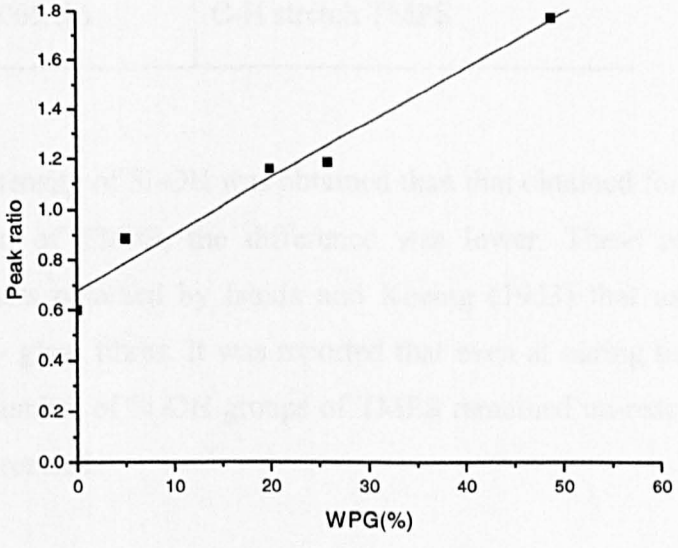


Figure 7.8: The ratio of the intensity of carbonyl group to the intensity of internal band at 1510 cm^{-1} versus WPG after leaching

Table 7.9: The peaks observed in the difference spectrum of TMPS treated wood

Peak (cm^{-1})	Assignment Treated wood
766 (a)	Si-C
About 900 (b)	Si-OH, which is strongly hydrogen bonded
1270 (c)	Si-C
1302 and 1322 (d)	C-H stretch from TMPS
1455 (e)	CH_2 stretch from TMPS
1636 (f)	C=C from TMPS
1736-1740 (g)	Carbonyl group due to ester from TMPS
2950 (e)	C-H stretch from TMPS
2800-3005 (h)	C-H stretch TMPS

For TMPS, a stronger intensity of Si-OH was obtained than that obtained for VTMS. The higher the concentration of TMPS, the difference was lower. These results are in agreement with the results obtained by Ishida and Koeing (1953) that used the same chemicals for treating E- glass fibres. It was reported that even at curing temperature as high as 150°C, a large number of Si-OH groups of TMPS remained un-reacted while Si-OH from VTMS mostly reacted.

A very small band at 1600 cm^{-1}due to the C=C group from TMPS confirms that the double bound of TMPS reacted effectively under the treatment conditions. More evidence about the reaction of the TMPS double bond will be given in the next section by on NMR spectroscopy of the wood.

7.8.7 CP-MAS ^{13} C-NMR spectroscopy of extensively leached silane modified wood

^{13} C-NMR spectra of VTMS and TMPS modified wood are shown in Figures 7.9 and 5.10. The liquid state spectrum for TMPS showed 9 signals (Table 7.10 and 7.11). In the spectrum of TMPS modified wood, some new signals were observed as explained in Table 7.4. Regarding as explained above, the result from FTIR and these results confirm the hydrolytic stability of the TMPS modified wood to the extensive leaching procedure at neutral pH.

As can be seen in Figure 7.9, signals at 125 and 136 ppm due to the double bond of TMPS which could be observed in the liquid state spectrum (Figure 7.9a) of the chemical had not disappeared in the solid state spectra of the modified wood (c). In addition to this, a new signal at 44 ppm in the NMR spectra of modified wood can be seen showing CH_2 from the TMPS organo-functional group after the occurrence of the free radical reaction. These confirm that the TMPS polymerised via the double bond the treatment conditions. These results are in line with the result obtained in Chapter 3.1. and the results obtained by FTIR.

Figure 7.14 (a) presents the ^{13}C MAS NMR spectra for VTMS. The spectrum of VTMS exhibits three narrow signals (Table 7.11). Figure 7.14 (c) presents the ^{13}C CP-MAS NMR spectra for VTMS modified wood. Two new signals at 130-136 ppm due to vinyl group from VTMS can be observed in the spectra of the modified wood. The **signifcant** reduction of signal at 49 ppm in the spectra's of VTMS modified shows the complete hydrolysis of the methoxy group of VTMS.

The presence of vinyl in the spectra confirmed the result obtained by FTIR that the vinyl group of VTMS remains un-reacted and VTMS stays in wood via Si-O after the extensive leaching procedure and solvent exchange.

Table 7.10: CP-MAS ^{13} C NMR spectroscopy of TMPS modified wood

	C=C	CH_3	CDCL3	C=O	CH_3O	CH_2	CH_3	CH	CH_2Si
NMR(solid)	-	44		176-80	67.79	44	17	21	9
NMR(liquid)	125-136	50	76-77	167	66	-	17	21	5

Table 7.11: CP-MAS ^{13} C NMR spectroscopy of VTMS modified wood

	C=C	CH_3O	$CDCL_3$
NMR(solid)	130-136	-	
NMR(liquid)	127-136	49	76

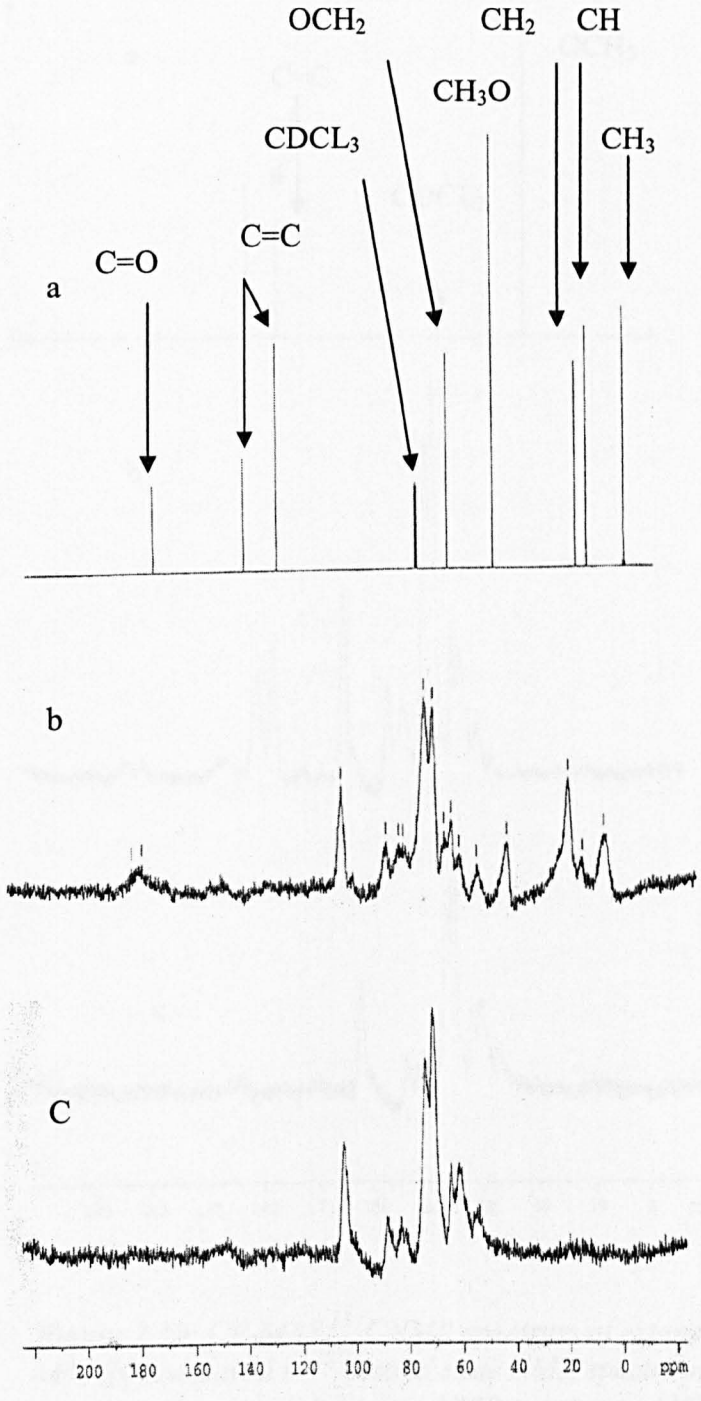


Figure 7.10: CP-MAS ^{13} CNMR spectrum of extensively leached silane modified wood with 49% (b) compared to ^{13} C solid state NMR spectrum of unmodified wood (c and Liquid NMR spectrum of TMPS (a).

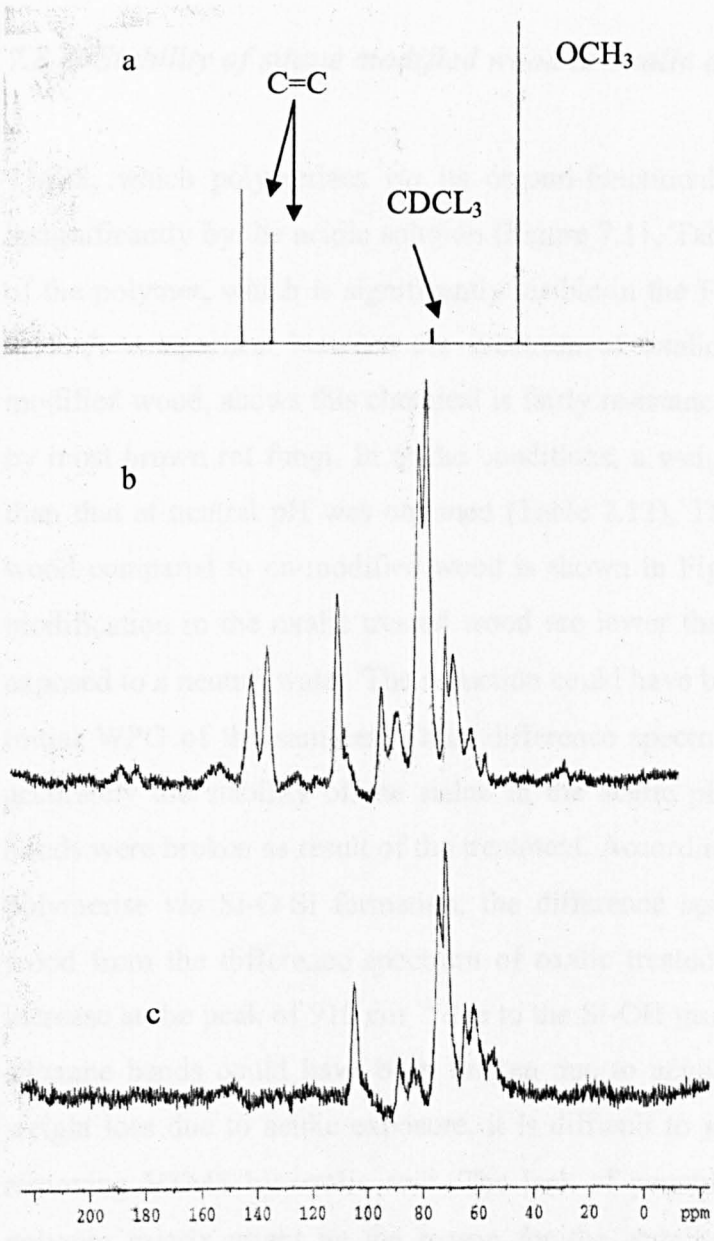


Figure 7.10: CP-MAS ^{13} CNMR spectrum of extensively leached silane modified wood 44% (b) compared to ^{13} C solid state NMR spectrum of unmodified wood (c) and Liquid NMR spectrum of VTMS.

7.8.8. Stability of silane modified wood to oxalic acid.

TMPS, which polymerises *via* its organo-functional group (Chapter 3), was leached insignificantly by the acidic solution (Figure 7.11, Table 7.12). The most important peak of the polymer, which is significantly visible in the FTIR spectrum is marked in Figure 7.11. A comparison between the spectrum of oxalic acid treated and untreated vinyl modified wood, shows this chemical is fairly resistance to the acidic conditions produced by most brown rot fungi. In acidic conditions, a weight loss slightly higher (about 1%) than that at neutral pH was obtained (Table 7.12). The spectra of the oxalic air treated wood compared to un-modified wood is shown in Figure 7.11, the bands due to VTMS modification in the oxalic treated wood are lower than those in VTMS modified wood exposed to a neutral water. The reduction could have been the result of a difference in the initial WPG of the samples. Thus, difference spectrum was taken to investigate more accurately the stability of the sialne in the acidic pH. This shows that some siloxane bonds were broken as result of the treatment. According to Chapter 3, VTMS is shown to polymerise *via* Si-O-Si formation, the difference spectrum of oxalic treated modified wood from the difference spectrum of oxalic treated unmodified wood shows a slight increase at the peak of 910 cm^{-1} due to the Si-OH group. This confirms that some of the siloxane bands could have been broken due to acidic pH. However, because of small weight loss due to acidic exposure, it is difficult to judge whether fungi are capable of removing VTMS by oxalic acid. The lack of penetration of the acid solution into the polymer matrix might be the reason for the stability of the silane in wood after the treatment. A negative peak at 3600 cm^{-1} due to the hydroxyl group in the spectrum of VTMS modified wood from unmodified wood showing a reduction in the free hydroxyl group of wood was replaced with a positive peak after the treatment (Figure 7.13). This might mean that the chemical might protect wood against acidic degradation with preventing from the degradation of hemicellulose which is susceptible to acid (Green *et al.*, 1992).

Table 7.12: weight loss due to oxalic acid treatment compared to modified sample leached 5 times with water.

VTMS		
Treatment	WPG(%)	WL(%)
Oxalic treated	35.1	3.89
Water leached	44	2.8
TMPS		
Oxalic treated	52	5
Water leached	52	6.7

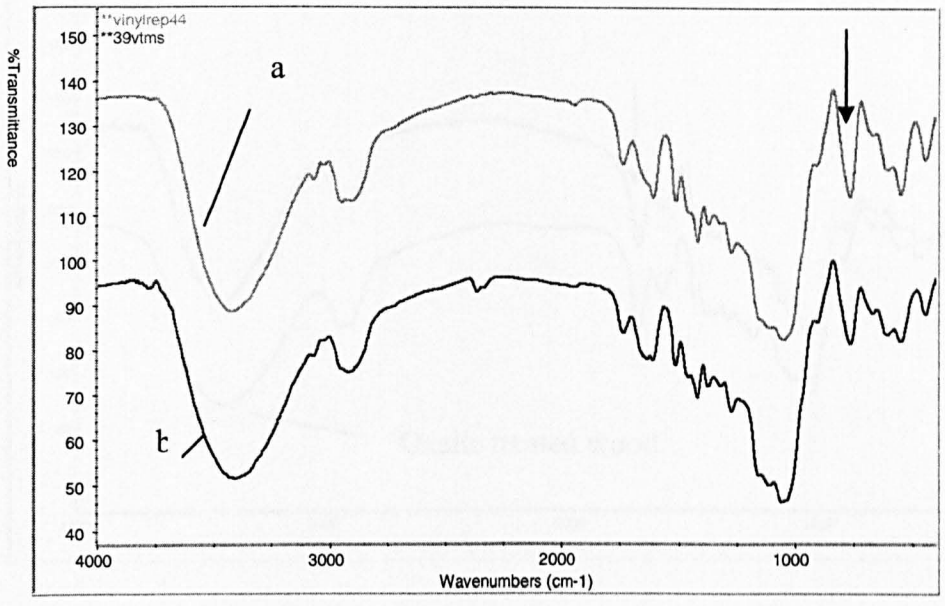


Figure 7.11: The spectra of VTMS modified wood (a) comared to VTMS modified wood treated with oxalic acid (b).

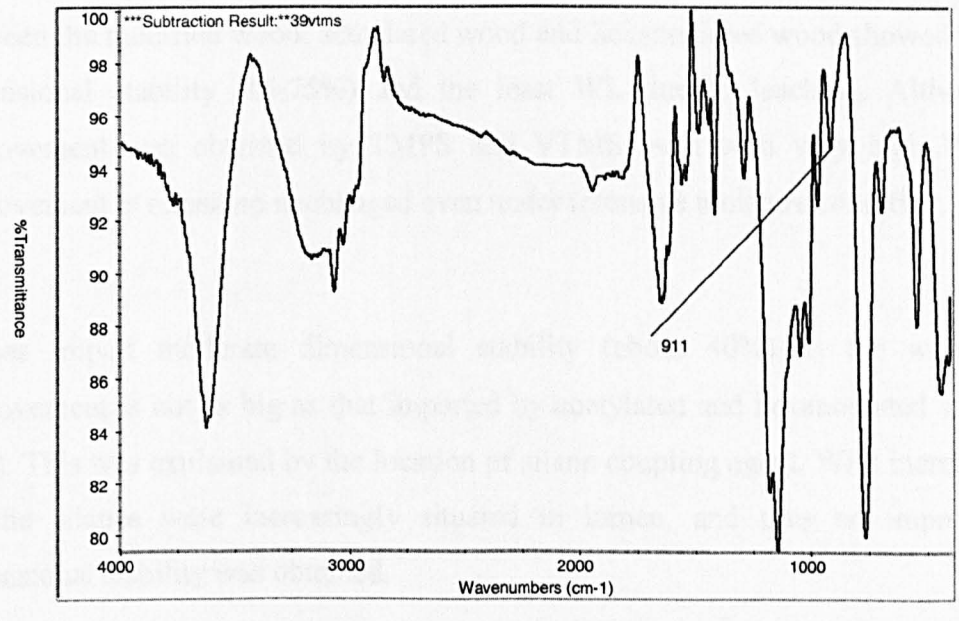


Figure 7.12: Difference spectrum of oxalic treated VTMS modified wood oxalic unmodified wood

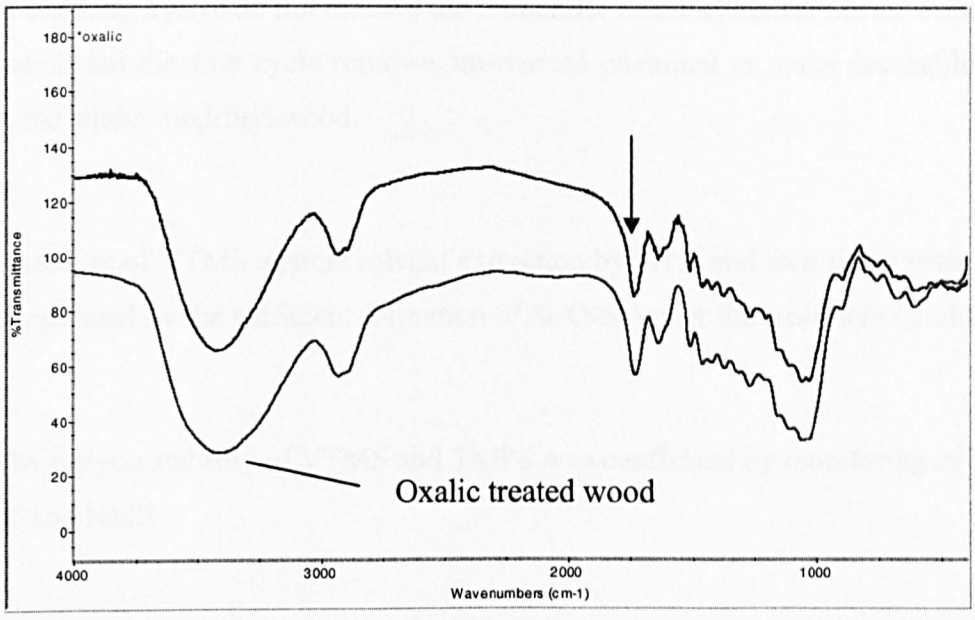


Figure 7.12: spectrum of oxalic treated TMPS modified wood compared to oxalic treated unmodified wood

7.9 Points raised from this chapter

Between the modified wood, acetylated wood and hexanoylated wood showed the highest dimensional stability (15-75%) and the least WL due to leaching. Although lower improvement was obtained by TMPS and VTMS even with very high WPG's, the improvement is remained unchanged even under intensive moisture condition.

Silanes impart moderate dimensional stability (about 40%) to the wood but the improvement is not as big as that imparted by acetylated and hexanoylated wood (about 70%). This was explained by the location of silane coupling agent. With increasing WPG for the silanes were increasingly situated in lumen, and thus no improvement in dimensional stability was obtained.

Since the stability of Si-O-C against hydrolysis is not high, the bulking effect by the treatment could be the main reason for the improvement.

Leaching in first cycle removes a little VTMS and TMPS from the treated wood but the other leaching cycles do not remove the remainder of the chemicals from wood. So it can be concluded the first cycle removes un-reacted chemical or water leachable oligomers from the silane-modified wood.

The stability of VTMS against solvent extraction by 4:1:1 and four times water extraction was explained by the sufficient formation of Si-O-Si under the treatment condition.

The hydrolytic stability of VTMS and TMPS was confirmed by monitoring of VTMS and FTIR and NMR.

BY FTIR and NMR, it was confirmed that silylation with VTMS under the treatment conditions can be achieved successfully.

By NMR and FTIR, it was confirmed that under the treatment condition the free radical of TMPS completely took place. The stability of TMPS to hydrolysis was explained by the occurrence of free radical reaction of the methacrylate group.

After 9 months exposure to water, nearly the same weight loss due to leaching as that after exposure to 5 cycles of water soaking. This shows the chemical are fairly stable to water leaching at neutral pH.

A slight increase in the intensity of Si-OH group as an evidence was found of the leaching of the silane VTMS in acidic water with a pH 1.7 was obtained, although mostly the silane remained in the wood even after two weeks exposure to oxalic acid solution.

Chapter 8

The hygroscopicity of heated wood

8.1 Introduction

In Chapters 4, 5 and 6, the biological effectiveness of the heated wood against basidiomycetes and soft rot fungi was examined. In this chapter, the effect of the heat treatments on the hygroscopicity of wood, which is an important factor in the decay of wood by fungi is assessed.

As was shown in Chapter 4, treatment temperatures above 200°C had a significant effect on the decay resistance of the wood, even when it was heated for the shortest time studied. In this chapter, an attempt was made to assess the hygroscopicity of wood heated at temperatures above 200°C for 2 hours only.

In addition to this, no attempt has been reported of an estimation of the FSP of heated wood. In this study, the application of the Hailwood-Horrobin Model (one hydrate form) for modelling the sorption isotherm of modified wood was investigated.

8.2 Materials and Methods

8.2.1 Heated wood

For the sterile control samples incubated for two months over malt and agar, some samples heated at 140, 200, 230 and 250°C were chosen based on the performance of heated wood against *Coniophora puteana* (Chapter 4), the most aggressive fungus which was studied.

8.2.2 Klason Lignin Determination

The heated wood was milled to a fine mesh and then approximately 1g of the oven dry flour was weighed out a four figure balance, transferred to a 100 ml beaker, and 15ml of a 6:1 (Vol.) mixture of concentration sulphuric and phosphoric acid was added. The mixture stirred with a glass rod until gelatinised. The beaker contents were transferred using 350 ml of deionised water to a 600 ml beaker and then brought to boil on a hotplate and left boiling for 20 min. The beaker was then removed from the heat source and allowed to stand for 30 min, then the contents filtered through a pre-weighed oven dry glass filter pad, the lignin was washed with deionised water, oven dried at 105°C overnight and weighed.

8.2.3 FTIR

FTIR spectroscopy was performed as explained in Section 7.2.4.

8.2.4 The Hailwood Horrobin (H-H) model

The H-H model was chosen because this model has been extensively used for studying chemically modified wood with good results being obtained (Spalt, 1958; Martins, 1992). In addition, with using this model it is possible partition the total sorbed moisture into monomolecular and poly-molecular phases and also provides a measure of the sorptive site accessibility within the wood structure. The model gives a good extrapolation of the observed sigmoidal sorption isotherm.

8.2.5 Isotherm determination

The heated wood was milled to a fine mesh and then the sorption isotherms were obtained by an automated moisture and organic vapour sorption analyser at 19 different relative humidities at a temperature of 25.5°C.

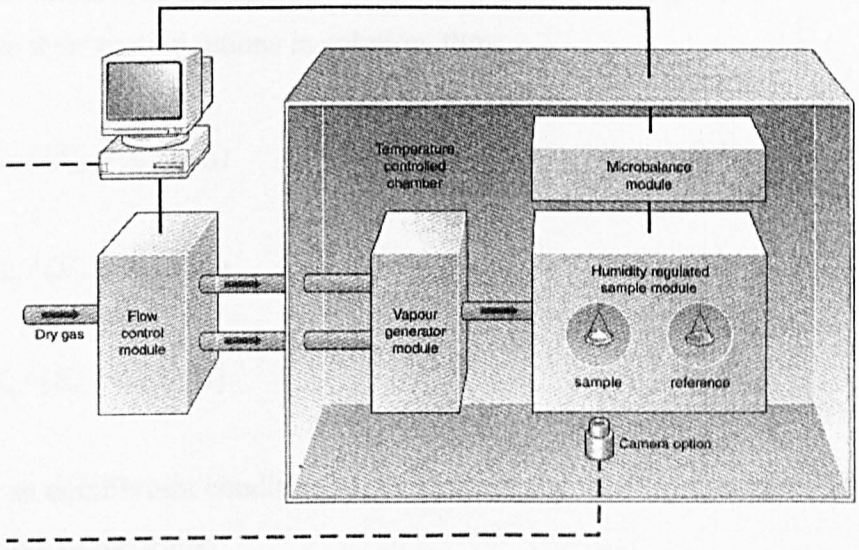


Figure 8.1: Schematic of the automated moisture and organic vapour sorption analyser

8.2.6 Hailwood Horrobin (H-H) model (one hydrate form).

Derivation of this model is fully explained in the original paper (Hailwood and Horrobin, 1946). It is has also been reviewed (Skaar, 1988). According to the model, the total sorbed water m (g of water per 100 g of sample dry weight) exists in two states: water of hydration (M_h) and water of solution (M_s).

