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Dimensional stabilisation by chemical modification of wood

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DIMENSIONAL STABILISATION BY CHEMICAL MODIFICATION OF WOOD

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by

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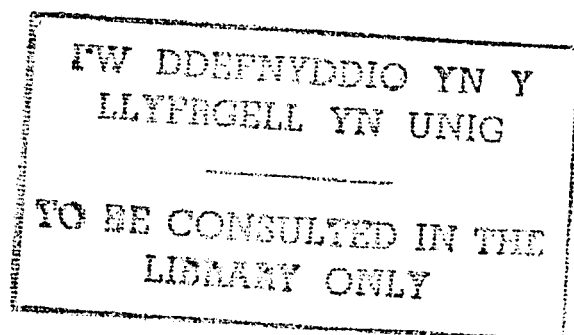
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DEDICATION

To my wife Thaís

and my daughter Carolina

SUMMARY

Corsican pine (*Pinus nigra*) and beech (*Fagus sylvatica*) wood specimens were modified with n-butyl isocyanate (n-Bu-NCO), phenyl isocyanate (Ph-NCO), 1,6-diisocyanatohexane (HDI) and tolylene 2,4-diisocyanate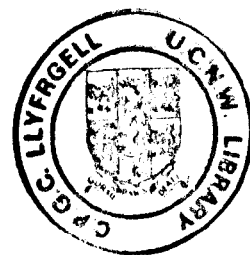 (TDI), using pyridine as the swelling agent and catalyst. Several levels of weight gain were achieved by varying the reaction time. For each species the approximate general reaction rate order based on hydroxyl substitution was Ph-NCO > n-Bu-NCO > HDI > TDI for Corsican pine, and HDI > Ph-NCO > n-Bu-NCO > TDI for beech.

The effect of chemical modification in the sorption properties and in the associated dimensional stability of wood was investigated by determining sorption isotherms and measuring the respective volumetric swelling at each relative humidity (RH) level. The treatment depressed the isotherms evenly over the entire range of RH for all levels of reaction, however, the difunctionally modified wood tended to show lower reduction in sorption at low RH's. The reduction in sorption was closely accompanied by a reduction in swelling indicating that within the accuracy of the experiment no voids were formed within the cell walls due to the treatment.

The TDI treated specimens showed higher reduction in swelling under RH conditions than at saturation in liquid water. This was interpreted as to be caused by the formation of rigid TDI crosslinkages.

The mechanisms of reduction in wood hygroscopicity were investigated by fitting data to the Hailwood-Horrobin sorption model. It was shown that the chemical modification treatment affects both monomolecular and polymolecular sorption. The accessibility of bonding sites was also reduced. Regression analysis revealed that the reduction in monomolecular sorption is chiefly governed by the decrease in site accessibility and that the reduction in polymolecular sorption is governed by the increase in the adduct volume in the cell wall.

Investigation of the causes of the reduction in site accessibility by analyzing the sorption isotherms for wood modified with n-Bu-NCO and with a bulkier monofunctional isocyanate (octadecyl isocyanate) suggest that the accessibility of the internal wood surfaces is related to the weight gain and not to the fraction of hydroxyl groups (OH) reacted. This suggests that the reduction in accessibility is caused by a "shielding effect" where the adducts physically cover some of the adjacent unreacted sorption sites.

With difunctionally modified wood no evidence of crosslinking effectiveness was indicated at saturation in liquid water. However, when the samples were soaked in pyridine, the crosslinkages seemed to influence super-swelling in comparison to that shown by monofunctionally reacted wood.

Finally, tensile strength testes carried out on modified and unmodified wood strips revealed that with the exception of n-Bu-NCO treated samples, the wood strength is slightly but significantly reduced by the treatments.

LIST OF ABBREVIATIONS

A_d	Activity of dissolved water
A_h	Activity of the hydrate
Ads.	Adsorption
ANOVA	Analysis of variance
A_o	Activity of dry wood
Approx.	Approximately
ASE	Anti-swelling efficiency
BET	Brunauer-Emmet-Teller sorption theory
C. pine	Corsican pine
$CH_3.COOK$	Potassium acetate
Chem.	Chemical
Des.	Desorption
DF	Degrees of freedom
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DS	Degree of substitution
EMC	Equilibrium moisture content
Fig.	Figure
FSP	Fibre saturation point (mass of water/unit wood dry weight)
G_o	Oven-dry specific gravity
G_{oe}	Effective specific gravity
h	Relative vapour pressure
HDI	1,6-diisocyanatohexane
Hemicell.	Hemicelluloses
HH	Hailwood-Horrobin sorption model
HR	Reduction in hygroscopicity
IPDI	Isophorone diisocyanate
IRH	Integral reduction in hygroscopicity
K_1	Equilibrium constant of the primary water in the Dent model.
K_2	Equilibrium constant of the secondary water in the Dent model
K_2CO_3	Potassium carbonate
KBr	Potassium bromide
K_d	Equilibrium constant of the dissolved water in the HH model.
K_h	Equilibrium constant of the hydrates in the HH model
KOH	Potassium hydroxide

KNO_3	Potassium nitrate
LiCl	Lithium chloride
m	Total moisture content (in both Dent and HH models)
m_1	Primary water (Dent model)
m_2	Secondary water (Dent model)
Max.Theor.WPG	Maximum theoretical weight percent gain
m_d	Water of solution (HH model)
Me-NCO	Methyl isocyanate
M_f	Fibre saturation point (volume of water/unit wood dry weight)
m_h	Water of hydration (HH model)
M_o	Moisture content corresponding to complete polymer hydration (HH model)
M_o'	Moisture content corresponding to complete monolayer cover (Dent model)
Mol. Wt.	Molecular weight
Molec.	Molecular
Mono	Monomolecular sorption
Monom.	Monomer
NaCl	Sodium chloride
$Na_2Cr_2O_7$	Sodium dichromate
n-Bu-NCO	Butyl isocyanate
NCO	Isocyanate
OCDC-NCO	Octadecyl isocyanate
O.D.	Oven-dry
OH	Hydroxyl group
PEG	Polyethylene glycol
Ph-NCO	Phenyl isocyanate
Poly	Polymolecular sorption
r^2	Coefficient of determination
RH	Relative humidity
SD	Standard deviation
S_f	Total hygroscopic swelling
S_v	Volumetric swelling
TDI	Tolylene 2,4-diisocyanate
TEA	Triethylamine
Vol.	Volume
W_o	Apparent molecular weight of the sorbate per mole of sorption sites (HH model)
WPG	Weight percent gain
X_{vs}	Moisture expansion coefficient

CONTENTS

CHAPTER I

GENERAL INTRODUCTION AND OBJECTIVES OF THE STUDY

Wood is widely used as a building material, fuel and source of chemical. It is also renewable, strong and aesthetically pleasing. Despite these many advantages, two properties restrict its much wider utilization: dimensional changes upon changing conditions of relative humidity and degradation by a large variety of microorganisms and insects. Since these properties are a consequence of the chemical composition of the cell wall polymers, research has been addressed to the modification of the basic chemistry of wood and consequently the properties of these cell-wall polymers through chemical reactions. The gross molecular architecture of the fibres must remain substantially unaltered in order to retain major mechanical properties. However, it has been shown that many types of chemical reaction may be applied to several species of wood to chemically modify the cell wall polymer and bring about significant property enhancement. (Stamm, 1964 and 1977a; Rowell, 1975, 1983 & 1984 and references therein).

Chemical modification when applied to wood composites before they are reconstituted eliminates problems associated with solid wood such as drying to low moisture content (since fibres and particles need to be dried prior to product formation). This is costly, if it has to be carried out as a separate process, and can cause damage to wood structure. Furthermore, problems

associated with reagent penetration and recovery are minimized, because the chemical has only to travel small distances to achieve full wood penetration. It appears therefore, that the most promising use of this technology at present lies in reconstituted products such as flakeboard, particleboard and fibreboard (Rowell *et al*, 1988).

As defined by Rowell (1975), chemical modification is a chemical reaction between some reactive part of a wood component and a chemical reagent, with or without catalyst, to form a covalent bond between the two. The most abundant reactive chemicals sites in wood are the hydroxyl groups of its main components, cellulose, hemicellulose and lignin. Most of the research carried out in this area involves the reaction of these hydroxyl groups although the less abundant carbonyl groups offer another route of selective chemical modification (Kalnins, 1982). The chemical used is required to react quickly, producing stable chemical bonds preferably with no by-products and the desirable properties of the untreated wood must remain unchanged. One group of chemicals that meet the above mentioned criteria for chemical reagents are the isocyanates. As shown below, they react with wood hydroxyls yielding stable nitrogen-containing ester bonds known as carbamates or urethanes (Rowell, 1980):

$$\text{Wood--OH} + \text{R-N=C=O} \longrightarrow \text{Wood-O-}\overset{\overset{\textstyle O}{\|}}{\text{C}}\text{-NH-R}$$

A review of the chemical modification of wood with isocyanates is presented in section 2.1.1

Whilst much is documented about the effect of chemical modification on overall stabilisation in response to liquid water soaking (Stamm, 1964 and 1977a; Rowell, 1983; Rowell and Banks, 1985), there is limited work reported on the water sorptive properties of such modified woods, (see section 3.1.5). In view of the sparse evidence of how sorption is influenced by carbamo-esterification, the basic mechanisms of reduction in moisture sorption and in the corresponding reduction of the natural tendency of wood to swell or shrink remain incompletely understood. At present, data provided by studies of acetylated wood accounts for the most consistent explanation. From this work it appears that chemical modification influences sorption by a combined effect of decreased water activity of the internal wood surfaces and the bulking action of the ester formed in the cell wall. The first effect is believed to predominate at the lower relative humidities and the latter, at the intermediate and higher ranges of relative humidity (Spalt, 1958). Wangaard and Granados (1967) reported similar conclusions in their study of sorption by extracted and unextracted wood. In earlier studies (Stamm and Tarkow, 1947) it was suggested that the reduced polarity of acylated wood was less likely a cause of stabilization than the bulking effect.

Due to some similarities in the nature of the products formed in the cell wall, isocyanate treated wood

is likely to present sorption reduction mechanisms comparable to acetylated wood. Comprehensive work however, able to establish the relative importance of decrease in site accessibility and cell wall bulking in the reduction in water-vapour sorption within the entire range of relative humidity for such modified woods is lacking.

Of further interest in the study of the chemical modification of wood is the use of difunctional compounds. In the reaction between these chemicals and wood, bonding may occur with two hydroxyl groups, hence the reaction is called crosslinking. The possible crosslinking combinations are large and theoretically the bonding between the two hydroxyls can occur between and within the wood components (cellulose, hemicellulose and lignin), (Rowell, 1983). The principle of this process consists of tying together the structural units of the wood cell wall with stable molecular crosslinks in order to achieve great reduction in its tendency to swell, through the addition of only small amounts of chemical (Stamm, 1977a). The most commonly reported type of wood crosslinking is accomplished by using formaldehyde. The reaction however, is best catalysed by strong acids such hydrochloric acid, resulting in great loss in wood strength during reaction (Tarkow and Stamm, 1953). A definite embrittlement is also observed in formaldehyde-treated wood, may be due to the short inflexible crosslinking unit of the -O-C-O- type formed (Rowell, 1975). Diisocyanates with 4 to 10 carbon atoms chains are

expected to form crosslinking between the structural units similarly to formaldehyde treated wood. However, because of the larger carbon chain forming the crosslink (4-10, rather than 1), it is possible that the products formed may be less brittle than formaldehyde cross linked wood.   That is, the longer linkages may give rise to an "elastomer" type of structure (Schollenberger et al, 1981).

