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Swelling, cell wall porosity and chemical modification of wood.

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Swelling, Cell Wall Porosity and Chemical Modification of Wood

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DEDICATION

To my Anthi

and Callum

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"For every man the world is as fresh as it was the at first day, and as full of untold novelties for him who has the eyes to see them"

Thomas Huxley

ABSTRACT

Kinetic profiles were investigated for the pyridine catalysed reaction of Corsican (CP) and Scots pine (SP) sapwood with a homologous series of linear chain carboxylic anhydrides namely, acetic (AA), propionic (PA), butyric, valeric and hexanoic (HA). With AA, it has been found that the reaction profiles are described by a model where diffusion dominates the reaction process, that is to say that reaction of the reagent molecules with a specific reaction site is rapid compared with diffusion. With longer chain anhydrides, the rate of chemical reaction and diffusion both contributed to the reaction kinetics.

The reaction activation energies (Ea) were determined for the catalysed reaction of pyridine swollen pine sapwood samples and phenolic model compounds (in solution) with the series of anhydrides, using the methods of initial rates and rate constants. Both methods resulted in comparable values. The wood species did not influence the Ea. With wood samples, the Ea was largest for the reaction of AA, and decreased as the molecular weight of the anhydride increased. When the reactions were performed in homogeneous solutions, there was no correlation molecular weight of anhydride and Ea. It is suggested that the lower values obtained for the Ea for reaction with wood are related to the restricted space surrounding the accessible hydroxyl groups (OH).

The cell wall micropore network of oven-dried (OD) CP and SP sapwood was investigated by reaction with AA and PA in a non-swelling solvent (xylene) and with swollen wood. Significant differences in reactivity were found between species.

The volumetric changes in CP and SP sapwood due to modification with the series of anhydrides were studied. Again significant differences in the response of the wood cell wall were found between species.

A comprehensive investigation into the water sorptive properties and into the effect of molecular size of the substituent group upon the sorption of water vapour of softwood modified with the series of anhydrides was performed. The sorption isotherms for untreated and chemically modified wood were analysed using the Hailwood-Horrobin model. The results are interpreted by consideration of both the number of OH groups reacted and the volume occupied by adduct in the cell wall. It is considered that the latter effect is more important.

In the final part of this study, an approach was made to investigate the cell wall porosity of unmodified and modified wood, using the nitrogen adsorption technique. Results indicated that the true porosity of the cell wall was not determined by this technique.

LIST OF ABBREVIATIONS

BET	Brunaeur-Emmet-Teller theory
Ea	Activation Energy
EMC	Equilibrium moisture content
FSP	Fibre saturation point
H	Relative vapour pressure
HH	Hailwood-Horrobin model
K_1	Equilibrium constant of the hydrates (in the Hailwood-Horrobin model)
K_2	Equilibrium constant of the dissolved water (in the Hailwood-Horrobin model)
m	Total moisture content (in the Hailwood-Horrobin model)
m.c	Moisture content
m_h	Water of hydration (in the Hailwood-Horrobin model)
m_s	Water of solution (in the Hailwood-Horrobin model)
OD	Oven dried
OH	Hydroxyl groups
R^2	Coefficient of determination
RH	Relative Humidity
SA	Surface area
SED	Solvent Exchange Dried
VC	Volume change
V_f	Void volume introduced into wood due to modification
V_i	Volume occupied by the modifying chemical
Wo	Molecular weight of the sorbate per mole of sorption site (in the Hailwood-Horrobin model)
WPG	Weight percent gain

LIST OF PUBLICATIONS ARISING FROM THIS WORK

(a) Referred Journal Publications

1. Hill C.A.S and A.N. Papadopoulos (2002). Chemical modification employed as a means of probing the cell wall micropore of pine sapwood. *Wood Science and Technology* (in press).
2. Hill C.A.S and A.N. Papadopoulos (2002). The pyridine catalysed acylation of sapwood and phenolic model compounds with carboxylic acid anhydrides. Determination of activation energies and entropy of activation. *Holzforschung* (in press).
3. Hill C.A.S and A.N. Papadopoulos (2002). A review of methods used to determine the size of the cell wall microvioids of wood. *Journal of the Institute of Wood Science* (in press).
4. Papadopoulos A.N. and C.A.S Hill. The sorption of water vapour by chemically modified softwood. *Wood Science and Technology* (submitted).
5. Papadopoulos A.N. and C.A.S. Hill. The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against brown rot fungi. *Holz als Roh-und Werkstoff* (submitted).
6. Papadopoulos, A.N. Swelling, cell wall porosity and chemical modification of wood. *Journal of the Institute of Wood Science* (submitted).

(b) Conference Proceedings

1. Papadopoulos A.N. and C.A.S Hill (2001). The biological effectiveness of wood modified with linear chain carboxylic acid anhydrides against brown rot fungi. *Proceedings of the international Conference: FOREST RESEARCH: a challenge for an integrated European approach.* Thessaloniki, Greece. (in press).
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CHAPTER 1

Introduction

Although wood continues to remain a popular material due to its excellent properties, it has a number of disadvantages such as dimensional instability in the presence of moisture and susceptibility to decay organisms. These deficiencies are due to the nature of the cell wall polymers, which contain an abundance of hydroxyl groups (OH). Yet the presence of these functional groups allows for the possibility of exploring their reactive chemistry in order to alter the material properties, a process referred to as chemical modification. Chemical modification has been studied for over fifty years, with the most interest being directed to acetylation using acetic anhydride (Rowell, 1983; Kumar, 1994). Although the material process properties of modified wood have been extensively studied, there has been little attempt to investigate the reaction kinetics of the process (Hill and Jones, 1996b). In part, this perceived reluctance may be due to the complex nature of the substrate.

The wood cell wall exhibits considerable heterogeneity in its ultrastructure. A typical section of a softwood cell (tracheid) may be considered as a hollow tube, the hollow interior being referred to as the lumen. This is shown schematically in Figure 1. Tracheids are typically 10-70 μm in diameter, the cell wall of which vary from 2 to 6 μm in thickness. Earlywood, formed at the start of the growing season, has thinner cell walls, and a higher diameter lumen, to facilitate the transport of sap and nutrients. Towards the end of the growth period, latewood is created, which has thick cell walls and a narrow lumen, imparting strength to the wood. Tracheid lengths typically vary from 1 to 5 mm. The cell wall is composed of several layers, of which the majority of the volume is contained within the S_2 layer. This consists of many layers of spiral wound microfibrils which are themselves composed of crystalline cellulose and other materials (Fengel and Wegener, 1984; Eaton and Hale, 1993). Attached to the surface of the microfibrils are the hemicelluloses, which act as an interfacial coupling agent between the highly ordered cellulose of the microfibrils and lignin, which is an amorphous hetero-polymer composed of phenolic units. Although the hemicelluloses are (like cellulose) polysaccharides, they differ in that they are composed of many

different sugar residues, have a lower molecular weight, and generally exhibit an amorphous structure. The lignin, which is highly crosslinked, provides stiffness to the cell wall and additionally acts to bond cell walls together *via* the middle lamella.

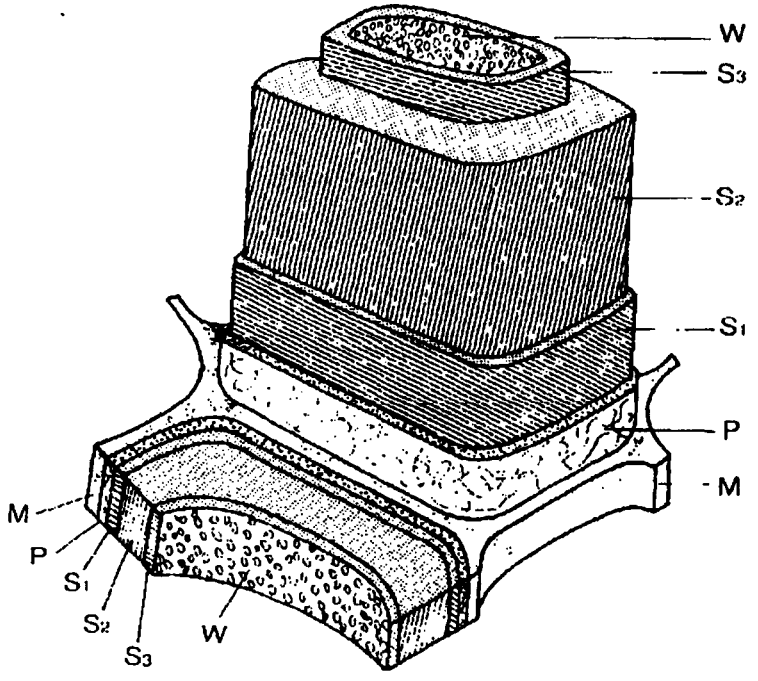


Figure 1: Schematic representation of cell wall layers in a tracheid with respective orientation of microfibrils (M, middle lamella; P, primary wall; S_1, S_2, S_3 layers of the secondary wall; W, warty layer). (Tsoumis, 1991).

Within the cell wall, there are regions between the cell wall polymers which constitute the cell wall pore structure. The detailed geometry of these micropores, which have dimensions in the nm range, is not known with any certainty, although a large number of studies in this area have been reported. The geometry of these micropores is of great importance, since this parameter has a substantial influence upon a number of processes of relevance to the wood processing industries (e.g. wood drying, pulping and bleaching, preservative distribution, biological decay processes, chemical modification etc.). Chapter 2 discusses the various experimental methods available for investigating the cell wall microvoids.

Chemical modification of wood has been the subject of many investigations and continues to be of interest (Rowell, 1983;1984; Hon, 1996). Essentially, this process involves the reaction of chemical reagents with the cell wall polymers of wood, resulting in the formation of covalent bonds between the wood and reagent. Many reagents have been investigated including anhydrides, isocyanates, epoxides etc. Potentially, the most useful and therefore widely studied, is the reaction of anhydrides with wood. At the present time, acetylation (i.e. reaction of wood with acetic anhydride) is close to being commercialised. Despite major research efforts investigating the reaction of acetic anhydride with wood, very little attention has been given to the fundamental aspects of the process. In particular, the reaction kinetics has not been studied in any detail. Reaction of chemicals within the cell wall of wood requires that those must travel and react within the porous network of the cell wall. It follows therefore, that this porous network must influence the reaction kinetics, this is investigated in Chapters 3 and 4. As reaction proceeds, the reacted molecules occupy space within the cell wall, resulting in wood that is swollen to larger dimensions than in the oven dry state.

Apart from potentially affecting the reaction kinetics, the micropore network geometry may also control accessibility of molecules to the cell wall interior. Different sized molecules would be expected to heve different accessibility to the cell wall. In Chapter 5, a study of reactivity of Corsican and Scots pine with two different sized reagents is reported, with differences between the two species found.

The degree of swelling depends upon the extent of reaction, volume of space occupied by the molecules and how the wood cell wall responds to the modification. This is covered in Chapter 6, where differences in the response of the two species used in this study (Corsican and Scots pine) were found.

The modification of wood is known to affect water vapour sorption. Two possible mechanisms are responsible for this effect: blocking of sorption sites, or swelling of the cell wall by reagent. In Chapters 7 and 8, the phenomenon of water vapour sorption of chemically modified wood is described.

Hydroxyl accessibility also has a major influence on chemical reactivity. This is studied in Chapter 9, by using deuterium exchange experiments. Attempts to determine lignin composition and porosity are also mentioned.

Finally, Chapter 10 brings together results from the studies, draws conclusions regarding this work and makes suggestions for future research.

CHAPTER 2

Pores in wood cell wall

2.1. Introduction

Wood is a porous material. The pore space in wood consists of macroscopic and microscopic voids such as cell lumena, intercellular spaces and pits. Resin and gum ducts also add to these voids. In addition, submicroscopic microvoids, also known as microcapillaries exist in the cell wall (Figure 2.1).

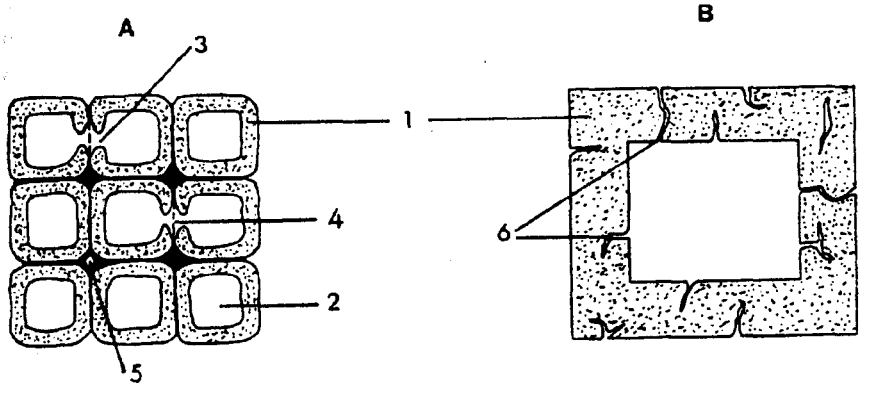


Figure 2.1: Simplified diagrams showing the pore space in a cross-section of wood. (A) and the microvoids existing in the cell wall (B). 1:cell wall, 2:cell lumena, 3:pit aperture and chamber, 4:pit membrane, 5:intercellular space; 6:microvoids of different shape and size in the cell wall. (Tsoumis, 1991).

The total volume and surface area of pores, distribution of pore size, and pore shape and location are factors affecting any treatment of wood by liquids, or reagents.

The measurement of pore size in wood is very difficult, due to the heterogeneous nature of the material and also because of the varying geometry of the pores when conditions change.

2.2. Void volume in the cell wall

The cell wall is partly porous as the result of an incomplete filling of the space between microfibrils by lignin, hemicellulose and extractives. The porosity in the cell wall is in the form of long and small diameter cavities, which are known as microvoids (Panshin and de Zeeuw, 1980). Various attempts have been made to provide experimental evidence for the existence of the microvoids, and to measure their diameters and volumes in natural cellulose, wood and wood pulps, using various techniques. These are reviewed herein. Each method has particular factors which must be considered when analysing results and these are discussed.

2.2.1. Density considerations

Density is by definition the mass contained in a unit volume of material. The density of wood is influenced by the presence of voids. In consideration of these voids the terms 'density of wood substance' and 'density of cell wall' are appropriate. The former refers to the substance (material) that constitutes the cell wall (without voids) and the latter to the wall with voids.

2.2.1.1. Density measured by displacement media

The density of cell walls may be measured by the displacement of liquids. Various liquids have been used as displacement media and various values have been obtained depending on whether the liquid enters the microvoids connected to the cell wall surface.

Density values for purified cotton measured with non-polar liquids such as toluene and benzene range from 1.52 to 1.59 g/cm^3 (Davidson, 1927 cited by Stamm 1967; Hermans, 1946; Stamm, 1950), values for wood pulps range from 1.54 to 1.56 g/cm^3 (Stamm, 1964), and values for wood are about 1.46 g/cm^3 (range from 1.42 to 1.48, Stamm, 1964; Wilfong, 1966; Stamm, 1967).

The situation is more complicated when water is used as the displacing medium. In all cases, water displacement values are higher than those using non-polar liquids, 1.60 to 1.62 g/cm^3 for cotton (Davidson, 1927 cited by Stamm 1967; Hermans, 1946; Stamm, 1950), 1.59 to 1.61 g/cm^3 for wood pulp (Stamm, 1964), and 1.53 (range from 1.50 to 1.55 g/cm^3) for various wood species (Stamm, 1964; Wilfong, 1966; Stamm, 1967). Two different explanations are given for the higher values obtained by water displacement. Stamm (1929, 1964) explains the higher values on the basis of the attractive force of cellulose for water being greater than the cohesive force of the water, which results in an effective compression, or orientation of the water molecules within the cellulosic structure. Hermans (1946) considered the higher values obtained in water to be the result of greater penetration of the fiber and discounted the concept of adsorption compression.

Displacement measurements have also been made using helium gas. Stamm (1929; cited by Stamm, 1967) appears to have been the first to make helium displacement determinations for wood. Stamm and Hansen (1937) obtained values of 1.46 g/cm^3 for white spruce, compared with 1.533 g/cm^3 with water. This difference was attributed to compression of the adsorbed water in the cell wall to an average density of 1.113 g/cm^3. Wilfong (1966) used an improved evacuation technique to remove air from his samples. The improved technique resulted in the non-polar displacement values being substantially the same as the helium displacement values, namely 1.46 g/cm^3.

Weatherwax and Tarkow (1968a), determined the cell wall density of dry Sitka spruce samples using two silicone polymers of low and high molecular weight (280 and 26,000 respectively) as the displacement liquids. The first one gave a cell wall density value of 1.465 g/cm^3, whereas the second one gave a slightly lower value. The authors concluded that the density of the dry wood cell wall was essentially independent of the molecular characteristics of the non-swelling fluids used in their study.

Weatherwax and Tarkow (1968a), attempted to explain the different values obtained by water and non-polar liquids on the basis of the factors cited by Stamm and Hansen (1937); i.e. (i) the compression of the bound water due to bonding forces at the sorption sites and (ii) the failure of non-polar liquids to penetrate the microvoids of the cell wall. They first measured the specific volumes by displacement with silicone

oil and toluene, obtaining equal values for both. In an attempt to measure the volume of microvoids only, they employed solvent exchange to replace water with ethanol, then ethanol with hexane. This allowed hexane to penetrate the microvoids, resulting in a specific volume which was 0.03 cm^3/g smaller than with silicone oil and toluene, namely 0.682 cm^3/g. This was assumed to be the volume of the microvoids (this corresponds to(0.030 / 0.682) x 100 = 4.4% microvoids). When the specific volume was measured by water displacement, the value obtained (0.647 cm^3/g) was 0.035 cm^3/g less than with silicone oil and toluene. The decrease of 0.005 cm^3/g was assumed to be due to water compaction.

The values of density, obtained by various displacement media described above, seem to be largely independent of the wood species used (Wilfong, 1966) and of whether the wood is in the form of fine particles or thin sections (Weatherwax and Tarkow, 1968a).

Table 2.1 summarises the dry cell wall density and volume values for wood and pulp obtained by various displacement media. It has to be stressed here that the pulps give higher density than wood and thus lower volume (see Table 2.1). There are two (contradictory) explanations for this observation: (i) the microvoids have collapsed in the pulp, and thus a true density for the cell wall substance is being measured, or (ii) the cell wall microvoids do not collapse and can be penetrated by swelling or non-swelling liquids to essentially the same extent. However, this difference was expected since the two materials, wood and pulp, have different chemical composition, i.e. the lignin has been removed in the pulp.

The above extensive discussion seems to imply that the void volume in the dry cell wall structure is equally inaccessible to all known non-swelling displacement media, since there is no significant difference between the density of the cell wall and that of wood substance in a dry condition, although a small void volume remains available only to water. This volume has been estimated to be about 1-5% of the cell wall volume by various authors, calculated as the total difference between the density of the dry cell wall and the density of the wood substance (Stamm, 1964; Wilfong, 1966; Stone *et al.* 1966; Weatherwax and Tarkow, 1968b; Wangaard, 1969; Kellogg and Wangaard, 1969; Tsoumis and Passialis, 1977). Although the porosity of the cell wall

Table 2.1: Summary of measurements of dry cell wall density and volume of wood and pulp by various displacement media.

Displacement media	Density (g/cm^3)	Volume (cm^3/g)	Reference
		Wood	
Water	1.53	0.653	Stamm and Hansen, 1937
Water	1.53	0.653	Wilfong, 1966
Water	1.55	0.647	Weatherwax and Tarkow, 1968a
Toluene	1.45	0.690	Kellogg and Wangaard, 1969
Benzene	1.44	0.693	Stamm and Hansen, 1937
Helium	1.46	0.684	Stamm and Hansen, 1937
Mercury	1.44-1.45	0.693	Stayton and Hart, 1965
Silicone oil	1.47	0.693	Weatherwax and Tarkow, 1968a
Hexane (by solvent exchange)	1.53	0.682	Weatherwax and Tarkow, 1968a
		Pulp	
Toluene	1.54-1.56	0.641-0.649	Stamm, 1964
Benzene	1.54-1.56	0.641-0.649	Stamm, 1964
Water	1.59-1.61	0.621-0.628	Stamm, 1964

is very small, it becomes much more significant when wood is treated with polar liquids such as water. As a result, 'transient pores' holding the water are created (Stamm, 1964) and the cell walls expand so that they are ultimately able to hold about 30% moisture based on their dry-weight in the fully swollen condition, at fibre saturation point (FSP).

Density measurements give evidence for the void volume in cell wall but they give no guide to the size of these voids.

2.2.1.2. *Density from microscopic measurements*

Jayme and Krause (1963), calculated the dry cell wall density of various woods from measurements of the fractional cell wall area made by planimeter measurements on highly magnified wood cross sections combined with measurements of the bulk density. They obtained values from 0.73 to 1.27 g/cm^3 indicating that the cell walls contain between 51.5% to 9.5% voids. Yiannos (1964), reported dry cell wall densities for several softwoods ranging from 1.04 for eastern spruce to 1.32 g/cm^3 for slash pine. Tsoumis (1964), has obtained a dry cell wall density of 0.967 g/cm^3 for

Eastern white pine. Cell wall density values considerably less than 1.0 g/cm^3 have been also reported for Douglas fir (Ifju and Kennedy, 1962) indicating that the cell wall has a void volume of about 30%.

Microscopic measurements of the dry cell wall density are obviously lower than those determined by the displacement method described previously. Many workers (Stayton and Hart, 1965; Wilfong, 1966; Stone *et al.* 1966; Stamm, 1967; Wangaard, 1969; Kellogg and Wanggard, 1969) have questioned these results and they wondered if the reported values actually represented the cell walls in a completely dry condition, as any swelling or bulking of the walls would considerably lower the apparent density.

A possible explanation for the difference between values obtained by optical and displacement methods, is that there exists in the dry cell wall a system of small pores which communicates with the cell lumena and is penetrated by the fluids, but which is not visible in the sections normally used for the microscope measurements.

2.2.2. Microscopic observations

Wardrop (1956), examined lignified and delignified fibers of spruce and flax impregnated with colloidal gold, and found the pore size to be about 10 nm (100 Å) in width. The crystals were found to be larger after delignification.

Wardrop and Davies (1961), used an electron microscope to investigate wood fibers, treated with gold chloride. They showed that there are capillaries between the microfibrils of wood, the width of which varied from 7 to 10 nm (70 to 100 Å) According to them, 20-30 water molecules can be accommodated in this distance.

By electron microscopic observations, Rollins *et al.* (1966) have shown that the pores visible between the lamellae in swollen cotton fibers resemble openings between parallel plates. On the other hand, the small pores between elementary fibrils and microfibrils in the lamellae have apparently more equilateral dimensions.

Rowland *et al.* (1984), pointed out the presence of small cracks and crevices in purified, sodium hydroxide-treated and liquid ammonia-treated cotton celluloses, revealed from scanning electron photomicrographs.

Microscopic observation of shadowed replicas of rapidly frozen, deep-etched primary cell walls from onion (*Allium)* parenchyma visualised pores as random gaps in the network of wall polymers rather than as specific structures (McCann *et al.* 1990). The pores were mostly 10 nm (100 Å) in diameter, but would have been artefactually enlarged during the deep etching process.

Frey-Wyssling (1937), based upon X-ray examination of delignified fibres, impregnated with gold or silver, concluded that the regions occupied by non-cellulosic components of the cell wall are 1 nm wide within the microfibrils and 10 nm between them, and that these regions are continuous and elongated in form. The data showed that the microvoids are parallel to the fibre axis.

Donaldson *et al.* (1988), used colloidal lanthanum and gold tracers of known particle size (2 nm and 5 nm, respectively) to study cell wall microvoid distribution in radiata pine (*Pinus radiata*). Cellulose regions were found to contain a large number of microvoids greater than 2 nm in diameter. In a study of the impregnation of the cell wall of Swedish pine (*Pinus sylvestris*) with silver nitrate/potassium glycerate, silver particles in the diameter range of 2-20 nm with a major axis as long as 1000 nm were observed (Wallstrom and Lindberg, 2000).

2.2.3. Nitrogen adsorption technique

Valuable information on the geometry of microvoids in native celluloses, wood and wood pulps can be obtained by adsorption of a gas near its boiling point. Nitrogen is particularly suitable as a gas, because it is chemically inert and the molecule is small enough in size to enter all but the smallest pores.

One method is to flow mixtures of helium and nitrogen over the sample at –195°C and measure the changes in pressure of the gas sample by a thermal conductivity meter. The partial pressure of nitrogen can be changed by changing either the composition of the mixture or by changing the total pressure. In this way an isotherm can be obtained relating the amount of nitrogen condensed onto the sample against the partial pressure, which allows an estimation of the total surface area of microvoids, ranging from those just accessible to nitrogen (0.36 nm) up to about 30 nm. The distribution of pore radii and the distribution of pore volume between these radii may also be determined (Stone and Scallan, 1965).

The observations can be made on both cell walls dried from water and on cell walls after solvent-exchange drying (SED). The latter was initially thought to remove the water from the cell wall while retaining its water-swollen structure. A typical procedure consists of the thorough removal of water with anhydrous methanol, the removal of methanol with pentane and the evaporation of the pentane in a stream of dry nitrogen. However, it was shown later that this solvent-exchange drying does not preserve the swollen cell wall structure and therefore does not preserve the total pore volume (Stone and Scallan, 1965; Stone and Scallan 1967). Wood or pulp produced by this method is commonly referred to as an aerogel.

By using this technique (SED), it has been reported that the surface area of wood when oven-dried from the water saturated state is about 1 $m^2 g^{-1}$ (Stone *et al.* 1966). When wood is dried by solvent exchange, a surface area of about 5 $m^2 g^{-1}$ is found, although a solvent exchange dried (SED) mechanical pulp may return values in excess of 40 $m^2 g^{-1}$ (Stone *et al.* 1969).

However, the use of this method has been criticised, in that a collapsing force is experienced by the microvoids due to surface tension forces operating at the liquid-vapour interface (Tarkow *et al.* 1966). Merchant (1957), studied the effect of solvent exchange drying upon fully bleached sulphite spruce pulp. A never-dried pulp was solvent exchanged from its water-swollen state using methanol and finally a liquid hydrocarbon. The fibres were studied using nitrogen adsorption. The surface areas of the fibres varied from 43 to 196 $m^2 g^{-1}$, with higher values recorded at higher drying temperatures. The amount of residual liquid trapped in the cell wall of the fibres

decreased as the measured surface area increased. The hydrocarbon used in the final stage also affected the measured surface area, with this property increasing in the sequence: (lowest surface area) benzene < toluene < cyclohexane < n-hexane < n-pentane (highest surface area). The change in surface area with drying temperature was attributed to the changing surface tensions of the final solvents. Partial collapse of the cell wall microvoids occurred as a result of these forces. When fibres were dried from water, re-soaked in water, then solvent exchange dried, they exhibited lower surface areas than never-dried fibres.

A superior drying method involves the use of carbon dioxide at the critical point, thereby avoiding the problems due the presence of a liquid vapour interface at the throat of the microvoid. Thus, Weatherwax and Caulfield (1971) investigated the drying of wood pulp using both conventional SED, and critical point drying. When the final solvent (hexane) was removed in a stream of dry nitrogen, a specific surface area of 43 $m^2 g^{-1}$ was recorded for the wood pulp. When the final solvent was CO_2 at the critical point, a surface area of 144 $m^2 g^{-1}$ was found. Similarly, with ball-milled wood pulps dried using solvent exchange (but not critical point drying), surface areas in the region of 100 $m^2 g^{-1}$ (increasing to 200 $m^2 g^{-1}$ after 250 minutes of ball-milling) were found (Thode *et al.* 1958). A maximum in the pore volume distribution curve was found at 3.8nm, which was not affected by the ball-milling. However, it is likely that this maximum is an artefact (Gregg and Sing, 1982).

Stone and Scallan (1965), applied this technique to oven-dried and solvent exchange dried microtomed sections of spruce. For oven-dried samples, surface areas in the range of 0.6 to 0.8 $m^2 g^{-1}$ were found, whereas for SED samples, the corresponding values were 3 to 6 $m^2 g^{-1}$. For SED pulp samples, values in the range of 100 to 200 $m^2 g^{-1}$ were reported. The most common pore diameter in every case was in the region of 3.2 to 4.0 nm.

The large difference found in surface area between wood and wood pulp dried using solvent exchange, indicates that the lignin has a very important role in both occluding and re-collapsing the microvoids when the final solvent is removed (Stone, 1964).

Haselton (1955), used nitrogen sorption for studying the microvoid volume distribution for SED (water to methanol to benzene) spruce flour, holocellulose derived therefrom, and KOH-extracted holocellulose. Surface areas of 4.0, 61.3 and 62.2 m^2g^{-1} were found respectively. Microvoid volume distributions for the holocellulose and KOH-extracted holocellulose were determined, which showed maxima at *ca.* 4-5 nm, with a tail in the distribution out to 10-12 nm.

An earlier study (Haselton, 1954), had shown that such samples, when dried conventionally, exhibited no detectable cell wall porosity. In a study of the delignification of Black spruce (*Picea mariana*) fibres, Stone and Scallan (1965) found that microvoids in the range of 2 to 4 nm were produced in the process.

Sawabe *et al.* (1973), investigated the micro-pore structure of various woods using nitrogen sorption. They found that most of the pores found were in the range 2.5 to 5.0 nm in diameter, with no essential differences in the pore size distribution between species. Weatherwax (1977), showed that pores in solvent exchange dried and critical point dried pulp ranged from 1.8 to 80 nm, with the majority being less than 3.2nm in diameter.

Nitrogen is not the only gas used for measuring surface area and pore size distribution in wood and wood constituents. Odintsov and Erinsh (1959), have used benzene and hexane as the adsorption gases and reported that the internal surface of sprucewood and spruce holocellulose to be 300 and 450-500 m^2g^{-1} respectively. They also found that pores with radii between 30 and 1000 Å are almost completely absent in sprucewood, but are produced by removing lignin from the wood. Partial removal of hemicelluloses caused an increase in the volume of pores having a radius over 200 Å. The volume distribution curve had a maximum at a radius of 17-18 Å.

Argon has also been used to study changes in specific surface area resulting from various chemical reactions on cellulose (Kudlacek and Ruzicka, 1962). However, analysis using this gas is difficult and results obtained are debatable .

2.2.4. Mercury porosimetry technique

Mercury porosimetry yields, in principle, the same kind of information as that afforded by gas adsorption, but it is applicable to a wider range of pore sizes. Because mercury does not wet wood and does not enter the pores therein, a positive pressure is required to penetrate the capillary structure. The method is based on the principle that when an evacuated sample is immersed in mercury, the mercury can be progressively forced into smaller and smaller pores by the application of the higher and higher pressures. The behaviour of a non-wetting liquid, such as mercury, in contact with a porous material, such as wood, is decribed by the Washburn equation (see below). A relationship between the applied pressure and the size of pore penetrated enables one to calculate the volume of pores in each size range.

$$P = \frac{-2\,\sigma\cos\theta}{r}$$ (Washburn equation)

Where: P is the applied pressure

r the pore radius

σ the surface tension

θ the contact angle.

With modern instrumentation, it is possible to achieve pressures up to 414 MPa (60,000 psi), wherein pores of 1.5 nm radius can theoretically be filled. Usually, cylindrical pores are assumed for most treatments using this technique. Stayton and Hart (1965), used this technique up to an applied pressure of 20.7 Mpa (3,000 psi), allowing for pores as small as 60 nm diameter to be penetrated. Cell wall densities in the region of 1.44-1.45 gcm^{-3} were determined, in close agreement with the values obtained by displacement using helium or non-polar liquids, showing that penetration of the cell wall had not occurred.

Stone *et al.* (1966), investigated several wood species, as well as wood pulp, using mercury intrusion porosimetry. Wood cell wall densities in the region of 1.5 g cm^{-3} were found. A maximum pressure of 100 psi allowed for the filling of pores up to 200

nm in diameter. The results indicated that there was no intrusion of mercury into the cell wall.

McKnight *et al.* (1958), applied this technique to sheets of paper and to mats of fibres evaporation dried from water, and sublimation dried from ice and solid benzene. Pressures up to 103.5 Mpa (15,000 psi) permitted the filling of pores as small as 7 nm radius and pore volume vs. radius distribution curves were obtained. It should be noted that the high pressures required to fill the smallest pores inevitably lead to compression of the wood, or pulp. This will almost certainly mean that the cell wall microvoids will collapse, and that as a consequence information regarding the microvoid geometry will not be obtained.

Quynn (1963) (cited by Stone, 1964), has applied the same technique to a variety of natural and synthetic fibers, yielding direct information about total pore volume and pore size distribution, and indirect information about the geometry of the pore structure.

Bariska (1975), used the mercury porosimetry technique, and found that pores with diameters of approximately 8 nm (80 Å) represented by far the largest part of the volume of air-dried beechwood (*Fagus sylvatica*); though radii of 50 to 300 nm and 1000 to 7000 nm were also relatively frequent. In a subsequent experiment, Bariska brought beechwood samples into contact with gaseous, anhydrous ammonia for an hour and he observed that the volume of pores with diameters of approximately 8nm was doubled. This was attributed to the fact that larger pores of the plasticized cell wall were reduced to smaller dimensions by the compression forces, which caused cell wall collapse. This was supported by the reduction by one half of the volume of the larger pores of 50 to 300 nm. Longer treatments gave evidence that the number of pores with radii below 7.5 nm were increased; however the volume of these pores could not be determined with the measuring method applied.

2.2.5. The solute exclusion technique

Direct microscopic observation of the cell wall structure, as well as mercury porosimetry and gas adsorption techniques, require the absence of water, so that if these techniques are to be used, it becomes necessary to remove the water from the cell wall. Removal of water by straightforward evaporation causes the collapse of pores (known as hornification) (Stayton and Hart, 1965; Stone *et al.* 1966). In this case, powerful capillary condensation forces operate to bring the walls of the micropores together (see Figure 2.2.a), resulting in the formation of extensive hydrogen bonding networks between the sides of the micropores. To try to avoid this difficulty, solvent exchange drying has been used to study the pore structure of the cell wall but this, as was discussed earlier, cannot preserve completely the pores in the swollen state (particularly with the lignified cell wall). During the solvent exchange process, a swelling solvent is gradually replaced by a non-swelling solvent, the molecules of which occupy the cell wall microvoids, thereby preventing collapse of the structure. However, if these occluding molecules are removed, then collapse of the structure occurs, although in this case there may not be such extensive hydrogen bonding networks formed (see Figure 2.2 b). In addition, the presence of lignin in the cell wall will also cause collapse of the cell wall microvoids.

A very interesting technique for assessing the accessibility of fibrous cellulose substrates in their swollen state was introduced by Aggebrandt and Samuelson (1964), who first studied the penetration of water-soluble polymers into cellulose. Stone and Scallan (1968b), perfected the solute exclusion technique, which derived from their work. The method measures the pore sizes in the water-swollen state by studying the penetration of solute molecules of differing molecular size into cellulosic substrates. If the water incorporated into the pores of the cellulosic sample is accessible to the small solute molecules, it will cause a dilution of the solute solution brought in contact with the water-swollen sample (Figure 2.3A). As solutions of increasingly larger solute molecules are applied to the swollen sample (Figure 2.3B and C) some of the smaller, and finally all pores, become impenetrable for the solute molecules. The water in the inaccessible pores cannot participate in the liquid and solvent exchange.

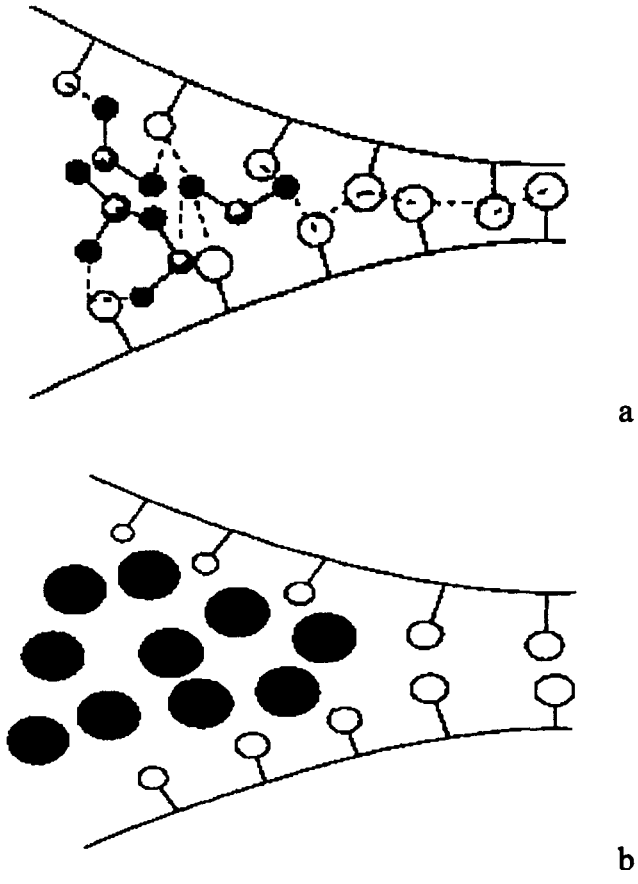


Figure 2.2: Schematic illustrating various models for cell wall pore collapse due to (a) drying from a water saturated state, (b) drying of wood via solvent exchange.

The observed dilution and concentration changes in the solution, in which the sample is immersed, allow the calculation of the amount of inaccessible water in relation to the molecular mass and the molecular dimensions of the solute molecules.

For best results, the solute molecules should not absorb chemically nor physically onto the cellulose and should be available over a wide range of molecular weights. Each solute should have a narrow molecular weight distribution and should also have a known size and geometry in solution, with a spherical shape being preferred. Most of the above conditions are met or approached by cross-linked dextrans (Stone and Scallan, 1968a).

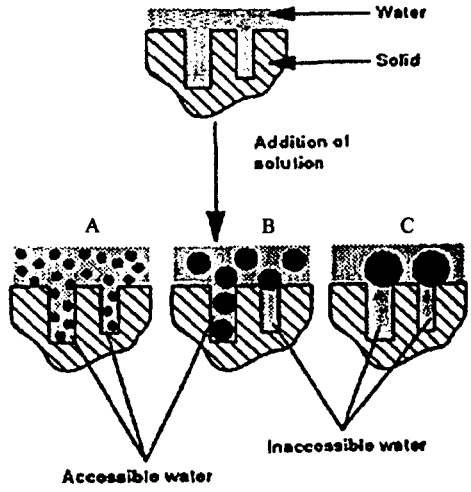


Figure 2.3: Principles of the solute exclusion technique (Stone and Scallan, 1968a).

According to Rowland and Bertoniere (1976), water-soluble solutes characterised by more limited hydrogen bonding capabilities than saccharides find only a fraction of the total water in accessible pores available as solvent water; the non solvent water is that which remains and is bound on cellulosic or polysaccharide surfaces. Rowland and Bertoniere (1976), also discussed the influence of electrostatic charge of the solutes on their penetration into pores. The presence of a carboxyl group in a solute causes negative sorption or repulsion of the solute from pores of the polysaccharide.

Two assumptions are made in this technique:

i) The concentration of solute in the accessible pores is equal to that in the solution surrounding the particle. This assumption depends upon the absence of specific interactions between the probe molecules and the cellulosic substrates and according to Allan *et al.* (1991) does not withstand scrutiny. According to them, the solutes with more limited capacity for hydrogen bonding would find only a fraction of the accessible water, whereas solutes with greater hydrogen donor ability would find all the accessible water and would interact with the cellulosic substrate.

ii) Complete penetration of solutes into the pores occurs when the solute diameter is less than the pore diameter. Day *et al.* (1979), however, showed that solute penetration is theoretically incomplete when the ratio of pore diameter to solute diameter is unity.

The apparent pore size distribution from this method reflects the shape as well as the size of the pores of wet cellulosic materials. A simple slit model is considered to be appropriate for cellulosic samples (Stone and Scallan, 1968a,b). Lin *et al.* (1987), in their study had also assumed a slit pore geometry. The choice of particular pore geometry is critical. Whereas the larger pores (>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 (this is discussed later in the section), the smaller (<25 Å) are of unknown configuration and have different properties (Stone and Scallan, 1968a,b).

A three dimensional computer model of macromolecular lignin structure was recently reported (Jurasek, 1995; 1996). The programme was designed to simulate lignin structures found in the middle lamella and secondary cell wall of wood fibres. The secondary wall lignin revealed a degree of orientation of the phenylpropane subunits in parallel with cellulose microfibrils. The middle lamella, on the other hand, was entirely randomly oriented and its structure was rather compact. However, some randomly distributed porosity was present in the structure and the pore sizes were within the range revealed experimentally in the literature. The sizes of these pores suggested that diffusion of small molecules (*e.g.* water, metal ions) might be possible.

Using the solute exclusion technique on never dried black spruce samples Stone and Scallan (1968a), found that the maximum cell wall pore diameter to be 3.6 nm (36 Å), though the median pore size (i.e., the pore size at which half of the cell wall pore volume is made up from less than that size) was 1.2 nm (12 Å).

Stone *et al.* (1969), calculated maximum pore sizes of never dried cellophane, textile rayon and super tire cord to be 20, 10, and 5 nm respectively; median pore sizes were 4, 2.5, and 1.2 nm respectively. It was also reported that these values were smaller after the drying and re-swelling of the material in water.

Kerr and Goring (1975a) and Grethlein (1985), found on white birch wood and on mixed hardwood (90% birch, 10% maple) respectively, a maximum pore diameter of about 10nm. Both reports, however, did not indicate whether the wood samples had ever been dried or not, but it is suspected that they had not been.

Flournoy *et al.* (1993), used the solute exclusion technique on previously dried sweetgum (*Liquidampar styraciflua)* and estimated the maximum pore diameter to be just 2nm and the median pore size 1 nm.

Weimer and Weston (1985), found the maximum pore size of six commercially available native celluloses to lay between 4.5 and 10 nm.

Caprita *et al.* (1979), applied the solute exclusion technique to five different cell types from cotton fibers to suspended cultured cells, and found remarkable consistency in the results with limiting pore diameters between 3.5 to 5.2 nm.

Many workers have used the solute exclusion technique to examine the effect of component removal upon the porous structure of the cell wall of wood. Thus, there are studies examining pore sizes in wood concerning themselves with changes that take place in the cell wall during the chemical pulping of wood. In the acid chlorite bleaching of white birch (*Betula papyrifera)*, it was found that the maximum pore diameter remained fairly constant throughout the delignification process and the median pore diameter started to increase only late in delignification and then only slightly (Kerr and Goring, 1975b). In spruce wood, the maximum pore diameter is increased in both Kraft and sulfite pulping and the median pore diameter greatly increased (Stone and Scallan, 1968a). These results demonstrate that chemical treatment of wood can have a substantial effect on cell wall pore volume and size distribution. Also there are studies examining pore sizes in wood, concerned with changes that take place during decay. It was reported that the cell wall void volume in white rot decayed sweetgum wood at 40 % weight loss was 0.6 ml/g and that the maximum pore diameter was more than 5 nm, whereas the corresponding values for undecayed wood were 0.35 ml/g and 2 nm respectively (Flournoy *et al.* 1993). It was suggested that the most of the cell wall void volume increase resulted from the creation of pores of 2 to 5 nm diameters.

Stone and Scallan (1968b), used the solute exclusion technique to suggest a structural model for water swollen delignified wood fibers. According to this, the pores in the cell wall are parallel slots between multiple lamellae. This leads to a surface model of parallel plates separated by a pore width; this width is measured by the solute exclusion technique. The larger pores are predominant between the concentric lamellae whose distances decrease continuously from the outer fiber surface to the internal lumen surface. Smaller pores are primarily located between the fibrils, forming the lamellae.

The solute exclusion technique has been criticised as a means of measuring pore diameter and volume. Alince (1991), argued that the concentration of a probe within a narrow pore would not be the same as that in bulk solution, stating that the only way that this would occur is if the probe molecule has a diameter infinitely smaller than the pore. He further stated that such an effect may account for the apparent porosity distributions measured by solute exclusion and that the porosity of cellulosic materials may be closer to monodisperse that is often believed. Alince (1991), also discussed problems that could affect solute exclusion measurements such as osmotic pressures or the 'ink bottle' effect where narrow pores could exclude probes from larger pores beyond. Walker (1993), suggests that solute exclusion may give a smaller than actual measure of pore diameter because the initial hydrogen bonded monolayer of water may not be accessible to probe molecules.

A recent development of the solute exclusion method has been the development of inverse size exclusion chromatography. This uses a series of probe molecules with different hydrodynamic molecular sizes, which are injected separately in sequence into an elution liquid. The liquid runs through a column that is packed with the pulp under investigation. The relative difference in elution time is recorded, which is analysed to give pore sizes and pore volumes. Berthold and Salmen (1997), used this technique, and obtained values comparable to those obtained using solute exclusion. The technique has also been applied to investigate the pore structure of various copolymers (Halasz and Vogtel, 1980).

2.2.6. Nuclear Magnetic Resonance

The diffusion of water within pulp fibres has been measured using a pulsed gradient spin-echo NMR technique (Li *et al.* 1992; 1995). This method can distinguish bulk water (between fibres and in the cell lumena) and fibre water (within the cell wall). The diffusion of water within the cell wall is restricted by the geometry of the microvoids. Such studies have indicated that the amount of fibre water is of the order of 1.4-1.6 g per g of cellulose fibre (in agreement with determinations using solute exclusion). Results also show that at least one dimension of the cell wall microvoids of pulp is in the micron range, showing that such microvoids are very elongated in form. This result is clearly in accordance with a lamellar model for the microvoid geometry in the delignified cell wall. Microvoid size distribution information can be obtained by determining the NMR relaxation time of the water in the microvoids. Water at (or close to) the surface of the microvoids (bound water) exhibits very different dynamic behaviour compared with water further from the surface, which behaves as free water. Microvoids of different sizes exhibit different relaxation times due to the different amounts of free and bound water (Li and Henriksson, 1993).

2.2.7. Thermoporosimetry

Maloney and Paulapuro (1998; 1999), have reported on the use of differential scanning calorimetry to provide information regarding the cell wall microvoids of pulp fibres (thermoporosimetry). This technique relies on the phenomenon that water located within the microvoids exhibits a depressed melting point compared with bulk water. The relationship between the melting point depression and radius of the microvoid (r) is given by the Gibbs-Thompson equation:

$$r = \frac{-V_m \sigma_{lm}}{\Delta H_m \ln\left(\frac{T}{T_o}\right)}$$

Where V_m is the specific molar volume of ice, T_o is the melting point of bulk water, T is the melting point of water located within the microvoid, σ_{ls} is the surface tension at

the liquid solid interface and ΔH_m is the specific melting enthalpy of water. Since it is necessary that the sample be frozen during such a measurement, it is possible that this may lead to an alteration of the structure of the fibres. Osmotic pressure effects may also lead to a melting point depression. However, thermoporosimetry studies have yielded credible values for the total volume of cell wall microvoids and shown that increases in the cell wall microvoid volume occur following lignin dissolution, in line with other studies.

A novel method for the investigation of the pore structure of paper and paper coating was described by Furo and Daicic (1999). The method is called NMR cryoporometry or cryoporosimetry and based on the principle of the freezing and melting temperature suppression of fluids entrapped within pores. The basic performance of the technique has been tested by comparing its results to those from the more established method of mercury porosimetry (Overloop and Gerren, 1993). In silica gels and in controlled pore glasses of 3-12 nm pore radii, the experimental average pore sizes supplies by the two methods did not differ more than 15%.

2.2.8. Other techniques

Wardrop and Davies (1961), observed that the uptake of dyes such as Congo red differ greatly in different regions of the cell wall of wood, being greater in the S_1 than the S_2 layer, and almost non-existent in the middle lamella. Congo red forms micelles, the size of which can be controlled by the nature of the solvent. The above observations indicate that the size, or number of microvoids in the S_1 layer is greater than in the S_2 and that these are also larger than the size of the dye micelle. In the middle lamella, the microvoids must be smaller than the dye micelles. This is presumably because the middle lamella is almost entirely lignin.

Stone (1964), notes that Cowling and Stamm (1962) have suggested a novel approach to the measurement of the cell wall porosity. This is based upon the measurement of the shrinkage properties of the material before and after diffusion of a series of polymeric solutes of increasing molecular weight into the cell wall. Molecules which

are smaller than the microvoids will enter the structure and by bulking, restrain the normal tendency of the cell walls to shrink upon drying. Dissolved molecules of progressively larger molecular size will enter the structure less readily and hence a lower anti-shrink efficiency will be observed. However, no experimental evidence was reported to indicate the feasibility of this procedure.

Palin and Petty (1981), measured the permeability to water of spruce (Picea abies) heartwood by applying a known osmotic pressure difference across specimens in which the cell walls were swollen and most of the void space was filled with paraffin wax. It was found that the wax-impregnated specimens swelled more than normal wood and that the swelling created more void space than existed in the dry wood. The relative moisture contents revealed that the water was taken up not only into the cell walls but also into some of the void space. In the water-swollen state the degree of filling with wax was found to be less than in the dry state by up to 10%. It was concluded that permeability was overestimated by about 10% owing to water entering some of the void space not filled by wax.

The adsorption of polyethyleneimine molecules of different sizes onto pulp fibres has been used as a means of determining cell wall microvoid structure (Alince and van der Ven, 1997). Results indicated a complete lack of porosity in the size range 3-40 nm, in contrast with results obtained using solute exclusion techniques.

Morisato *et al.* (1999), determined the heat of sorption for a series of solvents on oven dried wood. The results indicated that there are pre-existing microvoids or partially H-bonded regions within the cell wall of oven-dried wood.

2.2.9. Summary and conclusions

The determination of the microvoid geometry of wood presents problems due to the nature of the material, when compared to other porous materials. The microvoid geometry of wood is not constant, but varies depending upon the degree of swelling of the substrate. Techniques which rely upon the use of samples in an anhydrous state require careful preparation to ensure that collapse of the microvoids does not occur.

The presence of lignin in the material can result in such collapse, even when solvent exchange drying is employed. Determination of the microvoid geometry of wet samples would appear to be more appropriate. Solute exclusion techniques probably do not measure true microvoid geometries, but nonetheless provide information regarding cell wall accessibility. Methods such as NMR appear promising and further developments may be expected in this area.

2.2.10. Chemical modification

Chemical modification is a complementary technique, which can be applied for the same purpose. Chemical modification involves the linking of a reagent to the wood cell wall polymers via a covalent bond. The vast majority of methods investigated to date have involved the chemical reaction of a reagent with the cell wall polymer hydroxyl groups, which are by the far the most abundant reactive chemical sites in wood (Rowell, 1975). Thus, the chemical nature of the cell wall polymers is changed and this is reflected in new material properties. Chemical modification of wood has been the subject of a number of reviews (Rowell, 1983; 1984; Kumar, 1994; Hon, 1996).

The remainder of the Chapter describes chemical modification, in particular modification with anhydrides, discusses the kinetics of the chemical reaction and their complexity, and correlates chemical modification with wood porosity. Important factors related to the swelling of wood in both water and organic liquids are also covered. The swelling of wood and wood polymers in liquids is a complex process which is strongly influenced by both the wood substrate and the solvent. Finally the objectives of the work in this thesis are highlighted.

2.2.10.1. Requirements for chemicals considered for wood modification

A detailed set of requirements has been developed for chemicals considered for wood modification (Rowell, 1975; Rowell, 1982). In summary these include:

i. The chemicals must be capable of reacting with wood hydroxyls under neutral or mildly alkaline conditions at temperatures below 120^0C.
ii. The chemical system should be simple and capable of swelling the wood structure to facilitate penetration.
iii. The complete molecule must react quickly with wood components yielding stable chemical bonds.
iv. The treated wood must still possess the desirable properties of untreated wood, while improving one or more undesirable properties.

The result of the modification of wood first of all depends on the chemicals used. An equally, if not more important factor, is the process parameters applied during treatment. Chemicals with good wood modifying potential might not seem useful due to wrong treatment circumstances. In brief, the process parameters include:

(a) *Catalyst.*

Most chemical modifications of wood are performed with the addition of catalyst. The requirement of such a catalyst depends on the chemical used and chemical bond aimed for. The catalysts used in anhydride modification are discussed later in the chapter.

(b) Temperature.

Most chemicals react faster with hydroxyl groups of the wood at elevated temperatures. Temperatures applied usually range from 80^0C to 120^0C for most modifications.

(c) *Time.*

Most research in wood modification has been performed to see whether a certain chemical reacts with the cell wall components or not. Therefore long reaction periods of up to 24 hours have been applied. Attempts to find an optimum time for treatment have mainly been done with acetylation (Rowell, 1983). These results showed that a considerable amount of substitution takes place in the first 10 minutes of the reaction.

(d) Wood species.

Two major properties of wood species play an important role during wood modification. First of all, the permeability of the species used. Impregnation of wood species such as larch which are less accessible compared to pine sapwood or beech will have a lower uptake of chemical used and therefore, a lower degree of modification under equal process conditions (Beckers and Militz, 1994). Secondly, the chemical composition of the wood species. Wood extractives can react with the modifying chemical and prevent modification of the cell wall or result in the loss of a large amount of the chemical needed to modify. Research studies on acetylation of solid wood by Beckers *et al.* (1994), suggested that differences in lignin between softwood and hardwood species caused a difference in acetyl group distribution in lignin and holocellulose.

2.2.10.2. Anhydride modification

A wide variety of chemicals have been used to react with the hydroxyl groups in wood, including anhydrides, isocyanates, epoxides, aldehydes acid chlorides, carboxylic acids and others. Rowell (1975; 1982), Kumar (1994) and Hon (1996) have reviewed these modification reactions and the properties of the modified wood. The modifying chemicals attracting the greatest attention and those are of importance to this study are anhydrides.

Carboxylic acid anhydrides react with the wood cell wall hydroxyl groups *via* a nucleophillic reaction pathway (Bender, 1960; Satchell,1963). As a result of reaction with linear chain anhydrides, the corresponding carboxylic acid is produced as a reaction by-product (see Figure 3.4, presented in the following chapter).

The majority of research investigating this area has been concerned with the reaction of acetic anhydride with wood. Acetylation is a single site reaction, producing wood acetate and acetic acid as a by-product. Being a single site reaction, it means that one acetyl group is added per reacted hydroxyl group with no polymerisation. In other words, all weight gains caused by acetylation can be directly converted into units of hydroxyl groups substituted.

Acetylation has been studied since 1865, when Schutzenberger acetylated cellulose with acetic anhydride. Acetylation of wood (using wood flour or sawdust) was first investigated in the late 1920's through the work of Fuchs (1928) and Horn (1928), who used acetic anhydride that contained 0.25% sulphuric acid as a catalyst. Generally, the use of a strong acid as a catalyst is to be discouraged since it causes extensive degradation of the wood (Rowell, 1982). For this reason Suida (1928) used acetic anhydride alone or in mixture with pyridine. The first acetylation of whole wood (solid) is attributed to Stamm and Tarkow (1947), using pyridine as a catalyst. Many other catalysts have been tried including sodium acetate (Tarkow *et al.* 1950), magnesium perchlorate, trifluoacetic acid (Arni *et al.* 1961), boron trifluoride (Risi and Arseneau, 1957 a) and thioacetic acid (Singh *et al.* 1979) and several tertiary amine catalysts (Hill *et al.* 2000). Goldstein *et al.* (1961) claimed the best acetylation condition to be uncatalysed acetic anhydride in xylene at 100-130^{0}C.

Acetylation can be conducted in a liquid or vapour phase. However, the vapour phase treatment results in a product with poorer properties than the liquid phase (Rowell and Young, 1981; Rowell *et al.* 1985).

The efficiency of acetylation is affected by the moisture content of the wood (Clermont and Bender, 1957), since reaction with water generates acetic acid rather than resulting in wood modification. Acetic acid concentration within the anhydride also affects the degree of modification, with a slight increase in reaction rate occurring up to an acetic acid content of 15% and a decrease thereafter (Rowell *et al.* 1981). Recovery of acetic acid from the anhydride, following the reaction, is an important part of the economics of the process. On an industrial level, reagent recovery is accomplished by applying a vacuum on the sample whilst maintaining a temperature in the region of 120-130^{0}C (Goldstein *et al.* 1961).

Of the other linear chain anhydrides there have been a few papers published dealing with modification using propionic, butyric (Stamm and Tarkow, 1947; Risi and Arseneau, 1957b; Goldstein *et al.* 1961; Hill and Jones, 1996b; Li *et al.* 2000), and longer chain length anhydrides such as valeric, hexanoic and heptanoic (Hill and Jones, 1996b; Hill and Hillier, 1999; Cetin, 1999).

Reactions with cyclic anhydrides have also been investigated. Such reactions do not produce a by-product, leaving the modified wood polymers with a covalently bonded carboxylic group providing a site upon which further chemistry is possible. Cyclic anhydrides investigated include phthalic (Risi and Arseneau, 1958; Forster, 1998), maleic (Clemons *et al.* 1992) and succinic (Nakano, 1993; Hill and Mallon, 1998a).

2.2.10.3. Kinetics

The kinetics of a chemical reaction is of fundamental importance since the commercial viability of any chemical process is usually realised on the basis of adequate information obtained from such studies. This can also lead to the determination of the activation energy which is considered an energy barrier, and is defined as the minimum energy required by colliding molecules, in order that reaction will take place. This is further discussed in section 3.1.

Wood represents an exceedingly complex structure upon which to perform chemical reactions, and the kinetics would be expected to reflect this complexity. Any attempt to explain the nature of kinetic processes operating during wood modification may have to take account of a number of factors. These include (Hill and Hillier,1999):

(i) Differences between bulk and surface reactive sites. The reaction of a reagent with wood is considered to be dominated by two processes, namely surface and bulk effects (Hill and Jones, 1996a). The former is associated with reaction at or near the surface of the substrate and is assigned to the domination of the reaction kinetics by a first-order process (with respect to the wood hydroxyl groups). As the reaction proceeds, the bulk reactions assume increasing importance, and the kinetics will therefore be expected to display diffusion dominated processes. Whether diffusion kinetics are indeed observed will depend critically upon the relative rates of diffusion and reaction; if the former is the slower process, then the reaction will be diffusion limited, but if the latter is slower then a alternative kinetic process will be observed.

(ii) Differences in the chemical reactivities of the various hydroxyl groups. These, chemically, can be distinguished as being phenolic, benzylic or alcoholic on

the lignin regions and alcoholic in the carboydrate. The alcoholic groups may be either primary or secondary, the phenolic hydroxyls are attached to an aromatic ring which has various substituents attached. Thus, each of these groups will exhibit a different reactivity towards anhydrides. For example, it has been demonstrated that the primary hydroxyls of cellolose in cotton linters are more reactive to acetylation (Malm *et al.* 1953; cited by Hill and Jones, 1996a).

(iii) Various steric effects due to the different environments encountered in the material. The reaction rate within the wood bulk is affected by the rate of reaction of the anhydride units (and hence the production of the corresponding carboxylic acid), and the rate at which the carboxylic acid diffuses out of the wood matrix into the surrounding solvent.

(iv) The complex porous nature of the cell wall. The majority of the reactive hydroxyl sites of the cell wall are located within the interior; thus, in order for a reagent to react with these sites it is necessary for the molecules to travel *via* and react within the pore network.

2.2.10.4. Chemical modification and wood porosity

During the reaction of chemical reagents (such as anhydrides) with the cell wall of wood, it is necessary for the reagent molecules to travel via the cell wall micoporous network in order to react with the OH groups located within the interior of the cell wall (Patscheke and Dilg, 1958; Hill and Hillier, 1999). It is thus possible to investigate various properties of the cell wall microporous network by studying the wood modification process. If reaction takes place in a non-swelling solvent (e.g. toluene or xylene) and the wood has been previously dried, then the microporous network is in a collapsed state and ingress of reagent into the cell wall is controlled by the rate at which the micopores re-open. In this case the 'zipper' model (Krassig, 1985; West, 1988) is the most probable model explaining the reaction process. In such a model, the cell wall microvoids are effectively 'sealed shut' by extensive hydrogen bonding networks between the walls of the microvoid. In order that reagent molecules may penetrate the interior of the cell wall, it is necessary that these hydrogen bonds be

broken. If the rate of H-bond breaking is slow compared to the rate of reaction of reagent with the cell wall OH groups, then H-bond breaking is the rate limiting step of the reaction.

If however, the wood is in a swollen state, it is unlikely that hydrogen bond breaking plays any part in the reaction process. Hydrogen bonding networks only exist where hydroxyl groups are inaccessible, such as crystalline regions of cellulose, for example. In this case, the transfer of reagent molecules into the interior of the cell wall is affected only by the geometry of the cell wall micropores (in relation to reagent size). Obviously, other factors such as temperature and concentration of reagent are also important.

2.2.10.5. Swelling of wood in water and organic liquids

The wood cell wall is mainly composed of polymers with hydroxyl and other oxygen containing groups. When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to cell wall polymers through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionally to the volume of water added. Swelling increases until the cell wall is saturated with water. This point is called the fiber saturation point. This is further discussed in Chapter 7. Water added beyond this point remains as free water in the lumen and does not cause further swelling. This process is reversible and accounts for the dimensional changes that occur when wood comes into contact with water vapour or liquid.

As discussed so far, various techniques have been applied to investigate the microvoids within the wood cell wall. Some of them require the absence of water, so that if these techniques are to be used, it becomes necessary to remove water from the cell wall. Others can be applied in the swollen state.

In this section, important factors related to the swelling of wood in both water and organic liquids are discussed. The swelling of wood and wood polymers in liquids is a

complex process which is strongly influenced by both the wood substrate and the solvent.

2.2.10.5.1. Effect of wood substrate

The strong dependence of wood swelling in water on temperature was investigated by Mantanis *et al.* (1994a), using a computerised linear variable displacement transformer. They reported that by raising the water temperature above room temperature, the rate of swelling of wood was significantly increased. They suggested that the phenomenon of wood swelling is an activated process similar to a chemical reaction, since the temperature dependence of wood swelling in water closely obeyed the Arrhenius equation.

Mantanis *et al.* (1994a), West and Banks (1989) and Rowell and Ellis (1984), reported that the rate of wood swelling in various organic liquids is clearly dependent upon the temperature and, as above, closely obeys the classical Arrhenius equation. They showed that some liquids / solvents swell wood only slowly, or not at all, under room temperature conditions, but will be encouraged to do so by raising the temperature.

West (1988) and West and Banks (1989), noting the small induction period in most of the swelling profiles, proposed a 'zipper' model for the movement of water and organic liquids into wood structure causing swelling. According to them, the induction period reflects a gradual increase in the number of cell wall capillaries that participate in the swelling process as the liquid moves from the lumen into the cell wall and progresses slowly in the fiber direction.

During the reaction of chemical reagents (such as anhydrides) with the cell wall of wood, it is necessary for the reagent molecules to travel *via* the cell wall micoporous network in order to react with the hydroxyl groups located within the interior of the cell wall (Patscheke and Dilg, 1958; Hill and Hillier, 1999). It is thus possible to investigate various properties of the cell wall microporous network by studying the wood modification process. If reaction takes place in a non-swelling solvent (e.g. toluene or xylene) and the wood has been previously dried, then the microvoid network is in a collapsed state and ingress of reagent into the cell wall is controlled by

the rate at which the micopores re-open. In this case the 'zipper' model (Krassig 1985; West, 1988) is the most probable model explaining the reaction process. In such a model, the cell wall microvoids are effectively 'sealed shut' by extensive hydrogen bonding networks between the walls of the microvoid. In order that reagent molecules may penetrate the interior of the cell wall, it is necessary that these hydrogen bonds be broken. If the rate of hydrogen bond breaking is slow compared to the rate of reaction of reagent with the cell wall OH groups, then H-bond breaking is the rate limiting step of the reaction.

If however, the wood is in a swollen state, as is in the work considered in the bulk of this thesis, it is unlikely that hydrogen bond breaking plays any part in the reaction process. Hydrogen bonding networks only exist where hydroxyl groups are inaccessible, such as crystalline regions of cellulose, for example. In this case, the transfer of reagent molecules into the interior of the cell wall is affected only by the geometry of the cell wall micropores (in relation to reagent size).

The presence of extractives is another factor that affects wood swelling. Mantanis *et al.* (1994a; 1995a), found that removal of extractives from wood caused a significant increase in the wood swelling rate in both water and organic liquids. One of the reasons for this, might be the probable increase in size of the microscopic capillaries during the process of extraction as occluding molecules are removed.

Wood density appears to be correlated with maximum swelling. Mantanis *et al.* (1994a) showed that hardwoods swelled in water to a much greater extent compared to softwoods. They attributed this to the greater density of the hardwoods.

2.2.10.5.2. Effect of solvent factors

The molecular size of the solvent liquid is an important consideration in wood swelling. Stamm and co-workers (Stamm, 1964; Stamm and Tarkow, 1950) reported that an increase in molecular size in a series of liquids not only decreased the swelling rate, but the extent of swelling at equilibrium was also decreased. They attributed this to the greater difficulty for the larger molecules to diffuse into the fine capillary structure of the wood cell wall, since larger molecules need to break more hydrogen

bonds than smaller molecules in order to be adsorbed, leading to the higher energy consumption in the former process. Mantanis *et al.* (1994b), have further refined this work and reported that the logarithm of the rate of wood swelling in the liquids is inversely correlated with the molecular size of the solvent.

Studies of the penetration of liquids into the cell wall of oven-dried wood have indicated that molecules with molar volumes greater that 100 cm^3 per mole, do not penetrate the cell wall significantly (Mantanis *et al.* 1994b). Other studies have shown that molecules of molar volume greater that 100 cm^3 per mole which posses more than one H-bonding site per molecule are capable of penetrating the cell wall (Ishimaru and Maruta, 1996).

Solvent basicity (donor number) is found to be linearly correlated with the maximum tangential swelling of wood in organic liquids (Mantanis *et al.* 1994b). Mantanis *et al.* (1995b) proposed a statistical model for prediction of the maximum extent of the swelling of wood in organic liquids. Solvent basicity, solvent molecular volume, and density of wood appeared to be the most important parameters in the proposed model.

2.2.11. *Objectives of the study*

Previous studies of the kinetics of chemical modification of wood with anhydride reagents, have shown that reaction profiles are best described by considering both diffusion and reaction rates (Hill and Jones, 1996b; Hill and Hillier, 1999). Determinations of the activation energy (Ea) of reaction have suggested that the Ea decreases as size of reagent increases (Cetin, 1999; Hill and Hillier, 1998). However, no systematic study of a series of anhydride molecules in wood reactions has been performed. Furthermore, from the preliminary data it was not known how reproducible the Ea values obtained were, nor what effect changing the wood species had upon Ea. It is probable that molecular motions are restricted within the cell wall microporous network and that, as a consequence, would be expected to influence the velocity distribution of the reagent molecules. The results produced in this work (described in Chapter 3) have shown that the decrease in Ea as size of anhydride molecule increases is a real, reproducible effect. Data obtained from work on model

compounds (described in Chapter 4) has shown that this significant decrease in Ea with molecular size in wood, did not occur in solution. The reason for the decrease in Ea found in wood is not known at present. However, it is postulated that this occurs due to restrictions placed upon the transational motion of reagent molecules due to the reactions taking place within the cell wall microporous structure.

Different sized anhydride molecules will have varying accessibility to the cell wall because of differences in dimensions of the cell wall micropores. When wood is dried, the cell wall micropores collapse, severely reducing access. Yet previous studies have indicated that the cell wall of oven-dried Corsican pine is accessible by acetic anhydride (Hill *et al.* 2000). In Chapter 5, the issue of accessibility is addressed, where it is shown that there are significant differences between the behaviour of Corsican and Scots pine.

As reaction takes place with the hydroxyl (OH) groups, the cell wall swells because the bonded adduct occupies space. The degree of swelling depends upon:

(i) Extent of OH substitution
(ii) Size of adduct
(iii) Degree of ability of the cell wall polymers to deform around the bonded adduct.

In Chapter 6, a full analysis of the swelling properties of Corsican and Scots pine sapwood due to modification are presented. Important differences were found between the two species and some tentative explanations for this difference are presented.

When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to the cell wall polymers through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionally to the volume of water absorbed. Chemical modification changes the properties of wood due to the reaction of hydrophilic chemical groups within the wood and by bulking the cell wall.

Although a number of studies have investigated the sorption properties of acetylated wood (Spalt, 1958; Risi and Arseneau, 1957a; Popper and Bariska, 1972; Forster, 1998), there has not been a study of the effect of modifying the wood with different sized anhydride reagents. It is known that rate and extent of water vapour sorption is decreased by substitution of the hydroxyl sites with acetyl groups. Two mechanisms may be proposed:

(i) Blocking of sorption sites.
(ii) Bulking of the cell wall by acetyl groups resulting in less space being available to sorbed water.

However, in previous studies it was not possible to determine the influence of each effect. By modifying wood with a variety of anhydride molecules of different size, it is possible to produce similar levels of bulking at different levels of OH substitution. Therefore, it becomes possible to separate the two effects. Analysis of water vapour sorption isotherms was performed using the Hailwood-Horrobin model. As a consequence of this work, serious doubt is cast upon the validity of this model. Analysis of the relative influences of cell wall bulking and OH group blocking has been performed. This work is described in Chapters 7 and 8.

Analysis of the two wood species used in this study is presented in Chapter 9. Gross chemical analysis was performed, plus an attempt at determining micropore geometry using nitrogen adsorption/desorption. In addition, deuterium exchange (D_2O) was used to determine the accessible hydroxyl content in the two species.

Finally, Chapter 10 brings together results from the studies, draws conclusions regarding this work and makes suggestions for future research.

The objectives of this work therefore were:

- To determine if the freedom of motion of reagent molecules is restricted within the cell wall microporous network of wood.

- To address the issue of accessibility to the cell wall of different sized reagent molecules.

- To fully study and analyse the swelling properties of wood due to chemical modification.

- To study the water vapour sorption of chemically modified wood.

CHAPTER 3

Kinetic studies of the acylation of pine sapwood with linear chain anhydrides

3.1. Introduction

The energy of activation (Ea) of a chemical reaction contains important information regarding the kinetics and the mechanisms of reaction. In the collision theory of reactions, an ensemble of molecules at a given temperature has a range of different energies which is given by the Maxwell–Boltzmann distribution (Figure 3.1). The activation energy of a reaction is considered an energy barrier, and is defined as the minimum energy required by colliding molecules, in order that reaction will take place (Figure 3.2). Those molecules that have energies exceeding the activation energy for the reaction collide and react, whereas the vast majority (with energies below the Ea) collide but not react. As the temperature of the reaction medium is increased, a larger number of molecules have energies that exceed the Ea and thus react upon collision (Figure 3.1b).

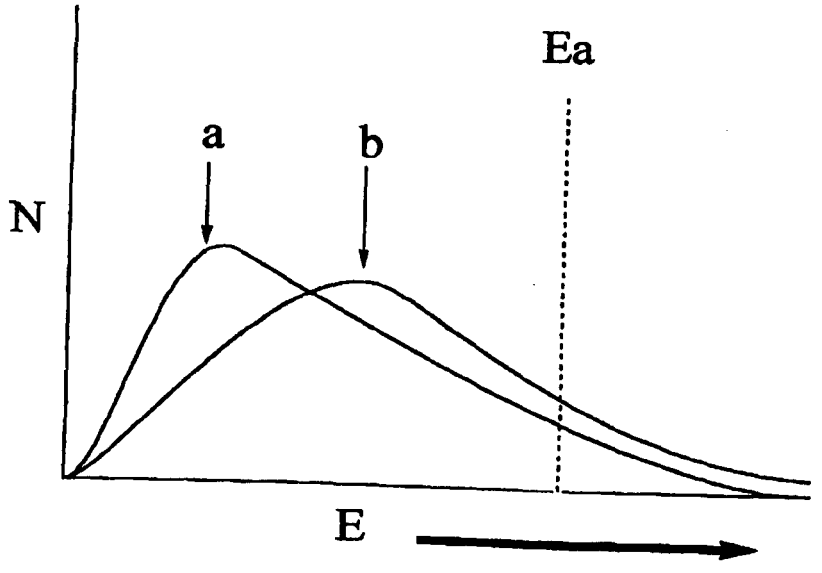


Figure 3.1: Maxwell-Boltzmann distribution and activation energy for low (a) and high (b) temperature.

This theory applies to reactions in the gas or solution phases, where the molecules have essentially unresticted freedom of movement in the solution. Reactions within the cell wall of wood differ. These take place within microvoids that exist between the polymeric cell wall components (Patscheke and Dilg, 1958; Hill and Hillier, 1999). Various attempts have been made to estimate the geometry of these pores, as extensively discussed in Chapter 2. In this case, the molecules that participate in the reaction are the hydroxyl groups of the cell wall components and the reagent molecule. The former are essentially fixed, the degree of freedom of the latter depends upon the amount of space surrounding the reacting hydroxyl group. It is therefore, reasonable to expect that there is a proportionally greater restriction upon translational motion in the region of the cell wall microvoids as the size of the reagent molecule used increases. The translational motion of molecules within the reactive region of these microvoids must be severely restricted where compared to the solution. There must therefore be some doubt as to the validity of applying conventional collision theory to reactions within the cell wall of wood.