The three chemical species present in the cell wall are assumed to be un-hydrated polymer (dry wood), hydrated molecules (hydrated wood) and dissolved water. It is convenient to treat this in terms of molar concentrations. X_o is assigned as the number of moles of un-hydrated polymer, X_h the number of moles of hydrated polymer (and therefore the number of moles of water of hydration, assuming one mole of water of hydration per mole of hydrated polymer), and X_s as the number of moles of dissolved or un-hydrated water.

The total number of moles of the three species is $X_o + X_h + X_s$. It is assumed that this solution behaves as an ideal solution; thus the activities A_o, A_h, A_h, of the three species are equal to their mole fractions in solution, thus:

$$A_h = X_h / (X_o + X_h + X_s) \qquad 8.1.$$

$$A_o = X_o / (X_o + X_h + X_s) \qquad 8.2.$$

$$A_s = X_s / (X_o + X_h + X_s) \qquad 8.3.$$

When an equilibrium condition exists between the three components, The equilibrium can be written in the form:

$$A_o + A_s \underset{}{\overset{K_1}{\rightleftharpoons}} A_h$$

Thus:

$$K_1 = A_h / A_o A_s = X_h / X_o A_s \qquad 8.4.$$

or

$$X_h = K_1 X_o A_s \qquad 8.5.$$

There also exists an equilibrium between the dissolved water and the water in the atmosphere given by its relative vapour pressure (p/p_o) or h. The equilibrium constant for this system is given as:

$$K_2 = A_s / h \qquad 8.6.$$

or

$$A_s = K_2 / h \qquad 8.7.$$

The ratio $X_h / (X_h + X_o)$ gives the mole X_h of hydrated wood (and thus water of hydration) per mole of dry wood. This is because the total number of moles of sites is equal to $X_h + X_s$. Thus, combining equations 8.5. and 8.7. gives:

$$\frac{X_h}{X_h + X_o} = \frac{K_1 X_o K_2 h}{K_1 X_o K_2 h + X_o} = \frac{K_1 K_2 h}{K_1 K_2 h + 1} \qquad 8.8.$$

The ratio $X_s / (X_h + X_o)$ gives the moles of dissolved water per moles of dry wood. This is obtained by rewriting equation 3 in inverted form and rearranging to give:

$$(X_h + X_o) / X_s = (1/A_s) - 1 = (1 - A_s) / A_s \qquad 8.9.$$

Inverting, and using equation 7 to eliminate A_s, gives:

$$\frac{X_s}{X_h + X_o} = \frac{K_2 h}{(1 - K_2 h)} \qquad 8.10.$$

The sum of equations 8.8 and 8.10 gives the total number of moles of water in the wood per mole of dry wood. This can be related to the wood moisture content M, since the moles of water are equal to the number of grams of water divided by the molecular weight of water (Eqn. 8.18), and that the moles of dry wood are equal to the number of grams of dry wood divided by the molecular weight of wood per mole of sorption sites. Since the latter is unknown, it will be represented by the symbol W. Thus:

$$\frac{X_h}{X_h + X_o} + \frac{X_s}{X_h + X_o} = [(\text{g hydrated water}/18) + (\text{g dissolved water}/18)]/(\text{g dry wood}/W) \qquad 8.11.$$

$$\frac{X_h + X_s}{X_h + X_o} = \frac{W}{18}[(\text{g hydrated water}) + (\text{g dissolved water})]/(\text{g dry wood}) \qquad 8.12.$$

$$\frac{X_h + X_s}{X_h + X_o} = (W / 18)(m_h + m_s) = (W / 18)m \qquad 8.13$$

Where m_h and m_s are the fractional moisture contents of the hydrated and dissolved water respectively, and m is the total fractional moisture content, all based on the dry weight of wood. Equation 13 can be combined with equations 8 and 10 to give:

$$m = m_h + m_s = \frac{W}{18}\left(\frac{K_1K_2h}{1+K_1K_2h} + \frac{K_2h}{1-K_2h}\right) \qquad 8.14$$

or, in terms of relative humidity, $H = 100h$, and percentage moisture content $M = 100m$:

$$M = M_h + M_s = \frac{1{,}800}{W}\left(\frac{K_1K_2RH}{100+K_1K_2RH}\right) + \frac{1{,}800}{W}\left(\frac{K_2RH}{100-K_2RH}\right) \qquad 8.15$$

The first term on the right is equivalent to M_h, the percentage moisture content consisting of water of hydration. The second term is equivalent to M_s, the percentage moisture content consisting of water of solution, or dissolved water.

The term $18/W$, is equal to the ratio of the grams of water per mole of water in the wood, to the grams of dry wood per mole of sorption sites. It is therefore equivalent to the fractional moisture content m_1 of the wood when there is one molecule of water on each sorption site, therefore:

$$m_1 = 18/W\,(\text{g/g});\ M_1 = 1{,}800/W\,(\%) \qquad 8.16$$

According to equations 14 and 15, there are three constants K_1, K_2, and W (or m_1) which determine what the relationship of M and H (the sorption isotherm) will be. These three constants also determine what proportion of the total moisture content M at any given humidity RH is water of hydration M_h and water of solution M_s.

Evaluation of these parameters is possible from the sorption isotherm but difficult. However, the equation 15 can be transformed thus:

$$\frac{RH}{M} = \frac{W}{1{,}800}\left[\frac{(100 + K_1K_2RH)(100 - K_2RH)}{K_1K_2\left(100 - K_2RH\right) + K_2(100 + K_1K_2RH)}\right] \qquad 8.17$$

or

$$\frac{RH}{M} = A + BRH - CRH^2 \qquad 8.18$$

where

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1 + 1)}\right] \qquad 8.19$$

$$7B = \left(\frac{W}{1{,}800}\right)\left[\frac{K_1 - 1}{K_1 + 1}\right] \qquad 8.20$$

$$C = \left(\frac{W}{180{,}000}\right)\left[\frac{K_1K_2}{K_1 + 1}\right] \qquad 8.21$$

From equation 8.19, it can be seen that the Hailwood Horrobin theory predicts a parabolic relationship between the ratio RH/M and RH. The constants A, B and C are obtained from the fitting parameters of the second order polynomial. From these parameters it is possible to determine the values of K_1, K_2 and W, and hence M_h and M_s.

The values of K_1, K_2 and W are derived from the fitting parameters thus:

$$K_1 = 1 + \frac{B^2 + \sqrt{B^2 + 4AC}}{2AC} \qquad 8.23$$

$$K_2 = \frac{200C}{B + \sqrt{B^2 + 4AC}} \qquad 8.24$$

$$W = 1800\left(\frac{4AC + B^2 + B\sqrt{B^2 + 4AC}}{B + \sqrt{B^2 + 4AC}}\right)$$

Alternatively, equation 7.15. can be written in the form (Okoh and Skarr 1980):

$M = +(Mok_2(K_1+1)\text{rh}\ /(1+K1K_2\text{rh})(1-K_2\text{rh})$ 8.25

Where: Mo=1800/Wo, M =100m, and RH= 100h

By using the formula h/m= A + Bh –Ch^2 8.26

The following relationships can be obtained:

$K2 = -B + \sqrt{B^2 + 4AC}\ /2AC$ 8.27

$K1 = 1/1-K_2\,(B/C)$ 8.28

$Mo = 100/\,(AK_2(K_1+1)$ 8.29

$Wo = 18[Ak2(k_1+1)]$ 8.30

$Mh = (MoK_1K_2\,h/1+K_1K_2\,h\,)$ 8.31

$Ms = MoK2\,h\ /1-K2\,h$ 8.32

The constant *Mo* is defined as the moisture content (percent of dry weight basis) corresponding to complete polymer hydration (one molecular of water attached to each hydratable polymer unit).

8.2.7 Fibre saturation point (FSP)

The equilibrium moisture content of wood at 100% RH as indicated by the sorption isotherm is sometimes used as a measure of FSP. However, using this method is not ideal. Stamm (1964), argues that since adsorption curves rise rapidly above a relative humidity of 90%, exploration above this level cannot be made with any confidence, even with the best adsorption data. Stamm (1960) and Skaar (1988), discuss several methods of measuring FSP and their advantages and disadvantages.

8.2.8 Reduction in the hygroscopicity of wood

The effect on hygroscopicity has been quantified by calculating the percentage reduction in the treated wood equilibrium moisture content *(EMC)* in relation to the controls equilibrium moisture content *(EMC)* at the same relative humidity *(RH)*, by means of equation, 3.10, as suggested by Stamm and Tarkow (1947) and Skarr (1988).

$$HR=100(EMC-EMC_t)/EMC \qquad 8.33$$

Where *HR* is the percentage hygroscopicity reduction, EMC and EMCt are respectively the equilibrium moisture content of the controls and of the treated specimens.

FSP of modified wood indicating the maximum capacity of the wood to hold water is of primary interest, as this will arguably have the greatest influence on the ability of fungi to decay wood. Thus, *EMC* at *FSP* was considered to calculate on the ability of the hygroscopicity of modified wood and un-modified wood.

$$HR=100(EMC\,u_{FSP}-EMC\,t_{FSP})/EMC\,u_{FSP} \qquad 8.34$$

A reduction of monomolecular and poly-molecular sorption was calculated from the relationship below:

$$HR=100(EMC\,u_{mono}-EMCt_{mono})/EMC \qquad 8.35$$

u_{mono}

$$HR=100(EMC\,u_{pol}-EMC\,t_{pol})/EMC\,u_{pol} \qquad 8.36$$

Where:

$EMCt_{mono}$ monomolecular absorption of treated wood

$EMC\,u_{mono}$ monomolecular absorption of untreated wood.

$EMC\,t_{pol}$ poly-molecular sorption of treated wood.

$EMC\,u_{pol}$ mono-molecular sorption of treated wood

8.2.9 Kelvin equation

The Kelvin equation was used to estimate the pore structure radius of modified wood by using adsorption isotherm data. The Kelvin equation gives the curvature of a drop of liquid and in the terms of its radius, r, and as a function of the relative vapour pressure, (p/p_o).

$$r = 2\sigma M/pRTln(p/p_o) \qquad 8.37$$

Where σ, is the surface tension of the liquid p, its density; and M, its molecular weight; R is the gas constant; T, the absolute temperature ; and ln is the symbol for the natural isotherm of what follows. In the case of water at 25.5 °C the equation reduces to

$$r = (0.454*10^{-7}) / [Log (p_o/p)] \qquad 8.38$$

Assuming the density of water in the cell wall is 1 gr/cm^3, then the calculated values were plotted versus volume of water (cm^3) per gram of oven dried wood to give a pore volume radius deformation.

.

8.3 Results and discussion

8.3.1 Isotherm Fitting

The moisture contents of the wood at each relative humidity are shown in the Figures 8.1 and 8.2. The experimental data was then transformed by dividing the relative humidity *(*RH*)* by the equilibrium moisture content *(EMC)*. A curve of the form of equation, 8.27 was fitted by using a second order polynomial function using Origin 6.1.

The calculated physical constants for untreated wood that were obtained were found to be in good agreement with those previously reported by Spalt (1958) and Wangaard and Granados (1967). K_2 expresses the activity of dissolved water per unit relative vapour pressure. According to Okoh and Skaar (1980), its value should be unity if it has the same activity as liquid water. The K_2 values calculated from adsorption and desorption data reduced from to 0.8 (Ad.) and 0.68 (Des.) to 0.7 and 0.56 respectively when the heat treatment temperature increased to 255°C. A reduction in the K_2 of heated wood suggests that the activity of dissolved water is reduced when temperature of the treatment was increased.

The extent of fitting, as measured by the coefficient of determination of determination (R) is remarkably high. The R values vary from 97.03 (from adsorption data) to 99.69 (from de-sorption data).

Figure 8.2: shows the worst fitting curve which was obtained for wood heated at 250°C for two hours. It should be mentioned that a better fitting curve was obtained for desorption.

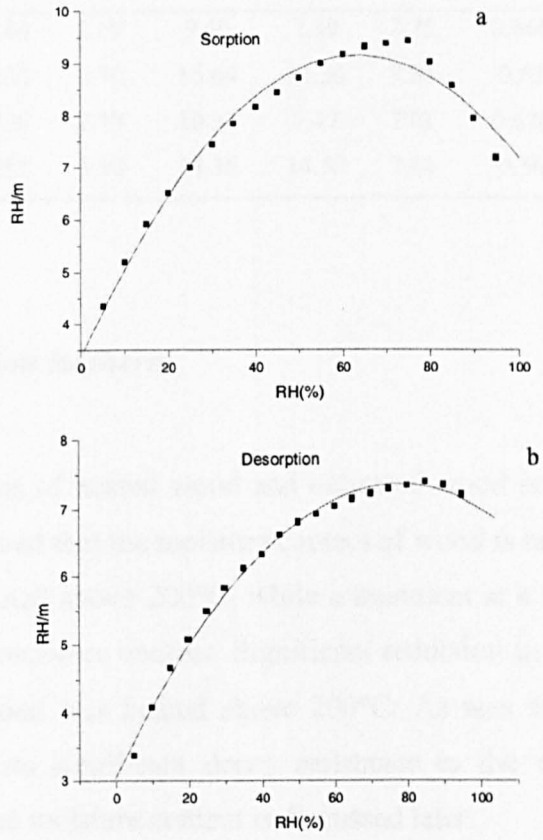


Figure 8.2 : Second order fit to h/m versus H plot for Corsican pine sapwood heated at 255°C for two hours showed the worst estimation of moisture by H- H model (a) sorption (b) de-sorption

Table8.1.: Fitted and physical constants calculated for H-H adsorption sorption isotherms.

wood		A	B	C	K1	k2	Wo	Mo	R2
unheated	0	3.25	13.85	13.10	6.347	0.80	342.53	5.25	95.94
heated	140	2.56	14.64	13.00	8.32	0.78	335.00	5.36	99.2
	200	2.70	16.64	14.30	9.06	0.76	373.00	4.80	97.94
	230	3.02	18.06	15.30	8.95	0.75	406.89	4.42	97.06
	255	3.38	18.35	14.50	8.76	0.70	415.00	4.33	97.61

Table8.2: Fitted and physical constants calculated for H-H desorption isotherms

wood		A_d	B_d	C_d	$K1_d$	$K2_d$	Wo_d	Mo_d	R2 (%)
Un-heated	0	3.25	13.85	13.10	5.19	0.682	215	8.37	99.69
heated	140	2.09	9.40	7.19	7.75	0.666	219	8.20	99.54
	200	2.70	16.64	14.30	7.34	0.62	220	8.14	99.03
	230	2.78	10.34	7.47	7.01	0.620	248	7.26	99.20
	255	3.38	18.35	14.50	7.44	0.56	259	6.93	99.48

8.3.2 Sorption isotherm

The isotherms of heated wood and unheated wood are shown in Figures 8.3 and 8.4. It can be observed that the moisture content of wood is reduced significantly when the wood was heat treated above 200°C, while a treatment at a temperature of 140°C only slightly reduces the moisture content. Significant reduction in the moisture content was obtained when the wood was heated above 200°C. As was shown in Chapter 4, heating above 200°C imparts significant decay resistance to the wood, the relation between decay resistance and moisture content is discussed later.

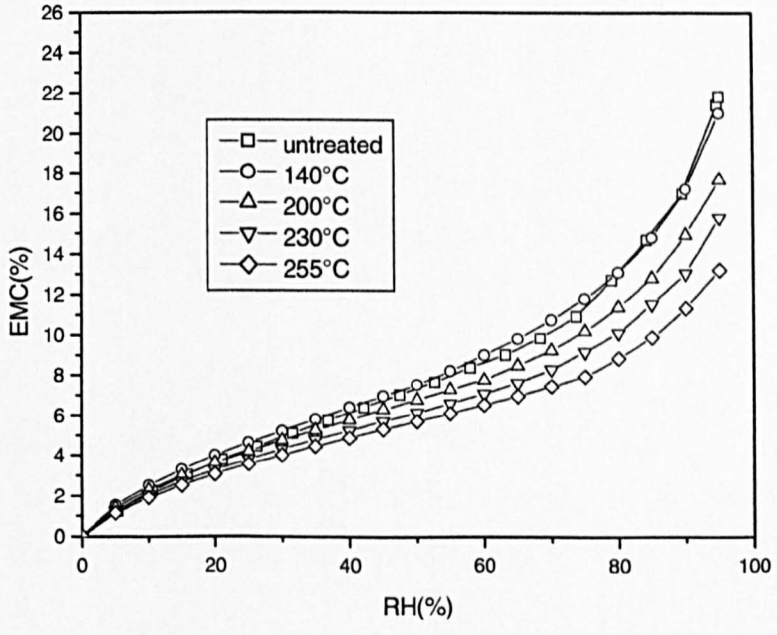


Figure 8.3: Sorption isotherms for Corsican pine sapwood untreated (controls) and treated at different temperatures for two hours.

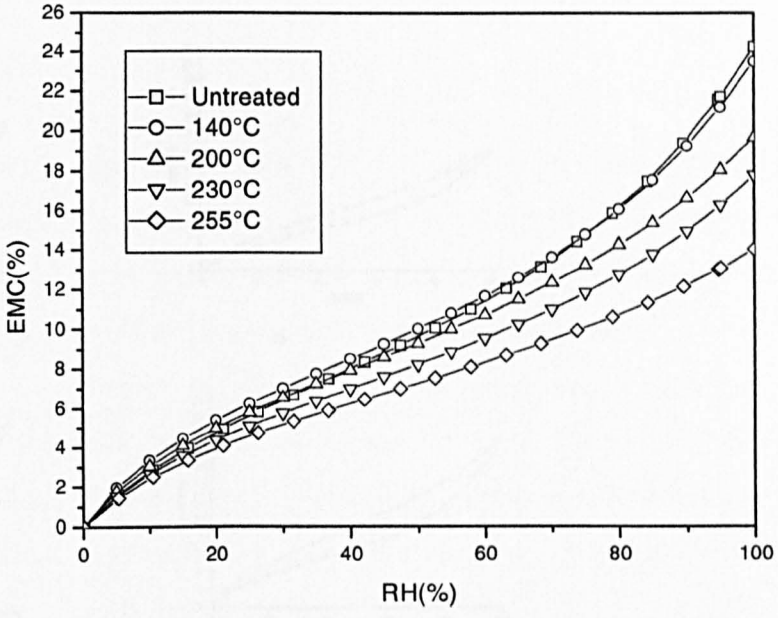


Figure 8.4: De-sorption isotherms for Corsican pine sapwood untreated (controls) and treated at different temperatures for two hours.

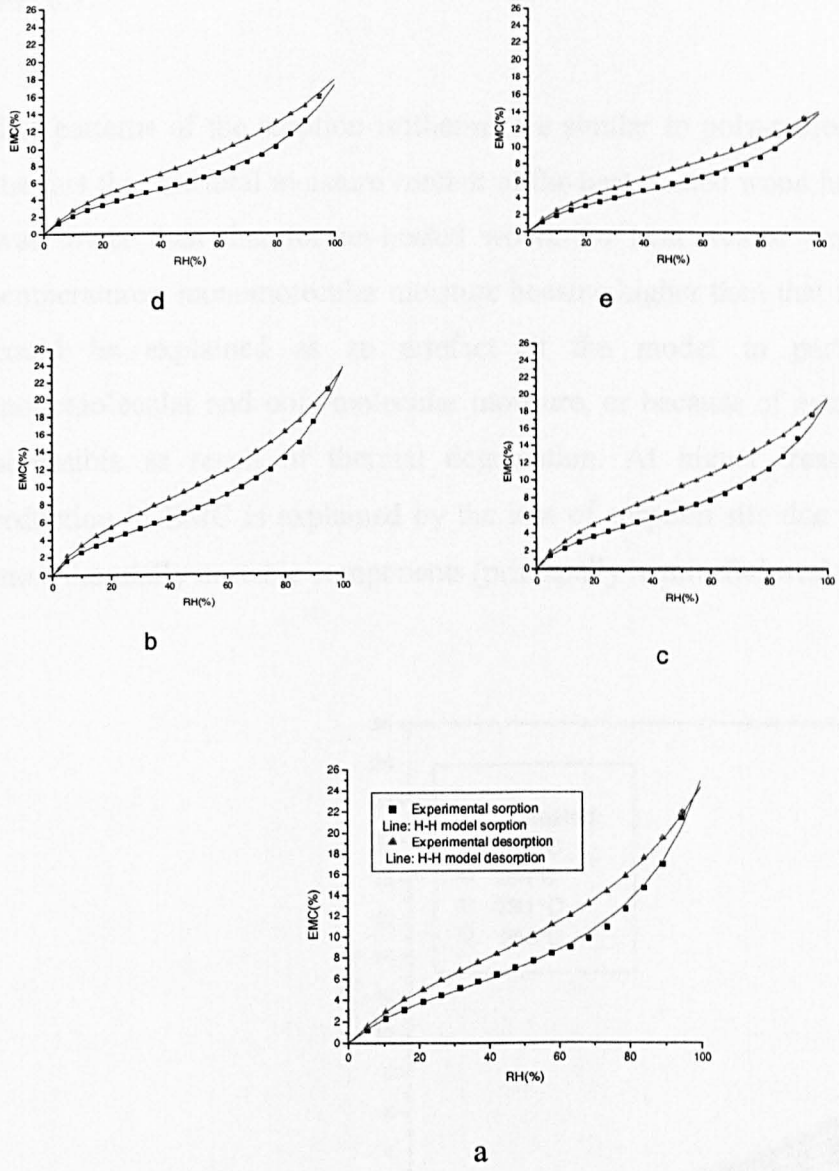


Figure 8.5: Sorption isotherms (experimental and model estimated), (a) control (b) 140 °C (c) 200 °C (d) 230 °C (e) 255°C

Figure 8.5 shows experimental and model estimated sorption isotherms of heated wood and unheated wood. In all cases, very good agreements between experimental sorption data and those obtained using the H-H model were obtained. However, a better estimation of moisture content at a given RH (%) was obtained from de-sorption data than that from sorption data.

The isotherms for monomolecular and poly-molecular adsorption calculated by equations 8.31. and 8.32. and plotted versus different relative humidity are depicted in Figures 8.6 and 8.7.

The patterns of the sorption isotherms are similar to poly-molecular isotherms. Despite the fact that the total moisture content of the heat treated wood heated at any temperature was lower than that for un-heated wood, for heat treated wood heated at treatment temperatures, monomolecular moisture became higher than that for unheated wood. This could be explained as an artefact of the model in partitioning moisture into monomolecular and poly-molecular moisture, or because of extra OH groups becoming accessible as result of thermal degradation. At higher treatment temperatures, the reduction in EMC is explained by the loss of sorption site due to decomposition of the most thermally unstable components (principally hemicelluloses).

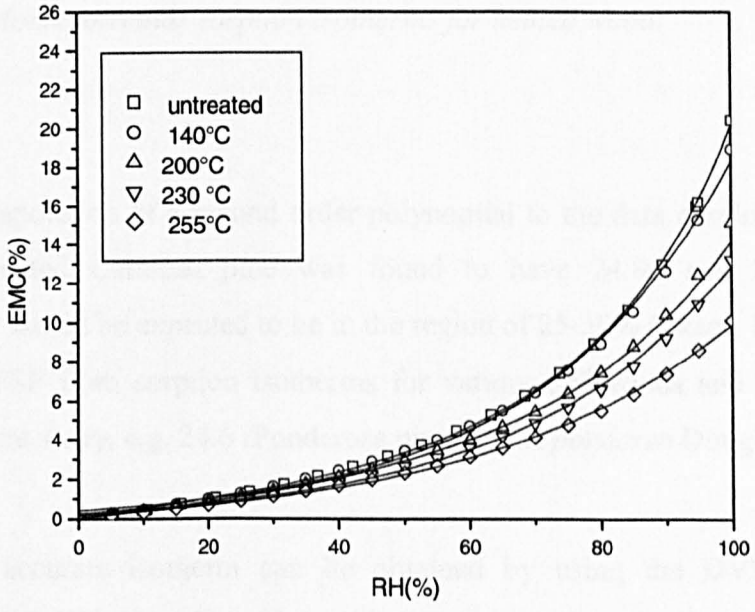


Figure 8.6: Poly-molecular sorption isotherms for heated wood.