According to the concept described above the mechanisms of holding the chains together should operate in addition to the proposed reduction in the hydrophilic nature of wood and the bulking effect, to increase dimensional stability. Previous work reported by Rowell (1984) however, showed no advantages of the difunctional isocyanates over the monofunctional ones. The reason for this apparent lack of difunctional effect is not clear. Further investigation of this interesting system within different treatment conditions seems to be justified.

Taking into consideration the above points the objectives of this work are:

1) To determine the effects of mono and difunctional urethane modification on the wood water-vapour sorption relationship and on the associated dimensional stability of wood.

2) From the data to develop a model of the mechanisms of these effects.

CHAPTER TWO

CHEMICAL MODIFICATION STUDIES

2.1 LITERATURE REVIEW

2.1.1 Wood-isocyanates reaction

Reactions of cellulosic materials with isocyanates have been described in the patent literature since the beginning of this century. Hearon, Hiatt and Fordyce (1943) cite three patents, dating from 1920, 1930, and 1935. All those patents relate to the cellulose carbamate preparations and the reactions described were based on phenyl isocyanate for preparing derivatives although the claims in several cases were of a general nature, e.g. aliphatic or aromatic isocyanates. In the same work Hearon *et al* compared the reactivity of aromatic and aliphatic isocyanates with cellulose materials, using partially substituted cellulose acetate with dry cyanic acid, methyl, ethyl, phenyl and alpha-naphthyl isocyanates in several concentrations of pyridine as a solvent and catalyst. The main conclusion of this work is that reaction under homogeneous conditions using soluble cellulose acetates with aromatic isocyanates went to completion with all hydroxyl groups in about 10 hours at 40-50°C. The aliphatics, in similar conditions, reacted slowly and incompletely even after 137 hours at 40°C. Clermont and Bender (1957) cite the work of Schnaebeli (1952) who claims to have reacted the free hydroxyl groups of cellulose with phenyl isocyanate

in the presence of pyridine at 80-100°C for 12-14 hours, yielding a cellulose triphenyl-carbamate.

Apparently inspired by earlier work on the preparations of carbamates of cellulose, Clermont and Bender (1957) report what seems to be the first work of a wood:isocyanate reaction: wood veneers of spruce, poplar and birch swollen in dimethylformamide (DMF) were exposed to vapours of phenyl isocyanate for 1-->2 hours at 100-125°C. Although no weight gains were reported, high dimensional stability (anti-shrink efficiency - ASE of up to 77%), increased mechanical strength and no change in colour were observed. It was also noticed that excess isocyanate increased the tendency for reaction and that the reaction rate was shown to be dependent on temperature.

Baird (1969) reports a work where a study of dimensional stabilisation by vapour phase chemical treatment was carried out. This was based on the reaction of spruce with ethyl, n-butyl, t-butyl, allyl and phenyl isocyanates. The swelling agent and catalyst was DMF used both by a one-step treating process (DMF in solution with the isocyanate) and also by soaking the samples in DMF prior to the treatment with vapours of the isocyanates. Baird stated that the one-step treatment was unsatisfactory with phenyl isocyanate (Ph-NCO) because "the isocyanate polymerised on the inside of the treating cell and on the surface of the wood samples" whenever that DMF was used. Without DMF in the treating solution, the Ph-NCO did not polymerise appreciably but in this

case "the samples would remain unswollen and the isocyanate could not enter and bulk the wood structure". The samples which were soaked in DMF prior to treatment with Ph-NCO showed a weight increase of 65% and an ASE of 77% in agreement with the work of Clermont and Bender (1957). Based on these latter results Baird concluded that in this case "only a small amount of the isocyanate polymerised outside the cell walls since the samples exhibited a bulking effect of the order expected from their chemical content".

Relating to the other isocyanates used, few data are given for reactions with ethyl, t-butyl and allyl isocyanates. These reactions were reported to occur much slower than with n-butyl isocyanate (n-Bu-NCO) which is reported as a more successful process. Baird reports that n-Bu-NCO was found much more adaptable to a completely vapour phase treating process than was Ph-NCO. Although DMF was used as the solvent and catalyst no homopolymerisation is reported. The reaction of the DMF pre-impregnated samples is related as faster than the one-step vapour phase treatment of oven-dried samples. Increasing the content of DMF in the samples from about 10 to 55% increases the rate of reaction but no further increase was evident from 55 to 81%. Baird, apparently with no supporting evidence, attributes this fact to a possible complete swollen state of the wood at 50% DMF. It is also reported that ASE increases with the weight percent gain (WPG) reaching a maximum of 76% at 51% WPG

and that the rate of weight gain decreases when approaching 50%.

Observing that the rate of weight increase dropped rapidly with increasing moisture content of the samples Baird makes no comment about the possibility of n-Bu-NCO reaction with easily accessible hydroxyl groups in water rather than with the less accessible hydroxyls groups in wood cell polymers. He assigns the reduction in rate of weight increase to the immiscibility of n-Bu-NCO with water and also because the moisture reduced the concentration of the isocyanate in the vapour surrounding the samples. Finally Baird reports a 25% reduction in toughness and abrasion resistance as a consequence of vapour phase treatment of spruce in the range 14 to 31% WPG.

Up to this point it was not clear in any of the literature on the modification of wood with isocyanates, whether or not a reaction took place between the isocyanates and a wood cell wall component. Later, Rowell and Ellis (1979) used methyl isocyanate (Me-NCO), the simplest isocyanate, to modify Southern pine by uncatalysed reaction. They stated that the calculated volume of chemical addition to the wood was in close agreement with the volume expansion of the wood and that treated samples submitted to water leaching or to extraction with benzene/ethanol retained a significant amount of the chemical. In the first case they concluded that the chemical addition took place in the cell wall.

In the second case, that a urethane bond stable to leaching was formed.

Rowell and Ellis (1979) showed that the WPG increases with reaction time and that the ASE attained with Me-NCO reaches a maximum when the WPG is about 28-30%. Electron micrographs at the higher WPG's showed evidence of cell wall splitting. These workers suggest that this damage leads to a decrease in ASE similar to that observed in alkylene oxide treated wood at high WPG (Rowell *et al*, 1976).

Rowell (1980) describes the distribution of chemicals in southern pine reacted with Me-NCO at various levels of WPG. He isolated holocellulose by the sodium chlorite method and lignin by the sulphuric acid procedure. By means of Kjeldahl nitrogen determinations on modified whole wood and on holocellulose and lignin fractions Rowell (1980) verified that the degree of substitution (DS) by carbamate was higher in the lignin fraction than in the holocellulose at each WPG. From infra-red spectra of Me-NCO modified southern pine wood he confirmed that reactions took place on the hydroxyl groups of lignin and holocellulose to form stable urethane bonds, as had been earlier assumed by Rowell and Ellis (1979).

In other work, Ellis and Rowell (1984) report the results of a large experiment on the reaction of Southern pine with some mono & difunctional aliphatic and aromatic isocyanates. The monofunctional isocyanates used were ethyl, n-propyl, isopropyl, n-butyl p-tolyl and

phenyl isocyanates. The difunctional isocyanates used were 1,6-diisocyanato hexane (HDI), tolylene 2,4-diisocyanate (TDI) and isophorone diisocyanate (IPDI). Solvents/catalysts used were triethylamine (TEA), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). All reactions were conducted at 120°C in the liquid phase. Although these workers expected that the difunctional isocyanates would act as crosslinking agents, showing a greater effect on dimensional stability of wood treated than do monofunctional isocyanates at similar weight gains, they observed that the difunctional isocyanates did not bond well to wood cell wall hydroxyl groups and did not improve dimensional stability any more than did the monofunctional isocyanates. With the exception of HDI the difunctional isocyanate reacted products exhibited no dimensional stability after the first or second water soak test.

The main conclusions of the work of Ellis and Rowell (1984) are:

-phenyl and p-tolyl isocyanates, 1,6 diisocyanato hexane, isophorone diisocyanate, and tolylene-2,4-diisocyanate formed mostly nonbonded polymers in the wood voids when 5% or less catalyst was present. These nonbonded lumen-filling polymers did not increase dimensional stability or decay resistance;

-ethyl, n-propyl and n-butyl isocyanates reacted with wood with no solvent or catalyst gave modified wood that had 30 to 50% better dimensional stability than

unmodified wood and high resistance to decay. Weight loss in a standard soil-block test was generally 4% or less; -phenyl isocyanate, 1,6-diisocyanatohexane, tolylene-2,4-diisocyanate and n-butyl isocyanate in the presence of 35% DMF reacted with wood to give increased weight, volume and dimensional stability. The catalysed n-butyl isocyanate modified wood at 30 to 35% weight gain was 70% more dimensionally stable than unmodified wood and had high resistance to decay. Only about two percent of specimen weight was lost in a standard soil-block decay test.

Stating that an increase in wood volume occurs only when an isocyanate reacts with the cell walls, Ellis and Rowell (1984) compared the increase in wood volume of the treated specimens with the theoretical volume of the isocyanate added (calculated from weight gains of specimens and densities of the isocyanates). They concluded that most of the chemical in the specimens modified with HDI, IPDI and TDI must be in voids since the increase in wood volume was much less than the volume of the chemical in the wood.

Comparison was also made between the calculated amount of nitrogen added to the wood (derived from the weight gain) and the amount of nitrogen estimated by Kjeldahl nitrogen analysis of the specimens after milling and solvent extraction (benzene/ethanol 2:1 vol./vol.). They suggested that only the ethyl, n-propyl and n-butyl isocyanate modified specimens which lost only 10% or less of the nitrogen by extraction, were bonded to the

cell walls. In the case of TDI, although the volume of the treated specimen increased by a negligible amount (4%) of the volume of the chemical added, the percentage of nitrogen calculated was in very good agreement with the amount estimated by the Kjeldahl method. This led to the conclusion that if the chemical added was in voids and the WPG resulted from 'nonbonded polymer' formation such a polymer must be insoluble in the benzene/ethanol mixture used for extraction.

The effects of moisture on the wood-isocyanate reaction were investigated by Rowell and Ellis (1984). They reacted southern pine at 0%, 5% and 10% moisture content, with n-butyl isocyanate in the presence of DMF, at $120^{\circ}C$ and 150 lb./in^2 pressure. Some of the treated samples were submitted to the double water soaking method (described earlier by Rowell and Ellis, 1978), some were conditioned at 90% relative humidity and $27^{\circ}C$ and equilibrium moisture content (EMC) and ASE were determined. A final set of the treated samples was ground and then extracted with refluxing benzene/ethyl alcohol in order to determine the amount of treating chemical not permanently bonded to the wood. From these experiments it was found that:

- the weight loss after extraction increased with the moisture content of the samples before treatment;
- the second water soak ASE value decreased with the increase in the original wood moisture content of the samples;

- after equilibration for 32 days at 90% RH/27°C, the treated specimens showed a significantly lower EMC (6 to 12%) than the control (19.4%)

The conditioning tests at 90% relative humidity were carried out on unextracted specimens (presumably containg bonded and nonbonded chemical) and the samples with originally highest moisture content (10%) showed the highest ASE. These results suggest that the reaction between water in the wood and chemical took place within the cell wall and therefore, contributed to the ASE increase (bulking effect).