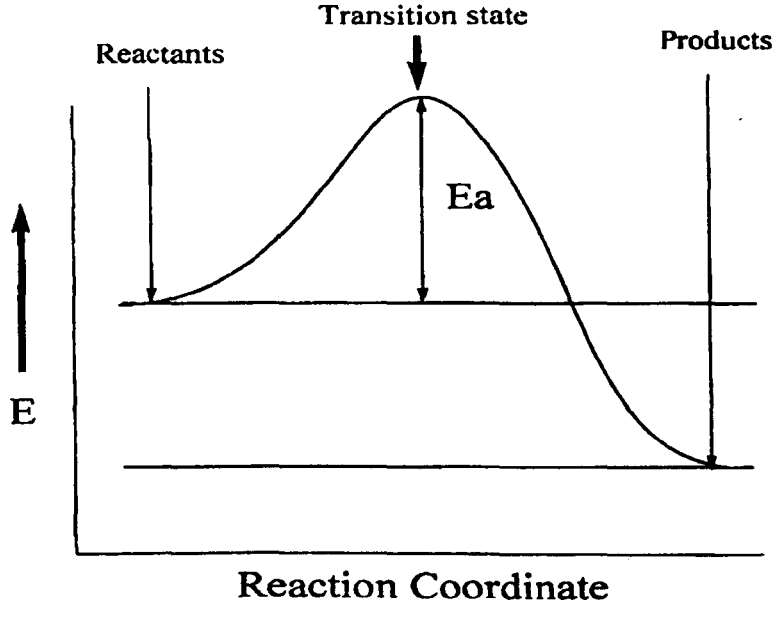


Figure 3.2: Variation of energy with reaction coordinate, showing activation energy (Ea).

In previous determinations of Ea for reaction of anhydrides (in pyridine) with wood, values of 41.6 kJ/mol and 31.3 kJ/mol, were obtained for acetic (Hill *et al.* 1998) and propionic anhydride (Hill and Jones 1996b). Whilst the value for acetic anhydride was considered to be close to what might be expected for a chemical reaction, the value of propionic anhydride was thought to indicate that hydrogen bond breaking was the rate determining step in this case.

In order to test the validity of this assumption, determine the reproducibility of the data and furthermore to test the validity of application of the Arrhenius equation to reactions within the cell wall of wood, a comprehensive study was performed.

Kinetic profiles were investigated for the pyridine catalysed reaction of Corsican and Scots pine sapwood with a homologous series of linear chain carboxylic anhydrides. Activation energies, for the initial stages of the reaction, were determined by the method of initial rates and from the rate constant data, by analysing reaction profiles over a series of temperatures from 120^0C to 60^0C. Additionally, the effect of the nature of substrate (Corsican and Scots pine) upon the activation energy was investigated.

3.2. Literature Review

3.2.1. Kinetic studies on homogeneous substrates

The kinetics of reaction of propionic anhydride with Corsican pine using pyridine as a catalyst, was found to obey pseudo first-order laws during the initial part of the reaction (Hill and Jones, 1996a). By determining reaction rates at different temperatures, the activation energy was calculated as 23.8 kJ/mol using rate constants. In addition, the method of initial rates was used to give a value of 31.3 kJ/mol. This discrepancy of the determined activation energies of these methods was attributed to the change in the number of the surface reactive sites with temperature.

Ramsden and Blake (1997), acetylated four softwoods (Larch, Southern yellow pine, Deal and Sitka spruce) with acetic anhydride in xylene (1:1 vol:vol.) and found a variation in the activation energy of the process from 42 (for Southern yellow pine) to 107 (for Larch) kJ/mol. The reaction kinetics was found to be zero order. Unfortunately, the use of only three data points in the Arrhenius plots used to obtain the activation energy casts serious doubt as to the accuracy of this observation. In addition, wood samples were not extracted prior to reaction which leads to complications in analysing the reaction kinetics.

Acetylation of Corsican pine using pyridine as a solvent/catalyst and with neat anhydride reagent has shown that the reaction kinetics are diffusion controlled, with no evidence of first-order kinetics during the initial stages of the reaction (Hill *et al.* 1998). Activation energies of 41.6 kJ/mol (pyridine catalysed) and 50.9 kJ/mol (uncatalysed) were obtained using the method of initial rates. Additionally activation energies of diffusion were determined as 20.5 (pyridine catalysed) and 34.2 kJ/mol (uncatalysed).

Pseudo first-order kinetics processes were also observed during the initial stages of the reaction of hexanoic and crotonic anhydride with Scots pine using pyridine as a catalyst. Activation energies were determined by the method of initial rates as 8.7 for hexanoic, 41.3 kJ/mol for crotonic anhydride and by the method of rate constants as 11.2 for hexanoic and 39 kJ/mol for crotonic anhydride (Cetin, *per. com.*). The values for hexanoic anhydride are exceptionally low for a classical reaction process, being more typically encountered when reactions are diffusion controlled.

The kinetics of reaction of cyclic anhydrides (succinic and octenyl succinic anhydride) with Scots pine using pyridine as a catalyst were also investigated (Hill and Mallon, 1998b). The analysis of the kinetics over extended times to determine if diffusion dominated the process, indicated complex behaviour which was not amenable to simple analysis. It is likely that substrate damage was the reason for the observed behaviour. The activation energies for surface reactions were determined by the method of initial rates as 79.5 and 29.6 kJ/mol for succinic and octenyl succinic anhydride respectively.

3.2.2. Other kinetic studies on acetylation of heterogeneous substrates

The kinetics of acetylation of jute and cotton fibre with acetic anhydride has been studied (Sen and Ramaswany, 1957). Acetylation was performed in both non-swelling (benzene) and swelling (acetic acid) media, in the presence of perchloric acid as a catalyst. It was found that the rate of reaction was diffusion controlled and activation energies of 54.3 and 71.7 kJ/mol were obtained for jute and cotton respectively.

A study of the perchloric acid catalysed acetylation of cellulose derived from wood pulp found that the kinetics of the process followed pseudo first-order rate laws, and an activation energy of 60.6 kJ/mol was measured (Frith, 1963). However, a study of the acetylation of cotton linters using acetic acid found that the reaction profile was found to be best described in terms of a combination of surface and bulk reactions (Hiller, 1954). The bulk reaction was considered to be controlled by diffusion. Energies of activation were determined as 60 kJ/mol for the surface reaction and 11 kJ/mol for the reaction with the bulk hydroxyl groups.

3.3. Materials and methods

3.3.1. Materials

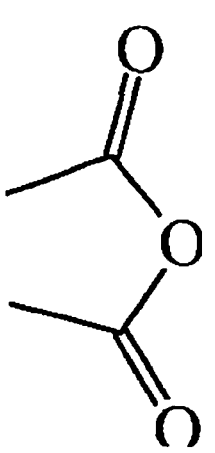
3.3.1.1. Modifying chemicals

Five linear chain carboxylic acid anhydrides were used in this study, namely acetic, propionic, butyric, valeric and hexanoic anhydride. All these yield the corresponding carboxylic acid as a by-product of their reaction with wood. The molecular structures of these anhydrides are shown in Figure 3.3.

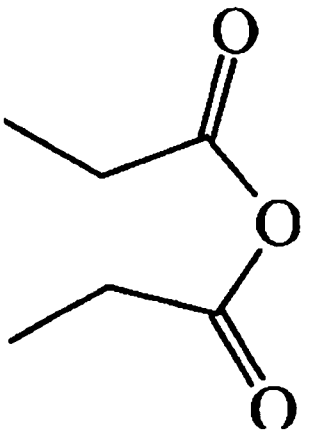
The reaction between wood and linear chain anhydrides is a single site reaction as depicted in Figure 3.4. However, Pizzi , Boonstra and co-workers (Pizzi *et al.* 1994; Boonstra *et al.* 1996; 1997) have questioned this. They suggest that in addition to the acylation reaction shown in Figure 3.4 substitution of the aromatic ring in lignin and cross linking reactions occur. In the present study the traditionally acknowledged reaction (Figure 3.4) was assumed.

All anhydrides were purchased from Aldrich and used as supplied.

The molecular size of the anhydrides chosen in this study is shown in Table 3.1. The limiting size for the penetration of water soluble material into water swollen cell wall is that of polyethylene glycol (PEG 300) (Tarkow *et al.* 1966). They suggested an approximation of the radius of gyration of such a molecule to be about 18-20 Å, based on intrinsic viscosity measurements. Hence, the diameter of the capillaries in the complete water swollen wood should be about 36-40 Å. To avoid any problem of penetration and diffusion into or through the cell wall, the anhydrides chosen take this limitation into consideration. The values in Table 3.1 show that the size of the chosen anhydrides meet the limiting size requirement. An approximation of the apparent diameter of the anhydride molecule obtained by means of simple calculation of the volume and diameter of a molecule based on the molecular weight, density, and Avogadro's number by assuming that the molecule is spherical is given in Table 3.1.



A



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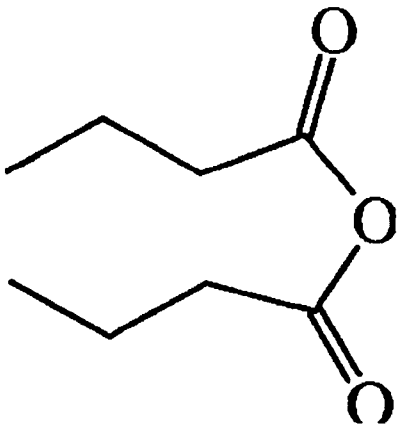
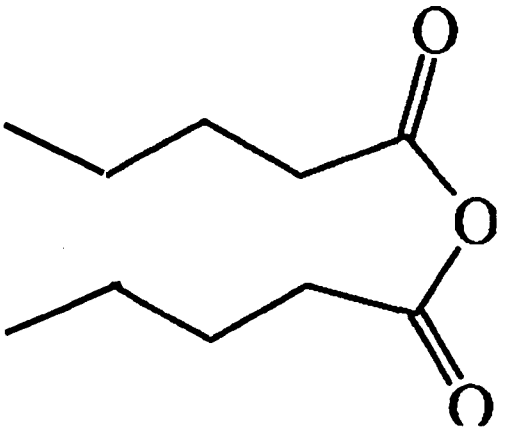
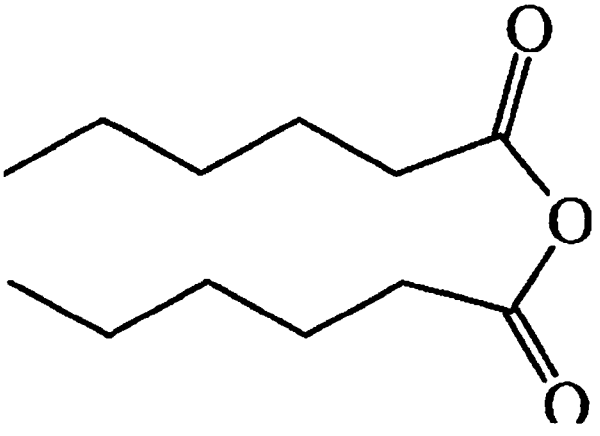


C



D



E

Figure 3.3: Molecular structures of the anhydrides used in this study: A: acetic; B: propionic; C: butyric; D: valeric; E: hexanoic.

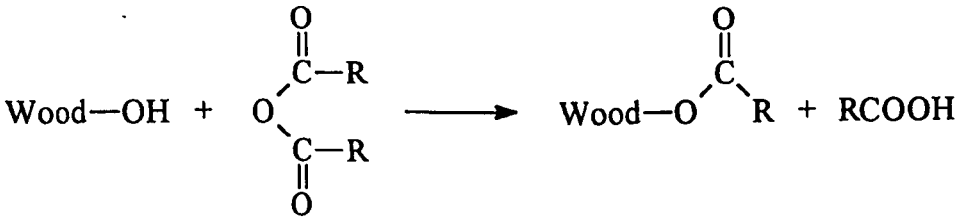


Figure 3.4: Anhydride modification scheme, where R=CH_3 (acetic anhydride), R= C_2H_5 (propionic anhydride), R=C_3H_7 (butyric anhydride), R= C_4H_9 (valeric anhydride), R=C_5H_{11} (hexanoic anhydride).

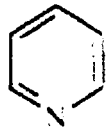
Table 3.1: Molecular size of the anhydrides used in this study. (For calculations see Appendix 1A).

Anhydride	Molecular Volume (Å^3)	Molecular Diameter (Å)
Acetic	156.9	6.68
Propionic	213.8	7.42
Butyric	271.6	8.02
Valeric	329.05	8.56
Hexanoic	384.2	9.02

3.3.1.2. Solvent

For comparison between modifying chemicals it was necessary to use the same reaction system, and therefore the same solvent.

Much work on acetic anhydride modification has involved the use of the undiluted anhydride or the use of xylene as solvent; a non swelling solvent considered by Goldstein *et al.* (1961) to the be ideal solvent for acetic anhydride modification of wood. To ensure each modifying chemical had the opportunity of accessing and reacting with wood cell wall polymers a swelling solvent was required. Pyridine (Figure. 3.5) was chosen for the following reasons:



M.W.: 79.1

b.p.: 115^0C

d= 0.978 g/cm^3

Figure 3.5: Molecular structure of pyridine.

i. Each of the modifying chemicals used in this study was found to be highly soluble or miscible with pyridine.
ii. Pyridine swells wood to a greater extent than water (approximately 25% greater; Stamm and Tarkow, 1947; Risi and Arseneau, 1957a) allowing even non-swelling modifying chemicals access to cell wall polymers.
iii. The longer chain anhydrides used in this study do not react with wood otherwise (Hill and Hillier, 1999).
iv. Pyridine is an organic tertiary amine, considered by Rowell (1983) to be ideal for the catalysis of wood modification of pine.

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

With regard to the swelling capacity of pyridine (point two 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 3.6).

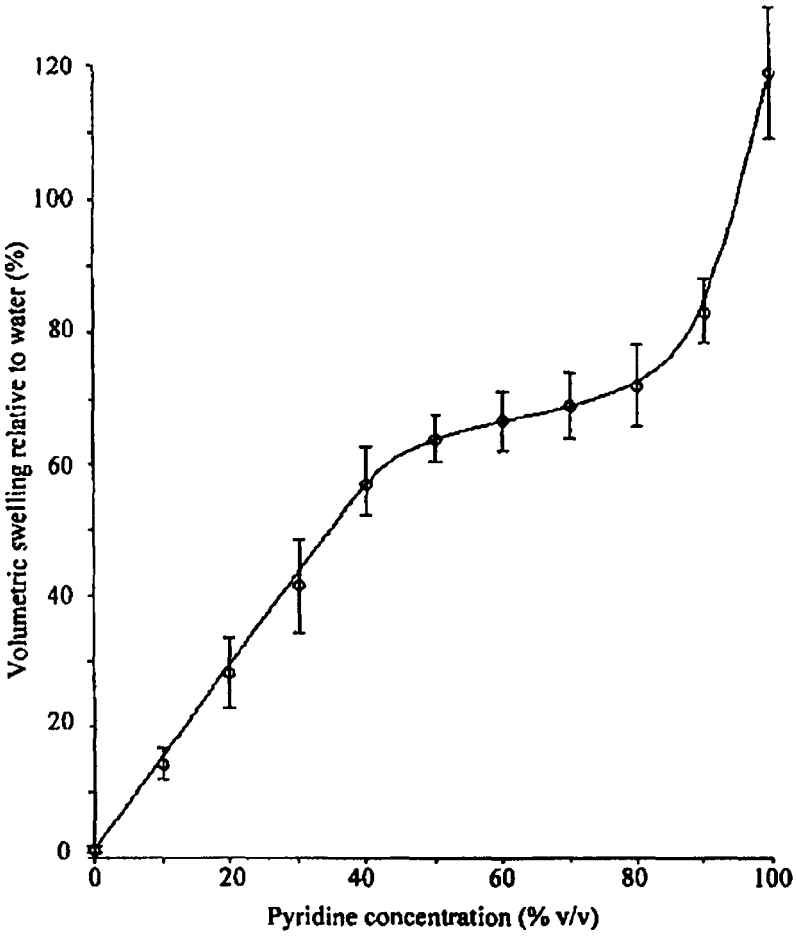


Figure 3.6: Graph of volumetric swelling relative to water with solutions of pyridine in toluene of varying concentrations (West, 1988).

Due to the requirement for modification reactions to take place in the absence of water, pyridine (purchased from Aldrich) was kept as dry as possible by storing it over KOH.

3.3.1.3. Wood

The wood used in the experiments was Scots Pine (*Pinus sylvestris*) and Corsican pine (*Pinus nigra*) sapwood obtained from North Wales forests. Pine sapwood was chosen because of its good permeability, essential in wood modification reactions.

In order to minimise any within species variability, the samples of each species, were prepared from a single board, from knot free sapwood. Also, samples with the same number of growth rings were preferentially chosen. Twelve thousand samples were screened for defects, such as small knots, sloping or curvy grain, and splits or cracks.

The specimen geometry was chosen in order to minimise the longitudinal dimension ensuring rapid reagent penetration into the cell lumen (average softwood fibre length is 3-4 mm). Hence, samples 20 x 20 x 5 mm (radial x tangential x longitudinal) were cut from kiln dried wood and carefully selected so that growth rings were parallel to the tangential face (Figure 3.7).

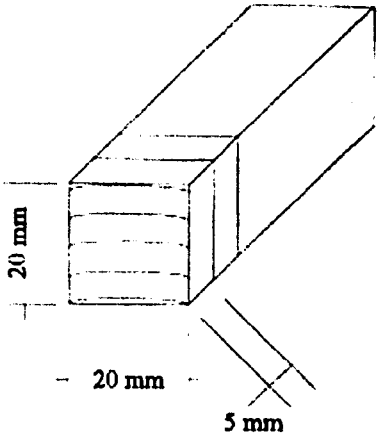


Figure 3.7: Preparation of wood samples.

3.3.1.4. Reaction mechanism

The reaction of an anhydride with the wood cell wall hydroxyl (OH) groups is one example of a generic class of reactions termed nucleophilic substitution at acyl carbon (Bender 1960; Satchell 1963). Reaction involves the attack on an electron deficient acyl carbon centre by a lone electron pair of a nucleophilic OH group associated with the cell wall polymers (Figure 3.8). This involves the formation of a four-centre intermediate (Figure 3.8). Reaction then proceeds by the cleavage of a carbon-oxygen bond to produce a carboxylic acid and covalently bonded acyl group (Figure 3.8). The rate of reaction of this step is dependent upon the nature of the leaving group. The four-centre intermediate (and associated transition states) has a higher energy than that of the two reactants, the difference between these two energies is the activation energy of reaction. In the case of pyridine catalysis, the lone electron pair of the nitrogen atom of the pyridine molecule attacks the acyl carbon of the anhydride to produce the acyl-pyridinium salt intermediate (Figure 3.8). The presence of the positive charge on the nitrogen atom proximal to the acyl carbon, makes the latter more susceptible to attack by a lone pair of the OH group (with no leaving group effect in this case). This has the effect of lowering the energy of the four-centre transition state, hence a lower activation energy for the reaction is observed. The acyl-pyridinium ion has been observed and established as a reaction intermediate in the aqueous hydrolysis of ethanoic anhydride (Bonner and Hillier 1973). However, this ion has not been detected in non-polar solvents and pyridine is more likely to act as a base catalyst in this case (Gold and Jefferson 1953).

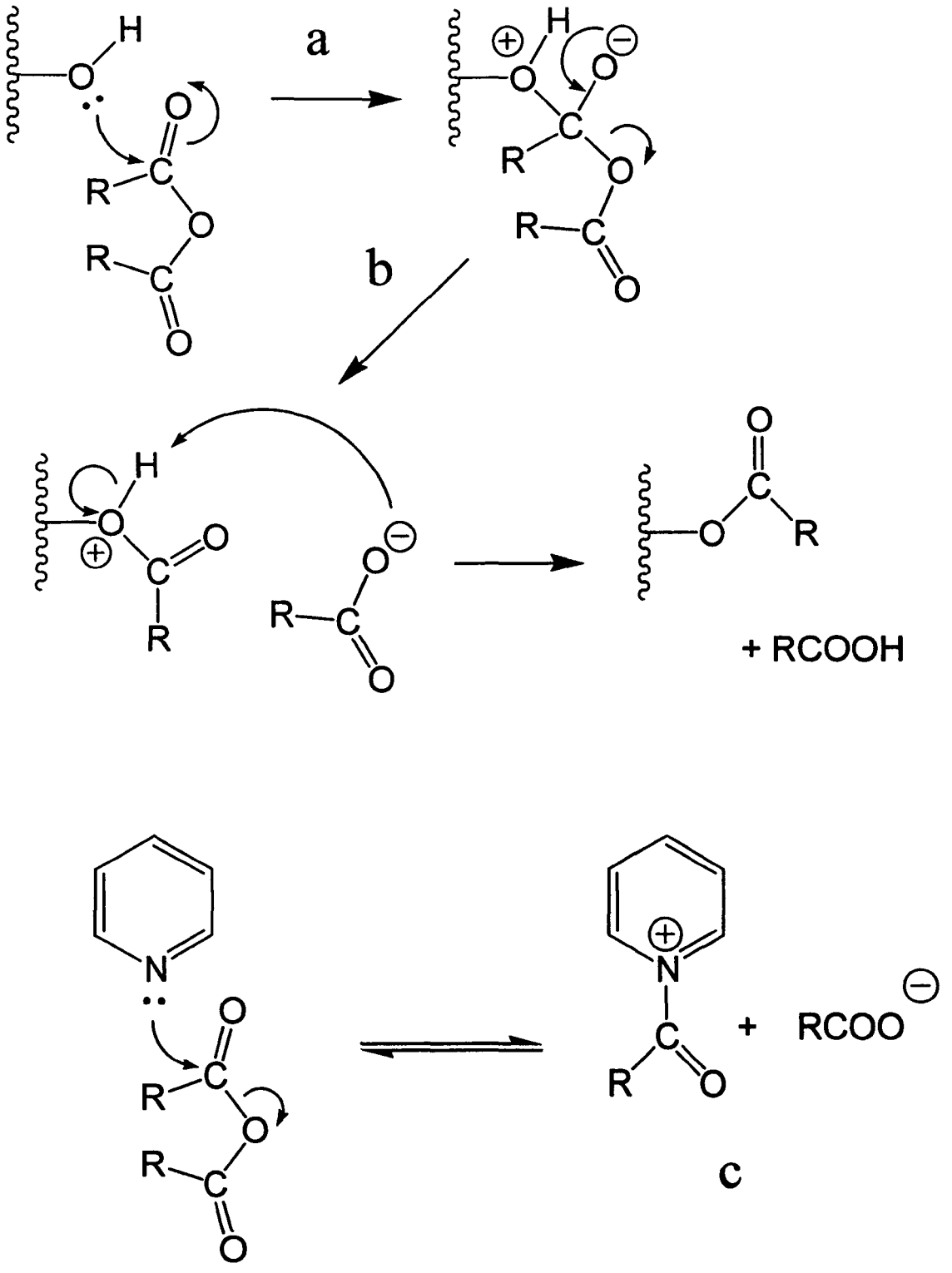


Figure 3.8: Reaction mechanism referred to in the text. (a). Nucleophilic attack of acyl carbon by oxygen lone pair of OH group. (b) Formation of ion pair from acetic anhydride. (c) Pyridine catalysed acetylation.

3.3.2. Reaction procedure

The purpose of the reaction procedure was to modify wood samples to a range of weight gains.

The procedure used for modifying samples is listed below:

- *Sample preparation*
  - Sanding
  - Soxhlet extraction
  - Labelling
  - Oven drying
  - Cooling to ambient temperature
  - Weight and dimension determination.
- *Impregnation*
  - Vacuum impregnation of samples with pyridine.
- *Reaction*
  - Preheating samples in excess of pyridine
  - Transferring to reactor for modification
  - Quenching in excess of acetone
- *Clean up*
  - Reflux in excess acetone.
  - Soxhlet extraction
  - Oven drying
  - Cooling to ambient temperature
  - Weight and dimension determination.

3.3.2.1. Sample preparation

After sawing, the samples were carefully lightly sanded to remove loose fibre which otherwise might be lost during reaction, affecting the weight gain measurements. Prior to use, all samples were subjected to Soxhlet extraction using a mixture of toluene: methanol: acetone (4:1:1 by volume) for six hours. Soxhlet extraction is required to remove extractives, which might otherwise be reacted in place of wood cell wall polymers (Rowell, 1975) or be extracted from the wood during the reaction

procedure, so affecting weight gain calculations. Where measures of weight gain are required to be as precise as possible such as in studies of reaction kinetics, prior extraction is essential. Following the extraction, the wood samples were labelled (2B pencil) and oven dried at 105^{0}C for 12 hours. The oven dried condition is essential since water reacts with anhydrides and needs to be removed prior to impregnation and reaction so all of the modifying chemical is available for reaction with wood polymers (Rowell, 1984) and will lead to depletion of effective reagent. Prior to modification, samples were transferred to a vacuum desiccator, containing silica gel, to cool to ambient temperature. Samples were then weighed on a four figure balance. Dimensions were determined using a micrometer accurate to +/- 0.01mm. Since wood is a natural material, it is inevitable that some sample to sample variation will occur. In order to take some account of this variation, yet limit the experiment to a managable number of samples, five replicates were used for each sample set and the results averaged.

3.3.2.2. Impregnation

The pre-weighed-measured oven dried wood samples were impregnated with dry (over KOH) pyridine prior to reaction, by subjecting samples to a vacuum of approximately 760 mmHg for 60 minutes, using a rotary vacuum pump.

The samples were then allowed to soak overnight in pyridine, after vacuum impregnation.

3.3.2.3. Reaction

The impregnated samples were pre-heated for one hour in a round bottom flask containing pyridine, set in an oil bath regulated to the desired temperature, i.e. 60, 70, 80, 90, 100, 110, 120^{0}C (+- 0.5^{0}C). For reaction temperatures, the upper limit was chosen to be 120^{0}C to minimise thermal degradation of the wood (Rowell, 1975a). The samples were then transferred in batches (5 replicates) to the reaction flask containing a one molar solution of the anhydride in pyridine, set in an oil bath as

above. A condenser, equipped with a drying tube containing anhydrous calcium chloride, was then fitted to the flask to minimise reaction of the modifier anhydride with atmospheric vapour. Samples were added at various time intervals so as to give a wide range of weight percent gains (reaction periods from 15 minutes to 7 hours). At the end of the reaction, the flask was removed from the oil bath and the still hot reaction solution decanted off. Ice cold acetone was then added to quench the reaction. The samples were left to stand in acetone for an hour.

3.3.2.4. Clean up

After reaction, it is necessary to remove solvent, unreacted modifying chemical and reaction by-product from the wood samples. For this reason, the samples were transferred to Soxhlet extractor and extraction performed using the standard 4:1:1 solvent system as above, for six hours. Although the wood was extracted prior to modification, one can assume that there remains the possibility that there are components within the wood that are removed by hot pyridine which are not extracted by the solvent system. Hill *et al.* (1998), performed a comprehensive series of experiments in order to determine the magnitude of this effect and they concluded that it is unlikely that extraction has any serious affect upon the kinetic data or activation energies derived therefrom. Following extraction, the samples were placed in an oven set at 105^0C and dried for 12 hours. After this, samples were transferred to a vacuum desiccator to cool to ambient temperature, then weighed and new dimensions were determined.

3.3.3. Calculations

The extent of the resulting modification was then measured in terms of the weight percent gain (WPG) of the wood sample associated with the reaction, and in terms of extent of hydroxyl (OH) substitution. This was done as follows:

$$WPG\ (\%) = \frac{Wmod. - Wunmod.}{Wunmod.} \times 100$$

Where Wmod. is the dry weight of modified wood and Wunmod. is the dry weight of unmodified wood

$$\text{OH substd. (mmoles/gm)} = \frac{\text{Wmod.} - \text{Wunmod.}}{\text{Wunmod.} \times M_w} \times 1000$$

Where M_w is the molecular weight of the adduct (-C(O)-R).

3.4. Results and discussion

3.4.1. Introduction

Any attempt to explain the nature of kinetic processes operating during wood modification has to take account of a number of factors, as discussed in detail in section 2.2.10.3. Briefly these include: (i) differences between surface and bulk reactive sites. (ii) differences in the chemical reactivities of the various hydroxyl groups (iii) various steric effects due to the different environments encountered in the material (iv) the complex porous nature of the cell wall.

Further complications arise since the substrate swells as modification proceeds, thus the substrate alters and additional reactive sites become available as a consequence. In addition, extensive hydrogen bonding networks exist within the cell wall and it is necessary for such bonds to be broken before reaction may proceed. The situation considered in this thesis is one in which the wood is already fully swollen with solvent before exposure to reagent, and this effect can therefore be ignored.

3.4.2. Kinetic profiles

The results for the reaction of a homologous series of linear chain carboxylic anhydrides with Corsican and Scots pine sapwood at a range of temperatures are shown in Tables 1 to 70 and in Figures A. 1.1 to A.1.5 (see Appendix 1).

Figure 3.9 shows a representative kinetic profile for the reaction of Corsican and Scots pine with acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e) anhydride at 120 ^{0}C. The units of y-axis are given as the number of hydroxyl groups substituted per gm of wood (in mmoles per gram). This is equivalent to the number of moles of acyl groups substituted, and calculated by dividing the weight gain per gram by the molecular weight of the substituting group (adduct) (see section 3.3.3).

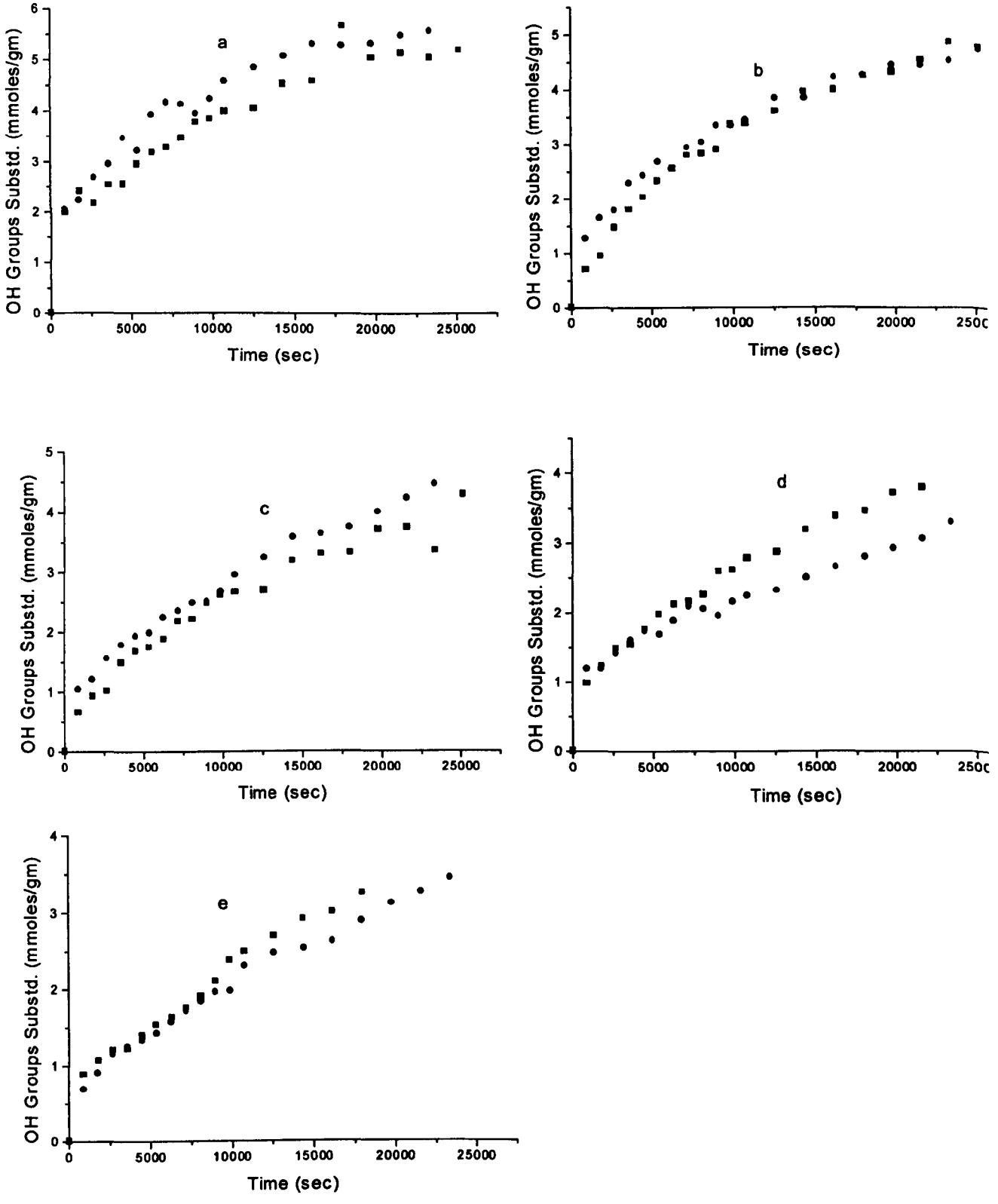


Figure 3.9: Kinetic profile for reaction of Corsican (squares) and Scots pine (circles) sapwood at 120 ^{0} with acetic (a), propionic (b), butyric (c), valeric (d), and hexanoic anhydride (e).

The kinetic profile of the reaction of the series of the anhydrides studied with Corsican (a) and Scots pine (b) sapwood at 120^0C is compared in Figure 3.10. From this, it can be seen that the reaction curves show an asymptotic profile, with lower rates of reaction and ultimate degree of substitution as size of anhydride increases. It can be also observed that the reaction profiles are very similar for the two wood species studied (see Figure 3.9). It can be also seen that most of the substitution does not take place in the first ten minutes of the reaction, in contrast to the report by Rowell (1975).

It has to be stressed that the standard deviations of the data are relatively very small (see Tables 1.1 to 1.70 in Appendix 1).

The understanding of the factors affecting the rate of reaction requires consideration of the reaction of two types of site with the reagent, namely surface and bulk sites. Reaction at the surface may be considered to be affected by the concentration of the reagents only, whereas reaction in the bulk of the material requires that the reagent molecule reaches a reactive site before reaction can proceed. These are discussed in detail herein.

3.4.3. Surface reactions

In such reactions, the two reagents are the anhydride molecules, and the wood hydroxyl groups. The rate of expression for such a reaction can be written (Atkins, 1987):

$$\text{Rate} = \frac{d[OH]}{dt} = -k\,[OH]\,[anhyd] \qquad (3.1)$$

Where [OH] is the concentration of hydroxyl groups and [anhyd] is the concentration of anhydride reagent. Such a reaction is referred to as second-order since the rate depends upon the concentration of two components.

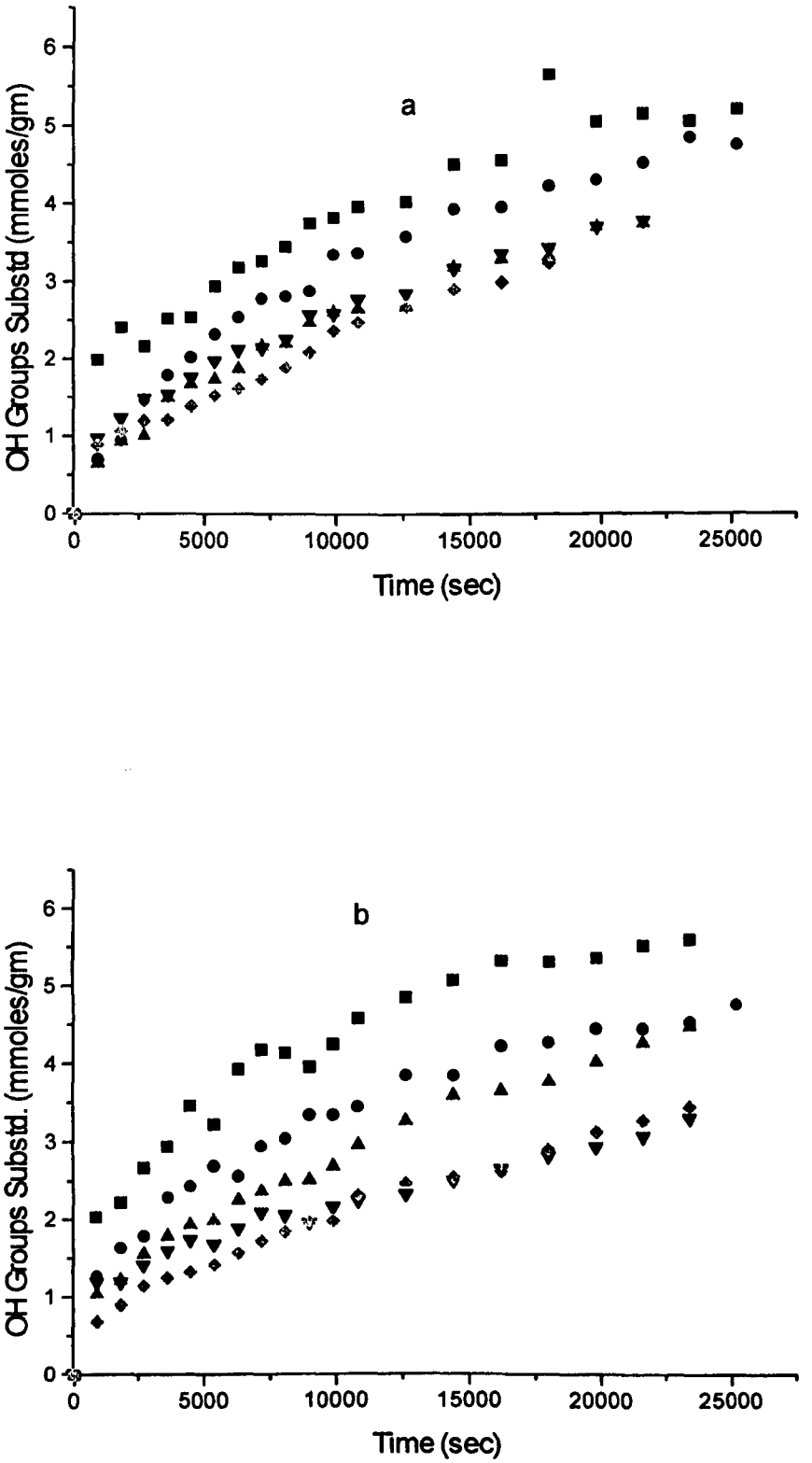


Figure 3.10: Kinetic profile for reaction of Corsican (a) and Scots (b) pine sapwood at 120°C with acetic anhydride (squares), propionic (circles), butyric (triangles), valeric (down triangles) and hexanoic anhydride (diamonds).

In a conventional homogeneous chemical reaction, the two reagents are dispersed throughout the solvent evenly. When performing the reactions on wood blocks, as is the case with the work presented in this thesis, the hydroxyl groups are located in a small volume within the solution; thus the concentration of anhydride reagent is in large excess compared with the number of surface sites which represent a small proportion of the total OH group content. This is to say that reaction has an insignificant effect on the 'reservoir' of reagent molecules in solution. Furthermore, during the initial stages of the reactions it is reasonable to assume that the 'surface' sites will dominate the kinetics (Hill and Jones, 1996a). Therefore, initially, the change in concentration of anhydride reagent will be very small and it is legitimate to write $[anhyd]_0=[anhyd]_t$; where $[anhyd]_0$ is the concentration of anhydride at time t=0. Under these circumstances the reaction becomes pseudo first-order, since the reaction is dependent upon the concentration of hydroxyl groups only, thus:

$$\text{Rate} = \frac{d[OH]}{dt} = -k'[OH] \qquad (3.2)$$

Where k' is the rate constant of the pseudo first- order reaction. Such an expression can be rearranged and integrated to yield the following expression:

$$\ln([OH]_t / [OH]_0) = -k't \qquad (3.3)$$

Where $[OH]_t$ and $[OH]_0$ are the concentrations of unsubstituted hydroxyl groups at time = t and time = 0 respectively, k' the pseudo first order rate constant, and t the reaction time.

The quantities $[OH]_t$ and $[OH]_0$ are calculated from the estimate of 14.9 mmoles/gm of OH groups in unreacted wood, based upon the chemical composition of the cell wall polymers (see Table 1.1.A and equation 1.1.A in Appendix 1B). This calculation, however, takes no account of the hydroxyl groups which are not accessible to reagent, such as the hydroxyl groups of the cellulosic component in the crystalline regions (within the interior of the microfibril) and possibly some hydroxyl groups of the hemicelluloses which are intimately associated with the microfibrils. In addition, the

absolute hydroxyl content of the lignin is not known with certainty, and will vary from species to species and within a wood sample. Thus, any attempt to determine the accessible OH content will inevitably lead to an error. However, the number of hydroxyl groups substituted is readily determined (see section 3.3.3).

It is possible to determine if first-order kinetics dominate the reaction process by plotting the natural logarithm of the concentration of hydroxyl groups substituted at time t, dividing by the concentration at time zero, against time in seconds; this will yield a straight line. The gradient of this line is equal to the rate constant, if first-order kinetics is obeyed. Since as noted above, the absolute OH content is not known accordingly, the absolute rate constant is not determined. However, for comparative studies on determination of Ea, this is not important.

The results for the analysis of the reaction profiles in terms of first-order kinetics for the series of anhydrides studies are shown in Figures A.1.6 to A.1.15 (see Appendix 1).

An example is given in Figures 3.11 and 3.12 for the reaction of the series of the anhydrides studied with Corsican and Scots pine sapwood at 120^0C. It can be seen in Figures 3.11 a and 3.12 a, that a first order relationship is not obeyed for acetylation, and it is not possible to obtain a rate constant from these plots. It will be demonstrated in section 3.4.4 that with acetic anhydride, the reaction process is diffusion. In contrast, with the other anhydrides studied (see Figures 3.11 b, c, d, e and 3.12 b, c, d, e) a linear relationship is indeed obtained, consistent with the hypothesis that first order kinetics are dominant during the initial stages of the reactions, and therefore, is possible to obtain a rate constant from these plots. This behaviour is typical for all the temperatures studied (see figures A.1.6 to A.1.15 in Appendix 1).

From the results presented in Figures A.1.6 to A.1.15 (see Appendix 1) the following general observations have been made:

(i) As reaction temperature decreases, first order kinetics is observed over longer time periods.

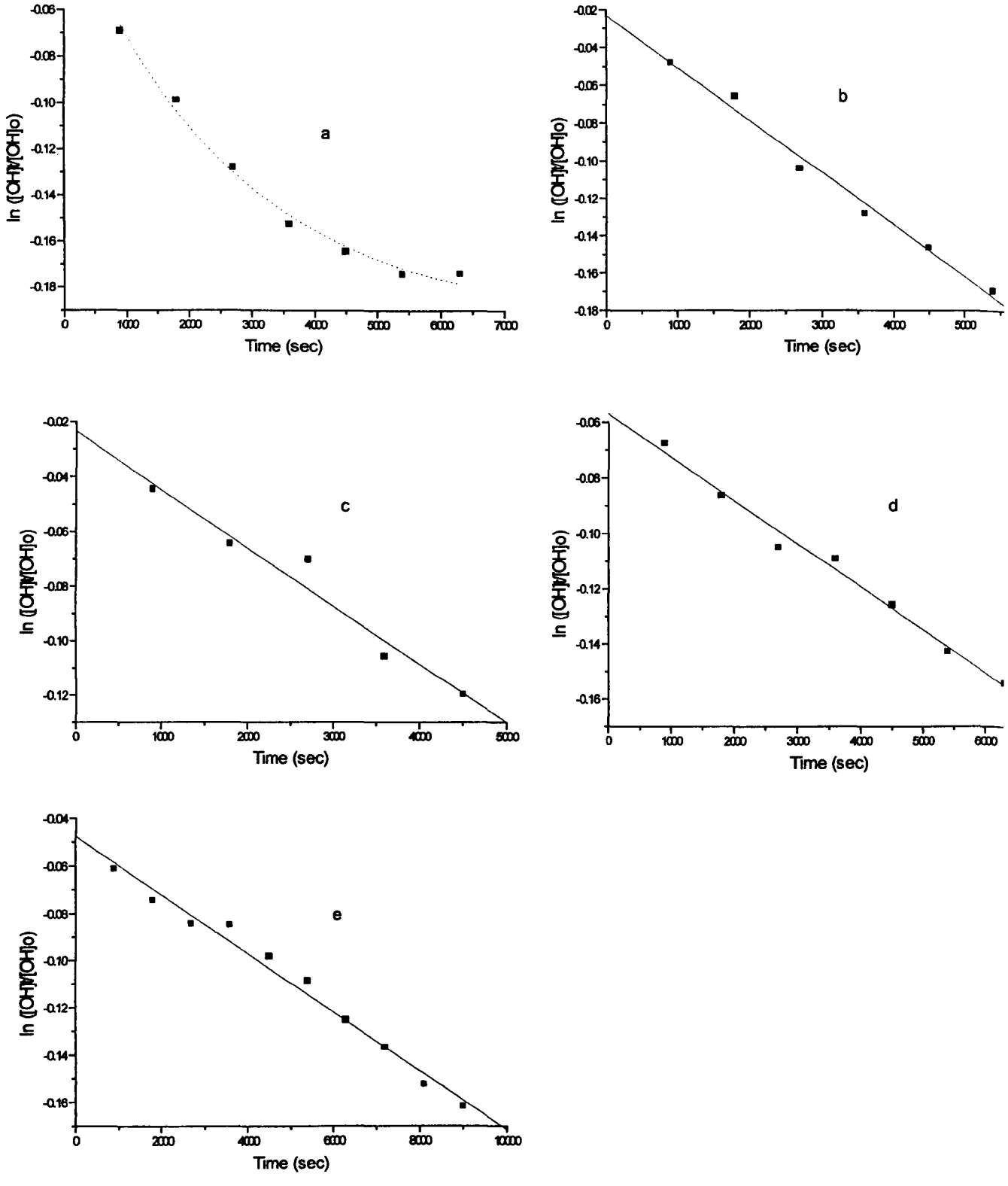


Figure 3.11: First order kinetic plot for reaction of Corsican pine sapwood at 120 ^{0}C with acetic anhydride (a), propionic (R^2=0.99) (b), butyric (R^2=0.98) (c), valeric (R^2=0.99) (d) and hexanoic anhydride(R^2=0.99) (e).

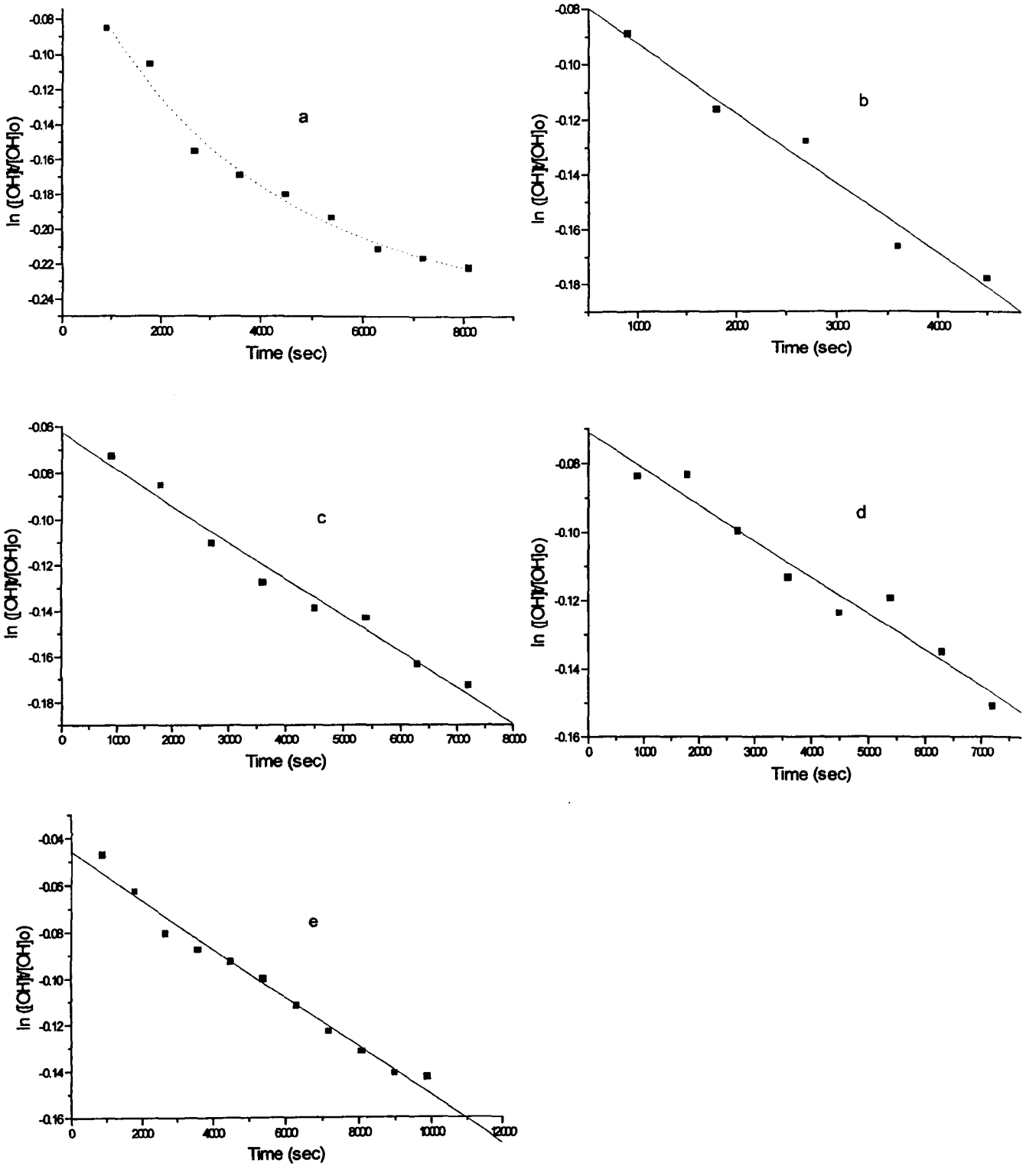


Figure 3.12: First order kinetic plot for reaction of Scots pine sapwood at 120 ^{0}C with acetic anhydride (a), propionic (R^2=0.98) (b), butyric (R^2=0.98) (c), valeric (R^2=0.99) (d) and hexanoic anhydride(R^2=0.99) (e).

(ii) As reagent size increases (for all but acetic anhydride) there is a greater likelihood of observing first order kinetics during the initial part of the reaction.

The activation energy for the surface reaction can be determined by measuring the rate constant at a series of temperatures, and evaluating using the Arrhenius expression:

$$k = A \exp(-Ea / RT) \quad (3.4)$$

Where Ea is the activation energy of the process, R the universal gas constant, T the absolute temperature, and A the pre-exponential or collision factor. Thus, by plotting the natural logarithm of the rate constant against reciprocal absolute temperature, a straight line of slope –Ea / RT is obtained, if the Arrhenius expression is obeyed.

Arrhenius data for reaction of the anhydrides with Corsican and Scots pine sapwood is shown in Tables 72 and 73 respectively (see Appendix 1).

Figures 3.13 and 3.14 show typical Arrhenius plots obtained from the rate constant data for the reaction of propionic anhydride with Corsican and Scots pine, respectively. Arrhenius plots for the series of the anhydrides studied are shown in Figures A1.16 to A1.25, in Appendix 1. From these plots, the gradient of the straight line was multiplied by a factor of 8.314 JK^{-1} mol^{-1} (the universal gas constant) in order to calculate the activation energies of the reactions. This has been done for the series of the anhydrides studied and the results are shown in Table 3.1, presented later in the chapter.

Although the rate constants could not be determined for the acetylation process in both substrates studied, as discussed earlier in the chapter, it is nonetheless still possible to evaluate an activation energy for the surface reaction processes only, by using the method of initial rates first developed for determining the Ea of swelling of wood by various solvents (West, 1988). The method relies upon determining the gradient of the rate curve at zero time to give the initial rate (Ro). The initial rate of

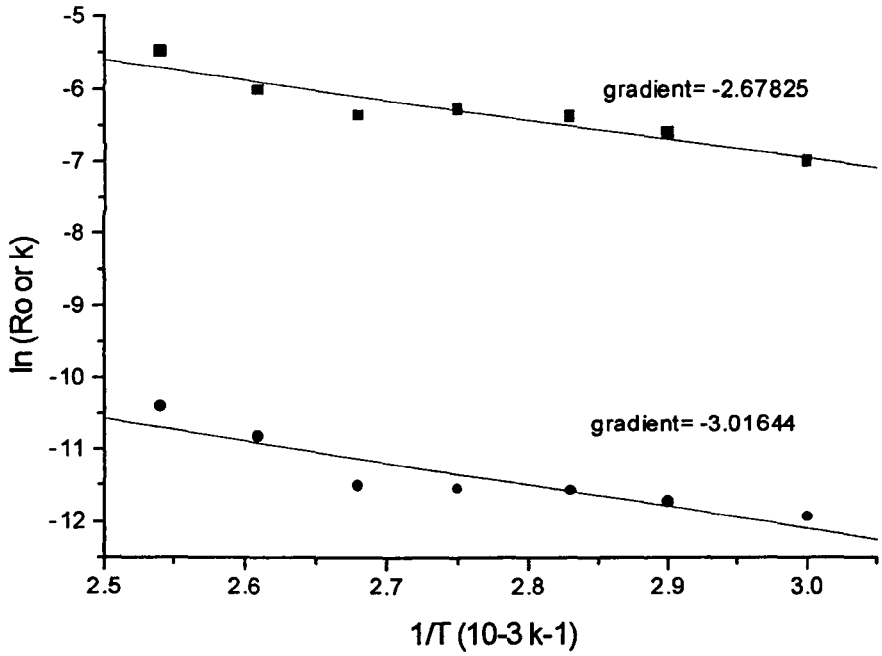


Figure 3.13: Arrhenius plot for reaction of propionic anhydride with Corsican pine (squares: initial rate data; circles: rate constant data).

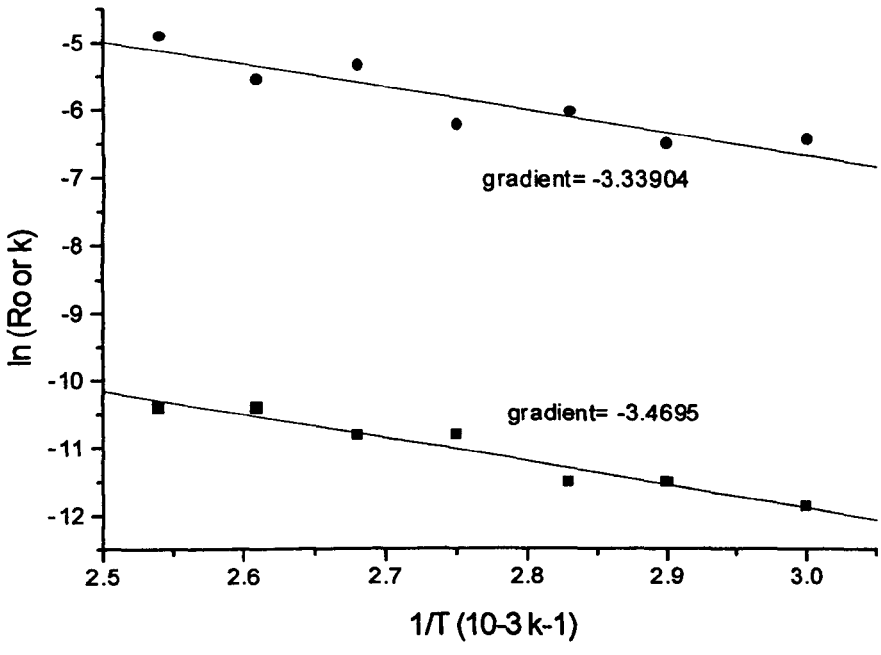


Figure 3.14: Arrhenius plot for reaction of propionic anhydride with Scots pine (circles initial rate data; squares: rate constant data).

the reaction is defined as the rate of the reaction at time zero, and is giving by the following relationship:

$$Ro = -k' [OH]_0 \quad (3.5)$$

Where $[OH]_0$ is the concentration of hydroxyl groups at time zero.

Since Ro is proportional to k', then it is legitimate to substitute initial rate for k' in the Arrhenius expression. This is because the Ea is determined from the slope of k' *vs* T). Assuming $[OH]_0$ is constant at different temperatures, thus allows for direct substitution of Ro for k' (West, 1988). The invariance of the hydroxyl group concentration with temperature cannot be assumed, since it is known that wood exhibits temperature dependent swelling with solvents such as pyridine (West, 1988; Mantanis *et al.* 1994b). The time to half-swell with pyridine has been estimated and varies from 13 min at 40^0C to 0.8 min at 100^0C. However, it has been proposed (Hill and Jones, 1996a) that it is possible to remove this variable from the experiment by allowing sufficient time for the wood blocks to equilibrate. Thus, it is expected that the assumption that $[OH]_0$ is invariant with temperature is true. If this is so, then the Ea's obtained by the two methods should be equal.

Typical rate curves for the reaction of the series of the anhydrides studied with Corsican and Scots pine sapwood at 120^0C are shown in Figures 3.15 and 3.16 respectively (Curves for the other temperatures studied are shown in Figures A.1.26 to A.1.35, in appendix 1). An exponential fitting function was used for the curve fitting, and the fit was limited to the early stages of the reaction only, since it was found that data points obtained thereafter distorted the fit. It should be stressed here, that an important factor for selecting the best fit, apart from fitting the data points, was that the curve must pass through the value of 14.9 mmoles/gm at zero time, otherwise the initial rate is not determined. It is apparent therefore that the calculation of activation energies by initial rate method is very sensitive to the curve fitting parameters. Therefore, the results obtained should be treated with caution.

Arrhenius data for modified Corsican and Scots pine sapwood is shown in Tables 74 and 75 respectively (see Appendix 1).

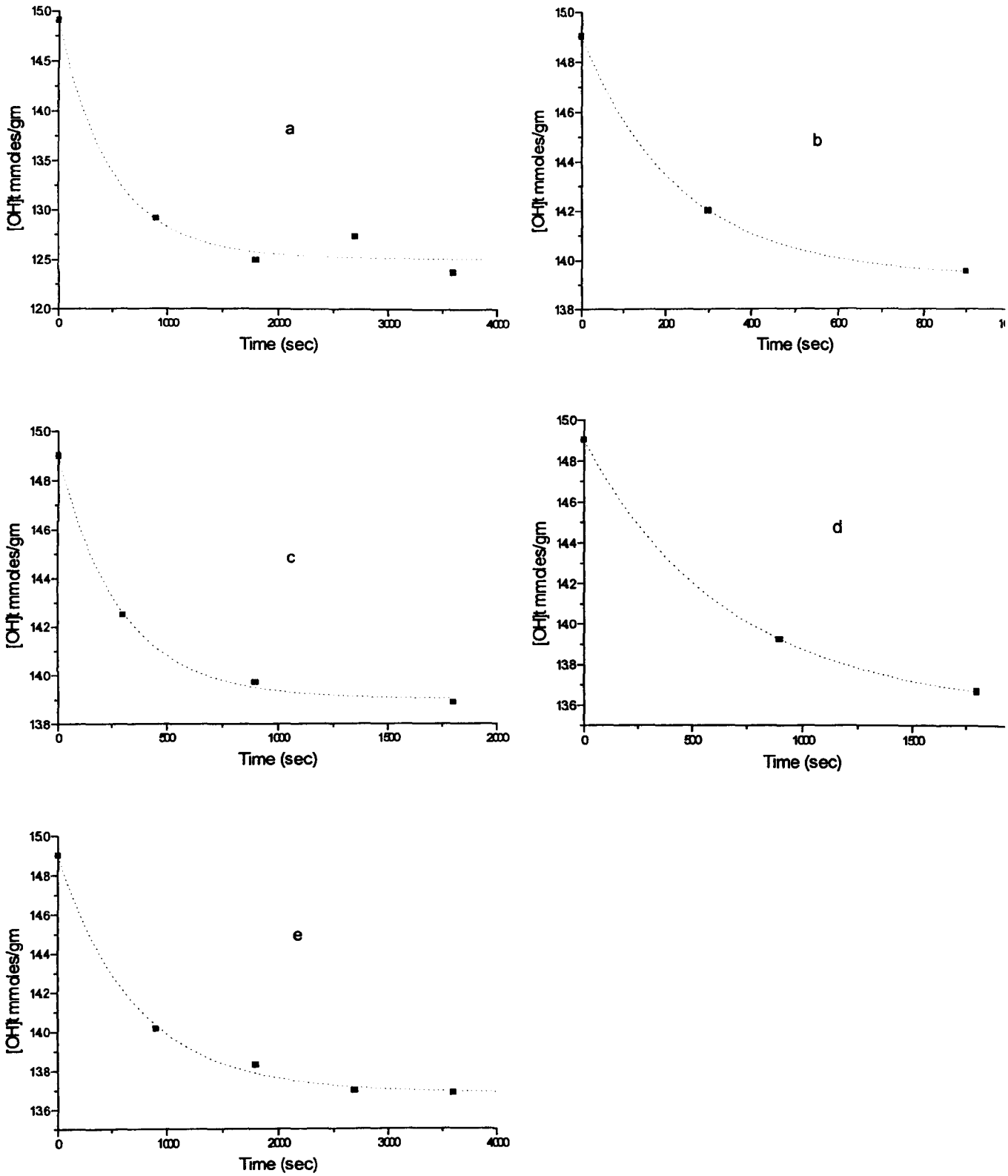


Figure 3.15: Exponential curve fit to kinetic data for reaction of Corsican pine sapwood at 120 ^{0}C, with acetic anhydride (a), propionic (b), butyric (c), valeric (d) and hexanoic anhydride (e).

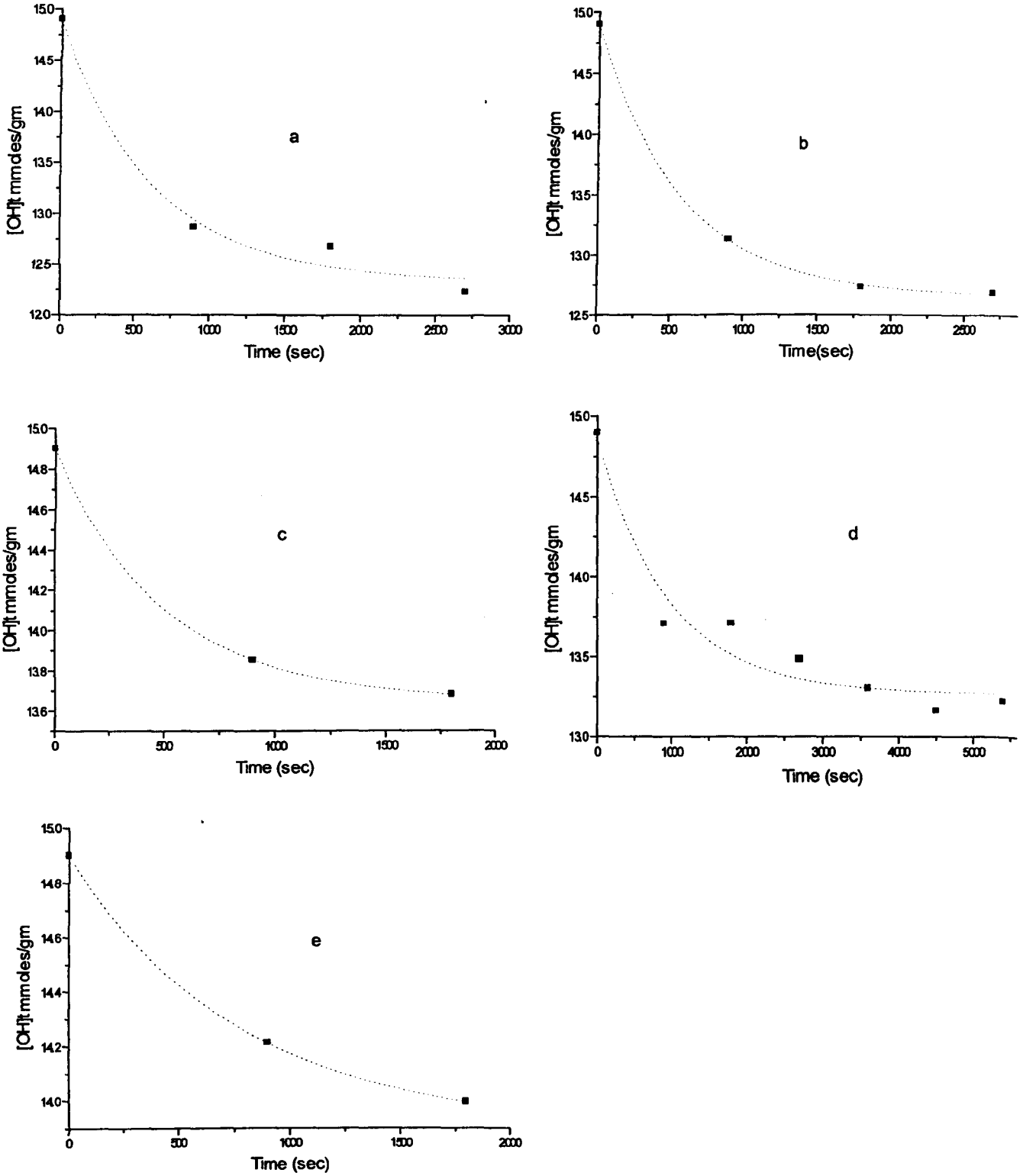


Figure 3.16: Exponential curve fit to kinetic data for reaction of Scots pine sapwood at 120 ^{0}C with acetic anhydride (a), propionic (b), butyric (c), valeric (d) and hexanoic anhydride (e).

Figures 3.13 and 3.14 (presented earlier in the chapter) show typical Arrhenius plots obtained from the initial rate data for the reaction of propionic anhydride with Corsican and Scots pine respectively. Arrhenius plots for the series of the anhydrides studied are shown in Figures A1.16 to A1.25, in Appendix 1. There is evidence of considerable scatter of the data using both methods. This scatter is an inevitable consequence of the variable nature of the substrate, and emphasises the need to obtain data at a sufficient number of temperatures, in order that confidence may be placed in the activation energies obtained. Since the gradient of the straight line must be multiplied by a factor 8.314 Jk^{-1} mol^{-1} in order to calculate the activation energies, it is inevitable that any error in the determination of the gradient will lead to a greater error in determining the activation energy.

The data obtained from this set of experiments is presented in Table 3.2. It is apparent that determination of activation energies of acylation by the methods of initial rates and rate constant have given comparable values, in contrast with earlier work on propionylation (Hill and Jones, 1996a).

Table 3.2: A comparison of activation energies for the reaction of linear chain anhydrides with Corsican and Scots pine sapwood, determined from rate constant and initial rate data. (Standard deviations in parentheses).

Substrate	**Anhydride**	**Activation energy ($kJmol^{-1}$)**	
		Initial rate data	Rate constant data
Corsican pine	Acetic	37.1 (+-5.1)	-
Corsican pine	Propionic	22.0 (+-3.9)	24.8 (+-6.2)
Corsican pine	Butyric	18.9 (+-4.9)	20.0 (+-3.6)
Corsican pine	Valeric	17.1 (+-1.9)	17.3 (+-5.8)
Corsican pine	Hexanoic	13.9 (+-1.3)	8.3(+-1.1)
Scots pine	Acetic	42.1 (+-10.8)	-
Scots pine	Propionic	27.5 (+-7.5)	28.5 (+-4.4)
Scots pine	Butyric	19.4 (+-2.6)	20.0 (+-3.7)
Scots pine	Valeric	17.3 (+-1.8)	13.0 (+-1.1)
Scots pine	Hexanoic	11.9 (+-0.5)	13.2 (+-0.9)

In acetylation, of both substrates studied, the method of initial rates has been found to yield values for activation energy which are in reasonable agreement with literature reported values for both heterogeneous and homogeneous reactions (see Tables 3.3 and 3.4 respectively), bearing in mind:

- Firstly, that the system under study here is a catalysed process and thus a lower activation energy for this process should be expected.

- Secondly, that even with homogeneous systems, activation energies are determined with an accuracy of no more than +/- 5 kJ/mol at best.

- and finally, that in some cases, data was not obtained at a sufficient number of temperatures compared with those in this thesis, and therefore reported values of Ea's on lignocellulosic materials (especially whole wood) should be treated with some caution.

Table 3.3: Literature values for the activation energy for reaction of acetic anhydride with cellulosic materials in heterogeneous systems.

Solvent system	**Substrate**	**Activation energy ($kJmol^{-1}$)**
$HClO_4$	Cellulose	60.6[a]
$HClO_4$	Jute	54.3[b]
$HClO_4$	Cotton	71.3[b]

a: Frith, 1963.

b: Sen and Ramaswamy, 1957.

Table 3.4: Literature values for the activation energy for acetylation of ethanol with acetic anhydride.

Solvent system	Activation energy ($kJmol^{-1}$)
CCl_4	57.7[a]
Ethanol	78.7[b]
Hexane	51.9[b]
CCl_4	66.1[b]
$CHCl_3$	70.6[c]
CCl_4	58.1[c]
Ethanol	72.3[c]
Heptane	47.2[c]

a: Janelli and Baretta, 1959.

b: Moelwyn-Hughes and Rolfe, 1932.

c: Ono, 1952.

Literature activation energies, for reaction of carboxylic acid anhydrides with wood are presented in Table 3.5. The reproducibility of the data is revealed by comparing this set of data with that presented in Table 3.2. It can be seen that there is excellent agreement between the two sets of data. Therefore, this work shows that it is possible to obtain reproducible activation energies for reaction of anhydrides with such an exceedingly complex substrate such as wood.

The values of activation energy obtained for the reaction of the larger anhydrides with Corsican and Scots pine compared with the values of acetylation under identical conditions are approximately 10-30 $kJmol^{-1}$ lower. This indicates that a different mechanism operates between acetylation and the acylation with larger anhydrides. The values of Ea's obtained for the reaction of wood with larger anhydrides are far lower than the values typically found in chemical processes, which are generally in the range 50-100 $kJmol^{-1}$.

Table 3.5: Literature activation energies for the reaction of linear chain anhydrides with Corsican and Scots pine sapwood.(Standard deviations in parentheses).

Substrate	Anhydride	Activation energy ($kJmol^{-1}$)	
		Initial rate data	Rate constant data
Corsican pine	Acetic[a]	41.6 (+-8.0)	-
Corsican pine	Propionic[b]	31.3 (+-0.4)	23.8 (+-0.3)
Corsican pine	Butyric[c]	20.2 (+-8.6)	13.7 (+-5.9)
Corsican pine	Hexanoic[d]	18.0 (+-2.8)	13.8(+-2.8)
Scots pine	Hexanoic[d]	8.7 (+-2.7)	11.2 (+-2.9)

a: Hill *et al.* 1998

b: Hill and Jones, 1996b

c: Hill and Strickland, unpublished results

d: Hill and Cetin, unpublished results.

The values of Ea for acylation with larger anhydrides than acetic, and indeed the activation energy obtained for propionylation, are close to that for the energy of the hydrogen bond in the wood matrix, which has been estimated at 20-25 $kJmol^{-1}$ (Morrison and Dzieciuch, 1959; Stamm, 1964).

It has been postulated that with propionic anhydride, the activation energy for reaction indicates that hydrogen bond breaking is the rate determining step of the reaction (Hill and Jones, 1996b). The validity of this hypothesis is discussed later in the chapter.

Table 3.2 shows that the molecular weight of the reagent clearly has an influence upon the activation energy, i.e. the activation energy decreases, as the molecular weight of the reagent increases.

At this stage, one may consider whether the interaction of anhydride with the substrate is important. For this reason, it was decided to perform reaction in solution using a series of phenolic model compounds. The methodology and the results of this study will be described in the chapter that follows, where it will be shown that the decrease in activation energy for the reaction of phenolic model compounds with anhydrides in any case will be far lower than that found for reactions with wood. It will be therefore concluded that the systematic decrease in activation energy as chain length of anhydride increases, is a consequence of performing the reactions with wood.

By referring to Table 3.2, it can be seen that the values obtained for propionic anhydride form part of a clear trend, which is more clearly illustrated by referring to Figures 3.17 and 3.18, where the relationship between molar volume of the anhydride *versus* the activation energy, determined by the initial rate method, has been plotted. An exponential relationship is obtained for all of the anhydrides and this holds for both substrates studied in this thesis, suggesting that the reagent volume is an important factor in determining the activation energy.

It was mentioned before, that it has been postulated that with propionic anhydride, the activation energy for reaction indicates that hydrogen bond breaking is the rate determining step of the reaction (Hill and Jones, 1996b). If hydrogen bond breaking was the rate determining step for longer chain anhydrides, then a random distribution (like the hypothetical one illustrated in Figure 3.19) of activation energies around the value of 25 kJ/mol (energy of hydrogen bond) would be expected.

It is concluded therefore, that hydrogen bond breaking is not the rate determining step for any of the reactions. It is unlikely that hydrogen bond breaking plays any part in the reaction process, since the wood samples are fully swollen with pyridine before the reaction is initiated. It is therefore probable that hydrogen bonding networks only exist where hydroxyl groups are inaccessible, such as crystalline regions of cellulose for example.