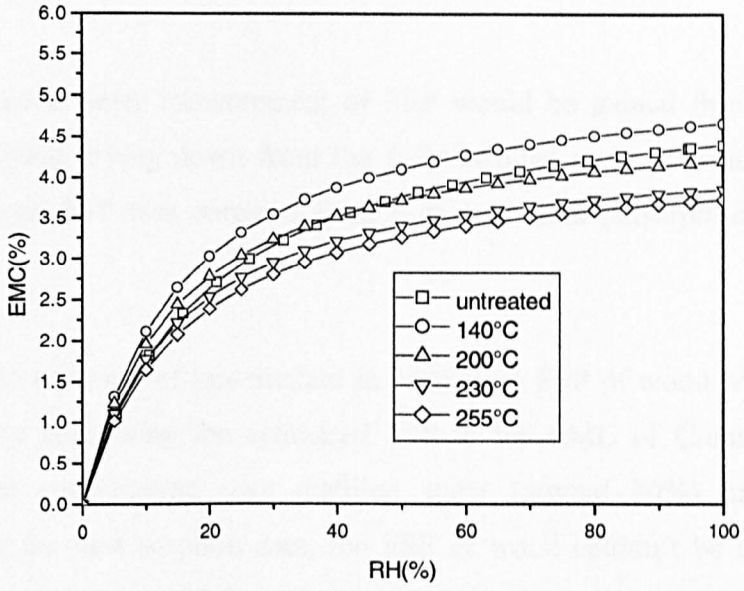


Figure 8.7: Monomolecular sorption isotherms for heated wood.

8.3.3 FSP

Using the method of extrapolation of a second order polynomial to the data obtained by the DVS machine, untreated Corsican pine was found to have 24.86 and 24.28, respectively. Usually FSP would be expected to be in the region of 25-30% (Skaar, 1998). Spalt (1958), measured FSP from sorption isotherms for various softwoods and found results similar to the present study, e.g. 24.6 (Ponderosa pine; *Pinus pondersa* Dougl.).

Because a much more accurate isotherm can be obtained by using the DVS, the extrapolation of the data (19 different relative humdities) was carried out to give a better determination of the Corsican pine sapwood FSP (24.86%) than those were reported by Forster (FSP, 22.8%), or Papadopoulos (FSP, 23.24%), who used only six different relative humidities. In addition, it should be mentioned that in this study, the isotherms were obtained at slightly higher temperatures (25.5°C) than those were used in the afore-mentioned studies (20°C). Since FSP, which is obtained by extrapolating the adsorption isotherm to 100% relative humidity, decreases proportionally with increasing temperature

(Rowell, 1983), a slightly higher FSP than 24.8% would be obtained if the measurement was done at a temperature of 20°C.

It has been reported that a better measurement of FSP would be gained from the de-sorption isotherm involving drying down from the fully swollen state (Martins, 1992). However, nearly the same FSP was obtained from both isotherms (adsorption and de-sorption).

By regarding the lack of accuracy of this method in estimating FSP of wood which was discussed earlier and by comparing the estimated FSP to the EMC of Corsican pine sapwood obtained after conditioning over distilled water (around 30%), it can be concluded that even by the best sorption data, the FSP of wood couldn't be estimated accurately. However, the estimated FSP for heated and unheated wood gave valuable data in comparing the ability of heat treatments in reducing the hygroscopicity of wood and the decay resistance of wood.

The estimated mono-molecular and poly-molecular and total (FSP) moisture content are given in the Tables 8.3. and 8.4. The FSP of heated wood extrapolated by sorption isotherms tends to decrease with increasing treatment temperature. However, a treatment temperature of 140°C decreased FSP slightly and the effect of treatment on hygroscopicity became much greater at a treatment temperature above 200°C. This could be explained by significant changes in the wood structure when it is heated at temperatures above 180°C.

	Sorption		
Temperature(°C)	Monomolecular(%)	Poly-molecular(%)	Total moisture(%)
0	4.38	20.48	24.86
140	4.62	19.00	23.65
200	4.23	14.55	18.75
230	3.85	13.26	17.11
255	3.70	10.12	13.86

Table 8.3. Mono-molecular, poly-molecular, total moisture (F.S.P.) at saturation which were extrapolated from adsorption data

Desorption			
Temperature(°C)	Monomolecular(%)	Poly-molecular(%)	Total moisture(%)
0	**6.5.00**	17.77	24.28
140	6.89	16.69	23.57
200	6.67	12.82	19.50
230	5.90	11.84	17.75
255	5.58	8.80	14.38

Table 8.4. Mono-molecular, poly-molecular, total moisture (F.S.P.) at saturation which were extrapolated from de-sorption data

The pattern of the total isotherm is similar to that for poly-molecular sorption. The result of this analysis, which is presented in Table 8.5, shows clearly that the variation in total sorption depends on both monomolecular and poly-molecular sorption. However, the higher F-ratio and R^2 values shown that variations in total sorption depend on both poly molecular and monomolecular sorption.

Table 8.5 Regression analysis of the relation between types of sorption and total sorption at saturation

*** *significant at 90%*

The others are Significant at 99%

Sorption		De-sorption	
F Statistic	R-Square(COD)	F Statistic	R-Square(COD)
2698.00	99.90	499.80	99.40
18.00	86.20	7.89***	74.46

As can be observed in Figure 8.8, the Klason lignin content of wood increased with increasing temperature of treatment, showing a reduction in the holocellulose content of

Sorption			
Temperature(°C)	Monomolecular(%)	Poly-molecular(%)	Total moisture(%)
0	4.38	20.48	24.86
140	4.62	19.00	23.65
200	4.23	14.55	18.75
230	3.85	13.26	17.11
255	3.70	10.12	13.86

wood, most probably pentoses which are sensitive to heating. High F and R^2 values were obtained from regression analyses between lignin content and total and poly-molecular sorption of wood (Table 8.6). This might suggest that an increase in the relative lignin content which has it's structure modified significantly at high temperatures (Bourgeois, 1988) might be the primary reason in the decreasing total and poly molecular sorption of wood. The correlation between lignin content and a reduction in mono-molecular sorption was not significant at the level of 90%. The lack of a significant correlation between a reduction in lignin content and monomolecular sorption could result from the failure of the model in exactly partitioning the moisture content to monomolecular and poly-molecular sorption.

However, regardless of the complicated effect of heat treatment on wood chemical structure and the accuracy of the H-H model, and regarding the good correlation obtained between the lignin content and poly-molecular and total sorption, it could be roughly concluded that a reduction in poly-molecular and total sorption of heated wood is mostly resulting from a reduction in the swelling of lignified micro-fibrils of heated wood in the presence of water resulting in a reduction in the cell wall space for condensed water rather than from a reduction in the hydrophilic sites due to the removal hemicelluloses. Since, an increase in the lignin content shows a reduction in holocellulose, mostly hemicelluloses), swelling could be reduced from both stress relaxation resulted from the removal of hemicelluloses and by cross linking of wood.

Table 8.6: Regression analysis of the relations between the types of water sorbed at saturation and sites accessibility (expressed as Wo)

Relation examined	Desorption (%)		Sorption (%)	
	F staistic	R-Square(COD) statistic	F	R-Square(COD)
Monomolecular vs lignin content	1.88**	48.44	3.06**	60.49
Pol vs lignin	40.57	95.30	74.11	97.37
Total	94.56*	97.93	56.51	96.58

*** significant at 99%*

** Not significant at the level of 90%*

The others are significant at the level of 95%.

A reduction in hydroxyl group as result of heating and cross-linking wood due to heating could reduce the site accessibility of wood. The regression analysis shows that the decrease in site accessibility depends on poly, monomolecular and total sorption. However a better correlation for Wo is found when this factor is related to monomolecular sorption. This indicated by the higher F-ratio and R^2 values obtained from sorption data (Table 8.7.).

Table 8.7.: Regression analysis of the relations between the types of water sorbed at saturation and sites accessibility (expressed as W_o)

	Sorption(%)		De-sorption(%)	
Realtion examined	F Statistic	R-Square(COD)	F Statistic	R-Square(COD)
Polymolecular vs Wo	50.4328*	94.00	32.04*	91.70
Monomolecualr vs Wo	84.8709*	97.00	12.04	85.30
W_0 vs total	39.0834*	93.00	17.43	80.50

**Significant at 99%*

***The others significant at 95%*

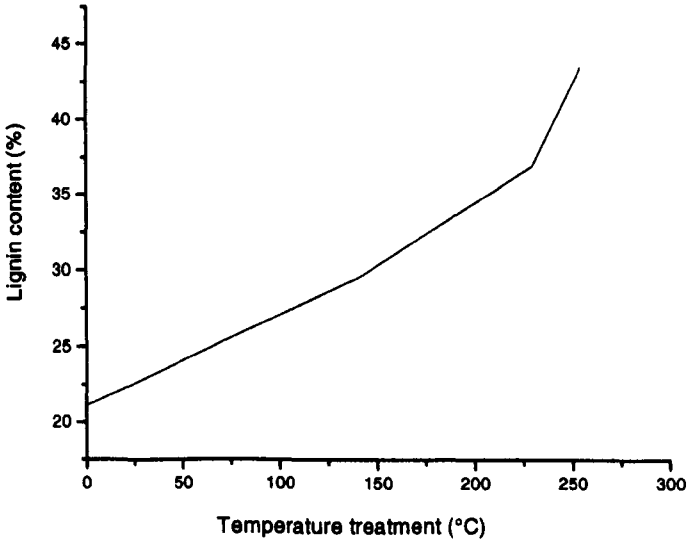


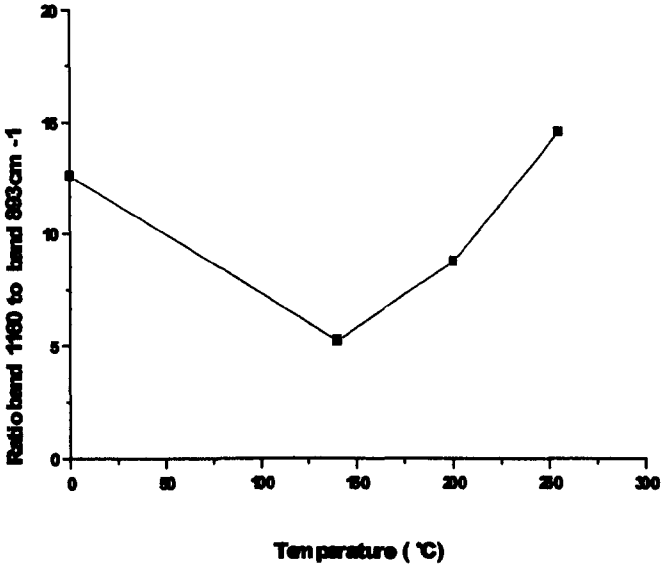
Figure8.8: changes in relative lignin content of wood as function of temperature treatment.

As mentioned above one the cross linking of the lignin in the wood during heating could be one of the factors in reducing the hygroscopity of wood (Terjssima, 1998). An increase in the wavelengths at 1160 cm^{-1} due to C-O-C and 1200-1270 cm^{-1} due to condensation of lignin (Figures 8.10 - 8.11) could be evidence of the condensation and cross-linking of heated wood, but variations in the trend of relationship between the band ratio's and the treatment temperatures did not permit the establishment of a relationship between a reduction in moisture content and the band ratio. However, the ratio increase at temperatures of 200°C after an initial decrease was coincidental with a significant increase in the reduction of the hygroscopicity of wood. Thus, cross-linking of wood due to heat treatment could be one of the possible reason for the reduction in the swelling of wood causing a decrease in the hygroscopicity.

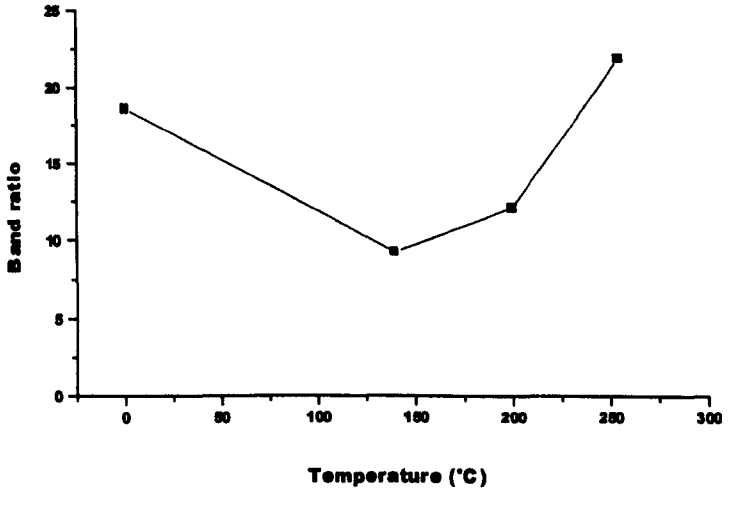
Sivonen *et al.* 2002, suggested that cross-linking of wood due to heat treatment could be the main reason for a reduction in the hygroscopicty of wood. They reported that the number of the stable free radicals of the phenoxy type which takes part in the condensation reactions leading to cross-links within the lignin and possibly between lignin and the other wood components, remarkably increased at temperatures above 200°C. In this study it was shown that hygroscopicity and decay resistance increased significantly with heat treatment above 200°C.

Table 8.8: Regression analysis of the relations between the water sorbed at saturation and the band ratio due to cross linking of wood.

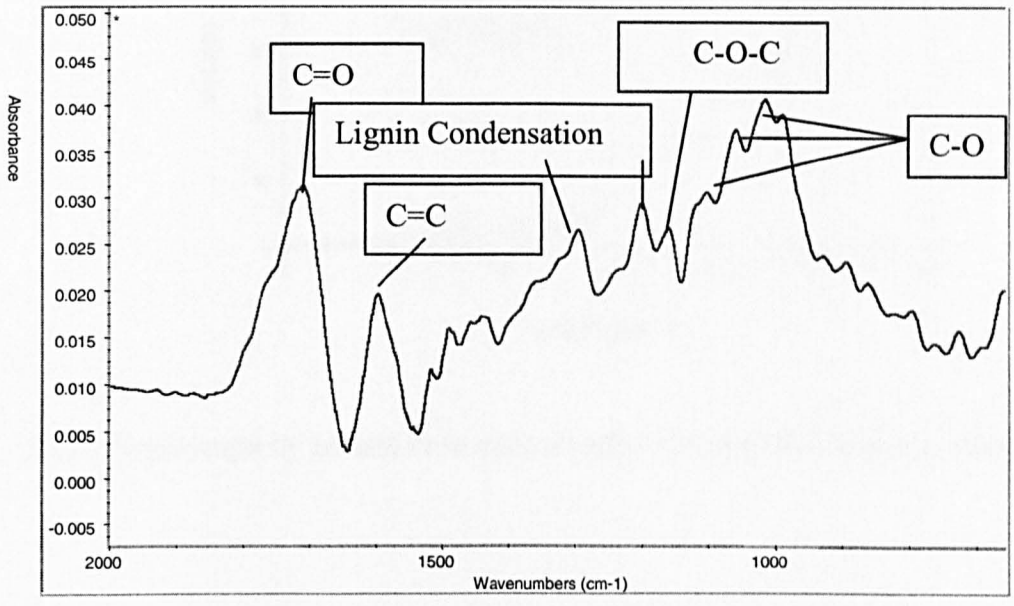
Relation examined	R-Square	P value	F Statistic
Monomolecular vs ratio 1230/839	77.90	0.136	5.90
Monomolecular vs ratio 1160/839	78.56	0.118	7.04



8.9: Variation in the ratio of the band at 1240 cm $^{-1}$ due to condensation to band at 839 cm $^{-1}$ as a function of treatment temperature (°C).



8.10: Variation in the ratio of the band at 1160 cm $^{-1}$ due C-O-C to the band at 839 cm $^{-1}$ as a function of treatment temperature.



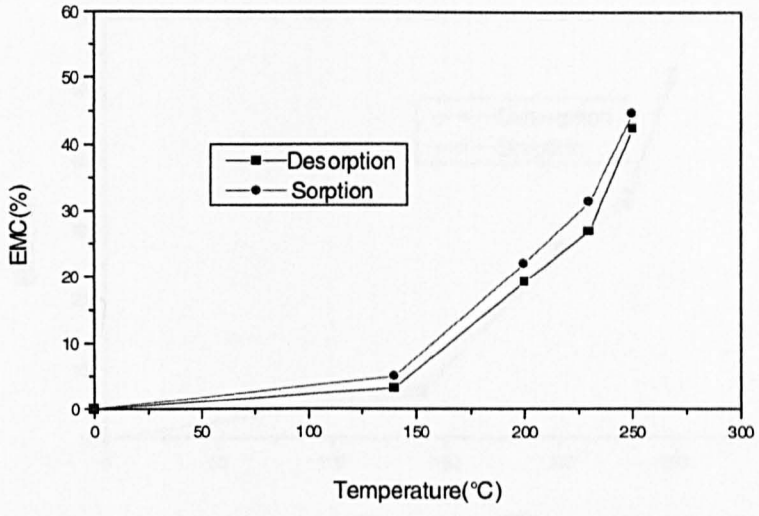
8.11: Subtraction spectra of thermally modified wood from unmodified wood

Of the most important changes in the FTIR spectra of heated wood, was an increase in the carbonyl group of heated wood, the correlation between the ratio and the total water was also not significant.

8.3.4 The reduction in the hygroscopicity of heated wood

Similar to FSP, the hygroscopicity tends to decrease with increasing treatment temperature. However, the treatment temperature at 140°C decreased hygroscopicity slightly and the effect of treatment on hygroscopicity became larger at temperatures above 200°C.

Hygroscopicity of heated wood slightly increases in de-sorption. As Figures 8.12, 8.13 and 8.14 shows that the increase was as result of a hygroscopicity increase in monomolecular sorption of heated wood.



8.12: Hygroscopicity reduction in total sorption as a function of temperature

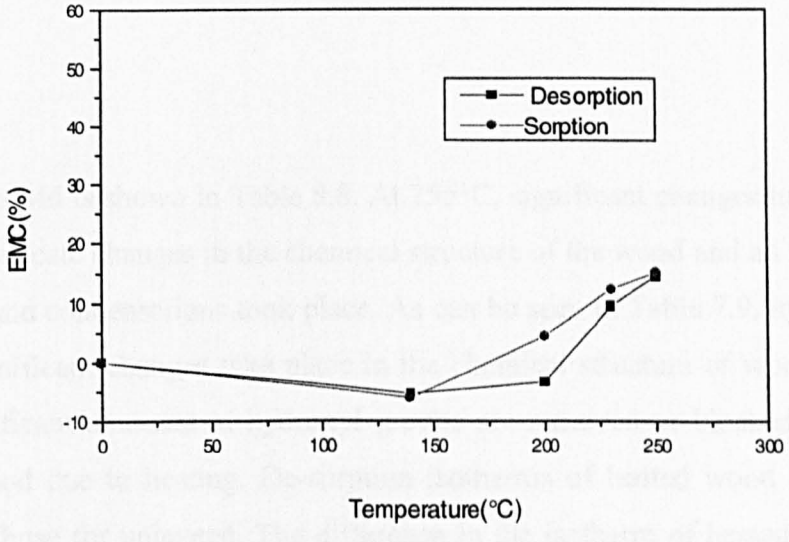


Figure 8.13: Hygroscopicity reduction in monomolecular sorption as a function of temperature

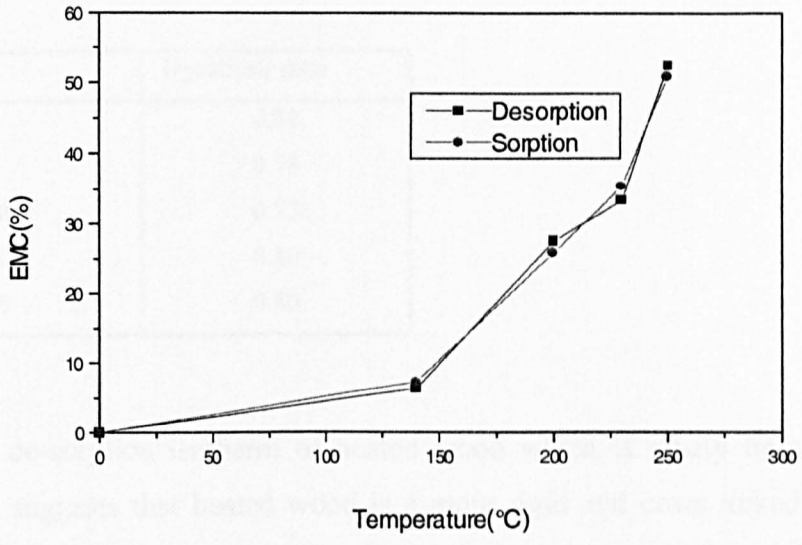


Figure 8.14: Hygroscopicity reduction in polymolecular sorption as a function of treatment temperature

8.3.5 Hysteresis

The average of Ma/Md is shown in Table 8.8. At 255°C, significant changes in the lignin content of wood indicate changes in the chemical structure of the wood and an increase in the cross-linking and condensations took place. As can be seen in Table 7.9, hysteresis is reduced when significant changes take place in the chemical structure of wood in other words when significant amounts of hydroxyl groups are removed or blocked by cross-linking of the wood due to heating. De-sorption isotherms of heated wood are in part more linear than those for unheated. The difference in the isotherm of heated wood and untreated wood suggests the wood as result of modification (most probably cross linking) due to heating, which has converted the wood to a more rigid material.

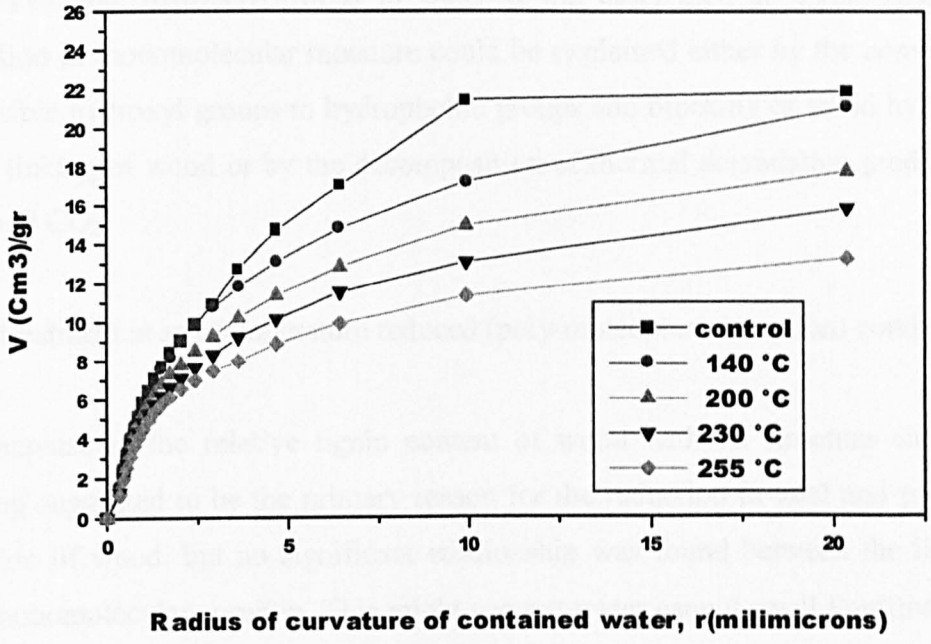
Table 8.9: Hysteresis of heated wood compared to untreated wood.

Temperature	Hysteresis ratio
0	0.80
140	0.78
200	0.77
230	0.80
255	0.80

The shape of the de-sorption isotherm of heated wood which is nearly linear at high relative humdities suggests that heated wood is a more rigid and cross linked material. This could be used as supportive evidence for the cross-linking of wood which were discussed earlier.

8.3.6 Estimation of pore radius from RH by Kelvin equation

The pore radius of heated and unheated wood estimated from RH (%) by the Kelvin equation were plotted against volume of water (cm^3)/g of wood. Figure 7.14 shows that the plots of pore radius and volume of water (cm^3)/ g of wood.



8.15: Volume of water per gram of wood versus pore radius obtained by Kelvin equation.

8.4 Points raised in this chapter

Heat treatment at 140°C reduced hygroscopicity slightly while heat treatment at temperatures above 200°C reduced the hygroscopicity significantly. This is in the agreement with the data obtained in Chapter 4. The relationship between hygroscopicity and decay resistance wood will be discussed in (Chapter 10).

In all cases, a very good agreement between experimental data and model for estimated sorption data was obtained. This shows this model could be used for the estimation of FSP.

Despite the fact that that the moisture content of the wood heated at any temperature was lower than that un-heated wood and good correlation between experimental and modelled sorption data was obtained, for treatments with low temperatures, monomolecular moisture content became higher than that for untreated wood. This is explained by either because of the fault of the model in portioning moisture into monomolecular and poly-

molecular moisture or by an increase in accessibility of the wood hydroxyl groups as result of thermal degradation. If the breaking down of some the wood components with more available hydroxyl groups to water is the case, then at higher temperatures, a reduction in monomolecular moisture could be explained either by the conversion of the accessible hydroxyl groups to hydrophobic groups and blocking of wood hydroxyl due to cross linking of wood or by the decomposition of thermal degradation products to acetic acid and CO_2.

Heat treatment at any temperature reduced (poly-molecular adsorption) condensed water.

An increase in the relative lignin content of wood with its structure changes during heating suggested to be the primary reason for the reduction in total and poly-molecular sorption of wood, but no significant relationship was found between the lignin content and monomolecular sorption. This might suggest water cannot swell lignified microfibrils of heated wood as much as the microfibrils of unheated wood. Thus, this causes a reduction in total and poly-molecular sorption of heated wood. In addition to this, a stress relaxation resulted from hemicellulose removal could be another effective factor in reducing swelling due to soaking.