West and Banks (1986) studied the rate of reaction of Scots pine with n-butyl isocyanate by the means of measuring WPG as a function of time, in order to obtain topochemical information from the reaction profile obtained from whole wood. Since the curve WPG vs time, in theory, is a combination of curves representing the reactions of each component of the wood, the authors split the reaction profile into its component curves to provide information about the rate and the extent of reaction within each fraction. Through the calculation with the mathematical equation provided these workers concluded that the lignin asymptote could be explained in terms of reaction of all available hydroxyls in this fraction to form urethane. Based on published data, that wood cellulose is about 65% crystalline and that hemicelluloses are completely amorphous, West and Banks data suggest that about one hydroxyl per non crystalline

sugar unit is available for reaction. Their data indicate that lignin reacts about 10 times faster than polysaccharide.

2.2 MATERIAL AND METHODS

2.2.1 Isocyanates

The main objective of this study is to assess how chemically modified wood is affected in its sorption properties and dimensional stability. The use of isocyanates different in molecular size, functionality, reactivity and physical properties may help to obtain a basic understanding of the mechanisms involved by providing a good matrix of performance data related to systematically varied treatment systems. Particularly, as is indicated on the introductory chapter, there is potential interest in using difunctional isocyanates to induce crosslinking and to assess the contribution of these croslinkages to improve dimensional stability. Aromatic isocyanates are also very interesting due to their greater reactivity compared to aliphatic reagents requiring milder reaction conditions. This apparent advantage may be offset by their greater tendency to undergo side reaction.

Four isocyanates were carefully chosen from those available in the market:

1- n-Butyl isocyanate (n-Bu-NCO) - $CH_3(CH_2)_3NCO$: aliphatic, monofunctional; molecular weight: 99.13g; density:0.88g/cc

2- 1,6 Diisocyanatohexane (HDI) - $OCN(CH_2)_6NCO$: aliphatic, difunctional; molecular weight 168.2g; density: 1.04g/cc

3-   Phenyl isocyanate (Ph-NCO) - C_6H_5NCO: aromatic, monofunctional; molecular weight: 119.12g; density: 1.096g/cc

4-   Tolylene 2,4-diisocyanate(TDI) - $CH_3C_6H_3(NCO)_2$: aromatic, difunctional; molecular weight: 174.16g; density: 1.225g/cc

The choice of these four isocyanates was based on variation in size, functionality and reactivity:

- size: according to Tarkow at al (1966), the limiting size for the penetration of water soluble material into water swollen cell-walls is that of polyethylene glycol (PEG) 3000. They suggest an approximation of the radius of gyration of such a molecule, based on intrinsic viscosity measurements, to be about 18-20 angstroms. Hence the diameter of the capillaries in the complete water swollen wood should be about 36-40 angstroms. To avoid any problem of penetration and diffusion into or through the cell walls the isocyanates were chosen taking into consideration this limitation. An approximation obtained by means of a simple calculation of the volume and diameter of a molecule based on the molecular weight, density and Avogadro's number shows that the size of the chosen isocyanates meet the limiting size requirement (an assumption of spherical molecules was made for the diameters calculation - see Table 2.1)

- Functionality and reactivity: the use of a monofunctional and a difunctional isocyanate is needed in order to make possible a comparative study of the

mechanism(s) of reduction in water sorption by bulking and by crosslinking agents. The study of the "pure chemistry" of isocyanates reaction is beyond the scope of this work. However the use of aliphatic along with the more reactive aromatic isocyanates may permit the assessment of any indirect effect on wood-water sorption caused by this higher reactivity (e.g. effects caused by by-products formed by side-reactions).

Table 2.1 Molecular size of the isocyanates chosen[*]

Isocyanate	Molecular volume (Å^3)	Molecular diameter (Å)
n-Bu-NCO	187	7.1
HDI	269	8.0
Ph-NCO	181	7.0
TDI	236	7.7

[*] For the assumptions made for the calculations, see text above.

2.2.2 Substrate

Between species variation in the performance of chemically modified wood species has been reported. Rowell (1984) related some difficulties found in achieving dimensional stability with chemically modified Red oak and Teak, in spite of the good weight gain obtained. Stamm and Tarkow (1947) also reported that softwoods required a higher degree of acetylation than hardwoods to achieve the same reduction in swelling. Structural differences between hardwoods and softwoods such as the presence of a specialised conducting tissue in hardwoods (the vessels or pores quite different from the fibres that provide mechanical transport) produce

significant variation mainly in the permeability of wood. Although important, permeability seems not to be critical in the case of chemical modification as long as: 1) polar systems (able to swell wood) are used and 2) specimens are of small dimensions, especially in the fibre direction. This is because the formation of transient capillaries in the swollen wood facilitates diffusive penetration of the chemicals into and through the cell-walls (Ellwood and Thomas, 1968). Some differences between wood species in effectiveness of diffusion pathways may be anticipated associated with variation in chemical composition, crystallinity of cellulose, compactness of the cell-wall and extractive content. These differences may interfere not only with chemical penetration and reactivity (Rowell, 1975) but also with the hygroscopicity of the wood (Wangaard and Granados, 1967; Spalt, 1958; Stamm, 1964 and 1971).

Aside from the fact that little research has been carried out on chemical modification of hardwoods, these differences make the study of a softwood and a hardwood under the same treatment conditions potentially useful from the point of view of understanding the sorption behaviour of chemically modified wood.

With these thoughts in mind, beech (*Fagus sylvatica*) and Corsican pine (*Pinus nigra*) were chosen as examples of permeable hardwoods and softwoods. In order to minimize any within species variability, the samples of each species were prepared from a single board, from knot free sapwood. Also, blocks with the same number of

growth rings were preferentially chosen. It is recognized however, that in view of the importance of the assessment of within species variability in reactivity further study using a more comprehensive sampling schedule is desirable.

It was decided to concentrate the work on whole wood instead of on isolated cellulose, hemicellulose and lignin. This is because the hygroscopic properties for the constituents while in the whole wood may be different from those in the chemically isolated fractions because of changes occurring during extracting the constituents and also because of the interaction between these constituents in the whole wood (Skaar, 1972).

The specimen geometry was chosen in order to minimize the longitudinal dimension ensuring rapid reagent penetration into the cell lumen. Hence, samples 20 x 20 x 5 mm (radial by tangential by longitudinal) of each species were prepared from air dried sticks ensuring that the growth rings were parallel to the edges. After sawing, the blocks were carefully lightly sanded to remove loose fibre which otherwise might be lost during reaction, hence affecting the weight gain estimates.

2.2.3 Experimental procedure

The methodology used in the chemical treatment of the samples was that described by West (1988). However, some adjustment required by the use of

isocyanates other than n-Bu-NCO are presented below along with other aspects considered important.

2.2.3.1 Reaction vessel design

The experiments on chemical modification were carried out in conventional laboratory glassware (reaction vessel fitted with thermometer) under reflux in thermostatically regulated electric heating mantles. The ground glass joints were sealed with silicone grease and the condenser was protected with a guard tube with self indicator silica gel to minimize reaction of the isocyanates with atmospheric vapour.

2.2.3.2 Extent of reaction

The non-leachable weight gain (weight percent gain - WPG - defined as the amount of chemical taken up by the sample explicit as a percentage of its oven dried untreated weight) was chosen as the analytical procedure to assess the extent of the wood:isocyanate reaction. This method was complemented by a measure of the accompanying volume increase of the samples after treatment and by infra-red spectroscopy (see section 2.2.3.4) It is taken into account throughout this work that at a given level of reaction a reagent of lower molecular weight substitutes more hydroxyls groups and also that each difunctional isocyanate molecule may substitute two hydroxyls groups.

2.2.3.3 Extent of by-product formation

To ensure that the non-leachable weight gain is a true reflection of extent of reaction there is a need to assure that the adduct is chemically attached at the wood, since by-products formed in the cell wall, such as polymers with a molecular weight exceeding about 3500, may be merely entrapped as homopolymers (Stamm, 1977a). The catalysed reaction of n-Bu-NCO in pyridine 1:1 vol./vol. at $120^{\circ}C$ after 7hours under reflux in the presence and absence of 4 wood blocks (two beech and two Corsican pine samples), generated some residues. These were shown to be completely soluble in acetone. Infra-red spectra of milled wood samples after reaction and extraction with acetone showed absence on unreacted isocyanate and substituted urea. This confirms the effectiveness of acetone as a clean-up solvent for n-Bu-NCO and any by-products.

Since Ph-NCO, HDI and TDI show different reactivity to n-Bu-NCO, extent and nature of by-products was checked using the same methodology to confirm the efficacy of acetone as the clean-up solvent.

The HDI/Pyridine Reaction

25ml of HDI purchased from Aldrich Chemical Co., (stated purity 98% by weight) made up to 50ml with pyridine (BDH, stated purity 98% weight/weight) stored over KOH was heated at the boiling point of the solution ($\approx 120^{\circ}C$), for 7 hours under reflux in the presence and absence of 4 samples (2 beech and 2 C. pine samples,

total mass $\approx$5.0 g). After the 7hs reaction the liquid was transferred to weighing bottles and evaporated in a fan-oven at 105°C +/-2 $^{\circ}$C for 72 hours. In both cases, (presence and absence of samples), the liquid changed from white at room temperature to dark yellow after the 7hs time reaction and there were no precipitates in either reaction vessel. After the 72 hours evaporation in the oven the yield of residue in both cases was a transparent light brown very hard deposit, not soluble in acetone even after four hours under reflux (acetone boiling point $\approx$57°C). It seems that the portion of HDI that remained unreacted after the 7 hours under reflux polymerised due to the long evaporation period and maybe also reacted with moisture from the air in the oven.

The test was then repeated under the same conditions and at this time the liquid was evaporated for 16 hours only (simulating the conditions used do dry samples following clean-up). The residue, a transparent light brown viscous liquid in both cases (presence and absence of samples), was weighed. It was shown to be completely soluble in boiling acetone. Milled wood samples showed absence of any infra-red absorption band at 2275-2240 cm^{-1}. This confirms the absence of unreacted isocyanate remaining in the samples (Rowell, 1984) and the validity of the clean-up procedure.

Similar checks were carried out with Ph-NCO and TDI reagents. Here it was found a that very small amounts of acetone insoluble residue could form in the presence of wood. These amounted to only about 0.1% of the reagent

mass in the case of Ph-NCO and about 1.5% in the case of TDI reagent. In the case of TDI the residues formed may affect the weight gain achieved during the treatment when a higher amount of this reagent is used. The possible effect of these by-products in the volume increase and in the weight gain is discussed in section 2.3.3 and 2.3.4.

2.2.3.4 Evidence of cell wall bulking and bonding

The three criteria cited by Rowell (1975): volume change, permanence and infra-red spectra were chosen as evidence that chemical reaction has taken place in the cell wall and that bonding has occurred with the cell wall polymers.

Volume change - The presence of chemical in the cell wall is revealed by an increase in the oven dried volume of the samples. Strong evidence that most of the chemical ended up in the cell wall and not as a lumem-filling material is shown through a good agreement between the volume of the chemical added (calculated from weight gains of specimens and densities of free isocyanates) and the volume increase of the respective sample. It is assumed that molar volume of adduct is similar to that of reagents.

Permanence - Volume increase indicate the presence of chemical in the cell wall but this is by no means evidence of bonding, since non-bonded chemicals (e.g. polyethylene glycols) may be simply physically deposited within cell walls. However, such substances are removed by extraction with an appropriate solvent. The solvent

extraction followed by oven drying procedure described in the section 2.2.3.3 is therefore applied to produce evidence of chemical bonding.