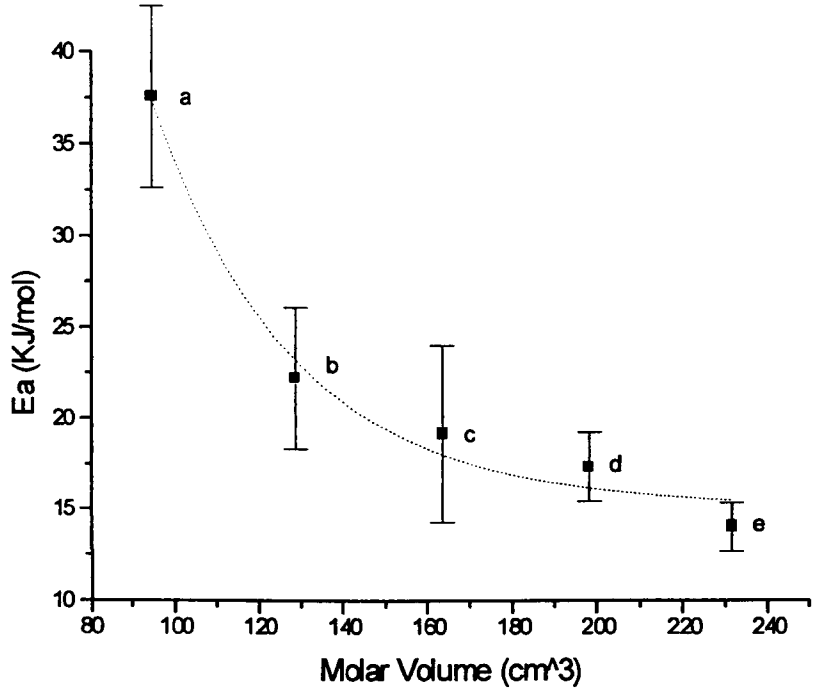


Figure 3.17: Relationship between activation energy and molar volume of reagent [(a) acetic, (b) propionic, (c) butyric, (d) valeric, (e) hexanoic anhydride] for reaction of Corsican pine, and using the activation energies determined from initial rate data.

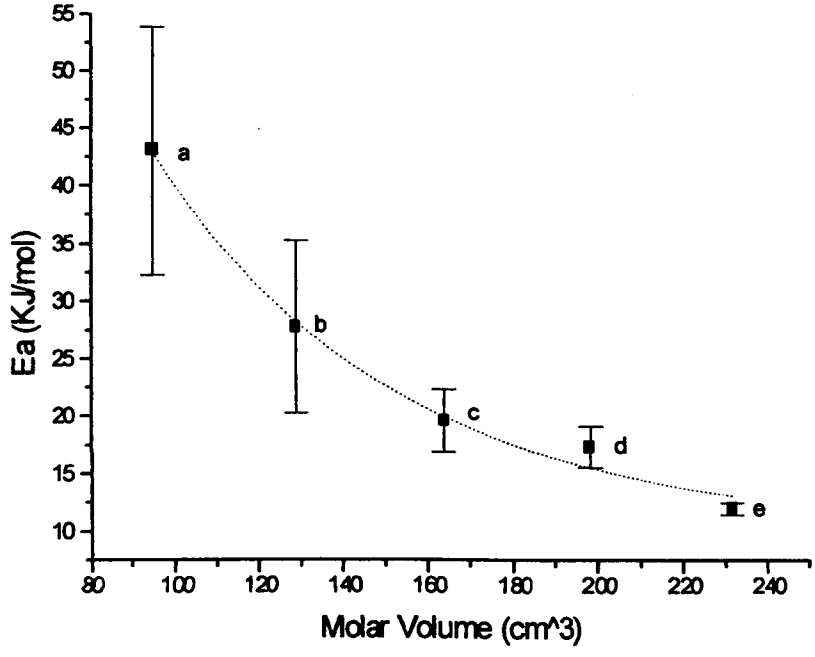


Figure 3.18: Relationship between activation energy and molar volume of reagent [(a) acetic, (b) propionic, (c) butyric, (d) valeric, (e) hexanoic anhydride] for reaction of Scots pine, and using the activation energies determined from initial rate data.

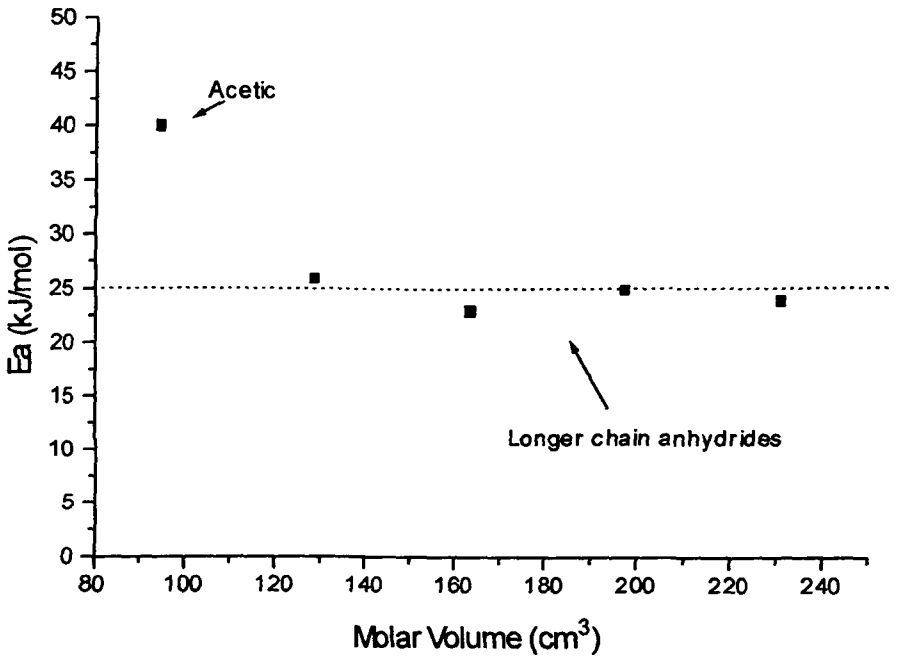


Figure 3.19: Relationship between activation energy and molar volume of reagent, applied to the hypothesis that hydrogen bond breaking is the rate determining step of the reaction between larger chain anhydrides and wood hydroxyl groups.

In addition to investigating the effect of different reagents upon the activation energy, the effect of substrate was also investigated. From the results presented in Table 3.2, it appears that there is no significant difference in activation energies for reaction with either of the two species used in this study.

The results obtained in this study show that for reaction with wood, as the molecular weight of the anhydride increases, the activation energy of the reaction decreases. It is clear that when the reaction is performed on wood, this has a profound effect upon the activation energy. This effect becomes more pronounced as the molecular weight (and hence size) of the anhydride increases. Reagent molecules within the cell wall polymeric network are clearly subject to considerable steric constraints. As size of reagent molecule increases, the freedom of motion within the cell wall microvoids proximal to the accessible hydroxyl groups decreases proportionately. It is therefore unlikely that as reagent size increases, the molecules present within the cell wall obey a classic Maxwell-Boltzmann type energy distribution as would occur in solution, where there is no such constraint upon molecular motion. Thus, as the temperature of reaction increases, the fraction of molecules having energies exceeding the activation energy of reaction will be influenced by the size of reagent in addition to the

temperature of reaction. As a result, the increase in the rate of reaction as the temperature of reaction increases, will be far lower that would be observed in homogeneous solution. As a consequence, the *apparent* energy of activation will be lower than would be observed in solution (since a small change in rate constant with temperature yields a low value for activation energy). With a small reagent molecule, such as acetic anhydride, the value for the energy of activation in wood is similar to that observed in solution (as will be shown in the following chapter), suggesting that the motion of the molecules within the cell wall microvoids is not significantly affected when compared with molecules in solution.

It is well known that the motion of molecules within pores is strongly influenced by the pore geometry. In a study of the motion of benzene molecules within graphite, it was shown that with pore widths greater than 3.5 nm, bulk behaviour was exhibited in the centre of the pore at 300 K, with the influence of the pore wall extending out to 1.7 nm (Steele, 1999). Other studies have shown that translational diffusivities of molecules are reduced by confinement within pores (Magda *et al.* 1988), particularly when pore widths are of the order of 3 nm and lower (Padilla and Toxvaerd, 1994). Motions of alkanes within the pores of zeolites have been shown to be influenced by molecular size (Schuring *et al.* 2000). The translational motions of water molecules within porous silica has been shown to be lower by a factor of two in 3.0 nm pores, compared with 10.0 nm pores, where such motion is comparable with the bulk phase (Takamuku *et al.* 1997). It is therefore reasonable to expect that the translational motion of molecules within the cell wall micropores must be severely restricted when compared to the solution phase, and there is a proportionally greater restriction upon translational motion in the micropores as the size of the molecule increases. There must therefore be some doubt as to the validity of applying conventional collision theory to reactions within the cell wall of wood

In conclusion, it is suggested that the lower values obtained for the activation energies for reaction of carboxylic acid anhydrides with wood are related to the restricted space surrounding the accessible hydroxyl groups. As a consequence of this, increasing the temperature of reaction has only a limited effect upon the motion of the longer chain length anhydrides. Hence, rather than determining a true activation energy, the value obtained is a consequence of the limited free space surrounding the hydroxyl groups.

3.4.4. Bulk reactions

It was stated in section 3.4.2, that the understanding of the factors affecting the rate of reaction requires the consideration of the reaction of two types of site with the reagent, namely surface and bulk sites. The former was extensively discussed in section 3.4.3, where activation energies for the surface reactions have been determined. This section discusses the reactions in the bulk of the wood matrix.

As reaction proceeds, the reagent will penetrate into the interior of the wood matrix, and reaction with bulk sites will occur. The driving force for such a process is the difference in concentration between reagent molecules distributed in the solvent at the surface of the cell wall, and the concentration of same within the cell wall. In the situation where the chemical reaction is rapid, compared with diffusion rate, the reaction will be under diffusion control. The process of heterogeneous kinetics limited by diffusion, has previously been described (Pannitier and Souchay, 1967). In this treatment, a derivation for the rate of reaction is obtained using Fick's law to describe the rate of diffusion. By considering the case of reaction on a plane front, the following expression is obtained:

$$m^2 = -2\, D\, \rho\, S^2\, c\, t \quad (3.6)$$

Where D is the diffusion coefficient, ρ the density of the reagent, S the surface area through which the reagent is diffusing, c the concentration gradient, and t the time. Assuming D, ρ, S, and c to be constant, the expression may rewritten more simply as:

$$m = a\, t^{1/2} \quad (3.7)$$

Where *m* is the mass change at time t, and a is a constant which is related to the diffusion coefficient. The surface area through which the reagent diffuses may not be a constant since the wood may swell to different degrees at different temperatures. However, in a study of pyridine swelling of wood it was noted that the ultimate degree of swelling was constant, although the time for maximum dimensional changes was temperature dependent (West, 1988). Since the samples were allowed to

equilibrate for one hour in pyridine before reagent was added, ample time was allowed for the blocks to achieve maximum swelling before reagent was added. Other treatments based upon Fick's law also give a square root time dependence for mass increase with diffusion dominated processes (Comstock, 1963). Thus a plot of mass change *versus* square root of time will indicate that diffusion is the limiting kinetic process, if a linear relationship of gradient (a) is observed.

Figure 3.20 is a diffusion plot for the reaction of the series of anhydrides studied with Corsican and Scots pine at 120^0C. (Diffusion plots for the temperatures 60^0C to 110^0C are shown in Figures A.1.36 to A.1.40 in Appendix 1). It must be stressed at this point, that for all but acetic anhydride, the first five data points which are associated with reactions at or near the surface of the substrate, have been omitted from the plots shown in Figure 3.20, since it was found earlier that reactions near the surface obeyed pseudo-first order kinetic laws. It can be seen that a linear relationship of gradient (a) is obtained (although there is considerable scatter of the data due to the inherent variability of the substrate) for all of the anhydrides studied, in both substrates, indicating that, as reaction proceeds, the reaction kinetics are dominated by diffusion processes. Thus, it is apparent that the rate of the reaction is rapid compared with the rate of the diffusion, i.e. that diffusion is the rate limiting step.

This observation suggests, therefore, that the degree of acylation within the wood ultrastructure depends upon the local density, since the rate of diffusion is inversely proportional to the density (Dinwoodie, 1981). This observation is in accordance with the results obtained measuring the distribution of chlorine using SEM-EXDA in chloroacetic anhydride modified wood, where it was found that the S_2 layer was modified more readily than the middle lamella at low wpg values. It is suggested therefore that the degree of acylation is more sensitive to the cell wall sub-microscopic structure than the chemical composition of the wood (Rowell, 1982).

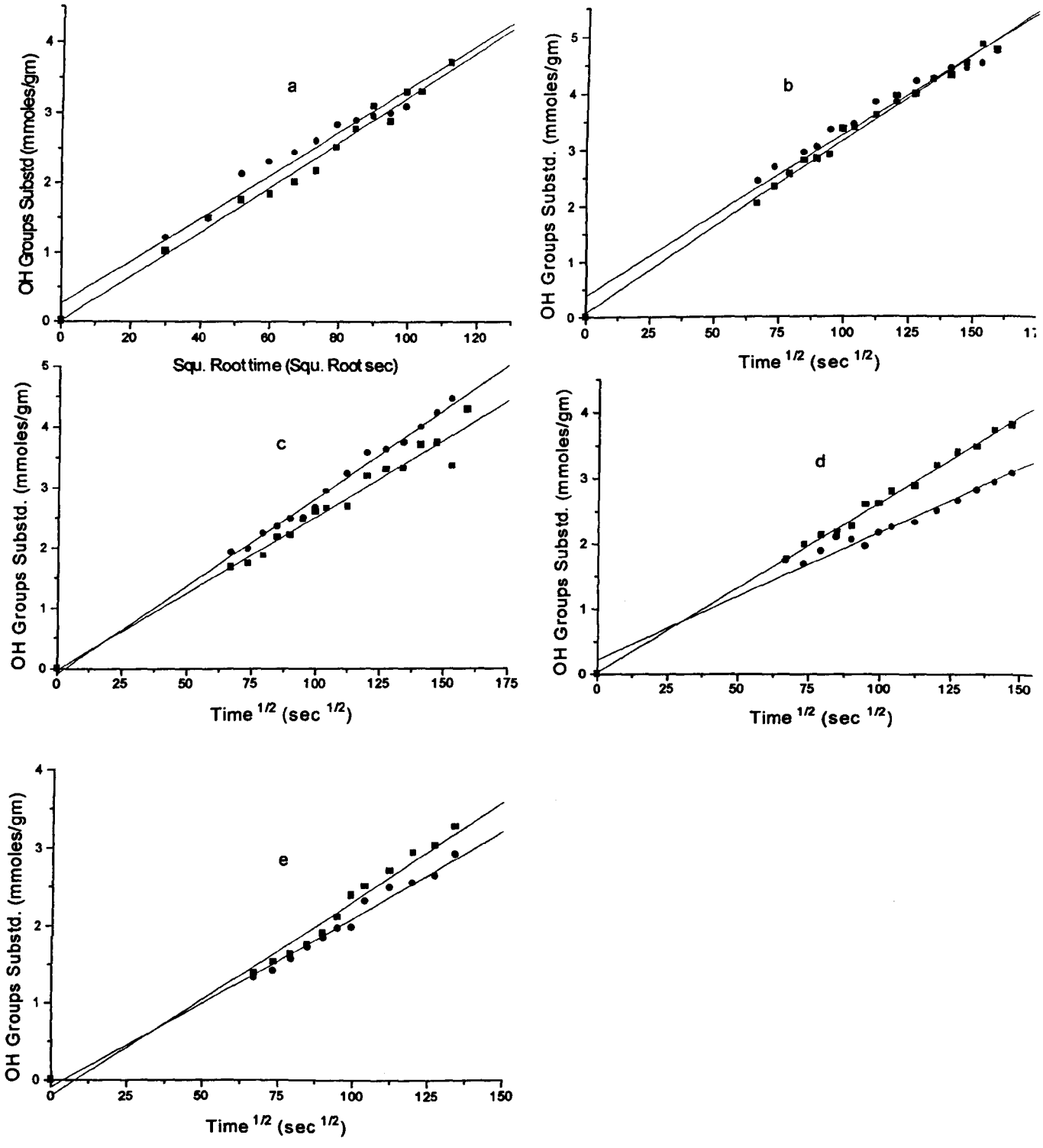


Figure 3.20: Diffusion profile for reaction of Corsican (squares) and Scots pine (circles) sapwood with acetic (a), propionic (b), butyric (c), valeric (d), and hexanoic anhydride (e) at 120^{0}C.

Diffusion can be considered an activated process, and expression (7) (see session 2.3) may be rewritten as

$$m = A \exp(-Ea/RT)\, t^{1/2} \quad (3.8)$$

Which can be rearranged thus:

$$\ln(m/t^{1/2}) = \ln(a) = \ln(A) - Ea/RT \quad (3.9)$$

Therefore, the activation energy of the diffusion process may be obtained by plotting the natural logarithm of (a) against the reciprocal absolute temperature, where if this relationship is obeyed, a straight line will be obtained with an intercept of ln(A) and gradient -Ea/RT.

Such a plot is shown in Figure 3.21 for the acetylation of Corsican and Scots pine (Arrhenius plots for the other anhydrides studied are shown in Figures A.1.41 to A. 1.45, in Appendix 1; Arrhenius data are presented in Tables 76 to 77, in Appendix 1).

From this set of data, activation energies for the diffusion process of acylation of Corsican and Scots pine were obtained; these are presented in Table 3.6. From this, it can be seen that activation energy for the diffusion process is not affected by the nature of the anhydride, unlike with the initial reaction, and in view of the magnitude of the errors associated with, it can be said that it is in the range of 10-15 kJ/mol. This proposed value is in agreement with that obtained from work on acid catalysed acetylation of cellulose, where a value of 11.7 kJ/mol was determined for the diffusion of acetic acid into cellulose (Hiller, 1954), and lower than that obtained from work on pyridine catalysed acetylation of Corsican pine sapwood, where a value 20.5 KJ/mol was determined for the diffusion process. In addition, the substrate does not have any significant effect upon the value of the activation energies of diffusion.

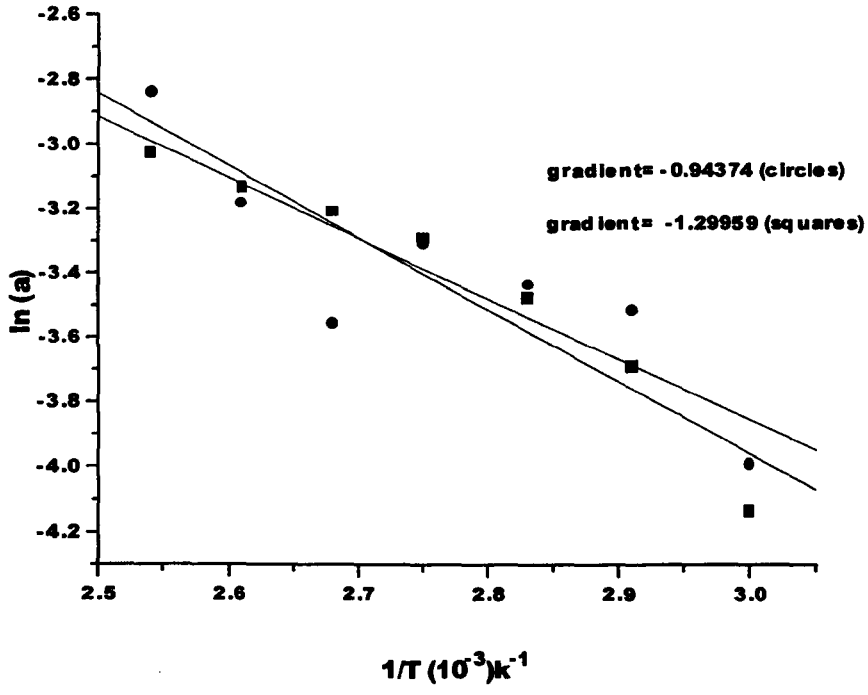


Figure 3.21: Arrhenius plots derived from the diffusion data for acetylation of Corsican (squares) and Scots pine (circles).

Table 3.6: Activation energies for the reaction of Corsican and Scots pine with linear chain anhydrides, determined from diffusion data. (Standard deviations in parentheses).

Anhydride	Corsican pine	Scots pine
Acetic	15.6 (+-2.9)	18.5 (+-2.2)
Propionic	10.6 (+-0.26)	7.7 (+-0.3)
Butyric	11. 5 (+-0.4)	11.3 (+-0.5)
Valeric	16.1 (+-3.7)	12.5 (+-1.5)
Hexanoic	16.4 (+-1.1)	14.9 (+-0.91)

3.5. Summary of points raised in Chapter 3

- The kinetic profiles for the reaction of a homologous series of linear chain anhydrides showed an asymptotic behaviour, with lower rates of reaction and ultimate degree of substitution as size of reagent increases.

- With propionylation, butyrylation, valerylation and hexanoylation, reactions at the 'surface' were found to obey pseudo first order kinetic laws. The reactions at the surface during acetylation did not contribute to the kinetic profile to any appreciable extent, since no evidence of first order kinetics was found.

- With acetic anhydride, it has been found that the reaction profiles are described by a model where diffusion dominates the reaction process, that is to say that reaction of the reagent molecules with a specific reaction site is rapid compared with diffusion.

- With longer chain anhydrides, the rate of chemical reaction and diffusion both contributed to the reaction kinetics.

- This work has shown that it is possible to obtain reproducible activation energies for reaction of carboxylic acid anhydrides with wood.

- Determination of the activation energies by the method of initial rates and rate constant has given comparable values, in contrast with earlier work on propionylation (Hill and Jones, 1996b).

- The activation energy of acetylation was close to what would be expected for a chemical reaction.

- An inverse relationship between the activation energy and molar volume of the reagent has been found with wood, suggesting that the reagent volume is an important factor in determining the activation energy for the reaction of carboxylic acid anhydrides with wood.

- The activation energy for the diffusion process has been found to be unaffected by the nature of the anhydride.

- No significant difference was found between the activation energies for reaction with either of the two species of this study.

- It is suggested that the lower values obtained for the activation energies for reaction of larger carboxylic acid anhydrides with wood are related to the restricted space surrounding the accessible hydroxyl groups. As a consequence of this, increasing the temperature of reaction has only a limited effect upon the motion of the longer chain length anhydrides. Hence, rather than determining a true activation energy, the value obtained is a consequence of the limited free space surrounding the hydroxyl groups.

- In view of the relationship found between anhydride size and activation energy, it was important to determine whether such a relationship would be exhibited for reactions in solutions. This study is the subject of the following chapter.

CHAPTER 4

Kinetic studies of the acylation of phenolic compounds with linear chain anhydrides

4.1. Introduction

The previous chapter has shown that it is possible to obtain reproducible activation energies for reaction of wood with carboxylic acid anhydrides. It was found that the molecular weight of the reagent clearly has an influence upon the activation energy, i.e. the activation energy decreases, as the molecular weight (and hence bulk) of the reagent increases.

The low values obtained for the activation energies for reaction of longer chain anhydrides with wood were considered to be related to the restricted space surrounding the accessible hydroxyl groups. As a consequence of this, increasing the temperature of reaction has only a limited effect upon motion of the longer chain anhydrides. It was concluded therefore, that rather than determining a true activation energy, the value obtained is a consequence of the limited surrounding the hydroxyl groups.

However, one may consider whether the interaction of anhydride with the substrate is important, or in other words, that the systematic decrease in activation energies as chain length of anhydride increases, is a consequence of the anhydride itself (nature of anhydride) and not to the limited space surrounding the hydroxyl groups. For this reason, it was decided to perform reactions in solution, using a series of phenolic compounds, where the molecules have the freedom of movement in the solution and therefore are not subject to steric constraints.

If it could be shown that the anhydride has no significant effect upon the activation energy of the reaction, then the systematic decrease in activation energies as chain length of anhydride increases, would be definitely a consequence of performing reactions with wood.

Furthermore, reaction under homogeneous conditions would allow an estimation of how accurate the method of initial rates is, since this has never been tested.

Therefore, kinetic profiles have been investigated for the reaction of a series of phenolic model compounds with linear chain carboxylic acid anhydrides. Activation energies were determined by the method of initial rates and from the rate constant data, by analysing reaction profiles over a series of temperatures.

4.2. Materials and methods

4.2.1. Materials

4.2.1.1. Modifying chemicals

Five modifying chemicals were used in this study. They include linear chain carboxylic acid anhydrides, namely acetic, propionic, butyric, valeric and hexanoic anhydride. Information about their molecular structure can be found in section 3.3.1.1.

4.2.1.2. Model compounds

Seven phenolic compounds were used in this study. These are listed in Table 4.1 along with some of their physical properties. Their structural formulae are presented in Figure 4.1.

All model compounds were purchased from Aldrich and used as supplied.

4.2.1.3. Catalyst

Pyridine was used as a catalyst for the reaction. Information about its molecular structure can be found is section 3.3.1.2.

Table 4.1: Physical properties of the phenolic model compounds used in this study.

Model Compound	Formula Weight	Purity	Physical state	Boiling point (^{0}C)	Density (g/cm^3)
Phenol	94.11	99%	Loose crystal	182	1.071
Guaiacol	124.14	98%	Liquid	205	1.129
2,6 Dimethoxyphenol	157.17	99%	Solid	261	1.182
3 methoxy phenol	124.14	96%	Liquid	113-115	1.131
2 methyl phenol	108.14	99%	Liquid	191	1.048
3 methyl phenol	108.14	99%	Liquid	203	1.034
4 methyl phenol	108.14	99%	Liquid	202	1.034

4.2.1.4. Experimental design

Reactions were performed between the five modifying chemicals namely acetic, propionic, butyric, valeric, hexanoic anhydride and 2,6 Dimethoxyphenol, and between butyric, valeric anhydride and phenol, guaiacol.

Furthermore, reactions were performed between acetic anhydride and 3 methoxyphenol, 2 methylphenol, 3 methylphenol and 4 methylphenol. These reactions were not extended to other anhydrides due to higher costs involved.

The above reactions were performed at a range of temperatures, from 50 to 100^{0}C (10^{0}C intervals). This restricted the number of individual reactions to 78.

4.2.2. Reaction procedure

A modification of the procedure reported by Haddadin *et al.* (1975) was used. A preheated solution of phenolic model compound and pyridine (both 0.1 molar) in relevant anhydride in 150 ml of acetic acid, set in an oil bath at a range of

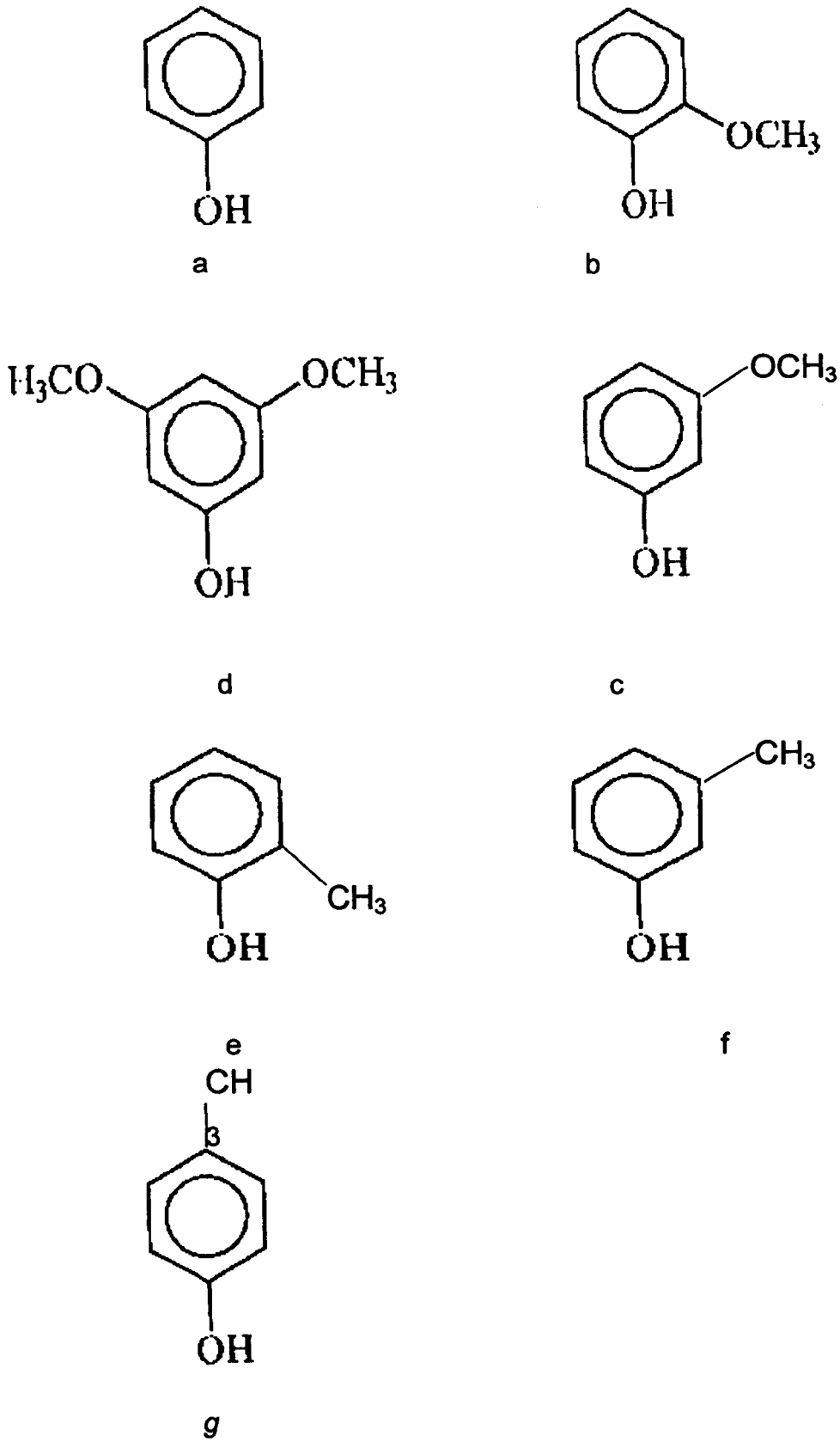


Figure 4.1: Structural formulae of the phenolic model compounds used in this study: a:phenol, b: guaiacol (2 methoxyphenol), c: 3 methoxyphenol, d: 2,6 Dimethoxyphenol, e: 2 methylphenol (o-Cresol),f: 3 methylphenol (m- Cresol) and g: 4 methylphenol (p-Cresol).

temperatures from 50^{0}C to 100^{0}C (10^{0}C intervals). Higher temperatures were not selected, in order to avoid possible interference with the acetic acid (boiling point 116^{0}C). The reactions were performed under an inert gas blanket of argon. Aliquots (1 ml) were periodically removed from the reaction mixture, and the samples diluted with 50 ml of ice-cold acetic acid (every 15 minutes for 3 hours reaction performed at 80, 90, 100^{0}C; and every 30 minutes for 4 hours reaction performed at 50, 60, 70^{0}C). The progress of the reaction was followed by monitoring the disappearance of the absorption band at 278 nm (indicative of the disappearance of the lignin content) (Pye-Unicam PU 8600 uv/vis spectrophotometer).

4.3. Results and discussion

4.3.1. Determination of activation energies

The activation energies for reaction of linear chain anhydrides with phenolic compounds were determined using the method of initial rates and the rate constant method, as described in section 3.3.

In order to determine the initial rate of the reaction, the kinetic data was plotted in terms of the change in concentration of the compound against time. A typical profile is shown in Figure 4.2, for the reaction of phenol with butyric anhydride at 100^{0}C. Kinetic profiles for all of the compounds studied are shown in Figures A.1 to A.13, in Appendix 2. An exponential fitting function was used for the curve fitting for determination of initial rate, and the fit was limited to the early stages of the reaction only, since it was found that data points obtained thereafter distorted the fit. It should be stressed here, that an important factor for selecting the best fit, apart from fitting the data points, was that the curve must pass through the value of concentration at zero time, otherwise the initial rate is not determined. It is apparent therefore that the calculation of activation energies by the initial rate method is very sensitive to the curve fitting parameters. Therefore, the results obtained should be treated with some caution.

Arrhenius initial rate data is shown in Tables A.1 to A.3 (see Appendix 2).

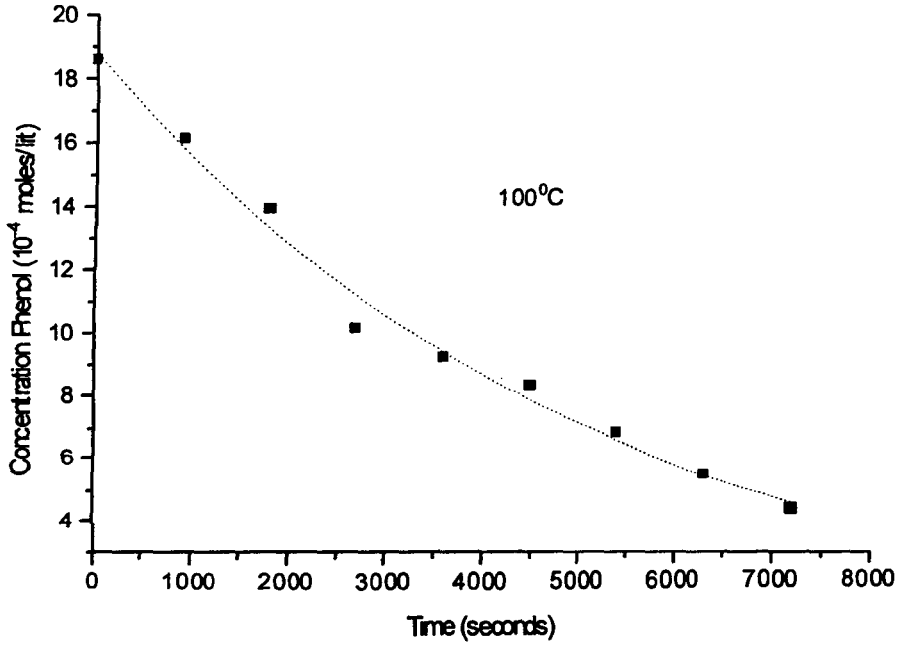


Figure 4.2: Kinetic profile for the reaction of phenol with butyric anhydride at 100°C.

Figure 4.3 shows a typical Arrhenius plot obtained from the initial rate data for the reaction of phenol with butyric anhydride. Arrhenius plots for the series of the phenolic compounds studied are shown in Figures A.14 to A.26, in Appendix 2. From these plots, the gradient of the straight line was multiplied by a factor of 8.314 JK^{-1} mol^{-1} (the universal gas constant) in order to calculate the activation energies of the reactions. This has been done for the series of the compounds studied and the results are shown in Table 4.2, presented later in the chapter.

It is possible to determine if first-order kinetics dominate the reaction process by plotting the natural logarithm of the concentration of phenolic hydroxyl groups substituted at time t, dividing by the concentration at time zero, against time in seconds; this will yield a straight line. The gradient of this line is equal to the rate constant, if first-order kinetics is obeyed.

The results for the analysis of the reaction profiles in terms of first-order kinetics for the series of the compounds studied are shown in Figures A.27 to A.39, in Appendix 2. An example is given in Figure 4.4 for the reaction of phenol with butyric anhydride

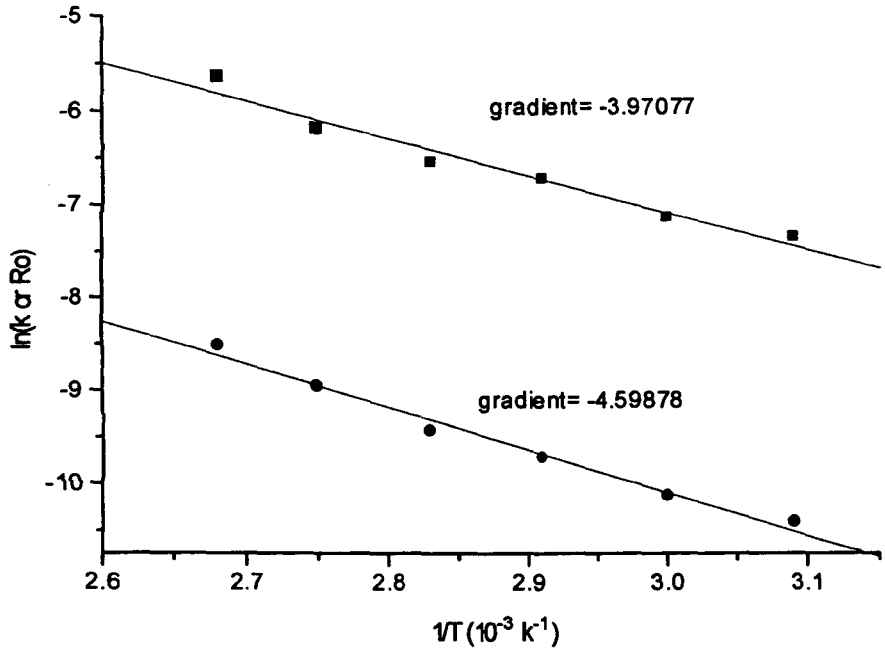


Figure 4.3: Arrhenius plot for reaction of phenol with butyric anhydride (squares: rate constant data, circles: initial rate data).

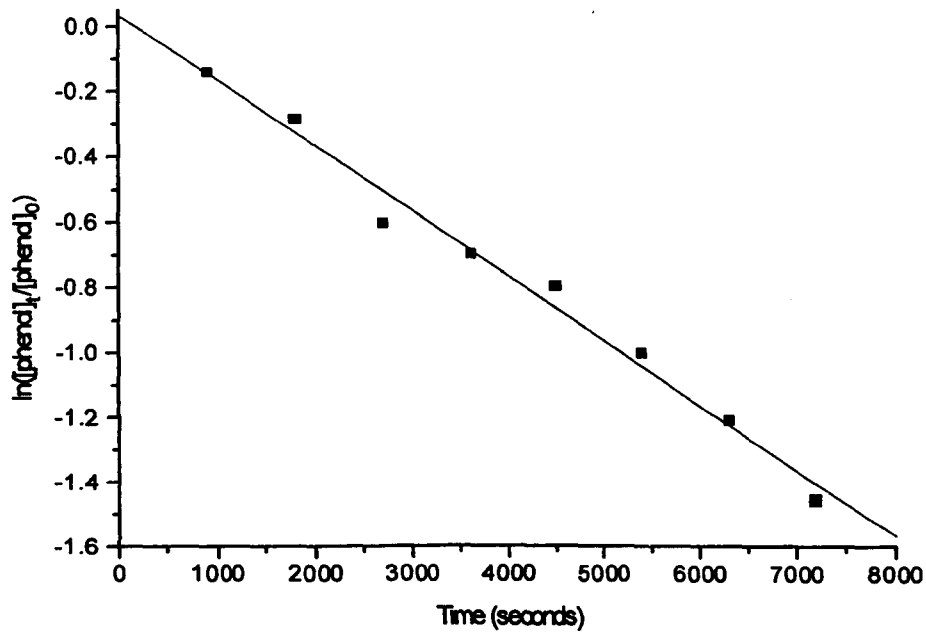


Figure 4.4: First-order kinetics plot for the reaction of phenol with butyric anhydride at 100^{0}C.

at 100^0C. It can be seen that a linear relationship is obtained, and therefore, it is possible to obtain a rate constant from this plot. This behaviour is typical for all of the compounds studied (see Figures A.27 to A.39, in Appendix 2).

Arrhenius rate constant data is shown in Tables A.4 to A.6 (see Appendix 2).

Figure 4.3 (presented earlier in the chapter) shows a typical Arrhenius plot obtained from the rate constant data for the reaction of phenol with butyric anhydride. Arrhenius plots for the series of the phenolic compounds studied are shown in Figures A.14 to A.26, in Appendix 2.

The data obtained from this set of experiments, and that available in the literature, are brought together and presented in Table 4.2. The values for activation energy for acetylation of phenolic model compounds are in reasonable agreement with literature values for both homogeneous and heterogeneous reactions (see Tables 3.2 and 3.3, respectively) and with the values obtained in this study, for reaction of linear chain anhydrides with whole wood (see Table 3.1). It is apparent that with a small reagent molecule, such as acetic anhydride, the value for the energy of activation in solution is similar to that observed in wood, indicating that the motion of the molecules within the cell wall microvoids is not significantly affected when compared with molecules in solution.

With both phenol and guaiacol, the anhydride has no significant effect upon the activation energy of reaction, when the rate constant method is used to determine the activation energy. When using the initial rate method, the activation energies determined for guaiacol show much grater variation than those with phenol. However, this does not correspond with the results obtained using rate constants, and in view of the considerable errors that may occur when using the method of initial rates, as discussed earlier in the chapter, the variation in the results is not thought to be of any significance. With 2.6-dimethoxyphenol there is evidence of a slight decrease in activation energy as the molecular weight of anhydride increases. This is found for activation energies calculated using both rate constant and initial rate methods, but the differences observed are small. The decrease in activation energy with anhydride

Table 4.2: activation energies (in kJ/mol) for reaction of phenolic model compounds with the series of anhydrides in pyridine (Standard deviations in parentheses).

Substrate	Acetic	Propionic	Butyric	Valeric	Hexanoic
Phenol (k)	37.3 (3.1) [a]	36.7 (4.0) [a]	33.01 (4.3)	36.49 (5.8)	33.7 (2.6) [a]
Phenol (Ro)	38.7 (3.4) [a]	38 (5.6) [a]	38.23 (3.6)	36.67 (2.2)	33.2 (3.2) [a]
Guaiacol (k)	43.9 (5.4) [a]	29.8 (2.7) [a]	38.66 (4.9)	28.07 (1.5)	30.6 (4.5) [a]
Guaiacol (Ro)	40.2 (5.5) [a]	27.1 (6.0) [a]	14.75 (2.5)	17.05 (2.86)	24 (6.2) [a]
3Methoxy Phenol (k)	35.95 (3.6)	-	-	-	-
3Methoxy Phenol (Ro)	36.97 (6)	-	-	-	-
2.6 Dimeth.Phenol (k)	38.54 (12.9)	36.49 (5.4)	30.15 (11.8)	29.57(3)	21.31 (3.5)
2.6 Dimeth.Phenol (Ro)	28.22 (5)	32.41 (5.3)	18.42 (3.8)	28.42 (5.9)	21.84 (2.3)
2 Methyl Phenol (k)	34.68 (10.7)	-	-	-	-
2 Methyl Phenol (Ro)	36.8 (11.3)	-	-	-	-
3 Methyl Phenol (k)	40.4 (7.1)	-		-	-
3 Methyl Phenol (Ro)	46.96 (16.9)	-		-	-
4 Methyl Phenol (k)	39.68 (6.6)	-	-	-	-
4 Methyl Phenol (Ro)	35.65 (7.8)	-	-	-	-

a: Hill and Hillier (1998).

when performing the reactions in solution, where the molecules have greater freedom of movement, in any case is far lower than that found for reactions with wood, where the molecules are subject to considerable steric constraints.

It is therefore, concluded that the systematic decrease in activation energies as chain length increases, is a consequence of performing the reactions with wood, since the interaction of anhydride with the substrate is of minor significance.

4.4. Summary of points raised in Chapter 4

- Activation energies derived using the rate constant or initial rate data were reasonably close, although the errors associated with the latter method are generally larger.

- Reaction of acetic anhydride with phenolic model compounds in solution yielded values for activation energies, which are comparable with those obtained in wood.

- With longer chain anhydrides, the values in solution were higher than those obtained in wood.

- When reaction was performed in solution, there was no correlation between anhydride molecular weight and activation energy of reaction, in contrast to what has been found in wood.

- Therefore, the systematic decrease in activation energy as chain length increases, is a consequence of performing reactions with wood.

CHAPTER 5

The accessibility of reagent molecules to the cell wall interior of pine sapwood

5.1. Introduction

During the reaction of chemical reagents, such as anhydrides, with the cell wall of wood, it is necessary for the reagent molecule to travel *via* the cell wall microporous network in order to react with the OH groups located within the interior of the cell wall.

In Chapter 3, the kinetics of the reaction of oven dried pine sapwood with a homologous series of carboxylic acid anhydrides have been investigated. In this case, a swelling agent such as pyridine was used as a catalyst/solvent. If reaction takes place in a non-swelling solvent (e.g. toluene or xylene) and the wood has been previously dried, then the microvoid network is in a collapsed state and ingress of reagent into the cell wall is controlled by the rate at which the micovoids re-open. In this case the 'zipper' model (Krassig, 1985; West, 1988) is the most probable model explaining the reaction process. In such a model, the cell wall microvoids are effectively 'sealed shut' by extensive hydrogen bonding networks between the walls of the microvoid. In order that reagent molecules may penetrate the interior of the cell wall, it is necessary that these hydrogen bonds be broken. If the rate of H-bond breaking is slow compared to the rate of reaction of reagent with the cell wall OH groups, then H-bond breaking is the rate limiting step of the reaction. If however, the wood is in a swollen state, then the transfer of reagent molecules into the interior of the cell wall is affected only by the geometry of the cell wall microvoids (in relation to reagent size), if other factors such as temperature and concentration of reagent are constant.

The investigation reported in this chapter was therefore undertaken to determine the effect of swelling of the cell wall of wood, upon the rate of reaction of the cell wall polymeric OH groups with two different anhydride reagents, namely acetic anhydride

(molar volume 94.4 cm^3) and propionic anhydride (molar volume 128.6 cm^3). Different sized anhydride molecules will have varying accessibility to the cell wall because of differences in dimensions of the cell wall micropores. When wood is dried, the cell wall micropores collapse, severely reducing access. Although there is evidence to show that acetic anhydride can react with a non-swollen wood cell wall, it has been shown that a swelling agent is required with propionic anhydride (Hill *et al.* 2000). In a recent study, reaction of wood with propionic or butyric anhydrides, it was found that reaction was possible at 140^{0}C (Li *et al.* 2000). Similarly, refluxing of wood in propionic anhydride (boiling point 167^{0}C) also resulted in reaction with the substrate (Dawson *et al.* 1999). However, this reported reactivity undoubtedly occurs due to degradation of the cell wall which occurs at such temperatures (Rowell, 1983; Hill and Jones, 1996a; Hill *et al.* 1998; Ramsden and Blake, 1997).

The study reported in this Chapter utilised extractive-free sapwood from Corsican pine (*Pinus nigra*) and Scots pine (*Pinus sylvestris*). Reactions were performed on oven-dry samples in the presence of water-free xylene, which does not swell the cell wall. Reactions were also performed under identical conditions, but on wood samples that had been dried under solvent exchange conditions, thereby retaining the swollen cell wall pore structure.

5.2. Materials and methods

5.2.1. Materials

5.2.1.1. Modifying chemicals

Acetic and propionic anhydride were used for this part of the study. Their molecular structure and their molecular diameter (Å) have been listed previously (see section 3.3.1.1.).

5.2.1.2. Solvent

Reactions were performed in the presence of water-free xylene (sodium dried). The xylene was purchased from Aldrich and used as supplied.

5.2.1.3. *Wood*

The wood used in the experiments was Scots Pine (*Pinus sylvestris*) and Corsican pine (*Pinus nigra*) sapwood obtained from North Wales forests.

The preparation of wood samples has been described in section 3.3.1.3.

5.2.2. Reaction procedure

Wood blocks of dimensions 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were cut from the sapwood of Corsican and Scots pine logs. The samples were carefully sanded and labelled, then transferred to a Soxhlet apparatus for extraction using a solvent system consisting of toluene/acetone/methanol (4/1/1, by volume) for 6 hours. Samples were then dried in an oven for 8 hours at 105°C. Prior to reaction, samples were removed from the oven and allowed to cool to room temperature in a desiccator over silica gel. In order to prepare the wood aerogel samples, an alternative procedure was employed. After Soxhlet extraction, the samples were left in a fume hood for several days to allow the organic vapours to evaporate off. The wood blocks were then vacuum impregnated with de-ionised water and allowed to soak for 48 hours with two water changes. Subsequent to this the samples were transferred to the Soxhlet apparatus and solvent exchanged with wet methanol (for 1 day), absolute (dry) methanol (for 1 day) and finally with dry xylene (for 1 day), xylene saturated samples were then added directly to the reaction flask. Apart from soaking in water and in wet methanol, all other procedures were carried out under a blanket of dry argon in sealed (parafilm) vessels fitted with drying tubes filled with calcium chloride. Reactions were performed in a 500 ml solution of the anhydride (4 molar) in dry xylene under a blanket of dry argon, at a temperature of 100^0. Oven-dried wood samples were pre-impregnated with the reaction solution under an argon blanket and added to the reaction vessel at suitable time intervals (5 replicates per addition). The reaction was then terminated by decanting off the hot reagent solution and adding the blocks to ice-cold acetone. After allowing the blocks

to sit in the acetone for one hour, they were then transferred to a Soxhlet apparatus for solvent extraction followed by oven drying as detailed above. After drying, the blocks were then transferred to a desiccator prior to reweighing. One further set of reactions was performed in a 4 molar solution of the anhydride in its corresponding acid. The blocks were treated as for the reaction of oven-dried blocks in xylene, but no attempt was made to exclude moisture from the reaction vessel.

5.2.3. Calculations

The extent of the resulting modification was then measured in terms of the weight percent gain (WPG) of the wood sample associated with the reaction, as described in section 3.3.3.

5.3. Results and discussion

The results from the experiments are shown in Figures 5.1 (acetic anhydride with Corsican pine), 5.2 (propionic anhydride with Corsican pine), 5.3 (acetic anhydride with Scots pine) and 5.4 (propionic anhydride with Scots pine). The raw data are presented in Tables 1 to 4, in Appendix 4.

In the reaction of acetic anhydride with Corsican pine, it can be seen that reaction occurred with the oven-dry wood samples as well as the swollen samples. However, in the case of reaction of propionic anhydride with Corsican pine, reaction only occurred when the wood was in a swollen state. With Scots pine, reaction with acetic anhydride and with propionic anhydride only occurred when the wood was in a swollen state. These results indicate that the cell wall micropores of the Scots pine samples used in this study were smaller than the acetic anhydride molecules. From the data on molar volumes given earlier (see section 3.3.1.1., also Appendix 1A), an apparent diameter for the anhydride molecule can be calculated, by assuming that the molecule is spherical. This equates to a diameter of 0.66 nm and 0.74 nm for acetic anhydride and propionic anhydride, respectively. The results therefore indicate the

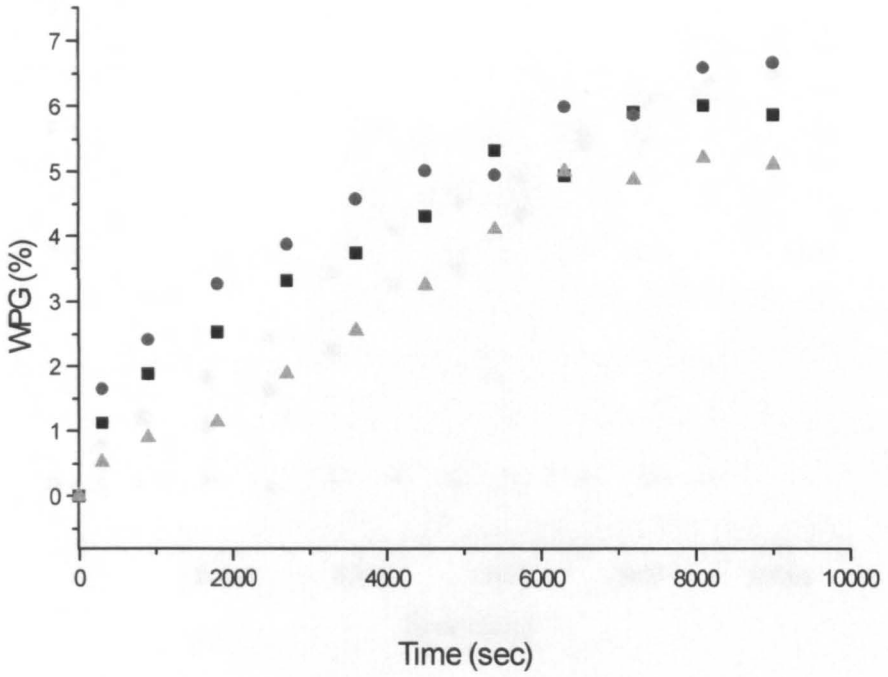


Figure 5.1: Reaction profiles for reaction of Corsican pine samples with acetic anhydride: solvent exchange dried samples (squares), oven-dried samples in xylene (triangles) and in the presence of acetic acid (circles).

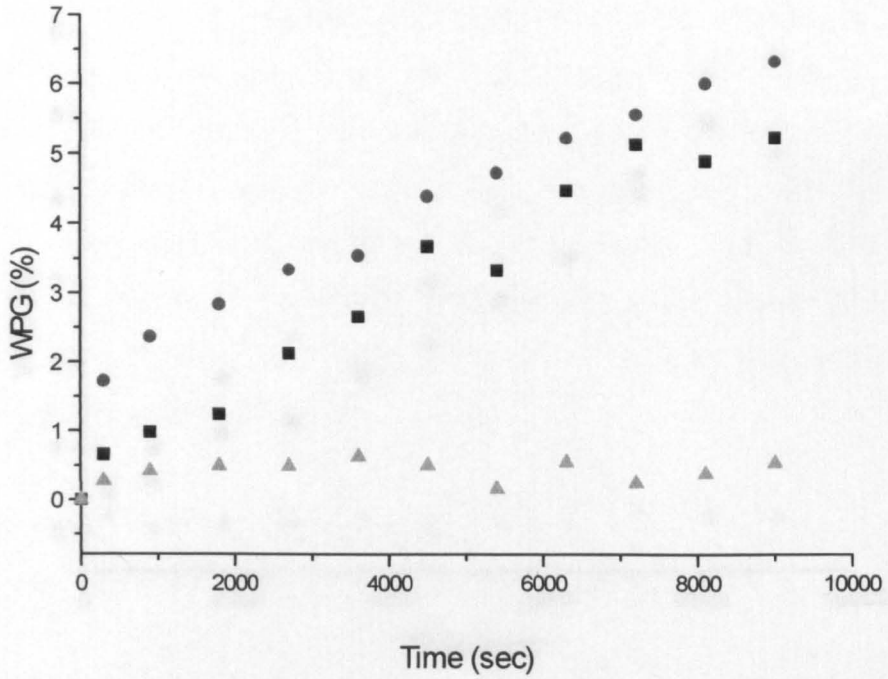


Figure 5.2: Reaction profiles for reaction of Corsican pine samples with propionic anhydride: solvent exchange dried samples (squares), oven-dried samples in xylene (triangles) and in the presence of propionic acid (circles).

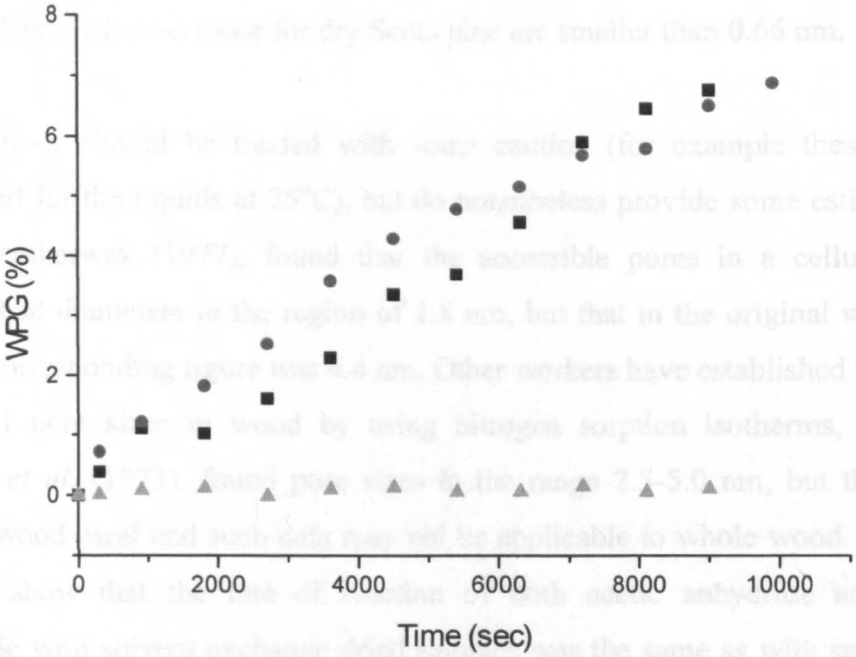


Figure 5.3: Reaction profiles for reaction of Scots pine samples with acetic anhydride: solvent exchange dried samples (squares), oven-dried samples in xylene (triangles) and in the presence of acetic acid (circles).

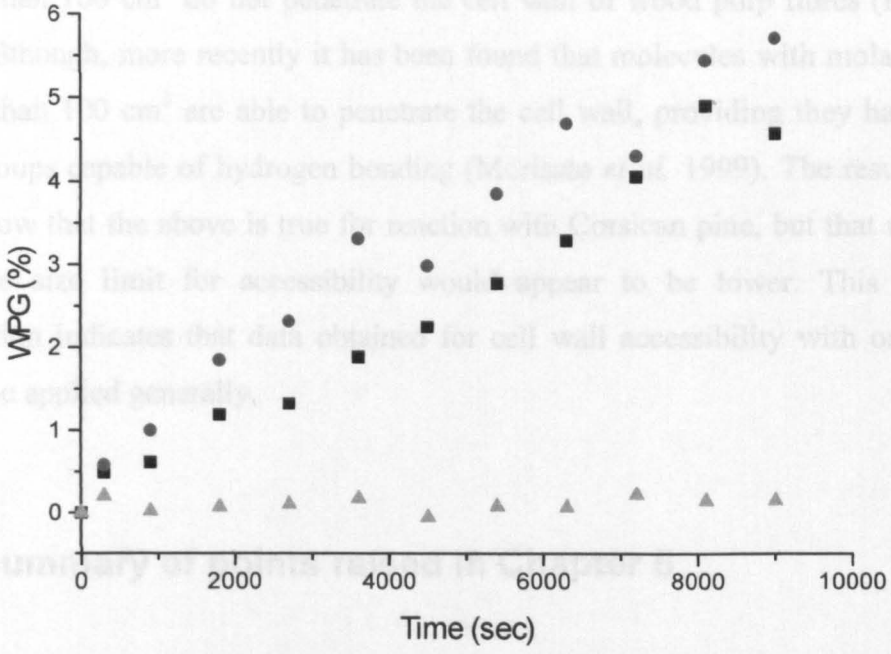


Figure 5.4: Reaction profiles for reaction of Scots pine samples with propionic anhydride: solvent exchange dried samples (squares), oven-dried samples in xylene (triangles) and in the presence of propionic acid (circles).

diameters of the micropores in the cell wall of oven dried Corsican pine are smaller than 0.74 nm, whereas those for dry Scots pine are smaller than 0.66 nm.

Such figures should be treated with some caution (for example these values are calculated for the liquids at 25°C), but do nonetheless provide some estimate of pore size. Weatherwax (1977), found that the accessible pores in a cellulose (WAC) aerogel had diameters in the region of 1.8 nm, but that in the original water swollen gel the corresponding figure was 4.4 nm. Other workers have established the median cell wall pore sizes in wood by using nitrogen sorption isotherms, for example Sawabe *et al.* (1973), found pore sizes in the range 2.5-5.0 nm, but this was with ground wood meal and such data may not be applicable to whole wood. The reaction profiles show that the rate of reaction of both acetic anhydride and propionic anhydride with solvent exchange dried samples was the same as with samples which were swollen with the corresponding carboxylic acid. This result shows that the cell wall pore structure of a solvent exchange dried aerogel cell wall is similar to that of the fully swollen equivalent, provided the solvent is not removed from the structure. The collapse of such structures must therefore occurs when the solvent molecules evaporate from the cell wall. It has been reported that molecules with molar volumes greater than 100 cm^3 do not penetrate the cell wall of wood pulp fibres (Robertson, 1970), although, more recently it has been found that molecules with molar volumes greater than 100 cm^3 are able to penetrate the cell wall, providing they have two or more groups capable of hydrogen bonding (Morisato *et al.* 1999). The results of this work show that the above is true for reaction with Corsican pine, but that with Scots pine, the size limit for accessibility would appear to be lower. This important observation indicates that data obtained for cell wall accessibility with one species cannot be applied generally.

5.4. Summary of points raised in Chapter 5

- The rate of reaction of acetic and propionic anhydrides was greater with swollen wood, compared with oven dried samples.

- When wood is preserved in a swollen state by solvent exchange drying, the rate of reaction is comparable with samples which are swollen with the corresponding carboxylic acid.

- Oven dried (unswollen) Scots pine sapwood did not react with acetic or propionic anhydride to any appreciable extent under the conditions used in these experiments.

- Oven dried Corsican pine sapwood did react with acetic but not with propionic anhydride.

- This indicates that the cell wall micoporous network of Corsican pine sapwood is accessible to some extent by acetic anhydride molecules, but not by propionic anhydride.

- It is concluded that the cell wall micropores of Corsican pine are sufficiently large to allow access of acetic anhydride but not propionic into the unswollen cell wall, but that with Scots pine both reagents are too large to gain access.

CHAPTER 6

Volumetric changes in Corsican and Scots pine sapwood due to chemical modification with linear chain anhydrides

6.1. Introduction

Acylation with linear chain anhydrides is a single site reaction, that is one acetyl group is added per reaction site with no associated polymerisation, as discussed in section 3.3.1.1. Therefore, the weight gain due to modification is related to the number of hydroxyl groups substituted. As the hydroxyl groups of the cell wall polymers are substituted, the cell wall of wood swells due to the volume occupied by the adduct. This swelling occurs because the covalently bonded hydroxyl groups occupy space within the cell wall and cause a localised deformation of the cell wall polymeric network.

Various studies of the relationship between the swelling of the material due to modification have been published. In studies of the acylation of spruce, maple and balsa, it has been found that the degree of swelling of the substrate exhibits a proportional relationship with the degree of substitution, up to an acetyl content of 16-18% (Stamm and Tarkow, 1947). Furthermore, the volume increase due to modification, has been found to be equal to the volume of the acetyl groups in the wood (Stamm and Tarkow, 1947; Rowell and Ellis, 1978).

More recently, this latter finding has been disputed, where it has been found that for Corsican pine modified wood, a volume increase larger than theoretically predicted is obtained (Hill and Jones, 1996a).

The volumetric swelling of wood due to esterification has been studied, and the effect of such modification upon the dynamic mechanical properties of wood determined (Nakano, 1994). In this reported work, it was considered that volume increase of the wood was the sum of volume occupied by chemically bonded reagent, plus a void volume created in the cell wall polymeric network around the adduct.

In this study, the volumetric changes in Corsican and Scots pine sapwood due to modification with a homologous series of linear chain anhydrides have been studied. Firstly, the relationship between percentage volume increase due to modification and WPG was investigated. Following that, the relationship of theoretical volume and measured volume of modified samples was compared. The results have also been interpreted in terms of the molar volume occupied by the substituent groups in the wood cell wall. Finally, determination of the apparent void volume created by the acyl groups within the wood cell wall polymeric network has been undertaken. It has to be stressed at this point that wood exhibits hysteresis, as will be discussed in section 7.2.3, and some of the volume change is not reversible.

6.2. Volume change *versus* weight percent gain

Volume change due to modification was calculated as follows:

$$VC\ (\%) = \frac{V_{mod.} - V_{unmod.}}{V_{unmod.}} \times 100$$

Where $V_{mod.}$ is the volume of chemically modified wood and $V_{unmod.}$ is the volume of unmodified wood.

Figure 6.1 illustrates the relationship between percentage volume increase, due to modification with a homologous series of linear chain anhydrides and WPG of both Corsican and Scots pine at 120^{0}C. It is revealed that, for all the anhydrides studied, there is a linear relationship between percentage volume increase and WPG. This was noted for all of the temperatures studied (60 to 110^{0}C), in the series of anhydrides (see Tables 3.2 to 3.11, Figures 3.1 to 3.5, Appendix 3). This behaviour is in agreement with previous reports (Stamm and Tarkow, 1947; Cetin, 1999) but contradicts recent findings by Hill and Jones (1999). In the latter case, a sigmoidal relationship was found between percentage volume increase and WPG of Corsican pine. This deviation from linearity at large wpg indicated some degree of substrate degradation at extended reaction times, since this deviation at *ca* 25% WPG occurred when the water saturated volume of the wood (*ca* 13%) was exceeded. No such behaviour was found in this study.

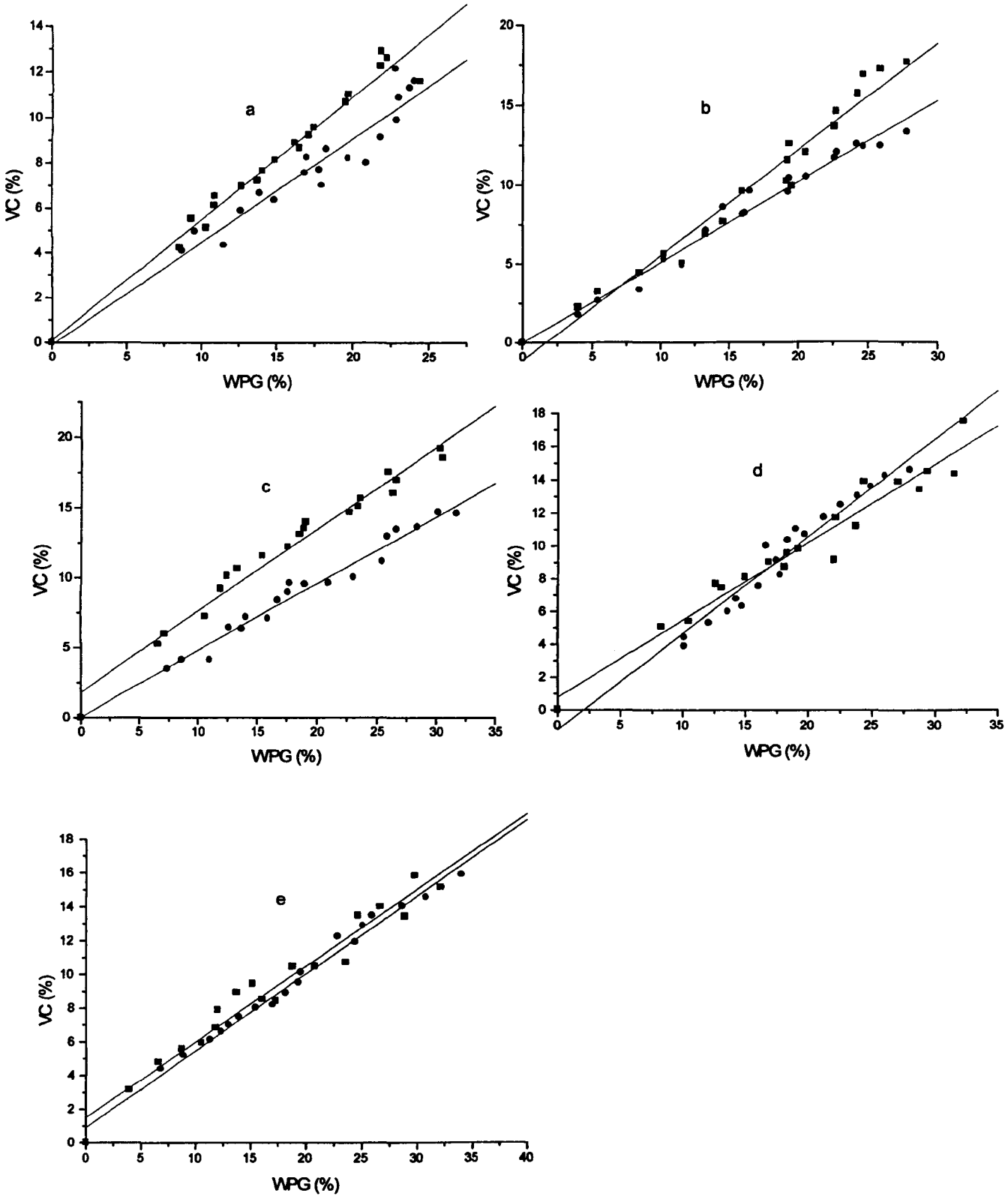


Figure 6.1: Relationship between percentage volume increase and WPG of Corsican pine (squares) or Scots pine (circles) modified with acetic (R^2=0.98 and R^2=0.99) (a), propionic (R^2=0.98 and R^2=0.98) (b), butyric (R^2=0.97 and R^2=0.99) (c), valeric (R^2=0.99 and R^2=0.97) (d) and hexanoic anhydride(R^2=0.99 and R^2=0.99) (e) at 120^0.

The percentage volume increase at a given WPG of Corsican pine sapwood was greater than the percentage volume increase of Scots pine sapwood modified with acetic, propionic and butyric anhydride; with wood modified with valeric and hexanoic anhydride, the volume increases at comparable wpg's were similar.

There are two possible explanations for this different degree of volume increase of the two substrates. Firstly, there may be ultra-structural differences between the two woods, which lead to differences in the accessibility of reactive sites to reagent, or to differences in the way that the wood responds to modification. Secondly, the difference in density of the wood between the two sample sets may be affecting this behaviour (see densities of Corsican and Scots pine in Table 3.1, Appendix 3). As reported earlier (Stamm, 1964), denser wood shows a higher swelling ratio than less dense wood.

6.3. Ratio of theoretical and measured volume increase V (rel) *versus* weight percent gain

Theoretical volume increase is calculated as follows:

$$V_{THEOR} = \frac{W_{mod.} - W_{unmod.}}{D}$$

Where $W_{mod.}$ is the weight of chemically modified wood and $W_{unmod.}$ is the weight of unmodified wood, and D the density of the relevant carboxylic acid (see densities of the carboxylic acids in Table 3.32, Appendix 3).

The values are shown in Tables 3.12 to 3.21 (in Appendix 3). This method relies upon the assumption that volume occupied by carboxylic acid molecules in the liquid state is equal to the volume occupied by the carboxylate groups in the wood bulk. With single site reactions such as anhydride modification, it has been stated that chemical modification produces a net swelling proportionate to the amount of the reagent bonding to wood. It has been further stated that, the measured volume increase

correlates well with the theoretical (or calculated) volume increase in uncatalysed acetylation reactions (Rowell and Ellis, 1978). Dividing the theoretical volume increase by the measured volume increase after modification gives the ratio $V_{(rel)}$, as follows,

$$V_{(rel)} = \frac{V_{THEORETICAL}}{V_{MEASURED}}$$

Figures 3.6 to 3.15 (in Appendix 3) show the relationship between the ratio of theoretical and measured volume increase V (rel) and weight percent gain of Corsican and Scots pine sapwood modified with a homologous series of linear chain anhydrides at various temperatures (60 to 110^{0}C). The curves shown in the figures represent best fit curves through the relevant data points.

The relationship between V (rel) and WPG of Corsican and Scots pine modified at 120^{0}C is compared for all the anhydrides studied in Figures 6.2 and 6.3 respectively. The behaviour is typical for all of the temperatures studied, as can be seen in Figures 3.6 to 3.15 (in Appendix 3). It is apparent that a variety of curves were obtained which exhibited lower values of V(rel) at low weight percent gains, which tended towards a maximum value of 0.9 for Corsican pine and 1.0 for Scots pine, at higher levels of substitution.

A small but noticeable decrease in the ratio noted for butyric, valeric and hexanoic anhydrides substituted samples at WPG value in excess of 25-30% was also observed. This drop may be an artefact of the polynomial curve fit used.

The behaviour of the two species studied is different in that with Scots pine, the ratio does not fall below 0.8 (see Figure 6.3), but with Corsican pine values as low as 0.6 were observed (with acetic anhydride modified samples, see curve a in Figure 6.2). The curves associated with the modified Corsican pine samples also show a much greater distribution of values.

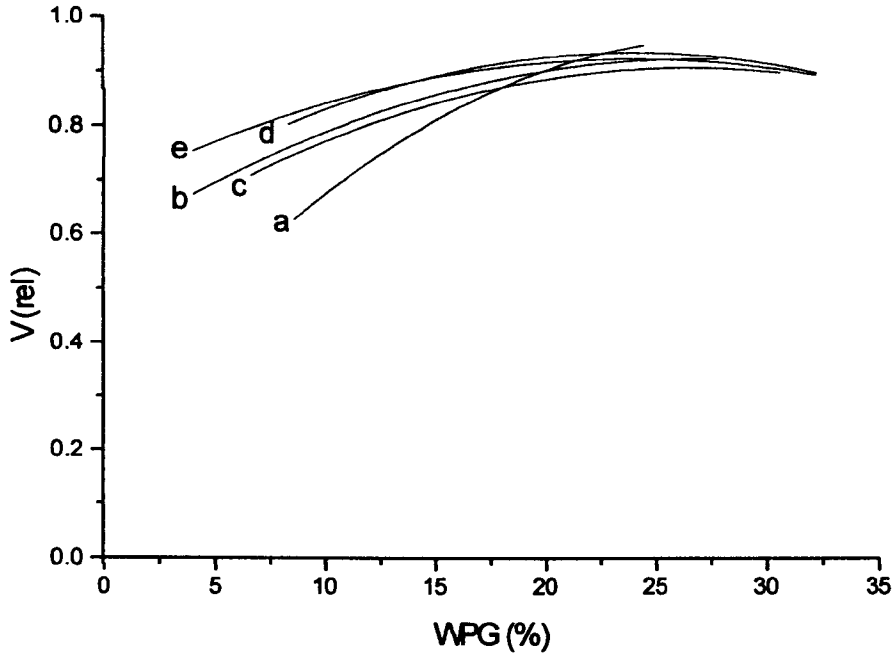


Figure 6.2: Relationship between ratio of theoretical to measured volume increase V(rel) and weight percent gain WPG of Corsican pine samples modified with the following anhydrides. Acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e).