By regression analysis of the sorption data, a reduction in the site accessibility of wood (W_o) was found to be the primary reason for a reduction in monomolecular sorption of wood as result of heating.

From FTIR band ratio's at different treatment temperatures, no significant relation between the band ratios at 1734 cm^{-1} due to esterifcation, carboxylic acid, and 1160 cm^{-1} due to C-O-C and moisture content at the level of 95% were obtained. Thus, the effort to correlate a reduction in moisture content and an increase in bands due to condensation by using FTIR failed. However, a rather high R^2 obtained from regression analysis between the ratio due to cross linking wood and mono-molecular sorption could suggest that the cross linking of wood due to heat treatment is an important factor in reducing the mono-molecular sorption of wood.

Heating at 255°C both reduced hysteresis and changed significantly the chemical structure of wood.

More or less the same estimation of FSP was obtained from adsorption and de-sorption data, although a better agreement between experimental data and model estimated FSP was obtained from de-sorption data than that from adsorption data.

Hygroscopicity of heated wood slightly increases in de-sorption. The increase was as result of an increase in monomolecular moisture content of heated wood.

Chapter 9

The hygroscopicity of chemically modified wood

9.1 Introduction

In the previous Chapter, the hygroscopicity of heated wood was investigated, in this Chapter, the hygroscopicity of wood modified with silanes and linear carboxylic anhydrides are investigated.

In this Chapter, in order to a restriction in time, DVS method was not used and the hygroscopicity of the chemically modified woods were studied at six different relative humidities and sorption isotherms were calculated from measured equilibrium moisture content. In this study, hysteresis was not measured as this was not considered important to the durability of the modified wood. Only EMC's in sorption isotherms for the various modified woods calculated.

9.2 Materials and Methods

9.2.1 Chemically modified wood

Blocks with dimension of 20x20x5mm were chemically modified as explained in Sections 33.2.1, 3.3.2.2 and 3.3.3. For each WPG, 2 blocks were chosen.

9.2.2 The control of relative humidity

The method for controlling relative humidity was the same method used by Martins, 1992. Test blocks were kept above saturated solution of selected salts in desiccators stored in a conditioning room set at 20°C (variation +/-1°C). Six salts were chosen and

these are listed in Table 9.1. Together with the relative humdities of the atmosphere above each saturated solution at 20°C (according to Kaye and Lab, 1973 in Simon, 1998).

Excess salt was present within each solution to ensure saturation was maintained. The solution and air in the container were agitated by stirring the solution within the conditioning period by a magnetic bar.

Since thin wood wafers reaches to equilibrium with its humid environment much quicker than blocks with dimensions of 20x20x5mm, thin Corsican pine and Scots sapwood wafers were used in each container to monitor any variation in humidity above a particular salt solution. The variation in humidity was checked by measuring moisture content (%) of the wafers after each week or two weeks.

An attempt was made to measure relative humidity within the containers by using a hygrometer and a wet and dry bulb psychometer. Neither of these proved accurate, and both gave inconsistent readings. The psychomotor was not suitable for use in this experiment due to lack of sufficient airflow required to evaporate water at the wet bulb. The relative humidities listed in Table 9.1 were therefore assumed to be correct.

The lack of an accurate measure of relative humidties for verification in this experiment was unfortunate, but this doesn't affect the comparisons made between modified (and unmodified), wood sample exposed under identical conditions.

9.2.3 Sample conditioning

The oven-dried blocks were placed in the desiccators above saturated salt solutions. They were left for 6 weeks and then weighed once a week on a four-place analytical balance until they showed constant moisture content (E.M.C). Equilibrium moisture content was reached within 6 weeks for all but the two highest humidities, which required a longer exposure time (16 weeks).

Table 9.1: Saturated salts used for adjusting relative humidity and their resultant relative humidity at 20°C.

Salt	Relative Humidity (%)
Potassium nitrate (KNO_3)	93
Sodium Chloride(NaCl)	76
Sodium Dichromate(Na_2CrO_7)	55
Potassium Carbonate(K_2CO_3)	44
Potassium acetate(CH_3COOK)Lithium chloride (LiCl)	23
Lithium Chloride	12

9.2.4 Model

The H-H model was used for the isotherm fitting of chemically modified wood because the model has been applied successfully for chemically modified wood, as it was mentioned earlier.

9.3 Results and Discussion

9.3.1 Isotherm fitting

The physical constants K_1, K_2 and Mo obtained by H-H model are shown in Tables 9.2-9.3. For linear carboxylic and VTMS the modified wood, Mo is reduced as the WPG increases, indicating that a proportion of sites are made un-available for water sorption. For TMPS modified wood, Mo didn't decrease at low WPG. This could be as result of an increase in the hydrophylic sites produced by un-reacted hydroxyl group of silane

Table 9.2: Fitted and physical constants calculated for H-H adsorption isotherms of linear carboxylic modified wood

adduct	WPG	A	B	C	K1	K2	Mo
control		3.23	11.019	10.1	5.53	0.75	6.3
acetic	9.40	5.70	13.68	13.8	4.14	0.76	4.46
	12.40	5.40	15.70	15.2	4.79	0.77	4.17
	15.80	7.440	17.30	17.10	4.11	0.75	3.52
	21.80	10.24	18.30	19.60	3.37	0.75	2.96
hexanoic	4.20	4.09	10.74	10.10	4.57	0.73	5.97
	7.30	5.64	9.90	9.96	3.45	0.71	5.57
	15.70	6.44	18.90	18.20	4.84	0.76	3.48
	21.00	10.71	16.52	17.90	3.10	0.73	3.11

Table 9.3: Fitted and physical constants calculated for H-H adsorption isotherms of Silane modified wood

*a*dduct		A	B	C	K1	K2	Mo
control		3.23	11.02	10.10	5.54	0.75	6.30
TMPS	6.	3.53	10.77	9.51	5.27	0.72	6.32
	27	5.56	14.44	14.00	4.45	0.75	4.39
	52	8.41	15.44	16.00	6.19	0.78	3.59
VTMS	4	4	18.20	16.40	4.57	0.73	5.97
	8.9	4.5	14.49	13.90	5.19	0.77	4.67
	25	4	18.20	16.40	6.90	0.77	4.10

9.3.2 Isotherms for Carboxylic anhydride wood

Figures 9.1 and 9.2, show the sorption isotherm families for each adduct of linear carboxylic modification. The isotherms for monomolecular and poly-molecular adsorption are plotted as described in the pervious Chapter.

Monomolecular, poly-molecular and total sorption for linear- carboxylic modified wood is shown in Figures 9.1 and 9.2.

In Figures 9.1 and 9.2, an obvious trend of decreasing hygroscopicity with increasing WPG for linear carboxylic anhydride modification can be observed. As can be seen in Figures 9.3-9.6, both adducts reduced monomolecular, poly-molecular and total sorption when WPG increased. The anhydrides one of different size, but nearly equally reduced the hygroscopicity of the wood proportional to WPG. This bulking due to modification could be the primary reason for the reduction. This is in the line with the results obtained by Papadopoulos (2001). Papadopoulos (2001), studied the mechanism by which linear carboxylic anhydrides reduce the hygroscopicity of wood, and concluded that bulking is the primary reason for the reduced hygroscopicity.

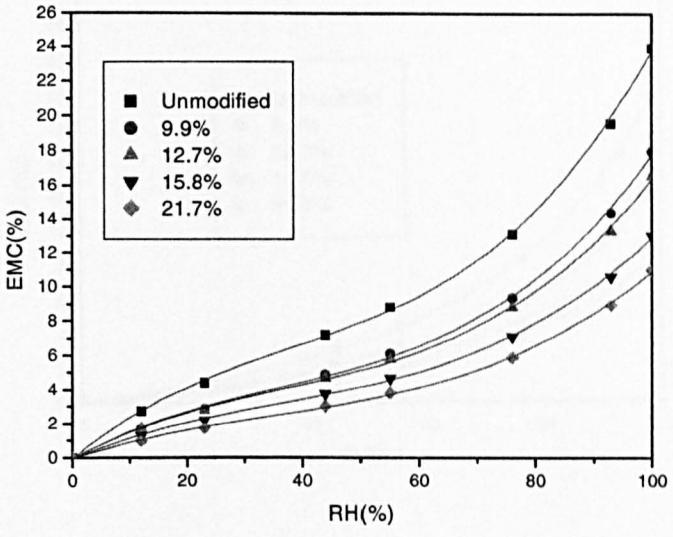


Figure 9.1: Sorption isotherms for Corsican pine sapwood acetylated with WPG's compared to unmodified wood.

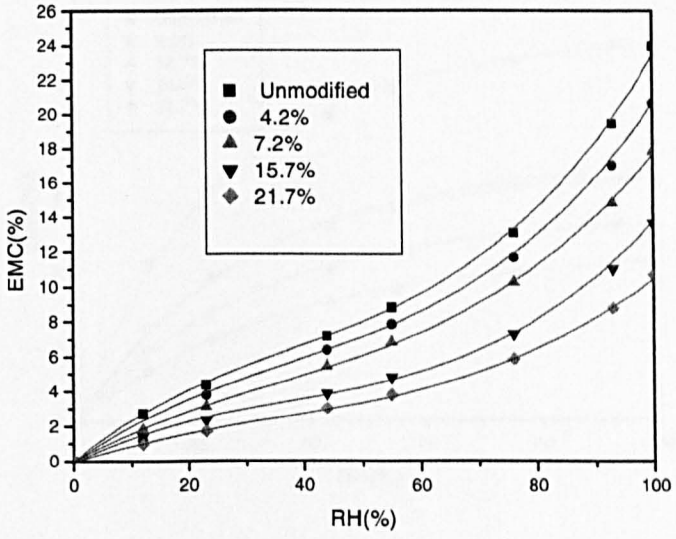


Figure 9.2: Adsorption isotherms for Corsican pine sapwood hexanyolated with various WPG's compared to unmodified wood (Control).

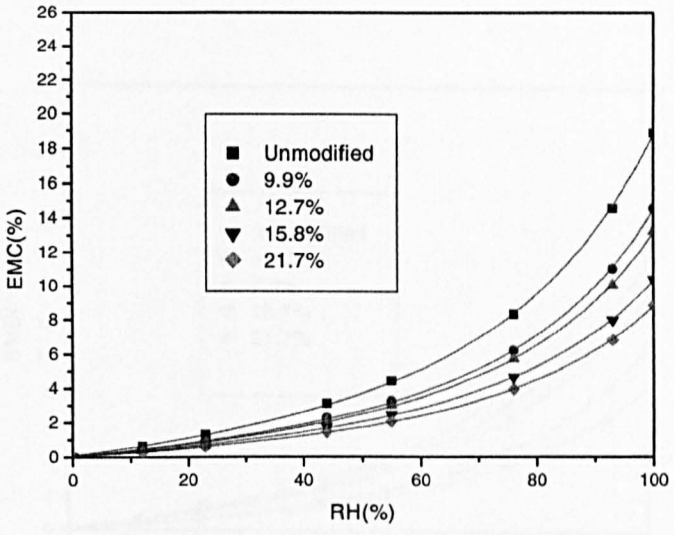


Figure 9.3: Polymolecular adsorption isotherms for Corsican pine sapwood acetylated with various WPG's compared to Unmodified wood

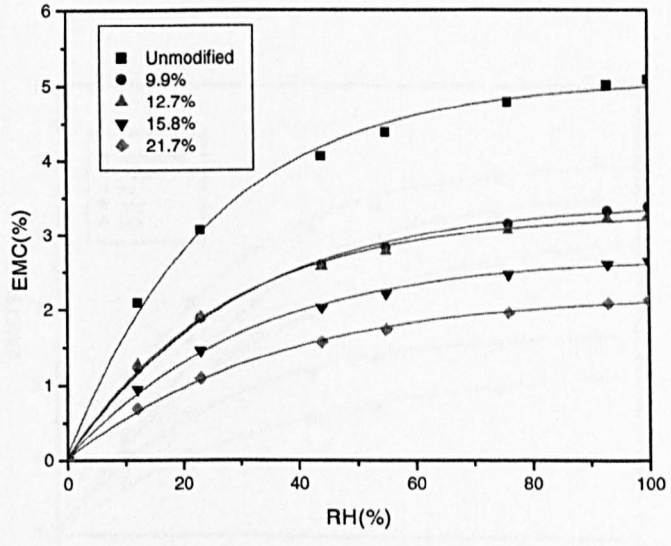


Figure 9.4: Monomolecular adsorption isotherms for Corsican pine sapwood acetylated with various WPG's compared to unmodified wood (Control).

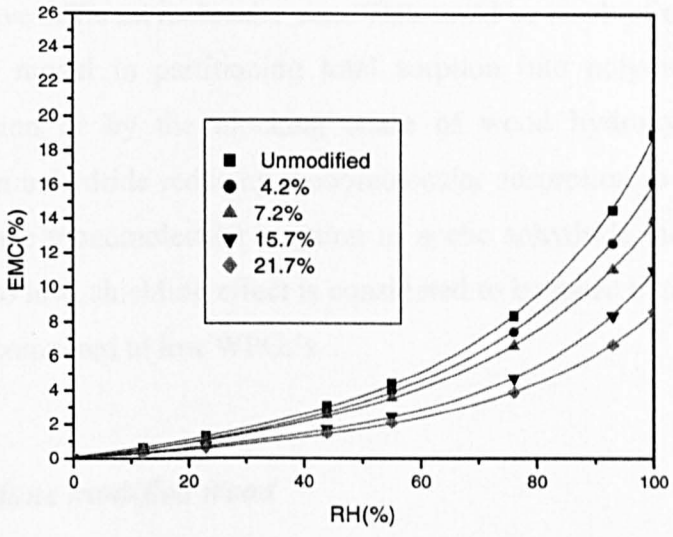


Figure 9.5: Polymolecular adsorption isotherms for Corsican pine sapwood untreated (controls) and hexanyolated with WPG's.

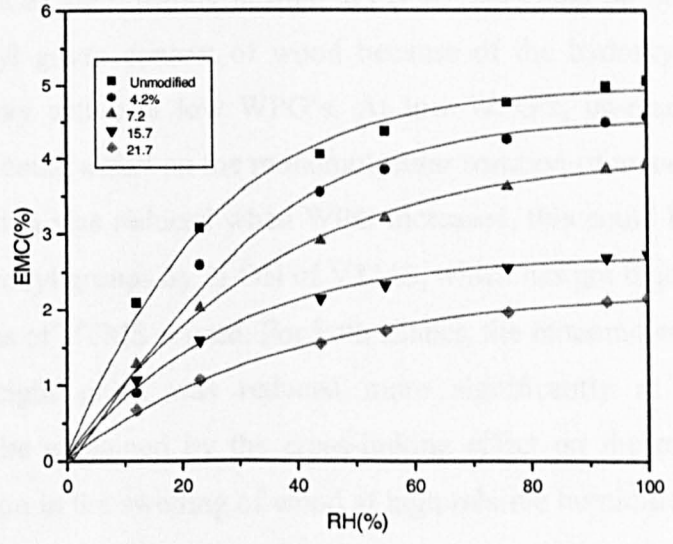


Figure 9.6: Monomolecular adsorption isotherms for Corsican sapwood pine hexanolytated with different WPG's compared to unmodified wood

Both adducts had nearly the same effect on monomolecular and poly molecular adsorption while they have different molecular size. This could be result of either the lack of the accuracy of the model in partitioning total sorption into poly-molecular and monomolecular adsorption or by the blocking some of wood hydroxyl groups by shielding of longer chain anhydride reducing monomolecular adsorption as much as that by acetic anhydride. Since monomolecular sorption of acetic anhydride more similar at high WPG's compared to low, shielding effect is considered to be more important for the adducts at high WPG's compared to low WPG.'s.

9.3.3 Isotherms for Silane modified wood

Figures 9.7 and 9.8, shows that the sorption isotherm families for each silane used. For both silanes, as it can be clearly observed that hygroscopicity reduced when WPG increased. For TMPS, monomolecular adsorption was not suppressed significantly at low WPG while it was reduced significantly at high WPG's. This could be the result of an increase in the hydroxyl group content of wood because of the hydroxyl group from TMPS which is not very active at low WPG's. At low WPG's, un-reacted hydroxyl groups from the TMPS could affect on the monomolecular sorption of wood. For VTMS, monomolecular adsorption was reduced when WPG increased, this could be result from the blocking wood hydroxyl groups by Si-OH of VTMS, which has got high activity even when low concentrations of VTMS is used. For both silanes, the monomolecular sorption, especially at high weight gains was reduced more significantly at high relative humidities, this could be explained by the cross-linking effect on the monomolecular adsorption. The reduction in the swelling of wood at high relative humidities due to cross linking could have prevented from the opening up of new hydrophilic sites. In addition to the cross linking effect, the shielding effect of TMPS could be one of the reasons for the comparable reduction of monomolecular adsorption at high WPG's.

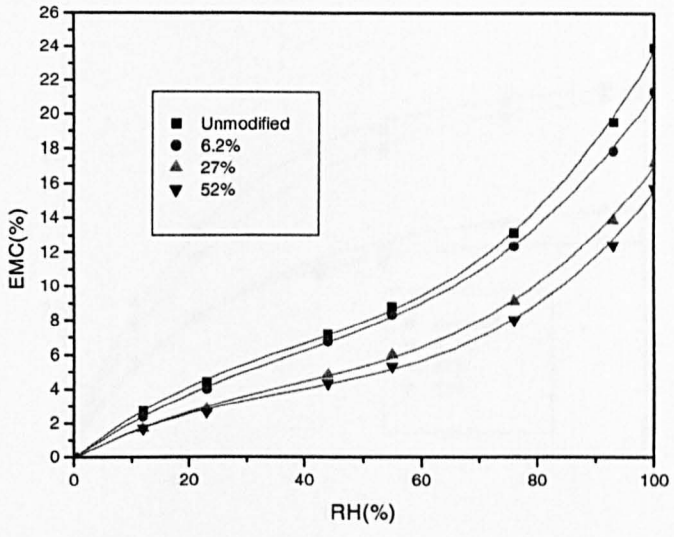


Figure 9.7: Sorption isotherms for Corsican pine sapwood modified with TMPS at different WPG's compared to unmodified wood

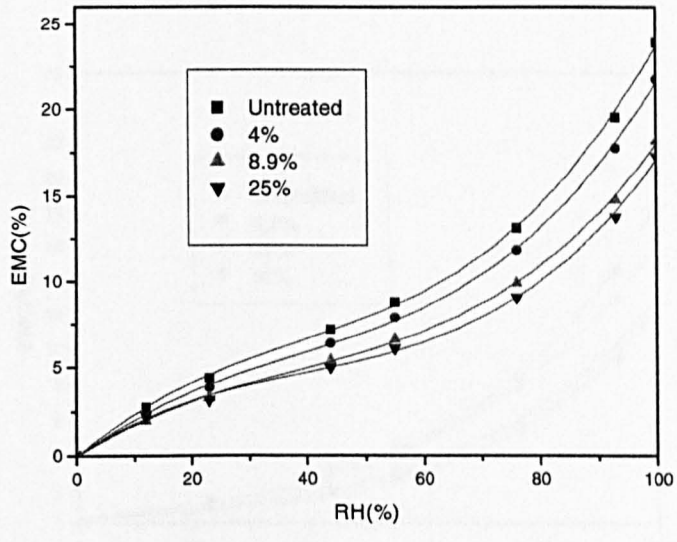


Figure 9.8: Sorption isotherms for Corsican pine sapwood modified with VTMS at different WPG's compared to unmodified wood

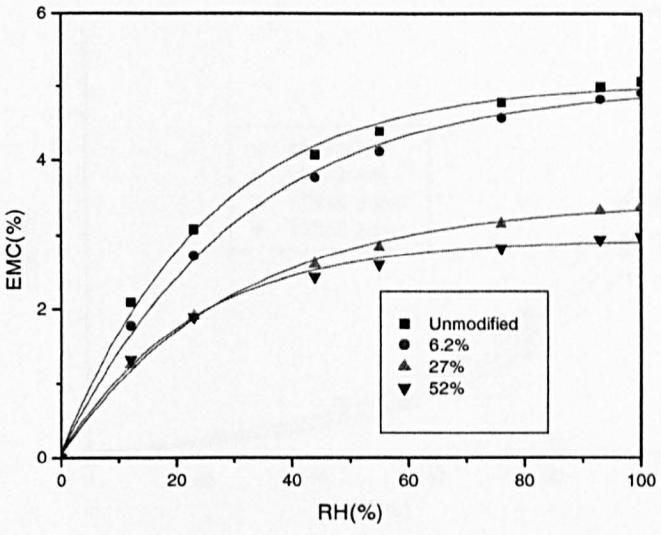


Figure 9.9: Monomolecular sorption isotherms for Corsican pine sapwood treated with TMPS at different WPG's compared to unmodified wood

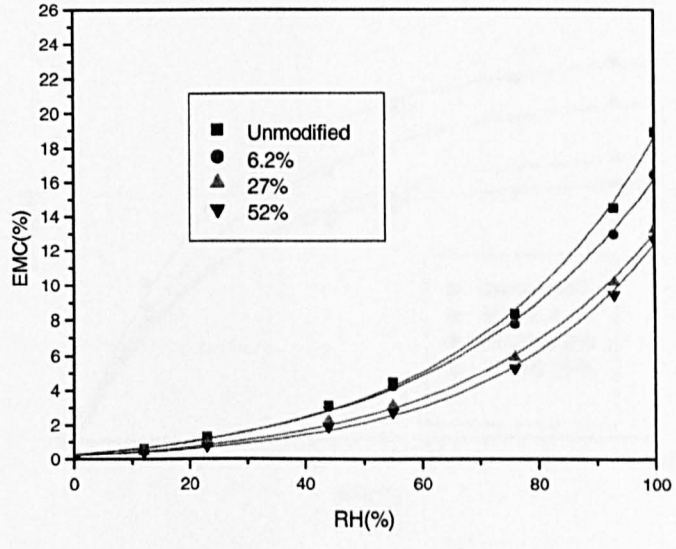


Figure 9.10: Poly-molecular sorption isotherms for Corsican pine sapwood treated with TMPS at different WPG's compared to unmodified wood

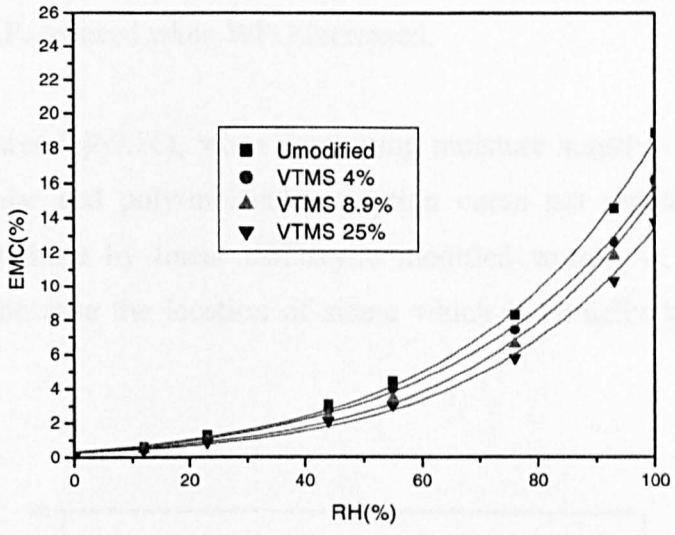


Figure 9.11: Poly-molecular sorption isotherms for Corsican pine sapwood treated with VTMS at different WPG's compared to unmodified wood

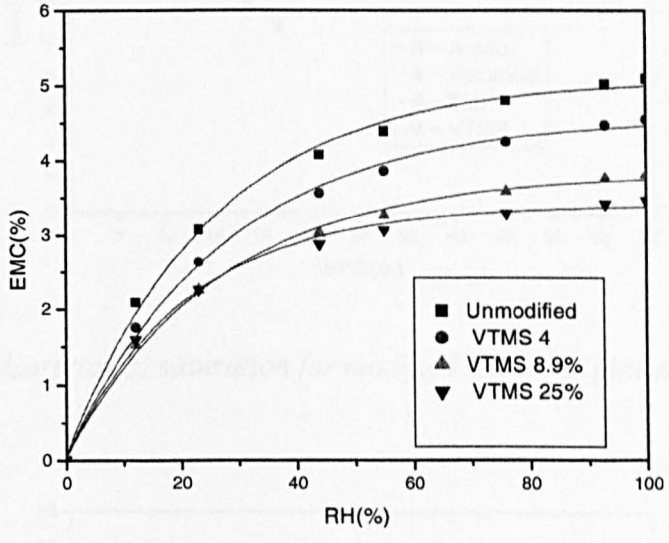


Figure 9.12: Monomolecular sorption isotherms for Corsican pine sapwood treated with VTMS at different WPG's compared to unmodified wood

9.3.4 F.S.P

In this section of studies, by using just six data points at 20°C, a FSP of 23.9% for Corsican pine was measured which is in accordance to the literature in which the

same methods were used but slightly lower than the amount obtained by the DVS at 25°C. In the all cases, F.S.P. reduced when WPG increased.

As can observed in (Figures 9.9-9.16), when comparing moisture sorptive properties vs WPG, FSP, monomolecular and poly-molecular sorption curve not reduced by silane modification as much as those by linear carboxylic modified wood. As discussed in Chapter 6, this must be because the location of silane which is partially located in the lumen at higher WPG's.