Infra-red spectra - By recording infra-red spectra of wood flour prepared from treated blocks (KBr disk technique) further evidence of cell wall bonding can be produced. After a wood-isocyanate reaction the carbonyl band in the wave number region of 1730 cm^{-1} becomes stronger due to carbamate formation. Other absorption bands can be found at 1550 cm^{-1} due to -N-H- deformation and at 1270 cm^{-1} due to -C-N vibration. If any unreacted isocyanate remains in the sample it produces adsorption at 2275 - 2240 cm^{-1} (Rowell, 1984). Whilst substituted ureas formed by reaction between isocyanate and water give vibrations at 1645 cm^{-1} (Bayley and Critchfield, 1981).

2.2.3.5 Treatment

Before treatment, the blocks (10 replicates for each treatment) were solvent extracted by refluxing in toluene/acetone/ethanol (4:1:1 vol./vol.), oven dried overnight (103+/-2 ^{o}C for approx. 16 hours) weighed using a 4-place analytical balance and measured using a micrometer accurate to 0.02mm. Solvent extraction is required to reduce the possibility of extractive interference with chemical penetration referred by Rowell (1975). The oven dried condition is essential since the hydroxyl in water is more accessible than the hydroxyl groups available in wood components (Rowell

Table 2.2. Chemical composition of the species (source: Sjöströn, 1981). All values as percentage of dry weight.

	BEECH	CORSICAN PINE*
Total extractives	1.2	3.5
Lignin	24.8	27.7
Cellulose	39.4	40.0
Glucomannan (a hexosan)	1.3	16.0
Glucuronoxylan (a pentosan)	27.8	8.9
Other polysaccharides	4.2	3.6
Residual contents	1.3	0.3

* Data for Scots pine

Table 2.3 Assumed composition of the extracted species

Component	% Dry Weight of whole wood		Molec. Weight of monom. unit	Mean nº of OH/monom.unit
	BEECH	C.PINE		
Lignin	25(1)	28(1)	194(2)	1.16(2)
Cellulose	40(1)	40(1)	162(1)	3(1)
Hemicell.	35(3)	32(1)		
Hexosans	5(3)	17(2)	162(1)	3(2)
Pentosans	30(3)	15(2)	132(1)	2(2)

(1)- Sjöströn (1981)
(2)- Rowell (1980)
(3)- Assumed values for calculation purposes based on data by Sjöströn (1981)

Table 2.4 Maximum theoretical WPG based on single site --OH substitution(1). Crosslinking formation is assumed for the difunctional isocyanates.

Species	Moles OH/g	NCO	Mol. Wt.(g)	Max. WPG
Beech	0.0144	n-Bu-NCO	99.13	143
		Ph-NCO	119.12	172
		HDI	168.2	122
		TDI	174.16	125
C. Pine	0.0145	n-Bu-NCO	99.13	144
		Ph-NCO	119.12	173
		HDI	168.2	122
		TDI	174.16	126

(1)- 100% accessibility is assumed for all --OH groups including those in the cellulose fraction.

1984) and will lead to depletion of effective reagent. The blocks were then transferred to the apparatus described in 2.2.3.1 containing an amount of pre-heated isocyanate:anhydrous pyridine mixture (one molar solution in pyridine as swelling solvent and basic catalyst) sufficient to provide a three-fold excess of isocyanate over total hydroxyl groups (calculation based on data of Tables 2.2, 2.3 and 2.4). The data of Table 2.3 are derived from published work of Sjöström (1981) and Rowell (1980). For the calculations it is assumed that cellulose and the hexosans have 3, pentosans 2 and lignin approximately 1.2 hydroxyl groups per monomer unit (Rowell, 1980).

In the absence of more specific data, it is assumed that Corsican pine is similar in chemical composition to Scots pine. Since the analytical data are used only to calculate the amount or reagent needed to provide an approximate 3-fold excess, these assumptions are reasonable. According to Table 2.4, the number of moles of --OH/g calculated is 0.0144, for beech and 0.0145 for Corsican pine. The closely similar values to species with relatively different chemical composition illustrate the insensitivity of such values to the assumptions referred to above. The reaction times to achieve desired weight gain with each reagent were determined by means of preliminary reactions in which some blocks were removed at measured intervals of time. After reaction, the specimens were rinsed twice in cold acetone and then cleaned by refluxing in fresh acetone

for 3-4 hours to remove excess reagent and by-product, oven dried at 103+/-2 $^{\circ}$C and again weighed and measured.

2.3 RESULTS AND DISCUSSION

2.3.1 Extent of reaction

Five levels of reaction were carried out for each wood species by varying reaction time (Table 2.5), over the approximate range 5 to about 37 percent weight gain. These samples were used in the sorption and dimensional stability experiments described later. Higher weight gains were avoided in order to minimise the possibility of cell wall splitting with the consequent decrease in dimensional stability, described by Rowell and Ellis (1979).

Wood is a heterogeneous material and inherent variations among and within the various sets of samples (e.g. earlywood/latewood ratio, density and chemical composition) are expected to produce variability in weight gain. The weight gains achieved within sets however, show relatively small variation as indicated by the standard deviations. This may reflect the effectiveness of the sampling procedure.

Control blocks refluxed with the solvent and catalyst pyridine, showed insignificant weight gains, (about 0.5 percent with beech and virtually no weight gain with Corsican pine). Slightly higher retention of pyridine by beech wood has been reported by Ashton, (1974) although under different experimental conditions. It is suggested by this worker that "a low-boiling water soluble solvent such as acetone or methanol might be more effective than water in removing

Table 2.5 Weight percent gain (WPG) and treated samples volume increase compared to the calculated volume of chemical added (reaction temperature ≈118°C).

Species	Reagent	Reaction time (minutes)	WPG**	SD	Volume increase (% of O.D. untreated volume)	Theoretical chem. vol.
C. Pine	n-Bu-NCO	12	7.5	0.3	4.8	4.6
"	"	30	11.3	0.4	6.4	6.9
"	"	80	19.7	0.4	11.7	12.1
"	"	140	24.1	0.5	14.4	14.9
"	"	270	34.3	0.9	18.2	21.3
Beech	"	17	7.9	0.4	6.6	6.5
"	"	40	11.7	0.2	10.7	9.8
"	"	90	18.0	0.5	14.2	15.1
"	"	180	23.3	0.5	16.4	19.5
"	"	300	25.7	0.4	19.2	20.3
"	"	240	37.3	0.2	25.6	31.2*
C. Pine	Ph-NCO	6	9.6	0.3	5.3	4.7
"	"	10	17.6	0.4	8.5	8.7
"	"	13	19.3	0.9	10.1	9.5
"	"	20	25.9	1.7	13.3	12.8
"	"	45	29.6	1.2	13.8	14.6
Beech	"	10	7.7	0.5	5.4	5.2
"	"	15	12.9	0.8	9.1	8.7
"	"	30	15.4	1.0	10.2	10.4
"	"	60	22.8	0.7	16.6	15.4
"	"	150	26.3	1.3	20.9	17.7
C. Pine	HDI	8	6.1	0.2	4.1	3.1
"	"	70	12.9	0.8	8.1	6.7
"	"	120	17.5	0.8	9.0	9.1
"	"	180	19.5	0.5	9.6	10.1
"	"	420	22.6	0.3	10.1	11.7
Beech	."	10	9.3	0.4	6.1	6.6
"	"	30	12.2	0.5	7.9	8.7
"	"	50	16.0	0.3	10.7	11.4
"	"	150	19.3	0.4	12.0	13.7
"	"	420	23.1	0.4	14.5	16.4
C. Pine	TDI	15	5.0	0.2	2.2	2.3
"	"	20	6.4	0.3	1.2	2.9
"	"	90	7.0	0.3	1.8	3.2
"	"	240	10.7	0.7	2.0	4.9
"	"	360	8.6	0.4	1.9	3.9
Beech	"	20	4.0	0.2	1.4	2.4
"	"	30	5.9	0.3	2.8	3.6
"	"	40	7.5	0.3	2.8	4.5
"	"	90	9.3	0.3	4.2	5.6
"	"	180	11.0	0.5	4.8	6.6

* (n-Bu-NCO) = 1:2 vol:vol   ** mean of 10 replicates

the last of the retained polar compounds". This suggestion is supported by the low pyridine retentions observed in this work after acetone extraction. It is assumed that the retention of pyridine in the chemically modified wood is of similar magnitude to that in unmodified wood and therefore its contribution to the weight gain achieved is considered to be negligible.

2.3.2. Infra-red spectra

Infra red spectra were recorded using flour ground from control and treated specimens by the KBr disk technique. Each spectrum recorded was analyzed according to the criteria previously cited (section 2.2.3.4) and the relevant spectral data are summarized in Figures 2.1.a and 2.1.b. These data suggest strongly that the wood has reacted to form urethane and that no free isocyanate remain in the samples. All spectra retained the broad absorption of O--H stretch centred at 3400 cm^{-1} indicating that substitution was not complete. These findings are in line with published work of Rowell (1980) where carbamate formation was reported to occur in methyl-isocyanate modified whole wood.