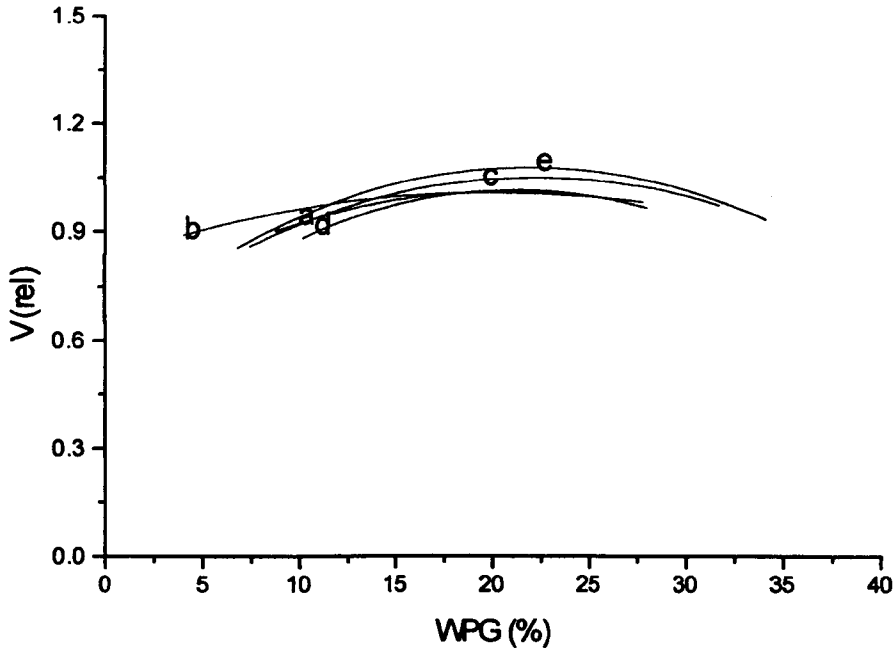


Figure 6.3: Relationship between ratio of theoretical to measured volume increase V(rel) and weight percent gain WPG of Scots pine samples modified with the following anhydrides. Acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e).

From the above, it is concluded that the degree of swelling of Corsican pine sapwood due to modification with a homologous series of linear chain anhydrides is not equal to the volume of the chemical added; but it is for Scots pine. With Corsican pine, larger volume changes than theoretically predicted were observed, whereas with the Scots pine samples the volume changes were close to those predicted.

The decrease in $V_{(rel)}$ at low WPG values, suggests that there are presumably additional factors contributing to the volume increase due to modification other than bulking by reagent alone. The opposite behaviour would be expected at low WPG values (i.e. the ratio would exceed 1.0) if bulking by reagent is considered to be the only contributor to the volume change, since the proportion of molecules occupying surface sites is much greater at low WPG values (short reaction times). The possibility that the decrease in ratio of theoretical to measured volume increase at low WPG values is due to the alteration of the wood with the hot pyridine solvent (i.e. removal of extractives), which may lead to an irreversible volume increase of the samples, was considered previously (Hill and Jones, 1996a). It was found that heating of wood blocks in neat pyridine for 3 hrs. at 120^0C led to a volume decrease of 1.7% and weight loss of 2.8%, indicating that such treatment does not contribute to any additional volume increase but only serves to remove extractives or thermally degraded components not removed during the Soxhlet procedure.

As mentioned in section 6.1, Nakano (1994) considered that volume increase of wood due to esterification was the sum of volume occupied by reagent, plus a void volume created in the cell wall polymeric network. Since it was found in this study, that increases in volume due to modification were larger than theoretically predicted, it can be argued that the volume increase (V) observed in the wood samples due to anhydride modification has contributions both from the volume occupied by the reagent (V_i) and a void volume (V_f) created by the presence of adducts within the wood cell wall.

The concept of void volume, which has also been used by others (Hill and Mallon, 1998 a; Hill and Jones, 1999) to explain dimensional changes in anhydride modified wood, was introduced by Nakano (1994) in order to explain the mechanism of

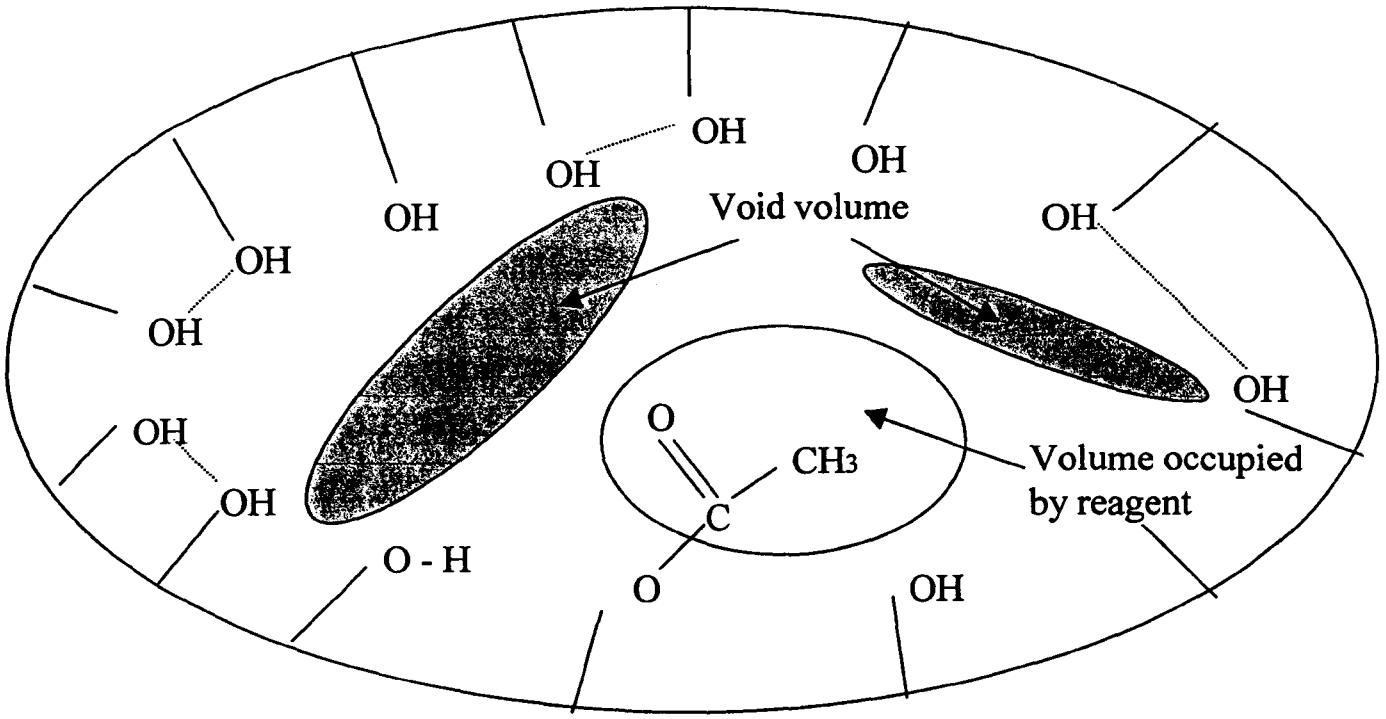


Figure 6.4: The concept of void volume as used in this study.

thermoplasticity imparted to wood by chemical modification, and is expressed by the formula:

$$V = k (V_i + V_f) \qquad (k = \text{constant})$$

The concept of void volume (see Figure 6.4) implies that there is a region around the acyl groups which is not occupied by cell wall polymers, and that the acyl groups have some freedom of movement within this space. The magnitude of the void volume may therefore be a measure of the compliance of the cell wall polymers in the vicinity of the adduct.

Bearing in mind the above observation, the following conclusions are drawn from Figures 6.2 and 6.3. Firstly, that a greater proportion of the volume increase due to modification with linear chain anhydrides in Corsican pine sapwood is attributable to void volume than in Scots pine sapwood. Secondly, that the proportion of the volume increase attributable to void volume, increases at low WPG (below *ca.* 20%).

The variation in the ratio of theoretical to measured volume increase between Corsican and Scots pine can be attributed to the ultra-structural differences between the two substrates. This is further discussed in the following section. Similar findings with Corsican pine modified wood were reported in previous work (Hill and Jones, 1999), where it was found that the theoretical to measured volume ratio decreased at low WPG values, and exhibited a maximum of 0.8. The results obtained in this study are also in agreement with those reported by Cetin (1999). He stated that the ratio of theoretical to measured volume increase was about 0.87 and 1.0 for Corsican and Scots pine respectively, both modified with crotonic and hexanoic anhydride. He further stated that the reaction temperature also affected the ratio of theoretical to measured volume increase of Scots pine samples modified with crotonic anhydride, since it was found that at lower reaction temperatures (90^0C and below), in the early stages of the reaction, the ratio was higher than 1.0 and in some cases reached the value of 2.0. No such behaviour was detected in this study.

6.4. Molar volume *versus* weight percent gain

Modification with reagent leads to an increase in the volume of the wood samples, as discussed in section 6.2. By determining the volume increase, and dividing this by the number of moles of adduct in the modified samples, a value for the molar volume for each of the reagents at different wpg's is obtained, as follows: (see Tables 3.22 to 3.31 in Appendix 3). This value represents the volume occupied by one mole of reagent in the modified wood samples.

$$V_{MOLAR} = \frac{V_{mod.} - V_{unmod.}}{M}$$

Where $V_{mod.}$ is the volume of chemically modified wood , $V_{unmod.}$ is the volume of unmodified wood, and M is the number of moles of adduct.

Figures 3.16 to 3.25 (see Appendix 3) show the relationship between molar volume and weight percent gain of Corsican and Scots pine samples modified with a homologous series of linear chain anhydrides at various temperatures (60 to 110^0C).

The curves shown in the figures represent best fit curves through the relevant data points.

The variation in molar volume in modified Corsican and Scots pine samples at 120^0C with extent of modification for the range of anhydrides studied, is illustrated in Figures 6.5 and 6.6, respectively. All of the anhydrides in this series showed the same behaviour, in that larger molar volumes were found at lower levels of substitution, with an asymptotic decrease to a stable value at higher wpg's. This observation reaffirms the previous one that larger volume increases are observed at lower weight gains than would be theoretically predicted (see session 6.3). The stable value of molar volume at higher wpg's is temperature independent, although lower temperatures resulted in generally slightly larger molar volumes at low wpg values (and hence short reaction times, see Figures 3.16 to 3.25, in Appendix 3). However, there were cases (3 out of 70, nearly 4%) where the molar volumes obtained at lower wpg's were very close to those obtained at higher ones (see Figures 3.21 a, 3.22 a, 3.23 a, in Appendix 3).

The increase in molar volume and hence the larger volumetric swelling of the material at low weight percent gain, is believed to be a phenomenon related to the modification process, as discussed by Hill and Jones (1999), since at low levels of substitution (and hence short reaction times) it was to be expected that the reaction will occur at surface sites; thus, less swelling of the material would occur at low wpg's, the opposite of what is observed in this study.

It is known from studies of chloroacetic anhydride modified wood, that at low wpg's the substituent is located predominantly in the S_2 layer of the cell wall (Rowell 1984). The location of the reagent within the wood cell wall depends upon the relative rates of diffusion of reagent molecules in the micropores of the wood cell wall, and the rate of reaction of such molecules with active sites located within the cell wall. As was found in this study (see section 3.3.4), the reaction kinetics of acetylation are diffusion dominated; due to the dominance of diffusion, the rate of reaction will be a function of the density of the wood, which varies from region to region (it is known that the rate of diffusion is inversely proportional to the density (Dinwoodie, 1981). Thus, reaction initially will occur in less lignified regions of the cell wall where

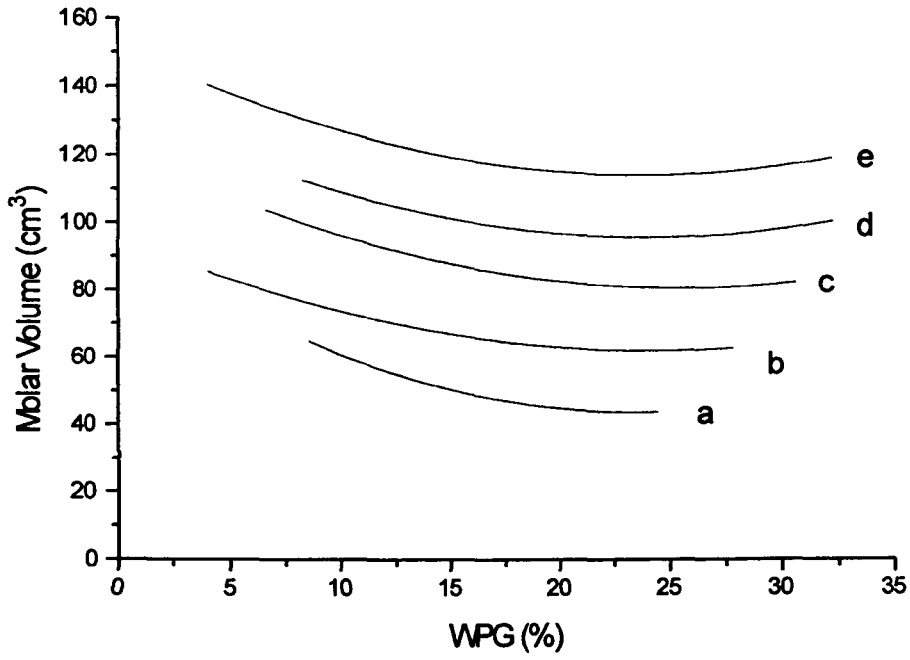


Figure 6.5: Variation in molar volume with weight percent gain for Corsican pine modified with the following anhydrides. Acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e).

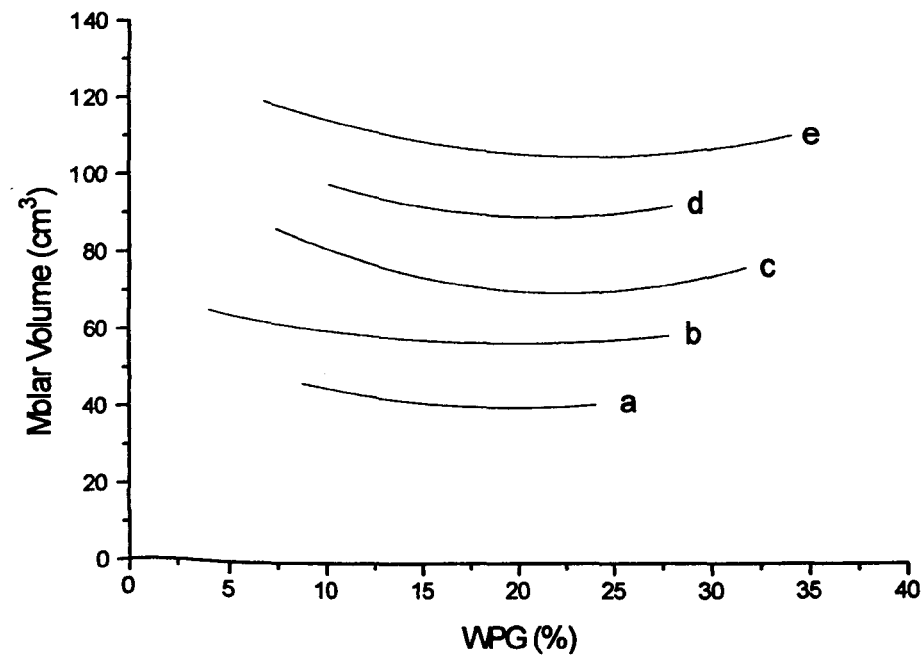


Figure 6.6: Variation in molar volume with weight percent gain for Scots pine modified with the following anhydrides. Acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e).

penetration of the reagent is facilitated, such as the S_2 layer of the cell wall, which is of lower density than the middle lamella. In these regions which are of lower lignin content, it is probable that the wood exhibits greater elasticity, and as a consequence, larger volumetric changes are observed. At higher wpg's, more highly lignified regions, such as the middle lamella are substituted and the associated volumetric changes are of lower magnitude.

Bearing in mind the observation made in section 6.3, that the volume increase due to modification has contributions both from the volume occupied by the reagent and a void volume created by the presence of adducts within the wood cell wall, it is apparent that the latter is larger at lower levels of substitutions.

It is also revealed that the volume occupied by the reagent in the wood cell wall due to modification is higher in Corsican pine than in Scots pine samples, regardless of the anhydride used (see Figures 3.16 to 3.25, in Appendix 3). This reaffirms the previous statement that a greater proportion of the volume increase due to modification is attributable to void volume in Corsican pine than in Scots pine modified wood. This is further discussed in the next section, where determination of the apparent void volume created by the acyl groups within the wood cell wall polymeric network has been undertaken.

6.5. Molar volume and ultimate OH substitution

Since the molar volumes vary with degree of substitution (Figures 6.5 and 6.6), the following procedure was adopted to determine the average molar volumes for each of the reagents. For each adduct there is a wpg above which there is no observable trend in the variation of molar volume (Figures 6.5 and 6.6); the data for molar volume above this wpg were averaged. These data was then used to produce the plot shown in Figure 6.7. The degree of ultimate OH substitution was determined from the rate curves for each of the modification reactions with the different anhydride reagents. It can be seen that a linear relationship is obtained between these two parameters.

From this relationship, it is possible to estimate the number of theoretically accessible OH groups as *ca* 6.30 (+-0.08) and 6.38 (+-0.14) mmoles/gm for Corsican and Scots pine respectively. In previous reports, the theoretical number of OH groups in Corsican pine was estimated as 14.9 mmoles/gm (Hill and Jones, 1996a). Since some of these OH groups are associated with crystalline regions of the cellulose, this will be an over-estimate of the number of OH groups accessible for reaction. The crystalline content of cellulose in wood has been estimated at around 65% (Fengel and Wegener, 1989), which suggests that a total of 8.6 mmoles/gm of OH groups should be theoretically available for reaction (Hill and Jones, 1996b). This estimate takes no account of OH groups which are inaccessible for other reasons (steric hindrance etc.). Since these values of 6.30 and 6.38 mmoles/gm were obtained experimentally, they are deemed to have greater significance than the theoretical value. It should be noted that determination of degree of OH groups substituted was obtained from rate curves at a time of reaction of 7 hours. A more precise determination of the ultimate OH substitution should be obtained from rate curves at more extended reaction times (several weeks), but again there will be an error associated with this, since the effect of substrate degradation will ensure that new reactive sites are created.

6.6. Calculation of void volume

As discussed in section 6.3, the volumetric changes in Corsican and Scots pine sapwood due to modification are due to the volume occupied by the reagent and an associated void volume. The determination of the apparent void volume created by the acyl groups within the wood cell wall polymeric network requires the use of theoretically calculated volumes for the attached acyl groups. These values are reported in the literature (Nakano, 1988) and have been also used by Hill and Jones (1999). Those values not reported were obtained by extrapolation.

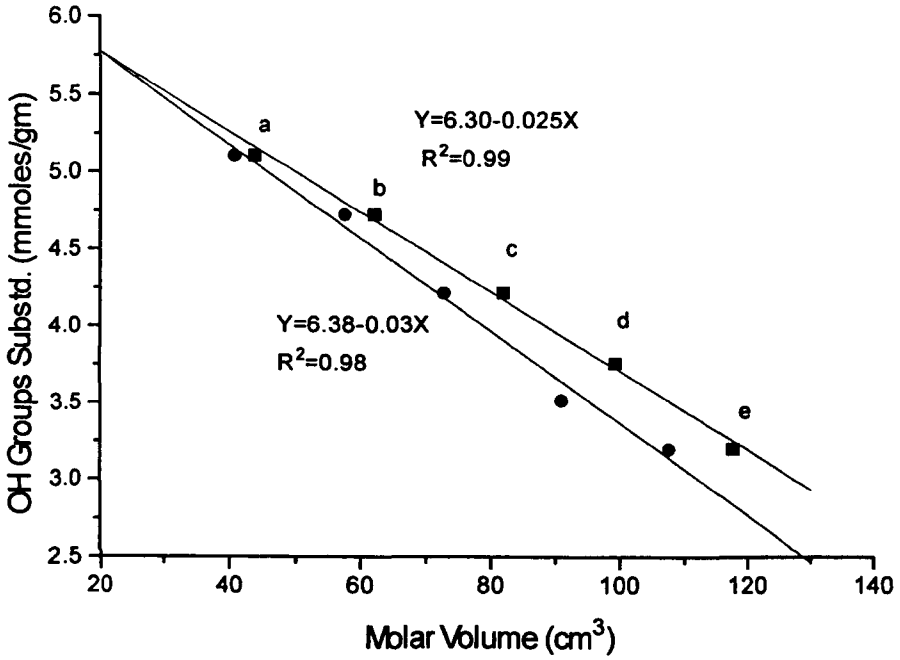


Figure 6.7: Relationship between ultimate degree of hydroxyl substitution and molar volume for a series of linear chain anhydrides. Acetic (a), propionic (b), butyric (c), valeric (d) and hexanoic (e). Corsican pine (■), Scots pine (●).

Void volumes (V_f) have been calculated for the various anhydride modified Corsican and Scots pine wood samples, by substracting the theoretical volumes (Vi) obtained from the literature (for each of the acyl groups) from the stable values of molar volumes (V) obtained from Figures 6.5 and 6.6. The results are given in Table 6.1 and are further illustrated in Figure 6.8.

From the results illustrated in Figure 6.8, the following conclusions are drawn. Firstly, that a larger void volume is created within the Corsican pine cell wall than in the Scots pine cell wall. This information indicates that there are differences in the way that the lignin-carbohydrate network deforms to accommodate the bonded acyl group.

Table 6.1: A comparison of measured molar volume (V), calculated molar volume (V_i) and void volume (V_f) for Corsican and Scots pine samples modified with different anhydride reagents (Units are cm^3 per mole).

R	V		V_i	V_f	
	Corsican	*Scots*		*Corsican*	*Scots*
CH_3	45	39	27.2	17.8	11.8
C_2H_5	62	57	37.5	24.5	19.5
C_3H_7	81	73	47.8	33.2	25.2
C_4H_9	98	89	58.1	39.9	30.9
C_5H_{11}	115	107	68.4	46.6	38.6

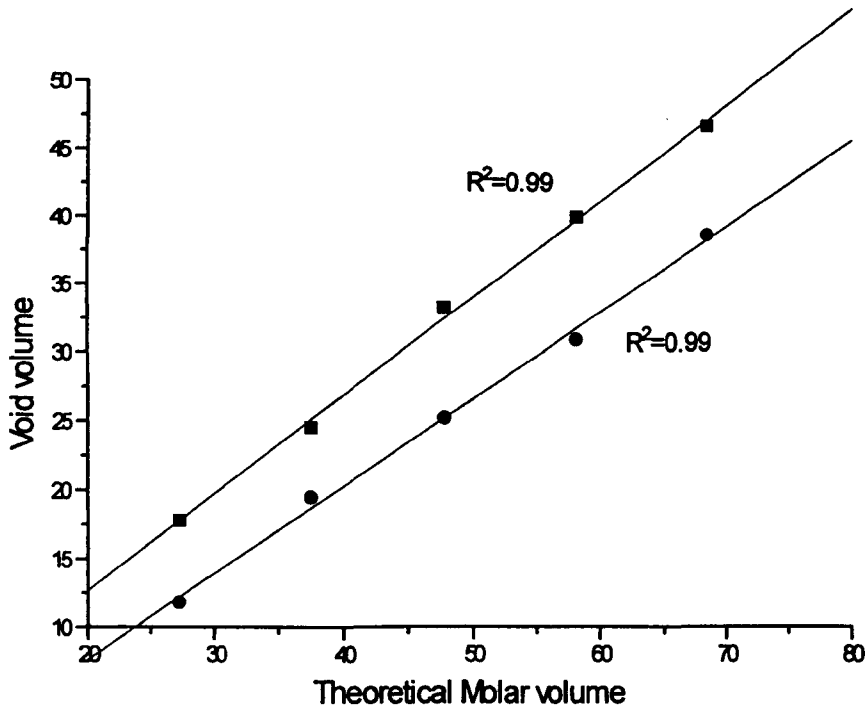


Figure 6.8: Relationship between void volume (V_f) and calculated molar volume (V_i) of acyl group of Corsican (■) and Scots pine (●) modified samples as the size of the anhydride increases. (Units are cm^3 per mole).

Secondly, it is apparent that void volumes created within the cell wall of both substrates studied, increase as the molecular size of the substituent increases. This observation is in agreement to the findings of Hill and Jones (1999).

Thirdly, there is a linear relationship between calculated molar volume (V_i) and void volume (V_f) which correlated with the chain length of adduct, in both substrates studied. This observation is in line with that made by Nakano (1988), but contradicts recent findings by Hill and Jones (1999) where a non-linear relationship was found between V_I and V_f. The linear relationship observed by Nakano was attributed to degradation of the lignin network, suggesting that a similar phenomenon may be occurring here. However, careful analysis of the volume increase as the level of modification increases shows this is not to be the case in this study, since a linear relationship was obtained between volume change due to modification and WPG (see Figure 6.1, and Figures 3.1 to 3.5, in Appendix 3). If degradation of the lignin network was the case, a deviation from linearity at high weight gains, and hence extended reaction times would be expected. The explanation may be due to the higher concentration of anhydride used in this study compared to that used by Hill and Jones. This will affect the rate of diffusion of anhydride molecule into the cell wall and hence the topochemical distribution of acyl groups.

6.7. Summary of points raised in Chapter 6

- With Corsican pine, larger volume changes than theoretically predicted were observed, whereas with the Scots pine the volume changes were close to those predicted.

- Volumetric changes due to modification with a homologous series of linear chain anhydrides were found to be due to the volume occupied by the reagent and an associated void volume created by the acyl groups within the cell wall.

- Larger volumetric changes and larger void volumes were found at lower levels of substitution.

- As the size of the reagent molecule increases so does the void volume created in the wood matrix.

- A linear relationship has been found between the void volume and the volume occupied by the adduct as the size of the reagent increases.

- Larger void volume is created by the acyl groups within the Corsican pine cell wall than in the Scots pine cell wall. This suggests that there are sub-microscopic differences between the two substrates, which lead to differences in the accessibility of reactive sites to reagents, or to differences in the way that the wood responds to modification.

- The volume occupied per molecule is larger in modified Corsican pine compared with modified Scots pine. This suggests that there are differences in the way that the lignin-carbohydrate network deforms to accommodate the bonded acyl group.

- Finally, by determining the relationship between average molar volume at high weight gains and ultimate level of hydroxyl substitution, for the range of anhydrides studied, it was possible to estimate the number of accessible hydroxyl groups at 6.30 and 6.38 mmoles/gm for Corsican and Scots pine respectively. These contrast with a theoretically calculated value of 8.6 mmoles/gm.

CHAPTER 7

The sorption of water vapour by chemically modified pine sapwood

7.1. Introduction

The wood-water relationship is one of the more important physical properties of wood. When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to cell wall polymers through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionally to the volume of water added. Chemical modification changes the properties of wood due to the reaction of the hydrophilic chemical groups within the wood and by bulking the cell wall.

Although a number of studies have been investigated the sorption properties of acetylated wood (Spalt, 1958; Risi and Arseneau, 1957a; Popper and Bariska, 1972; Forster, 1998; Chauhan *et al.* 2001), there has not been a study of the effect of modifying the wood with different sized anhydride reagents. It is known that rate and extent of water vapour sorption is decreased by substitution of the hydroxyl sites with acetyl groups. Two mechanisms may be proposed:

(i) Blocking of sorption sites.
(ii) Bulking of the cell wall by acetyl groups resulting in less space being available to sorbed water.

However, in previous studies it was not possible to determine the relative influence of each effect. By modifying wood with a variety of anhydride molecules of different size, it is possible to produce similar levels of bulking at different levels of OH substitution. Therefore, it becomes possible to separate the two effects.

Several models for fitting sorption isotherms to empirical data have been proposed. One such model is that proposed by Hailwood and Horrobin (1946). This model is described in section 7.3.4. Due to the close fit found when the Hailwood-Horrobin model has been applied to e.m.c data for wood (Spalt, 1958; Simpson, 1980) and for chemically modified wood (Martins, 1992; Forster, 1998), this model was also used in the present study.

A further advantage of the Hailwood and Horrobin model is the ease which the total water sorbed can be attributed to monomolecular and polymolecular sorption (Martins, 1992). This is potentially of great use when assessing and comparing wood reacted with a variety of modifying chemicals.

7.2. Literature Review

7.2.1. How moisture is held in wood

Moisture is found in wood in two forms: as liquid water in the cell wall, and as liquid and/ or vapour in the cell cavities. The basic reason for moisture entering into the mass of wood is the attraction of water molecules to the hydroxyl groups of its chemical constituents. As a result, a monomolecular layer of water is formed and held to these hydroxyls by hydrogen bonds (Figure 7.1 A). Formation of this layer results in the pushing apart of chains of cellulose molecules in the amorphous regions and between the crystallites of the microfibrils, so that wood starts to swell. Under the effect of secondary attractive forces, more water molecules enter and form a polymolecular layer (Figure 7.1 C). An additional part may also enter by capillary condensation in cell wall voids and pit features (Stamm, 1964).

The above phases (monomolecular, polymolecular layer, capillary condensation) are not clearly separated, but a distinction is made between water held in cell walls and in cell cavities: water held in cell walls is called 'bound water' and that which is held in cavities 'free water' (Tsoumis, 1991).

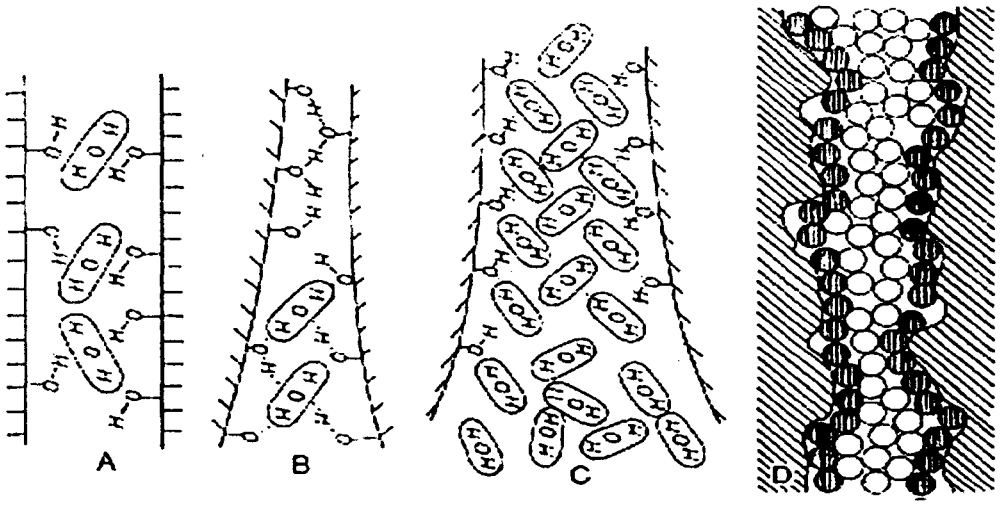


Figure 7.1. Water in wood. (A) Monomolecular layer of water held by free hydroxyls of cellulose chain molecules. (B). Gradual formation of the monomolecular layer by breaking the hydrogen bonds between adjucent cellulose molecules. (C). Polymolecular layer. (D). Schematic representation of monomolecular (dark circles) and polymolecular layer (white circles). (Tsoumis, 1991).

7.2.2. The fibre saturation point (F.S.P)

Skaar (1984) and Stamm (1971) discuss definitions and methods of measuring FSP in detail. The common definition of FSP is that it is the moisture content corresponding to saturation of the cell wall with no free water in the lumen.

The concept of fibre saturation point is useful from a practical point of view, because most properties change when the moisture content of wood is below this point. This relationship allows experimental determination of the FSP by measurement of a certain property (i.e. shrinkage, mechanical property, electrical resistance) at successively higher or lower moisture contents, until this property stops changing. However, the FSP cannot always be measured with accuracy. For practical purposes the critical moisture content of wood is taken as about 30% based on dry weight of wood, but it has been found to vary among species generally between 20 and 40%. (Stamm, 1971).

7.2.3. Water sorption and sorption isotherms

The mechanism by which water attaches to sites in the wood cell wall in response to changes in temperature or relative humidity is known as sorption. When wood is exposed to constant conditions of temperature or relative humidity, for a sufficient time, it desorbs or adsorbs moisture depending on its original hygrometric condition and finally retains a certain quantity of moisture; this is called the equilibrium moisture content (EMC) (Venkateswaran, 1970).

EMC shows differences when wood loses moisture for the first time, or adsorbs moisture after drying, or desorbs moisture when it has been previously adsorbed. EMC is greater in desorption than adsorption at a given relative humidity (Figure 7.2a). This phenomenon is called hysteresis (Spalt, 1958). It should be noted here that after the initial desorption of green wood, its hygroscopicity is permanently reduced at high relative humidities. In Figure 7.2a, curve *a* is not repeated, in contrast to curves *b* and *c*.

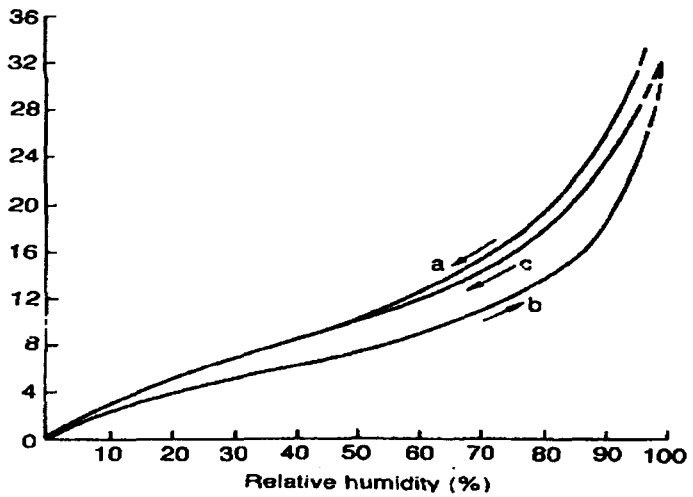


Figure 7.2 a. Moisture sorption isotherms for basswood (32^{0}C, 90F): a *initial desorption,* b *adsorption,* c *desorption following drying and saturation (Spalt, 1958).*

Various attempts have been proposed to explain moisture hysteresis. These are reviewed elsewhere (Martins, 1992). A simple explanation is that the phenomenon is due to linkage of free hydroxyls of the wood constituents when there is no moisture or very little moisture in wood. Thus, during subsequent adsorption, the number of available hydroxyls groups is lower (Skaar, 1988; Stamm, 1964).

The relationship between EMC and relative humidity, at a constant temperature, is called a sorption isotherm, and for wood exhibits a characteristic sigmoid shape, described by Urquhart (1960) as a type II sorption isotherm. Its sigmoid shape, always exhibiting hysteresis (irreversibility), indicates the polymolecular nature of sorption and the large forces of attraction between the wood and water molecules (Stamm, 1964). According to Skaar (1988), three kinds of sorption isotherms from the five described by Urquhart (1960) are applicable to water-wood relationships. Types I, II, III are depicted in Figure 7.2b. The relevance of type I and type III isotherms is discussed later in the section.

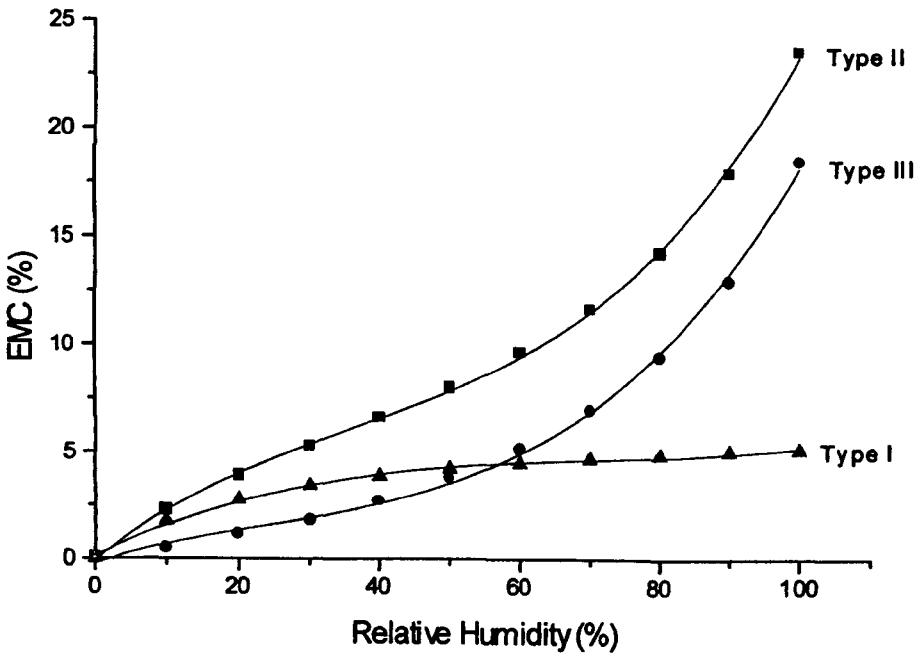


Figure 7.2 b: Type I, II and III adsorption isotherms calculated from data for unmodified Corsican pine.

There are several methods that have been used for fitting isotherms to experimental data for relative humidity and EMC. Skaar (1988) has reviewed those that have been used for wood. According to him, the various theories can be divided into two classes, namely the surface sorption theories represented by the BET theory (Brunauer, Emmet, and Teller,1938) and solution theories represented by the Hailwood-Horrobin theory (1946).

Both of these theories consider bound water in wood to be held in two separate ways. These are monomolecular sorption (forms a type I isotherm), in which a single layer of water molecules forms hydrogen bonds to available sorption sites on the wood polymers; and polymolecular sorption (forms a type III isotherm), in which water is sorbed within the cell wall but is not in direct contact with the sorption sites. The sigmoid shape of the type II isotherm appears to be an amalgam of the types III and I.

Adsorption at the monomolecular layer, at low relative humidities, is considered to be the dominant form, as an increasing number of sorption sites is exposed. As humidity increases, polymolecular sorption becomes increasingly important (Wangaard and Granados, 1967). True capillary condensation is believed to take place at the upper range of relative humidities as the isotherm rises steeply when the saturation condition is approached. The major part of capillary condensation occurs in the microscopically visible capillary structure of wood and to a limited degree, within the cell walls (Stamm, 1964).

The main difference between the BET and Hailwood-Horrobin theories is the way in which they assume that the polymolecular water is held with in the cell wall. The BET theory considers polymolecular sorption to take the form of additional layers building up on a first monolayer, bonded to the wood polymers. The Hailwood-Horrobin theory considers monomolecular sorption to take the form of a hydrate of the cell wall polymers while polymolecular water is assumed to be in solution with the wood polymers (Hartley *et al.* 1992).

Other sorption theories are often based on either of these two.

The Hailwood-Horrobin model allows for the formation of a multiple hydrate with a single unit of a polymer. Applying the model to wood, Spalt (1958) assumed the formation of a single hydrate, and found this to give a good fit to EMC data for various wood species.

Simpson (1980), has tested a number of the most widely known theories, including the Hailwood-Horrobin and BET models. Since all models include simplifying assumptions necessary in order to derive a mathematical model, the agreement between the measured heat of sorption and that predicted by the model was poor. With the exception of the BET model, all models tested gave an excellent fit to the EMC data; in addition the Hailwood-Horrobin model showed a particularly good fit between model and experiment.

In practice, if relative humidities above 99.5% are used, then condensation occurs in the microscopically visible capillary structure of the wood after the cell walls have became saturated (Stamm, 1964). Equilibrium moisture content at a relative humidity of 100% is equivalent to complete saturation of the wood. When fitting a Hailwood-Horrobin isotherm to data such as that used in this study (i.e. highest e.m.c reading at 93%) the isotherm forms an extrapolation to 100% relative humidity at a much lower moisture content. The 100% relative humidity value calculated from such an extrapolation is often used as an estimate for F.S.P (Stamm, 1964).

In order to correctly measure hysteresis using this model, it must be fitted separately to e.m.c data measured in adsorption and desorption (Spalt, 1958).

All models have limitations and are at best approximations of what happens in the cell wall. Two such limitations of the Hailwood-Horrobin model are that it does not predict hysteresis and does not take account of capillary condensation.

7.2.4. Water sorption characteristics of chemically modified wood

A method used to assess wood-water relationships in modified wood has been through studies of sorption characteristics. There have been several studies of sorption that have involved wood modified with anhydrides.

Stamm and Tarkow (1947), measured the equilibrium moisture content (e.m.c) of unreacted and vapour phase acetylated (30% acetyl content) Sitka spruce at various humidities and found a 67% reduction in water sorbed at 95% relative humidity.

In research carried out by Risi and Arseneau (1957a), vapour phase acetylated Balsa fir samples were exposed to a series of relative humidities produced over saturated salt solution. They found that increased levels of modification lead to greater reductions in e.m.c. This effect was attributed to the combined effects of bulking and decreased hygroscopicity as a result of the introduction of the acetyl groups into the cell walls. They also measured swelling at each relative humidity and found a linear relationship between moisture content and swelling for each WPG, which was not the same for different levels of modification, i.e. at higher levels of reaction, swelling was lower for the same quantity of water in the cell wall, regardless of the relative humidity.

Spalt (1958), used the Hailwood –Horrobin model to fit isotherms to sorption data for sixteen unmodified wood species and to modified white spruce. Acetylation was carried out with acetic anhydride in an evacuated reaction tube in the vapour phase, using pyridine at the solvent catalyst (1:1 vol:vol.). The treated samples with 32% acetyl content were oven dried to constant weight and taken through a single desorption-adsorption cycle. From the results of the analysis, he concluded that the effect of acetylation to this level was to reduce e.m.c at saturation by 63%. Separating isotherms into the two components, he measured a 67% reduction in surface sorption (monomolecular sorption) at saturation and 62% reduction in capillary condensed water (here Spalt is referring to polymolecular sorption and not to the capillary condensation in the existing, non transient, capillaries as defined by Stamm, 1964).

He also found that at saturation, 76% of the reduction in the total water sorbed was due to cell wall bulking (as opposed to reduction in sorption sites).

The sorption properties of modified white fir with acetic and phthalic anhydride were measured by fitting isotherms to sorption data using the BET and Hailwood–Horrobin models (Popper and Bariska, 1972). It was found that the reaction with acetic anhydride significantly reduced monomolecular adsorption, as the hydrophilic hydroxyl groups were replaced. In contrast, wood modified with phthalic anhydride gave monomolecular adsorption isotherms similar to untreated wood. This was attributed to the hydrophilic acid hydroxyl introduced during reaction with phthalic anhydride. Reduction in sorption due to phthalic anhydride modification was found to be almost solely due to bulking, thereby causing a reduction in polymolecular sorption.

Martins (1992), measured the adsorption and desorption characteristics of Corsican pine and Beech (*Fagus sylvatica*) modified with mono- and difunctional isocyanates. Isotherms were fitted using the Hailwood-Horrobin model. In all cases increasing WPG caused a reduction in sorption. Martins attributed this to:

- The increasing number of hydroxyl groups blocked (having a particular effect on monomolecular sorption).
- Bulking (affecting polymolecular sorption).
- Cross-linking restricting swelling (in the case of difunctional isocyanates).

The latter of these only affected polymolecular adsorption at high relative humidities. On saturation however, blocks reacted with difunctional isocyanates were found to swell fully. Martins concluded that cross-linking does not prevent swelling but hinders it, causing lower adsorption at humidities up to saturation. Measuring swelling at various relative humidities, he found similar results to those of Risi and Arseneau (1957a) for acetylated wood. Swelling and equilibrium moisture content formed a linear relationship for all the isocyanates used, with lower swelling per unit increase in moisture content for the wood reacted to higher weight gains.

Martins (1992), in order to test the effect of size of modifying chemical on sorption, compared water sorption of wood with butyl (molecular weight 99.13) and octadecyl isocyanate (molecular weight 295.1). He found the sorption isotherms to be almost identical for the two chemicals at equivalent WPG. Monomolecular adsorption isotherms were very similar, despite the significantly lower numbers of hydroxyl reacted by the octadecyl isocyanate. This was attributed to site shielding by the large hydrophobic chain introduced into the wood cell wall, causing hydroxyls to become inaccessible to monomolecular adsorption. Monomolecular desorption isotherms were found to differ slightly, with the octadecyl isocyanate modified wood sorbing more water at the monomolecular layer. Martins concluded that at saturation, the octadecyl chain may move slightly away from the sorption sites within the cell wall, making some extra sites available for sorption.

7.3. Materials and methods

7.3.1. Modified wood

Samples of the two wood species, Scots pine (*Pinus sylvestris*) and Corsican pine (*Pinus nigra*) unmodified and modified to different WPG's with the five carboxylic linear chain anhydrides (see Table 7.1) comprised the basic matrix of variants. Approximately equivalent WPG'S were carefully selected for the wood samples modified with the different anhydrides in order to assess the effect of molecular size of the substituent group on site accessibility.

Two samples from each reaction set were selected, oven dried overnight at 105^0C and oven dry weights recorded. In the cases where swelling was measured (see selected weight gains in Table 7.1, indicated with bold font), as described in the following Chapter, oven dry dimensions of unmodified and modified samples were recorded.

Table 7.1: Experimental design.

Wood species	Modifying chemical	WPG (%)
Corsican pine	Acetic anhydride	**5.2**, 11.4, **15.8**, 19.6, **22.5**
	Propionic anhydride	5.3, 11.2, 15.3, 20.1, 25.7
	Butyric anhydride	5.5, 11.1, 16, 20.1, 26.1
	Valeric anhydride	4.9, 10.9, 15.5, 19.8, 26.2, 28.9
	Hexanoic anhydride	**5.7**, 12.1, **15.7**, 19.5, **25.4**, 29.1
Scots pine	Acetic anhydride	**5.7**, 10.7, **16.1**, 20.1, **21.9**
	Propionic anhydride	6.1, 10.9. 15.6, 19.7, 24.5
	Butyric anhydride	5.8, 11.3, 16, 19.9, 25.2
	Valeric anhydride	5.9, 11.4, 16.2, 20.4, 24.9, 27.5
	Hexanoic anhydride	**6.2**, 11.1, **15.7**, 20.5, **25.3**, 28.6

7.3.2. Control of relative humidity

The method for controlling relative humidity was identical to that used by Martins (1992) and Forster (1998). Test samples were kept above saturated solutions of selected salts in containers stored in a controlled temperature room set at 20^0C (variation +/- 1 ^{0}C). Pure water results in the saturated vapour pressure corresponding to 100% relative humidity. The addition of a solute to water reduces its vapour pressure in proportion to its mole fraction in the case of diluted solutions. When a saturated solution at a controlled temperature is used, a constant relative humidity is maintained (Siau, 1995).

This technique which is described by Stamm (1964), has been widely used and was selected for being simple, economical and reasonably precise. The relative humidity within a container may be alternatively controlled by other means such as by controlling the dry-bulb temperature with thermostatically-operating heating and cooling devices and by thermostatically regulating the wet-bulb temperature or the dew point (Siau, 1995).

Six salts were chosen and these are listed in Table 7.2 along with the relative humidity of the atmosphere above each saturated solution at 20^0C (according to Kaye and Laby, 1966). They were chosen on the basis of giving minimum relative humidity variation with changes in the temperature (Stamm, 1964). Data published by Kaye and Laby (1966) show the equilibrium relative humidity above saturated solutions of these salts to be insensitive to any variation in temperature expected in the controlled temperature room (a variation around 20^0C of +/-5^0C causing a maximum variation of +/- 1% relative humidity).

Excess salt was always present within each solution to ensure saturation was maintained. The solution and air in the container were agitated by bubbling air through the solution.

Table 7.2: Saturated salt solutions used and their resultant relative humidities at 20 ^{0}C.

Salt	Relative humidity (%)
Potassium nitrate (KNO_3)	93
Sodium chloride (NaCl)	76
Sodium dichromate ($Na_2Cr_2O_7$)	55
Potassium carbonate (K_2CO_3)	44
Potassium acetate (CH_3COOK)	23
Lithium chloride (LiCl)	12

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 psychometer 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 7.2 were therefore assumed to be correct.

Thin wood wafers were used in each container alongside the test samples, to monitor any variation in humidity above a particular salt solution. These wafers were expected to equilibrate much faster than the test samples and so give an indication of any unexpected variation. No such variation was detected.

The lack of an accurate measure of relative humidity for verification in this experiment was unfortunate, but this does not affect the comparisons made between modified (and unmodified) wood samples exposed under identical conditions.

7.3.3. Sample conditioning

The oven dry wood samples were placed in the containers above saturated salt solutions. They were left to equilibrate for 4 weeks and then weighed once a week,

using a four-place analytical balance until it became obvious that no significant weight change had occurred since the last weight was recorded (and e.m.c had been attained).

To minimise moisture gain from the surface of the samples during weighing, the samples were placed in closed weighing bottles. Care was taken to minimise the number of times the samples were removed from the container.

Equilibrium moisture content was reached within 6 weeks for all but the two highest humidities, which required longer exposure times. Furthermore, it was observed that at each relative humidity, the time required for the samples to attain e.m.c increased as the molecular size of the adduct increased, i.e. samples modified with acetic anhydride attained e.m.c quicker than those modified with hexanoic anhydride.

7.3.4. Description of the Hailwood-Horrobin model and isotherm fitting

This model was designed to explain the sigmoid sorption isotherm observed with the sorption of water vapour on polymers, particularly with textiles (Hailwood and Horrobin, 1946). It has been applied to the sorption of water vapour into wood, for which it has proved to be useful; although it has been criticised for some of the assumptions used in its derivation. Good descriptions of this model can be found in Spalt, 1958; Skaar, 1972; Skaar, 1988; Okoh and Skaar, 1980; and Simpson, 1980. The Hailwood Horrobin (HH) model considers that water sorbed by wood can exist in two forms:

Water of hydration
Solid solution

Three chemical species are present: 'dry' polymer, hydrated polymer (chemisorbed water), and dissolved water. These three components are considered to act as an ideal solution. It is convenient to treat this in terms of molar concentrations. If X_o is

assigned as the number of moles of unhydrated polymer, X_h as the number of moles of hydrated polymer, and X_s as the number of moles of dissolved or unhydrated water.

Note that, water of hydration corresponds to water molecules that are H-bonded to the cell wall polymeric OH groups, whereas dissolved water corresponds to 'free' water molecules that are less constrained.

The molecular weight (W_o) of the wood cell wall polymers is unknown, but it is possible to calculate this in terms of the molecular weight of polymer per mole of water sorption sites (i.e. accessible OH groups).

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_s, of the three species are equal to their mole fractions in solution, thus:

$$A_h = X_h / (X_o + X_h + X_s) \qquad \textbf{(7.1)}$$

$$A_o = X_o / (X_o + X_h + X_s) \qquad \textbf{(7.2)}$$

$$A_s = X_s / (X_o + X_h + X_s) \qquad \textbf{(7.3)}$$

When an equilibrium condition exists between the three components, an equation of the form can be written:

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

Thus:

$$K_1 = A_h / A_o A_s = X_h / X_o A_s \qquad \textbf{(7.4)}$$

or

$$X_h = K_1 X_o A_s \qquad (7.5)$$

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:

$$K_2 = A_s / h \qquad (7.6)$$

or

$$A_s = K_2 / h \qquad (7.7)$$

The ratio $X_h / (X_h + X_o)$ gives the moles 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 7.5 and 7.7 gives:

$$\frac{X_h}{X_h + X_o} = \frac{K_1 X_o K_2 h}{K_1 X_o K_2 h + X_o} = \frac{K_1 K_2 h}{K_1 K_2 h + 1} \qquad (7.8)$$

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 7.3 in inverted form and rearranging to give:

$$(X_h + X_o) / X_s = (1/A_s) - 1 = (1 - A_s) / A_s \qquad (7.9)$$

Inverting, and using equation 7.7 to eliminate A_s, gives:

$$\frac{X_s}{X_h + X_o} = \frac{K_2 h}{(1 - K_2 h)} \qquad (7.10)$$

The sum of equations 7.8 and 7.10 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 (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_o. Thus:

$$\frac{X_h}{X_h + X_o} + \frac{X_s}{X_h + X_o} = [(\text{g hydrated water}/18) + (\text{g dissolved water}/18)]/(\text{g dry wood}/W) \quad \textbf{(7.11)}$$

$$\frac{X_h + X_s}{X_h + X_o} = \frac{W}{18}[(\text{g hydrated water}) + (\text{g dissolved water})]/(\text{g dry wood}) \quad \textbf{(7.12)}$$

$$\frac{X_h + X_s}{X_h + X_o} = (W/18)(m_h + m_s) = (W/18)m \quad \textbf{(7.13)}$$

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 7.13 can be combined with equations 7.8 and 7.10 to give:

$$m = m_h + m_s = \frac{W}{18}\left(\frac{K_1K_2h}{1 + K_1K_2h} + \frac{K_2h}{1 - K_2h}\right) \quad \textbf{(7.14)}$$

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

$$M = M_h + M_s = \frac{1{,}800}{W}\left(\frac{K_1K_2H}{100 + K_1K_2H}\right) + \frac{1{,}800}{W}\left(\frac{K_2H}{100 - K_2H}\right) \quad \textbf{(7.15)}$$

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 $18/W_o$, 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:

$m_1 = 18/ W_o$ (g/g); $M_1 = 1{,}800/ W_o$ (%) **(7.16)**

According to equations 7.14 and 7.15, there are three constants K_1, K_2, and W_o (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 H 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 7.15 can be transformed thus:

$$\frac{H}{M} = \frac{W}{1{,}800}\left[\frac{(100 + K_1K_2H)(100 - K_2H)}{K_1K_2(100 - K_2H) + K_2(100 + K_1K_2H)}\right] \quad \textbf{(7.17)}$$

$$\frac{H}{M} = \frac{W}{18}\left[\frac{1}{K_2(K_1 + 1)}\right] + \frac{W(K_1 - 1)H}{1{,}800(K_1 + 1)} - \frac{W}{180{,}000}\left(\frac{K_1K_2H^2}{K_1 + 1}\right) \quad \textbf{(7.18)}$$

or

$$\frac{H}{M} = A + Bh - Ch^2 \quad \textbf{(7.19)}$$

where

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1 + 1)}\right] \quad \textbf{(7.20)}$$

$$B = \left(\frac{W}{1{,}800}\right)\left[\frac{K_1 - 1}{K_1 + 1}\right] \quad \textbf{(7.21)}$$

$$C = \left(\frac{W}{180{,}000}\right)\left[\frac{K_1K_2}{K_1 + 1}\right] \quad \textbf{(7.22)}$$

From equation 7.19, it can be seen that the Hailwood Horrobin theory predicts a parabolic relationship between the ratio H/M and h. 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_o, and hence M_h and M_s.

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

$$K_1 = 1 + \frac{B^2 + \sqrt{B^2 + 4AC}}{2AC} \tag{7.23}$$

$$K_2 = \frac{200C}{B + \sqrt{B^2 + 4AC}} \tag{7.24}$$

$$W = 1800\left(\frac{4AC + B^2 + B\sqrt{B^2 + 4AC}}{B + \sqrt{B^2 + 4AC}}\right) \tag{7.25}$$

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

$$M = \frac{M_o K_2(K_1 + 1)h}{(1 + K_1K_2h)(1 - K_2h)} \tag{7.26}$$

Where: $M_o = 1800/W_o$, $M = 100m$, and $H = 100h$.

By using the formula $h/m = A + Bh - Ch^2$, (7.27)
the following relationships can be obtained:

$$K_2 = \frac{-B + \sqrt{B^2 + 4AC}}{2A} \tag{7.28}$$

$$K_1 = \frac{1}{1 - K_2(B/C)} \tag{7.29}$$

$$M_o = \frac{100}{AK_2(K_1 + 1)} \tag{7.30}$$

$$W_0 = 18\,[A\,K_2\,(K_1 + 1)] \tag{7.31}$$

$$M_h = \frac{M_o K_1 K_2 h}{1 + K_1 K_2 h} \tag{7.32}$$

$$M_s = \frac{M_o K_2 h}{1 - K_2 h} \tag{7.33}$$

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

7.4. Results and discussion

7.4.1. Isotherm fitting

The mean moisture contents (of 2 wood blocks) at each relative humidity are given in Tables 7.3 and 7.4 for Corsican and Scots pine respectively. The experimental mean values were then transformed by dividing the relative vapour pressure (h) by the equilibrium moisture content (m). A curve of the form of equation 7.27 was fitted to these data points, as depicted in Figure 7.3, and values of A, B, C and R^2 obtained. Values for the physical constants K_1, K_2, W_o, M_o were calculated using the equations 7.28 to 7.31.

All these values are listed in Tables 7.5 and 7.6 for Corsican and Scots pine respectively.

The physical constants K_1, K_2, W_o, M_o obtained were found to be in good agreement with those previously reported by Spalt (1958); Wangaard and Granados (1967) for unmodified control wood, and by Martins (1992); Forster (1998) for modified wood. For the modified wood, the M_o values decrease as the WPG increases, indicating that a proportion of sites are made unavailable for water sorption.

As defined in section 7.3.4, the constant 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 vary approximately between 0.7 and 0.82 for Corsican pine and between 0.71 and 0.79 for Scots pine wood, indicating that the dissolved water shows a lower activity than the liquid water. This suggests that the freedom of motion of water in the pores (dissolved water) is not the same as that in liquid water.

The goodness of fitting, as measured by the coefficient of determination (R^2) is remarkably high, considering the complexity of the matrix of data, where wood samples of two species were chemically modified at several levels of reaction with different anhydrides. The R^2 values (given in Tables 7.5 and 7.6) range from 0.890 to 0.996 for both Corsican and Scots pine, indicating good fit to the experimental results.

Table 7.3: Mean (and standard deviation) values for experimentally derived e.m.c's at various levels of relative humidity for the unmodified and modified Corsican pine samples.

Reagent	WPG(%)	EMC (%)					
		12	23	44	55	76	93
Control	0	2.59 (.18)	4.35 (.02)	7.27 (.08)	8.49 (.08)	13.01 (.08)	19.29 (.12)
Acetic	5.2	2.19 (.05)	3.64 (.02)	6.01 (.05)	7.25 (.05)	10.87 (.02)	16.01 (.15)
	11.4	1.91 (.0.4)	3.07 (.04)	5.27 (.08)	6.35 (.08)	9.62 (.09)	15.01 (.11)
	15.8	1.63 (0.7)	2.54 (.05)	4.39 (.05)	5.16 (.05)	7.77 (.16)	12.02 (.12)
	19.6	1.24 (.11)	2.13 (.02)	3.74 (.08)	4.43 (.08)	6.71 (.14)	10.37 (.08)
	22.5	0.99 (.08)	1.73 (.02)	3.28 (.05)	3.91 (.05)	6.05 (.11)	9.54 (.09)
Propionic	5.3	2.06 (.02)	3.51 (.01)	5.82 (.08)	7.09 (.02)	10.69 (.09)	15.85 (.05)
	11.2	1.77 (.07)	2.66 (0.8)	4.99 (.05)	5.89 (.05)	9.21 (.01)	14.26 (.09)
	15.3	1.48 (.08)	2.34 (.01)	4.21 (.11)	4.89 (.14)	7.52 (.19)	11.83 (.12)
	20.1	1.14 (.04)	1.99 (0.8)	3.52 (.11)	4.11 (.11)	6.49 (.05)	10.09 (.18)
	25.7	0.91 (.11)	1.58 (0.5)	2.97 (.05)	3.69 (.04)	5.81 (.09)	9.21 (.19)
Butyric	5.5	1.98 (.04)	3.31 (.02)	5.61 (.14)	7 (.04)	10.42 (.18)	15.77 (.05)
	11.1	1.62 (.04)	2.77 (.07)	4.88 (.02)	5.94 (.08)	9.01 (.14)	13.28 (.04)
	16	1.39 (.09)	2.22 (.09)	4.01 (.11)	4.67 (0.1)	7.33 (.08)	11.01 (.11)
	20.1	1.17 (.04)	2.06 (.07)	3.69 (.01)	4.24 (.12)	6.57 (.07)	10.32 (.09)
	26.1	0.85 (.04)	1.42 (.04)	2.71 (.12)	3.54 (.02)	5.61 (.07)	8.78 (.18)
Valeric	4.9	2.21 (.02)	3.62 (.02)	6.11 (.05)	7.33 (.04)	11.01 (.08)	16.16 (.21)
	10.9	1.74 (.05)	2.73 (.02)	4.78 (.05)	5.99 (.05)	8.64 (.05)	14.39 (.15)
	15.5	1.57 (.07)	2.4 (.07)	4.57 (.07)	5.31 (.07)	7.95 (.07)	12.22 (.120
	19.8	1.21 (.02)	2.12 (.05)	3.33 (.04)	4.21 (.08)	6.77 (.07)	10.23 (.02)
	26.2	0.91 (.02)	1.39 (.05)	2.73 (.08)	3.62 (.05)	5.53 (.08)	8.99 (.05)
	28.9	0.98 (.07)	1.66 (0.4)	3.09 (.08)	4.01 (.07)	5.88 (.05)	9.19 (.09)
Hexanoic	5.7	1.99 (.02)	3.21 (.01)	5.61 (.07)	7.15 (.05)	10.51 (.19)	15.33 (.09)
	12.1	1.65 (.05)	2.75 (.08)	4.96 (.05)	5.88 (.01)	8.49 (.05)	13.67 (.08)
	15.7	1.49 (.05)	2.49 (.02)	4.39 (.05)	5.12 (.02)	7.72 (.09)	12.04 (.5)
	19.5	1.11 (.05)	2.01 (.05)	3.49 (.04)	4.01 (.07)	6.72 (.02)	10.39 (.08)
	25.4	1.01 (.04)	1.65 (.09)	3.12 (.04)	3.79 (.05)	5.61 (.07)	9.01 (.16)
	29.1	1.02 (.01)	1.59 (.05)	3.06 (.05)	3.73 (.05)	5.55 (.07)	8.92 (.02)

Table 7.4: Mean (and standard deviation) values for experimentally derived e.m.c's at various levels of relative humidity for the unmodified and modified Scots pine samples.

Reagent	WPG(%)	EMC (%)					
		12	23	44	55	76	93
Control	0	2.33 (.05)	4.19 (.09)	7.02 (.02)	8.38 (.09)	12.68 (.19)	18.95 (.28)
Acetic	5.7	2.05 (.07)	3.48 (.08)	5.79 (.04)	7.12 (.14)	10.64 (.07)	15.88 (.18)
	10.7	1.88 (.04)	2.86 (.09)	5.06 (.08)	6.41 (.08)	9.55 (.08)	13.2 (.26)
	16.1	1.55 (.08)	2.42 (.09)	4.51 (.12)	5.23 (.12)	7.65 (.05)	12.12 (.16)
	20.1	1.15 (.08)	1.99 (.04)	3.55 (.09)	4.35 (.12)	6.6 (.07)	10.22 (.14)
	21.9	0.94 (.04)	1.65 (.09)	3.2 (.11)	3.82 (.14)	5.99 (.08)	9.38 (.12)
Propionic	6.1	2.01 (.08)	3.45 (.08)	5.62 (.14)	6.88 (.05)	10.45 (.05)	15.62 (.24)
	10.9	1.81 (.08)	2.71 (.09)	5.19 (.05)	6.15 (.14)	9.33 (.14)	13.86 (.15)
	15.6	1.33 (.05)	2.1 (.12)	4.05 (.14)	5.01 (.15)	7.62 (.12)	12.01 (.18)
	19.7	1.19 (.09)	2.11 (.05)	3.32 (.09)	4.01 (.11)	6.55 (.08)	9.98 (.15)
	24.5	0.9 (.12)	1.62 (.05)	2.77 (.15)	3.65 (.05)	5.71 (.08)	9.42 (.12)
Butyric	5.8	1.88 (.11)	3.15 (.09)	5.81 (.16)	7.21 (.12)	10.29 (.14)	15.65 (.05)
	11.3	1.69 (.05)	2.99 (.08)	5.01 (.21)	6.11 (.11)	9.15 (.18)	13.66 (.12)
	16	1.25 (.14)	2.02 (.14)	3.89 (.05)	4.45 (.08)	7.15 (.11)	10.85 (.22)
	19.9	1.19 (.09)	1.99 (.08)	3.54 (.08)	4.15 (.08)	6.38 (.08)	10.01 (.12)
	25.2	0.92 (.05)	1.52 (.04)	2.61 (.05)	3.39 (.16)	5.51 (.07)	8.65 (.14)
Valeric	5.9	2.15 (.05)	3.52 (.14)	6.02 (.14)	7.02 (.04)	10.79 (.14)	15.89 (.16)
	11.4	1.58 (.08)	2.53 (.02)	4.58 (.05)	5.88 (.05)	8.33 (.08)	13.22 (.09)
	16.2	1.45 (.04)	2.36 (.08)	4.29 (.08)	5.11 (.12)	7.85 (.09)	12.01 (.16)
	20.4	1.11 (.12)	2.01 (.21)	3.19 (.04)	4.02 (.18)	6.48 (.22)	9.92 (.22)
	24.9	0.93 (.07)	1.44 (.07)	2.63 (.11)	3.55 (.08)	5.55 (.18)	9.19 (.25)
	27.5	0.89 (.04)	1.41 (.11)	2.66 (.06)	3.44 (.07)	5.68 (.09)	9.12 (.18)
Hexanoic	6.2	2.01 (.04)	3.15 (.07)	5.41 (.12)	7.25 (.09)	10.62 (.24)	15.02 (.18)
	11.1	1.57 (.07)	2.62 (.09)	4.55 (.08)	5.66 (.04)	8.66 (.12)	13.11 (.14)
	15.7	1.32 (.09)	2.29 (.12)	4.11 (.12)	5 (.16)	7.49 (.012)	11.85 (.22)
	20.5	1.19 (.05)	2.02 (.22)	3.66 (.09)	4.12 (.15)	6.52 (.15)	10.02 (.14)
	25.3	1.06 (.07)	1.58 (.05)	3.02 (.09)	3.55 (.05)	5.81 (.25)	8.88 (.18)
	28.6	0.82 (.09)	1.39 (.15)	2.72 (.09)	3.39 (.09)	5.71 (.15)	9.01 (.08)

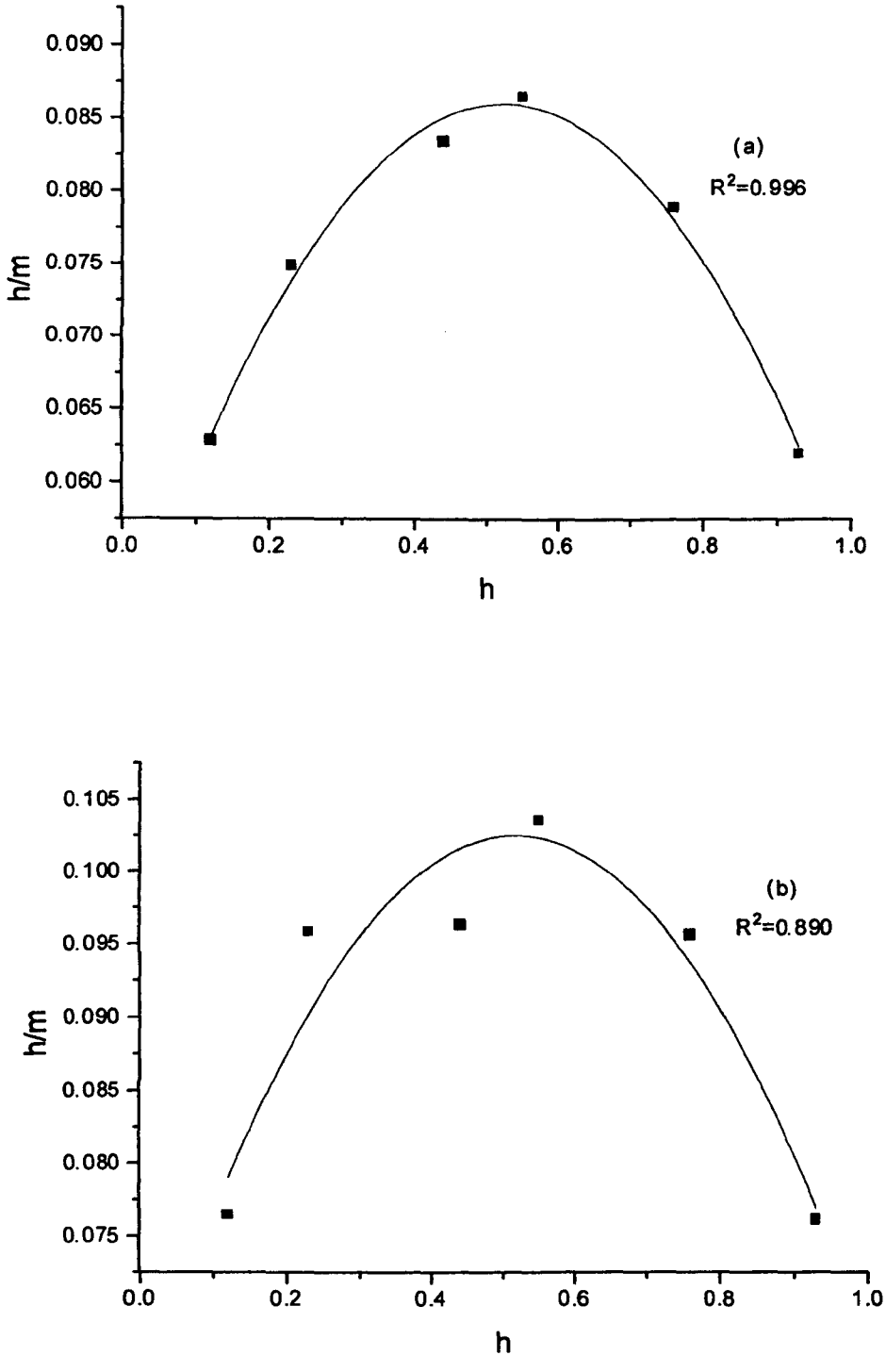


Figure 7.3: Selected plots of the form of h/m against h, in order to obtain A, B, C and R^2 values. (a) Best fit to data points (data from Corsican pine wood modified with acetic anhydride at 5.2 WPG); (b) Worst fit to data points (data from Scots pine wood modified with valeric anhydride at 15.5 WPG).

Table 7.5: Fitted and physical constants calculated for the Hailwood –Horrobin adsorption isotherms (Corsican pine data).

Reagent	WPG	A	B	C	K_1	K_2	W_o	M_o	R^2
Control	0	3.44	10.54	9.71	5.13	0.74	281.5	6.39	0.976
Acetic	5.2	4.1	12.47	11.42	5.12	0.73	333.2	5.40	**0.996**
	11.4	4.72	14.89	14.25	5.10	0.76	398.7	4.51	0.99
	15.8	5.4	19.04	17.7	5.61	0.76	491.2	3.661	0.976
	19.6	7.67	17.81	17.5	4.12	0.74	526.0	3.427	0.968
	22.5	10.47	15.61	17.43	3.001	0.74	561.6	3.20	0.955
Propionic	5.3	4.46	12.11	11.38	4.67	0.73	336.5	5.34	0.993
	11.2	5.45	15.1	15.03	4.56	0.77	424.3	4.24	0.925
	15.3	6.21	18.64	18.05	4.89	0.77	507.7	3.54	0.956
	20.1	8.37	18.83	19.15	3.95	0.76	567.9	3.16	0.956
	25.7	11.53	16.74	19.57	2.89	0.76	619.0	2.90	0.989
Butyric	5.5	4.76	12.14	11.12	4.56	0.71	341.1	5.27	0.998
	11.1	6.11	12.16	12.03	3.74	0.721	378.3	4.75	0.993
	16	6.83	18.11	17.63	4.50	0.75	512.1	3.51	0.956
	20.1	8.18	17.65	17.81	3.88	0.74	538.2	3.34	0.924
	26.1	12.78	17	20.93	2.71	0.77	663.5	2.716	0.973
Valeric	4.9	4.14	12.05	11.09	4.96	0.73	326.4	5.51	0.994
	10.9	5.27	16.3	15.98	4.95	0.78	441.8	4.07	0.957
	15.5	6.25	15.46	14.96	4.32	0.74	445.6	4.03	**0.89**
	19.8	7.33	22.41	22.2	4.88	0.78	611.2	2.948	0.964
	26.2	11.91	19.96	23.37	3.10	0.79	699.8	2.57	0.897
	28.9	10.92	14.99	17.05	2.85	0.73	560.4	3.21	0.973
Hexanoic	5.7	4.99	11.04	10.66	4.04	0.72	329.2	5.46	0.973
	12.1	5.77	13.81	13.42	4.22	0.74	402.6	4.47	0.923
	15.7	6.23	16.51	15.87	4.53	0.74	465.2	3.86	0.957
	19.5	8.47	19.26	20.14	3.91	0.77	584.1	3.08	0.921
	25.4	10.05	19.32	20.21	3.55	0.75	619.8	2.90	0.933
	29.1	9.98	20.82	21.71	3.73	0.76	649.0	2.77	0.908

Table 7.6: Fitted and physical constants calculated for the Hailwood–Horrobin adsorption isotherms (Scots pine data).