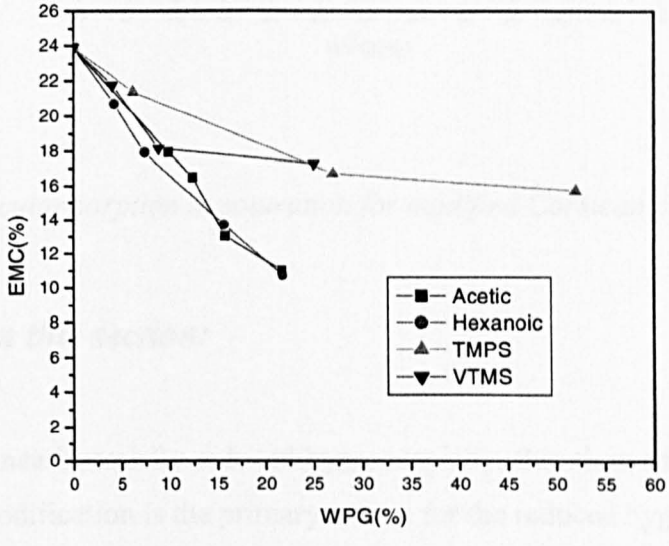


Figure 9.13: Total adsorption at saturation for modified Corsican pine sapwood

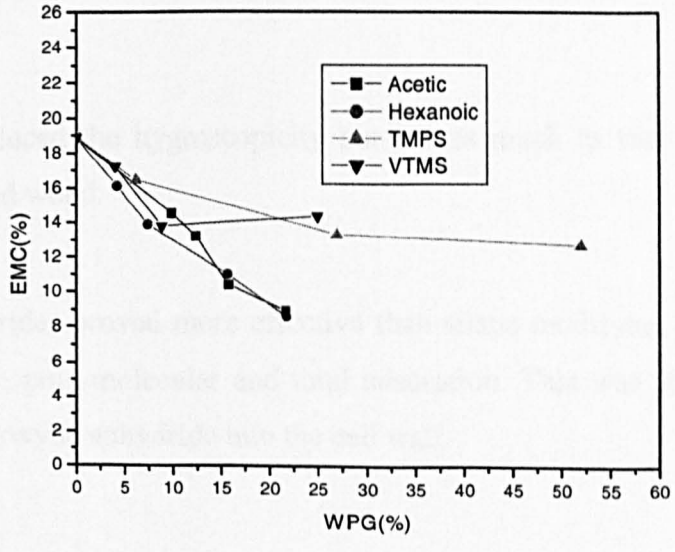


Figure 9.14: Poly-molecular sorption the modified Corsican pine sapwood

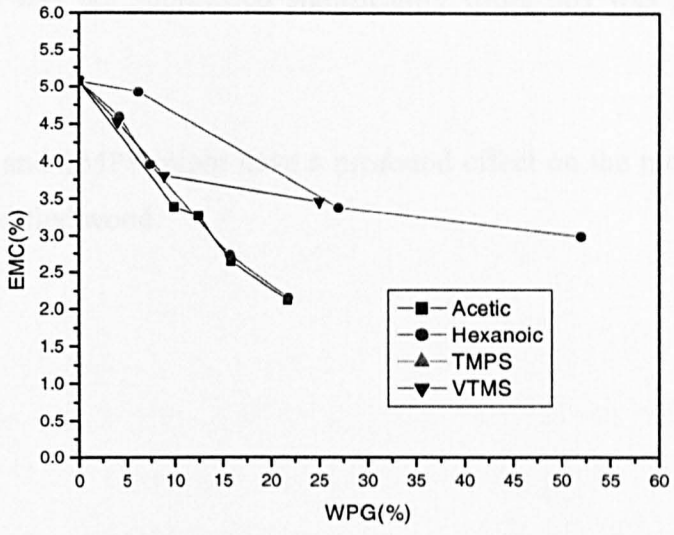


Figure 9.15: Mono-molecular sorption at saturation for modified Corsican pine sapwood

9.4 Points raised from this section:

Both anhydrides studied nearly equally reduced hygroscopicity, this showed that bulking of the wood due to the modification is the primary reason for the reduced hygroscopicity.

Both anhydrides reduced the monomolecular sorption of wood by the same extent. This was explained by the blocking of some hydroxyl groups with shielding effect of the longer chain anhydrides.

Silane treated wood, reduced the hygroscopicity but not as much as that achieved by linear carboxylic modified wood.

Linear carboxylic anhydrides proved more effective than silane modifying chemicals at reducing monomolecular, poly-molecular and total adsorption. This was attributed to a better penetration of carboxylic anhydride into the cell wall.

At low WPG's, presumably, because of un-reacted free hydroxyl groups of TMPS, the monomolecular sorption was not suppressed significantly while this was not observed with VTMS.

Cross linking of VTMS and TMPS might have a profound effect on the monomolecular sorption of the silane modified wood.

Chapter 10

Cell wall pore accessibility of modified wood

10.1 Introduction

It has been shown that the bulking of wood due to chemical modification caused a reduction in the moisture content of the modified wood by reducing the volume available for condensed water in the cell wall (Chapters 7 and 9). The presence of chemical adducts in the cell would also be expected to cause a reduction in the cell wall micropore volume. Since white and brown rot fungi degrade wood by the diffusion of degrading agents into the cell wall (see Section 2.9), the presence of adducts due to the modification might block the pore structure preventing these degradative agents penetrating the cell wall.

For the thermal modification, which causes the cell wall to shrink, it was interesting to see whether the shrinkage would change the total cell wall volume (as was explained in Chapter 6). Heat treatment shrinks wood, causing an increase in the pore structure of latewood and closure of the pore structure of spring wood. Cross-linking and condensation of lignin due to heat treatment would therefore be expected to cause cell wall micropore closure.

To assess whether cell wall micropore blocking, or closure is a likely mechanism of protection of wood by the different modifications, a measurement of the accessibility of these micropores to probes of various sizes was attempted. This is known as the solute exclusion technique. This was developed by Stone and Scallon (1968a, b) and used for investigations of decayed wood by Flournoy *et al.* (1991, 1993) as discussed in (Sections 2.9.1 and 2.9.2)

10.2 Materials and methods

10.2.1 Modified wood

Samples with dimensions of (5mm x 20mm x 20mm) (log. x rad. x tang.) were reacted as described in Chapter 8. In the sample selection for this experiment, it was tried to select samples cut from just one log. The wood used for heat treatment came from a different log. Time restrictions meant that only weight gains by which significant decay resistance was imparted to the wood against brown rot and white rot were selected.

In the case of heat treatment, only wood heated at 250°C for two hours (which showed significant decay resistance against white rot and brown rot) was chosen. Unextracted and extracted wood were also tested as controls for the modification. Four blocks were selected from each relevant treatment. Samples were oven dried and oven dry weight was recorded.

10.2.2 Determination of pore size

The weighed blocks were vacuum impregnated with a solution of 0.05% sodium azide and soaked for 4 months to ensure complete saturation. Sodium azide was used as a preservative to prevent bacterial attack of the wood (or probes) during the initial soaking or the experiment. Before incubation with probe solutions, the soaking solution had been changed five times during the soaking in water in an attempt to remove any leachable material from the blocks, so that this would not contaminate the solutions used in the experiment.

The same probes used by Flournoy *et al.* (1991) were used in this study and are listed, along with their molecular weights and diameters, in Table 10.1. Flournoy used dextran (Pharmacia T10) but this was not available, thus it was not used in this study. Of the five (non-water) probes, three are sugars and two (the two largest probes) are dextrans.

Table 10.1 Molecular weights and diameters of probes

Probe	Molecular weight	Probe diameter (Å)*
Water	18	4
Glucose	180	8
Maltose	342	10
Raffinose	504	12
Fluka AG	6000	38
Polysciences 15-20K	17500	61

* Probe diameters from sources cited by Flournoy *et al.* (1991)

For the best results with the solute exclusion technique, Stone and Scallon (1968b) list three properties of probes that are necessary:

1. Each solute molecule should have a known size and geometry in solution, with spherical being preferred. For linear dextrans of the type used in this study, this has been found to be the case (Grotte, 1956, cited by Stone and Scallon, 1968b).

2. Each solute should have narrow molecular diameter distributions (governed by the molecular weight range for a given dextran) compared to the range of pore sizes within the porous body being examined. Stone and Scallon (1968b) concluded that the dextrans used (similar to those used here) satisfied this condition, because the wood and pulp fibres they measured had a comparatively wide pore distribution. Although it was expected that chemical modification would reduce pore size (rather than increase it as in the case of pulping), the relative distributions of the probes and the modified wood pores was not considered further in the present study. The dextrans used in this study were not expected to be able to penetrate the modified wood cell wall to any significant extent. Flournoy *et al.* (1991), found the same three dextrans did not penetrate unmodified un-decayed wood. The three probes expected to penetrate the wood cell wall were all sugars, having no molecular weight variation within a sample.

3. Probe molecules should not sorb chemically nor physically onto the wood, as this would cause a reduction in the concentration of the solution and an apparent increase in accessibility. Stone and Scallon (1968b) found sorption to be negligible for wood and pulp fibre, and in this study it was assumed also to be negligible for modified wood samples.

Stock solutions (1% concentration) of each probe were prepared in aqueous 0.05% sodium azide solution. Wet modified wood samples were dabbed dry and weighed in a sample tube to 4 decimal places. Probe solution was then added (20ml per sample) and the weight (4 d.p.) recorded. Sample tubes were then sealed and incubated in a temperature controlled room (20°C) for two weeks. Preliminary tests had shown this time to be sufficient for the penetration of the sample by the probes and equilibrium concentration of the solution to be reached. After this period, the solution was decanted from the sample and set aside for solute concentration measurement. Wood samples were then soaked in aqueous 0.05% sodium azide (approx. 100ml of solution per sample) for one week to remove the probe from the wood. To ensure that the probe was fully removed, the soaking solution was changed after two and five days. The procedure was then repeated for each subsequent probe.

The quantity of water in each modified wood sample was calculated by subtracting the oven-dry weight from the saturated weight of the sample. The quantity of this water accessible to each probe was calculated from the change in the concentration of the probe solution after incubation with the wood block. This was determined using a Knauer differential refractometer in a temperature controlled room (20°C) with the undiluted 1% stock solution of the given probe in the control cell. A comparison of the differential refractometer reading with readings on a calibration curve prepared by adding known quantities of water (containing 0.05% sodium azide) to the stock solution gave the quantity of water in the wood sample which had diluted the stock solution during incubation.

The quantity of water in the sample which had diluted the probe solution during incubation, as measured above, was the accessible water in the sample for that given probe. This was divided by the original (unmodified) oven-dry weight of the wood block to give a measure of the volume of accessible water per gram of wood (ml/g). By

presenting this measure as accessible volume it has been assumed that the specific gravity of water in the sample (and in the wood cell wall) is 1. The original (pre-modification) weight of the sample was calculated on the basis of modified weight and WPG as in Chapter 4. The unmodified weight was used in preference to modified wood weight, because it was decided that this would give a better measure of the accessible water in a given volume of swollen cell wall material.

In the calculation of accessible volume in the cell wall to probes of a given size a further assumption has been made. This is that the concentration of the solute in the accessible pores is equal to that in the solution surrounding the sample. This assumption has been criticised by Alince (1991) as discussed in Section 2.2.3. Since each probe would have been subjected to the same effects for each modification type, as presumably would degradative agents diffusing into the wall from fungal hyphae, the measurement of the apparent accessible volume was still considered valuable.

10.2.3 Results and discussion

Table 10.2 gives the average accessible pore volumes available to each probe in water swollen modified wood. Despite the fact that the wood blocks came from the same log, in some cases, high variation was observed. As can be observed in Table 10.2, some meaningless results were obtained for silane and heat treated wood. This was probably because of the leaching of tiny amounts of chemical or heat degradation products from silane and thermally modified wood respectively. This is discussed more in the next sections.

Table 10.2: Average (and standard deviation) pore volumes of chemically modified wood accessible to probes of various sizes

Modification	WPG (%) or Time(min)	Accessibility (ml/g) to probes of increasing diameter					
		4Å	8Å	10Å	12Å	38Å	61 Å
Control (extracted wood)	0	1.93 (0.04)	1.84 (0.03)	1.8 (0.03)	1.77 (0.06)	1.57 (0.06)	1.56 (0.04)
Acetylation	9.2	1.83 (0.1)	1.74 (0.15)	1.73 (0.15)	1.65 (0.15)	1.52 (0.07)	1.49 (0.09)
	21.8	1.25 (0.06)	1.19 (0.06)	1.18 (0.02)	1.18 (0.06)	1.1 (0.03)	1.04 (0.07)
Hexanoylation	7.2	1.42 (0.02)	1.33 (0.01)	1.3 (0.02)	1.27 (0.07)	1.11 (0.05)	1.08 (0.07)
	22.7	1.21 (0.04)	1.16 (0.06)	1.15 (0.07)	1.14 (0.04)	1.08 (0.02)	1.02 (0.02)
Silylation VTMS	44	1.12 (0.06)	MS	MS	1.01 (0.1)	MS	MS
Silylation TMPS	28	1.6 (0.06)	MS	MS	1.54 (0.05)	1.3 (0.1)	1.33 *
Control (Unextracted)	0	1.86 (0.06)	1.79 (0.07)	1.75 (0.04)	1.7 (0.06)	1.52 (0.07)	1.51 (0.09)
Heat treatment at 250°C	120min	1.69 (0.2)	MS	MS	1.54 (0.2)	1.44 *	1.22 *

MS: Meaningless

* Just one replicate

10.3 Fibre saturation point

The fibre saturation point in the present study can be calculated from the accessible volume listed for water (4Å diameter probe) in Table10.3 or the accessible volume at 4Å in Figure 10.2 This was done by subtracting the accessible pore volume of each probe in water from the dextran that showed the highest accessible volume. The results are depicted in the Figure 9.1. The fibre saturation points of the silane and heated wood because of some meaningless results obtained (in some cases) are not represented in this section. However, the cell wall accessible volume to water (FSP) of heated and TMPS modified wood are represented in the next section. The calculated FSP for the extracted and un-extracted wood were 36% and 35% respectively. These are high compared to unmodified wood but are in agreement with the results obtained by the other workers. Flournoy *et al.* (1991) calculated FSP of Sweetgum (*Liquidambar styraciflua*) to be 35% and Stone and Scallon (1967) calculated FSP of Black spruce (*Picea mariana*) to be 40%. Possible reasons for the high FSP measures obtained from the solute exclusion technique are given by Siau (1996) (see Section 2.7.3).

As can be observed, the FSP of carboxylic anhydride modified wood, was reduced when the WPG, increased. Insignificant differences were observed between the anhydrides studied.

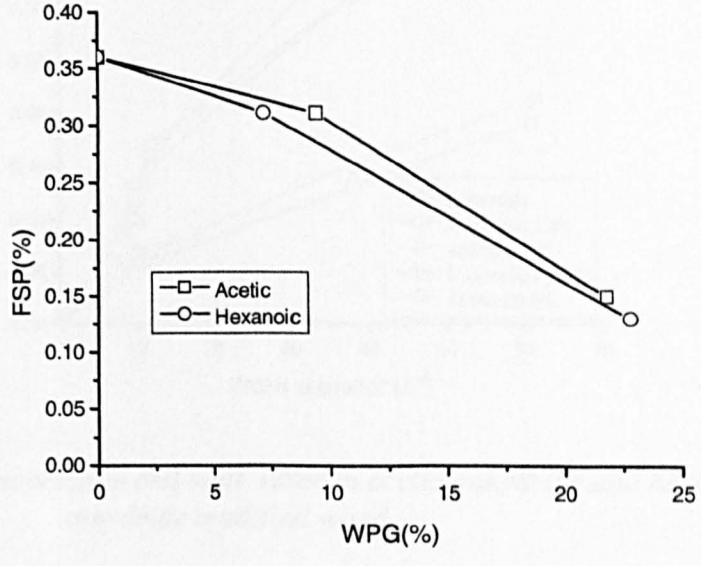


Figure 9: FSP of carboxylic anhydride modified wood.

9.4 Pore accessibility of modified wood

As can be seen in Table 10.2, all modified wood had lower cell wall accessibility than that for unmodified wood. The accessible and non-accessible water of carboxylic anhydride modified wood are shown in Figures 10.2 and 10.3, respectively.

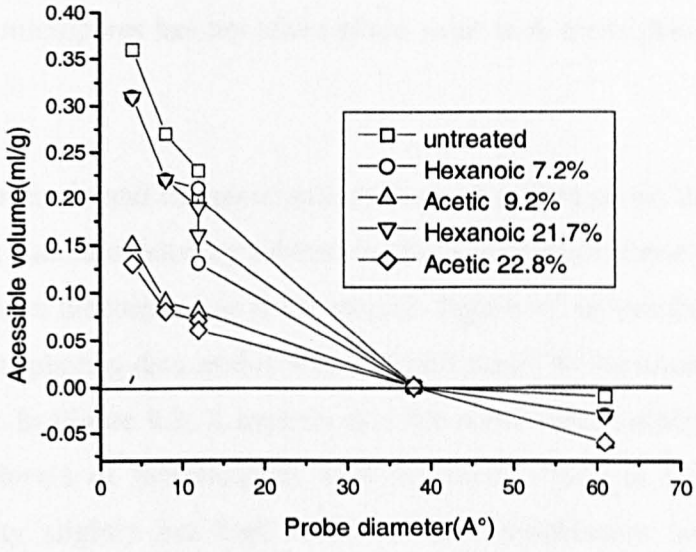


Figure 10.2: Average accessible cell wall water in acetic anhydride and hexanoic anhydride modified wood

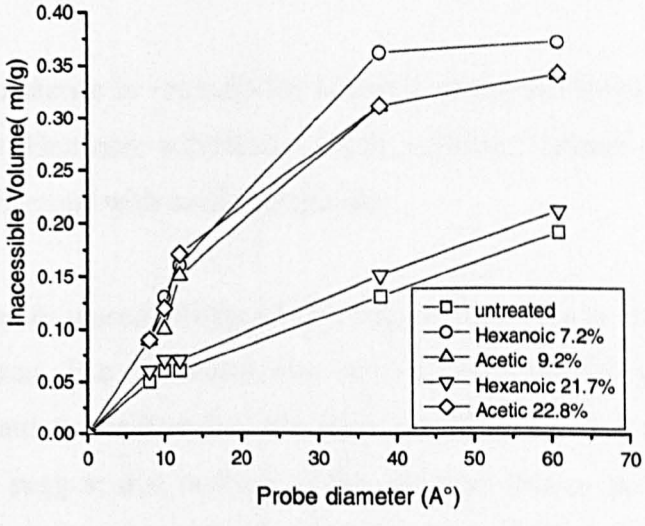


Figure 10.3: Average inaccessible cell wall water in acetic anhydride and hexanoic anhydride modified wood

As can be observed, the accessibility of the cell wall of the modified wood to glucose and maltose reduced very little at low levels of modification but at the high WPG's, the accessibility reduced significantly. Since a high variation was obtained between the replicates for the low weight gains, it is hard to say whether any effective blocking of wood cell wall micropores has occurred, but significant cell wall micropore blocking has taken place with the modification at the high WPG's. However, the results show that complete blocking of the micropores has not taken place, even with the highest levels of modification.

Figure 9.2, shows data for acetic and hexanoic anhydride modified wood on the basis of inaccessible volume. This was calculated by subtracting the accessible volume to a given probe in a single sample from the total water in the sample. Figure 9.2 shows the averages for each set of samples. Displaying data in this way makes it easier to see changes in the distribution of pore sizes. In Figure 9.2, it appears that the water inaccessible to the all probes decreased at all levels of modification. Low levels of chemical modification reduced the inaccessibility slightly but high levels of the modification reduced the inaccessibility significantly. This might suggest that at higher weight gains, reaction occurs in the most of the pores, and the total volume of the pores is reduced. The inaccessibly of acetic anhydride modified wood at low levels of modification to raffinose increased slightly, but this could be the result of experimental error.

In Figure 10.1, a small difference in accessibility between acetic and hexanoic anhydride modified wood is evident. Hexanoic anhydride, which is bulkier, caused slightly higher inaccessibility than that observed with acetic anhydride.

As can be observed, the pore inaccessibility of the biggest dextran was higher than that that for the smaller dextran. The difference was not very obvious for the unmodified wood but it was significant for carboxylic anhydride modified wood at high levels of modification. This might suggest that bulking of the cell wall due to the modifications reduces the micropores with diameters of 61Å to smaller sizes which were accessible to the probes with a diameter of 31Å.

For VTMS modified wood, the accessibility of the pores to raffinose was reduced significantly, although because of the problems mentioned above, the accessibility of

dextrans used for the calculation of the accessibility of the cell wall was not possible to calculate. For example, the pore volume to the water was 1.1 g/ml, but the water accessible volume to Dextran was calculated as 1.5 g/ml or 1.8 g/ml, thus the data was excluded and is not reported. The leaching data reported in Chapter 7, shows that just 1% percentage more of material from the modified wood was leached in the solute exclusion test than when the wood was exposed to a five times water extraction. In the guide book for the refractometer, it has been recommended that extra care should be taken about impurities because the refractive index is extremely sensitive to impurities. In order to remove any leachable material, it is recommended that the modified wood be leached according to EN 81 for more than two weeks. The inaccessibility of the modified wood to the probes is not presented in this study. However, the accessible pore volume of the sample to raffinose reduced significantly. This might be because of the accumulation of high amounts of VTMS in the lumen instead of a high reduction of the accessibility in the cell wall of VTMS modified wood. This would restrict access to the cell wall without actually blocking the micropores.

For TMPS modified wood, the accessibility of the cell wall was reduced at the WPG studied (Table 10.3). Because of unknown reasons (most likely leaching), some of the replicates of the modified wood gave meaningless results. However, from the data, it is evident that the water accessible to the cell wall was reduced.

Table 10.3: The accessibility of the cell wall of TMPS modified wood compared to unheated wood.

	The cell wall accessibility (ml/g) to probes of increasing diameter	
	4 Å	12 Å
Extracted	0.36	0.27
TMPS	0.29	0.23

In the case of heat treated wood, because of the high standard deviation (0.2) and some meaningless results (Table 10.2), the accessible volume of the cell wall was calculated based on the average of the accessibility of the heated wood to the two dextran probes used.

By using NMR spectroscopy, an increase in the pore size of wood heated at 230°C has been observed (Hietala *et al.*, 2002). In this study, a slight increase in the accessibility of the cell wall to raffinose between thermally modified wood and un-extracted wood are evident (Table, 10.4), though due to the questionable sensitivity of this test and the high variation in the data this is not a conclusive result.

Table 10.4: The accessibility of the cell wall of heated wood compared to unheated wood.

	The cell wall accessibility (ml/g) to probes of increasing diameter	
	4 Å	12 Å
Un-extracted	0.35	0.19
Heated	0.27	0.21

10.6 Points raised from this chapter.

Fibre saturation point was measured for the extracted and un-extracted control samples to be 36% and 35% respectively. This is high in relation to other methods of determination (e.g. that measured in Chapter 4), but in line with the results of other workers using the solute exclusion technique.

Wood modification with acetic and hexanoic anhydrides, caused a reduction in FSP from that measured for the extracted controls.

Significant cell wall micropore blocking at a high level of modification with carboxylic anhydrides was observed although, the data shows that complete blocking of the micropores has not taken place with these modifications at the WPG's studied.
Probably, leaching of VTMS and TMPS during soaking of the silane modified wood in the experiments caused the data to be meaningless. The problem was not observed with the last sugar studied. It was inferred that for the last sugar, all the leachable material had been removed. Since the total leaching of the silanes was not high, it was concluded that even tiny amounts of modifying chemical could ruin the data from the solute exclusion technique. In addition, the questionable sensitivity of the measurements also should be considered. The sensitivity of the method weakens the ability of the method to study the micropore structure of the modified wood or any other modified wood.

For VTMS wood modified to a WPG of 44%, the micropore accessibility to raffinose was reduced significantly, although the calculation of micropore accessibility of the cell wall was not carried out because of some meaningless results obtained with the dextrans studied. Since the treatment reduced the pore accessibility more than the other modifications studied, it was concluded that the accumulation of the chemical in the lumen might be the main reason for the reduction.

For TMPS modified wood, a reduction in the accessibility of the wood to water was observed.

Heat treated wood exhibited a reduced accessibility of the cell wall to water, but increased the micropore accessibility to raffinose. However, because of high variation observed between the replicates and other problems, these are not conclusive results.

Chapter 11

Discussion, conclusions and recommendations

11.1 Introduction

The main purpose of the study was to try to further understand the mechanisms by which thermal modification and chemical modification impart decay resistance to the wood. This is not a straightforward task, due in part to the fact that that the mechanism by which fungi decay wood is itself not fully understood.

A reduction in hygroscopicity is one of the proposed mechanisms for the decay resistance of wood treated with either of the modifications studied (thermal and chemical modifications). Before entering into the discussion about the mechanism by which modification imparts decay resistance to the wood, the reasons why water is required by decay fungi, as introduced in Chapter 1, are recalled below.

Water is required for the growth of fungal hyphae, as has been explained by Forster (1998).