2.3.3. Volume increase caused by reaction

Volume increases due to the treatments were assessed. They were compared to the theoretical volume of the chemical added, on the assumption that all adduct is located within the cell wall and also that carbamate adducts have the same specific volumes as the parent
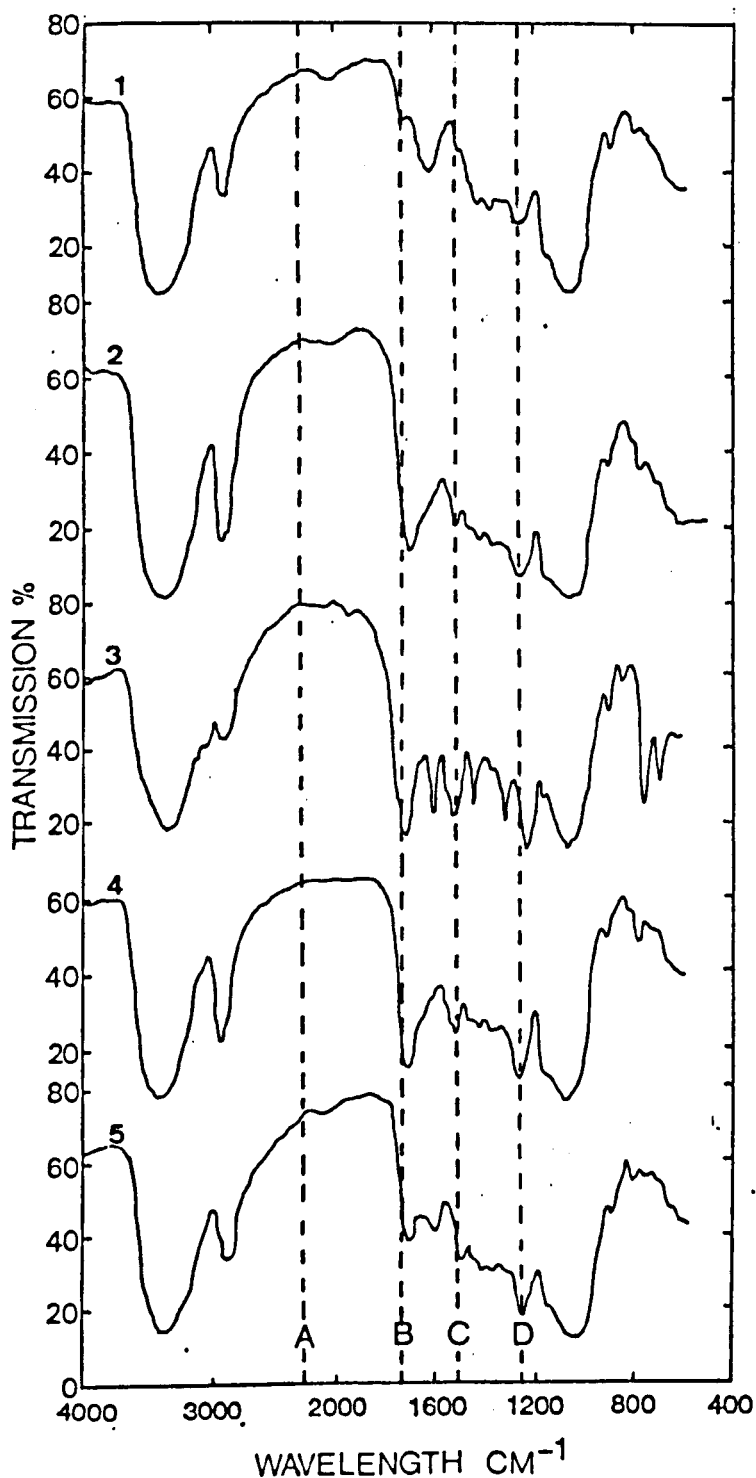
Fig. 2.1-a Infra-red spectra of isocyanate-modified Corsican pine wood. 1- Untreated (control). 2-Modified to 11.3 WPG with n-Bu-NCO. 3- Modified to 17.6 WPG with Ph-NCO. 4- Modified to 16.0 WPG with HDI. 5- Modified to 7.0 WPG with TDI. Main spectral regions are shown by the vertical lines: Line A (2275-2240 cm^{-1}): absence of unreacted reagent; Line B (1730 cm^{-1}): carbonyl (C=O) stretching in the urethane bond; Line C (1550 cm^{-1}): N-H deformation; Line D (1270 cm^{-1}): C-N vibration.
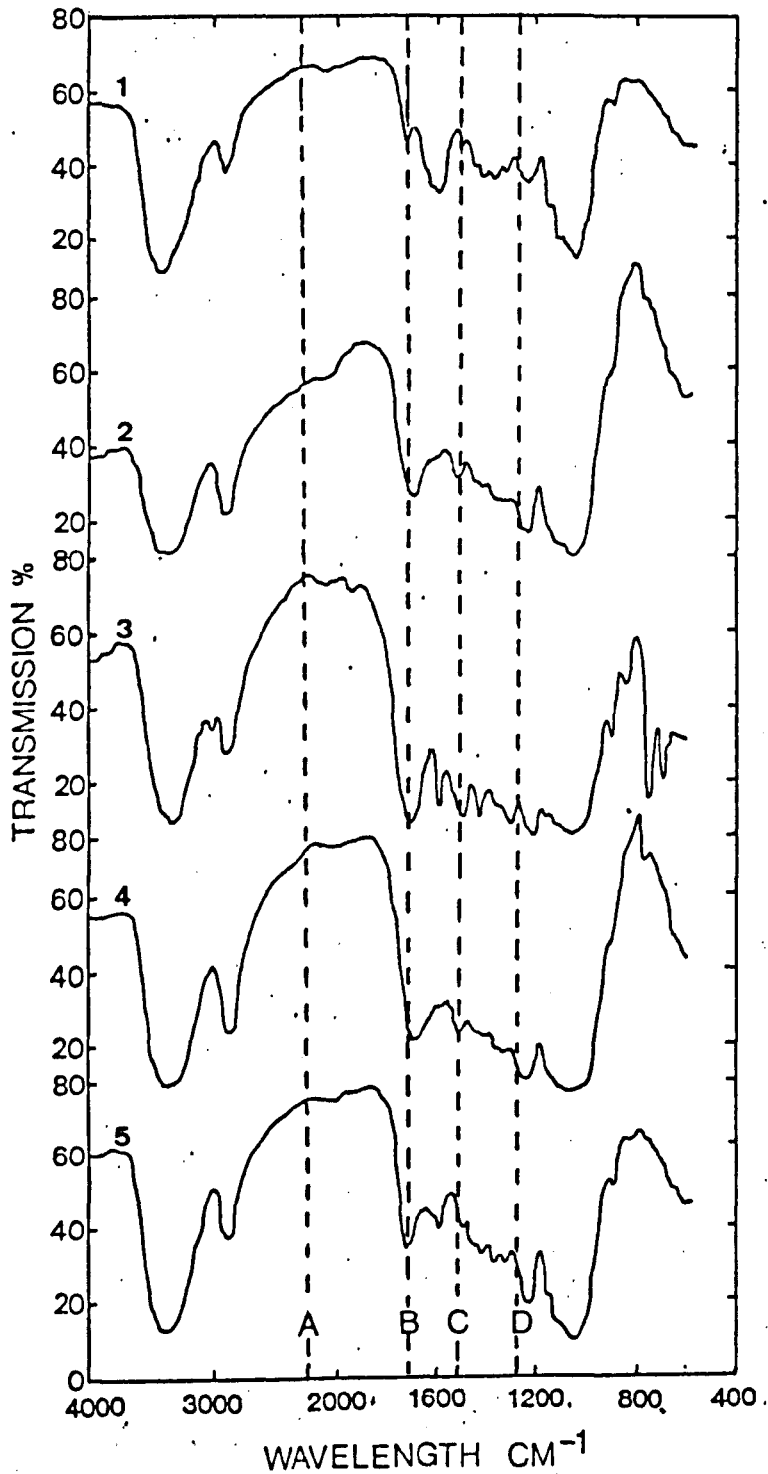
Fig. 2.1-b Infra-red spectra of isocyanate-modified beech wood. 1- Untreated (control). 2-Modified to 18 WPG with n-Bu-NCO. 3- Modified to 15.4 WPG with Ph-NCO. 4-Modified to 19.3 WPG with HDI. 5- Modified to 7.5 WPG with TDI. Main spectral regions are shown by the vertical lines: Line A (2275-2240 cm^{-1}): absence of unreacted reagent; Line B (1730 cm^{-1}): carbonyl (C=O) stretching in the urethane bond; Line C (1550 cm^{-1}): N-H deformation; Line D (1270 cm^{-1}): C-N vibration.