Reagent	WPG	A	B	C	K_1	K_2	W_o	M_o	R^2
Control	0	4.03	9.16	8.77	4.13	0.72	270.1	6.66	0.955
Acetic	5.7	4.51	12.04	11.36	4.61	0.73	336.6	5.34	**0.996**
	10.7	5.33	12.64	11.78	4.31	0.71	364.8	4.93	0.914
	16.1	6.14	16.35	15.61	4.57	0.74	459.1	3.92	0.901
	20.1	8.64	16.56	17.16	3.56	0.74	530.0	3.39	0.987
	21.9	11.32	14.24	16.78	2.69	0.74	558.4	3.22	0.955
Propionic	6.1	4.49	12.95	12.21	4.85	0.74	354.0	5.08	0.989
	10.9	5.57	13	12.68	4.15	0.74	382.4	4.70	**0.890**
	15.6	7.73	14.46	15.62	3.44	0.76	473.5	3.80	0.928
	19.7	7.22	23.85	23.3	5.18	0.78	634.2	2.83	0.952
	24.5	10.99	20.77	23.56	3.36	0.79	689.4	2.61	0.985
Butyric	5.8	5.49	9.11	9.15	3.35	0.70	303.3	5.93	0.936
	11.3	5.6	12.72	12.22	4.12	0.72	375.6	4.79	0.979
	16	8.08	16.27	16.93	3.66	0.75	512.8	3.50	0.906
	19.9	7.91	20.1	19.86	4.34	0.76	578.3	3.11	0.965
	25.2	10.49	26.02	27.92	4.06	0.80	773.9	2.32	0.986
Valeric	5.9	4.22	12.61	11.67	5.03	0.74	339.6	5.29	0.977
	11.4	6.33	13.62	13.69	3.88	0.74	415.2	4.33	0.927
	16.2	6.72	15.64	15.59	4.09	0.75	463.7	3.88	0.968
	20.4	8.18	21.91	22.26	4.40	0.78	625.7	2.87	0.955
	24.9	10.91	24.71	27.66	3.75	0.82	767.4	2.34	0.947
	27.5	11.83	21.37	25.06	3.23	0.80	729.5	2.46	0.956
Hexanoic	6.2	5.01	11.2	10.82	4.06	0.72	333.0	5.40	0.899
	11.1	6.16	14.36	14.37	4.08	0.75	426.0	4.22	0.998
	15.7	7.49	14.52	15.02	3.59	0.74	462.7	3.89	0.971
	20.5	7.96	19.09	18.87	4.18	0.75	559.2	3.21	0.917
	25.3	9.29	24.47	25.14	4.33	0.79	704.7	2.55	0.907
	28.6	13.23	17.05	21.86	2.62	0.79	684.8	2.62	0.977

R^2 is a statistical measure of the proportion of variation that can be explained by the regression line (i.e. for unmodified control Corsican pine, the regression line accounted for 97.6% of variation); the lower the R^2 value the lower the proportion of total variation accounted for the fitted regression line. Therefore, an example representing the worst overall variation in EMC attained through the model in this study, was chosen to assess the sensitivity of the EMC obtained by means of equation 27 to the degree of fitting. The example in Table 7.7, shows deviations between experimental and calculated data of about 0.24% moisture content or less, that is of a similar magnitude as the experimental standard deviation. This is in good agreement with the work of Simpson (1980), who found that the worst deviation between experimental and calculated sorption data was about 0.8% moisture content, by analysing experimental sorption data from the USDA Wood Handbook, using the Hailwood-Horrobin model.

Table 7.7: Example showing the sensitivity of the EMC calculated by means of equation 6.2 to the degree of fit, for the lowest R^2 value (0.890). Data for Corsican pine wood modified at 15.5 WPG with valeric anhydride.

RH (%)	EMC (%)		Deviation from exp.
	Experimental	Calculated	value (% of m.c)
12	1.57	1.52	-0.05
23	2.40	2.42	+0.02
44	4.57	4.33	-0.24
55	5.31	5.37	+0.06
76	7.95	8.12	+0.17
93	12.22	12.09	-0.13

7.4.2. Isotherms for chemically modified wood

Figures 7.4 to 7.8 and 7.19 to 7.23 show the sorption isotherm families for each modification type, for Corsican and Scots pine respectively. The isotherms for monomolecular and polymolecular adsorption are plotted, as described in section 7.3.4, in Figures 7.9 to 7.18 and 7.24 to 7.33 for Corsican and Scots pine respectively.

For the unmodified woods, the isotherms produced by monomolecular sorption rise rapidly in the range of low R.H, levelling off asymptotically at higher R.H showing the characteristic shape of a Type I isotherm. The curves produced by polymolecular sorption approach an asymptote to the moisture content axis at saturation and present the shape of the Type III isotherm. The isotherms for total sorption (the amalgam of monomolecular and polymolecular sorption) are of Type II, exhibiting the well known sigmoid shape (see section 7.2.3). Figure 7.2b shows clearly that polymolecular sorption predominates at the intermediate and higher R.H, while monomolecular sorption predominates at the lower ones.

Figure 7.4 indicates an obvious trend of reducing hygroscopicity with increasing WPG for acetic anhydride. This also holds for the monomolecular and polymolecular isotherms in Figures 7.9 and 7.10. Similar trends were found for all of the anhydrides studied, in both Corsican and Scots pine wood.

Of interest is the behaviour of Corsican pine wood modified with valeric and hexanoic anhydride at the highest WPG (26.2%, 28.9%; 25.4%, 29.1 respectively), where the sorption isotherms in Figures 7.7 and 7.8 cross one another indicating higher monomolecular adsorption (see Figures 7.15 and 7.17), and higher polymolecular adsorption (see Figures 7.16 and 7.18). This also holds for the Scots pine modified wood (see Figures 7.22 and 7.23, for valeric and hexanoic anhydride respectively). This behaviour, which occurs when a value of approximately 26% WPG is exceeded, may indicate some degree of cell wall degradation. As a consequence of this, new sorption sites were made available in the wood cell wall. Thus, despite the higher quantity of chemical being introduced in the cell wall, higher monomolecular and polymolecular adsorption were observed; the opposite of what would be predicted.

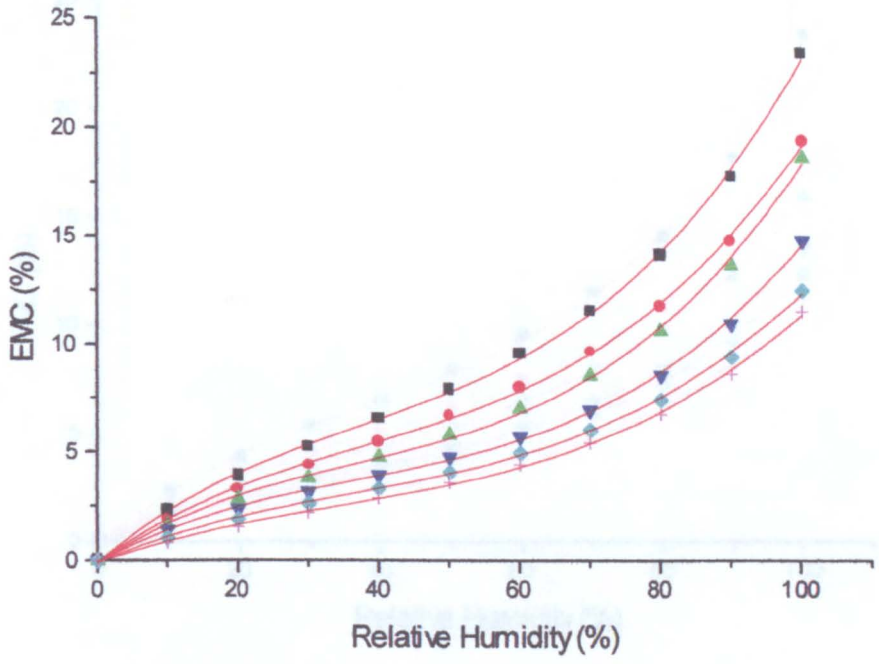


Figure 7.4: Adsorption isotherms for Corsican pine control (■) and acetic anhydride modified wood: 5.2 WPG (●); 11.4 WPG (▲); 15.8 WPG (▼); 19.6 WPG (◆); 22.5 WPG (+).

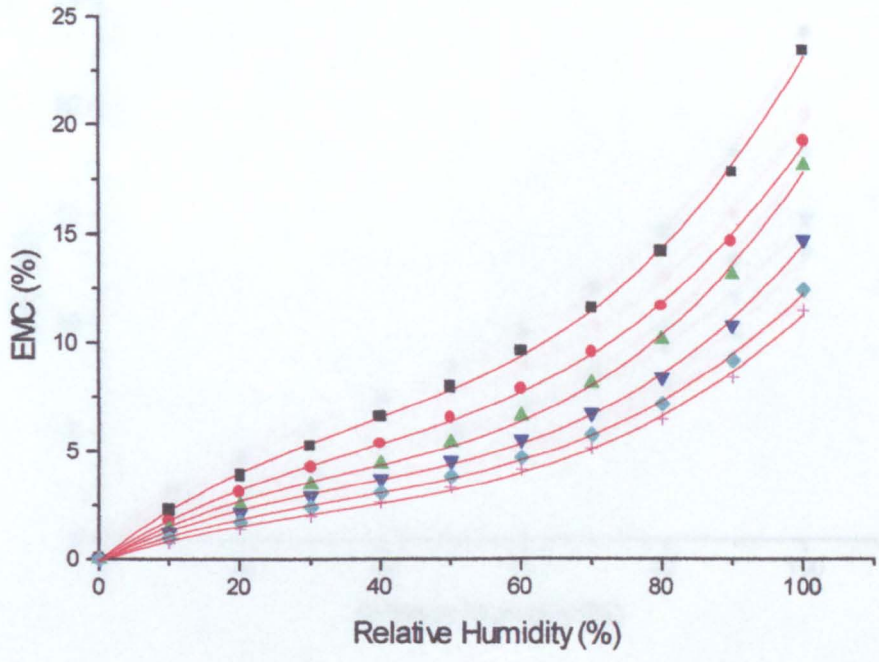


Figure 7.5: Adsorption isotherms for Corsican pine control (■) and propionic anhydride modified wood: 5.3 WPG (●); 11.2 WPG (▲); 15.3 WPG (▼); 20.1 WPG (◆); 25.7 WPG (+).

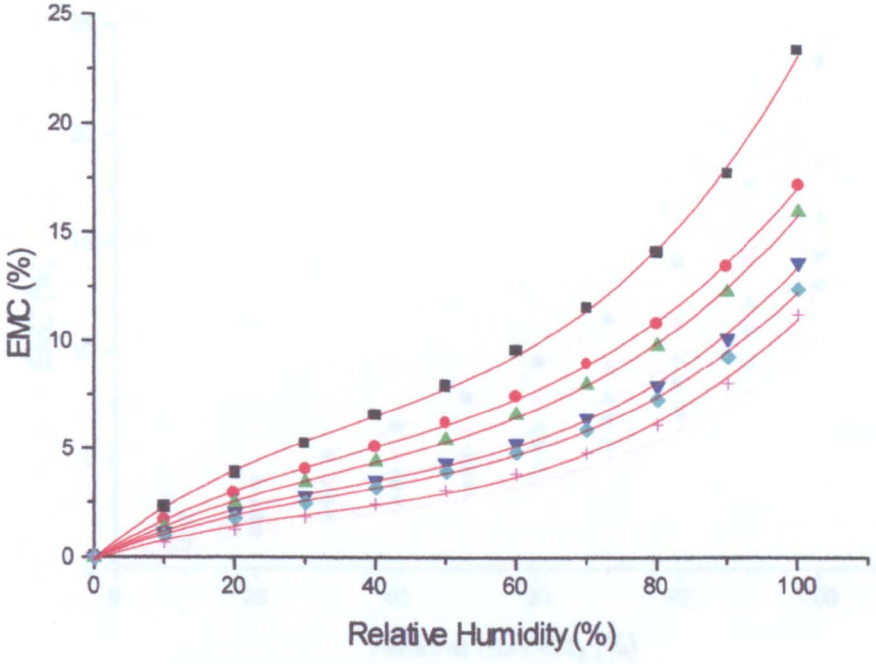


Figure 7.6: Adsorption isotherms for Corsican pine control (■) and butyric anhydride modified wood: 5.5 WPG (●); 11.5 WPG (▲); 16 WPG (▼); 20.1 WPG (◆); 26.1 WPG (+).

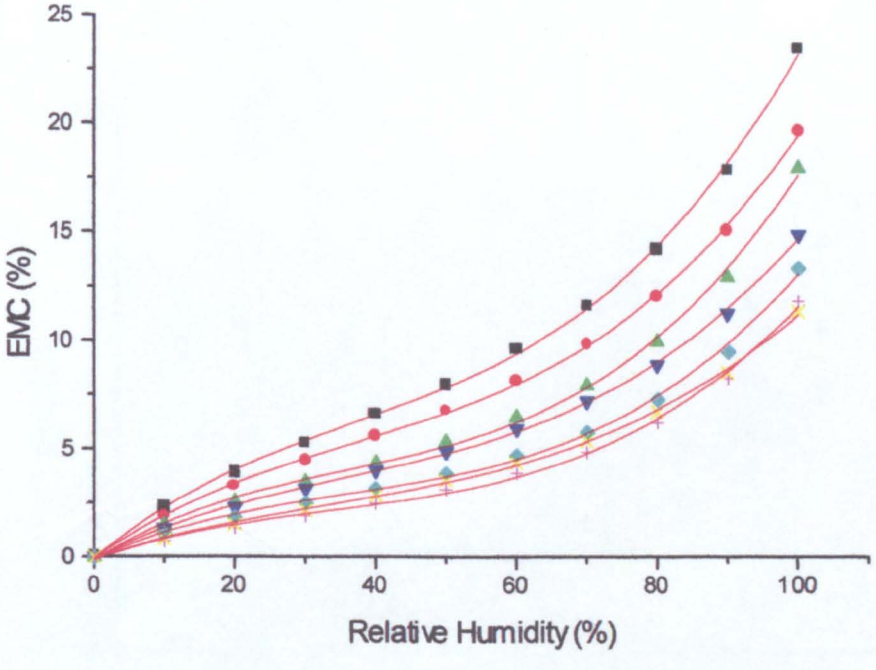


Figure 7.7: Adsorption isotherms for Corsican pine control (■) and valeric anhydride modified wood: 4.9 WPG (●); 10.9 WPG (▲); 15.5 WPG (▼); 19.8 WPG (◆); 26.2 WPG (+); 28.9 WPG (X).

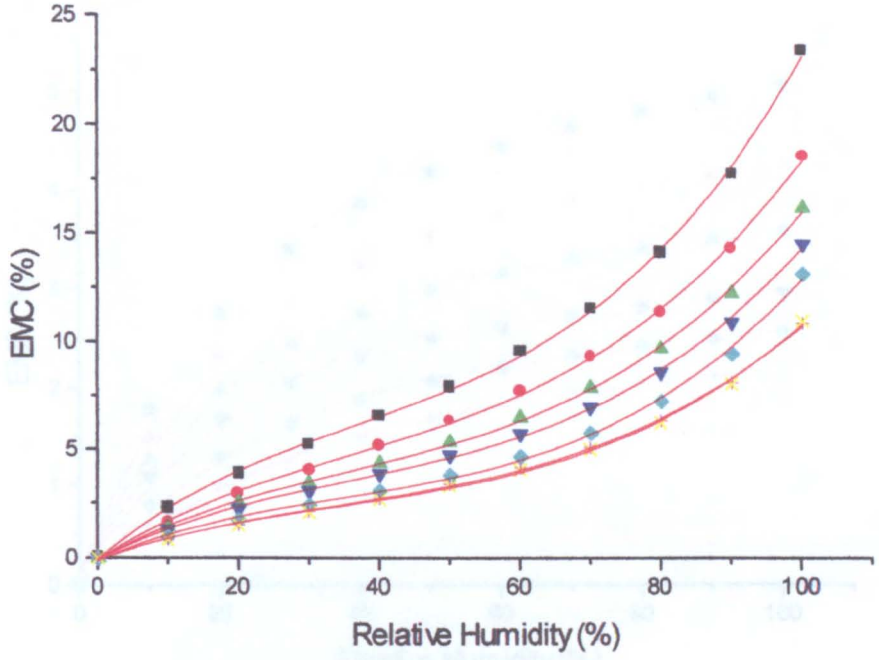


Figure 7.8: Adsorption isotherms for Corsican pine control (■) and hexanoic anhydride modified wood: 5.7 WPG (●); 12.1 WPG (▲); 15.7 WPG (▼); 19.5 WPG (◆); 25.4 WPG (+); 29.1 WPG (*).

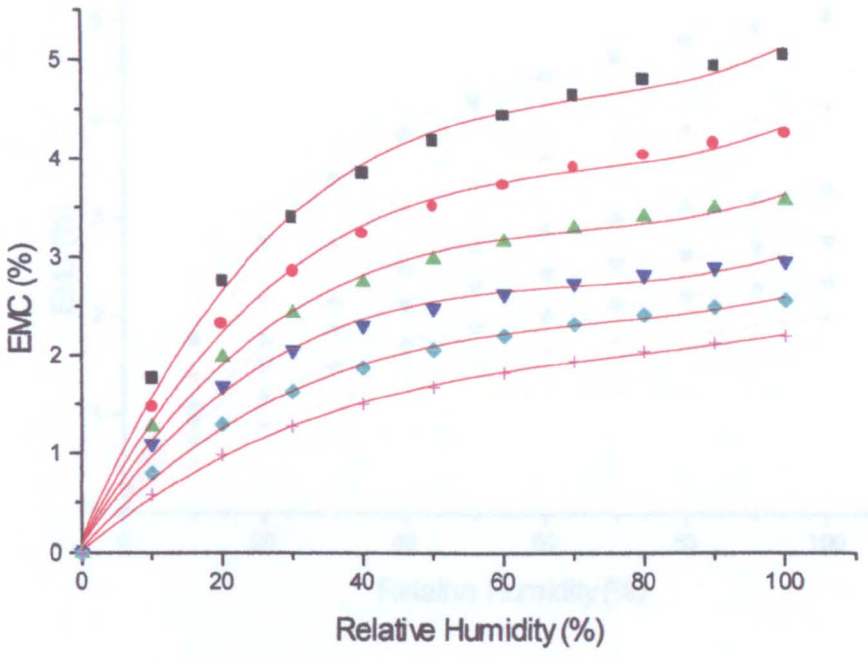


Figure 7.9: Monomolecular adsorption isotherms for Corsican pine control (■) and acetic anhydride modified wood: 5.2 WPG (●); 11.4 WPG (▲); 15.8 WPG (▼); 19.6 WPG (◆); 22.5 WPG (+).

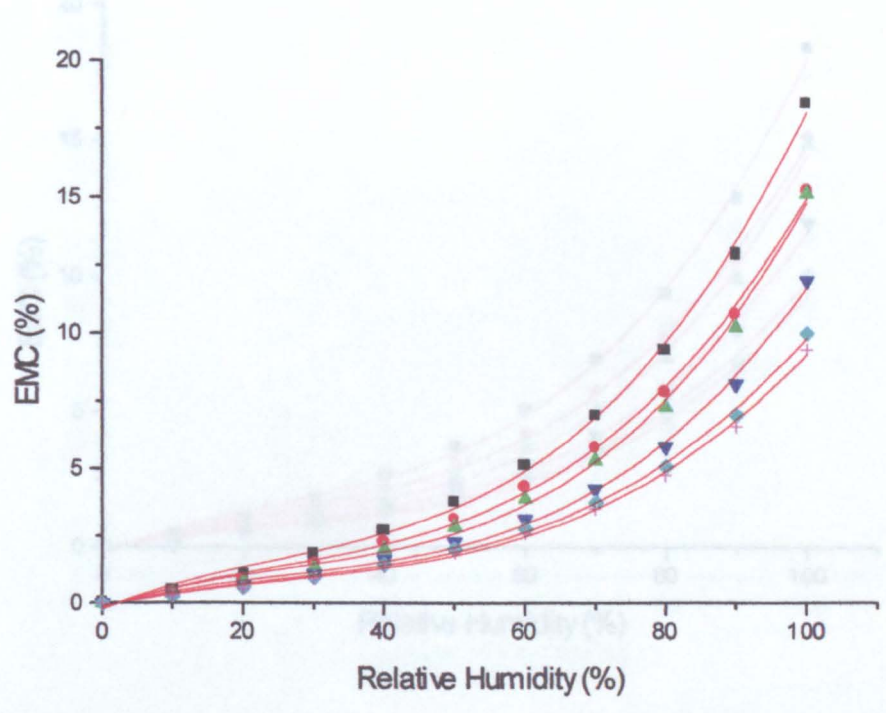


Figure 7.10: Polymolecular adsorption isotherms for Corsican pine control (■) and acetic anhydride modified wood: 5.2 WPG (●); 11.4 WPG (▲); 15.8 WPG (▼); 19.6 WPG (◆); 22.5 WPG (+).

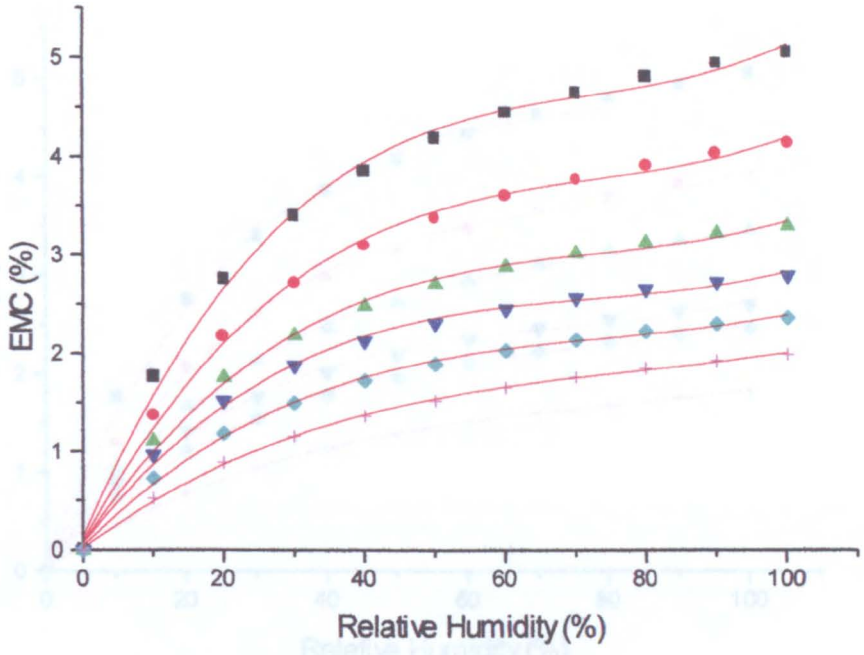


Figure 7.11: Monomolecular adsorption isotherms for Corsican pine control (■) and propionic anhydride modified wood: 5.3 WPG (●); 11.2 WPG (▲); 15.3 WPG (▼); 20.1 WPG (◆); 25.7 WPG (+).

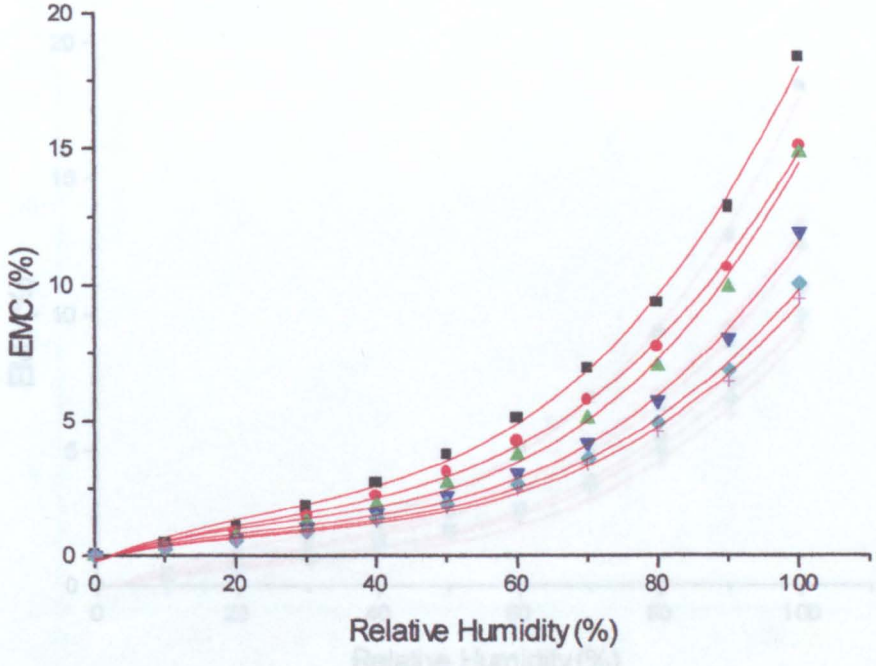


Figure 7.12: Polymolecular adsorption isotherms for Corsican pine control (■) and propionic anhydride modified wood: 5.3 WPG (●); 11.2 WPG (▲); 15.3 WPG (▼); 20.1 WPG (◆); 25.7 WPG (+).

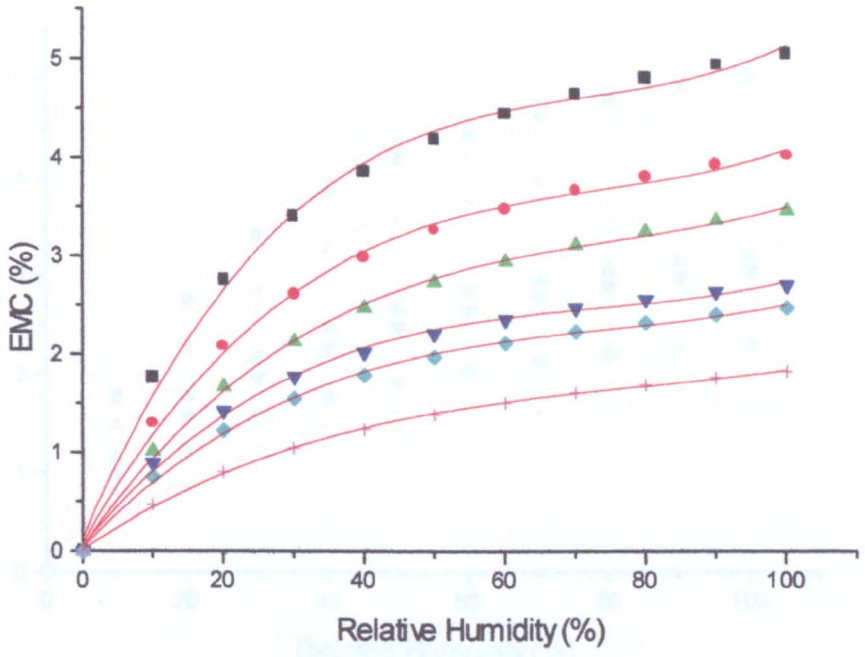


Figure 7.13: Monomolecular adsorption isotherms for Corsican pine control (■) and butyric anhydride modified wood: 5.5 WPG (●); 11.5 WPG (▲); 16 WPG (▼); 20.1 WPG (◆); 26.1 WPG (+).

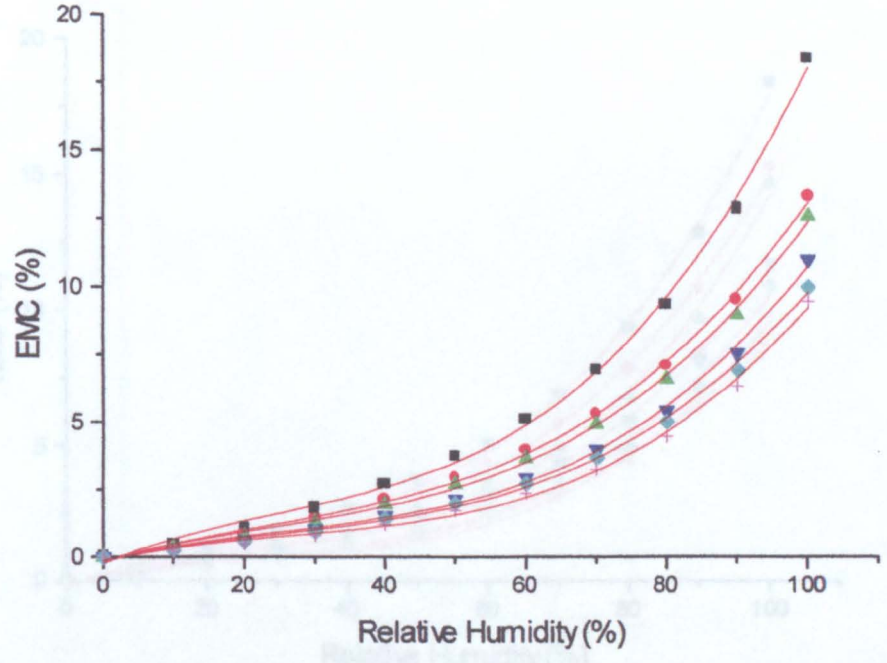


Figure 7.14: Polymolecular adsorption isotherms for Corsican pine control (■) and butyric anhydride modified wood: 5.5 WPG (●); 11.5 WPG (▲); 16 WPG (▼); 20.1 WPG (◆); 26.1 WPG (+).

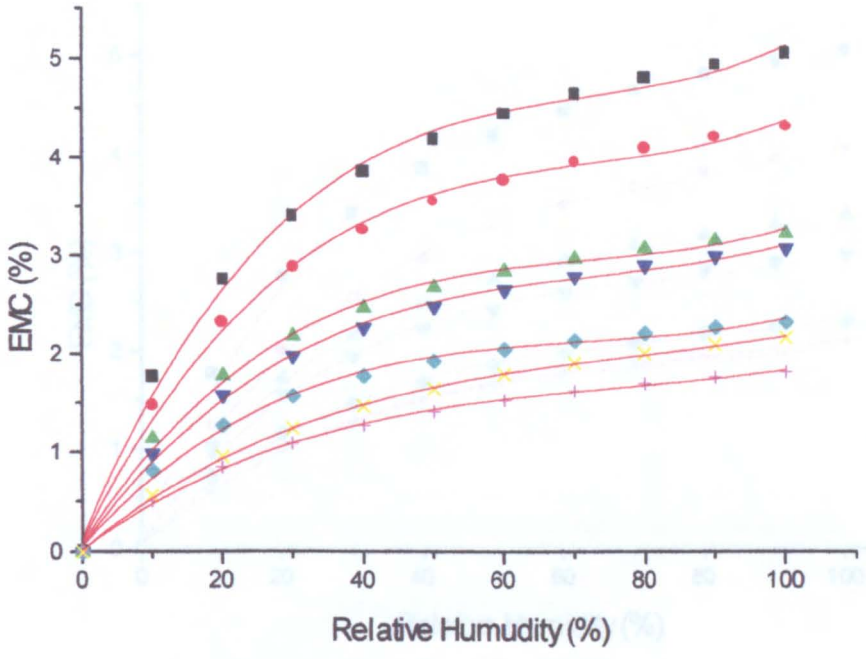


Figure 7.15: Monomolecular adsorption isotherms for Corsican pine control (■) and valeric anhydride modified wood: 4.9 WPG (●); 10.9 WPG (▲); 15.5 WPG (▼); 19.8 WPG (◆); 26.2 WPG (X); 28.9 WPG (+).

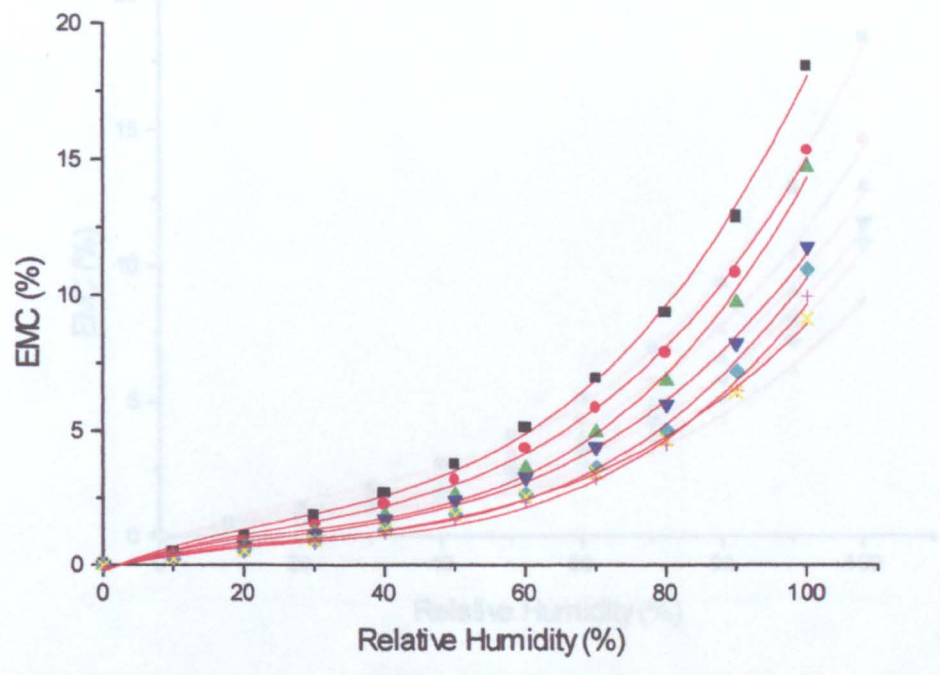


Figure 7.16: Polymolecular adsorption isotherms for Corsican pine control (■) and valeric anhydride modified wood: 4.9 WPG (●); 10.9 WPG (▲); 15.5 WPG (▼); 19.8 WPG (◆); 26.2 WPG (X); 28.9 WPG (+).

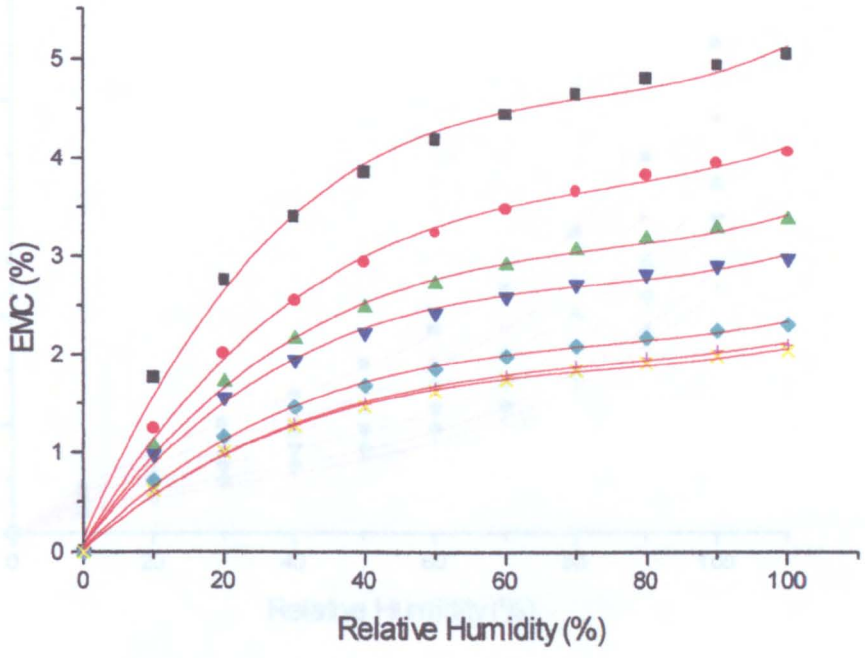


Figure 7.17: Monomolecular adsorption isotherms for Corsican pine control (■) and hexanoic anhydride modified wood: 5.7 WPG (●); 12.1 WPG (▲); 15.7 WPG (▼); 19.5 WPG (◆); 25.4 WPG (+); 29.1 WPG (X).

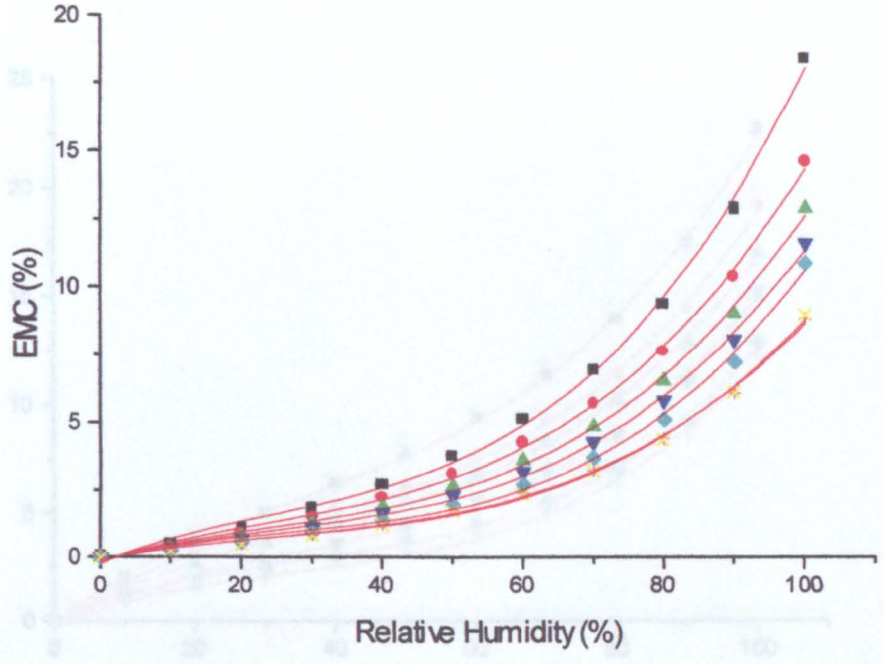


Figure 7.18: Polymolecular adsorption isotherms for Corsican pine control (■) and hexanoic anhydride modified wood: 5.7 WPG (●); 12.1 WPG (▲); 15.7 WPG (▼); 19.5 WPG (◆); 25.4 WPG (+); 29.1 WPG (X).

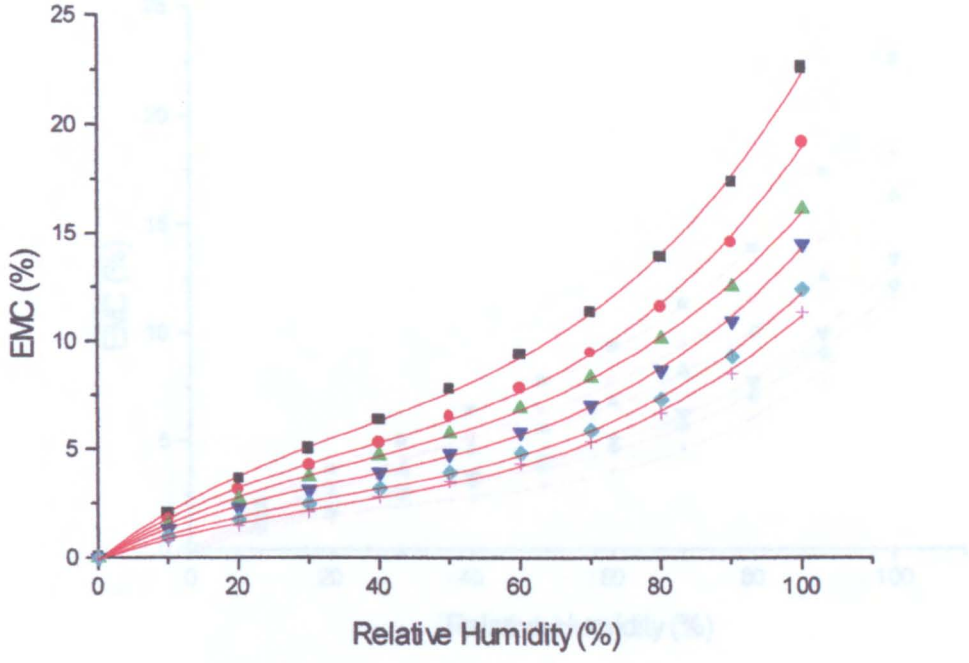


Figure 7.19: Adsorption isotherms for Scots pine control (■) and acetic anhydride modified wood: 5.7 WPG (●); 10.7 WPG (▲); 16.1 WPG (▼); 20.1 WPG (◆); 21.9 WPG (+).

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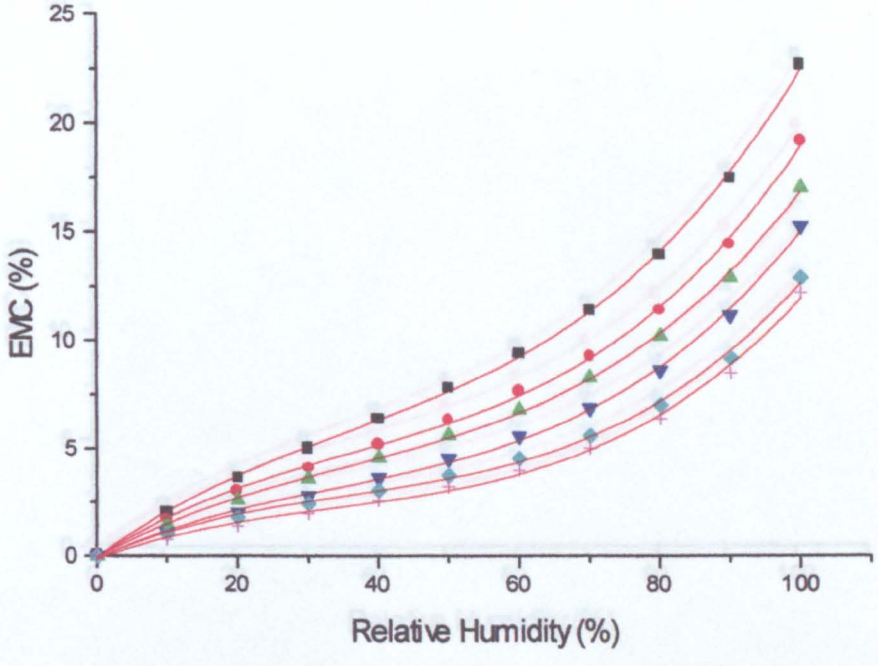

Figure 7.20: Adsorption isotherms for Scots pine control (■) and propionic anhydride modified wood: 6.1 WPG (●); 10.9 WPG (▲); 15.6 WPG (▼); 19.7 WPG (◆); 24.5 WPG (+).

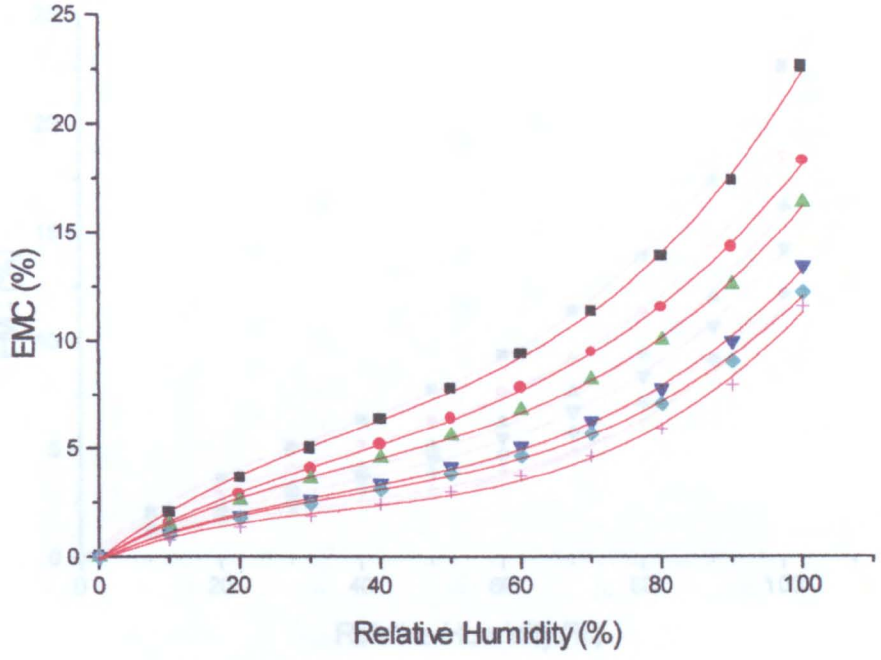

Figure 7.21: Adsorption isotherms for Scots pine control (■) and butyric anhydride modified wood: 5.8 WPG (●); 11.3 WPG (▲); 16 WPG (▼); 19.9 WPG (◆); 25.2 WPG (+).

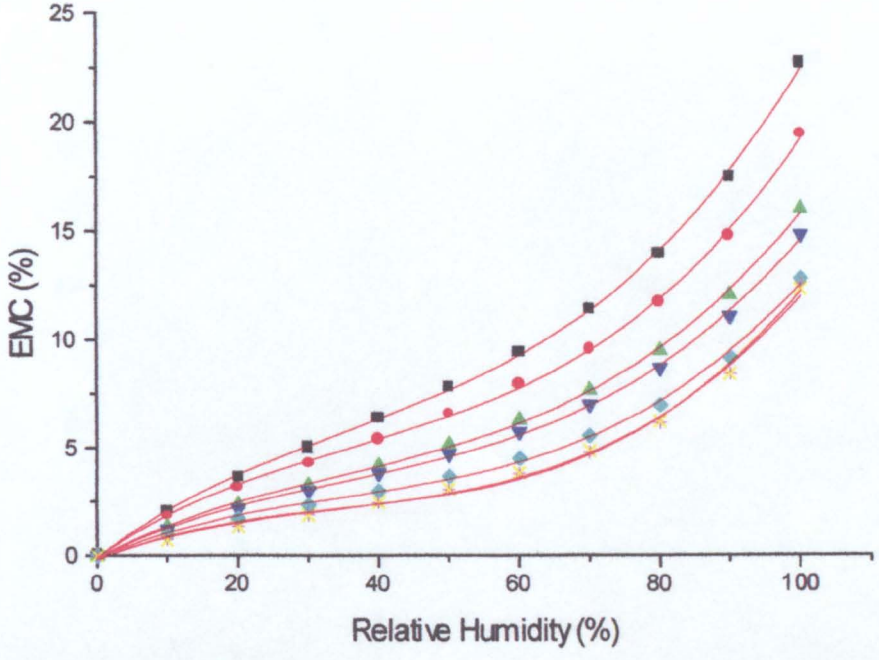

Figure 7.22: Adsorption isotherms for Scots pine control (■) and valeric anhydride modified wood: 5.9 WPG (●); 11.4 WPG (▲); 16.2 WPG (▼); 20.4 WPG (◆); 24.9 WPG (+); 27.5 WPG (X).

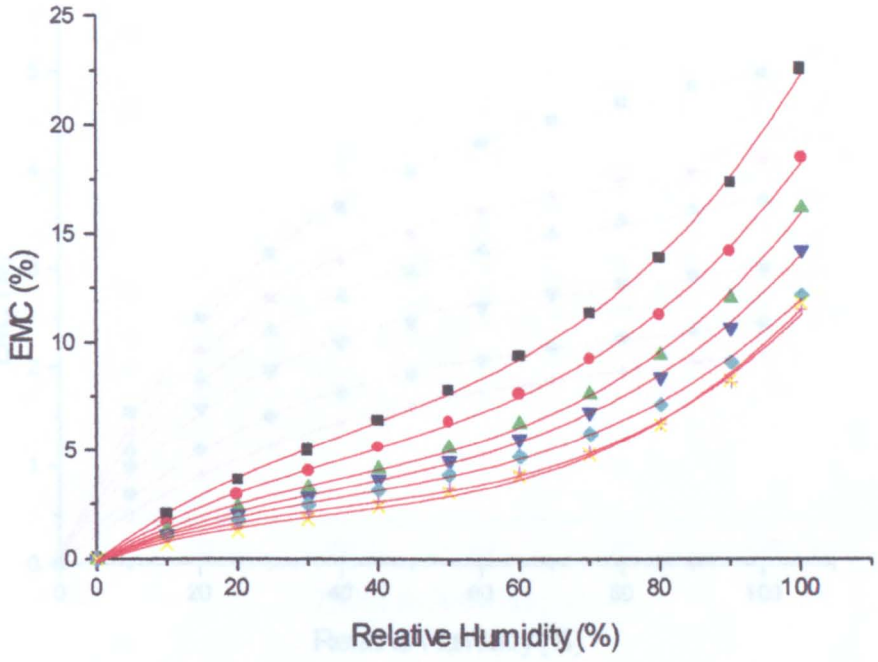

Figure 7.23: Adsorption isotherms for Scots pine control (■) and hexanoic anhydride modified wood: 6.2 WPG (●); 11.1 WPG (▲); 15.7 WPG (▼); 20.5 WPG (◆); 25.3 WPG (X); 28.6 WPG (+).

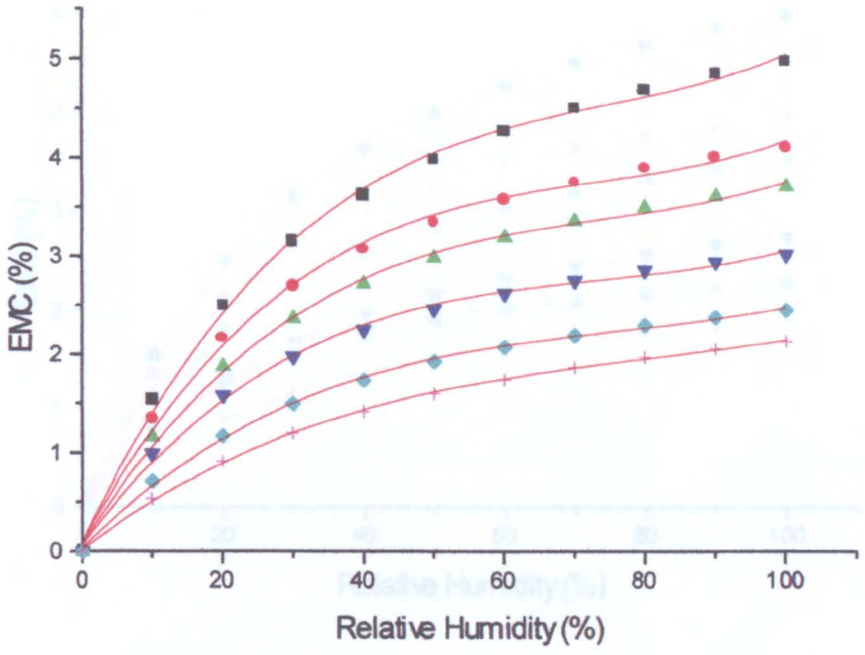

Figure 7.24: Monomolecular adsorption isotherms for Scots pine control (■) and acetic anhydride modified wood: 5.7 WPG (●); 10.7 WPG (▲); 16.1 WPG (▼); 20.1 WPG (◆); 21.9 WPG (+).

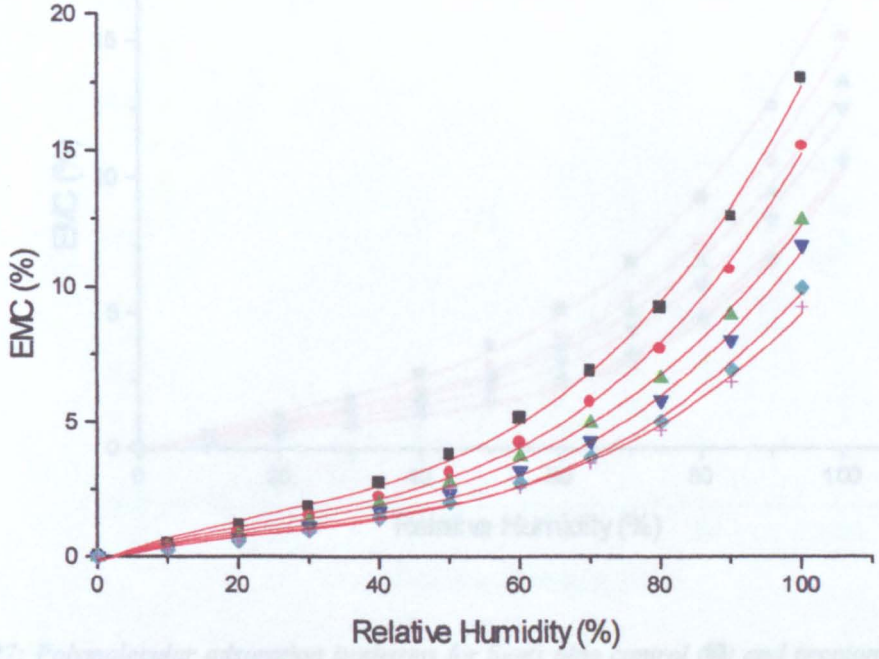

Figure 7.25: Polymolecular adsorption isotherms for Scots pine control (■) and acetic anhydride modified wood: 5.7 WPG (●); 10.7 WPG (▲); 16.1 WPG (▼); 20.1 WPG (◆); 21.9 WPG (+).

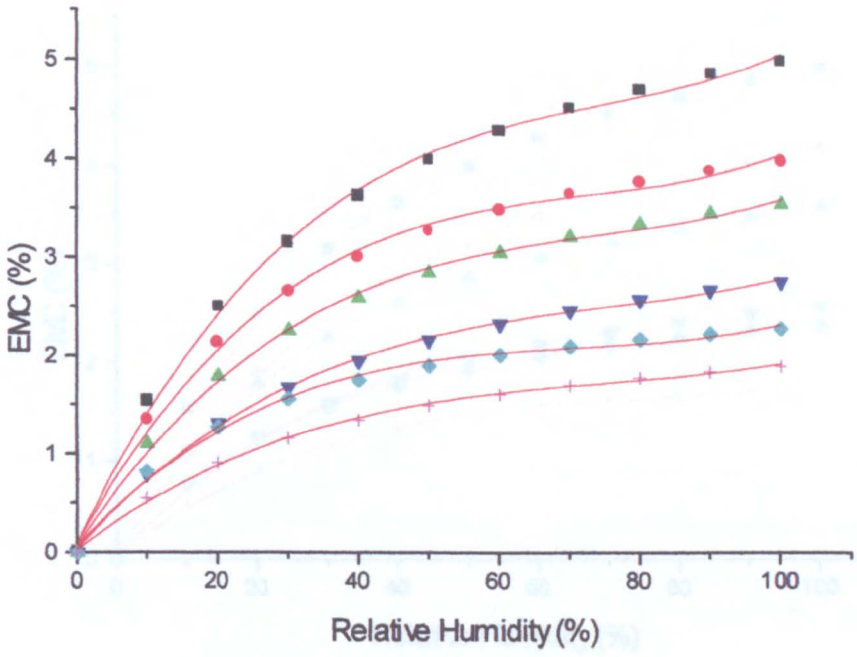

Figure 7.26: Monomolecular adsorption isotherms for Scots pine control (■) and propionic anhydride modified wood: 6.1 WPG (●); 10.9 WPG (▲); 15.6 WPG (▼); 19.7 WPG (◆); 24.5 WPG (+).

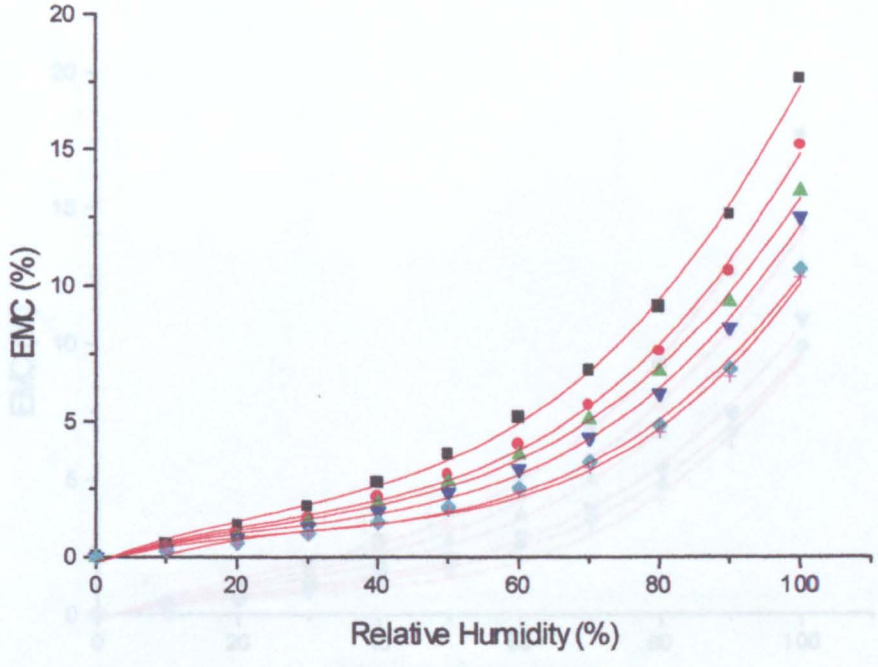

Figure 7.27: Polymolecular adsorption isotherms for Scots pine control (■) and propionic anhydride modified wood: 6.1 WPG (●); 10.9 WPG (▲); 15.6 WPG (▼); 19.7 WPG (◆); 24.5 WPG (+).

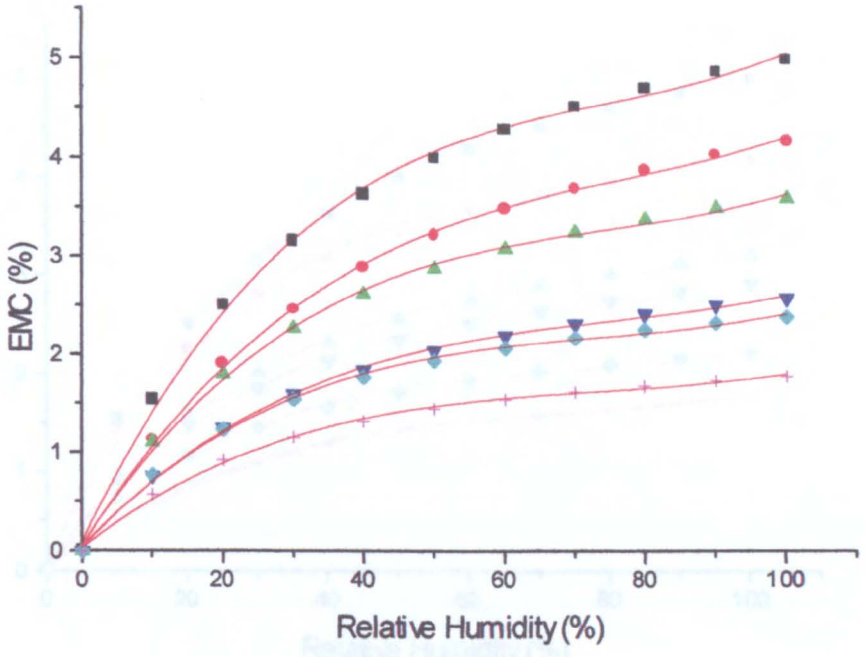

Figure 7.28: Monomolecular adsorption isotherms for Scots pine control (■) and butyric anhydride modified wood: 5.8 WPG (●); 11.3 WPG (▲); 16 WPG (▼); 19.9 WPG (◆); 25.2 WPG (+).

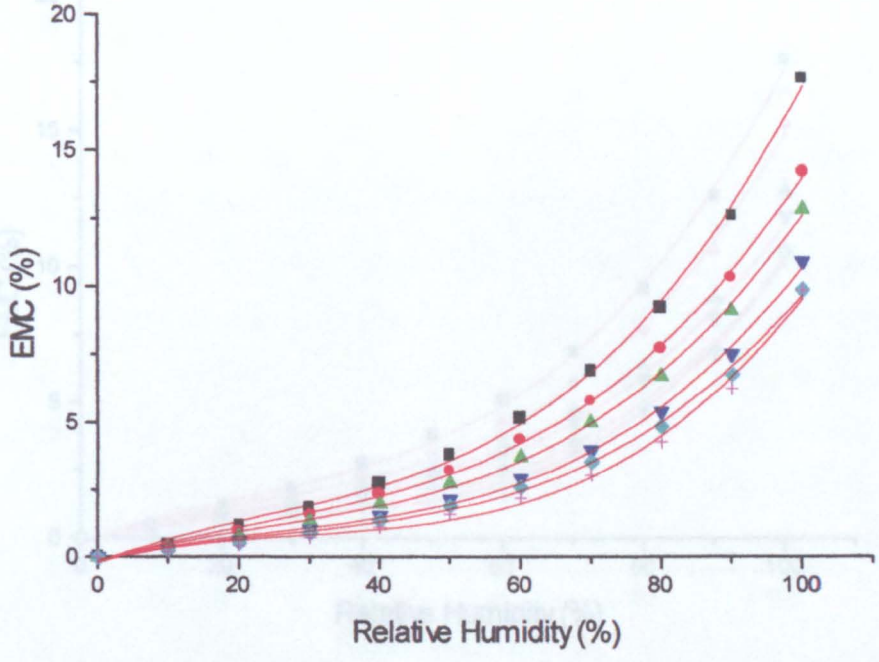

Figure 7.29: Polymolecular adsorption isotherms for Scots pine control (■) and butyric anhydride modified wood: 5.8 WPG (●); 11.3 WPG (▲); 16 WPG (▼); 19.9 WPG (◆); 25.2 WPG (+).

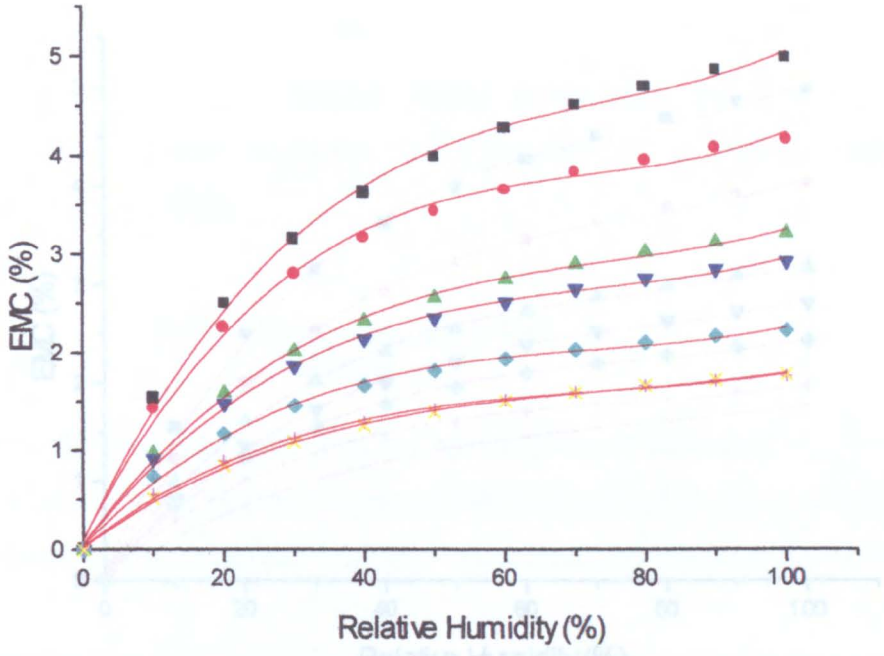

Figure 7.30: Monomolecular adsorption isotherms for Scots pine control (■) and valeric anhydride modified wood: 5.9 WPG (●); 11.4 WPG (▲); 16.2 WPG (▼); 20.4 WPG (◆); 24.9 WPG (+); 27.5 WPG (X).

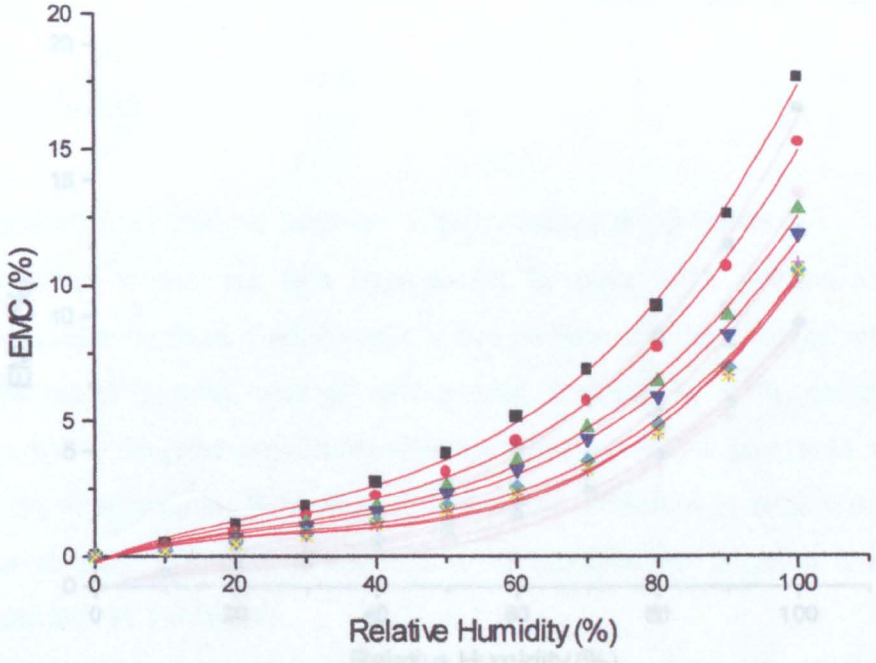

Figure 7.31: Polymolecular adsorption isotherms for Scots pine control (■) and valeric anhydride modified wood: 5.9 WPG (●); 11.4 WPG (▲); 16.2 WPG (▼); 20.4 WPG (◆); 24.9 WPG (+); 27.5 WPG (X).

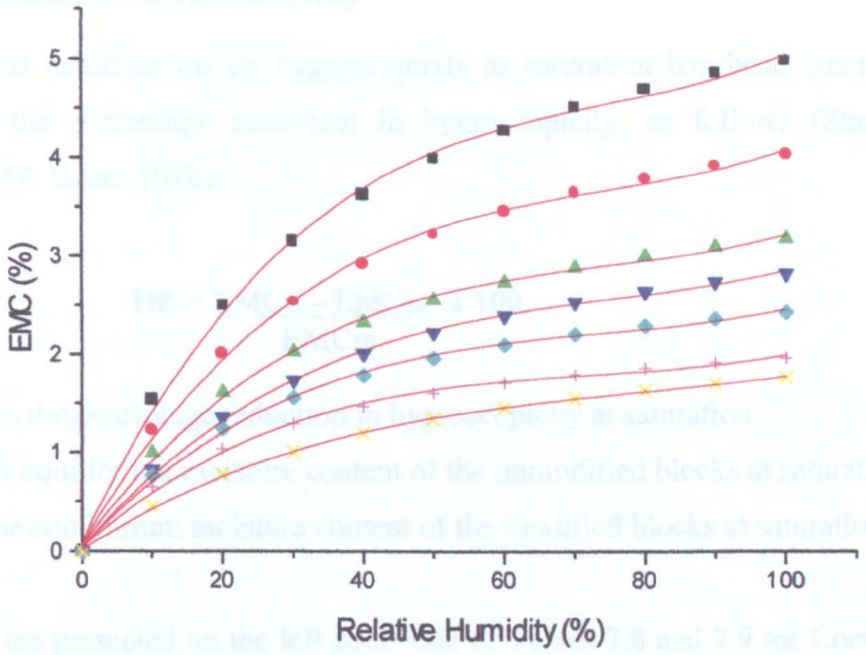

Figure 7.32: Monomolecular adsorption isotherms for Scots pine control (■) and hexanoic anhydride modified wood: 6.2 WPG (●); 11.1 WPG (▲); 15.7 WPG (▼); 20.5 WPG (◆); 25.3 WPG (X); 28.6 WPG (+).

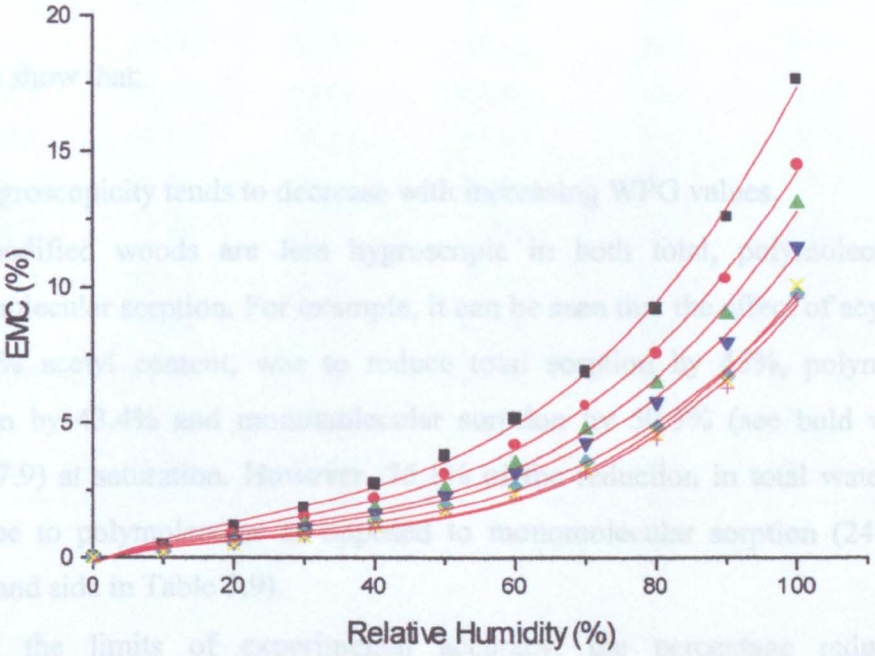

Figure 7.33: Polymolecular adsorption isotherms for Scots pine control (■) and hexanoic anhydride modified wood: 6.2 WPG (●); 11.1 WPG (▲); 15.7 WPG (▼); 20.5 WPG (◆); 25.3 WPG (+); 28.6 WPG (X).

7.4.3. Mechanisms of reduction in hygroscopicity

7.4.3.1. Reduction in hygroscopicity

The effect of modification on hygroscopicity at saturation has been quantified by calculating the percentage reduction in hygroscopicity, as follows (Stamm and Tarkow, 1947; Skaar, 1988):

$$HR = \frac{EMCu - EMCm}{EMCm} \times 100$$

Where HR is the percentage reduction in hygroscopicity at saturation
EMCu is the equilibrium moisture content of the unmodified blocks at saturation
EMCm is the equilibrium moisture content of the modified blocks at saturation.

The results are presented on the left hand side of Tables 7.8 and 7.9 for Corsican and Scots pine respectively. On the right hand side, the data are also presented in terms of percent in total change in moisture content, calculated as follows:

$$\text{Total Change in m.c (mon/lar or pol/lar) (\%)} = \frac{\text{EMCu- EMCm (mon/lar or pol/lar)}}{\text{EMCu- EMCm (total)}}$$

The results show that:

- The hygroscopicity tends to decrease with increasing WPG values.
- The modified woods are less hygroscopic in both total, polymolecular and monomolecular sorption. For example, it can be seen that the effect of acylation to a 20.1% acetyl content, was to reduce total sorption by 45%, polymolecular sorption by 43.4% and monomolecular sorption by 50.5% (see bold values in Table 7.9) at saturation. However, 75.1% of the reduction in total water sorbed was due to polymolecular as opposed to monomolecular sorption (24.8%, see right hand side in Table 7.9).
- Within the limits of experimental accuracy, the percentage reduction in hygroscopicity and the total change in moisture content, are of the same magnitude for all of the anhydrides studied, at equivalent WPG values.

Table 7.8: Reduction in the hygroscopicity (%) and percent of total change in moisture content at saturation of Corsican pine as a result of acylation with linear chain anhydrides, at various WPG.

Reagent	WPG	Reduction in Hygroscopicity (%)			Total decrease in m.c (%)		
		Total	Polymolecular	Monomolecular	Total	Polymolecular	Monomolecular
Acetic	5.2	17.08	17.48	15.63	100	80.21	19.78
	11.4	20.33	17.96	28.94	100	69.23	30.76
	15.8	36.64	35.36	41.30	100	75.63	24.36
	19.6	46.49	45.79	49.03	100	77.20	22.79
	22.5	50.63	49.08	56.25	100	75.98	24.01
Propionic	5.3	17.72	17.62	18.08	100	77.95	22.04
	11.2	22.64	19.34	34.62	100	66.94	33.05
	15.3	37.20	35.15	44.65	100	74.05	25.94
	20.1	46.95	45.28	53.01	100	75.59	24.40
	25.7	50.91	48.30	60.41	100	74.35	25.64
Butyric	5.5	26.12	27.75	20.19	100	83.28	16.71
	11.1	31.57	31.63	31.32	100	78.55	21.44
	16	41.58	40.28	46.32	100	75.92	24.07
	20.1	46.75	45.62	50.85	100	76.49	23.50
	26.1	51.75	48.467	63.65	100	73.40	26.59
Valeric	4.9	16.27	16.75	14.52	100	80.71	19.28
	10.9	23.61	20.18	36.03	100	67.01	32.98
	15.5	36.74	36.08	39.13	100	76.97	23.02
	19.8	43.36	40.48	53.83	100	73.16	26.83
	26.2	49.76	45.88	63.83	100	72.27	27.72
	28.9	51.80	50.38	56.94	100	76.23	23.76
Hexanoic	5.7	20.48	20.77	19.43	100	79.49	20.50
	12.1	30.68	30.02	33.05	100	76.71	23.28
	15.7	37.84	36.99	40.94	100	76.61	23.38
	19.5	43.74	40.87	54.15	100	73.23	26.76
	25.4	53.38	52.04	58.24	100	76.41	23.58
	29.1	53.02	51.25	59.44	100	75.76	24.23

Table 7.9: Reduction in the hygroscopicity (%) and percent of total change in moisture content at saturation of Scots pine as a result of acylation with linear chain anhydrides, at various WPG.