As a reactant in the hydrolytic degradation of wood polymers: cellulose and hemicellulose degradation enzymes are hydrolytic enzymes which require water to degrade glycosidic linkages in wood carbohydrates. It is generally thought that brown rot decay is caused by an oxidative system that is involved in the initial de-polymerisation reactions and that the hydrolytic enzymes cannot penetrate the wood cell wall, even at an advanced stage of decay (Srebotnik and Messner, 1991). If these enzymes operate only at the lumen/cell wall boundary or in the hyphal sheath to break down de-polymerisation fragments, then they would be unaffected by the water content within the wood cell wall. Thus, under these circumstances the decay resistance achieved by the modification

against brown rot fungi would be attributable to causes other than a reduction in cell wall moisture content.

Water is required as a diffusion medium in the wood cell wall so that low molecular weight degrading agents can get into the cell wall.

11.2 Thermally modified wood

Corsican pine sapwood properties (decay and dimensional stability) wood were enhanced by heat treatment. In Chapter 4, it was shown that heat treatment temperature plays a more important role in the improvement of decay resistance than the treatment time. Heat treatment imparted decay resistance to the wood against the fungi tested, but significant decay resistance was only achieved with very intensive heat treatments (255°C above 2 hours).

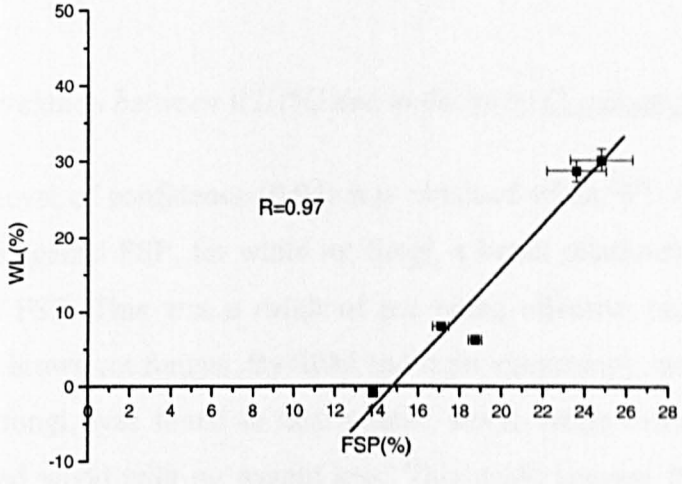
Zero weight loss due to decay by brown rot and white rot fungi was obtained when the wood was heated at a temperature of 255°C for 2 hours. Thus, further attempts were made to investigate the decay resistance of Corsican pine sapwood heated at a temperature 250°C for less than two hours (0.5, 1 and 1.5 and 2 h). By exposing the heat treated wood to brown rot, soft rot and the white rot fungi, it was found that the wood heated at 250°C for 1.5 h was significantly resistant against *C. puteana* and *P. chrysosporium* and soft rot fungi, while a longer treatment (2 h) was required to prevent decay by *T. versicolor*.

Heat treatment above 200°C decreased the hygroscopicity of the modified wood and significantly increased the decay resistance of wood against basidiomycetes.

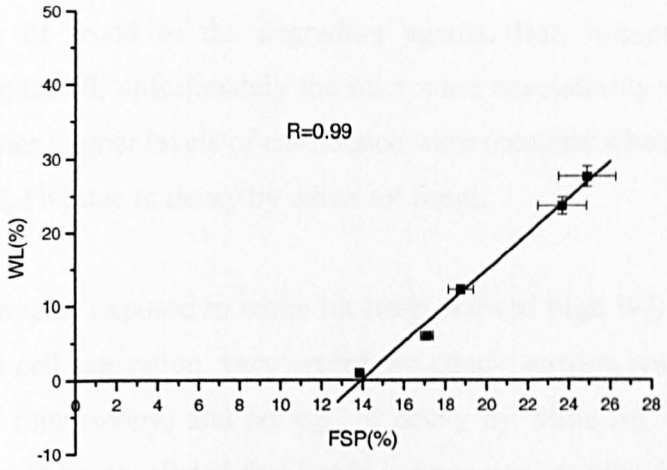
In Chapters 4, and 5, it was shown that although the end moisture content in decay tests was reduced proportionally to WL (%) due to decay, the end moisture content of even those samples that had been protected by the heat treatment, was mostly at a level regarded as being sufficient to allow decay. Thus, the reduction of water in the wood which is required for the growth of fungi could not be the main reason for the improvement of decay resistance. As mentioned in Chapter 4, the end moisture content gives no accurate indication of the position of moisture within the wood. It could be that

wood decay fungi require a certain amount of water in the cell wall itself and the end test moisture content is of lesser importance, a possibility suggested by Stamm and Bachler (1960). The theoretical maximum cell wall moisture content is the fibre saturation point. Two of the tests in this study provided measures of FSP; the sorption tests (Chapter 8) and pore size exclusion analysis (Chapter 10). Due to the problems mentioned in Chapter 10, the FSP of heat treated wood samples were not measured successfully by the solute exclusion technique, thus, this data is not used here.

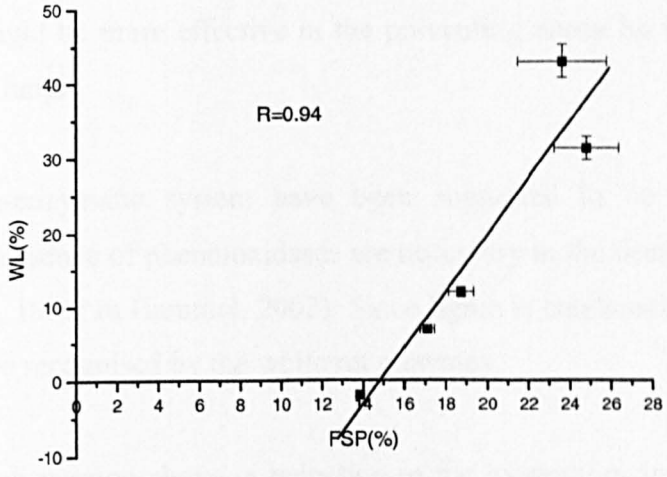
In Figures 11.1 to 11.3, the FSP's calculated by using the H-H model are plotted against the WL's due to decay. In all cases, good correlations between a reduction in the FSP of wood and a reduction in the weight loss were obtained, showing that a reduction in the hygroscopicity of the wood may explain the main reason for the improved decay resistance. The EMC limit required by fungi to degrade wood and FSP are theoretical measurements, in addition, FSP values vary depending upon, the method used for the estimation (this was discussed in Chapter 2). Thus, the FSP value cannot be used for making a decision as to whether the EMC of heated wood is lower that than the limit required by the fungi. However, it was shown that effective heat treatments which reduced the end test moisture content of control samples incubated over sterile malt agar to below or around the limit required by fungi.



11.1: The correlation between WL (%) due to decay by P. chrysosporium and FSP(%).



11.2: The correlation between WL (%) due to decay by T. versicolor and FSP (%).



11.3: The correlation between WL (%) due to decay by C. puteana and FSP (%).

Although a high level of confidence (0.94) was obtained when WL due to attack by *C. puteana* is plotted against FSP, for white rot fungi, a better relationship was established between WL and FSP. This was a result of not being effective heat treatment below 200°C against the brown rot fungus. By SEM and light microscopy, no evidence of decay due to white rot fungi, was found in heat treated wood, while evidence of decay was found in the heated wood with no weight loss. This could suggest that complete decay resistance against brown rot fungi might not be possible by heat treatment (although longer treatments times might confer full protection). Since, it has been reported that heat treatment opens up the cell wall in early wood (Fengel and Wegner, 1989), despite a reduction in the moisture content, the oxidative agent of brown rot could degrade slightly the cell wall in the areas where micro-cracks form. In Chapter 7, it was shown that heat

treatment reduces the volumetric swelling of wood in water and thus, it might reduce the pore accessibility of wood to the degrading agents. But, because of the problems mentioned in Chapter 10, unfortunately the micropore accessibility was not determined. As mentioned earlier, higher levels of confidence were obtained when hygroscopicity was plotted against WL (%) due to decay by white rot fungi.

Since untreated samples exposed to white rot fungi showed high WL's due to decay (this was confirmed by cell separation, very severe ray attack, erosion and so on, which were observed by light microscopy) and no sign of decay by white rot was observed in the heated wood, it could be concluded that lignin is protected completely by heat treatment. Since white rot fungi degraded the heat-treated wood extensively in decay tests with high levels of moisture (direct contact worked well with the fungi), a reduction in the hygroscopicity might be more effective in the preventing decay by white rot fungi than that by brown rot fungi.

Although, a non-enzymatic system have been suggested to be involved in lignin degradation, the presence of phenoloxidases are necessary in the decay of wood by white rot fungi (Tanaka, 1999; in Hammel, 2002). Since lignin is condensed due to heating, the lignin might not be recognised by the white rot enzymes.

According to the discussion above, a reduction in the hygroscopicity might be the main reason for the improved decay resistance. Thus, the primary reason for the improved hygroscopicity monitored by a reduction in FSP could be the main reason for the improved decay resistance reported in Chapter 7. By using the H-H model, it was shown that the removal of accessible hydroxyl sorption sites could not be the primary reason for the reduced hygroscopicty. A good correlation between proportional lignin content, which increased due to heat treatment and a reduction in the poly-molecular adsorption was established, suggesting that the change in hygroscopicity is as result of a reduction in the swelling of the cell wall due to a more rigid matrix of condensed lignin surrounding the wood microfibrils. The reduction in the swelling could be explained by two theories put forward by Kamdem (1999), and Tjeerdsma (1998) (see Section 2.12). The evidence obtained by FTIR and DVS, suggests that heated wood is a more rigid and cross linked material Thus, the cross-linking of lignin due to heat treatment could be the main reason

for the reduction of wood swelling due to water-soaking and the improved decay resistance.

By using DRIFT spectroscopy of heated wood exposed to decay tests compared to unexposed heated wood, Weiland *et al.* (2003), studied two of the theories by which heat treatment imparts decay resistance to the wood (hemicellulose removal and lignin modification in such a way that the degrading system of enzymes cannot recognise the substrate). Since cellulose was degraded significantly when the hemicellulose is removed due to heating, they suggest that hemicellulose removal cannot be the main reason for the improved decay resistance. They suggested that the modifications of lignin lead to an obsoleteness of the fungal enzymatic system against retified woods. They did not study the decay resistance of wood in connection with the hygroscopicity, but in this present study, a good correlation between a reduction in the hygroscopicity and decay improvement was obtained, suggesting the main reason for the improved decay resistance could also be the same reason for the improved hygroscopicity. In addition, a good correlation between an increase in the lignin content and a reduction in the poly-molecular sorption was obtained, suggesting an increase in the condensed lignin that surrounds the microfibrils. The condensed lignin might have improved contact with cellulose in heated wood (because of the removal of hemicellulose), which could be the main reason for the improved hygroscopicity and probably for the improved decay resistance. These results support the theory put forward by Weiland *et al.* (2003) stating that lignin modification could be the main reason for the improved decay resistance. However, the separation of the direct role of lignin modification in decay resistance from its role in the hygroscopicity was not possible by this study. In addition, in the study that was done by Weiland *et al.* (2003), it was not shown whether isolated lignin could be degraded or not. For this, more studies are required which are discussed later.

Kamdem, (2000a), reported that Retified wood contains very low concentrations of toxic substances, which might contribute to the decay resistance of the modified wood. He subsequently reported that the toxicants didn't contribute in the decay resistance (Kamdem *et al.*, 2000b). Since the retified wood showed only moderate decay resistance, the question of whether higher decay resistance could be achieved without the contribution of toxicants was not answered. Thus, in this present study, a more intensive

heat treatment (heat treatment at high temperatures for longer treatment times than those used in the Retification treatment) was used to examine whether high decay resistance could be achieved without the contribution of any toxicants. Insignificant differences were found between WL due to decay of heated wood which was post-extracted and that without any extraction. In addition, mycelia were found in heated wood exposed to white rot and brown rot fungi, showing that heat-treated wood is not a toxic material.

In Chapter 8, it was shown that heat treatment increases the proportional lignin content of the wood. Since hemicelluloses are the most heat sensitive component of wood, an increase in the lignin of wood showed that hemicellulose had been degraded. As mentioned earlier, by using the H-H model it was shown that a reduction in the hydroxyl groups could not be the main reason for the improved hygroscopicity and probably the decay resistance. Weiland *et al.* (2003), showed that when hemicellulose was removed significantly, the cellulose was still decayed dramatically *by Postia placenta,* which is capable of degrading pure cellulose under suitable conditions (Highley, 1988). *C. puteana* (used in the present study) has also been reported to degrade pure cellulose, thus, it is unlikely that hemicellulose removal has any direct effect on the decay resistance achieved.

It is proposed that a reduction in the hygroscopicity of wood so that the water swelling of the cell wall due to a rigid matrix of condensed lignin and hemicelluloses surrounding microfibrils could be the main reason for the improved decay resistance.

11.3 Anhydride modification

It is well known that acetylation can impart decay resistance to the wood. In this study, the decay resistance of wood modified with two linear carboxylic anhydrides with different sizes was studied. Decay by white rot fungi was more easily controlled than decay by brown rot fungi. In the case of acetylation, since the wood at the lowest WPG studied, showed complete or significant decay resistance against the white rot fungi, there were not enough data points obtained to calculate an accurate threshold. Takahashi *et al.* (1989), reported a WPG of 6% for the protection of a soft wood against *T. versicolor.* By

comparing this result with the threshold level of 8% obtained for hexanoic anhydride modified wood in the present study against *T. versicolor*, it can be said that there is little difference between the performance of the two adducts against white rot fungi.

No difference was also observed in the performance of hexanoylated and acetylated wood against the brown rot fungus (*C. puteana*). Papadopoulos (2001), also reported the same efficacy for a range of linear chain carboxylic anhydrides in imparting decay resistance against brown rot fungi.

In the un-sterile soil test, in which soft rot was the predominant attack, acetic anhydride was slightly more effective at providing protection than hexanoic anhydride. Acetic anhydride modification ranked between the threshold WPG values (%) figures reported in Chapter 5 for white rot (below 9%) and brown rot fungi (around 17.7%). But for hexanoylated wood, the WPG (17%) threshold was nearly the same as that found for brown rot fungi.

In Figure 9.16, the available monomolecular sorption sites obtained using the H-H model (at 100% RH), are plotted against WPG for each type of modification. The results of the sorption study suggest that at the WPG required for full protection of wood against white rot fungi, about 40% of available hydroxyl groups have been substituted. However, it was not possible to determine the location of the substitution sites. In addition, the sorption data shows the water accessible hydroxyl groups, but water molecules are smaller than the suggested low molecular weight agents required for the Fenton's reaction (non-enzymatic system). Thus, not all of the hydroxyl groups of wood which are available to water are accessible to the degrading agents. But, the sorption data is used as evidence for estimating the reduction of the total available hydroxyl groups in the modified wood.

By using NMR spectroscopy, it has been reported that lignin substitution occurs at very low WPG's in the contrast with cellulose and that the degree of substitution increases when WPG increases, although there is some dispute whether full substitution is ever achieved (Ohkoshi and Kato, 1997). It is assumed that the phenolic groups of the lignin react more rapidly compared to the polysaccharides OH's, this would presumably result in the lignin being more resistant to degradation at low WPG levels. Takahashi *et al.*

(1989), proposed that preferential substitution of lignin in the reaction procedure could account for the lower WPG's required for the protection of wood from decay by white rot fungi.

There is some dispute as at what WPG level all of the lignin OH groups are substituted (Hill, 2003) (or indeed whether full substitution is ever achieved (Ohkoshi and Kato, 1997). At the WPG's at which decay resistance against white rot is imparted, there is some difference between the monomolecular sorption of hexanoic and acetic anhydride modified wood, However, at high WPG's, no significant difference could be seen in the monomolecular sorption of hexanoic and acetic anhydride modified wood. This suggests that a shielding effect becomes more important at high WPG's than that at low WPG's. In the decay tests, as was mentioned earlier, since decay resistance against white rot fungi was achieved at the lowest WPG with acetylated wood, calculation of the threshold level was not achieved. Thus, in this work, the presence of any significant difference between the anhydrides with different sizes was not established, although the limited data suggest that the difference is not very significant.

In addition to the blocking of the accessible hydroxyl groups of lignin, since hemicellulose substitution occurs at very low WPG's (Ohkoshi and Kato, 1997), and carbohydrates are required for the degradation of lignin by both fungi studied (Thomas, 1981; Erikson, 1988), the modification of wood in a way so that the degrading system of the fungi are not able to attack the substrate could be another possible reason contributing to the decay resistance against white rot fungi.

In contrast with the white rot fungi, high threshold levels were required to fully protect wood against the brown rot fungus. At the WPG's, required to protect wood against *C. puteana*, about 60% of available hydroxyl groups are substituted. In addition, since the weight loss due to decay by brown rot fungi is reduced when the WPG is increased, and cellulose participates in the reaction at above a WPG of 20% (Ohkoshi and Kato, 1997), there is some possibility that cellulose substitution may be an important reason for the improved decay resistance against brown rot fungi. Since cellulose is not very reactive to acetylation (as mentioned above), decay resistance must be imparted to the wood by acetylation in a way in which the non-enzymatic system of the *C. puteana* degrading system becomes inactive in the S_3 layer (degrading agents diffuse from S_3 and decay starts

from S_2). No significant difference was found between the performance of hexanoic and acetic anhydrides against brown rot fungi which surely means that the level of OH substitution is unimportant.

It is well established that chemical modification can cause wood to become more hydrophobic (Sections 2.15.2 and 2.15.3). In this study, an attempt was made to verify any link between decay resistance and hygroscopicity. Swelling and sorption characteristics of modified wood were measured.

In the pure culture test (Chapter 5), it was shown that the end moisture content in the sterile jars was reduced proportionally with WPG, so that at high WPG's, the end moisture content was reduced to below the limits theoretically required by fungi to degrade wood. But in the jars with white rot and brown rot fungi, the end of test moisture contents even in the samples that had been protected from decay (brown rot and white rot) by modification were theoretically high enough for decay (especially in the white rot tests in which samples were incubated directly over malt agar). However, a high wood MC doesn't necessarily mean that the cell wall MC is sufficiently high to allow decay.

Similar to thermally modified wood, for chemically modified wood, two of the tests in this study provided measures of FSP; the sorption test (Chapter 9) and pore size exclusion analysis (Chapter 10). For reasons described previously, sorption gave relatively low measures of FSP and pore size exclusion gave relatively high measures of FSP. However, the solute exclusion technique data supports the idea that decay resistance against brown rot fungi, is imparted when the cell wall MC is below the limit required by fungi while decay resistance against white rot fungi takes place when cell wall MC is high enough for the fungi to degrade wood. Since, two 2 WPG's were studied by the solute exclusion technique, not enough data points were obtained to establish a relation between the solute exclusion calculated FSP's and WL's due to decay. Further work is required here.

Figure 11.4 shows the weight losses due to decay by the brown rot fungus (*C. puteana*) in the pure culture tests (Chapter 5) plotted against FSP of un-exposed modified wood (at the same WPG's) calculated from sorption studies (Chapter 9). It was expected that if

moisture exclusion from the cell wall was the mechanism of the increased decay resistance, then the relationships for the different linear carboxylic anhydrides would be identical (regardless of WPG and the adduct).

As shown in Figure 11.4, the variation between WPG of the samples studied for the sorption and decay tests caused the mean WPG's of the selected test sample to differ very slightly. The effect of this variation was found to be negligible. As can be observed in Figure 11.4, there is significant agreement in the data between the two different linear anhydrides.

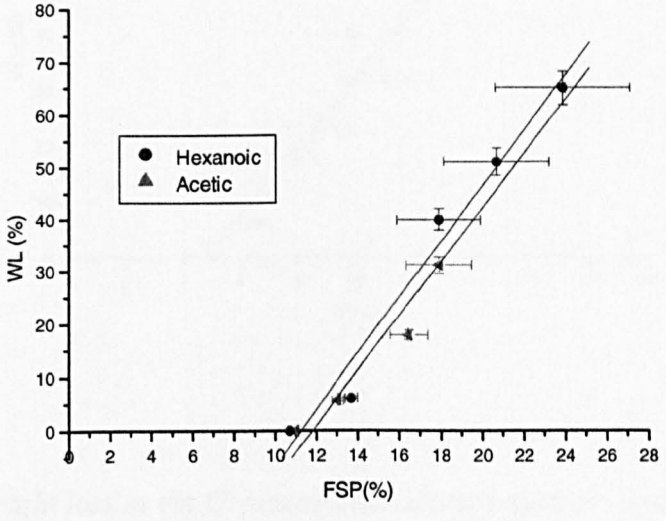


Figure 11.4: Weight loss in the C. puteana test plotted against FSP (from sorption) for a range of WPG's.

As mentioned earlier, in order that decay can take place, water is required to swell the wood cell wall so that degrading agents can enter the cell wall. In the absence of sufficient water, the cell wall micropores would be too small for the diffusion of the degrading agents into the wood cell walls. Figure 11.5, shows weight losses in pure culture decay tests plotted against the volumetric swell, S (%), from water soak tests (from Chapter 7.). There is again good agreement between the two different linear

carboxylic anhydrides, but slightly better agreement than that obtained between weight loss and FSP.

In Chapter 9, it was reported that the hygroscopicity of the anhydride modified wood was dependent on wood cell wall bulking rather than the OH substitution, thus any correlation between the reductions in FSP and weight loss does not disagree with an explanation that pore blocking due to bulking is the reason for the increased decay resistance against brown rot fungi.

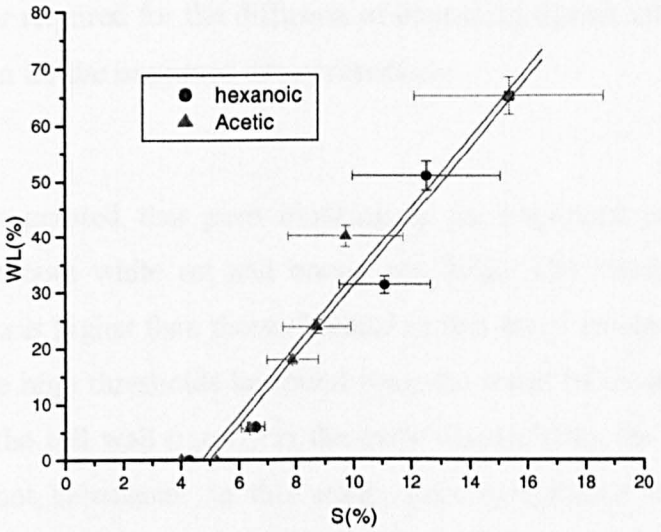


Figure 11.5: Weight loss in the C. puteana test plotted against volumetric swelling for samples with a variety of WPG's.

In Chapter 10, it was shown that at the WPG's where significant decay resistance against white rot fungi is imparted, the cell wall micropores, which are accessible to degrading agents of the fungi are not closed significantly, although some significant pore closure takes place against raffinose (which was used as a probe with the size of 12 Å). Although there is not a clear understanding of the non-enzymatic system which is involved in the degradation of wood, the same low molecular agents suggested for brown rot fungi have been extracted from white rot fungi (Hammel *et al.* 2002; Enoki *et al.*, 2003). Regarding the agents involved in the non-enzymatic system of white rot and brown rot fungi, if cell wall micropore blocking was the most important mechanism by which modification

imparts decay resistance against white rot fungi, the same WPG threshold level as required for brown rot should have been obtained. Cell wall micropore blocking could be considered an important reason for providing in the decay resistance against white rot if it is shown that higher molecular weight agents are involved in the degradation of wood by white rot compared with those by brown rot fungi.

In the case of brown rot fungi, at the WPG's where decay resistance is imparted, the number of micropores accessible to the fungal degradation agents are significantly reduced. However, complete cell wall micropore closure was not observed. Thus, a reduction in water required for the diffusion of degrading agents into the cell wall could be the main reason for the improved decay resistance.

Forster (1998), suggested that pore blocking is an important reason for the decay resistance against both white rot and brown rot fungi. The threshold he reported for acetylated wood was higher than those obtained in this study and in previous studies. He suggested that the high thresholds he found were the result of an uneven distribution of acetyl groups in the cell wall (mostly in the early wood). Thus, the actual thresholds for the fungi were not calculated. In this study, pre-impregnation with undiluted acetic anhydride was used, which has been reported to distribute more evenly in wood. In the case of hexanoic anhydride, which was used with a pyridine catalyst system, should also have shown more regular distribution with the sample sizes used. As a result, uneven distribution of the chemical, which would interfere with actual WPG required for the complete decay resistance against fungi, was not observed and the decay resistance against white rot fungi were obtained at very low WPG's.

In this study, un-sterile soil tests according to ENV807 were used for the soft test experiment. With no pure culture test, and the control of conditions involved with it, the analysis of the mechanism of protection of chemically modified wood against soft rot is not easy. In addition, the mechanism by which decay resistance to the wood occurs against soft rot fungi has not been studied as extensively as those for brown rot and white rot fungi.

However, it is interesting that under the test conditions observed the point at which the modified wood samples exhibited an end moisture content around or below the limit required by fungi, also showed zero weight losses due to decay. This might suggest that hygroscopicity is an important factor in the decay resistance against soft rot fungi.