isocyanates. A comparison between theoretical and experimentally determined volume changes, expressed as percentage of the respective oven-dry untreated volume of the samples, is presented in Figs. 2.2 and 2.3. The figures show convincingly that, with the exception of TDI, there is close agreement between theoretical and experimentally values, suggesting that the adducts are located within the specimen cell walls throughout the treated range and are therefore acting as bulking agents. The n-Bu-NCO results are in agreement with the published literature (Baird, 1969 and Ellis and Rowell, 1984). With HDI and Ph-NCO however, these data are in contrast with those reported by Ellis and Rowell. Ellis and Rowell (1984) found that the volume increase shown by specimens modified with these isocyanates was much less than the theoretical volume of the chemicals in the wood. From this, they concluded that most of the adduct was in voids and not bonded within the cell wall. This contrast is believed to be at least in part explained by the different reaction conditions and catalysts (dimethyl formamide and triethylamine) used by these workers. Baird (1969) has reported that some homopolymerization occurs with Ph-NCO when dimethyl formamide (DMF) is used as the solvent/catalyst. Furthermore, Ellis and Rowell did not report drying the catalysts. If moisture was present during their experiments side reactions to form ureas is a real possibility. In other work, Rowell and Ellis (1984) report that when moisture is present during isocyanate reactions with wood, significant non-bonded,
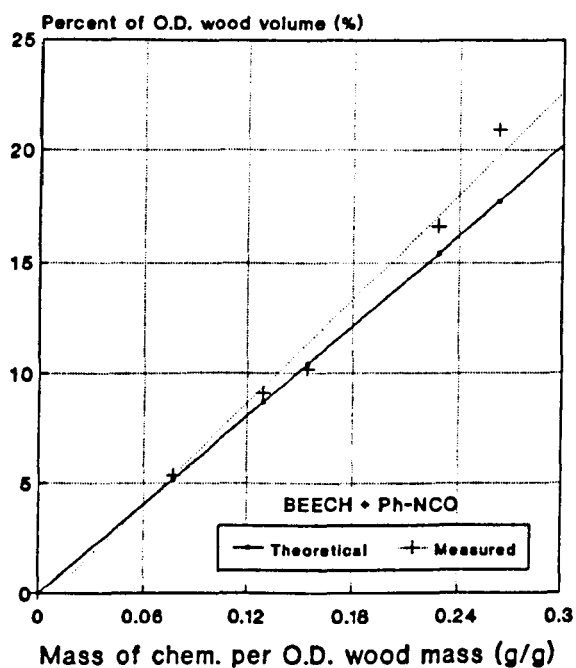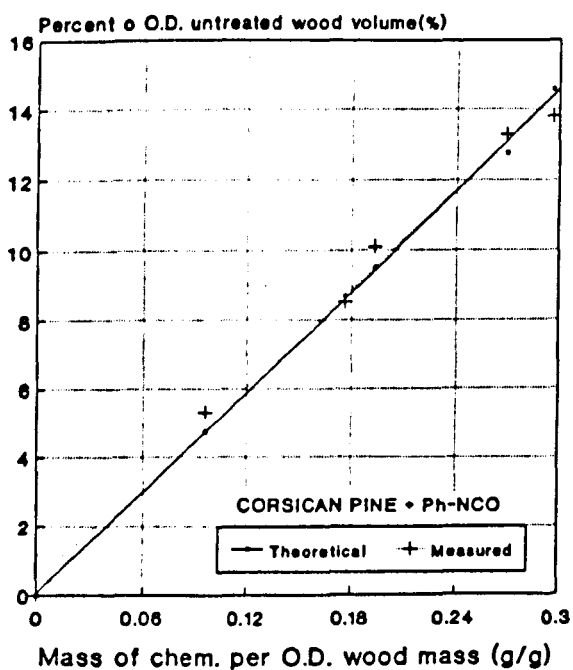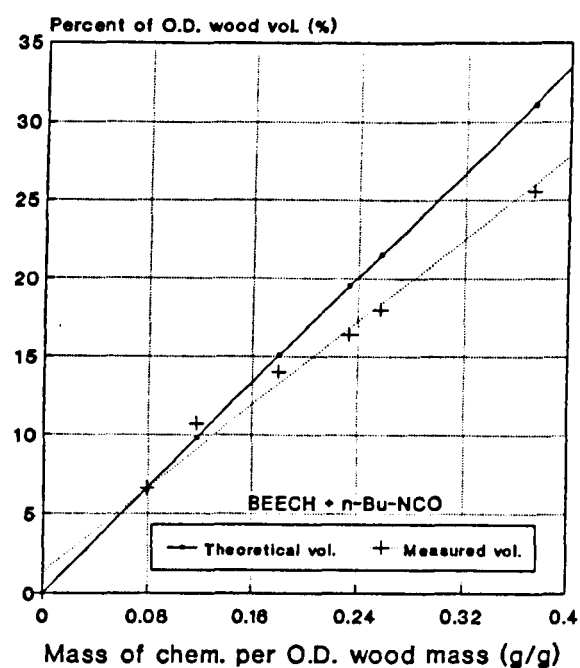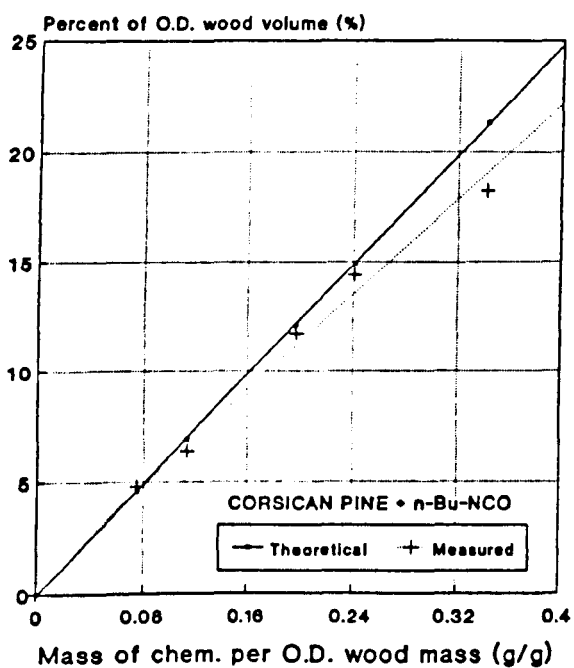
Fig. 2.2 Comparison between theoretical and measured volume increases - monofunctional isocyanates.
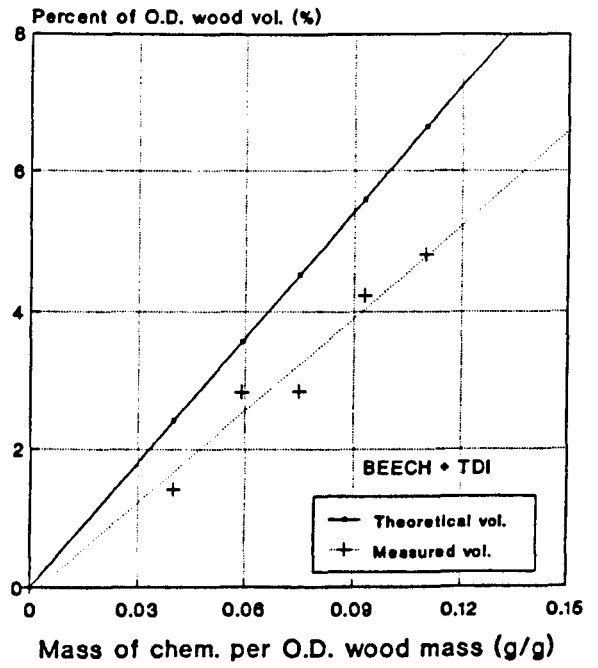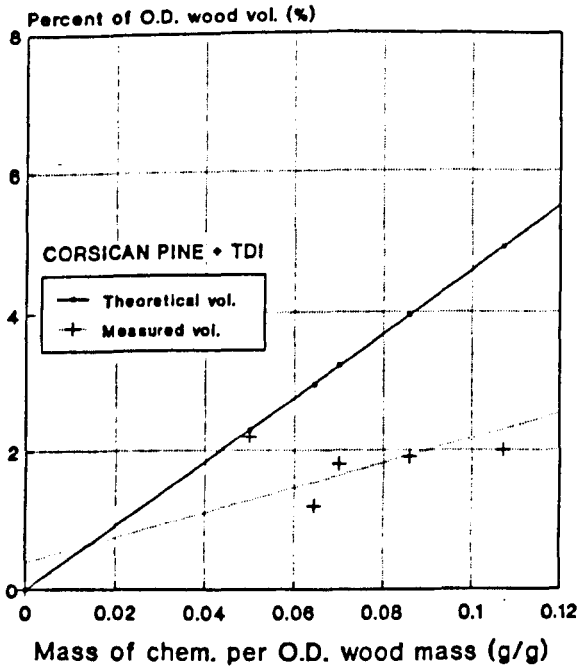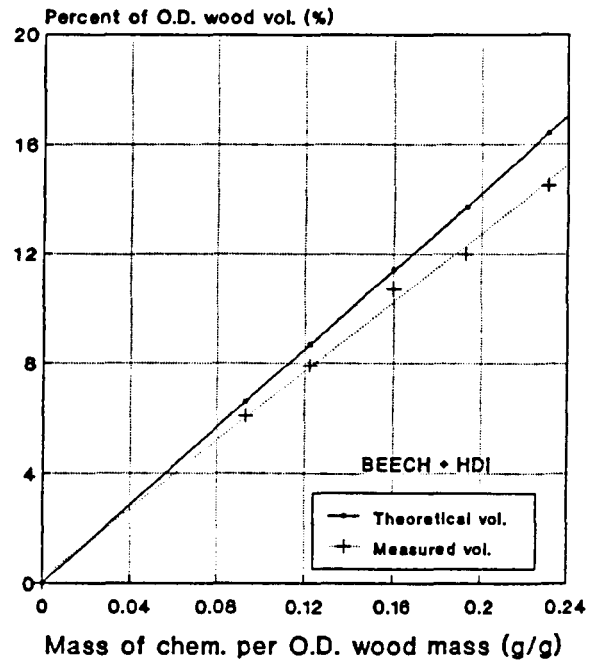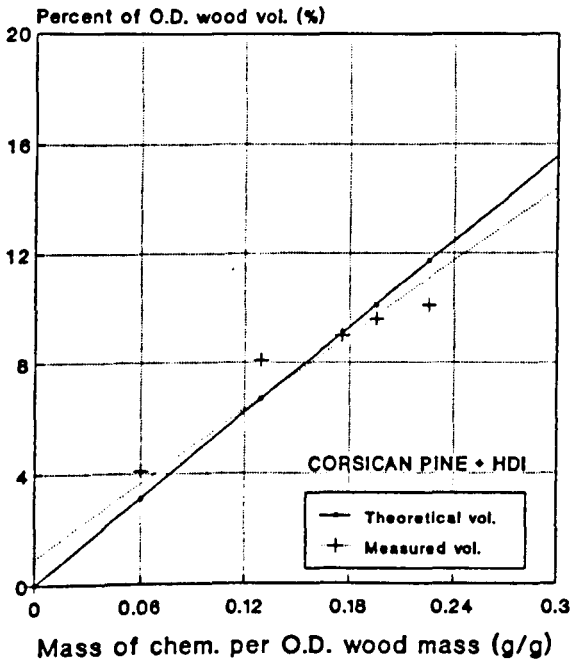
Fig 2.3 Comparison between theoretical and measured volume increases - difunctional isocyanates.

soluble adduct may be formed by the reaction between the isocyanate and free water.

In the present work, TDI reacted samples show inconsistent volume increases when compared to the theoretical chemical volume (Fig. 2.3). Similar inconsistency was found by Ellis and Rowell (1984) for a series of isocyanates including TDI. During the experiment with TDI described in section 2.2.3.3 it was found that a by-product, non-soluble in acetone, was formed. The discrepancy found between the volume increase and the calculated chemical volume suggests that a similar by-product was probably formed within the cell lumens during the TDI reactions. It is likely therefore, that the total mass insoluble is proportionally higher than that found during the preliminary test accounting for the above-mentioned divergences. Since these by-products are located in the lumem they are not producing volume increase and therefore, are not acting as bulking agents. Hence, unless TDI acts as an effective crosslinking agent its efficacy as a dimensional stabiliser is likely to be relatively poor.

2.3.4. Reaction rates

The reaction between the wood specimens and the four isocyanates occurred readily. The relationships between weight gains and treating time, as would be expected, varied appreciably with the wood species treated and with the isocyanate used. These relationships are shown in Fig. 2.4 where weight gain (WPG) versus
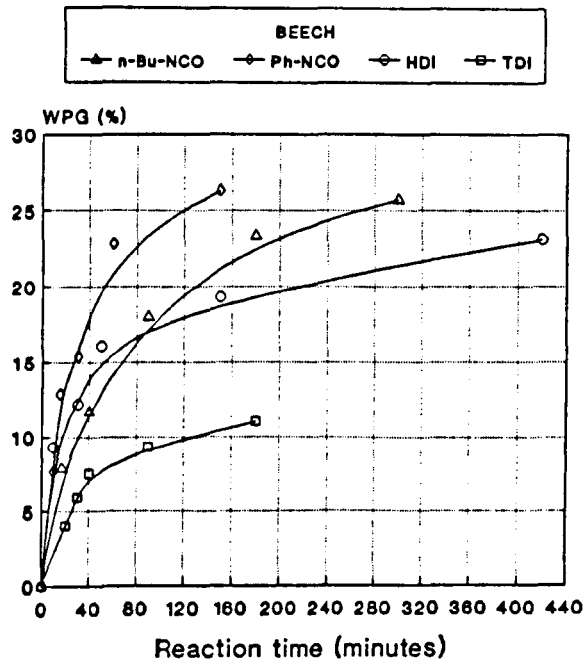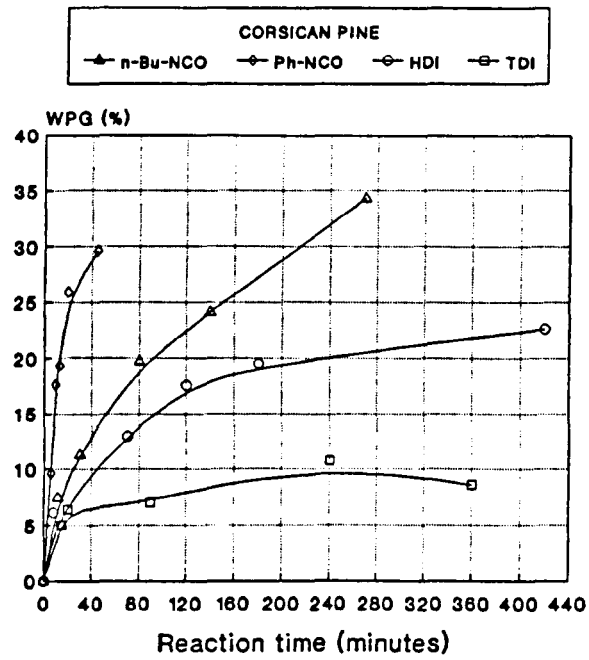
Fig. 2.4 Reaction rate based on the weight percent gain (WPG) for the four isocyanates with the two wood species.

reaction time curves are plotted for each isocyanate and wood species. The monofunctional isocyanates seem to react faster than the difunctionals with both wood species. With beech wood however, the difunctional HDI appears to react slightly more rapidly than n-Bu-NCO in the early stages. As the reaction proceeds, n-Bu-NCO becomes faster. In general, the monofunctional reagents react slightly faster with the softwood than with the hardwood whereas the difunctional ones seem to react quicker when beech samples are used. Parallel experiments, when samples of the two wood species were reacted together with each isocyanate in the same reaction vessel confirmed the above observation. The cause of this difference in behaviour has not been further investigated.

Due to differences in molecular weight and functionality, comparison between reaction rates of the various isocyanates based on WPG may be misleading. From the point of view of interpretation of the results concerning the reaction rates of the four isocyanates it is better to assess the extent of reaction, expressing the uptake as a fraction of the total (theoretical) hydroxyls reacted. Assuming that all adducts are in the cell wall and carbamate bonds only are formed, with no polymerization, a linear relationship between percent of --OH depleted and weight gain must exist. Hence the percentage of --OH depleted may be calculated from each WPG by simply dividing the actual WPG by the theoretical maximum. The theoretical maximum WPG (Table 2.4) was

calculated for each isocyanate and for the two wood species based on data of Table 2.3, assuming total accessibility for the cellulose fraction. For the difunctional isocyanate it is also assumed that the two functional groups react with wood --OH groups forming single crosslinks (i.e., monomeric croslinking).