Reagent	WPG	Reduction in hygroscopicity (%)			Total decrease in m.c (%)		
		Total	Polymolecular	Monomolecular	Total	Polymolecular	Monomolecular
Acetic	5.7	14.83	14.14	17.27	100	74.29	25.70
	10.7	28.59	29.49	25.42	100	80.36	19.63
	16.1	35.75	34.74	39.33	100	75.70	24.29
	20.1	**45.02**	**43.44**	**50.59**	100	**75.18**	**24.81**
	21.9	49.65	47.57	56.99	100	74.65	25.34
Propionic	6.1	15.48	14.14	20.22	100	71.16	28.83
	10.9	24.95	23.83	28.92	100	74.40	25.59
	15.6	32.72	29.29	44.83	100	69.74	30.25
	19.7	43.11	39.92	54.35	100	72.15	27.84
	24.5	46.09	41.61	61.91	100	70.33	29.66
Butyric	5.8	18.89	19.57	16.52	100	80.68	19.31
	11.3	27.54	27.38	28.07	100	77.48	22.51
	16	40.43	38.17	48.38	100	73.56	26.43
	19.9	45.76	43.94	52.18	100	74.81	25.18
	25.2	48.54	44.07	64.301	100	70.74	29.25
Valeric	5.9	14.34	13.77	16.35	100	74.82	25.17
	11.4	29.39	27.66	35.49	100	73.33	26.66
	16.2	34.71	32.83	41.34	100	73.69	26.30
	20.4	43.55	40.21	55.32	100	71.94	28.05
	24.9	44.47	38.78	64.54	100	67.94	32.05
	27.5	45.70	40.43	64.27	100	68.94	31.05
Hexanoic	6.2	17.99	17.68	19.10	100	76.55	23.44
	11.1	28.13	25.86	36.13	100	71.63	28.36
	15.7	36.76	34.92	43.26	100	74.01	25.98
	20.5	45.96	44.51	51.09	100	75.44	24.55
	25.3	48.72	45.40	60.43	100	72.60	27.39
	28.6	47.50	42.70	64.46	100	70.03	29.96

7.4.3.2. *Mechanisms of reduction*

EMC values at saturation for monomolecular, polymolecular and total sorption are shown in Tables 7.10 and 7.11, for Corsican and Scots pine respectively. The relation between total sorption and the ways in which it is held within the cell walls at saturation was verified by regression analysis of the data for the modified woods from Tables 7.10 and 7.11.

The results of this analysis which are presented in Table 7.12, show clearly that the variation in total water sorbed is dependent on both monomolecular and polymolecular sorption. However, the higher F-ratios and R^2 values shown by the relationship between polymolecular and total sorption indicate that the variation shown in the water sorbed at the polymolecular level plays the main role in the variation in total water sorbed. This observation is in line with that made by Martins (1992) in wood modified with monofunctional isocyanates.

It is of interest at this point to assess how the decrease in site accessibility and the increasing volume of adducts in the cell wall (an expression of the degree of bulking) affect both total, monomolecular and polymolecular sorption.

In the Hailwood-Horrobin model, W_o is the molecular weight of the sorptive substance associated with one mole of water in hydrate form at saturation. Accordingly, sorption site accessibility decreases with increasing W_o values. As the level of modification increases, the increasing values shown for W_o in tables 7.10 and 7.11, for Corsican and Scots pine respectively, indicate that the availability of bonding sites is progressively reduced, resulting in decreasing monomolecular sorption. This is because as the level of modification increases, the proportion of sorption sites occupied by the acyl groups introduced in the cell wall also increases, and therefore less free hydroxyl sites are left available for hydrogen bonding to water molecules. Additionally, as the level of modification increases, both polymolecular and total sorption are reduced. The presence of the adducts not only reduces monomolecular sorption by decreasing site accessibility as discussed above, but also causes a great degree of bulking in the wood cell wall. Therefore, the reduction in site accessibility is accompanied by cell wall bulking. Thus, regression analysis of the

Table 7.10: EMC values at saturation for monomolecular, polymolecular and total sorption for Corsican pine modified wood.

Reagent	WPG	EMC values at saturation			W_o
		Total	Polymolecular	Monomolecular	
Acetic	5.2	19.41	15.14	4.27	333.2
	11.4	18.65	15.05	3.59	398.7
	15.8	14.83	11.86	2.97	491.2
	19.6	12.53	9.95	2.58	526.0
	22.5	11.56	9.34	2.21	561.6
Propionic	5.3	19.26	15.12	4.14	336.5
	11.2	18.11	14.80	3.30	424.3
	15.3	14.70	11.90	2.80	507.7
	20.1	12.42	10.04	2.37	567.9
	25.7	11.49	9.49	2.00	619.0
Butyric	5.5	17.30	13.26	4.03	341.1
	11.1	16.02	12.54	3.47	378.3
	16	13.67	10.96	2.71	512.1
	20.1	12.46	9.98	2.48	538.2
	26.1	11.29	9.45	1.83	663.5
Valeric	4.9	19.60	15.28	4.32	326.4
	10.9	17.88	14.65	3.23	441.8
	15.5	14.81	11.73	3.08	445.6
	19.8	13.26	10.92	2.33	611.2
	26.2	11.76	9.93	1.83	699.8
	28.9	11.28	9.10	2.17	560.4
Hexanoic	5.7	18.62	14.54	4.07	329.2
	12.1	16.23	12.84	3.38	402.6
	15.7	14.55	11.56	2.98	465.2
	19.5	13.17	10.85	2.32	584.1
	25.4	10.91	8.80	2.11	619.8
	29.1	11.00	8.94	2.05	649.0

Table 7.11: EMC values at saturation for monomolecular, polymolecular and total sorption for Scots pine modified wood.

Reagent	WPG	EMC values at saturation			W_o
		Total	Polymolecular	Monomolecular	
Acetic	5.7	19.27	15.13	4.13	336.6
	10.7	16.15	12.42	3.72	364.8
	16.1	14.53	11.50	3.03	459.1
	20.1	12.43	9.96	2.46	530.0
	21.9	11.38	9.24	2.14	558.4
Propionic	6.1	19.12	15.13	3.98	354.0
	10.9	16.97	13.42	3.55	382.4
	15.6	15.22	12.46	2.75	473.5
	19.7	12.87	10.58	2.28	634.2
	24.5	12.19	10.29	1.90	689.4
Butyric	5.8	18.34	14.17	4.17	303.3
	11.3	16.39	12.79	3.59	375.6
	16	13.47	10.89	2.57	512.8
	19.9	12.26	9.88	2.38	578.3
	25.2	11.64	9.85	1.78	773.9
Valeric	5.9	19.37	15.20	4.17	339.6
	11.4	15.97	12.75	3.22	415.2
	16.2	14.77	11.84	2.93	463.7
	20.4	12.77	10.53	2.23	625.7
	24.9	12.56	10.79	1.77	767.4
	27.5	12.28	10.49	1.78	729.5
Hexanoic	6.2	18.55	14.51	4.04	333.0
	11.1	16.26	13.06	3.19	426.0
	15.7	14.30	11.47	2.83	462.7
	20.5	12.22	9.78	2.44	559.2
	25.3	11.60	9.62	1.97	704.7
	28.6	11.87	10.10	1.77	684.8

Table 7.12: Regression analysis results of the relation between types of sorption and total sorption at saturation.

Reagent	Relation Examined	Corsican pine		Scots pine	
		F-ratio[1]	R^2	F-ratio[1]	R^2
Acetic	Monomolecular *vs* Total	54.81	94.8	84.4	96.6
	Polymolecular *vs* Total	645.84	99.5	672.44	99.6
Propionic	Monomolecular *vs* Total	45.06	93.8	157.5	98.1
	Polymolecular *vs* Total	466.42	99.4	865.93	99.7
Butyric	Monomolecular *vs* Total	209.7	98.6	133.93	97.8
	Polymolecular *vs* Total	761.16	99.6	534.1	99.4
Valeric	Monomolecular *vs* Total	37.44	90.3	116.81	96.7
	Polymolecular *vs* Total	312.86	98.7	450.01	99.1
Hexanoic	Monomolecular *vs* Total	138.66	97.2	70.92	94.7
	Polymolecular *vs* Total	1082.57	99.6	422.29	99.1

1. All values shown are significant at 99 percent level of probability.

data presented in Tables 7.10 and 7.11 was carried out in order to assess the effect of decreasing site accessibility (expressed as W_o) in the cell wall upon the total, polymolecular and monomolecular sorption.

The results of the analysis, which are presented in Table 7.13, show that the decrease in site accessibility is dependent on both monomolecular, polymolecular and total sorption. However, better correlation for W_o is found when this factor is related to monomolecular sorption. This is indicated by the higher F-ratios and R^2 values in all relationships considered, and it is particularly evident for Corsican and Scots pine modified with acetic anhydride. It seems therefore, that only the reduction in monomolecular sorption can be primarily attributed to the decrease in site accessibility.

The effect of increasing volume of the adducts in the cell wall, which is an expression of bulking, on both monomolecular, polymolecular and total sorption was assessed by regression analysis. The volume occupied by the acyl groups in the cell wall due to modification (an expression of the degree of bulking) was calculated as follows:

$$\text{Bulking } (cm^3/g \text{ of wood}) = (V_{mod} - V_{unmod}) / W_{unmod}$$

Where V_{mod} is the volume of the sample after modification, V_{unmod} is the volume of the sample before modification and W_{unmod} is the weight of the sample before modification.

These values are presented in Table 7.14.

Table 7.13: Regression analysis of the relations between the types of water sorbed at saturation and sites accessibility (expressed as W_o).

Reagent	Relation Examined	Corsican pine		Scots pine	
		F-ratio	R^2	F-ratio	R^2
Acetic	*Wo vs* Monomolecular	423.28	99.3	464.52	94.4
	W_o *vs* Polymolecular	41.51	93.3	26.39	89.9
	W_o *vs* Total	74.51	96.1	42.68	93.4
Propionic	*Wo vs* Monomolecular	431.05	99.3	48.81	94.2
	W_o *vs* Polymolecular	44.86	93.7	39.89	93
	W_o *vs* Total	97.72	97	48.05	94.1
Butyric	*Wo vs* Monomolecular	129.61	97.7	47.53	94.1
	W_o *vs* Polymolecular	50.12	94.4	14.26*	82.6
	W_o *vs* Total	76.6	96.2	20.7*	87.3
Valeric	*Wo vs* Monomolecular	50.7	92.7	61.31	93.9
	W_o *vs* Polymolecular	8.91*	69	12.75*	76.1
	W_o *vs* Total	13.94*	77.7	20.07*	83.4
Hexanoic	*Wo vs* Monomolecular	252.93	98.4	66.12	94.3
	W_o *vs* Polymolecular	68.05	94.4	20.24*	83.5
	W_o *vs* Total	109.83	96.5	31.13	88.6

* Significant at 95 percent level of probability. All the other values are significant at 99 percent level of probability.

The results of the analysis, which are presented in Table 7.15, show that the increasing volume of adducts in the cell wall is dependent on both monomolecular, polymolecular and total sorption. However, the higher F-ratios and R^2 values shown when this factor is related to polymolecular and total sorption, suggest that only the reduction in polymolecular and total sorption can be primarily attributed to the increasing volume of adducts in the cell wall.

Table 7.14: Calculated values for bulking (cm^3/g of unmodified wood).

CORSICAN PINE									
ACETIC		PROPIONIC		BUTYRIC		VALERIC		HEXANOIC	
WPG	*Bulking*	*WPG*	*Bulking*	*WPG*	*Bulking*	*WPG*	*Bulking*	*WPG*	*Bulking*
5.2	0.08523	5.3	0.08962	5.5	0.08588	4.9	0.07081	5.7	0.08814
11.4	0.1101	11.2	0.12255	11.1	0.13325	10.9	0.13726	12.1	0.15376
15.8	0.18823	15.3	0.17558	16	0.1739	15.5	0.18368	15.7	0.1901
19.6	0.21522	20.1	0.222	20.1	0.25533	19.8	0.21477	19.5	0.2118
22.5	0.22963	25.7	0.29985	26.1	0.30022	26.2	0.30752	25.4	0.28103
-	-	-	-	-	-	28.9	0.34048	29.1	0.36284
SCOTS PINE									
5.7	0.06875	6.1	0.07325	5.8	0.06422	5.9	0.06233	6.2	0.05962
10.7	0.14155	10.9	0.14889	11.3	0.14522	11.4	0.14999	11.1	0.14222
16.1	0.17555	15.6	0.16985	16.	0.17335	16.2	0.17888	15.7	0.18332
20.1	0.20552	19.7	0.20055	19.9	0.18996	20.4	0.19979	20.5	0.21752
21.9	0.2255	25.4	0.23955	25.2	0.20522	24.9	0.21788	25.3	0.22832
-	-	-	-	-	-	27.5	0.23955	28.6	0.23021

Table 7.15: Regression analysis of the relations between the types of water sorbed at saturation and increasing volume in the cell wall (an express of bulking).

Reagent	Relation Examined	Corsican pine		Scots pine	
		F-ratio	R^2	F-ratio	R^2
Acetic	Volume *vs* Monomolecular	74.84	94.9	40.35	90.8
	Volume *vs* Polymolecular	101.33	97.1	540.65	99.4
	Volume *vs* Total	188.56	98.4	288	99.0
Propionic	Volume *vs* Monomolecular	29.72	88.0	35.22	94.6
	Volume *vs* Polymolecular	30.42	90.8	52.87	94.6
	Volume *vs* Total	38.34	92.7	53	89.5
Butyric	Volume *vs* Monomolecular	46.29	91.9	23.43	84.9
	Volume *vs* Polymolecular	64.37	95.5	31.55	91.3
	Volume *vs* Total	66.67	95.7	32.01	91.4
Valeric	Volume *vs* Monomolecular	24.29	82.3	71.02	93.1
	Volume *vs* Polymolecular	44.03	91.7	96.97	96
	Volume *vs* Total	56.64	93.4	140.67	97.2
Hexanoic	Volume *vs* Monomolecular	20.22*	79.4	66.74	92.9
	Volume *vs* Polymolecular	36.28	90.1	82.71	95.4
	Volume *vs* Total	33.04	89.2	142.29	97.3

* Significant at 95 percent level of probability. All the other values are significant at 99 percent level of probability.

These observations are supported by the work of Martins (1992) in wood modified with isocyanates, and by the work of Wangaard and Granados (1967) concerning the effect of extractives on these types of sorption. In the former study, it was shown that the reduction in monomolecular sorption is chiefly governed by the decrease in site accessibility, whereas the effect of polymolecular and total sorption is of secondary importance. In the latter study, it was found that the presence of extractives in the cell wall cause a slight increase in monomolecular sorption and a great decrease in polymolecular and total sorption. Since the extractives are themselves hygroscopic, the hygroscopicity of the cell wall is slightly increased resulting in increased monomolecular sorption. The reduction in polymolecular and total sorption, despite the increased site accessibility, clearly indicated that the bulking effect of extractives prevented water from occupying the same space in the cell wall.

It is suggested therefore that, in the case of wood modified with linear chain anhydrides, the two effects, namely site accessibility and bulking, are complementary to each other, i.e. the presence of the adducts in the cell wall causes a decrease in the hygroscopicity of the internal surfaces, decreasing site accessibility and therefore sorption at the monomolecular layer. At the same time, it decreases polymolecular and total sorption by bulking the cell walls. These effects suggest that in wood modified with linear chain anhydrides, the reduction in moisture sorbed at the monomolecular layer is chiefly governed by the decrease in availability of sorption sites. The reduction attained at the polymolecular level and in total water sorbed, seems to be highly influenced by the degree of bulking brought about by the presence of the adducts in the cell wall.

The influence of the reduction in site accessibility (expressed by the decline in monomolecular sorption) and of bulking (expressed by the decline in polymolecular sorption) in total sorption, within the range of relative humidity is revealed by splitting the isotherms for total water sorbed in its two components predicted by the model (see session 7.4.2.). For the unmodified woods, the isotherms produced by monomolecular sorption rise rapidly in the range of low R.H, levelling off asymptotically at higher R.H showing the characteristic shape of a Type I isotherm. The curves produced by polymolecular sorption approach an asymptote to the moisture content axis at saturation and present the shape of the Type III isotherm. The

isotherms for total sorption (the amalgam of monomolecular and polymolecular sorption) are of Type II, exhibiting the well known sigmoid shape (see section 7.2.3). Figure 7.2b shows clearly that polymolecular sorption predominates at the intermediate and higher R.H, while monomolecular sorption predominates at the lower ones.

As was mentioned in section 7.4.2., the two types of sorption, namely monomolecular and polymolecular, and consequently the total sorption are affected by the treatment, since the two complementary isotherms are clearly depressed when compared to those produced by the controls. This is illustrated more clearly in Figure 7.34 where the isotherms of unmodified control and acetic anhydride modified Corsican pine (22.5 WPG) were superposed. Lines A, B, C illustrate the reduction

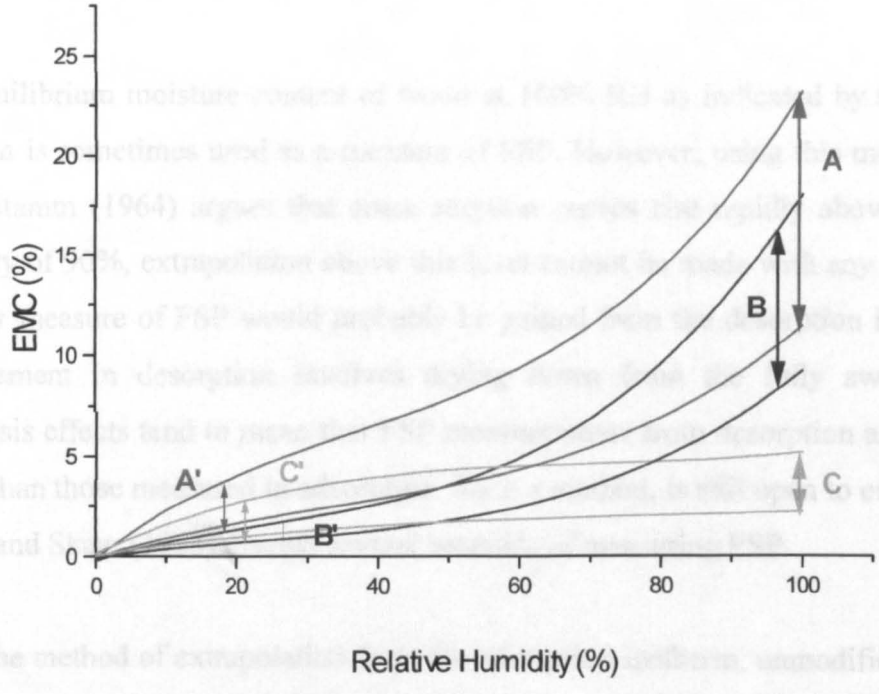

*Figure 7.34: Superposition of the isotherms produced by unmodified control pine and modified Corsican pine with acetic anhydride (22.5 WPG), showing the shift in the relative contribution of the reduction in monomolecular and **polymolecular** sorption to the reduction in total water sorbed. A, B, C and A'. B', C' represent the reduction in total, **polymolecular** and monomolecular sorption respectively at high and low relative humidity.*

in total, polymolecular and monomolecular sorption respectively at high relative humidity and lines A', B', C' at low relative humidity.

As the relative contribution of polymolecular to total sorption increases with increasing relative humidities, so does the relative contribution of the decrease in this type of sorption, to the total reduction achieved by the modified wood. This reflects the moisture exclusion caused by the bulking effect (lines B and B'). At saturation this contribution reaches a maximum. Conversely, the relative contribution of monomolecular to total sorption increases as the relative humidity decreases and therefore, the relative contribution of the reduction in this type of sorption also increases (lines C and C'), making clear that the decline in total sorption achieved at lower relative humidities is chiefly due to a reduction in site accessibility.

7.4.4. Fiber 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 sorption curves rise rapidly above a relative humidity of 90%, extrapolation above this level cannot be made with any confidence. A better measure of FSP would probably be gained from the desorption isotherm, as measurement in desorption involves drying down from the fully swollen state. Hysteresis effects tend to mean that FSP measurements from desorption are generally higher than those measured in adsorption. Such a method, is still open to error. Stamm (1964) and Skaar (1988) discuss several methods of measuring FSP.

Using the method of extrapolation from the adsorption isotherm, unmodified Corsican and Scots pine sapwood were found to have a FSP of 23.4% and 22.6% respectively. Usually FSP would be expected to be 25-30% (Skaar, 1988). Spalt (1958) measured FSP from sorption isotherms for various softwoods and found results similar to the present study, e.g. 22.8% (Redwood; *Sequoia sempervirens*), 24.6% (Ponderosa pine; *Pinus ponderosa*) and 23.9% (Western white pine; *Pinus monticola*). In most cases, Spalt found FSP measured from desorption to be 3 to 5% higher than the adsorption

measure (i.e. much closer to the expected measure). Forster (1998) found a similar value for FSP as well, namely 22.8%, for unmodified Corsican pine measured from adsorption.

The e.m.c. values at 100% RH measured here from extrapolation of the sorption isotherms, though not accurate measures of FSP, serve as an indication of relative values of FSP. These values are plotted for total, polymolecular and monomolecular sorption in Figures 7.35 to 7.40, for both Corsican and Scots pine.

The behaviour for total sorption (see Figures 7.35, 7.38) very much reflects that for polymolecular adsorption (see Figures 7.36, 7.39). This is as expected, due to the much larger proportion of polymolecular sorption compared to monomolecular sorption at high relative humidities, and is in line with findings of Spalt (1958) and Forster (1998). In the present study, monomolecular sorption of different modified woods (see Figures 7.37, 7.40) also showed a similar pattern, in line with the findings of Forster (1998).

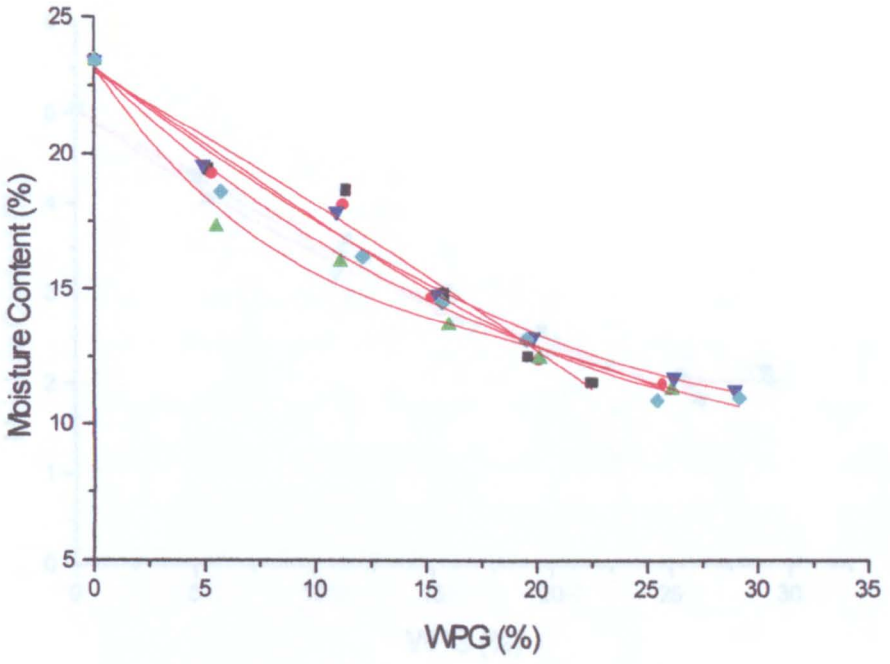

Figure 7.35: Total water adsorbed at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

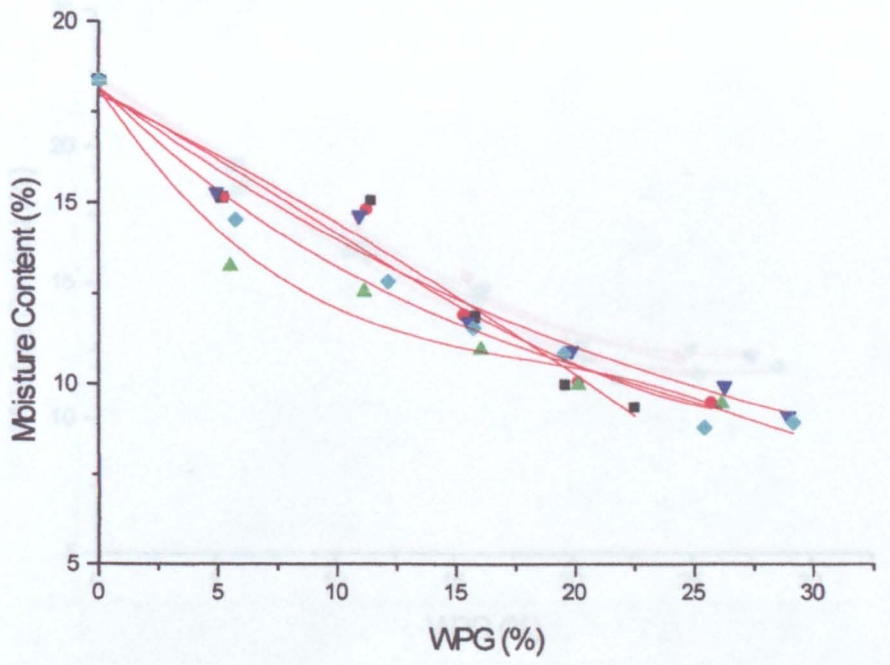

Figure 7.36: Polymolecular adsorption at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

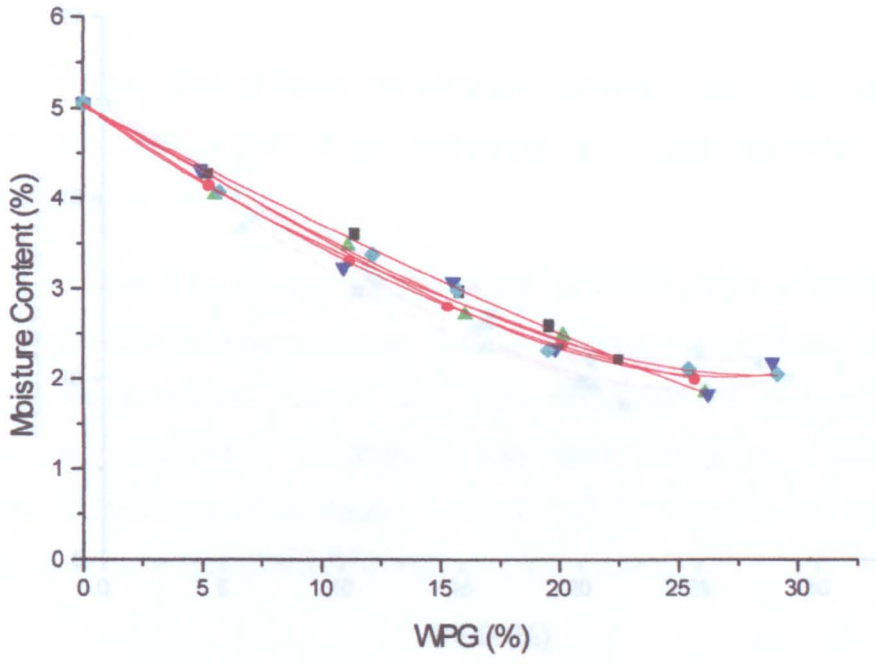

Figure 7.37: Monomolecular adsorption at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

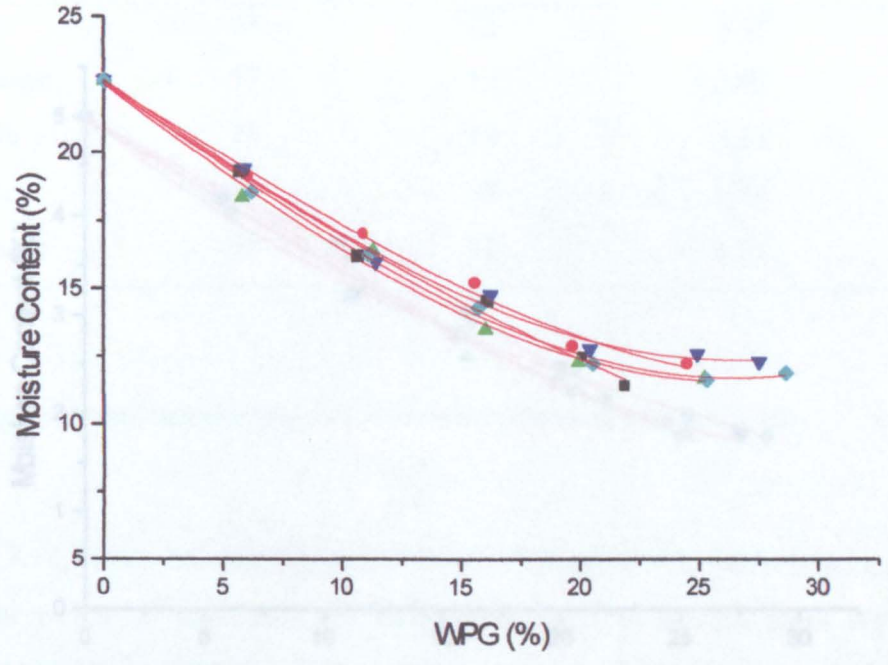

Figure 7.38: Total water adsorbed at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

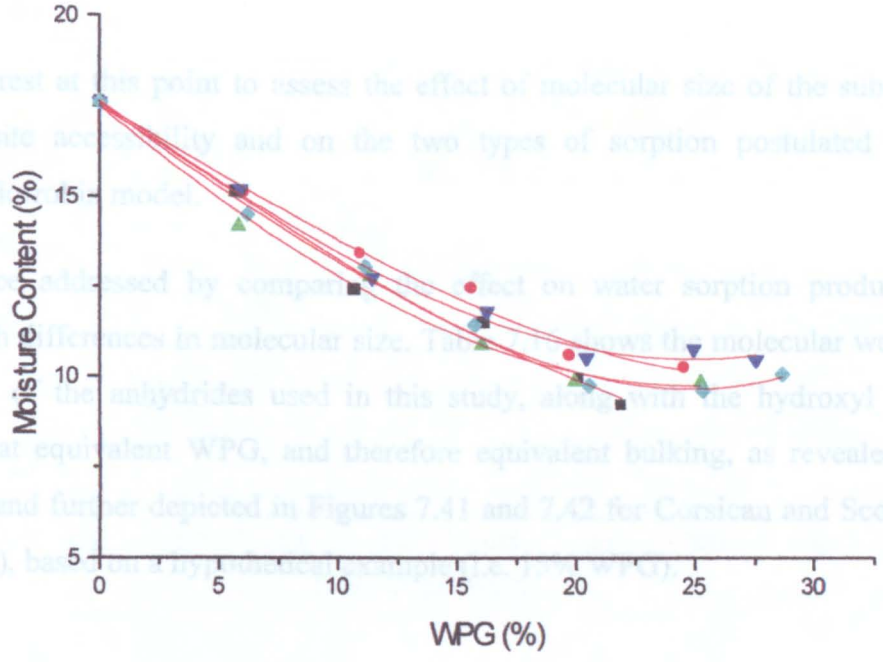

Figure 7.39: Polymolecular adsorption at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

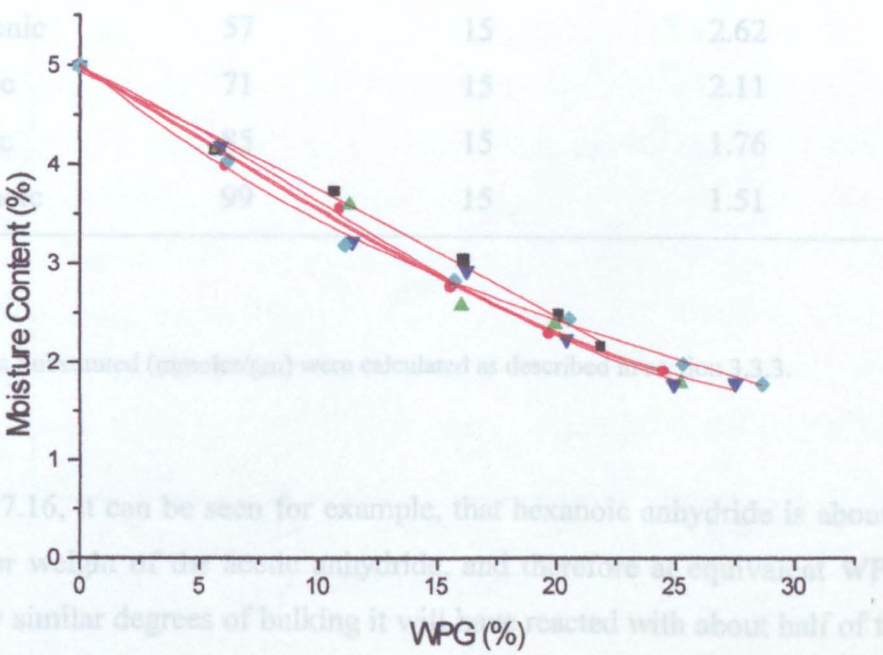

Figure 7.40: Monomolecular adsorption at saturation: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

7.4.5. Effect of molecular size of the substituent group on site accessibility

It is of interest at this point to assess the effect of molecular size of the substituent group on site accessibility and on the two types of sorption postulated by the Hailwood-Horrobin model.

This may be addressed by comparing the effect on water sorption produced by adducts with differences in molecular size. Table 7.16 shows the molecular weight of the adducts of the anhydrides used in this study, along with the hydroxyl groups substituted at equivalent WPG, and therefore equivalent bulking, as revealed from Table 7.14 and further depicted in Figures 7.41 and 7.42 for Corsican and Scots pine respectively), based on a hypothetical example (i.e. 15% WPG).

Table 7.16: Molecular weight of the adducts of the anhydrides used in this study.

Anhydride	Molecular Weight	WPG (%)	OH Groups Substd.[1]
Acetic	43	15	3.48
Propionic	57	15	2.62
Butyric	71	15	2.11
Valeric	85	15	1.76
Hexanoic	99	15	1.51

1. OH Groups Substituted (mmoles/gm) were calculated as described in section 3.3.3.

From Table 7.16, it can be seen for example, that hexanoic anhydride is about twice the molecular weight of the acetic anhydride, and therefore at equivalent WPG and consequently similar degrees of bulking it will have reacted with about half of the OH groups substituted by acetic anhydride. Conversely, hexanoic anhydride may react with an equivalent amount of OH groups but bringing about twice as much bulking than the acetic anhydride.

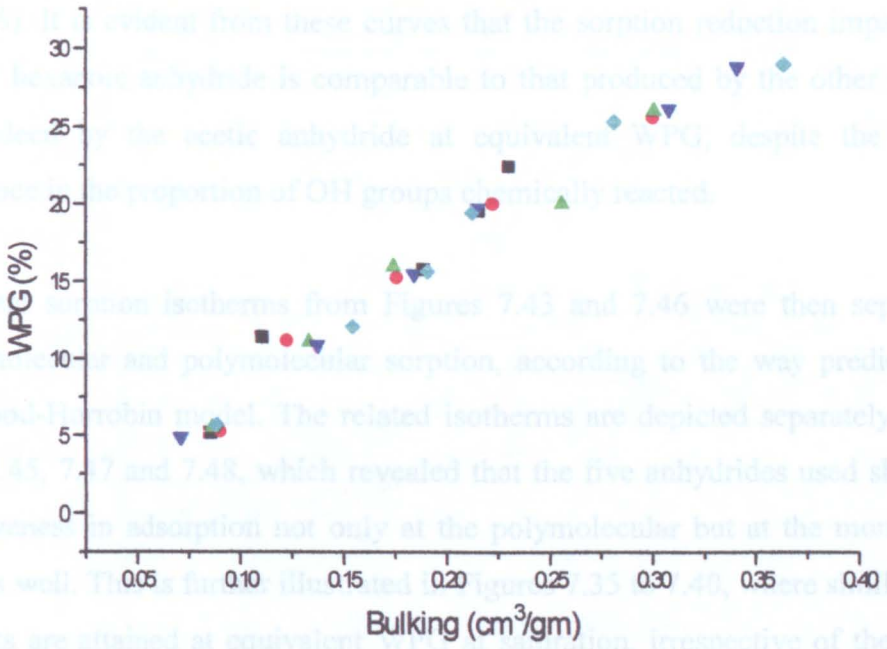

Figure 7.41: Relationship between WPG% and bulking: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

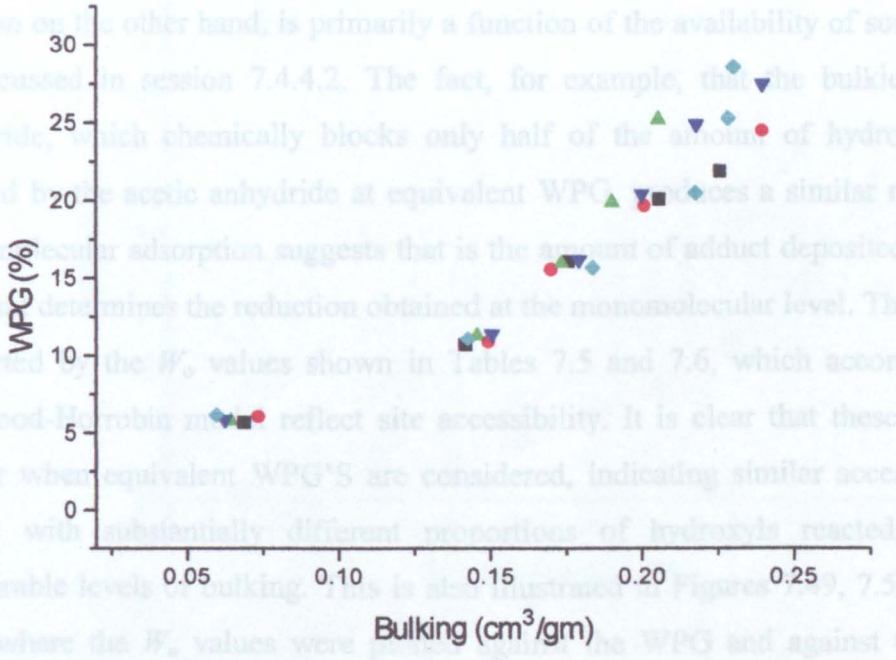

Figure 7.42: Relationship between WPG% and bulking: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

Figures 7.43 and 7.46 show selected total sorption isotherms for Corsican and Scots pine respectively, modified with the linear chain anhydrides at equivalent WPG (*ca* 15-16%). It is evident from these curves that the sorption reduction imparted by the bulkier hexanoic anhydride is comparable to that produced by the other anhydrides, and indeed by the acetic anhydride at equivalent WPG, despite the substantial difference in the proportion of OH groups chemically reacted.

The total sorption isotherms from Figures 7.43 and 7.46 were then separated into monomolecular and polymolecular sorption, according to the way predicted by the Hailwood-Horrobin model. The related isotherms are depicted separately in Figures 7.44, 7.45, 7.47 and 7.48, which revealed that the five anhydrides used show similar effectiveness in adsorption not only at the polymolecular but at the monomolecular level as well. This is further illustrated in Figures 7.35 to 7.40, where similar moisture contents are attained at equivalent WPG at saturation, irrespective of the modifying chemical used.

This is not surprising at the polymolecular level, since this type of sorption is affected by the bulking, as shown in section 7.4.4.2, and at equivalent WPG the five anhydrides produce similar bulking (see Figures 7.41 and 7.42). Monomolecular sorption on the other hand, is primarily a function of the availability of sorption sites, as discussed in session 7.4.4.2. The fact, for example, that the bulkier hexanoic anhydride, which chemically blocks only half of the amount of hydroxyl groups blocked by the acetic anhydride at equivalent WPG, produces a similar reduction in monomolecular adsorption suggests that is the amount of adduct deposited in the cell wall that determines the reduction obtained at the monomolecular level. This is further supported by the W_o values shown in Tables 7.5 and 7.6, which according to the Hailwood-Horrobin model reflect site accessibility. It is clear that these values are similar when equivalent WPG'S are considered, indicating similar accessibility for woods with substantially different proportions of hydroxyls reacted, but with comparable levels of bulking. This is also illustrated in Figures 7.49, 7.50 and 7.51, 7.52, where the W_o values were plotted against the WPG and against the bulking respectively. Therefore, no trends can be identified to indicate the advantage of using one of the anhydrides used in this study in preference to another in reducing hygroscopicity.

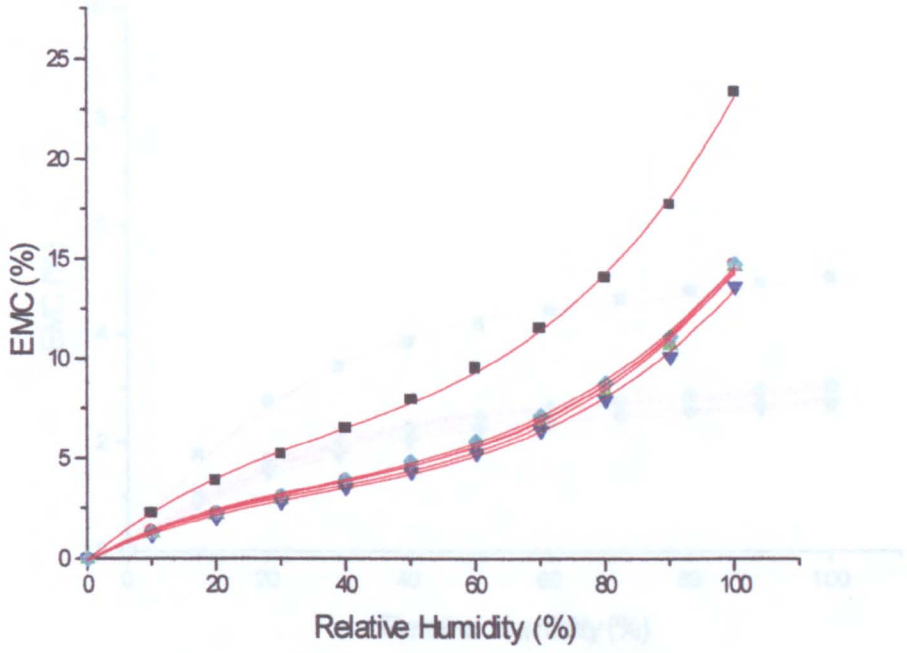

Figure 7.43: Total adsorption isotherms for Corsican pine wood: control (■); acetic 15.8% WPG (●); propionic 15.3% WPG (▲); butyric 16% WPG (▼); valeric 15.5% WPG (◆); hexanoic 15.7% WPG (+).

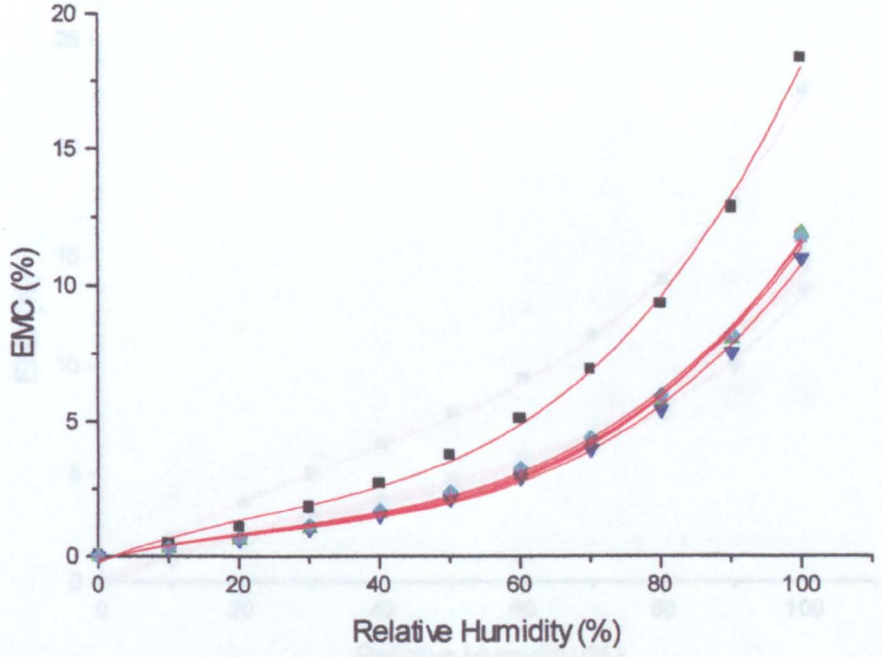

Figure 7.44: Polymolecular adsorption isotherms for Corsican pine wood: control (■); acetic 15.8% WPG (●); propionic 15.3% WPG (▲); butyric 16% WPG (▼); valeric 15.5% WPG (◆); hexanoic 15.7% WPG (+).

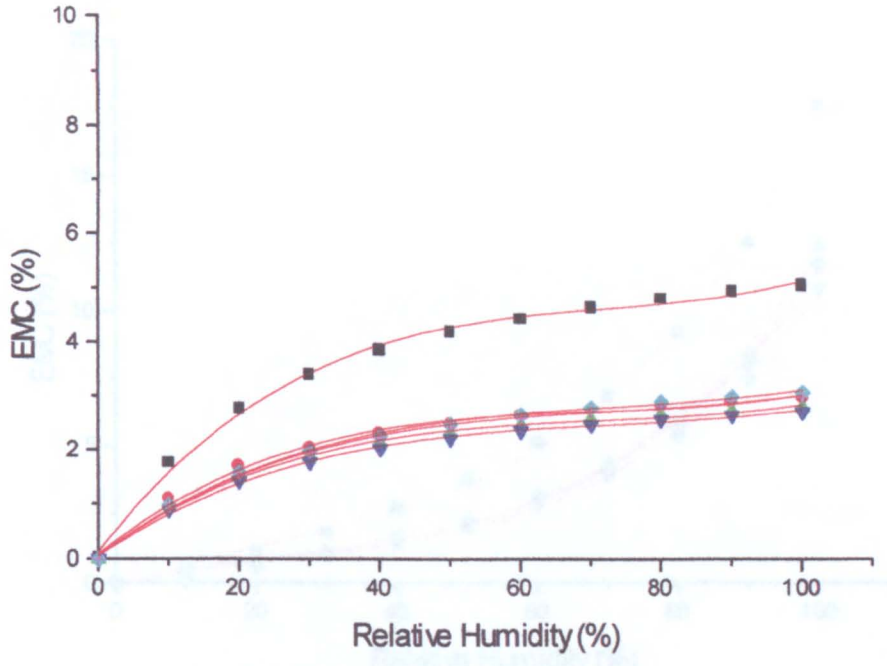

Figure 7.45: Monomolecular adsorption isotherms for Corsican pine wood: control (■); acetic 15.8% WPG (●); propionic 15.3% WPG (▲); butyric 16% WPG (▼); valeric 15.5% WPG (◆); hexanoic 15.7% WPG (+).

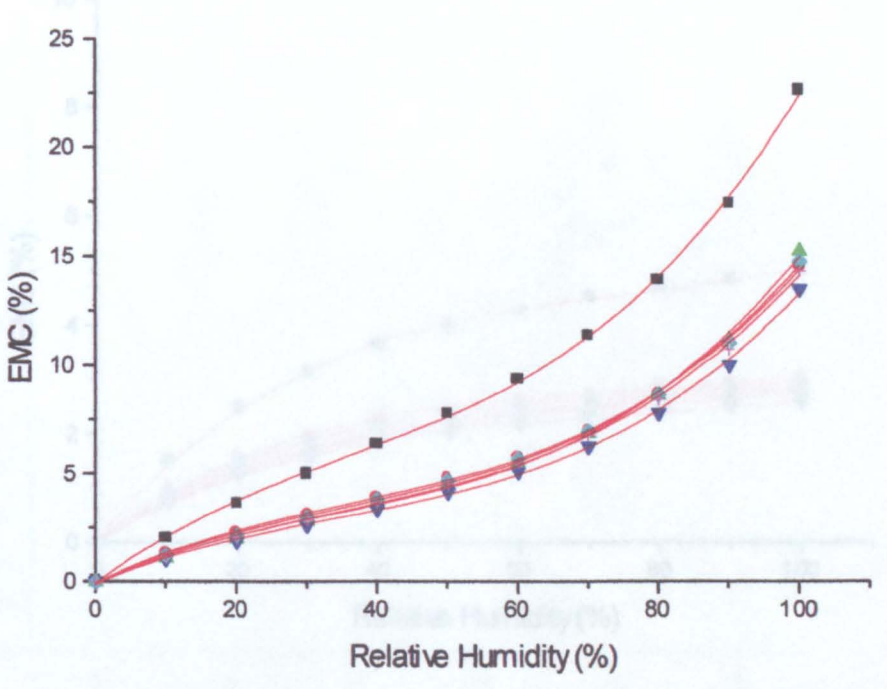

Figure 7.46: Total adsorption isotherms for Scots pine wood: control (■); acetic 16.1% WPG (●); propionic 15.6% WPG (▲); butyric 16% WPG (▼); valeric 16.2% WPG (◆); hexanoic 15.7% WPG (+).

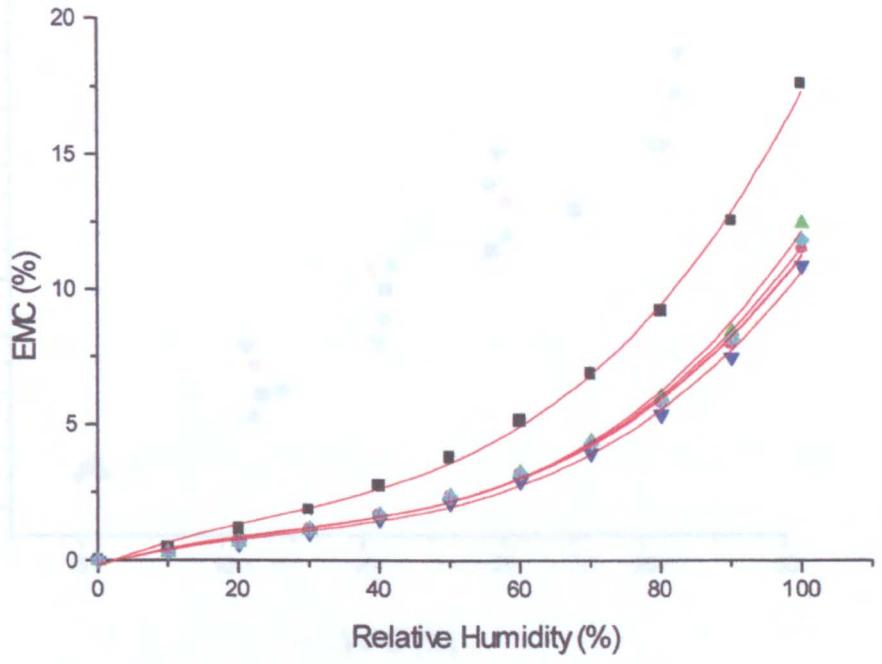

Figure 7.47: Polymolecular adsorption isotherms for Scots pine wood: control (■); acetic 16.1% WPG (●); propionic 15.6% WPG (▲); butyric 16% WPG (▼); valeric 16.2% WPG (◆); hexanoic 15.7% WPG (+).

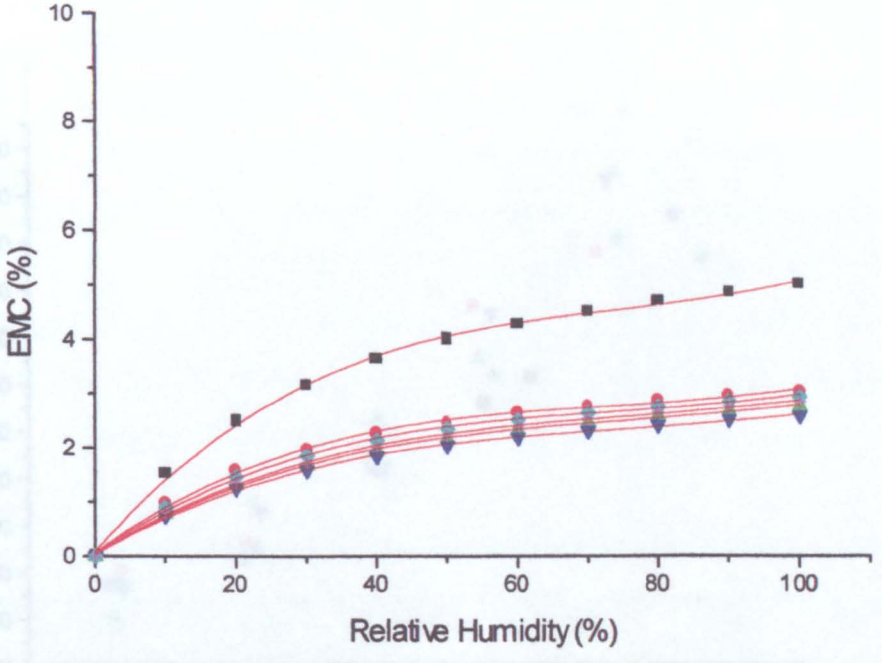

Figure 7.48: Monomolecular adsorption isotherms for Scots pine wood: control (■); acetic 16.1% WPG (●); propionic 15.6% WPG (▲); butyric 16% WPG (▼); valeric 16.2% WPG (◆); hexanoic 15.7% WPG (+).

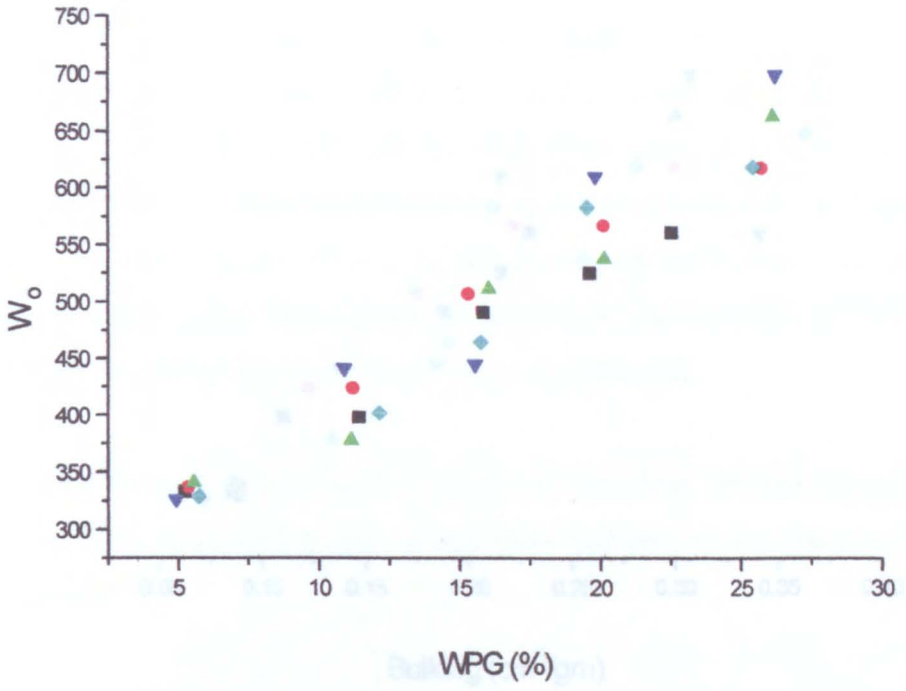

Figure 7.49: Relationship between W_o values and WPG: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

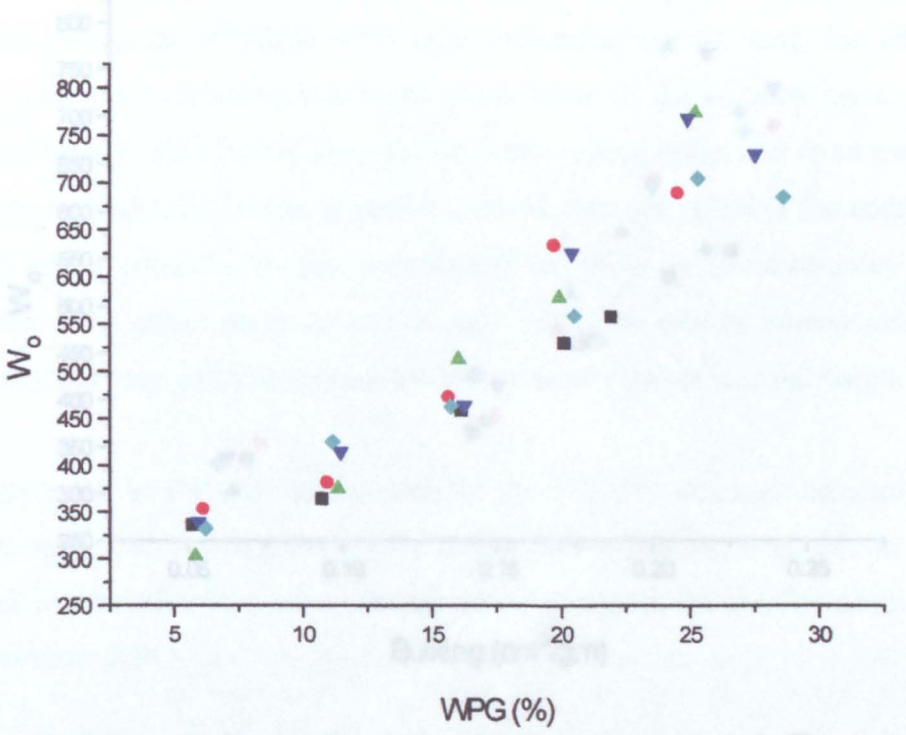

Figure 7.50: Relationship between W_o values and WPG: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

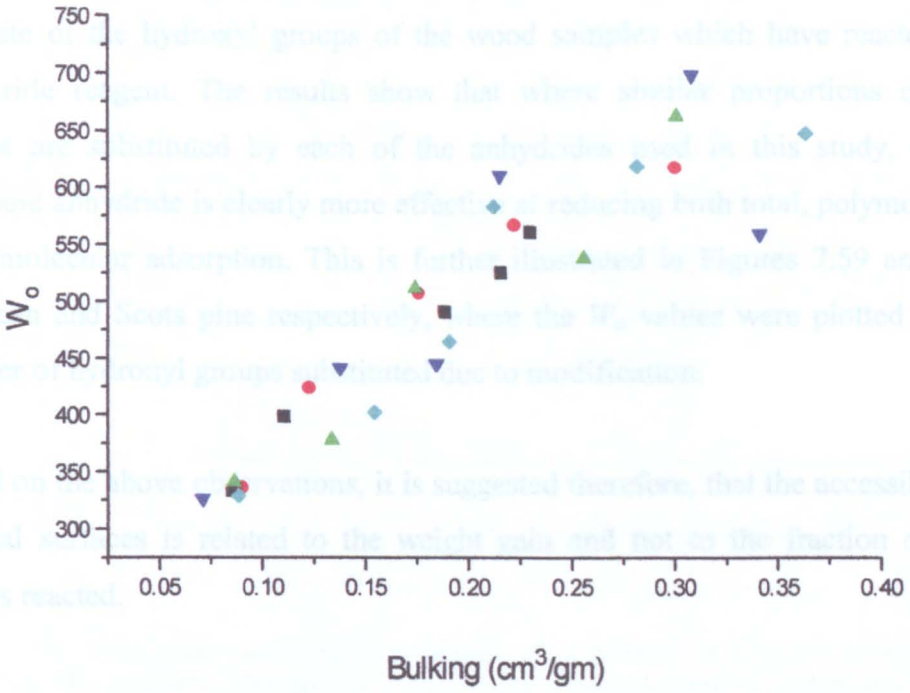

Figure 7.51: Relationship between W_o values and bulking: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

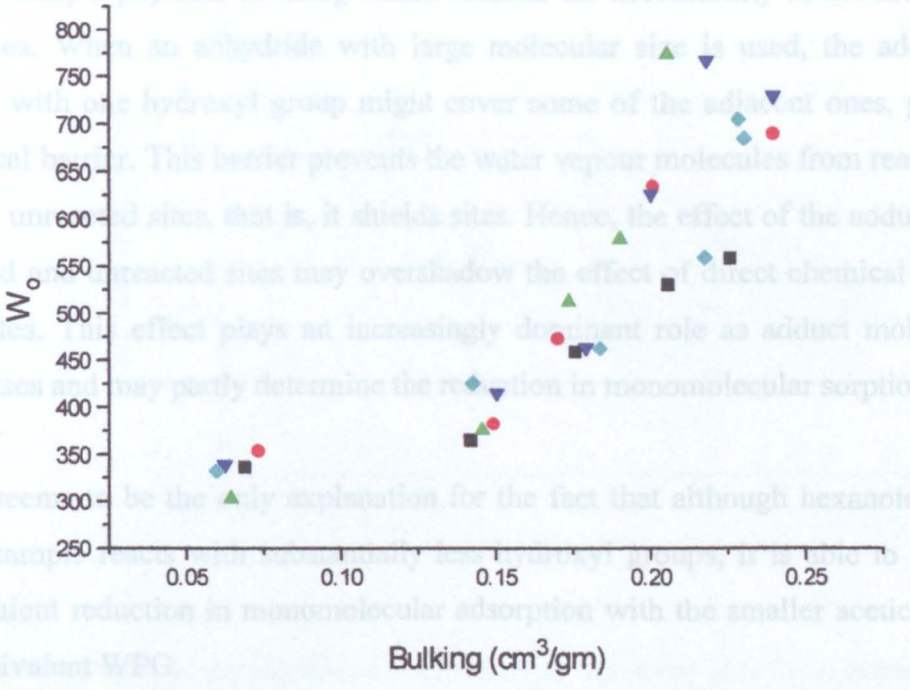

Figure 7.52: Relationship between W_o values and bulking: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

The data shown in Figures 7.35 to 7.40, is replotted in Figures 7.53 to 7.58, where account is taken of the molecular weight of the reacting chemical in order to obtain an estimate of the hydroxyl groups of the wood samples which have reacted with the anhydride reagent. The results show that where similar proportions of hydroxyl groups are substituted by each of the anhydrides used in this study, the bulkier hexanoic anhydride is clearly more effective at reducing both total, polymolecular and monomolecular adsorption. This is further illustrated in Figures 7.59 and 7.60, for Corsican and Scots pine respectively, where the W_o values were plotted against the number of hydroxyl groups substituted due to modification.

Based on the above observations, it is suggested therefore, that the accessibility of the internal surfaces is related to the weight gain and not to the fraction of hydroxyl groups reacted.

From the above discussion, it appears that the reduction in monomolecular adsorption produced by the linear chain anhydrides is primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted. An additional contributor to this behaviour, may be the simple physical covering which reduces the accessibility of the internal wood surfaces. When an anhydride with large molecular size is used, the adduct which reacts with one hydroxyl group might cover some of the adjacent ones, providing a physical barrier. This barrier prevents the water vapour molecules from reaching some of the unreacted sites, that is, it shields sites. Hence, the effect of the adduct covering reacted and unreacted sites may overshadow the effect of direct chemical bonding to the sites. This effect plays an increasingly dominant role as adduct molecular size increases and may partly determine the reduction in monomolecular sorption.

This seems to be the only explanation for the fact that although hexanoic anhydride for example reacts with substantially less hydroxyl groups, it is able to produce an equivalent reduction in monomolecular adsorption with the smaller acetic anhydride, at equivalent WPG.

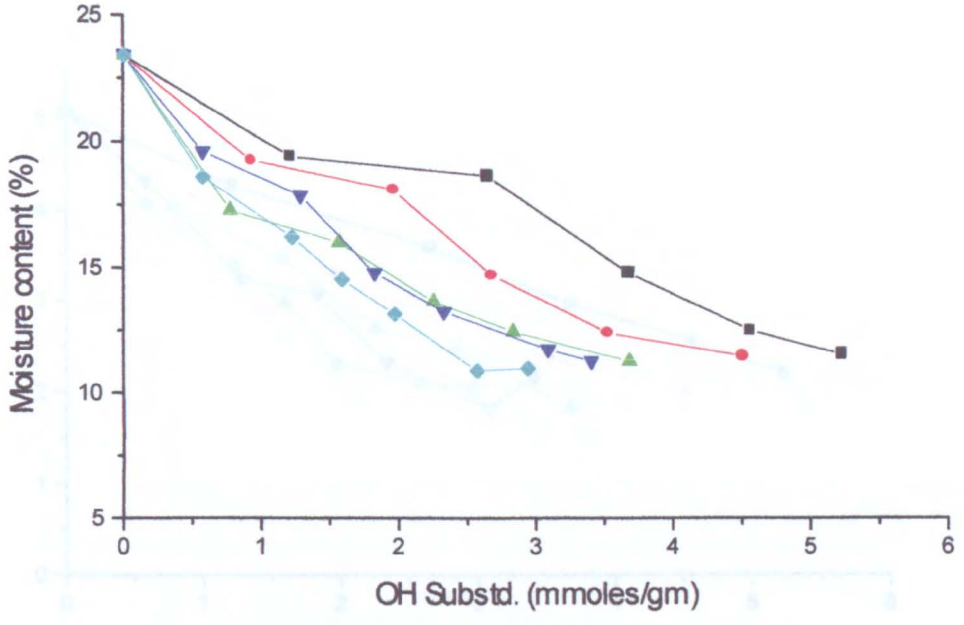

Figure 7.53: Total water adsorbed at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆) (Corsican pine data).

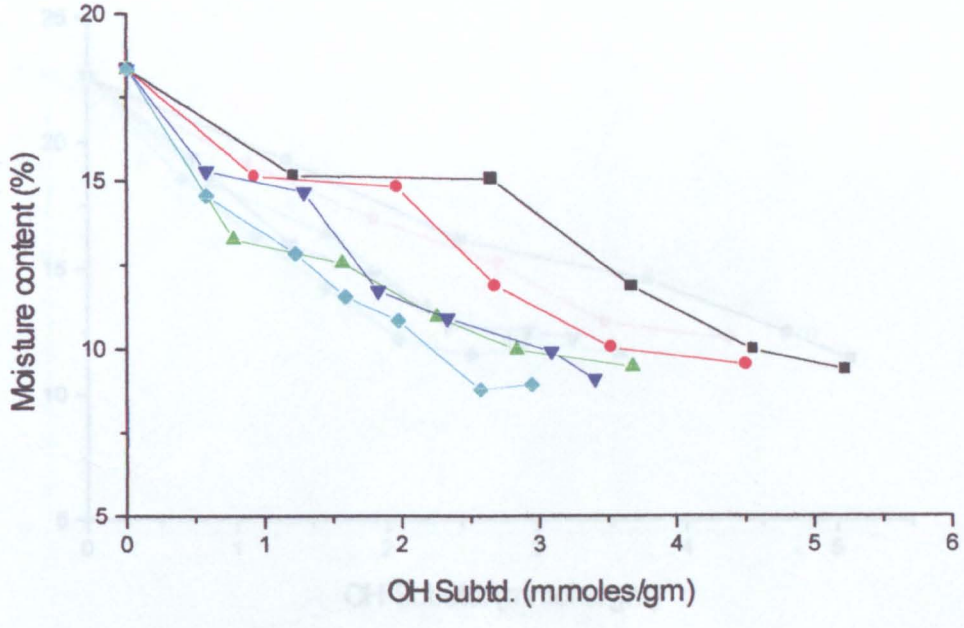

Figure 7.54: Polymolecular adsorption at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆) (Corsican pine data).

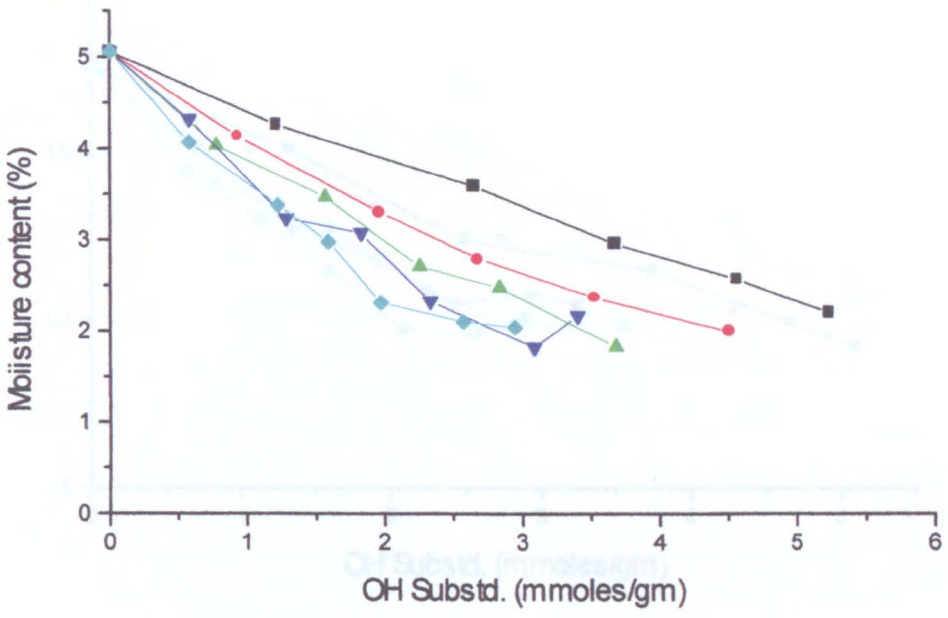

Figure 7.55: Monomolecular adsorption at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆) (Corsican pine data).

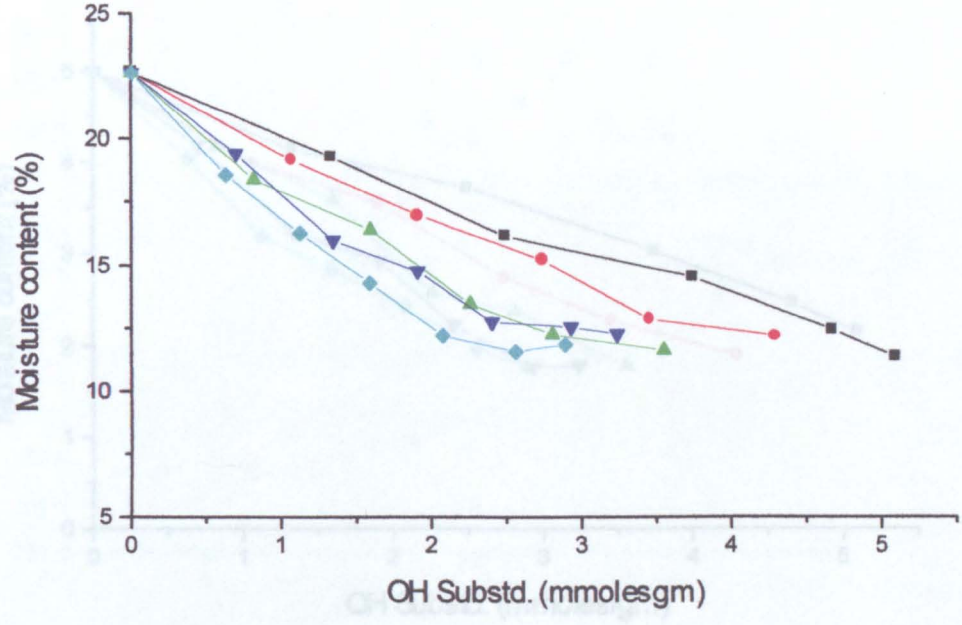

Figure 7.56: Total water adsorbed at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆) (Scots pine data).

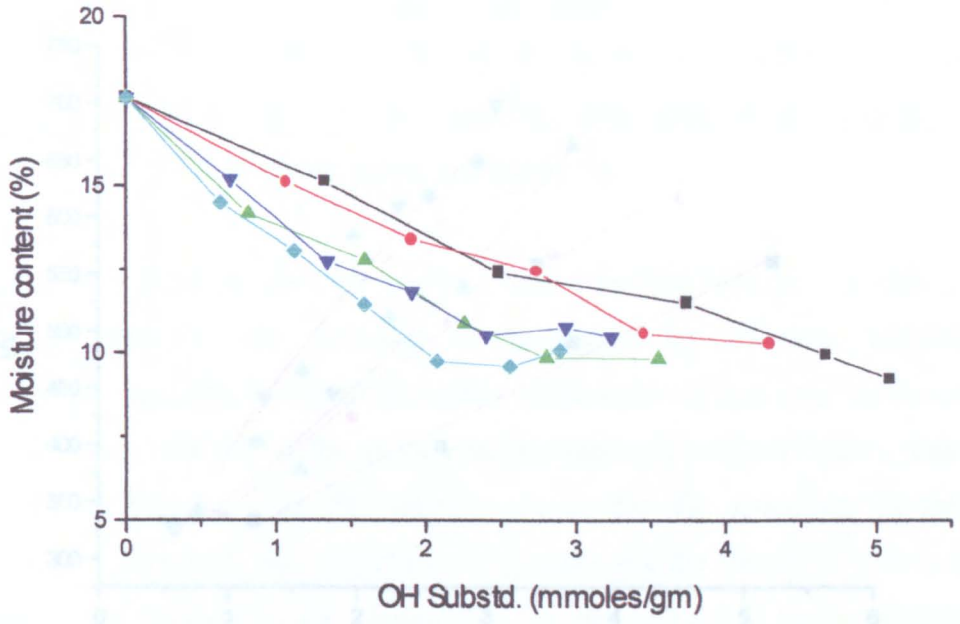

Figure 7.57: Polymolecular adsorption at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆) (Scots pine data).

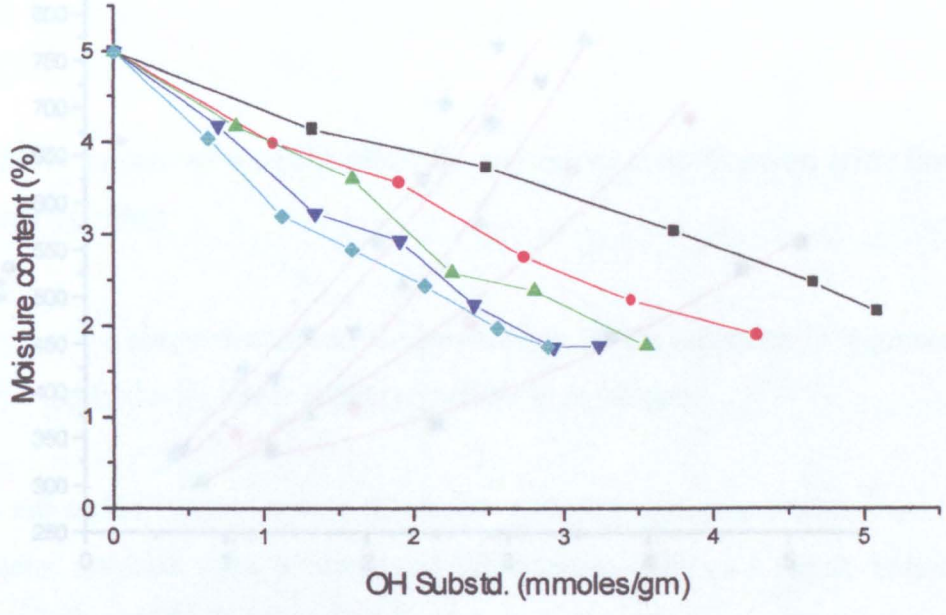

Figure 7.58: Monomolecular adsorption at saturation as a function of hydroxyl substitution: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

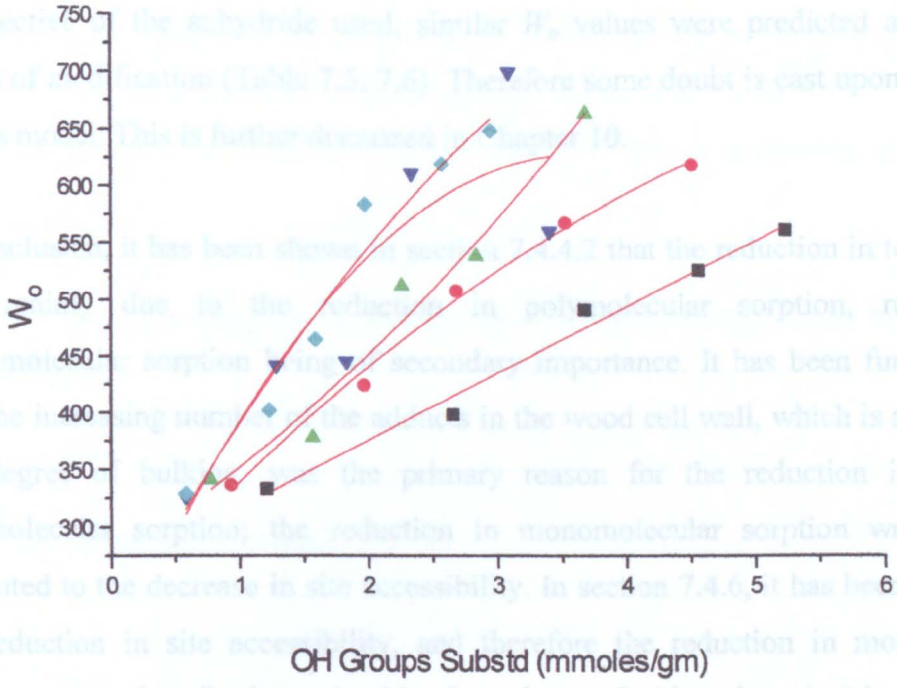

Figure 7.59: Relationship between W_o values and number of hydroxyl groups substituted: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Corsican pine data).

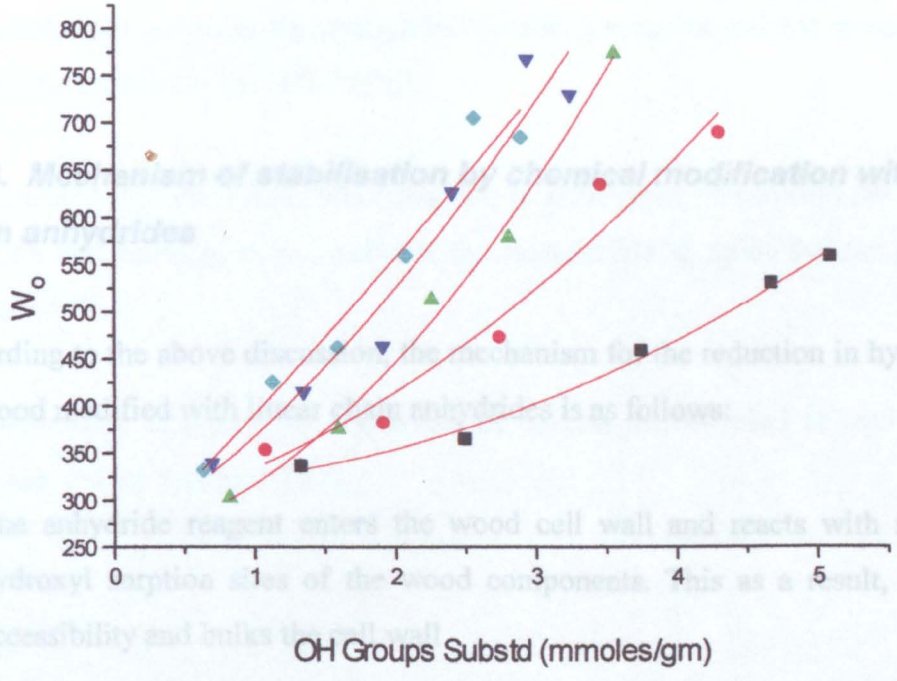

Figure 7.60: Relationship between W_o values and number of hydroxyl groups substituted: acetic anhydride (■), propionic anhydride (●); butyric anhydride (▲); valeric anhydride (▼), hexanoic anhydride (◆). (Scots pine data).

Another explanation may be the inability of the Hailwood-Horrobin model to fully predict monomolecular and polymolecular sorption of modified wood, since irrespective of the anhydride used, similar W_o values were predicted at equivalent levels of modification (Table 7.5, 7.6). Therefore some doubt is cast upon the validity of this model. This is further discussed in Chapter 10.

In conclusion, it has been shown in section 7.4.4.2 that the reduction in total sorption was mainly due to the reduction in polymolecular sorption, reduction in monomolecular sorption being of secondary importance. It has been further shown, that the increasing number of the adducts in the wood cell wall, which is a measure of the degree of bulking, was the primary reason for the reduction in total and polymolecular sorption; the reduction in monomolecular sorption was primarily attributed to the decrease in site accessibility. In section 7.4.6, it has been shown that the reduction in site accessibility, and therefore the reduction in monomolecular sorption, was primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted. Combining the above observations, it is concluded that the reduced moisture uptake of wood modified with linear chain anhydrides is mainly a bulking phenomenon.

7.4.6. Mechanism of stabilisation by chemical modification with linear chain anhydrides

According to the above discussion, the mechanism for the reduction in hygroscopicity for wood modified with linear chain anhydrides is as follows:

- The anhydride reagent enters the wood cell wall and reacts with some of the hydroxyl sorption sites of the wood components. This as a result, reduces site accessibility and bulks the cell wall.

- Sorption at the monomolecular level is primarily reduced by reduction in site accessibility, while sorption at the polymolecular level is reduced by bulking.

- The accessibility of the internal surfaces to water molecules is primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted, and at the same time by a shielding effect when the adduct physically covers some of the adjacent unreacted sorption sites. The latter is of less importance compared to the bulking effect.

- The shielding effect plays an increasingly dominant role as adduct molecular size increases.

7.4.7. Species comparison

The effect of modification on hygroscopicity on two substrates used in this study, namely Corsican and Scots pine, has been compared.

The results are shown in Figures 7.61, 7.62, 7.63, for total, polymolecular and monomolecular sorption, for unmodified (control) samples and for samples modified with acetic anhydride (*ca* 16% WPG).

It is revealed that the e.m.c values attained in both types of sorption are identical for Corsican and Scots pine, not only for the unmodified samples but for the modified ones as well.

This behaviour is typical for the series of the anhydrides used at equivalent WPG (compare Tables 7.10 and 7.11).

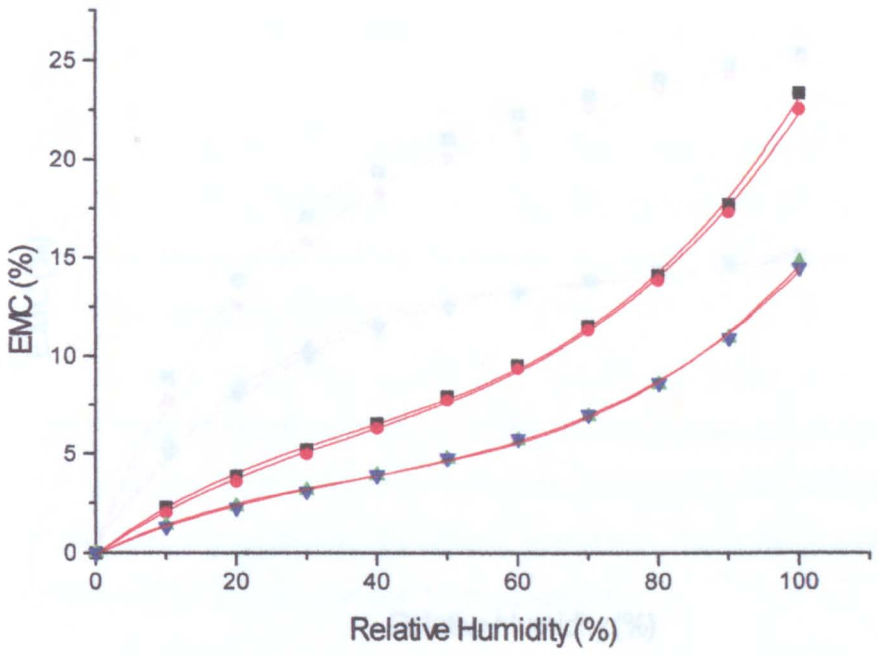

Figure 7.61: Total water adsorbed at saturation: Corsican pine control (■), Scots pine control (●); Corsican pine modified with acetic anhydride 15.8 WPG (▲), Scots pine modified with acetic anhydride 16.1 WPG (▼).

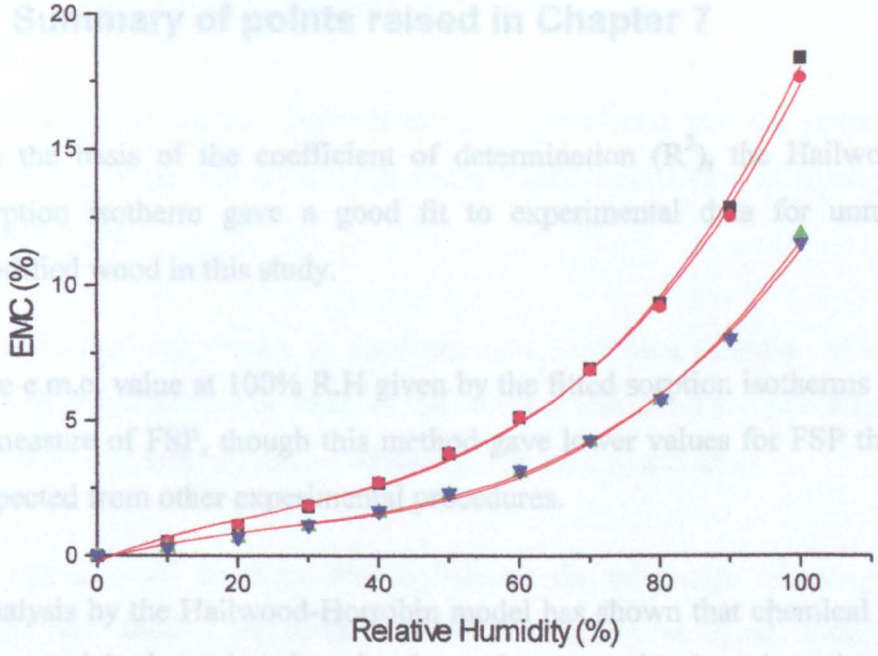

Figure 7.62: Polymolecular adsorption at saturation: Corsican pine control (■), Scots pine control (●); Corsican pine modified with acetic anhydride 15.8 WPG (▲), Scots pine modified with acetic anhydride 16.1 WPG (▼).

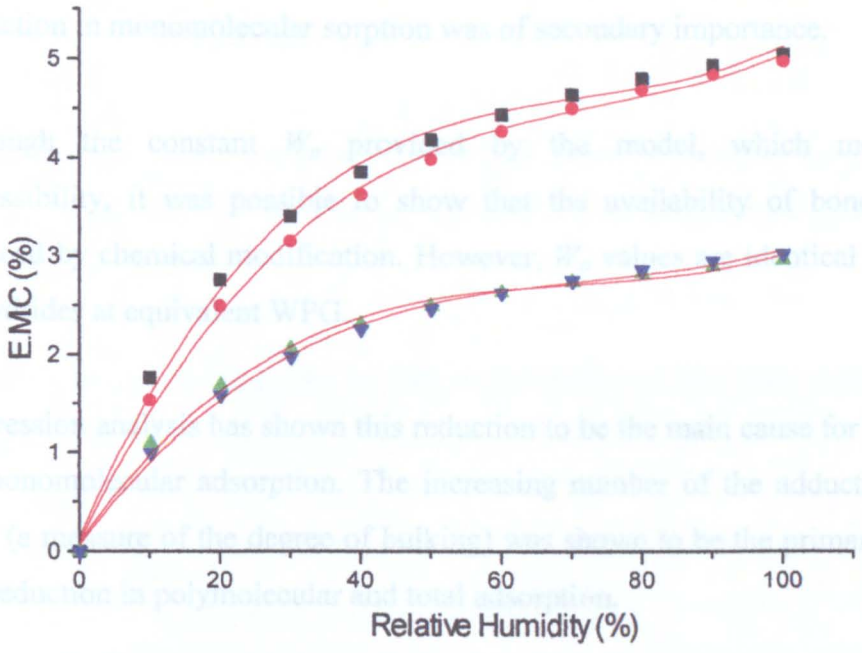

Figure 7.63: Monomolecular adsorption at saturation: Corsican pine control (■), Scots pine control (●); Corsican pine modified with acetic anhydride 15.8 WPG (▲), Scots pine modified with acetic anhydride 16.1 WPG (▼).

7.5. Summary of points raised in Chapter 7

- On the basis of the coefficient of determination (R^2), the Hailwood-Horrobin sorption isotherm gave a good fit to experimental data for unmodified and modified wood in this study.

- The e.m.c. value at 100% R.H given by the fitted sorption isotherms was taken as a measure of FSP, though this method gave lower values for FSP than would be expected from other experimental procedures.

- Analysis by the Hailwood-Horrobin model has shown that chemical modification decreased both total, polymolecular and monomolecular adsorption. This effect increased with increasing WPG.

- Analysis by the Hailwood-Horrobin model suggests that the reduction in total sorption at saturation was mainly due to the reduction in polymolecular sorption, reduction in monomolecular sorption was of secondary importance.

- Through the constant W_o provided by the model, which measures site accessibility, it was possible to show that the availability of bonding sites is reduced by chemical modification. However, W_o values are identical for different anhydrides at equivalent WPG.

- Regression analysis has shown this reduction to be the main cause for the decrease in monomolecular adsorption. The increasing number of the adducts in the cell wall (a measure of the degree of bulking) was shown to be the primary reason for the reduction in polymolecular and total adsorption.

- Investigation of the causes of the reduction in site accessibility by analysing the sorption isotherms suggests that the accessibility of the internal wood surfaces, and therefore monomolecular sorption, was primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted.

- Combining the above observations, it is concluded that the reduced moisture uptake of wood modified with linear chain anhydrides is mainly a bulking phenomenon.

- An additional contributor to this behaviour, may be a shielding effect where the adducts physically cover some of the adjacent unreacted sorption sites. The effect played an increasingly role as adduct molecular size increases.

- No trends could be identified to indicate the advantage of using one of the anhydrides studied in preference to another in reducing hygroscopicity at equivalent WPG.

- Where similar proportions of hydroxyl groups were substituted by each of the anhydrides used in this study, the bulkier hexanoic anhydride was more effective at reducing hygroscopicity.

- Identical e.m.c values were attained in both types of sorption for Corsican and Scots pine, at equivalent WPG, not only for the unmodified samples but for the modified ones as well.

- Some doubt was cast upon the validity of the Hailwood-Horrobin model.

CHAPTER 8

Analysis of the swelling behaviour of chemically modified pine sapwood

8.1. Introduction

The previous chapter studied the reduction in equilibrium moisture content caused by increasing weight gains of modifying chemical. This was attributed mainly to the bulking action of chemical in the cell wall displacing water that would otherwise be adsorbed in the cell wall as bound water. The aim of this chapter was to present an analysis of the swelling behaviour of chemically modified wood due to water vapour sorption.

When wood takes up moisture into the cell wall, the walls swell volumetrically in proportion to the volume of the water absorbed (Skaar, 1988). This is based on the assumptions that the cell lumena are constant in size and that there are no voids in the cell wall and therefore, water simply adds its volume to that of dry wood. It was shown in Chapter 6 that volumetric changes due to modification with a homologous series of linear chain anhydrides were found to be due to the volume occupied by the reagent and an associated void volume created by the acyl groups within the cell wall. Additionally, it was shown that as the size of the reagent increases, so does the void volume created in the wood matrix.

The first assumption relies on modification either causing an increase in swelling (due to saturation) into the cell lumena or a reduction in the way in which the lumen size increases due to water swelling. Cell lumena in some wood species have been found to enlarge or shrink when wood is saturated and swells, though where this occurs it is often only by a small amount, and negligible compared to the swelling of the cell wall (Stamm, 1964; Siau, 1984; 1996). It was assumed therefore that no such change

occurred. Any change in dimension due to water swell was considered to be solely due to the swelling of the wood cell wall.

It was the aim of this Chapter to test the validity of the second assumption.

8.2. Materials and methods

The relationship between EMC and swelling was assessed by measuring the volume (derived from the three dimensions) of samples (unmodified and modified, see Table 8.1) at the moisture content achieved in equilibrium with each relative humidity during the adsorption tests described in section 7.3.3.

Due to time constraints, only samples modified with acetic and hexanoic anhydride to three selected weight gains, as indicated in Table 8.1, were tested.

Table 8.1: Experimental design

Wood species	Modifying chemical	WPG (%)
Corsican pine	Acetic anhydride	5.2, 15.8, 22.5
	Hexanoic anhydride	5.7, 15.7, 25.4
Scots pine	Acetic anhydride	5.7, 16.1, 21.9
	Hexanoic anhydride	6.2, 15.7, 25.3

Swelling was then calculated in two ways:

(i). As total swelling due to exposure to relative humidity

$$S_1\ (\%) = \frac{\text{Volume of wet modified wood} - \text{Volume of dry modified wood}}{\text{Volume of dry modified wood}} \times 100$$

(ii). As the aggregate swelling, i.e. that due to modification plus exposure to relative humidity.

$$S_2\ (\%) = \frac{\text{Volume of wet modified wood - Volume of dry unmodified wood}}{\text{Volume of dry unmodified wood}} \times 100$$

8.3. Results and discussion

8.3.1. Equilibrium moisture content (EMC) and swelling

The percent volumetric swelling values in equilibrium with each relative humidity obtained for the controls and for the three selected levels of weight gain modified with acetic and hexanoic anhydride are shown in Tables 8.2 and 8.3 for Corsican and Scots pine, respectively. From these, it can be seen that the decrease in EMC is accompanied by a decrease in swelling.

The variation of volumetric swelling over the relative humidity range is depicted in Figures 8.1 to 8.2 and 8.3 to 8.4 for Corsican and Scots pine, respectively. The curves are of similar shape to the sorption isotherms presented in section 7.4.2, indicating a close relationship between EMC and swelling. On closer inspection, it was revealed that the volumetric swelling of the modified woods approximately parallels the swelling of the controls, that is, the curves are depressed evenly over the entire experimental range, as the weight gain increases. This is in good agreement with the results reported by Risi and Arseneau (1957a) and by Martins (1992) for various isocyanate modified woods and indicates that bulking influences swelling over the entire course of the relative humidity.

The relationship between EMC and volumetric swelling is illustrated in Figures 8.5 to 8.6 and 8.7 to 8.8 for Corsican and Scots pine, respectively. From this, it can be seen that as the weight gain increases, the samples swell less at each EMC attained. At very low WPG's (*ca* 5-6%) a non-linear relationship is obtained; however at higher WPG's the relationship is linear. A linear relationship was also reported by Martins (1992) for various isocyanates and by Risi and Arseneau (1957a) for acetic and phthalic

Table 8.2: Equilibrium moisture content and Volumetric swelling values for Corsican pine sapwood modified with acetic and hexanoic anhydride. (Standard deviation in parentheses).

	Control		Acetic 5.2%		Acetic 15.8%		Acetic 22.5%	
R.H (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)
12	2.59	1.3 (.12)	2.19	0.8 (.05)	1.63	0.6 (.12)	0.99	0.4 (.12)
23	4.35	2.4 (.13)	3.64	1.4 (.08)	2.54	1.1 (.19)	1.73	0.7 (.15)
44	7.27	3.9 (.21)	6.01	2.3 (.12)	4.39	1.7 (.22)	3.28	1.1 (.2)
55	8.49	4.6 (.22)	7.25	2.7 (.2)	5.16	2.1 (.28)	3.91	1.6 (.18)
76	13.01	7.2 (.31)	9.62	4.8 (.25)	7.77	3.2 (.22)	6.05	2 (.2)
93	19.29	11.4 (.5)	15.01	8.2 (.3)	12.02	5.1 (2)	9.54	3.5 (.15)
	Control		**Hexanoic 5.7%**		**Hexanoic 15.7%**		**Hexanoic 25.4%**	
R.H (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)
12	2.59	1.3 (.11)	1.99	0.7 (.05)	1.49	0.5 (.01)	1.01	0.4 (.02)
23	4.35	2.4 (.2)	3.21	1.5 (.09)	2.49	1 (.02)	1.65	0.8 (.05)
44	7.27	3.9 (.15)	5.61	2.3 (.1)	4.39	1.5 (.05)	3.12	1.2 (.1)
55	8.49	4.6 (.22)	7.15	2.8 (.11)	5.12	1.9 (.1)	3.79	1.7 (.11)
76	13.01	7.2 (.3)	10.51	4.9 (.15)	7.72	2.9 (.12)	5.61	2.1 (.12)
93	19.29	11.4 (.5)	15.33	8 (.2)	12.04	4.8 (.33)	8.92	3.4 (.22)

Table 8.3: Equilibrium moisture content and Volumetric swelling values for Scots pine sapwood modified with acetic and hexanoic anhydride. (Standard deviation in parentheses).

	Control		Acetic 5.7%		Acetic 16.1%		Acetic 21.9%	
R.H (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)
12	2.33	1.1 (.02)	2.05	0.7 (.01)	1.55	0.5 (.01)	0.94	0.4 (.01)
23	4.19	2.3 (.05)	3.48	1.3 (.03)	2.42	1.1 (.05)	1.65	0.6 (.01)
44	7.02	3.7 (.32)	5.79	2.1 (.1)	4.51	1.5 (.05)	3.2	1.1 (.03)
55	8.38	4.3 (.22)	7.12	2.5 (.2)	5.23	1.9 (.05)	3.82	1.5 (.05)
76	12.68	6.9 (.3)	10.64	4.5 (.25)	7.65	3 (.1)	5.99	1.9 (.08)
93	18.98	11.1 (.5)	15.88	7.9 (.3)	12.12	4.8 (.2)	9.38	3.3 (.09)
	Control		**Hexanoic 6.2%**		**Hexanoic 15.7%**		**Hexanoic 25.3%**	
R.H (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)	EMC (%)	Swell (%)
12	2.33	1.1 (.03)	2.01	0.6 (.01)	1.32	0.6 (.01)	1.06	0.5 (.01)
23	4.19	2.3 (.1)	3.15	1.3 (.02)	2.29	0.9 (.01)	1.58	0.7 (.01)
44	7.02	3.7 (.25)	5.41	2.1 (.02)	4.11	1.4 (.03)	3.02	1.1 (.03)
55	8.38	4.3 (.4)	7.25	2.6 (.05)	5	1.8 (.04)	3.85	1.5 (.04)
76	12.68	6.9 (.54)	10.62	4.5 (.08)	7.49	2.7 (.05)	5.81	1.9 (.06)
93	18.98	11.1 (.6)	15.02	7.6 (.09)	11.85	4.5 (.1)	8.88	3.2 (.07)

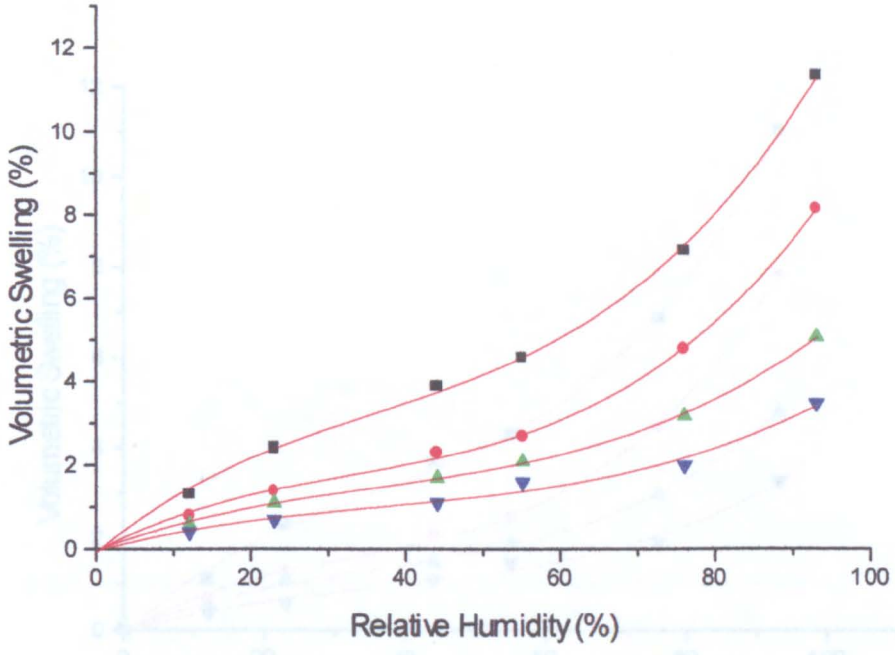

Figure 8.1: Relationship between the relative humidity and percent volumetric swelling of Corsican pine sapwood modified with acetic anhydride: Control (■): 5.2 WPG (●); 15.8 WPG (▲); 22.5 WPG (▼).

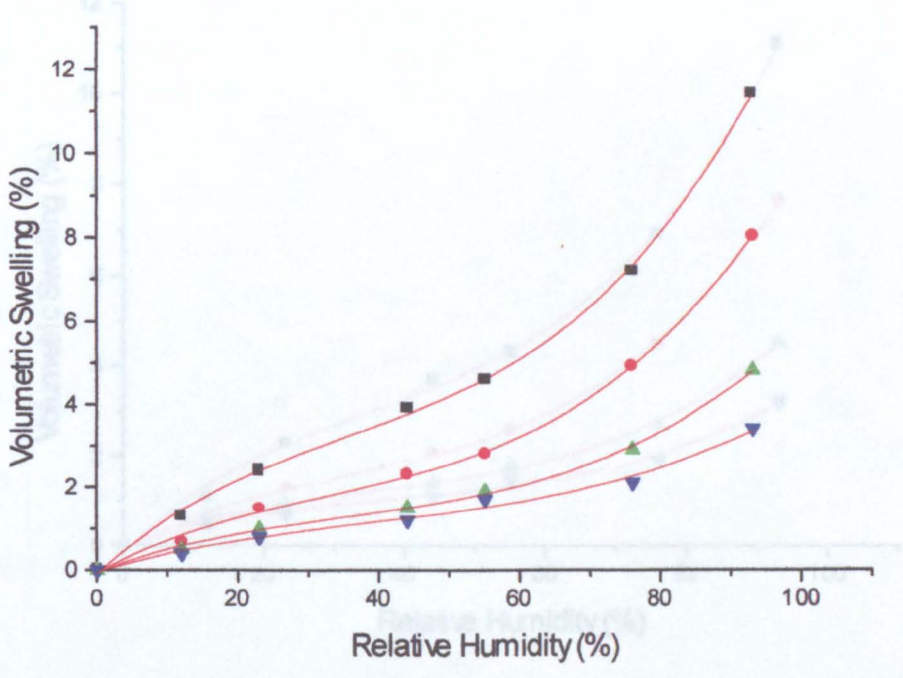

Figure 8.2: Relationship between the relative humidity and percent volumetric swelling of Corsican pine sapwood modified with hexanoic anhydride: Control (■): 5.7 WPG (●); 15.7 WPG (▲); 25.4 WPG (▼).

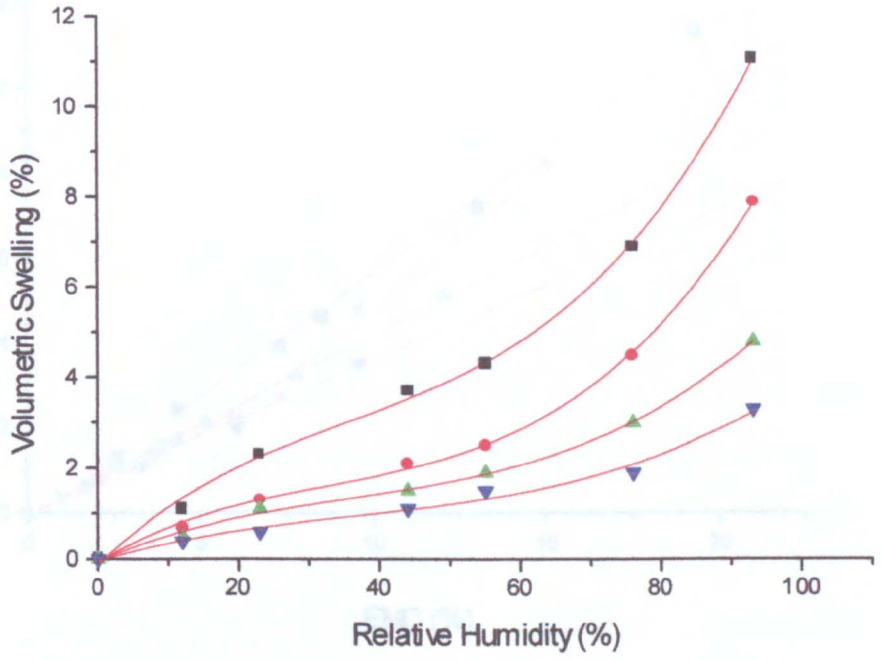

Figure 8.3: Relationship between the relative humidity and percent volumetric swelling of Scots pine sapwood modified with acetic anhydride: Control (■): 5.7 WPG (●); 16.1 WPG (▲); 21.9 WPG (▼).

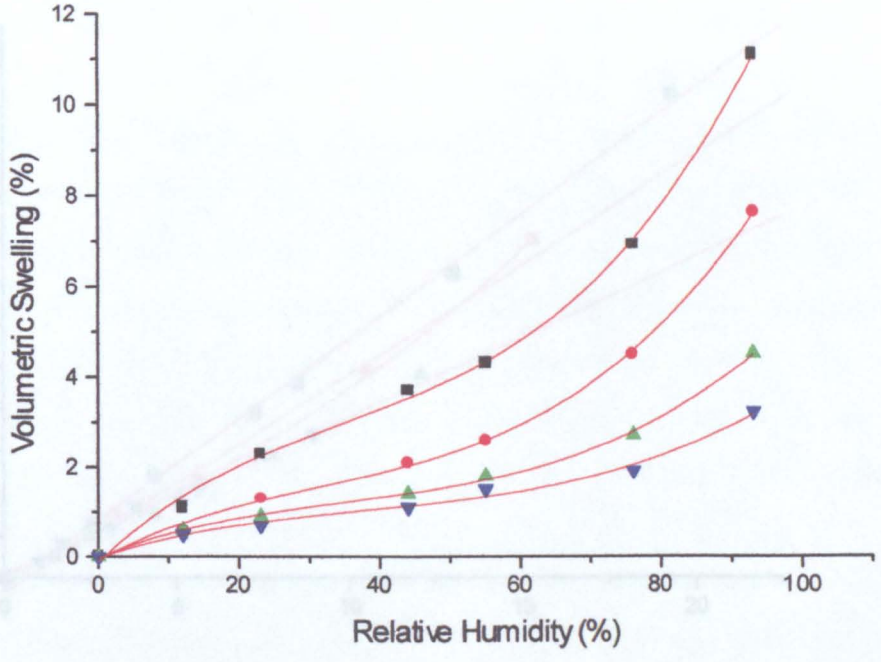

Figure 8.4: Relationship between the relative humidity and percent volumetric swelling of Scots pine sapwood modified with hexanoic anhydride: Control (■): 6.2 WPG (●); 15.7 WPG (▲); 25.3 WPG (▼).

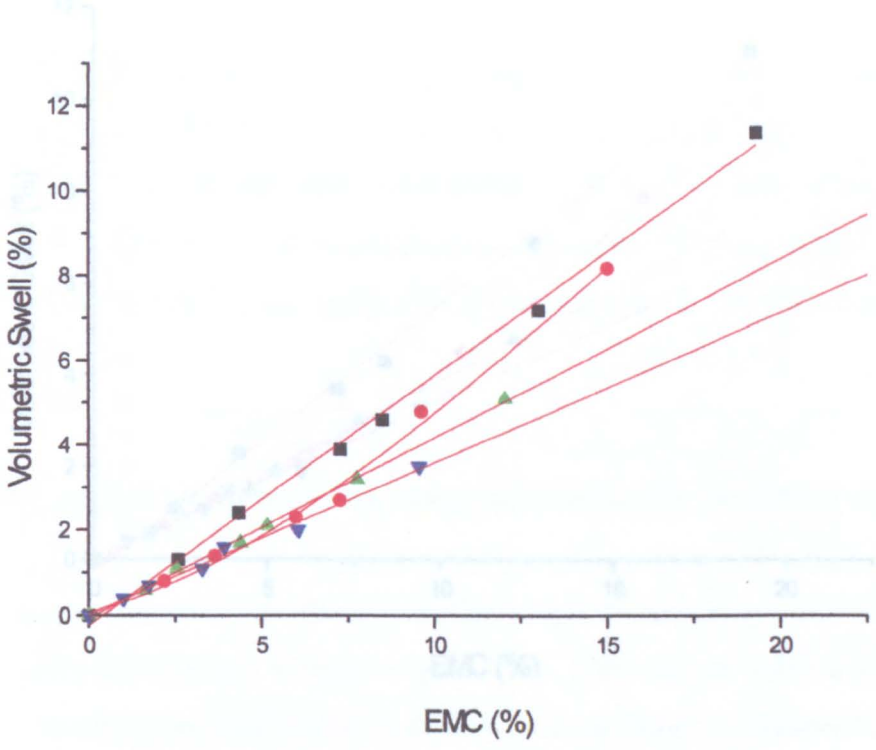

Figure 8.5: Relationship between EMC and percent volumetric swelling of Corsican pine sapwood modified with acetic anhydride: Control (■): 5.2 WPG (●); 15.8 WPG (▲); 22.5 WPG (▼).

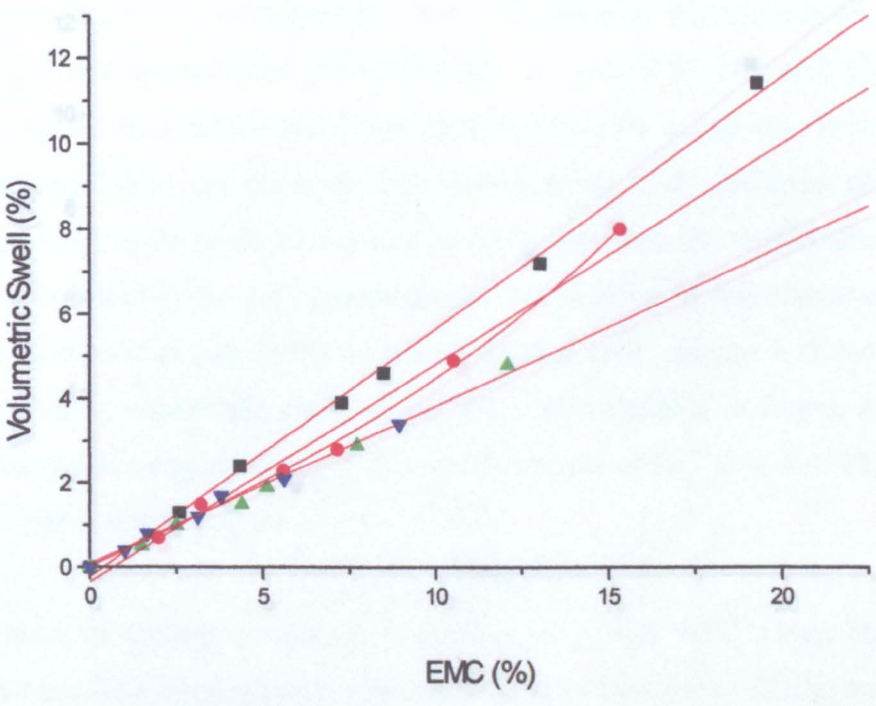

Figure 8.6: Relationship between EMC and percent volumetric swelling of Corsican pine sapwood modified with hexanoic anhydride: Control (■): 5.7 WPG (●); 15.7 WPG (▲); 25.4 WPG (▼).

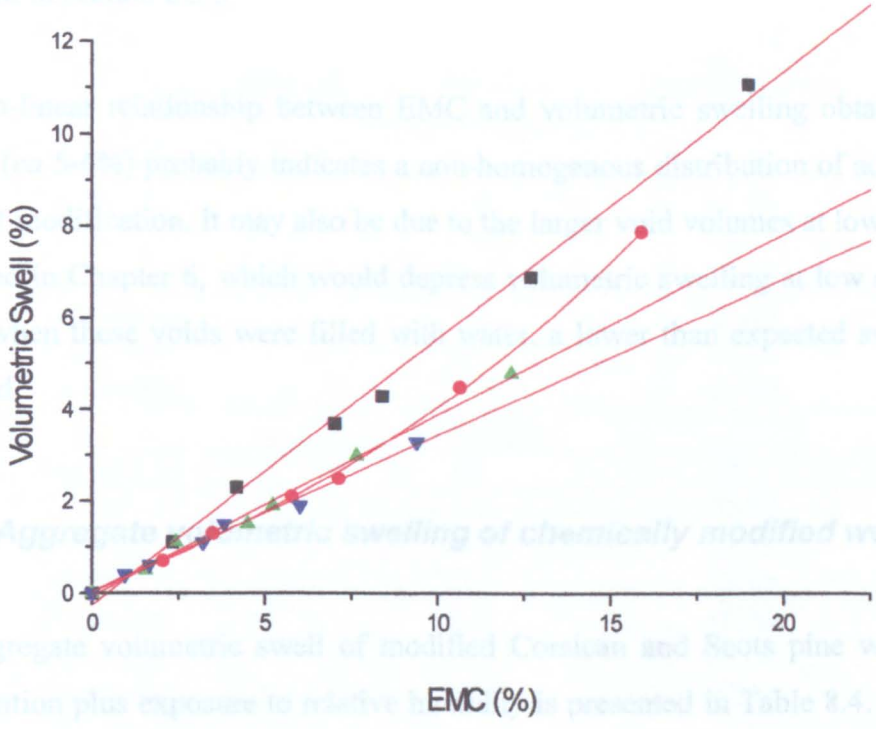

Figure 8.7: Relationship between EMC and percent volumetric swelling of Scots pine sapwood modified with acetic anhydride: Control (■): 5.7 WPG (●); 16.1 WPG (▲); 21.9 WPG (▼).

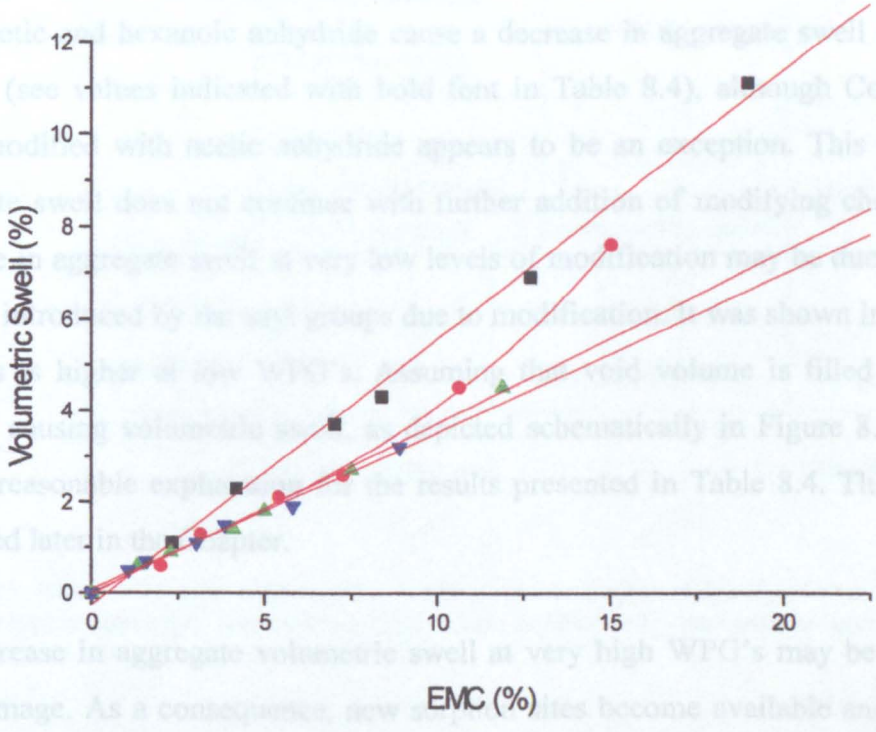

Figure 8.8: Relationship between EMC and percent volumetric swelling of Scots pine sapwood modified with hexanoic anhydride: Control (■): 6.2 WPG (●); 15.7 WPG (▲); 25.3 WPG (▼).

anhydrides, though no explanation appears to have been offered. This is further discussed in section 8.3.3.

The non-linear relationship between EMC and volumetric swelling obtained at low WPG's (*ca* 5-6%) probably indicates a non-homogenous distribution of adduct at low levels of modification. It may also be due to the larger void volumes at low WPG's, as discussed in Chapter 6, which would depress volumetric swelling at low emc's. As a result, when these voids were filled with water, a lower than expected swelling was observed.

8.3.2. Aggregate volumetric swelling of chemically modified wood

The aggregate volumetric swell of modified Corsican and Scots pine wood due to modification plus exposure to relative humidity is presented in Table 8.4. Swelling at saturation was obtained from extrapolation of the data shown in Figures 8.5 to 8.8 (the EMC values were first extrapolated to 100% relative humidity and consequently from the Figures 8.5 to 8.8, a value for the volumetric swell at 100% relative humidity was obtained).

Both acetic and hexanoic anhydride cause a decrease in aggregate swell at very low WPG's (see values indicated with bold font in Table 8.4), although Corsican pine wood modified with acetic anhydride appears to be an exception. This decrease in aggregate swell does not continue with further addition of modifying chemical. The decrease in aggregate swell at very low levels of modification may be due to the void volume introduced by the acyl groups due to modification. It was shown in Chapter 6, that this is higher at low WPG's. Assuming that void volume is filled with water without causing volumetric swell, as depicted schematically in Figure 8.9, this may offer a reasonable explanation for the results presented in Table 8.4. This is further discussed later in the Chapter.

The increase in aggregate volumetric swell at very high WPG's may be due to cell wall damage. As a consequence, new sorption sites become available and there may be some disruption of the cell wall polymeric network, which allows extra expansion.

Table 8.4: Aggregate volumetric swelling (%) of modified Corsican and Scots pine sapwood at saturation.

Modifying Chemical	WPG	Aggregate Swell
	Corsican pine	
Control	0	13.66
Acetic	5.2	14.60
Acetic	15.8	14.33
Acetic	22.5	14.46
Hexanoic	5.7	**13.49**
Hexanoic	15.7	14.18
Hexanoic	24.5	17.89
	Scots pine	
Control	0	12.9
Acetic	5.7	**10.93**
Acetic	16.1	14.49
Acetic	21.9	15.96
Hexanoic	6.2	**11.26**
Hexanoic	15.7	16.04
Hexanoic	25.3	17.38

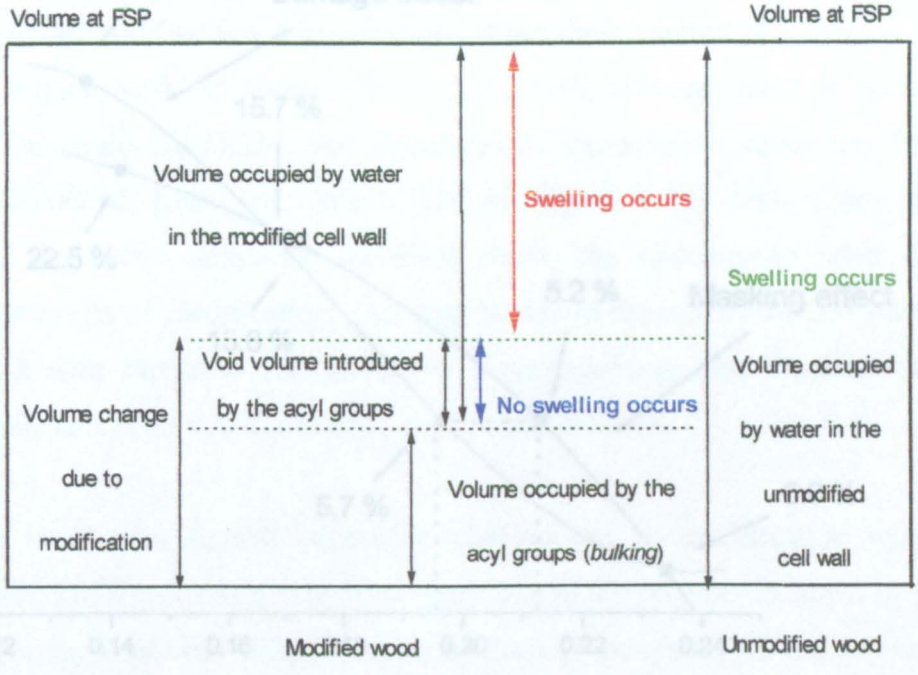

Figure 8.9: Schematic representation of the swelling behaviour of unmodified and chemically modified wood, using the concept of void volume. Void volume is filled with water without causing volumetric swell.

8.3.3. Analysis of the swelling behaviour of modified softwood

Figure 8.10 illustrates the relationship between weight of water in the cell wall due to exposure to relative humidity at saturation and bulking. Weight of water and bulking were calculated as follows:

$$\text{Weight of water} = \frac{\text{Weight of wet modified wood} - \text{Weight of dry modified wood}}{\text{Weight of dry unmodified wood}}$$

$$\text{Bulking} = \frac{\text{Volume of dry modified wood} - \text{Volume of dry unmodified wood}}{\text{Weight of dry unmodified wood}}$$

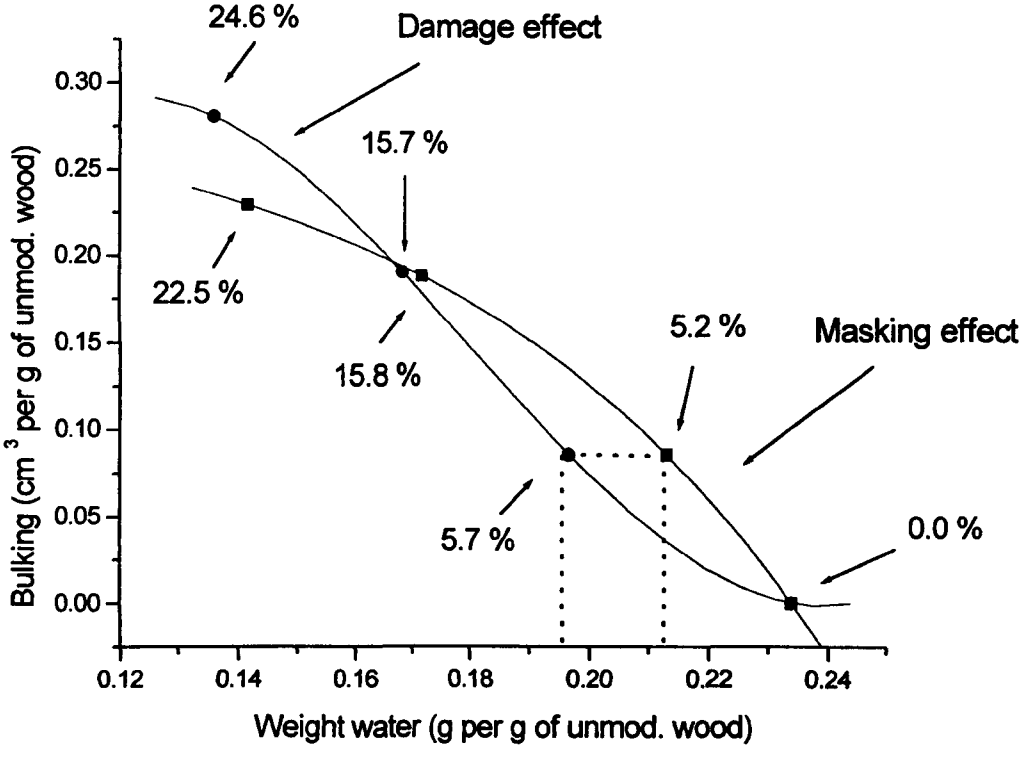

Figure 8.10: Relationship between weight of water in the cell wall due to exposure to relative humidity at saturation and bulking. Squares: acetic anhydride; Circles: hexanoic anhydride. (Corsican pine data).

From this, it can be seen that for both chemicals, a non-linear relationship is obtained. If it is assumed that the volume available in the cell wall for water decreases as a result of volume occupied by adduct, then a linear relationship between the two values would be expected. Thus, as more volume in the cell wall is occupied by adduct, there is less volume available for water.

On closer inspection, the results depicted in Figure 8.10 indicate that at low WPG's (*ca* 5-6%) more water is accommodated in the cell wall in acetic anhydride modified wood than in hexanoic anhydride modified wood. This indicates a shielding or masking effect with hexanoic anhydride modified wood, as extensively discussed in section 7.4.5. It appears therefore, that the adduct of the larger molecular size hexanoic anhydride, reacts with one hydroxyl group but covers some of the adjacent ones, providing a physical barrier. This barrier prevents the water vapour molecules from reaching some of the unreacted sites, that is, it shields sites. Hence, the effect of the adduct covering reacted and unreacted sites may overshadow the effect of direct chemical bonding to the sites. At intermediate WPG's (*ca* 16%) both acetic and hexanoic anhydride modified wood accommodated the same amount of water, as can be seen from Figure 8.10. At higher WPG's (*ca* 22.5%, although there is no data available for hexanoic anhydride, and therefore an approximate value has been obtained as indicated from the dotted line in Figure 8.10) less water was accommodated by acetic anhydride modified wood, the opposite to what was observed at low levels of modification. This may be due to damage of the cell wall in wood modified with hexanoic anhydride. As a consequence, new sorption sites become available and extra space is created in the wood cell wall.

It was shown in Chapter 6, that volumetric changes due to modification with a homologous series of linear chain anhydrides were due to the volume occupied by the reagent and an associated void volume created by the acyl groups within the cell wall. If it is assumed that this void volume can accommodate water without concomitant swelling of the cell wall, then clearly account must be taken of this. This is shown schematically in Figure 8.9, where void volume was deducted from the value of bulking (see y-axis in Figure 8.10) to give a figure for the apparent volume occupied by acyl groups in the modified cell wall. This apparent volume per gm of unmodified wood, was then plotted against weight of water per gm of unmodified wood in the

same way that bulking was plotted in Figure 8.10. These recalculated data are given in Figure 8.11. These recalculated data points, for acetic anhydride modified wood, were found to lie reasonably close to a straight line ($R^2 = 0.99$); this was not the case for hexanoic anhydride modified wood. It has to be stressed at this point, that the line for the acetic anhydride data points goes through the origin, however this is not the case for hexanoic anhydride. An explanation for this deviation is again the masking effect at low levels of modification and the damage of the cell wall at the higher ones. At the intermediate levels, the two lines cross over.

It seems therefore that the free volume model introduced in Chapter 6, offers a reasonable explanation of the differences in swelling recorded for Corsican pine sapwood modifying to varying WPG's with acetic anhydride.

However, when the same data analysis was performed for the Scots pine data, no linear relationship was found, as depicted in Figure 8.12. The reason behind this behaviour is unknown. Therefore, a definite conclusion regarding the application of the free volume model cannot be drawn from this study.

A wider range of weight gains, a larger number of replicates, and swelling measurements during desorption would be required for a comprehensive study of this phenomenon.

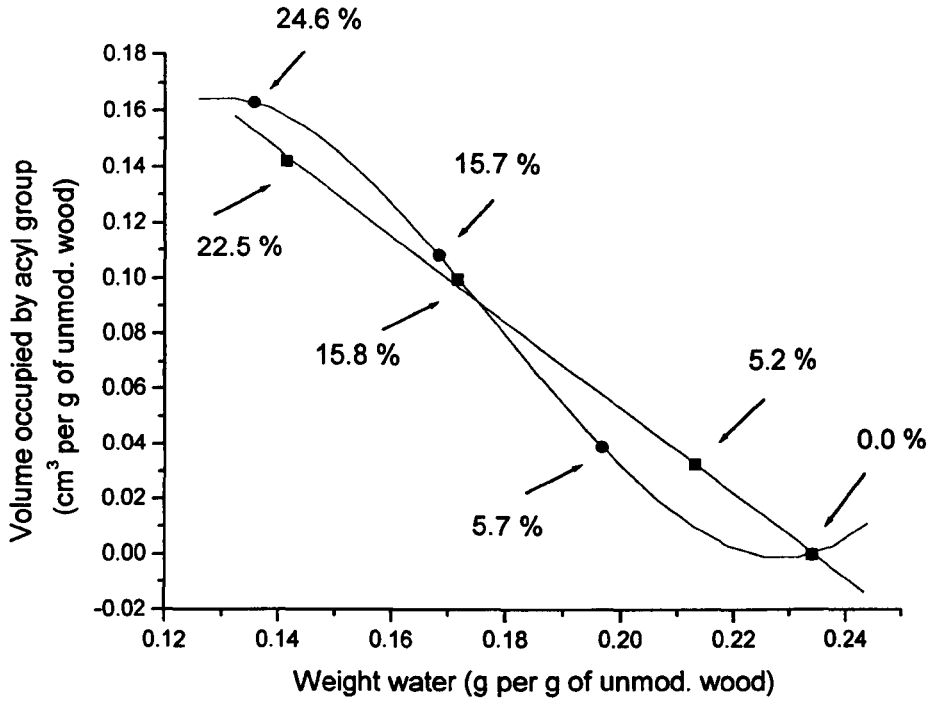

Figure 8.11: Relationship between weight of water in the cell wall due to exposure to relative humidity at saturation and volume occupied by acyl groups. Squares: acetic anhydride; Circles: hexanoic anhydride. (Corsican pine data).

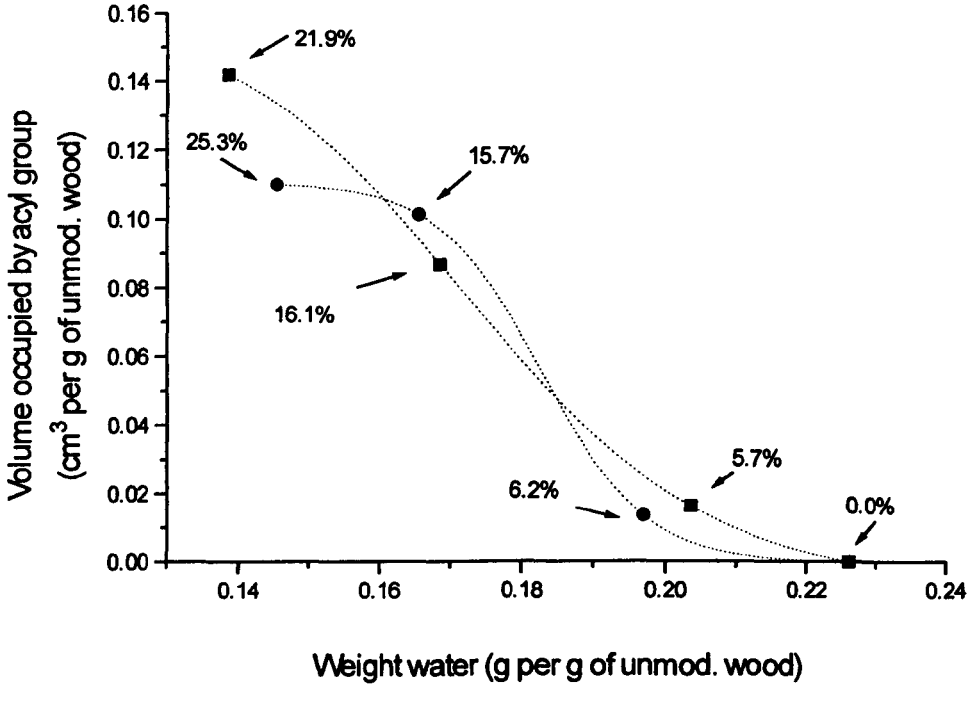

Figure 8.12: Relationship between weight of water in the cell wall due to exposure to relative humidity at saturation and volume occupied by acyl groups. Squares: acetic anhydride; Circles: hexanoic anhydride. (Scots pine data).

8.4. Summary of points raised in Chapter 8

- Examination of the relationship between volumetric swelling and relative humidity revealed that the volumetric swelling of modified woods approximately parallels the swelling of the controls.

- Good agreement was found between EMC and swelling, for different WPG's of different chemicals. In particular, it was found that as the weight gain increases, the samples swell less at each EMC attained.

- Weight of water per gm of unmodified wood fell with increasing WPG for both acetic and hexanoic anhydride modified wood.

- Less weight of water per gm of unmodified wood was accommodated by hexanoic anhydride modified wood than by acetic modified wood, at low WPG's.

- A non-linear relationship was found between weight of water per gm of unmodified Corsican pine wood and bulking, whereas a linear relationship would be predicted. However, this takes no account of void volume.

- When the value of void volume, calculated in Chapter 6, is deducted from the bulking a linear relationship was indeed obtained with acetic anhydride modified Corsican pine, but not with hexanoic anhydride modified Corsican pine.

- It seemed therefore that the free volume model introduced in Chapter 6, offers a reasonable explanation of the differences in swelling recorded for Corsican pine sapwood modifying to varying WPG's with acetic anhydride.

- However, when the same analysis was performed for the Scots pine data, no such correlation was found. Therefore, a definite conclusion regarding the application of the free volume model cannot be drawn from this study.

- A wider range of weight gains, a larger number of replicates, and swelling measurements during desorption would be required for a comprehensive study of this phenomenon.

CHAPTER 9

Lignin analysis and determination of the surface area and pore volume of unmodified and modified wood flour using the nitrogen adsorption technique

9.1. Introduction

In Chapter 6, it was shown that the volume occupied in the cell wall per reagent molecule is larger in modified Corsican pine compared with modified Scots pine. It was suggested that the cell wall polymeric network surrounding the acyl groups exhibits different flexibility between the two species. Additionally, it was shown in Chapter 5, that the cell wall micropores in Corsican pine are sufficiently large to allow access of acetic anhydride but not propionic into unswollen cell wall, but that with Scots pine both reagents are too large to gain access. It was the aim of this chapter to find possible explanations for this behaviour. A first approach was made by determining the chemical composition of Corsican and Scots pine, since a possible lower lignin content in Corsican pine will partially explain the different flexibility of the Corsican pine cell wall polymeric network surrounding the acyl groups. A second approach was made by qualitatively determining the S:G ratio (Syringyl: Guaiacyl) of lignin. A higher syringyl content, and therefore higher ratio, denotes less crosslinking and therefore more flexibility of the lignin. A third approach, involved exposure of Corsican and Scots pine samples to deuterium (D_2O) exchange, in order to estimate the number of available hydroxyl groups. The choice of deuterium oxide was based on its good accessibility to wood cell wall and to its ease to handle.

The previous Chapter studied the reduction in equilibrium moisture content caused by increasing weight gains of modifying chemical. This was attributed mainly to the bulking action of chemical in the cell wall occupying space that would otherwise be available in the cell wall to bound water. In addition, the extent of swelling of modified wood was studied. It was thought possible that the bulking of the cell wall by modifying chemical, along with reduced swell, could be causing a restriction in

cell wall pore volume and in total surface area. This was investigated in this Chapter using the nitrogen adsorption technique. The technique has largely been used in the past with pulp samples and no substantive work using this technique (on wood or pulp) has appeared in the literature in the past decade.

9.2. Materials and methods

9.2.1. *Determination of chemical composition of Corsican and Scots pine sapwood*

9.2.1.1. *Preparation of wood flour*

Corsican or Scots pine sapwood were ground using a hammer mill and sieved to a size of 40 mesh. Before grinding, each piece of wood was dipped into liquid nitrogen for approximately 20 seconds to avoid excess heat generation.

9.2.1.2. *Determination of holocellulose content* (Browning, 1902)

Approximately 1 g of extractive-free, oven dry wood flour (Corsican or Scots pine) was weighed out on a four figure balance and transferred to a 250ml Erlenmeyer flask to which was added 160ml of deionised water, 0.5ml of glacial acetic acid and 10ml of a 15% solution of sodium chlorite. A beaker was placed over the neck of the flask and the contents transferred to a water bath set at 75^{0}C, and heated with occasional stirring for 1h. Three further additions of 0.5ml acetic acid and 10ml sodium chlorite were made at hourly intervals. After heating for 4h in total, the flask was transferred to an ice bath and the contents cooled to below 10^{0}C. The delignified flour was filtered through a pre-weighed glass sinter crucible, washed with 200ml of 95% ethanol, 200ml ice cold deionised water and finally 200ml acetone. The crucible and contents were oven dried overnight at 50^{0}C, before weighing. The mass of the residue corresponds to the mass of holocellulose.

9.2.1.3. *Determination of cellulose content* (Browning, 1902)

A sample (*ca* 1g) of oven dry holocellulose was weighed on a four figure balance and transferred to a 250ml Erlenmeyer flask, then 100ml of a solution of 10% NaOH / 15% $Na_2B_4O_7$ was added. The flask was flushed with argon and the neck sealed with parafilm. The flask was maintained at a temperature of 20^0C for 2h, and contents agitated every 10min during this period. The contents were then poured into a preweighed glass sinter crucible, washed with 50ml of the NaOH / $Na_2B_4O_7$ solution, then several times with 100ml portions of deionised water and finally with 100ml of ethanol. The crucible and contents were oven dried overnight at 105^0C, then weighed to give the amount of cellulose.

Weight of hemicellulose was calculated by substracting weight of cellulose from weight of holocellulose.

9.2.1.4. *Determination of lignin content* (Browning, 1902)

Approximately 1 g of extractive free oven dry wood flour (Corsican or Scots pine) was weighed out on a four figure balance, transferred to a 100ml beaker, and 15ml of a 6:1 (vol:vol) mixture of concentration sulphuric/phosphoric acid added. The mixture was stirred with a glass rod until gelatinised. The beaker was transferred to a water bath set at 35^0C for 2 min, then added to 350ml of deionised water in a 600ml beaker. The contents of the beaker were then brought to the boil on a hotplate and left boiling for 20 min. The beaker was 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 105^0C overnight and weighed.

9.2.2. Qualitative determination of S:G ratio (Syringyl: Guaiacyl)

9.2.2.1. Nitrobenzene oxidation (Browning, 1902)

1mole of NaOH was transferred to a 100ml beaker to which was added 30ml of deionised water. The mixture was stirred with a glass rod until gelatinised. Subsequently, the beaker was transferred in the hot plate set in an oil bath at 60^0C for 10 min to dissolve the NaOH. The contents of the beaker were transferred to a 100 ml volumetric bottle to which was added deionised water to a total volume of 100ml.

Approximately 20mg lignin (from Corsican or Scots pine sapwood) was weighed out on a four figure balance, transferred to a pressure vessel, then 7ml of the NaOH solution from the volumetric flask, and 0.4 ml nitrobenzene added. The pressure vessel was sealed and transferred to an oil bath set at 175^0C for 3 hr. Afterwards, the vessel was removed from the oil bath and allowed to stand for 30 min, then the contents filtered through a glass filter pad in a 100ml conical flask, and washed with 7ml of 0.2M NaOH and 10 ml deionised water. Then 30 ml chloroform was added to the flask and the mixture allowed to stand for 2 hr. The organic phase was transferred to a 50 ml round bottom flask and subsequently to a rotary evaporator for drying. To the conical flask was then added few droplets of 20% HCl to decrease the pH to 2. Three further additions of 30 ml chloroform were made at 2 hr intervals, all the extractives were combined together and transferred to evaporator for drying. Afterwards, the extractives were transferred to a sample tube and 3ml of methanol added. The tube was then placed in a fridge until required for HPLC analysis for the qualitative determination of the S:G ratio (Syringyl: Guaiacyl).

9.2.2.2. HPLC Separation

A Kontron System 525 (pump 525, detector 535, Software Kromosystem 2000) was used for HPLC (High Performance Liquid Chromatography) analysis. Separations were performed on a LiChrosorb RP-18 (250 x 4.60mm), using a mixture of methanol water (4:1 vol:vol) as solvent. The flow rate was 1ml/min. All tests were performed at ambient temperature.

9.2.3. Deuterium Exchange

Oven dried (for 12 hr at 105^0C) unmodified and modified, with hexanoic anhydride, Corsican and Scots pine samples were weighed in a four figure balance and placed above deuterium oxide (D_2O), in a 500 ml jar. The jar was sealed then with parafilm. The samples were left in the jar for 12 weeks. After that, samples were removed from the jar, oven dried as above, and weight percent gain due to deuterium exchange determined.

9.2.4. Determination of surface area and pore volume of holocellulose and wood flour

9.2.4.1. Preparation of aerogels

Extractive free wood flour (or holocellulose) (Corsican or Scots pine) was left in a fume hood for several days to allow the organic vapours to evaporate off. The wood flour (or holocellulose) was then vacuum impregnated with de-ionised water and allowed to soak for 48 hours with two water changes. Soaking time was not found to be an important parameter in surface area determination (Merchant, 1957). Subsequent to this the wood flour (or holocellulose) was put into extraction thimbles, transferred to Soxhlet apparatus and solvent exchanged with wet methanol (for 1 day), absolute (dry) methanol (for 1 day) and finally with dry toluene (or pentane) (for 1 day). During the exchange with absolute methanol, linde molecular sieves (4 Å) were put in the flask in order to adsorb all water diffusing from the wood flour (or holocellulose). Apart from soaking in water and in wet methanol, all other procedures were carried out under a blanket of dry nitrogen in sealed (parafilm) vessels. Toluene (or pentane) saturated wood flour (or holocellulose) were then transferred directly to a drying apparatus set in an oil bath at 50^0C, and dried for 5 hr under a stream of dry nitrogen. Prepurified nitrogen was dried by passage through a tube of magnesium perchlorate during the period of drying. Samples were kept under nitrogen for 1 h to cool down, before being transferred to a glove box. Subsequent to this, approximately 0.3 g of solvent exchange dry wood flour (or holocellulose) was weighed out, under nitrogen, on a four figure balance, set inside the glove box, and transferred to the sample tube ready for the determination of surface area as described below.

9.2.4.2. Determination of surface area and pore volume

A Micromeritics Gemini 2375 surface analyser was used for the determination of surface area (Figure 9.1). The machine provides single point and multipoint BET surface area.

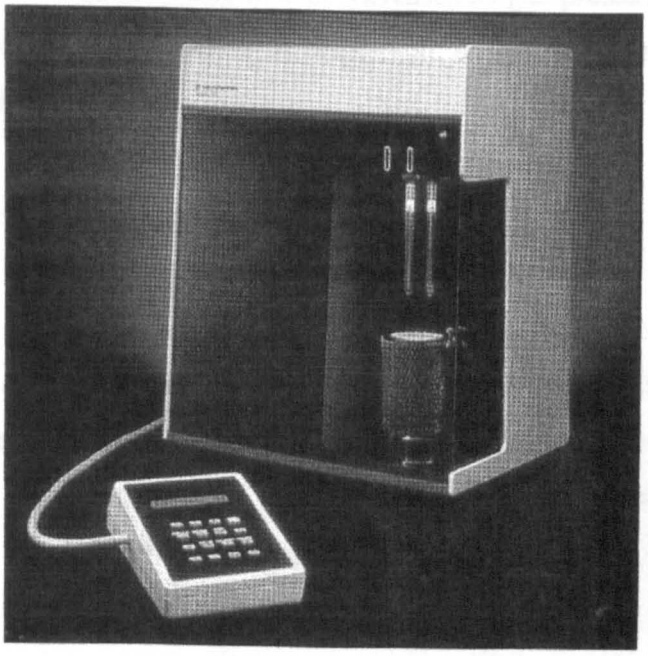

Figure 9.1: The Micromeritics Gemini 2375 surface analyser used in this study.

The machine first frees the samples of moisture and atmospheric gases. Then the sample temperature is reduced to that of liquid nitrogen for the gas to be adsorbed. The adsorbing gas (N_2) is admitted in incremental doses to various pre-set partial pressures (Webb and Orr, 1997). The accumulated gas quantity adsorbed *versus* gas pressure data at one temperature are then graphed to generate the adsorption isotherm. The data are then treated in accordance with gas adsorption theories (BET) to arrive at a specific surface area value for the sample in units of square metres per gram (m^2/g).

Classical adsorption theory assumes that gas molecules admitted under increasing pressure to a clean, cold surface form a layer one molecule deep on the surface before forming a second layer. The data treatment technique finds the quantity of gas forming this first layer, and then the area covered is calculated from the number of molecules of the gas and gas molecule dimensions. Actually, adsorbed gas molecules do not attach to a solid surface and thereafter remain attached while other molecules build upon them. In the first place, there are regions on all surfaces that are more attractive to gas molecules and regions that are less so. What is called adsorption is really the manifestation of a continual exchange between gas molecules temporarily residing on a solid surface and those nearby in the gas phase. The number of

molecules attached to a solid at any instant increases as gas pressure increases until a point is reached where statistically it is reasonable to consider a monolayer to have formed (Webb and Orr, 1997).

9.2.4.2.1. Description of the apparatus

The design of the Gemini analyser utilises a dual sample/balance system so that the sample tube and balance tube are identical in every way including the conditions they undergo during the analysis. Each tube produces exactly the same behaviour, the only differences being those introduced by the sample. This duplicate operation is combined with an accelerated delivery of the analysis gas in which the sample uptake controls the rate at which the gas is delivered.

9.2.4.2.2. Method of operation

Gemini uses an adaptive rate, static volumetric technique of operation. It adapts the rate at which gas is delivered to the sample to the rate at which it is adsorbed. Each pressure point completely equilibrates before the next point is taken. The Gemini has, as illustrated in Figure 9.2, two gas reservoirs (A), which are filled with equal volumes of nitrogen. From the reservoirs, nitrogen is dosed into the sample and balance tubes. A transducer (B) on the sample side monitors the target pressure. As the sample adsorbs nitrogen, the pressure would tend to decrease in the sample tube except that transducer (B) causes a fast response servo valve (C) to hold the pressure constant. Transducer (D), located between the sample and balance tubes, detects any pressure difference between the two tubes and causes another servo valve (E) to balance the pressures in both tubes. A third pressure transducer (F) monitors the pressure between the two reservoirs to determine the amount of nitrogen that is adsorbed on the sample. Before proceeding to measurements for the surface area of wood and holocellulose samples, materials of known porosity (zeolites, clay) were used in order to calibrate the machine.