11.4 Silane modified wood

The two silanes investigated in this study showed completely different reactivity, in that TMPS polymerised mostly *via* its vinyl group, while VTMS polymerised *via* its Si-OH groups. Both silanes penetrated the cell wall at low WPG's but at high WPG's, the silanes were predominantly located in the lumen. Both silanes showed reasonable stability against extensive leaching procedures. The performance of the two silanes against basidomycetes were nearly the same. The improvement of dimensional stability, hygroscopicity and decay resistance against basidiomycetes by the treatments were restricted to the penetrability of the adducts into the cell wall. The correlation between weight loss, and hygroscopicity and water swelling of the modified wood are shown in Figures 11.6 to 11.8, where the results are compared to heat treated and anhydride modified samples. Since different WPG's of VTMS were used in the decay and hygroscopicity tests, the end moisture contents of the chemically modified wood incubated over sterile malt agar was only considered and the FSP of the VTMS modified wood was not plotted against white rot fungi.

As can be observed, the treatment of wood by methanolic solutions of silanes does not reduce the swelling and hygroscopicity of the wood to as great an extent compared with anhydrides at the point where full protection against *C. puteana* was obtained. When anhydride modification reduced the end moisture contents to about 12% and S % to 5% respectively, complete decay resistance was imparted. With *T. versicolor*, for the all treatments, at end moisture contents of 20-25% and an S (%) of about 10%, complete decay resistance was imparted. For (*P.chrysosporium*), for all the treatments, except for TMPS, complete decay resistance was imparted when the end moisture content and S (%) was reduced to 20-25% and to about 10%, respectively. For TMPS, a lower MC (about 16%) and a higher S (about 8%) were required to stop decay by (*P.chrysosporium*). Since

P.chrysosporium, preferentially degrades lignin, and the OH of TMPS is not very reactive (Chapters 3 and 7), the lack of reaction of TMPS with lignin at a WPG of 27% could be a possible reason for the poorer performance against the selective white rot fungi. When, heated wood was exposed to white rot fungi, at nearly the at the same MC and S (%) as TMPS treated wood, weight loss due to decay was zero, heated wood showed significant decay resistance against *C. puteana*. The results of this study are in line with the results obtained by Stamm *et al.* (1960). Stamm and *et al.* (1960), reported that heated wood at an ASE% of about 50% showed complete decay resistance against brown rot fungi while acetylated wood showed a complete decay resistance at an ASE of about 70%.

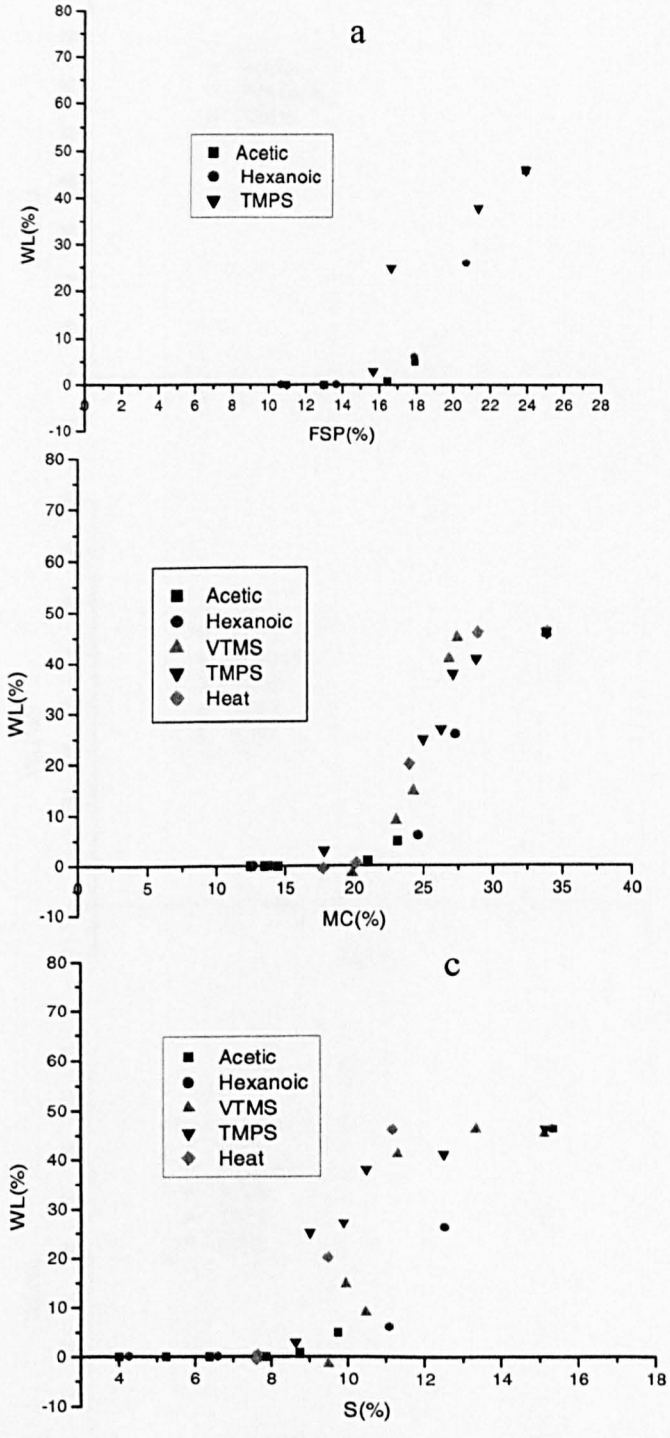


Figure 11.6: Weight loss due to decay by P. chrysosporium, and moisture content, volumetric swelling and FSP in chemically modified wood (a) FSP of TMPS treated, acetylated and hexanyolated wood. (b) the end moisture content of sterile controls versus WL (c) Swelling average of the modified wood after exposure to 5 water soaking cycles versus WL

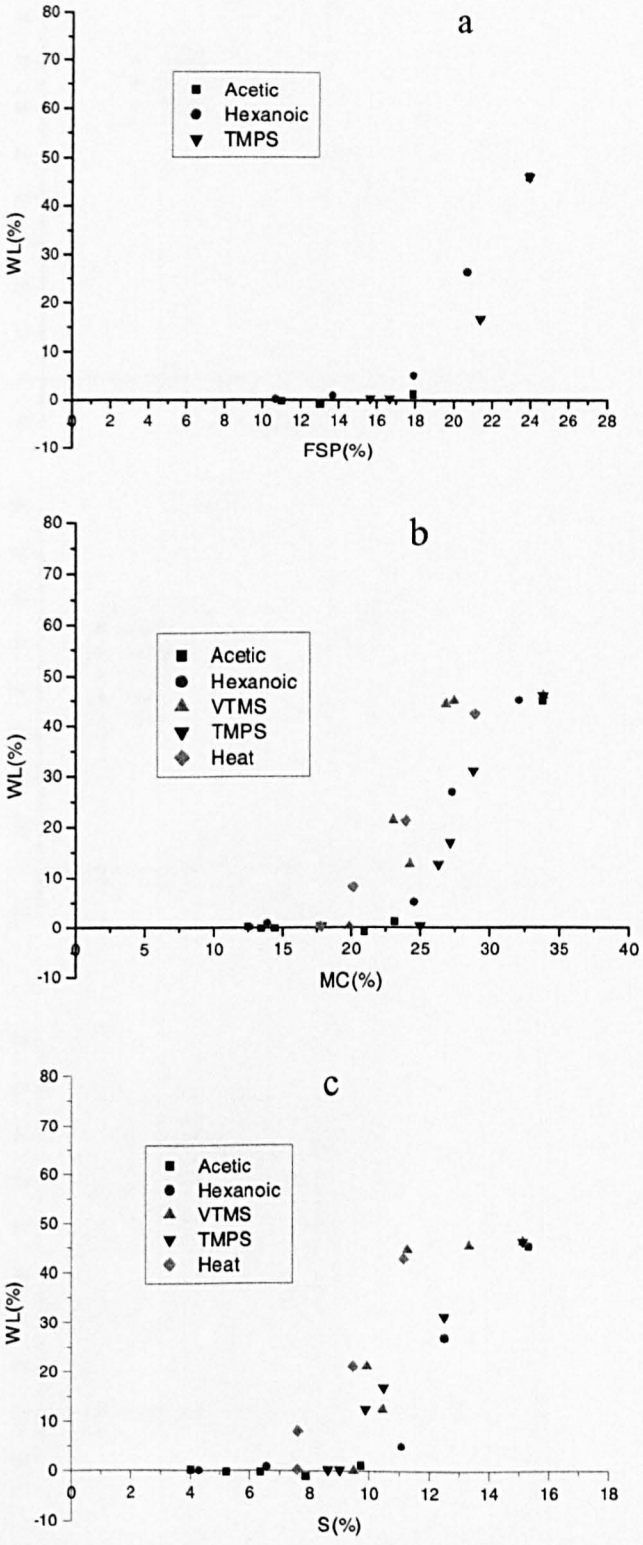


Figure 11.7: Weight loss due to decay by T. versicolor , and moisture content, volumetric swelling and FSP modified wood (a) FSP of TMPS treated, acetylated and hexanyolated wood (b) The end moisture content of sterile controls versus WL (C) Swelling average of the modified wood after exposure to 5 water soaking cycles

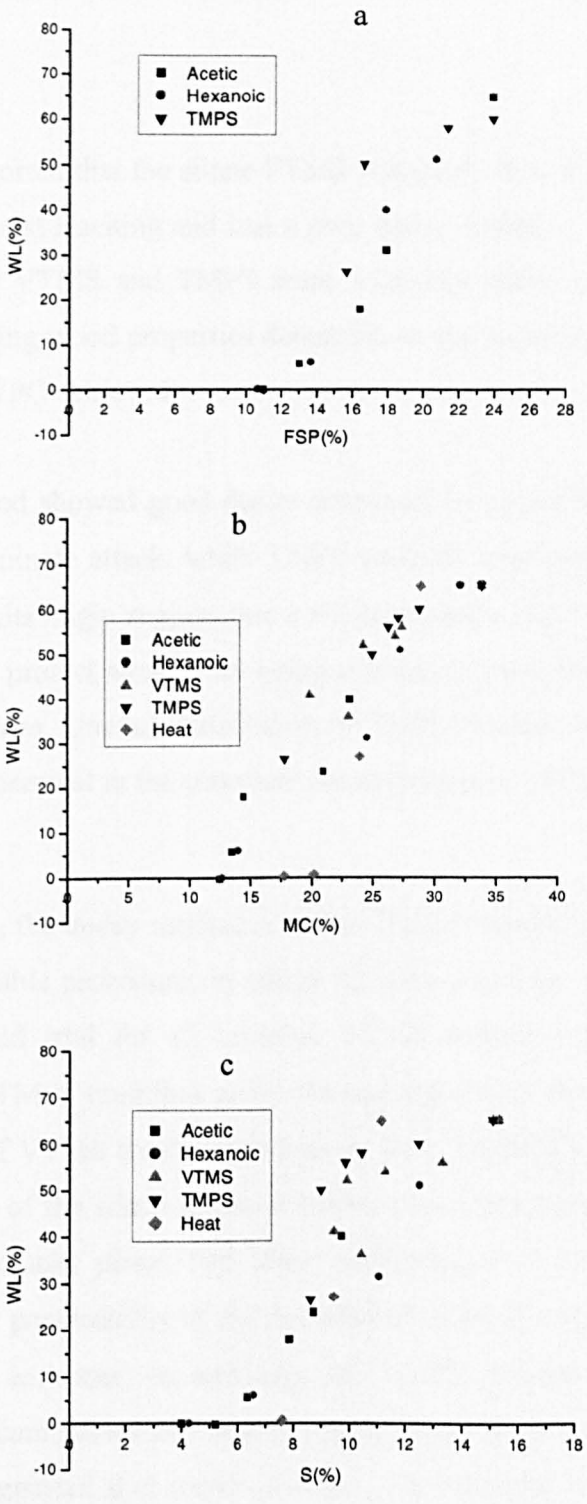


Figure 11.7: Weight loss due to decay by C. puteana, and moisture content volumetric swelling and FSP in modified wood (a) the end moisture content of sterile controls versus WL (b) Swelling average of the modified wood after exposure to 5 water soaking cycles versus WL(C) FSP of TMPS treated, acetylated and hexanoylated wood

Steven (1994), reported that the silane PTMS polymerised to form a poly-siloxane which was not stable against leaching and had a poor decay resistance but in this present study, it was shown that VTMS and TMPS were relatively stable against leaching and their efficacy in improving wood properties depended on the penetration of the chemical in the cell wall and the WPG achieved.

VTMS treated wood showed good decay resistance in un-sterile soil tests in which soft rot was the predominate attack, while TMPS partially improved the decay resistance of the wood. The results might suggest that a polymer matrix with high amounts of silicon in the cell wall could protect wood from being soft rotted, even more effectively than linear carboxylic anhydrides. Uneven distribution of TMPS treated wood was recognised to be the failure of the chemical in the complete decay resistance of the wood.

In additional work, the decay resistance of the silane treated wood modified with a more industrially acceptable procedure, in which aqueous solutions of silanes were used, was assessed by a field trial for 12 months. VTMS treated wood showed some decay resistance but the TMPS modified wood showed significant decay resistance. The poorer decay resistance of VTMS treated wood under these treatment conditions was attributed to oligomerisation of the silane in water before significant penetration of the silane into the cell wall could take place. The better performance of TMPS modified wood was attributed to better penetrability of the hydrolysed silane for which its silanol groups are not very reactive in water. In addition, the TMPS distribution problem which was observed in the vacuum dessicator method, didn't seem to be a problem with the pressure treatment. It is suggested that under pressure, the chemical could penetrate the denser wood (late wood).

In conclusion, silanes are effective in enhancing wood properties such as the decay resistance and dimensional stability, provided that they penetrate sufficiently into the cell wall. An industrially acceptable method was established which worked well with TMPS

but didn't work with VTMS, although VTMS treated wood in laboratory conditions (methanolic solution and vacuum desiccators) showed better decay resistance.

11.5 Recommendations for further work

In this study, it was shown that silanes, have potential to be used as wood preservatives, but since silanes are expensive, the industrial application of them is restricted. It has been shown that by using silanes, less toxic preservatives such as boron compounds could be fixed in wood without being leached (Saka *et al.*, 2001). In this study, it was also shown that VTMS is capable of the polymerisation via Si-OH groups under mild conditions. Thus, a study of the decay resistance of boron-VTMS composites containing a low amount of VTMS, which would be more industrially applicable, is suggested.

In addition, in the glass fibre industries, silanes are cured at high temperatures which would damage wood. In this study it was shown that treatment temperatures above 200°C impart significant decay resistance to wood. Thus, a study of decay resistance of wood treated with the silanes and cured at moderately high temperatures between 150-200°C is also suggested.

Due to restrictions in time, no spectroscopic method was used determine the location of silicon in the treated wood. Further studies by SEM-EDAX are required to compare accurately the capability of the silanes in penetrating into the cell wall under different treatment conditions.

Treatment with a methanolic solution of VTMS at low WPG's was recognised to be more effective in controlling soft rot attack than acetic anhydride (. A study of the combination of the both treatments (acetylation and silylation) in imparting decay resistance against different types of attack is also suggested.

In Chapter 8, H-H model was used to estimate the FSP of heated wood. Since good agreement between the experimental data and H-H calculated data was obtained, the model would give a valid comparison of the ability of heat treatments with

different temperatures in reducing the FSP of wood. This was confirmed when a good correlation between weight loss due to decay and hygroscopicity was obtained. In order to confirm the important role of poly-molecular sorption in the hygroscopicity of heated wood, another model which was recently used by Nakano (2003) is suggested to be used for the partitioning of total adsorption to monomolecular and poly-molecular.

In Chapter 6, it was shown that TMPS pressure treated wood showed significant decay resistance in the field test. Further studies are required to measure the decay resistance of silane pressure treated wood against basidomycetes (by pure culture tests).

For chemically modified wood, the sorption of water vapour by modified pine sapwood was studied at just six different relative humidities. It's suggested that sorption of water vapour of the chemically modified is also studied at more relative humidities and higher relative humidities than those which were studied in this thesis. Using models other than the H-H model is suggested to analyse the moisture content data.

The two white rot fungi applied in this study, which were only capable of degrading lignin in the presence of carbohydrate, which acts as a lignin degradation inducer for the fungi (Erikson, 1988). With heat treated wood, the improved decay resistance could arise as a result of the removal of hemicellulose, or due to a lower MC of the cell wall. However, in this study, the separation of the effect of hemicellulose removal on hygroscopicity from the direct effect of the hemicellulose removal on the decay resistance of the wood was not possible. This could be recognised by using other white rot fungi, which are capable of the degradation of pure cellulose, compared to the white fungi which need carbohydrates as inducers for the degradation. In addition, it has been reported that fungi from coniophoroid, are capable of degrading pure cellulose. However, in heated wood cellulose is not only depolymerised but also, it is slightly modified and it's structure is changed. In addition, heat treatment removes large part of the hemicellulose which might put cellulose in contact with lignin and therefore, some cross linking between the cellulose and lignin could have happened. Thus, the exposure of isolated lignin, or

cellulose or mixture of lignin and cellulose heated at high temperatures to *C. puteana* or white rot fungi is required to find whether brown rot fungi or white rot fungi are capable of degrading thermally modified cellulose or lignin.

In Chapter 10, the attempts to measure the pore structure of heated, or silane modified wood by solute exclusion technique was not successful and the solute exclusion method was recognised to be very sensitive to any leachable material that might contaminate the sugar solution. Another study by solute exclusion technique, in which the pore structure of heated and silane modified wood is exposed to more extensive leaching procedures is suggested.

Appendixes:

Appendix 1 Tabel

A.1.a Results from preliminary silane treatment studies showing weight percentage gain after silane treatment and with subsequent extraction (in parentheses)

Silane	Curing temp. (°C)	AIBN	Wood moisture content 0%	12%	33%
TMPS	50		20.2 (2.1)	20.1 (2.1)	29.4 (0.1)
TMPS	50	Yes	33.4 (0.6)	22.9 (2.0)	24.7 (2.0)
TMPS	100		4.9 (4.9)	12.0 (6.0)	9.5 (5.0)
TMPS	100	Yes	21.9 (19.9)	21.2 (18.8)	10.4 (8.4)
VTMS	50		7.4 (1.9)	10.1 (2.2)	16.5 (10.7)
VTMS	50	Yes	6.7 (0.1)	10.4 (4.0)	17.3 (10.2)
VTMS	100		2.5 (0.6)	4.9 (3.4)	17.1 (13.7)
VTMS	100	Yes	2.5 (1.8)	6.0 (3.8)	14.2 (11.2)

A.1.b WPG's of modified wood which were used in the Soft rot test

	WPG(%)				
VTMS	3.05	6.4	11.35	11.44	36.9
TMPS	8	17.34	27.6	65	
Acetic	3.4	14.9	16.5	20.33	23.9
Hexanoic	6	10	15	28	

A.1.c WPG's of modified wood which were used in solute exclusion technique

WPG(%)			
TMPS	VTMS	Hexanoic	Acetic
28	44	9.2	7.2
		21.8	22.7

A.1.d WPG's of modified wood which were used in isotherm tests

	WPG(%)			
VTMS	25	11	8	3
TMPS	52	27	11	6
Acetic	21.7	15.9	12.7	9.4
Hexanoic	21.8	15.7	7.2	4.2

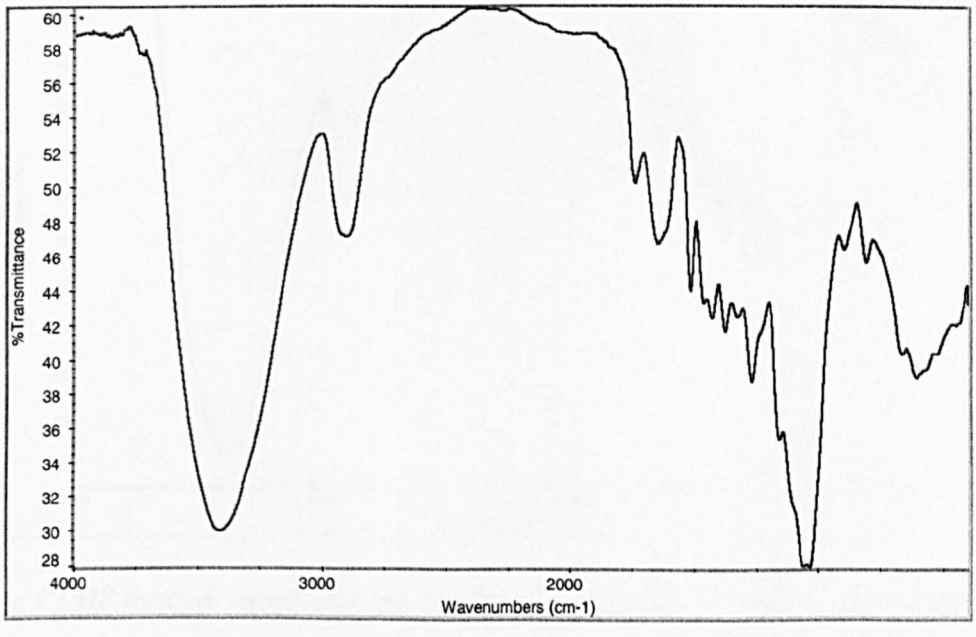
A.1.e WPG's of modified wood which were used in pure culture tests.

WPG(%)			
Acetic	Hexanoic	VTMS	TMPS
9.9	4.2	2.7	6.1
12.7	7.2	6.2	11.0
13	15.7	16.5	20.8
15.8	21.7	18.7	27.6
21.8		48.0	52.0

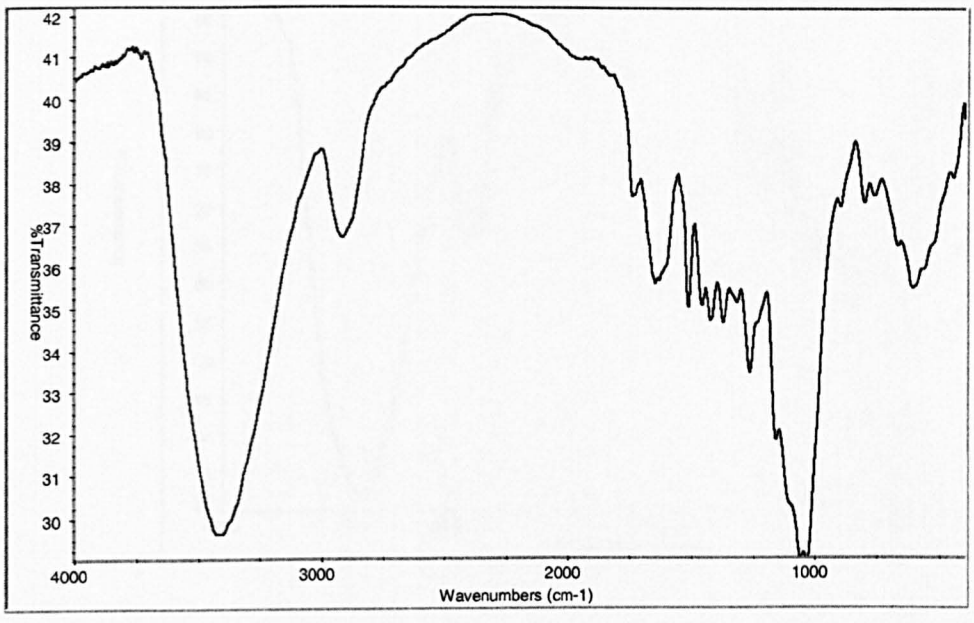
A.1.f The uptake of VTMS and TMPS

	TMPS(Kgr/m3)
6	439.375
4	436.5625
7	381.25
	VTMS(Kg/m3)
1	521.875
2	308.75*
3	240.625*

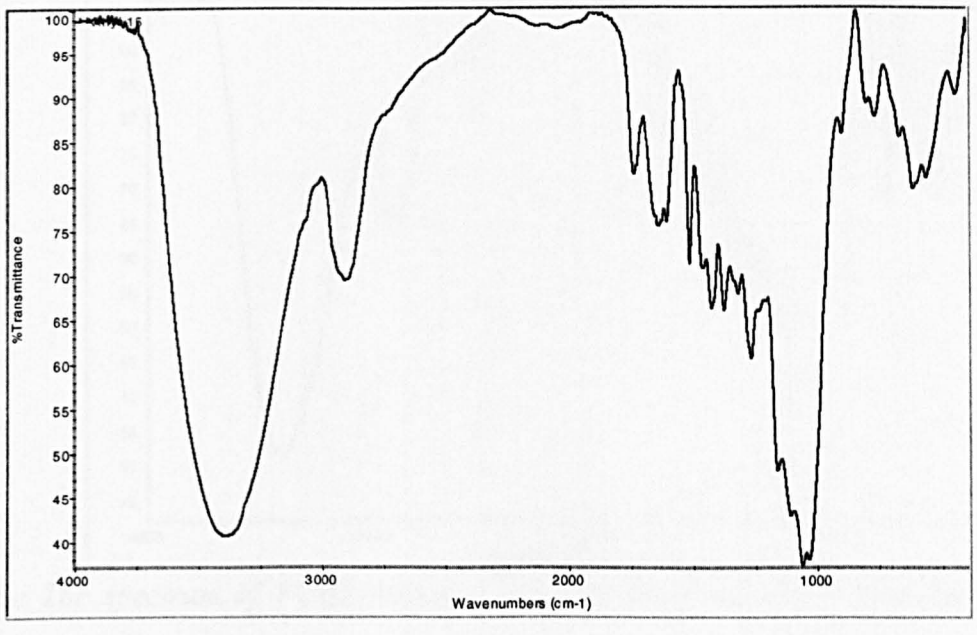
Appendix: 2 The FTIR Spectroscopy of silane modified wood