Figure 2.5 shows the reaction rates of the four isocyanates reacted respectively with Corsican pine and beech woods, plotting the percentage of --OH depleted as a function of reaction time. These curves are not extrapolated beyond the range of experimental points determined. The rates are greater at the lower levels of addition tending to decrease at different extents of reaction (depending on reagent and species) as the reactions proceed. Since these curves were obtained under conditions of excess isocyanate this decline in reaction rate is likely to be caused by a decrease in the amount of --OH available (West and Banks, 1986).

Substantial differences in the reaction rate are visible between the four isocyanates and also between the wood species within the range of WPG shown. Because of the higher rate of the difunctional reagents and the lower rate of the monofunctional reagents with the hardwood (see above), HDI appears to react at a slightly higher rate than Ph-NCO with beech. With Corsican pine however, Ph-NCO reacts faster. The order for Corsican pine wood reaction rate is Ph-NCO > n-Bu-NCO > HDI > TDI. For beech wood the order is HDI > Ph-NCO > n-Bu-NCO > TDI; Even when the reaction rates are
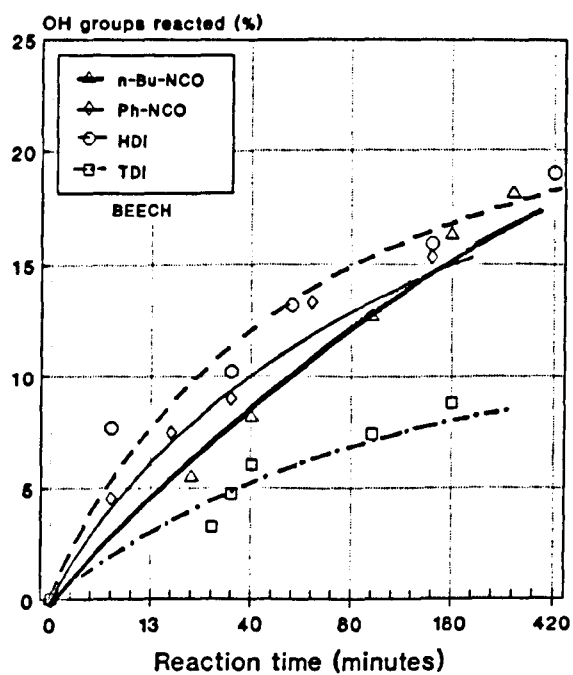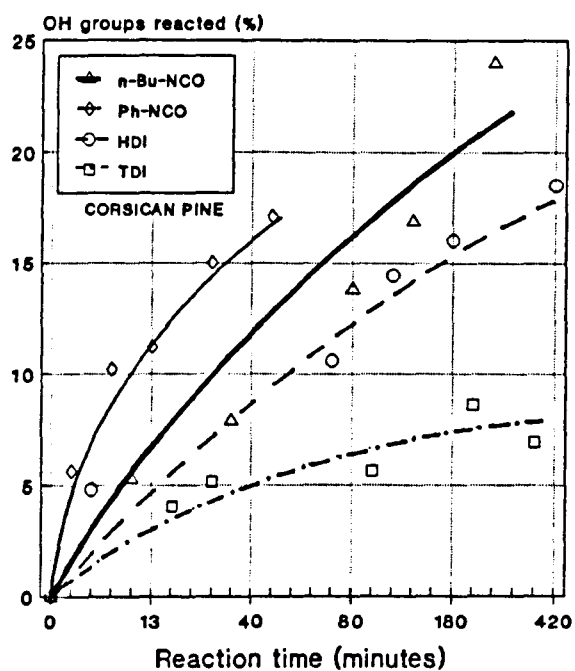
Fig 2.5 Reaction rate based on percent of total hydroxyl groups reacted, for the four isocyanates with the two species.

expressed in this more systematic way, no totally consistent trend between rate and molecular property is apparent. It seems likely that the overall rate of reaction is influenced by several factors, e.g. reactivity of the isocyanate group due to inductive effects; molecular size; molecular shape; molecular flexibility. It is beyond the scope of this work to investigate these factors.

The assumption of exclusive carbamate formation by the adducts probably overestimates the TDI reaction rate, since it appears that part of this chemical is probably polymerized outside the cell walls. Notwithstanding this effect, TDI still shows the lowest reaction rate with wood of the four isocyanates studied. This is an example of how reactivity is influenced by environment. Although more reactive in homogeneous reactions than n-Bu-NCO and HDI (Arnold et al, 1957), TDI did not react quickly in the heterogeneous wood environment. This may be the result of its bulky molecular size and relatively high rigidity. However, the low final weight gain may be the consequence of rapid addition occurring with this reagent early in the reaction precluding other molecules from reacting by simple steric blocking making access to remaining --OH groups difficult. The higher homogeneous reactivity may also induce TDI to undergo side reaction very easily with traces of water, forming loose complexes (e.g. soluble urea derivatives), as pointed out by Rowell and Ellis,

1984.　　These　are　leached　out　during　the　acetone
extraction resulting in low bonded WPG.

CHAPTER THREE

SORPTION STUDIES

3.1 LITERATURE REVIEW

3.1.1 Sorption phenomena

According to McLaren and Rowen (1951), sorption is the process in which vapour molecules are attached to sites distributed throughout the bulk phase of an amorphous or partially crystalline solid. The term sorption makes no distinction between adsorption and desorption, respectively the gain and loss of adsorbate. The take up may be monomolecular or polymolecular but in general rarely exceeds an average of ten molecules thickness (Stamm, 1964).

The internal surface of dry wood is quite large, amounting to 0.2 m^2 per gram for wood with a specific gravity of 0.4 (Stamm, 1952); The internal surface of wood swollen by water or other polar liquid is very much larger corresponding to 200-300 m^2 per gram (Stamm and Millet, 1941). Since sorption is proportional to the surface area of the sorbent, wood and other cellulosic materials e.g. paper, are highly adsorbent materials specially in the case of polar adsorbates like water vapour which cause swelling with consequent increase in specific surface. As these materials sorb water vapour they undergo change in dimensions and other properties (McLaren and Rowen, 1951).

3.1.2   Sorption isotherms

Although sorption is in fact a surface property meaning that the amount sorbed is proportional to the surface area of the sorbent, for the wood-water system, the sorptivity is usually expressed as a fraction or percent of the wood dry weight, i.e. the ratio of the mass of water vapour sorbed to the oven-dry mass of the wood. This avoids the difficulties associated with measurement of internal surface areas (Prichananda, 1966). This ratio is usually defined as the moisture content of wood and when this moisture content is at equilibrium with the ambient atmosphere is designated as the equilibrium moisture content (EMC) of wood. At a given temperature it is approximately proportional to the ambient relative humidity (RH) or relative vapour pressure (h). When the EMC is plotted against RH or h at constant temperature the resulting curve is the sorption isotherm (Skaar, 1988). Sorption isotherms are generally temperature-dependent. Specifically, the amount of vapour sorbed decreases as temperature increases. At equal relative humidities, differences of up to 5% in EMC exist between different temperatures (Simpson, 1979). Skaar (1988), citing results of several workers, reports decreases in EMC varying from 1 to 1.3% per $10^{\circ}C$ increase, in the temperature range 20 to $100^{\circ}C$.

Pidgeon and Maass (1930), Stamm and Hansen (1937), Barkas (1949), Higgins (1957), Kelsey (1957), Spalt (1957 and 1958) Wangaard and Granados (1967) and Prichananda (1966) are among the investigators who

showed that all wood water vapour sorption curves are characterized by the sigmoid shape described by Urquhart (1960) as type II sorption isotherms. Actually, according to Skaar (1988), three kinds of sorption isotherms from the five described by Urquhart (1960) are applicable to the wood water system, as postulated by several sorption theories discussed by Simpson (1979) and Skaar (1972 and 1988). The sigmoid shape of the type II appears to an amalgam of the types I and III. Type I characterizes the sorption of a molecular monomolecular layer of vapour (Langmuir, 1918) and Type III is obtained when several layers of sorbate are formed on the substratum (polymolecular sorption). In the Type I sorption the attraction between the sorbent and the sorbate is greater than between the sorbate molecules themselves in the liquid state. In the Type III this attraction is considered to be minimal.

The monomolecular layer can also be considered as a hydrate formed by the vapour with the substrate (wood), and the polymolecular sorption may also be viewed as a solution of the sorbent in the hydrated water. This model is proposed by Hailwood and Horrobin (1946) (see section 3.1.4).

The sigmoid shape of the type II isotherm is determined by regions of relative vapour pressure in which these two types successively become dominant. The line of demarcation between the types of sorption is by no means sharp, since there are some indications that adsorption takes place in the second layer long before

the first layer becomes completely filled (Babbitt, 1942). Stamm (1964) analyzing polymolecular adsorption on the basis of the surface theory of Brunauer-Emmett-Teller-(BET), (1938) states that different sorptions sites may exert different attractive forces for the vapours, making it possible for the most active site to take its second molecule before a less active site takes on its first. In the same way, at the upper ranges of relative humidities, condensation may overlap the region of multilayer sortion (Browning, 1963).

According to Wangaard and Granados (1967) monomolecular or surface sorption predominates at the low relative humidities and polymolecular sorption, held in solid solution or as multilayers built up successively on the monolayer, predominates in the intermediate and higher ranges of relative humidities. True capillary condensation is believed to take place at the upper range of relative humidities as the isotherm rises steeply when the saturation pressure is approached. The extent of condensation is not yet fully understood. The Kelvin equation, relating the condensation of water vapour to relative vapour pressure and capillary size predicts that true capillary condensation can occur in pre-existing capillaries down to sizes approaching molecular dimensions. According to Stamm (1964), the major part of capillary condensation occurs in the microscopically visible capillary structure of wood and just to a limited degree, within the cell walls. Basing his opinion on studies of specific gravity of the wood substance and of

the cell walls he concluded that most of the true capillary condensation taking place within the cell walls must be confined to the relative vapour pressure range of about 0.90 to 0.995 and cannot exceed 2 percent of the volume of the dry cell wall in the wood. Weichert (1963) however, found a decrease in the swelling rate with increasing moisture content in the relative range above 90 percent suggesting that a significant volume of pre-existing voids exists in the cell walls where water may condense without causing correspondent swelling.

3.1.3 Sorption hysteresis

It has long been recognized that the wood sigmoid sorption isotherms differ depending upon whether moisture is being adsorbed or desorbed. Several investigators, working with small specimens under carefully controlled conditions extending from saturation to practically zero relative vapour pressure, found higher moisture-content values during desorption than during adsorption for the same equilibrium relative vapour pressure (Stamm, 1952). This phenomenon known as sorption hysteresis has been widely studied and has been variously explained as being caused by: a reduction in the number of surface sites due to lateral hydroxyl-to-hydroxyl bonding upon desorption to dryness (Urquhart and Williams, 1924 and Urquhart 1960); differences in the degree of aggregation or dispersion attained by the gel respectively in dry and saturated conditions (Barkas, 1949 and Spalt, 1958); differences between advancing and

receding contact angles of water against the capillary
walls producing higher wettability under desorption than
under adsorption conditions (Zsigmondy, 1912 and Chen and
Wangaard, 1968).