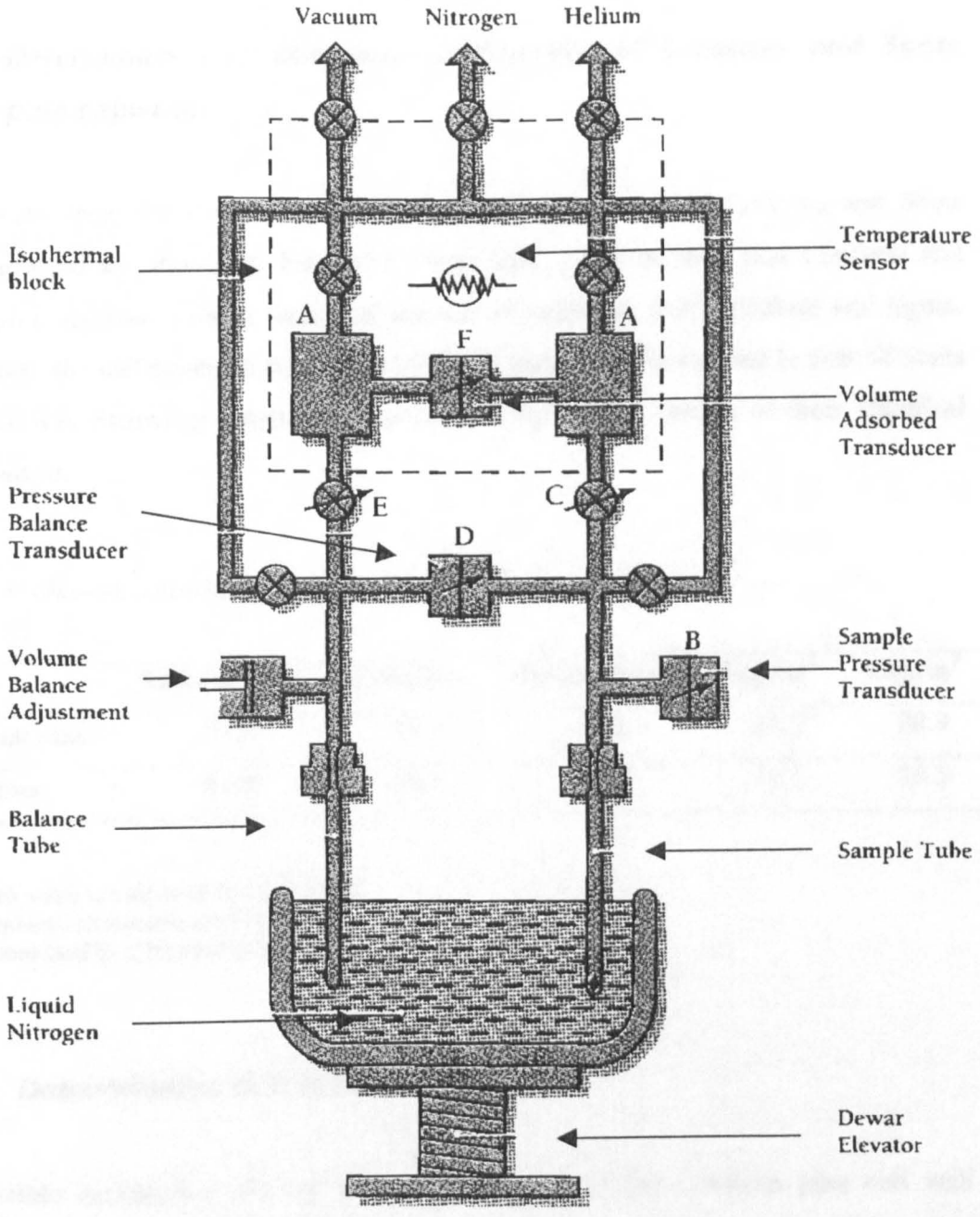

Figure 9.2: Plumbing diagram of the surface analyser.

9.3. Results and discussion

9.3.1. Determination of chemical composition of Corsican and Scots pine sapwood

The results from the determination of chemical composition of Corsican and Scots pine sapwood are shown in Table 9.1. From this, it can be seen that Corsican and Scots pine sapwood contain identical amount of cellulose, hemicellulose and lignin. Therefore, the difference in behaviour of the Corsican pine compared to that of Scots pine, as was shown in Chapter 6, cannot be explained in terms of their chemical composition.

Table 9.1: Chemical composition (%) of Corsican and Scots pine sapwood [1].

	Holocellulose	Cellulose	Hemicellulose	Lignin[2]	Lignin[3]
Corsican pine	71.1	39.3	31.8	28.7	28.9
Scots pine	69.8	38.4	32.1	29.1	29.5

1. Each value is a mean of five replicates.
2. Sulphuric/phosohoric acid lignin.
3. Determined by difference from holocellulose.

9.3.2. Determination of S:G ratio

A possible explanation for the different flexibility of the Corsican pine cell wall polymeric network surrounding the acyl groups may involve the lignin, and in particular the S:G ratio (Syringyl: Guaiacyl, see structures in Figure 9.3). A higher syringyl content, and therefore a higher S:G ratio, denotes less cross-linking and therefore more flexibility of the lignin.

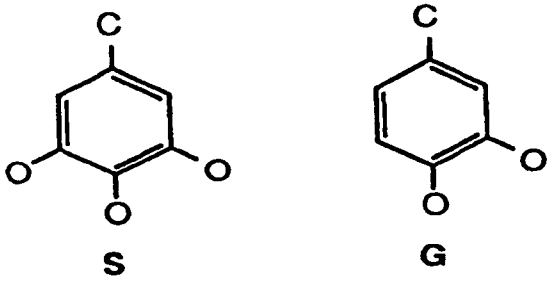

Figure 9.3: Syringyl (S) and Guaiacyl (G) lignin.

The results from the HPLC analysis are shown in Figures 9.4 and 9.5 for Corsican and Scots pine respectively. In these figures, the syringyl and guaiacyl compounds were easily identified from Figures 9.6 and 9.7 respectively, using the individual peaks that these compounds produced. From Figures 9.4 and 9.5, it can be seen that the S:G ratio is significantly higher in Corsican pine. This is, however an indicative result; a more definite conclusion would have drawn from this experiment, if all the peaks in Figures 9.4 and 9.5 had been identified. Time restrictions and high costs involved meant that this was not possible with the confines of this study.

9.3.2. Deuterium exchange results

The results due to deuterium exchange are presented in Table 9.2. From this it can be seen that exposure to deuterium exchange caused a higher weight percent gain in Corsican pine samples. This is true for both unmodified and modified, with hexanoic anhydride, samples. This contrasts with the finding of Chapter 6 (see section 6.5), where the same values of theoretically accessible hydroxyl groups was obtained for Corsican and Scots pine.

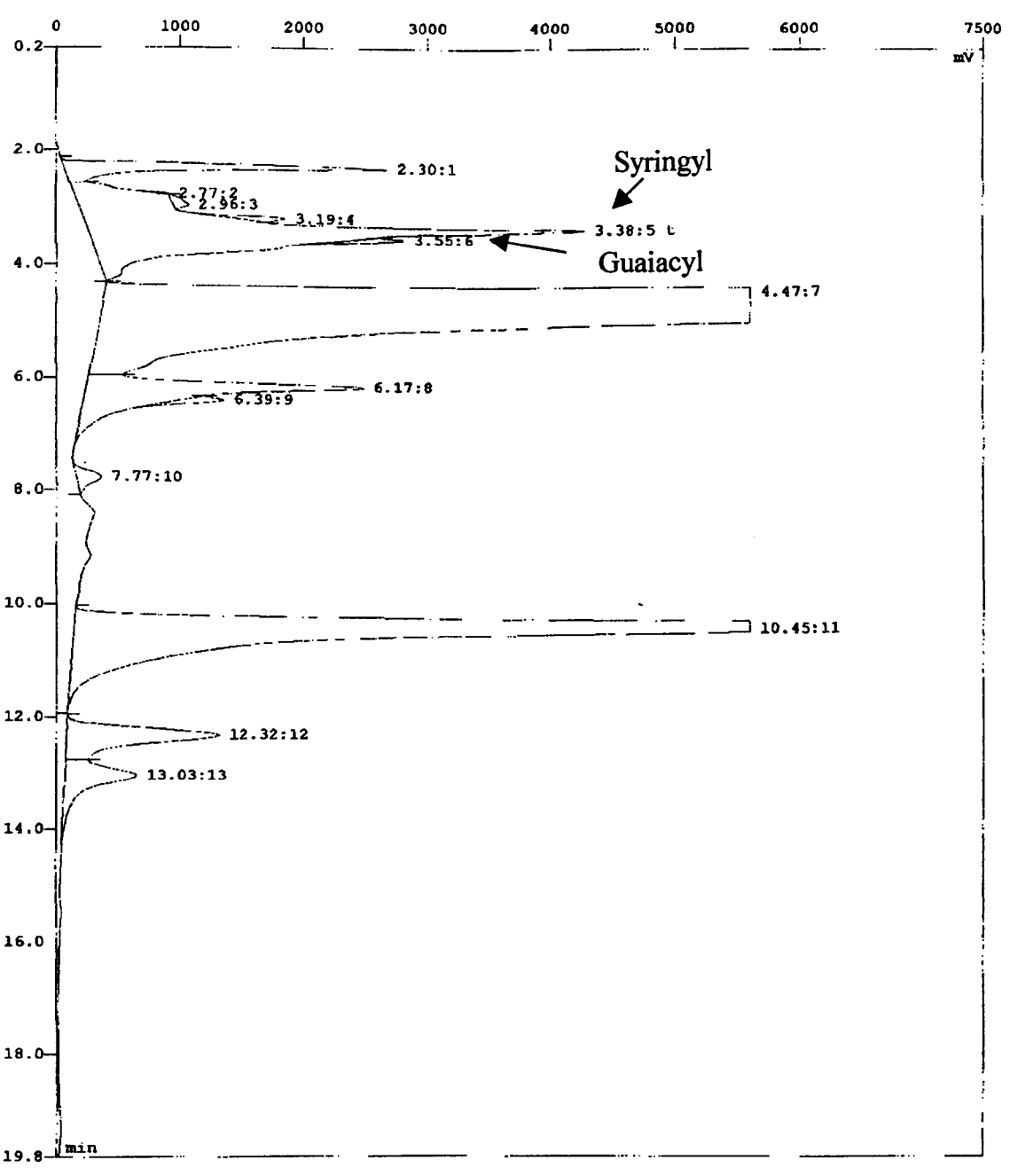

Figure 9.4: HPLC analysis for Corsican pine sapwood.

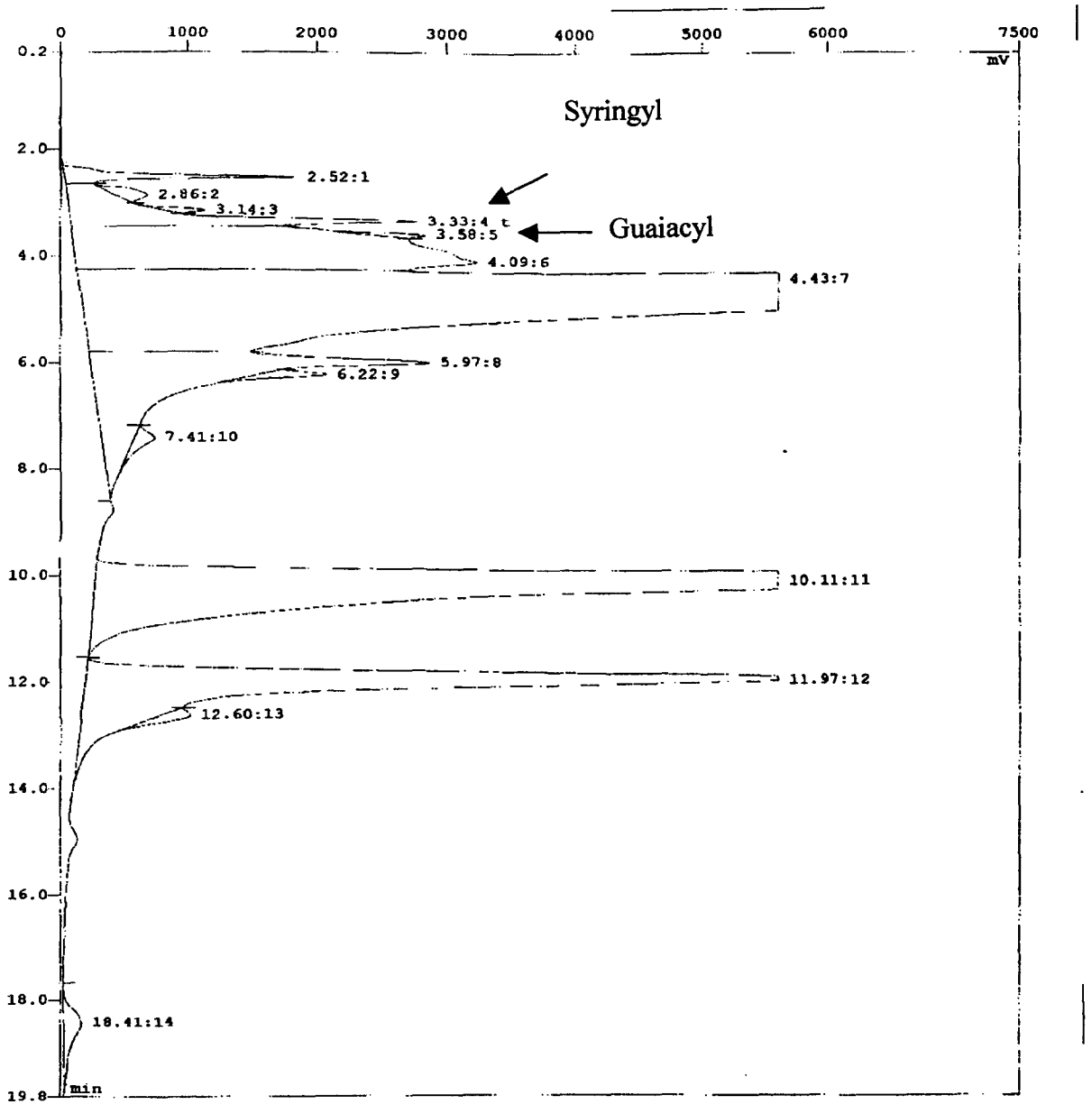

Figure 9.5: HPLC analysis for Scots pine sapwood.

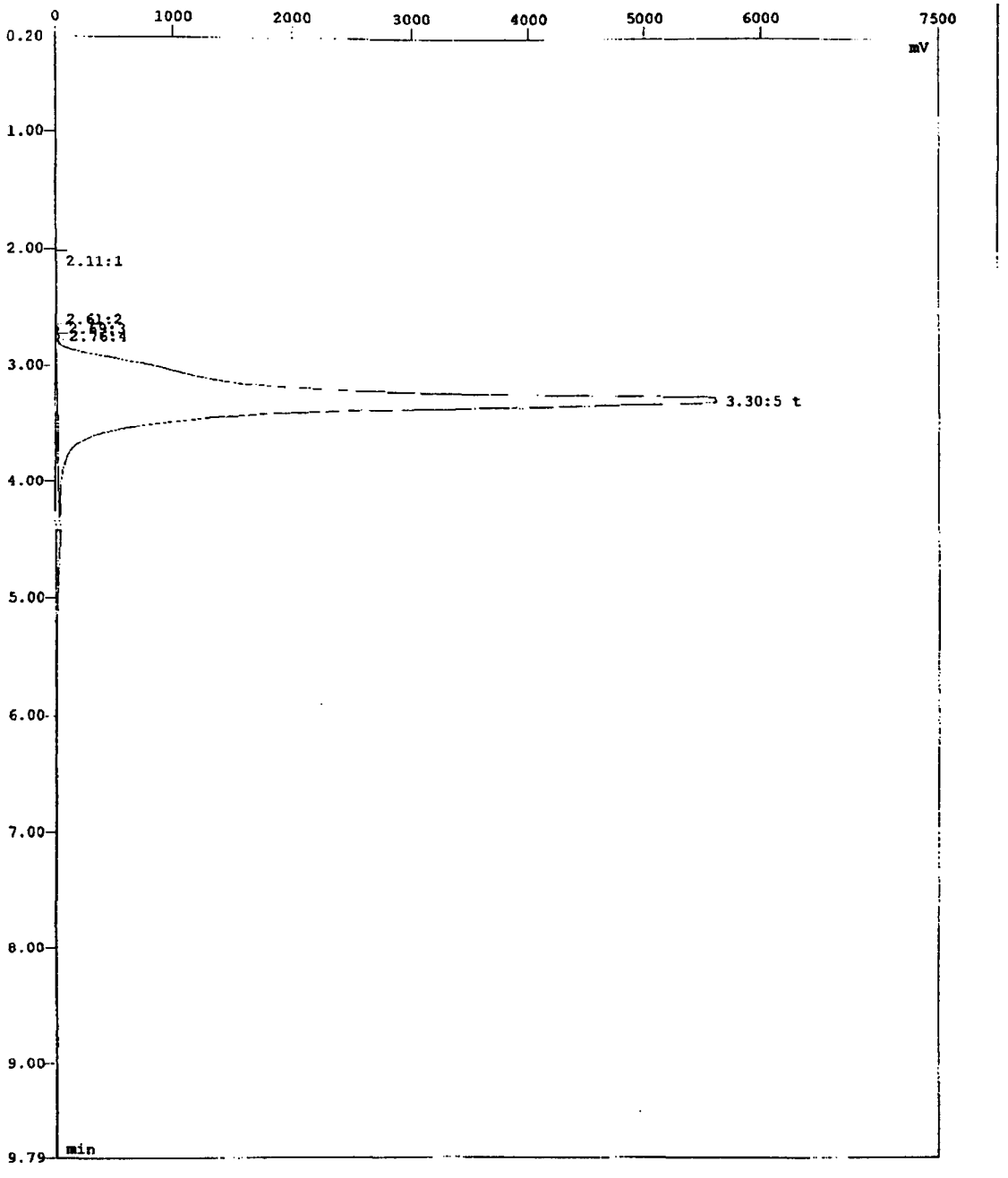

Figure 9.6: HPLC analysis for syringyl compound.

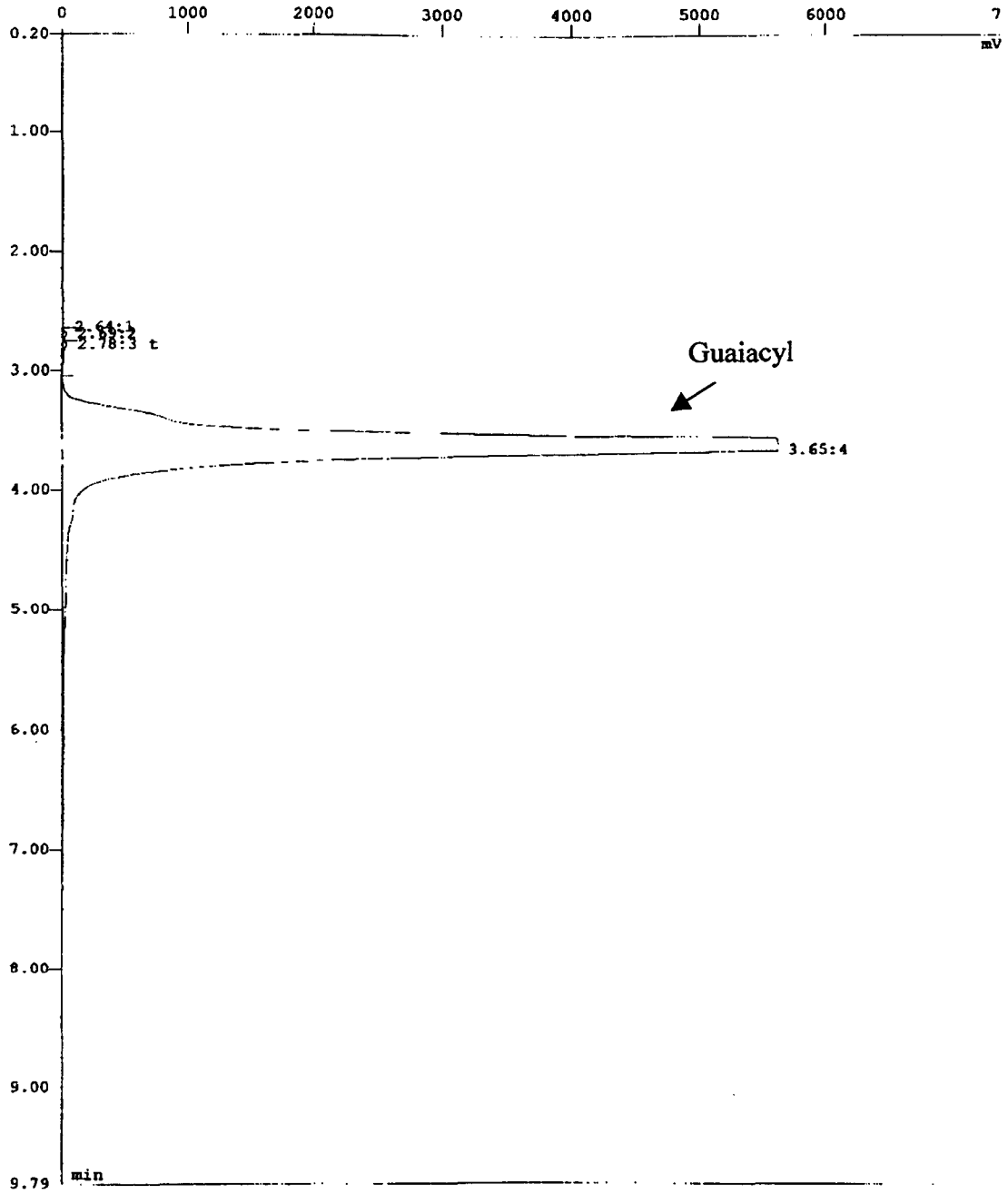

Figure 9.7: HPLC analysis for guaiacyl compound.

Table 9.2: Weight gain (%) of unmodified and modified with hexanoic anhydride samples after exposure to deuterium exchange.

Sample History	Weight Gain (%)
Corsican pine	
Unmodified	3.48
Modified (8.7% WPG)	0.42
Modified (25.1% WPG)	0.25
Scots pine	
Unmodified	1.38
Modified (7.3% WPG)	0.37
Modified (21.9% WPG)	0.19

From the data for unmodified wood presented in Table 9.2, it is possible to estimate the number of accessible hydroxyl groups, based on the fact that 1 gm weight gain per gm of sample due to deuterium exchange is equal to 1 mole of hydroxyl groups per gm of unmodified sample. This yields a figure of 0.0348 and 0.0138 moles/gm for unmodified Corsican and Scots pine, respectively. The value obtained for Corsican pine is approximately twice the theoretically calculated value, namely 0.0149 moles/gm, whereas the value obtained for Scots pine is close to 0.0149. However, both values obtained from this experiment are considered too high, since the theoretically calculated value of 0.0149 is an over-estimate of the number of OH groups accessible for reaction, as discussed in section 6.5. Therefore, caution is cast upon the validity of this experiment.

9.3.4. Determination of surface area and pore volume

9.3.4.1. Surface area and pore volume determination of unmodified wood flour and holocellulose

The results from the determination of surface area and pore volume of oven dried and solvent exchange dried unmodified Corsican and Scots pine wood flour and holocellulose are presented in Table 9.3. From this, it can be seen that a very low surface area (*ca* 0.5 m^2/g) and a low pore volume (*ca* 0.002 cm^3/g) have been obtained for oven dried wood and this is in agreement with the results reported in the literature (Stone *et al.* 1966; Stone and Scallan, 1968a). This is a result of the micropore network in the cell wall collapsing when the wood is dried. During the oven-drying of water saturated wood, powerful capillary condensation forces operate to bring the walls of the micropores together (Figure 9.8A), resulting in the formation of extensive hydrogen bonding networks between the sides of the micropores. To quote Tarkow *et al.* (1966) a 100 Angstrom void, on losing its water, experiences a collapsing force of about 150 atmospheres.

Table 9.3: Surface area (m^2/g) and pore volume (cm^3/g) *of oven dried (OD) and solvent exchange dried (SED) unmodified wood flour and holocellulose.*

Species	History	Final Solvent	Surface area	Pore Volume
		Wood flour		
Corsican pine	O.D	-	0.58	0.0024
Corsican pine	SED	Pentane	1.12	0.006
Corsican pine	SED	Toluene	6.63	0.015
Scots pine	O.D	-	0.51	0.0021
Scots pine	SED	Pentane	1.21	0.009
Scots pine	SED	Toluene	5.93	0.013
		Holocellulose		
Corsican pine	SED	Pentane	77.7	0.061
Corsican pine	SED	Toluene	23.2	0.044

The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was the final solvent. However, the resulted surface area (*ca* 6 m^2/g) and pore volume values (*ca* 0.015 cm^3/g) indicated that such a structure is in no way representative of a fully swollen cell wall and were in agreement with published results (Stone and Scallan, 1965; 1968b; 1971; Stone *et al.* 1968). The effect of final solvent on surface area is discussed later.

During the solvent exchange process, a swelling solvent (dry methanol) is gradually replaced by a non-swelling solvent (toluene or pentane), the molecules of which occupy the cell wall microvoids, thereby preventing collapse of the structure. However, if these occluding molecules are removed, then collapse of the structure occurs, although in this case there may not be such extensive H-bonding networks formed (Figure 9.8B). The collapse of the porous structures is controlled by surface tension forces at the liquid vapour interface; thus if supercritical drying is employed then such collapse is prevented (at least as far as wood holocellulose or pulp is concerned, see later). An additional factor in this latter case is the elasticity of the cell wall, which is largely controlled by the lignin. When a bleached wood pulp is solvent exchange dried from a never dried state, surface areas in the region of 100-200 m^2/g and pore volumes of 0.2-0.4 cm^3/g are reported (Stone and Scallan 1965b). In this study, a surface area of 77.7 m^2/g was obtained for SED of holocellulose using pentane as a final solvent (see Table 9.3). This larger measured surface area is undoubtedly partly a result of the removal of the lignin leading to the increase in the void content of the cell wall, but there is also a contribution from the reduced elasticity of the cell wall (Stone 1964). In this latter case, collapse of the micropores is incomplete when solvent exchange drying is employed (Figure 9.8C). It should be noted that the conditions under which the final solvent are removed from the substrate affect the pore structure considerably. Tarkow *et al.* (1966), citing Stamm and Hansen (1935), noted that shrinkage of the substrate occurs when the final replacement liquid is evaporated from the material below the critical temperature of the liquid.

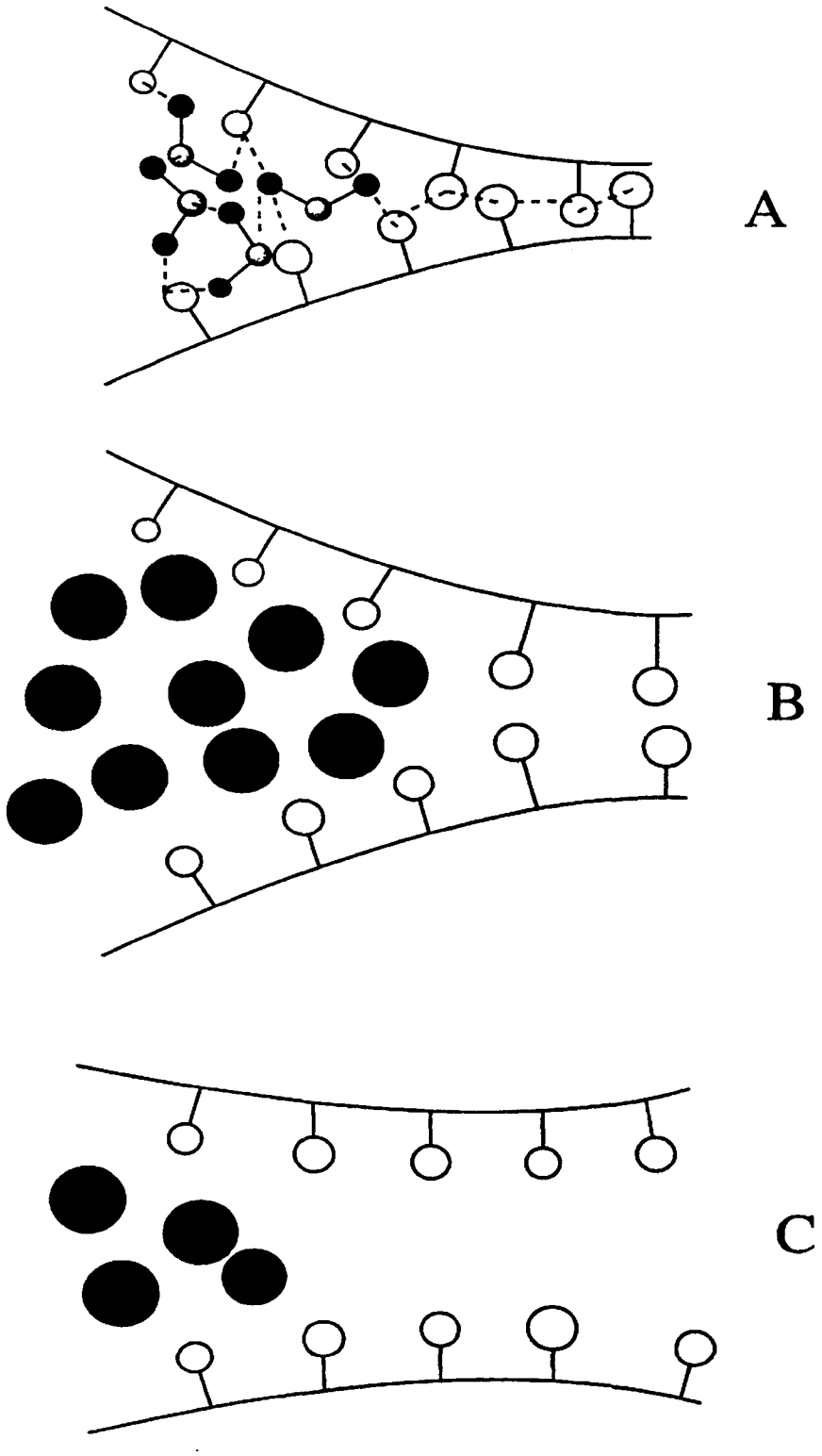

Figure 9.8: Schematic illustrating various models for cell wall pore collapse due to (A) drying from a water saturated state, (B) drying of wood via solvent exchange and (C) drying of wood pulp via solvent exchange.

Weatherwax and Caulfield (1971), found that the specific surface area of solvent exchange dried wood pulp was dependent upon the method of removal of the final solvent. Thus when hexane was removed in a stream of nitrogen, a lower specific surface (43 m^2/g) was recorded compared with a method where the final solvent was carbon dioxide (WAC aerogel), which was carefully removed above the critical temperature (specific surface 144 m^2/g). This difference arises due to liquid/air surface tension forces acting upon the capillary walls and partially collapsing the pores, when drying is attempted below the critical temperature of the final solvent. Note however, that a very large difference is found in the surface area between solvent exchange dried wood and wood pulp, indicating the importance of lignin in both occluding and collapsing the pores.

9.3.4.2. The effect of final solvent on surface area

The effect of final solvent on surface area is presented in Table 9.3. From this, it can be seen that with holocellulose samples, a larger surface area was obtained using pentane as a final solvent. However, the opposite was true with wood flour, where larger surface area was obtained using toluene as a final solvent. Merchant (1957), reported increased surface area values of water-swollen and SED cellulose fibres with increased molecular size of the final solvent, and concluded that this behaviour was the result of differences in properties of the different solvents; however, further details were not given. Such properties may include polarity, surface tension and viscosity of the final solvent.

The same behaviour was observed in this study on SED wood flour samples. However, the opposite was true on holocellulose samples. This behaviour may be due to other than molecular size and shape factors, since the opposite would have been observed if molecular size and shape had an effect on surface area. In that case, the presence of lignin would have prevented the larger and more rigid molecule of toluene to gradually replace the non-swelling agent (methanol) during the solvent exchange process, and as a result lower surface area would have been obtained.

9.3.4.3. Surface area and pore volume of modified wood

Although the SED process did not fully preserve the swollen pore structure of the wood cell wall, as discussed above, it was still thought that comparison between the surface area and pore volume of unmodified and modified wood flour samples would be of interest. For this reason, Corsican and Scots pine sapwood, heavily modified with hexanoic anhydride, was selected and solvent exchange dried with toluene as a final solvent, as described in session 9.2.3.1. The choice of heavily modified wood with hexanoic anhydride was based in the observation made in Chapter 5, that the apparent void volumes created within the cell wall increase as the molecular size of the substituent increases.

The results from the determination of surface area and pore volume of modified Corsican and Scots pine wood with hexanoic anhydride are presented in Table 9.4, along with the results of unmodified wood. It can be seen that chemical modification resulted in significant reduction in surface area and pore volume. This may be a result of blocking pores due to chemical modification. It may be that such void volume that is created is inaccessible to the gas (ink-bottle bottles).

Table 9.4: Surface area (m^2/g) and pore volume (cm^3/g) *of solvent exchange dried (SED) modified and unmodified samples using toluene as a final solvent.*

Species	Surface area	Pore Volume
Corsican Unmodified	6.63	0.018
Corsican modified with hexanoic anhydride (29.6 WPG)	1.65	0.015
Scots Unmodified	5.93	0.013
Scots modified with hexanoic anhydride (32 WPG)	1.78	0.01

Overall it appears, as extensively discussed in section 9.3.4.1, that in order to fully preserve the swollen pore structure of the wood cell wall, it is imperative to partially degrade the lignin to various extents without extraction of the lignin fragments. By

breaking up the cross-linking network of the lignin macromolecule, it may be that this will limit the ability of this molecule to shut the cell wall pores after drying. Several approaches are possible including exposure to UV radiation and exposure to white rot fungi attack. Time restrictions meant that this was not possible within the confines of this study.

9.4. Summary of points raised in Chapter 9

- Examination of the chemical composition of Corsican and Scots pine sapwood revealed that both species contained identical amount of cellulose, hemicellulose and lignin.

- Corsican pine lignin contained a significantly higher syringyl content than Scots pine lignin. This is, however an indicative result; a more definite conclusion would have been drawn from this experiment, if all the peaks in Figures 9.4 and 9.5 had been identified.

- Exposure of Corsican and Scots pine samples to deuterium exchange resulted in higher weight percent gain in Corsican pine samples. This contrasts with the finding of Chapter 6 (see section 6.5), where the same values of theoretically accessible hydroxyl groups was obtained for Corsican and Scots pine.

- Very low surface area (*ca* 0.5 m^2/g) and a low pore volume (*ca* 0.002 cm^3/g) have been obtained for oven dried wood, using the nitrogen adsorption technique.

- The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was used as a final solvent. However, the resulted surface area (*ca* 6 m^2/g) and a pore volume values (*ca* 0.015 cm^3/g) indicated that such a structure is in no way representative of a fully swollen cell wall.

- By using solvent exchange drying (SED), it is possible to preserve the swollen pore structure of holocellulose samples. However, with samples which contain significant amounts of lignin, such as native wood, it is not possible to prevent re-collapse of the pores. This problem arises because as micropore swelling occurs, the surrounding lignin network of the cell wall is stretched. When the molecules occupying the micropores are removed, the lignin returns to its original configuration, re-collapsing the micropores in the process.

- Chemical modification resulted in significant reduction in surface area and pore volume, possibly a result of pore blocking by the large acyl group. No evidence for void volume was found using this technique.

CHAPTER 10

General discussion, conclusions and recommendations

10.1 General discussion and conclusions

The main objectives of this study were outlined in section 2.2.11. These objectives have been achieved.

10.1.1. Kinetic studies of the acylation of pine sapwood and phenolic compounds with linear chain anhydrides

Previous studies of the kinetics of chemical modification of wood with anhydride reagents, have shown that reaction profiles are best described by considering both diffusion and reaction rates (Hill and Jones, 1996b; Hill and Hillier, 1999). Determinations of the activation energy (Ea) of reaction have shown that the Ea decreases as size of reagent increases (Cetin, 1999; Hill and Hillier, 1998). However, no systematic study of a series of anhydride molecules in wood reactions has been performed. Furthermore, from the preliminary data it was not known how reproducible the Ea values obtained were, nor what effect changing the wood species had upon Ea. No study has ever been performed upon the relationship between size of anhydride molecules and Ea in homogeneous reactions. It is probable that molecular motions are restricted within the cell wall microporous network and that, as a consequence, would be expected to influence the velocity distribution of the reagent molecules.

In order to test the validity of this assumption, determine the reproducibility of the data and furthermore to test the validity of application of the Arrhenius equation to reactions within the cell wall of wood, a comprehensive study was performed.

Kinetic profiles were investigated for the pyridine catalysed reaction of Corsican and Scots pine sapwood with a homologous series of linear chain carboxylic anhydrides namely, acetic, propionic, butyric, valeric and hexanoic. Activation energies, for the initial stages of the reaction, were determined by the method of initial rates and from the rate constant data, by analysing reaction profiles over a series of temperatures

from 120^0C to 60^0C. Additionally, the effect of the nature of substrate (Corsican and Scots pine) upon the activation energy was investigated.

The kinetic profiles for the reaction of a homologous series of linear chain anhydrides showed an asymptotic behaviour, with lower rates of reaction and ultimate degree of substitution as size of reagent increases. With propionylation, butyrylation, valerylation and hexanoylation, reactions at the 'surface' were found to obey pseudo first order kinetic laws. The reactions at the surface during acetylation did not contribute to the kinetic profile to any appreciable extent, since no evidence of first order kinetics was found. With acetic anhydride, it has been found that the reaction profiles are described by a model where diffusion dominates the reaction process, that is to say that reaction of the reagent molecules with a specific reaction site is rapid compared with diffusion. With longer chain anhydrides, the rate of chemical reaction and diffusion both contributed to the reaction kinetics.

Table 3.2 presents activation energies from data obtained from the present study. Values of the activation energy have been calculated using the method of initial rates (West, 1988) and the more conventional rate constant method (Hill and Jones, 1996b; Hill *et al.* 1998). As with previous studies, it was not possible to interpret the data for acetic anhydride in terms of first order kinetics, and in this case, the values for the activation energy have been calculated using the method of initial rates only. Literature activation energies, for reaction of carboxylic acid anhydrides with wood are presented in Table 3.5. The reproducibility of the data is revealed by comparing this set of data with that presented in Table 3.2. It can be seen that there is excellent agreement between the two sets of data. Therefore, this work shows that it is possible to obtain reproducible activation energies for reaction of anhydrides with such an exceedingly complex substrate such as wood.

From the results presented in Table 3.2, it can be seen that the activation energies obtained by using the methods of initial rates, or by the rate constant method are consistent. Nor does the wood species appear to have any significant influence upon the activation energy. It is, however, clear that the activation energy decreases as the molecular weight of the anhydride reagent increases. Furthermore, it is apparent that the values of activation energy for higher molecular weight reagents are much lower

than would normally be found for classical chemical reactions (which are generally of the order of 50-150 kJ mol^{-1}). Indeed, such values as are observed with hexanoic anhydride are more typically encountered when reactions are diffusion controlled. However, previous studies have indicated that as the molecular weight of the anhydride increases, the initial stage of the reaction becomes rate limited rather than diffusion limited (Hill and Hillier, 1999). With acetic anhydride, it has been previously reported that there is no evidence of first order kinetics and that the reaction is diffusion limited throughout (Hill *et al.* 1998). This has also been found with the present study. Hence, it might be expected that activation energies with magnitudes typical of diffusion should be observed with acetic anhydride, which is not the case. It is important to note that the activation energy obtained using these techniques is related to the slowest process occurring in the reaction (the rate determining step). Hence, a rate limited reaction is observed if the rate of reaction is slower than diffusion. The factors affecting the rate of each process are complex, but it is likely that the nature of the rate determining step will change with time of reaction, since during the initial stages of the reaction process the most readily accessible OH groups will react, but as reaction proceeds reagent molecules have to diffuse further into the cell wall in order to react (Hill and Hillier, 1999).

The molecular weight of the reagent clearly has an influence upon the activation energy, and in order to determine whether the interaction of anhydride with the substrate was important, it was decided to perform reactions in solution using a series of phenolic model compounds, namely phenol, guaiacol, 2,6-dimethoxy phenol, 3 methoxy phenol, 2 methyl phenol, 3 methyl phenol and 4 methyl phenol. Table 4.2 shows the activation energies determined by using the rate constant method and the method of initial rates, for a variety of anhydrides with the phenolic compounds. With both phenol and guaiacol, the anhydride molecular weight has no significant effect upon the activation energy of reaction, when the rate constant method is used to determine activation energy. When using the initial rates method, the activation energies determined for reaction with guaiacol show much greater variation than for those with phenol. However, this does not correspond with the results obtained using rate constants, and in view of the considerable errors that may occur when using the method of initial rates (Hill *et al.* 1998), the variation in the results is not thought to be of any significance. With 2,6-dimethoxy phenol there is evidence of a slight

decrease in activation energy as the molecular weight of the anhydride increases. This is found for activation energies calculated using both rate constant and initial rates methods, but the differences observed are small. The decrease in activation energy with anhydride in any case is far lower than that found for reactions with wood. It is therefore concluded that the systematic decrease in activation energy as chain length of anhydride increases is a consequence of performing the reaction with wood. It has been postulated that with propionic anhydride, the activation energy for reaction indicates that hydrogen bond breaking is the rate determining step of the reaction (Hill and Jones, 1996b). By referring to Table 3.2, it can be seen that the values obtained for propionic anhydride form part of a clear trend, which is perhaps more clearly illustrated by referring to Figures 3.17 and 3.18, where all of the results have been combined. If H-bond breaking were the rate determining step for longer chain anhydrides (with acetic being rate controlled), then a random distribution of activation energies around the value of 25 kJ mol^{-1} (energy of hydrogen bond) would be observed, as this illustrated in Figure 3.19. It is concluded that H-bond breaking is therefore not the rate determining step for any of the reactions. It is unlikely that H-bond breaking plays any part in the reaction process, since the wood samples are fully swollen with pyridine before the reaction is initiated. It is therefore probable that H-bonding networks only exist where OH groups are inaccessible (such as crystalline regions).

The values of Ea observed with the longer chain length anhydrides are more typical of diffusion limited reactions. However, since activation energies determined by the method of initial rates rely upon determining the gradient of the rate curve at time zero, it is therefore unlikely that diffusion would be a rate limiting step at this time. In addition, as discussed previously, with acetic anhydride, the reaction kinetics are found to be diffusion limited throughout, whereas with longer chain anhydrides the initial stage of the reaction is rate limited. It is thus extremely unlikely that the activation energies obtained for the initial stages of the reaction are due to diffusion being the rate limiting step. As the reaction proceeds, it has been found that the reaction kinetics become diffusion limited, and from the reaction kinetics curves obtained from such an analysis, it is possible to derive activation energies (Hill *et al.* 1998); these values are shown in Table 3.6. From these values, it can be seen that the anhydride molecular weight has little influence upon the activation energy. In

addition, the substrate does not have any significant affect upon the value of Ea_{diff}. The values so obtained are typical of activation energies obtained for diffusion processes (Hiller, 1954).

The above results show that for reaction with pyridine swollen wood, the reaction activation energy of the reaction decreases, as the molecular weight of the anhydride increases. No significant difference was found between the energies of activation for reaction with either of the two species of this study. When the reactions were performed in homogeneous solution, there was no significant correlation between anhydride molecular weight and activation energy of reaction. It is clear that when the reaction is performed on wood, anhydride molecular weight has a profound effect upon the activation energy. This effect becomes more pronounced as the molecular weight (and hence size) of the anhydride increases. Reagent molecules within the cell wall polymeric network are clearly subject to considerable steric constraints which do not occur in solution. As the size of the reagent molecule increases, the freedom of motion within the cell wall micropores proximal to the accessible OH groups decreases proportionately. It is therefore unlikely that as reagent size increases, the molecules present within the cell wall obey a classic Maxwell-Boltzmann type energy distribution as would occur in solution, where there is no such constraint upon molecular motion. Thus, as the temperature of the reaction increases, the fraction of molecules having energies exceeding the activation energy of reaction will be influenced by the size of reagent in addition to the temperature of reaction. As a result, the increase in the rate of reaction as the temperature of reaction increases will be far lower than would be observed in homogeneous solution. As a consequence, the *apparent* energy of activation will be lower than would be observed in solution (since a small change in rate constant with temperature yields a low value for Ea). With a small reagent molecule (acetic anhydride), the value for the energy of activation in wood is similar to that observed in solution, suggesting that the motion of the molecules within the cell wall micropores is not significantly affected when compared with molecules in solution.

10.1.2. *The accessibility of reagent molecules to the cell wall interior of pine sapwood*

During the reaction of chemical reagents, such as anhydrides, with the cell wall of wood, it is necessary for the reagent molecule to travel via the cell wall microporous network in order to react with the OH groups located within the interior of the cell wall.

In Chapter 3, the kinetics of the reaction of oven dried pine sapwood with a homologous series of carboxylic acid anhydrides have been investigated. In this case, a swelling agent such as pyridine was used as a catalyst/solvent. If reaction takes place in a non-swelling solvent (e.g. toluene or xylene) and the wood has been previously dried, then the microvoid network is in a collapsed state and ingress of reagent into the cell wall is controlled by the rate at which the micovoids re-open. In this case the 'zipper' model (Krassig, 1985; West, 1988) is the most probable model explaining the reaction process. In such a model, the cell wall microvoids are effectively 'sealed shut' by extensive hydrogen bonding networks between the walls of the microvoid. In order that reagent molecules may penetrate the interior of the cell wall, it is necessary that these hydrogen bonds be broken. If the rate of H-bond breaking is slow compared to the rate of reaction of reagent with the cell wall OH groups, then H-bond breaking is the rate limiting step of the reaction. If however, the wood is in a swollen state, then the transfer of reagent molecules into the interior of the cell wall is affected only by the geometry of the cell wall microvoids (in relation to reagent size), if other factors such as temperature and concentration of reagent are constant.

The investigation reported in Chapter 5 was therefore undertaken to determine the effect of swelling of the cell wall of wood, upon the rate of reaction of the cell wall polymeric OH groups with two different anhydride reagents, namely acetic anhydride (molar volume 94.4 cm^3) and propionic anhydride (molar volume 128.6 cm^3). Different sized anhydride molecules will have varying accessibility to the cell wall because of differences in dimensions of the cell wall micropores. When wood is dried, the cell wall micropores collapse, severely reducing access. Although there is evidence to show that acetic anhydride can react with a non-swollen wood cell wall, it

has been shown that a swelling agent is required with propionic anhydride (Hill *et al.* 2000). In a recent study, reaction of wood with propionic or butyric anhydrides, it was found that reaction was possible at 140^{0}C (Li *et al.* 2000). Similarly, refluxing of wood in propionic anhydride (boiling point 167^{0}C) also resulted in reaction with the substrate (Dawson *et al.* 1999). However, this reported reactivity undoubtedly occurs due to degradation of the cell wall which occurs at such temperatures (Rowell, 1983; Hill and Jones, 1996a; Hill *et al.* 1998; Ramsden and Blake, 1997).

The study reported in Chapter 5 utilised extractive-free sapwood from Corsican pine and Scots pine. Reactions were performed on oven-dry samples in the presence of water-free xylene, which does not swell the cell wall. Reactions were also performed under identical conditions, but on wood samples that had been dried under solvent exchange conditions, thereby retaining the swollen cell wall pore structure.

It was found that no significant reaction occurred, except in the case of reaction between Corsican pine and acetic anhydride. However, when the wood samples were in a swollen state, reaction occurred between the wood and both anhydrides. It is concluded that the cell wall micropores of Corsican pine are sufficiently large to allow access of acetic anhydride but not propionic into the unswollen cell wall, but that with Scots pine both reagents are too large to gain access.

From the data on molar volumes given earlier (see section 3.3.1.1., also Appendix 1B), an apparent diameter for the anhydride molecule can be calculated, by assuming that the molecule is spherical. This equates to a diameter of 0.66 nm and 0.74 nm for acetic anhydride and propionic anhydride respectively. The results therefore indicate the diameters of the micropores in the cell wall of oven dried Corsican pine are smaller than 0.74 nm, whereas those for dry Scots pine are smaller than 0.66 nm.

Such figures should be treated with some caution (for example these values are calculated for the liquids at 25°C), but do nonetheless provide some estimate of pore size. Weatherwax (1977), found that the accessible pores in a cellulose (WAC) aerogel had diameters in the region of 1.8 nm, but that in the original water swollen gel the corresponding figure was 4.4 nm. Other workers have established the median

cell wall pore sizes in wood by using nitrogen sorption isotherms, for example Sawabe *et al.* (1973), found pore sizes in the range 2.5-5.0 nm, but this was with ground wood meal and such data may not be applicable to whole wood. The reaction profiles show that the rate of reaction of both acetic anhydride and propionic anhydride with solvent exchange dried samples was the same as with samples which were swollen with the corresponding carboxylic acid. This result shows that the cell wall pore structure of a solvent exchange dried aerogel cell wall is similar to that of the fully swollen equivalent, provided the solvent is not removed from the structure. The previously reported collapse of such structures must therefore occur when the solvent molecules evaporate from the cell wall. It has been reported that molecules with molar volumes greater than 100 cm^3 do not penetrate the cell wall of wood pulp fibres (Robertson, 1970), although, more recently it has been found that molecules with molar volumes greater than 100 cm^3 are able to penetrate the cell wall, providing they have two or more groups capable of hydrogen bonding (Morisato *et al.* 1999). The results of this work show that the above is true for reaction with Corsican pine, but that with Scots pine, the size limit for accessibility would appear to be lower. This important observation indicates that data obtained for cell wall accessibility with one species cannot be applied generally.

10.1.3. Volumetric changes in Corsican and Scots pine sapwood due to chemical modification with linear chain anhydrides

Acylation with linear chain anhydrides is a single site reaction, that is one acetyl group is added per reaction site with no associated polymerisation, as discussed in section 3.3.1.1. Therefore the weight gain due to modification is equal to the number of hydroxyl groups substituted. As the hydroxyl groups of the cell wall polymers are substituted, the cell wall of wood swells due to the volume occupied by the adduct. This swelling occurs because the covalently bonded hydroxyl groups occupy space within the cell wall and cause a localised deformation of the cell wall polymeric network.

Various studies of the relationship between the swelling of the material due to modification have been published. In studies of the acylation of spruce, maple and

balsa, it has been found that the degree of swelling of the substrate exhibits a proportional relationship with the degree of substitution, up to an acetyl content of 16-18% (Stamm and Tarkow, 1947). Furthermore, the volume change due to modification, has been found to be equal to the volume of the acetyl groups in the wood (Stamm and Tarkow, 1947; Rowell and Ellis, 1978).

More recently, this latter finding has been disputed, where it has been found that for Corsican pine modified wood, a volume increase larger than theoretically predicted is obtained (Hill and Jones, 1996a).

In Chapter 6, the volumetric changes in Corsican and Scots pine sapwood due to modification with an homologous series of linear chain anhydrides have been studied. Calculations of the theoretical volume increase due to modification, based on the density of the reagents, was found to yield theoretical volume increases less than those measured for Corsican pine, and close to those predicted with Scots pine sapwood. This observation indicated that there are contributions to the volume increase due to modification from the space occupied by the reagent and an associated void volume.

The results have also been interpreted in terms of the molar volume occupied by the substituent groups in the wood cell wall. It was found that larger void volumes occurred in the Corsican pine samples. This result indicates that the cell wall polymeric environment surrounding a reagent molecule is more compliant in the case of Corsican pine.

Larger volumetric changes and larger void volumes were found at low levels of substitution, in both Corsican and Scots pine. The increase in molar volume and hence the larger volumetric swelling of the material at low weight percent gain, is believed to be a phenomenon related to the modification process, as discussed by Hill and Jones (1999), since at low levels of substitution (and hence short reaction times) it was to be expected that the reaction will occur at surface sites; thus, less swelling of the material would occur at low WPG's, the opposite of what is observed in this study.

It is known from studies of chloroacetic anhydride modified wood, that at low wpg's the substituent is located predominantly in the S_2 layer of the cell wall (Rowell *et al.* 1994). The location of the reagent within the wood cell wall depends upon the relative rates of diffusion of reagent molecules in the micropores of the wood cell wall, and the rate of reaction of such molecules with active sites located within the cell wall. As was found in this study (see section 3.3.4), the reaction kinetics of acetylation are diffusion dominated; due to the dominance of diffusion, the rate of reaction will be a function of the density of the wood, which varies from region to region (it is known that the rate of diffusion is inversely proportional to the density (Dinwoodie, 1981). Thus, reaction initially will occur in less lignified regions of the cell wall where penetration of the reagent is facilitated, such as the S_2 layer of the cell wall, which is of lower density than the middle lamella. In these regions which are of lower lignin content, it is probable that the wood exhibits greater elasticity, and as a consequence, larger volumetric changes are observed. At higher wpg's, more highly lignified regions, such as the middle lamella are substituted and the associated volumetric changes are of lower magnitude.

Another important observation, raised in this part of the study, was that a linear relationship has been found between the void volume occupied by the adduct as the size of the reagent increases.

Finally, by determining the relationship between average molar volume at high weight gains and ultimate level of hydroxyl substitution, for the range of anhydrides studied, it was possible to estimate the number of accessible hydroxyl groups at 6.30 and 6.38 mmoles/g for Corsican and Scots pine respectively. These contrast with a theoretically calculated value of 8.6 mmoles/g.

10.1.4. *The sorption of water vapour by chemically modified pine sapwood*

When moisture comes into contact with wood, the water molecules penetrate the cell wall and become bound to cell wall polymers through hydrogen bonding. With addition of water to the cell wall, wood volume increases nearly proportionally to the

volume of water added. Chemical modification changes the properties of wood due to the reaction of hydrophilic chemical groups within the wood and by bulking the cell wall.

Although a number of studies have been investigated the sorption properties of acetylated wood (Spalt, 1958; Risi and Arseneau, 1957a; Popper and Bariska, 1972; Forster, 1998), there has not been a study of the effect of modifying the wood with different sized anhydride reagents. It is known that rate and extent of water vapour sorption is decreased by substitution of the hydroxyl sites with acetyl groups. Two mechanisms may be proposed:

(i) Blocking of sorption sites.
(ii) Bulking of the cell wall by acetyl groups resulting in less space being available to sorbed water.

However, in previous studies it was not possible to determine the influence of each effect. By modifying wood with a variety of anhydride molecules of different size, it is possible to produce similar levels of bulking at different levels of hydroxyl substitution. Therefore, it becomes possible to separate the two effects.

A comprehensive investigation into the water sorptive properties and into the effect of molecular size of the substituent group upon the sorption of water vapour of softwood modified with linear chain carboxylic acid anhydrides, namely acetic, propionic, butyric, valeric, hexanoic, has been described in Chapter 7. The sorption isotherms for untreated and chemically modified wood were analysed using the Hailwood-Horrobin model. The experimental analysis of the sorption isotherms showed that acylation affected both total, polymolecular and monomolecular sorption.

Analysis by the Hailwood-Horrobin model suggested that the reduction in total sorption at saturation is chiefly due to the reduction in polymolecular sorption, reduction in monomolecular sorption being of secondary importance.

Having assessed how the reduction in hygroscopicity is affected by the reduction in the two types of sorption by which water is assumed to be held by wood, the next step

was to determine the causes of the reduction in hygroscopicity in these two types of sorption. Through the constant W_o provided by the model, which measures site accessibility, it was possible to show that the availability of bonding sites is reduced by chemical modification. Regression analysis has shown this reduction to be the main cause for the decrease in monomolecular sorption, whereas the increasing volume of adducts in the cell wall (a measure of the degree of bulking) was shown to be the primary reason for the decrease in polymolecular sorption.

The effect of molecular size of the substituent group on site accessibility was addressed by comparing the effect on water sorption produced by adducts with differences in molecular size. Similar levels of bulking were produced at different levels of substitution, for the range of the anhydrides studied. Table 7.16 shows the molecular weight of the adducts of the anhydrides used in this study, along with the hydroxyl groups substituted at equivalent WPG. From this, it can be seen for example, that hexanoic anhydride acyl group is about twice the molecular weight of the acetic anhydride, and therefore at equivalent WPG and consequently similar degrees of bulking, it will have reacted with about half of the OH groups substituted by acetic anhydride. Conversely, hexanoic anhydride may react with an equivalent amount of OH groups but causing about twice as much bulking as the acetic anhydride.

The results showed that the reduction in total sorption imparted by the bulkier hexanoic anhydride is comparable to that produced by the other anhydrides, and indeed by the acetic anhydride at equivalent WPG, despite the substantial difference in the proportion of hydroxyl groups chemically reacted (see Figures 7.43, 7.44). The total sorption isotherms were then separated into monomolecular and polymolecular sorption, according to the Hailwood-Horrobin model. The related isotherms revealed that the five anhydrides used show similar effectiveness in adsorption not only at the polymolecular but at the monomolecular level as well (see Figures 7.45 to 7.48).

Account is then taken of the molecular weight of the reacting chemical in order to obtain an estimate of the hydroxyl groups of the wood samples, which have reacted with the anhydride reagent. The results showed that where similar proportions of hydroxyl groups are substituted by each of the anhydrides used in this study, the

bulkier hexanoic anhydride is clearly more effective at reducing both total, polymolecular and monomolecular adsorption (see Figures 7.53 to 7.58).

Based on the above observations, it is suggested that the accessibility of the internal surfaces is related to the weight gain and not to the fraction of hydroxyl groups reacted. This is further confirmed, when the W_o values were plotted against WPG and the number of hydroxyl groups substituted due to modification (see Figures 7.49, 7.50, 7.59, 7.60). It was found closer W_o values for similar weight gains than for similar fractions of hydroxyl groups.

From the above discussion, it appears that the reduction in monomolecular adsorption produced by the linear chain anhydrides is primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted. An additional contributor to this behaviour, may be the simple physical covering which reduces the accessibility of the internal wood surfaces. When an anhydride with large molecular size is used, the adduct which reacts with one hydroxyl group might cover some of the adjacent ones, providing a physical barrier. This barrier prevents the water vapour molecules from reaching some of the unreacted sites, that is, it shields sites. Hence, the effect of the adduct covering reacted and unreacted sites may overshadow the effect of direct chemical bonding to the sites. This effect plays an increasingly dominant role as adduct molecular size increases and may partly determine the reduction in monomolecular sorption.

This seems to be the only explanation for the fact that although hexanoic anhydride for example reacts with substantially less hydroxyl groups, it is able to produce an equivalent reduction in monomolecular adsorption with the smaller acetic anhydride, at equivalent WPG. Another explanation maybe the inability of the Hailwood-Horrobin model to fully predict monomolecular and polymolecular sorption of modified wood, since irrespective of the anhydride used, similar W_o values were predicted at equivalent levels of modification. Therefore some doubt is cast upon the validity of this model. This is further discussed later in the section.

In conclusion, it has been shown in section 7.4.3.2 that the reduction in total sorption primarily was mainly due to the reduction in polymolecular sorption, reduction in

monomolecular sorption being of secondary importance. It has been further shown, that the increasing number of the adducts in the wood cell wall, which is a measure of the degree of bulking, was the primary reason for the reduction in total and polymolecular sorption; the reduction in monomolecular sorption was primarily attributed to the decrease in site accessibility. In section 7.4.6, it has been shown that the reduction in site accessibility, and therefore the reduction in monomolecular sorption, was primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted. Combining the above observations, it is concluded that the reduced moisture uptake of wood modified with linear chain anhydrides is mainly a bulking phenomenon.

Based on the above, a mechanism of stabilisation by chemical modification with linear chain anhydrides has been proposed. This is as follows:

i. The anhydride reagent enters the wood cell wall and reacts with some of the hydroxyl sorption sites of the wood components. This as a result, reduces site accessibility and bulks the cell wall.

ii. Sorption at the monomolecular level is primarily reduced by reduction in site accessibility, while sorption at the polymolecular level is reduced by bulking.

iii. The accessibility of the internal surfaces to water molecules is primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted, and at the same time by a shielding effect when the adduct physically covers some of the adjacent unreacted sorption sites. The latter one is of less importance comparing to bulking effect.

iv. The shielding effect plays an increasingly dominant role as adduct molecular size increases.

Limitations of the model

It has been shown by other workers (Spalt, 1958; Wangaard and Granados, 1967; Simpson, 1980; Forster, 1998) and is further confirmed in this study, that the Hailwood-Horrobin model fits the experimental wood sorption data very well. However, it is not reasonable to assume the validity of the model, because it incorporates simplifying assumptions that are necessary in order to make its mathematical derivation feasible. For example, as pointed out in the original paper, the model assumes that W_o (the apparent molecular weight of the polymer associated to one mole of water), which provides a measure of site accessibility, is constant for a given sorption isotherm within the entire relative humidity range. However, Hailwood and Horrobin suggest that the fraction of inaccessible groups is not constant throughout the sorption process, since the wood structure is gradually opened as sorption and swelling proceed, thus increasing the proportion of accessible sites. In fact, increase in internal surfaces upon swelling with consequent developing of new sorption centres through the disruption of hydrogen bonding between wood components has been frequently reported in the literature (Spalt, 1958; Stamm, 1964). The validity of the model and its application to chemically modified wood remains speculation at present. Analysis of the set of data obtained in this study has to be conducted using other models.

10.1.5 Analysis of the swelling behaviour of chemically modified pine sapwood

Chapter 7 studied the reduction in equilibrium moisture content caused by increasing weight gains of modifying chemical. This was attributed mainly to the bulking action of chemical in the cell wall displacing water that would otherwise be adsorbed in the cell wall as bound water. The aim of this chapter was to present an analysis of the swelling behaviour of chemically modified wood due to water vapour sorption.

When wood takes up moisture into the cell wall, the walls swell volumetrically in proportion to the volume of the water absorbed (Skaar, 1972). This is based on the assumptions that the cell lumen is constant in size and that there are no voids in the

cell wall and therefore, water simply adds its volume to that of dry wood. It was shown in Chapter 6 that volumetric changes due to modification with a homologous series of linear chain anhydrides were found to be due to the volume occupied by the reagent and an associated void volume created by the acyl groups within the cell wall. Additionally, it was shown that as the size of the reagent increases, so does the void volume created in the wood matrix.

The first assumption relies on modification either causing an increase in swelling (due to saturation) into the cell lumina or a reduction in the way in which the lumen size increases due to water swelling. Cell lumina in some wood species have been found to enlarge or shrink when wood is saturated and swells, though where this occurs it is often only by a small amount, and negligible compared to the swelling of the cell wall (Stamm, 1964; Siau, 1984; 1996). It was assumed therefore that no such changed occurred. Any change in dimension due to water swell was considered to be solely due to the swelling of the wood cell wall.

The validity of the second assumption was the subject of Chapter 8. For this reason, swelling was calculated by measuring the volume (derived from the three dimensions) of samples (unmodified and modified with acetic and hexanoic anhydride at selected WPG's) at the moisture content achieved in equilibrium with each relative humidity during the adsorption tests described in section 7.3.3.

When the weight of water in the Corsican pine cell wall due to exposure to relative humidity at saturation was plotted *versus* bulking, a non linear relationship was obtained (see Figure 8.10). If it is assumed that the volume available in the cell wall for water decreases as a result of volume occupied by adduct, then a linear relationship between the two values would be expected. Thus, as more volume in the cell wall is occupied by adduct, there is less volume available for water.

It was shown in Chapter 6, that volumetric changes due to modification with a homologous series of linear chain anhydrides were due to the volume occupied by the reagent and an associated void volume created by the acyl groups within the cell wall. If it is assumed that this void volume can accommodate water without concomitant swelling of the cell wall, then clearly account must be taken of this.

When the value of void volume is deducted from the bulking, to give a figure for the apparent volume occupied by acyl groups in the modified cell wall, a linear relationship was indeed obtained with acetic anhydride modified Corsican pine, but not with hexanoic anhydride modified Corsican pine (see Figure 8.11). It seemed therefore that the free volume model introduced in Chapter 6, offers a reasonable explanation of the differences in swelling recorded for Corsican pine sapwood modifying to varying WPG's of different modifying chemicals.

However, when the same data analysis was performed for the Scots pine data, no linear relationship was found, as depicted in Figure 8.12. The reason behind this behaviour is unknown. Therefore, a definite conclusion regarding the application of the free volume model cannot be drawn from this study.

10.1.6 Lignin analysis and determination of the surface area and pore volume of unmodified and modified wood flour using the nitrogen adsorption technique

In Chapter 6, it was shown that the volume occupied in the cell wall per reagent molecule is larger in modified Corsican pine compared with modified Scots pine. It was suggested that the cell wall polymeric network surrounding the acyl groups exhibits different flexibility between the two species. Additionally, it was shown in Chapter 5, that the cell wall micropores in Corsican pine are sufficiently large to allow access of acetic anhydride but not propionic into unswollen cell wall, but that with Scots pine both reagents are too large to gain access. It was the aim of chapter 9 to find possible explanations for this behaviour.

A first approach was made by determining the chemical composition of Corsican and Scots pine, since a possible lower lignin content in Corsican pine will partially explain the higher flexibility of the Corsican pine cell wall polymeric network surrounding the acyl groups. Examination of the chemical composition of Corsican and Scots pine sapwood revealed that both species contained identical amount of cellulose, hemicellulose and lignin. Therefore, the difference in behaviour of the Corsican pine compared to that of Scots pine, as was shown in Chapter 6, cannot be explained in terms of their chemical composition.

A second approach was made by qualitatively determining the S:G ratio (Syringyl: Guaiacyl) of lignin. A higher syringyl content, and therefore higher ratio, denotes less crosslinking and therefore more flexibility of the lignin. The results from the HPLC analysis showed that the S:G ratio is significantly higher in Corsican pine. This was, however an indicative result; a more definite conclusion would have drawn from this experiment, if all the peaks in Figures 9.4 and 9.5 had been identified. Time restrictions and high costs involved meant that this was not possible with the confines of this study.

A third approach, involved exposure of Corsican and Scots pine samples to deuterium (D_2O) exchange. It was found that exposure to deuterium exchange caused a higher weight percent gain in Corsican pine samples. This contrasts with the finding of Chapter 6 (see section 6.5), where the same values of theoretically accessible hydroxyl groups was obtained for Corsican and Scots pine.

Chapter 7 studied the reduction in equilibrium moisture content caused by increasing weight gains of modifying chemical. This was attributed mainly to the bulking action of chemical in the cell wall displacing water that would otherwise be adsorbed in the cell wall as bound water. In addition, the extent of swelling of modified wood was studied, in Chapter 8. It was possible that the bulking of the cell wall by modifying chemical, along with reduced swell, could be causing a restriction in cell wall pore volume and in total surface area. This was investigated in Chapter 9 using the nitrogen adsorption technique. The technique has largely been used in the past with pulp samples and no substantive work using this technique (on wood or pulp) has appeared in the literature the past decade.

Very low surface area (ca 0.5 m^2/g) and a low pore volume (ca 0.002 cm^3/g) have been obtained for oven dried wood, using the nitrogen adsorption technique. This was a result of the micropore network in the cell wall collapsing when the wood is dried. During the oven-drying of water saturated wood, powerful capillary condensation forces operate to bring the walls of the micropores together (Figure 9.8A), resulting in the formation of extensive hydrogen bonding networks between the sides of the micropores.

The microporous structure of wood flour was partially preserved by the solvent exchange drying (SED) employed in this study, in particular when toluene was used as a final solvent. However, the resulted surface area (ca 6 m^2/g) and a pore volume values (ca 0.015 cm^3/g) indicated that such a structure is in no way representative of a fully swollen cell wall.

During the solvent exchange process, a swelling solvent (dry methanol) is gradually replaced by a non-swelling solvent (toluene or pentane), the molecules of which occupy the cell wall microvoids, thereby preventing collapse of the structure. However, if these occluding molecules are removed, then collapse of the structure occurs, although in this case there may not be such extensive H-bonding networks formed (Figure 9.8B). The collapse of the porous structures is controlled by surface tension forces at the liquid vapour interface; thus if supercritical drying is employed then such collapse is prevented (at least as far as wood holocellulose or pulp is concerned, see later). An additional factor in this latter case is the elasticity of the cell wall, which is largely controlled by the lignin. When a bleached wood pulp is solvent exchange dried from a never dried state, surface areas in the region of 100-200 m^2/g and pore volumes of 0.2-0.4 cm^3/g are reported (Stone and Scallan 1965b). In this study, a surface area of 77.7 m^2/g was obtained for SED of holocellulose using pentane as a final solvent (see Table 9.3). This larger measured surface area is undoubtedly partly a result of the removal of the lignin leading to the increase in the void content of the cell wall, but there is also a contribution from the reduced elasticity of the cell wall (Stone, 1964). In this latter case, collapse of the micropores is incomplete when solvent exchange drying is employed (Figure 9.8C).

It is concluded that, by using solvent exchange drying (SED), it is possible to preserve the swollen pore structure of holocellulose samples. However, with samples which contain significant amounts of lignin, such as native wood, it is not possible to prevent re-collapse of the pores. This problem arises because as micropore swelling occurs, the surrounding lignin network of the cell wall is stretched. When the molecules occupying the micropores are removed, the lignin returns to its original configuration, re-collapsing the micropores in the process

Although the SED process did not fully preserve the swollen pore structure of the wood cell wall, as discussed above, it was still thought that comparison between the surface area and pore volume of unmodified and modified wood flour samples would be of interest. The results from the determination of surface area and pore volume of modified wood with hexanoic anhydride indicated that chemical modification resulted in significant reduction in surface area and pore volume. This may be a result of blocking pores due to chemical modification.

10.2. Recommendations for further work

In Chapter 4, determination of Ea for a series of phenolic compounds was undertaken in order to consider if the interaction of anhydride with the substrate is important. It will be of interest to extend this work using a series of alcoholic compounds in order to reaffirm the conclusions drawn from the present work.

In Chapter 5, the issue of accessibility of reagent molecules to the cell wall interior of pine sapwood was addressed. It will be of interest to extend this work to other wood species, particularly with known lignin content, and to examine how accessibility is influenced by genetic factors, geographical factors and growing conditions. Also the accessibility and reactivity of abnormal wood, i.e. juvenile wood, compression wood may be examined, since this type of wood is expected to respond to modification with a different manner. All these are very important aspects in the commercialisation of the modification process.

In Chapter 7, the sorption of water vapour by chemically modified pine sapwood was studied and the e.m.c data was analysed using the Hailwood-Horrobin model. This model has been applied to e.m.c. data for wood chemically modified with anhydrides (Forster, 1998; Chauham, *et al.* 2001) and isocyanates (Martins, 1992), and fitted the experimental data very well; this is further confirmed in the present study. However, there has not been a study of the effect of modifying the wood with different sized anhydride reagents. The results obtained in the present comprehensive study of this phenomenon, and in particular the identical W_o values (the apparent molecular weight

of the polymer associated to one mole of water) at equivalent levels of modification with different reagents, cast some doubt upon the validity of the Hailwood-Horrobin model. Analysis of the set of data obtained in this study may be conducted using other models in order to test the validity of this. It is to be hoped that other investigators will accept the challenges that this work presents.

From the swelling analysis of the chemically modified wood, presented in Chapter 8, a definite conclusion regarding the application of the free volume model cannot be drawn. A wider range of weight gains, a larger number of replicates, and swelling measurements during desorption would be required in a comprehensive study of this phenomenon.

It was found in Chapter 9, that with samples which contain significant amounts of lignin, such as native wood, it is not possible to prevent re-collapse of the pores. This problem arises because as micropore swelling occurs, the surrounding lignin network of the cell wall is stretched. When the molecules occupying the micropores are removed, the lignin returns to its original configuration, re-collapsing the micropore in the process. By breaking up the cross-linking network of the lignin macromolecule, it is hoped that this will limit the ability of this molecule to shut the cell wall pores after drying. Several approaches are possible including exposure to UV radiation and exposure to white rot fungi attack.

In Chapter 5, it was found that the cell wall micropores of Corsican pine are sufficiently large to allow access of acetic anhydride but not propionic into the unswollen cell wall, but that with Scots pine both reagents are too large to gain access. In addition, in Chapter 6, it was suggested that there are differences in the way that the lignin-carbohydrate network deforms to accommodate the bonded acyl group. However, no such difference was detected in Chapter 9, using the nitrogen adsorption technique, where similar values of surface area were obtained for both Corsican and Scots pine. It is essential to find the reasons for this behaviour, probably looking at ways to improve the solvent exchange drying employed in this study.

In Chapter 9, it appeared that the final solvent during the solvent exchange drying has an important effect on the surface area determined using the nitrogen adsorption

technique. A wider choice of final solvents and classification according to their properties (i.e. polarity, viscosity etc) may be required in order to understand this phenomenon.

Deuterium exchange did not work properly in this study. A wider selection of WPG'S and an increased number of replicates may be required. Also a more suitable apparatus for the exchange, other than the jar used in the present study may be tried. Furthermore, the exposure time to deuterium exchange and drying time after the exchange may be re-examined in a comprehensive study of this phenomenon.

Delignification of wood samples from various seed origins and various provenances may be undertaken in order to determine whether genetic factors or site affect porosity of the cell wall or the ease of delignification of samples. The effect of removing lignin from samples upon the cell wall porosity can also be determined.

As noted in Chapter 2, the geometry of micropores is of great significance, since this parameter has a substantial influence upon a number of processes of great importance in the wood processing industries (e.g. wood drying, preservative distribution, pulping and bleaching, biological decay processes etc.). A very important example of this is the ability of enzymes to penetrate the cell wall in order to metabolise the polymeric components (cellulose, hemicelluloses, lignin). It is known that the enzymes are too large to enter the cell wall pores of undegraded wood, and in wood decay various low molecular weight agents are believed to be responsible for initiating degradation so that the cell wall pores are opened up. An understanding of the mechanisms by which this process occurs would have great benefits for developing new non-toxic preservation methods. Therefore, the effect of exposure of various wood samples to a variety of enzymes (cellulases, hemicellulases, ligninases) may be assessed and the effect of delignification and lignin degradation (as recommended above) upon the ability of such enzymes to degrade the cell wall may be undertaken. Enzymatic degradation can be assessed by changes in porosity of the samples, as well as assays for lignin and polysaccharides. It may be possible to determine pore size thresholds for the penetration of various enzymes into the cell wall.

Finally, samples exposed to lignin degradation, as described above, may also be exposed to various enzymes. This can be used to determine how changes in the void structure of wood following lignin degradation affects the ability of enzymes to penetrate the cell wall.

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