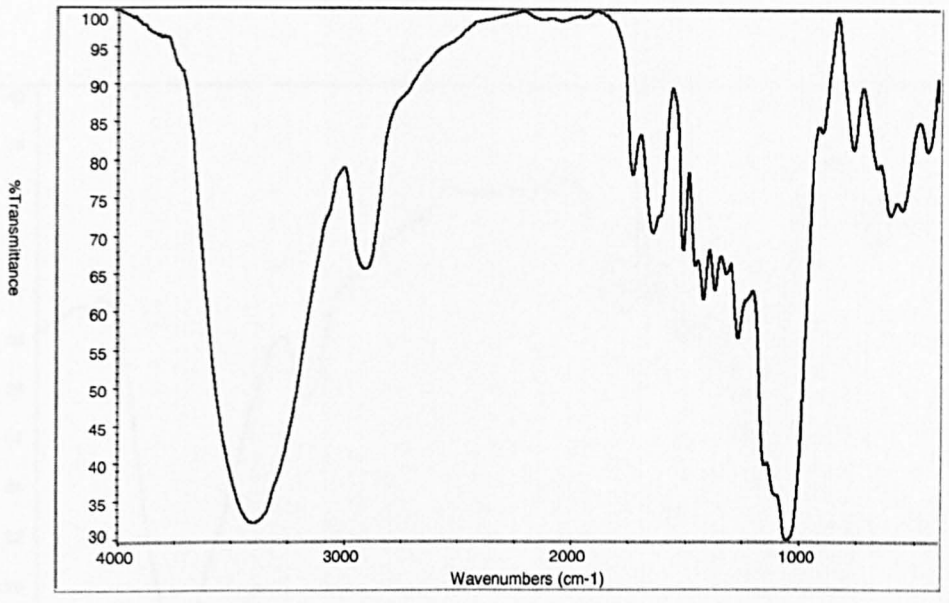
A.2.a Corsican pine sapwood extracted by 4:1:1 and five cycle of water extractions



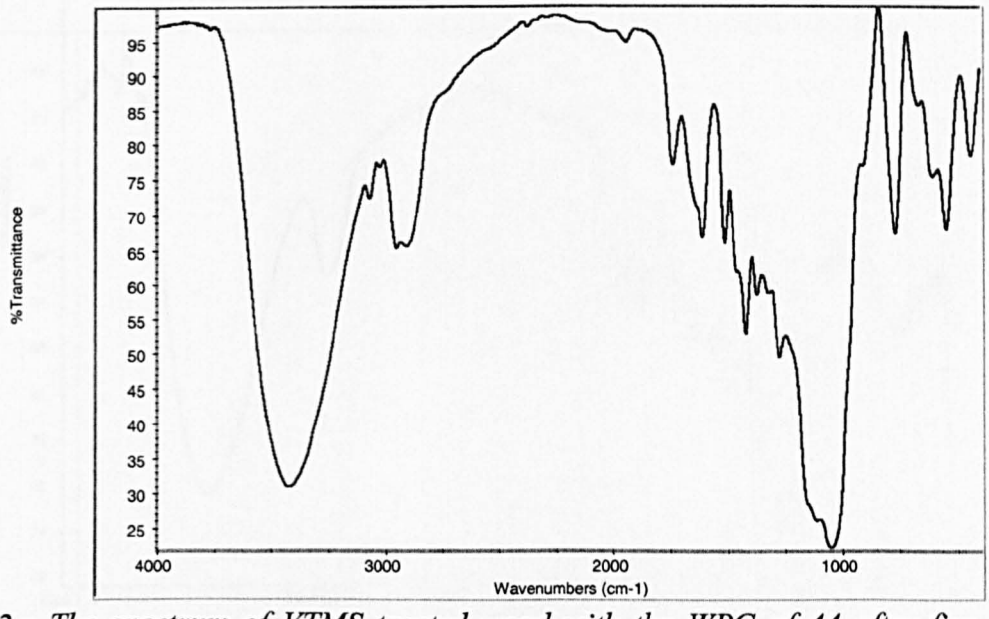
A.2.b VTMS treated wood with the WPG of 1.8 after five time water extraction



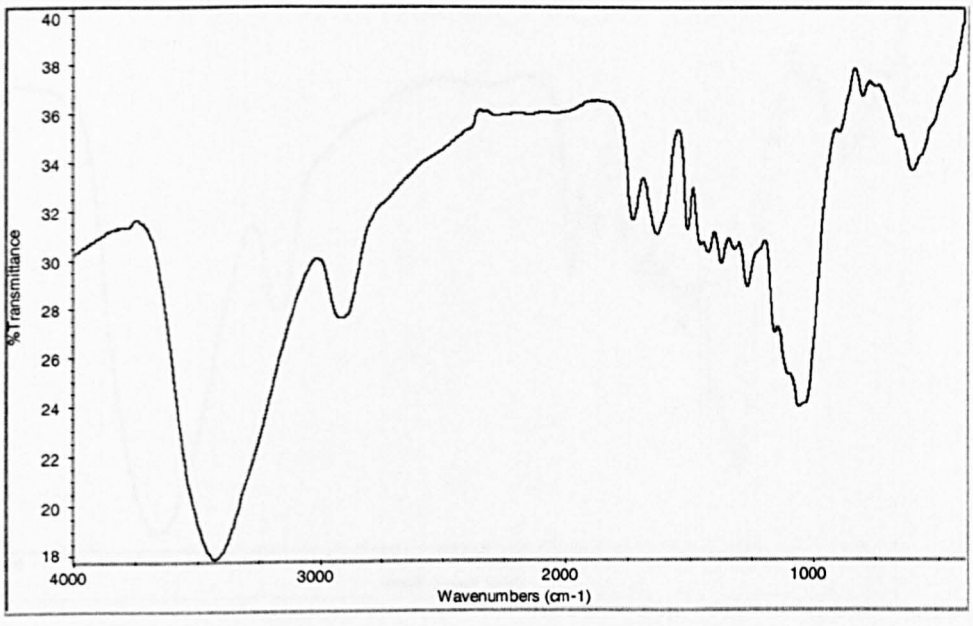
A.2.c VTMS treated wood with the concentration of 13.4 after five time water extraction



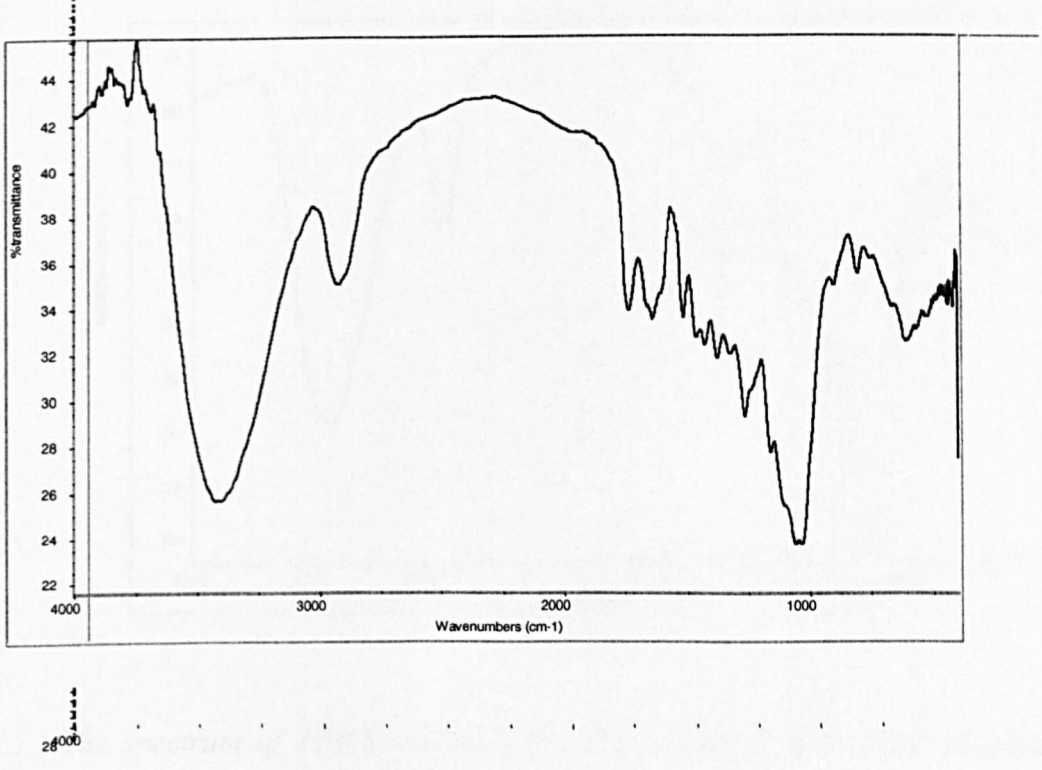
A.2.d VTMS treated wood with the WPG of 14.15 after five time water extraction



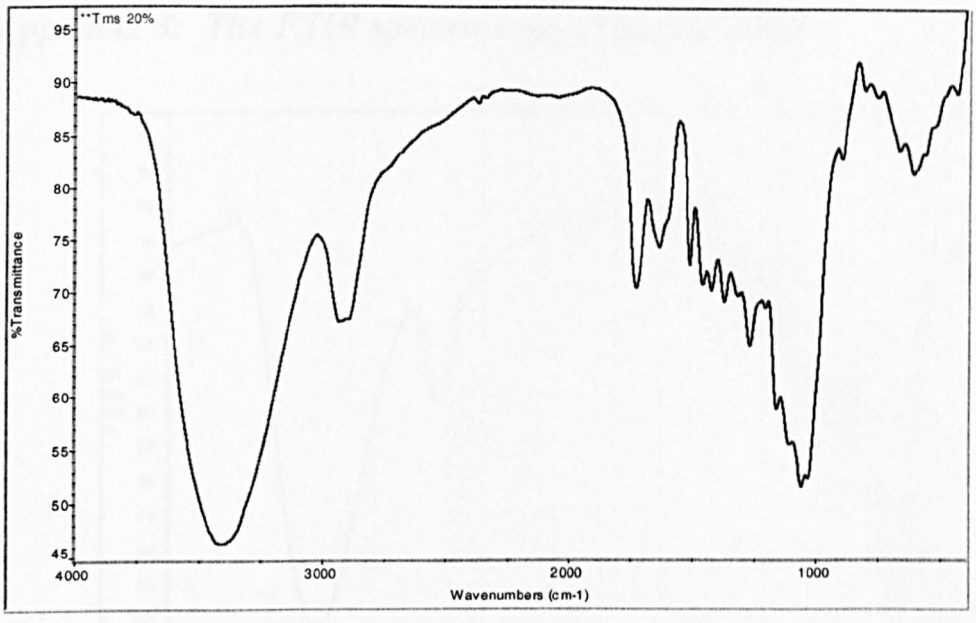
A.2.e The spectrum of VTMS treated wood with the WPG of 44 after five time water extraction



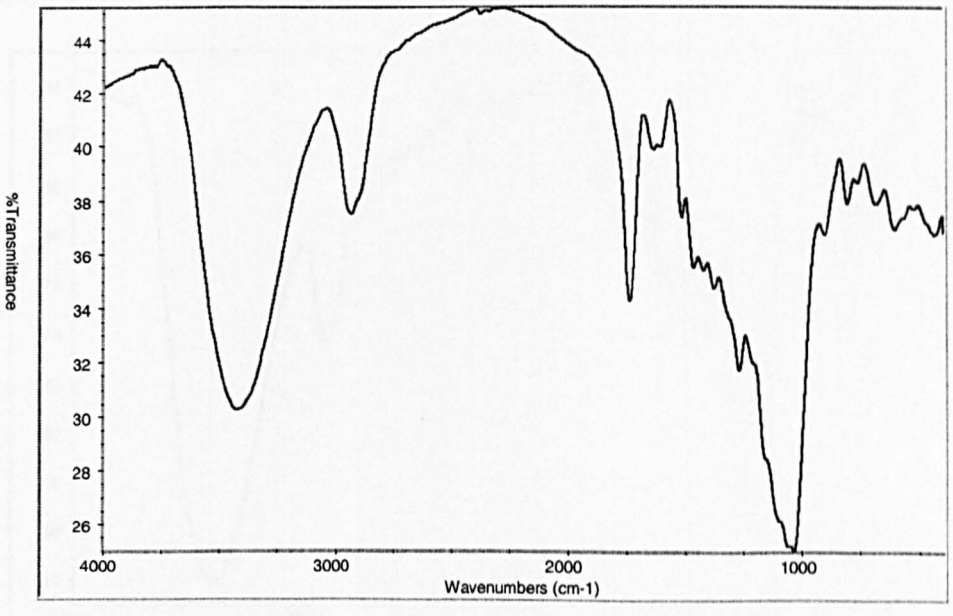
A.2.f The spectrum of TPMS treated wood with the WPG of 5% after five time water extraction



A.2.g The spectrum of TMPS treated wood with the WPG of 12.7 after five time water extraction

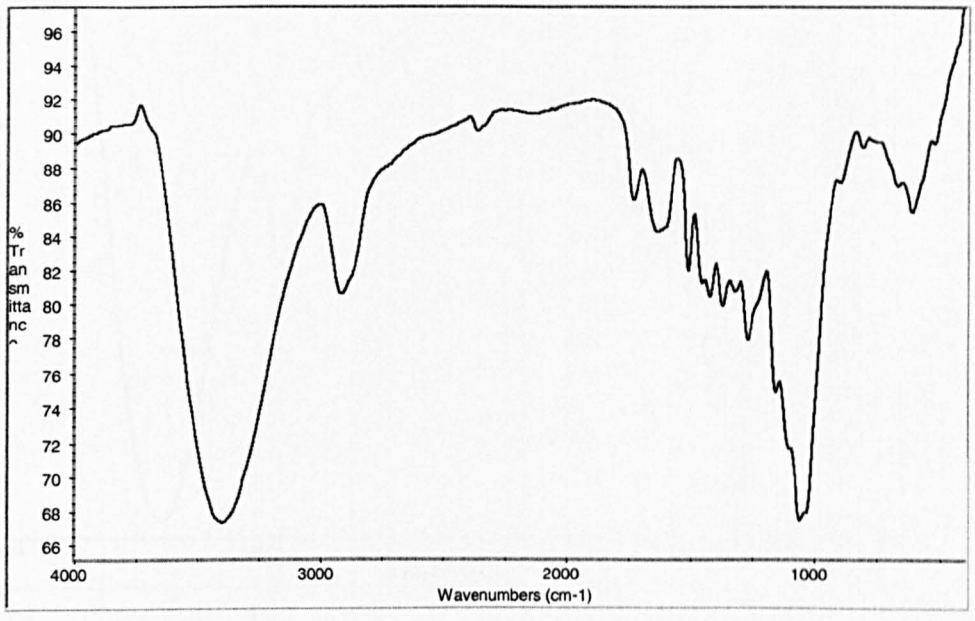


A.2.h The spectrum of TPMS treated wood with the WPG of 20% after five time water extraction

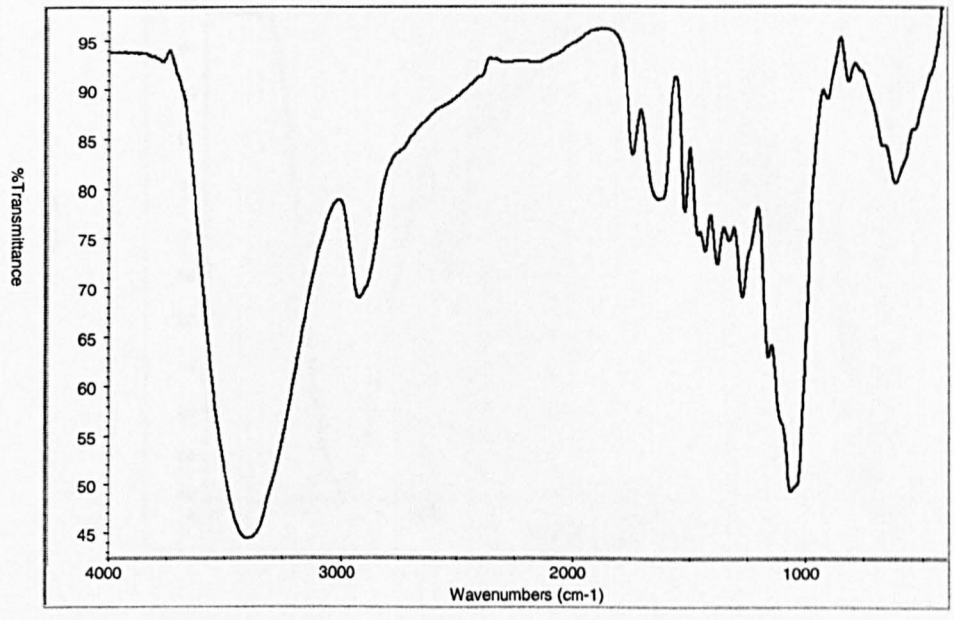


A.2.I The spectrum of TPMS treated wood with the WPG of 49 after five time water extraction

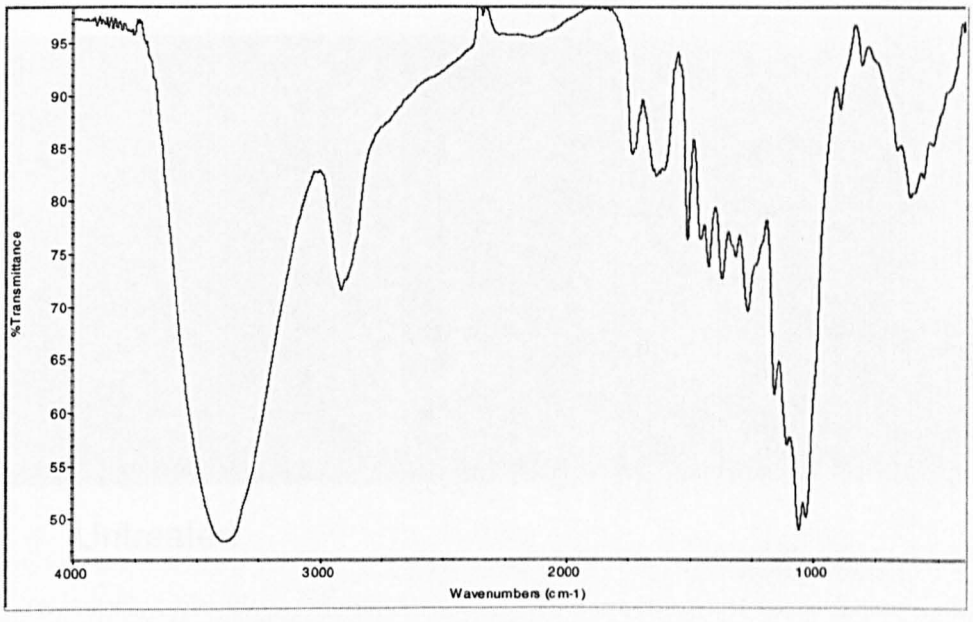
Appendix 3: The FTIR spectroscopy of heated wood



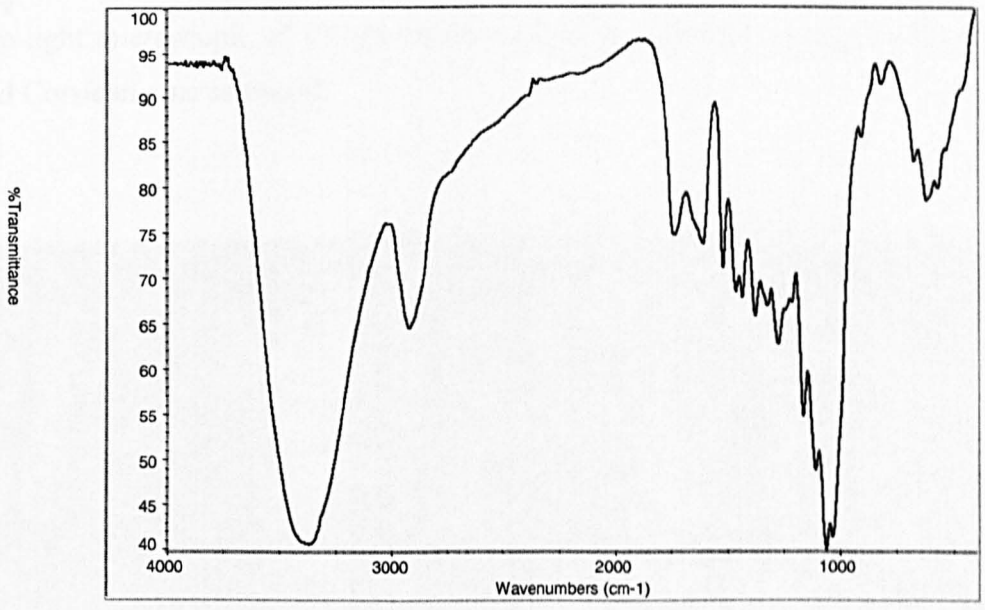
A.3.aThe spectrum of Corsican pine sapwood (Untreated)



A.3.b The spectrum of Corsican pine sapwood heated at 140°C for 2 hours

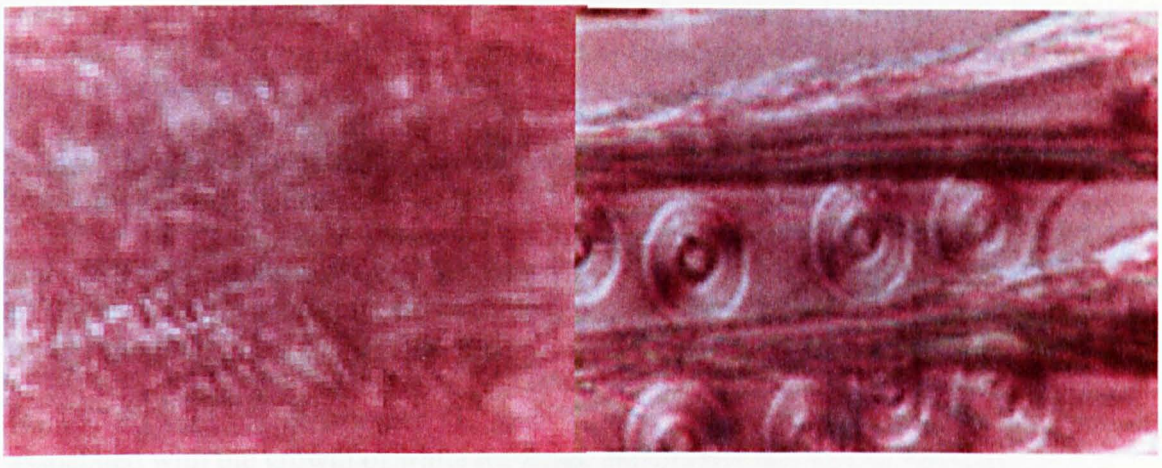


A.3.c The spectrum of Corsican pine sapwood heated at 200°C for 2 hours

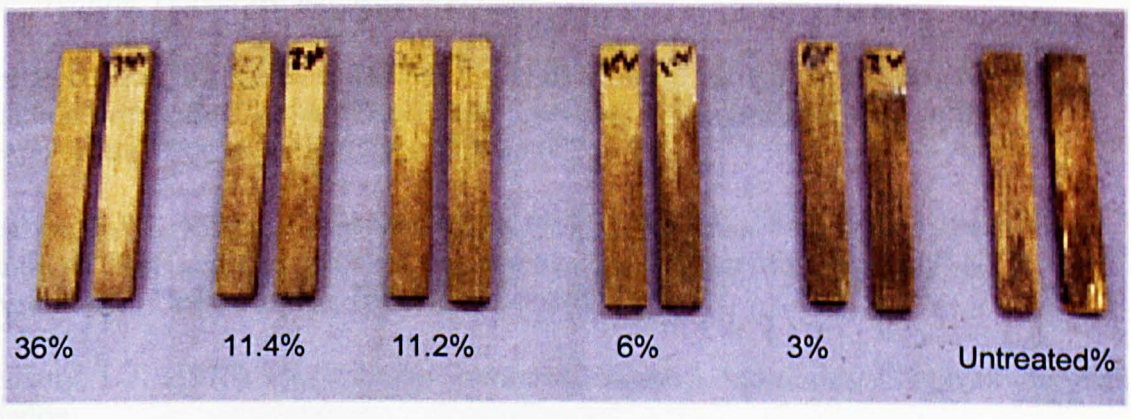


.3.dThe spectrum of Corsican pine sapwood heated at 255°C for 2 hours

Appendix 4: Un-sterile soil test of VTMS modified wood



A.4.aThe[Abs] light microscopic of VTMS wood exposed to un-sterile soil tests compared to untreated Corsican pine sapwood. .



.4.b VTMS modified wood which were exposed to un-sterile soil tests

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