According to Stamm (1964), the presently
favoured explanation for sorption hysteresis in cellulose
materials is that given by Urquhart and Williams (1924).
However, Spalt (1958), working with several softwoods and
hardwoods, found that hysteresis over the entire range
of relative humidity is predominantly influenced by
polymolecular sorption. Although stating that the basic
mechanism of hysteresis is most reasonably ascribed to
lateral bonding, he describes hysteresis as a result of
two series of equilibria attained by the cellulose
material, starting from a dispersed state in desorption
and from a more highly aggregated state in adsorption.
This explanation is essentially similar to that of Barkas
(1949), where hysteresis is explained in terms of plastic
deformation of the gel on the desorption of water vapour.
In this case the increased internal stresses are
believed to decrease the vapour pressure on the
desorption side of the loop in a way similar to the
effect of an external hydrostatic pressure on the vapour
pressure of a liquid.

The explanation concerning to the difference in
wettability was first presented by Zsigmondy (1912),
based on the behaviour of silica gel during desorption
and adsorption of water vapour. Barkas (1949) has
commented on the difficulties of this theory at low

vapour pressures, where capillary condensation is not possible. Stamm, (1964) also believes that differences in the curvature of the menisci involving the concept of angle of wetting, is meaningless due to the lack of solid-vapour interfaces in the wood capillary system.

Notwithstanding this effect, Chen and Wangaard, (1968), working with several tropical woods, found that in the upper range of relative humidities (above 60-70 percent), polymolecular and total sorption hysteresis, under isotherm condition, are positively correlated with wettability hysteresis. This suggests that sorption hysteresis is, at least in part, a consequence of the difference in the wettability of the cell wall capillaries when undergoing adsorption or desorption. The contribution of monomolecular sorption hysteresis to the total hysteresis was reported to be of minor importance in the range of relative humidities higher than 60%, as was found to be the case by Spalt (1958) and Wangaard and Granados (1967). These works give partial support to Zsigmondy's explanation of hysteresis as a phenomenon of capillary condensation.

3.1.4 Mechanisms and theories of sorption

Both lignin and hemicellulose, as well as cellulose contribute to the sorption of water vapour by wood. According to Christensen and Kelsey (1959), for wood of *Eucalyptus regans*, cellulose contributes 47 percent, the hemicelluloses 37 percent and lignin 16 percent to the total water sorption capacity of wood.

Cellulose however, is partially crystalline and water is adsorbed only in the noncrystalline regions and on the surface of the crystallites.

The noncrystalline regions and the surface of the crystallites appear to be responsible for initial adsorption brought about mainly by hydrogen bond formation with unbonded hydroxyl groups (Browning, 1963). These initial sorbed water molecules make the fibre start to swell. This leads to breakage of secondary hydrogen bonds between hydroxyl groups within the less ordered regions, with simultaneous surface development. The number of active sorption centre increases as more water is adsorbed and, since the crystalline regions are not swollen in water, ultimately the formation of more additional sorption centres is restricted by the network structure of the fibre (Howsman, 1954).

According to Morrison et al (1959), the potential surface of cellulosic materials is largely or completely developed at the water content corresponding to the completion of the first monolayer. The rapid rise in adsorption at higher relative humidity is only slightly influenced by the formation of new sorption centres during swelling. As further sorption occurs, it is supposed that multimolecular layers of water molecules are built up successively on the monolayer first formed (Brunauer et al, 1938) or that a solution of the water in the polymer is established (Hailwood and Horrobin, 1946 and Simha and Rowen, 1948). Multilayer formation or polymer-liquid mixing occurs even at very

low humidities and increases gradually with increasing relative vapour pressure, tending to become predominant in the higher ranges of relative humidity.

Although the sorption phenomena have been extensively treated in the literature, specially since about 1940, no theoretical approach has adequately described the sorption of water vapour by hygroscopic polymers such as wood and textile materials over the entire range of relative vapour pressures.

Skaar (1972 and 1988), Simpson (1973 and 1979), and McLaren and Rowen, (1951) have reviewed and discussed in detail most of the existent sorption theories. According to Skaar, (1988) the various theories of water sorption can be divided into two groups. The first group treats sorption principally as a surface phenomenon and the second group as a solution phenomenon. In the surface sorption theories, represented by the Brunauer et al (1938) (BET) theory, the fibre is considered to have a large amount of internal surface containing residual polar groups (mainly hydroxyl groups in the case of wood), which can strongly adsorb water forming a layer one molecule thick, (the monolayer). In order to account for the high relative humidity end of the isotherm, additional layers are assumed to build up as multilayers on the first monolayer. In the solution theories, represented by the Hailwood-Horrobin (1946) theory, the initial sorption is attributed to surface binding, with water combining with units of the polymer to form hydrates. In the following secondary phase, water is

assumed to be in solution with the polymer (dissolved water).

According to Howsman (1954), the two classes of sorption theory, surface sorption and solution sorption, are not so different as they appear since both classes postulate the presence of strong bonding with part of the water intimately associated with cellulose molecules (monolayer, hydrated water) and part distinctly less intimately associated (multilayer, dissolved or liquid water). In line with these items, Venkateswaran (1970) has listed the equations of a number of sorption models where two common assumptions are generally made in the derivation. Skaar (1988) expressed these assumptions in terms of water sorption by wood as follows: the existence of two kinds of sorbed water, primary and secondary where the energy of interaction of the primary sorbed water is higher than that of the secondary sorbed water; the secondary water is sorbed at a constant energy of interaction with the moist wood equal to the heat of condensation of liquid water. Furthermore, concerning the similarities between the two groups of theories, the mathematical expression for multilayer surface sorption and for extremely imperfect solutions have the same form, as pointed out by White and Eyring (1947).

Simpson (1973 and 1979) 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 models is poor. So far as the degree of fitting is concerned, with the exception of the BET, all models tested gave an excellent representation of the isotherms, the Hailwood-Horrobin model showing particularly good fit between model and experiment.

3.1.5 Chemically modified wood isotherms

Much of the work carried out with wood has been concerned with the influence of conditioning and treatment upon sorption isotherms and hysteresis. Wangaard and Granados (1967) refer to an extensive bibliography which led to the present concepts of sorption phenomena in wood. An excellent review is also included based on the works of Browning (1963), Kolmann (1959) and Stamm (1952 and 1964). The bulk of these works however, relate to the moisture content-relative humidity relationship of unmodified wood, (Spalt, 1957; Stamm, 1964; Skaar, 1972 and 1988; Siau, 1984 and references therein) although a few exceptions can be found.

Higgins (1957) describes a study where sorption isotherms were determined for 12 species by means of conditioning of the samples in several relative humidities controlled by saturated salt solutions in small sealed vessels. Among the species, he included samples of Southern yellow pine impregnated with phenolic resin (11.3 and 13.3 lb. of phenolic resin per cubic foot

of wood). He claims that a considerable reduction in EMC values, volumetric shrinkage and fibre saturation point was obtained. The EMC value reduction attained in impregnated pine was found to be proportionally greater at the higher relative humidities than at the lower. Hysteresis was still evident at the higher ranges of RH even with an impregnation of 13.5 lb/ft^3 of wood. Higgins also observed that the effects of impregnation of pine with the phenolic resin were probably due more to blocking of capillaries than to shielding of hydroxyl ions. No details of the 'phenolic resin' or of the method used to impregnate the wood is given in the work of Higgins. Stamm and Tarkow (1947) however, state that "phenolic resins have been formed within the intimate cell-wall structure of wood using an unpolymerized phenol-formalin-catalyst mix or a water-soluble phenol-formaldehyde resinoid of sufficiently low molecular weight to penetrate the cell-wall structure and sufficiently polar to bond to the active groups of the wood". Impreg (resin-treated uncompressed wood) and Compreg (resin treated compressed wood) are results of this treatment.

In research carried out by Risi and Arsenau (1957), vapour phase acetylated birch wood samples were exposed to adsorption in a series of relative humidities produced over saturated salt solution. The temperature of conditioning varied between 23 and $25^{o}C$. From the results they concluded that the dimensional stability of acetylated wood depends upon the combined effects of

bulking and decreased hygroscopicity as a result of the introduction oh the acetyl groups into the cell-walls. There is no allusion however of the extent to which each of these effects influence the dimensional stability achieved.

An important study in the area of isotherm determination for treated wood is that of Spalt (1958) who used a high vacuum apparatus and a basic experimental procedure described in earlier work (Spalt, 1957) to determine sorption data for 16 unmodified species and for acetylated spruce. Spruce acetylation was carried out with acetic anhydride in an evacuated reaction tube in the vapour phase, using pyridine as the solvent-catalyst (1:1 vol./vol.) The reaction was allowed to proceed at $90^{\circ}F$ for one month. The clean up procedure was described as 'prolonged evacuation of the vessel'. The treated samples with 32% acetyl content, were oven dried to constant weight and taken through a single desorption-adsorption cycle. The data were treated by means of the theoretical sorption model derived by Hailwood and Horrobin (1946). From the result of the analysis Spalt (1958) concluded that:

- an acetyl content of 32%, corresponding to a substitution number of 1.8 (Spalt assumed that all hydroxyl esterification was confined to cellulose) or to a 60% esterification of the hydroxyls, produced a 67% reduction in surface sorption and 62% decrease in capillary condensation;

- 76% of the reduction in the total water sorbed was caused by the bulking of capillaries by the ester i.e. the reduced hygroscopicity of acetylated spruce at saturation was predominantly attributable to the bulking of capillary voids.

- at saturation, 98% of the variation between species in the total water sorbed is accounted for by the amount of capillary-condensed water in the cell wall.

Also observing that the magnitude of water condensed in capillaries was independent of crystallinity when species with higher extractive content were considered, he pointed to a contrast between his work and that of Segal, Nelson and Conrad (1951). These workers, studying the effect of cellulose crystallinity on the sorption of water at 81% RH, found that the total water sorbed decreases linearly with increasing crystallinity. However, Spalt's conclusion was confirmed later in the work of Wangaard and Granados (1967). Comparing sorption characteristics of extracted and unextracted species they found no significant relation between total sorption and accessibility of bonding sites for either high or low extractive content material.

3.1.6 Chemically modified wood hysteresis

All the above mentioned causes of sorption hysteresis in cellulose materials are expected to be affected by the chemical modification process. The reaction and consequent deactivation of the hydroxyl groups is expected to reduce lateral hydroxyl-to-

hydroxyl bonding upon drying. At the same time, the bulking effect of adducts in the cell wall reduces void volume and keeps the cell walls in a partially swollen state reducing the degree of aggregation attained during desorption. Spalt (1958), working with white spruce acetylated to 32% weight gain, found a reduction in the hysteresis represented by an increase in the ratio adsorption to desorption from 0.790 to 0.816. These ratios were calculated by integrating the equations from the isotherms and are thus based on the ratios of the areas under the adsorption and desorption isotherms respectively. This reduction was proposed to be the result of a decrease in the number of sorption sites available and of a decline in the degree of aggregation that may be attained by the wood upon drying, caused by the bulking action of the ester.

Since polymolecular sorption hysteresis is a predominant factor influencing total sorption hysteresis (Chen and Wangaard, 1968) and the bulking effect is the main cause of reduction in polymolecular sorption (Spalt, 1958 and Wangaard and Granados, 1967), it seems reasonable to believe that the reduction in total hysteresis is at least in part, caused by the bulking of the cell wall capillaries.

According to Wenzl (1970), the lignin fraction shows greater sorption hysteresis than the carbohydrates although the shapes of the respective isotherms are quite similar. According to the results of Rowell (1980) obtained by analysis of wood reacted with methyl

isocyanate, lignin appears to react faster and to a higher degree of substitution than the holocellulose. It is possible therefore, that the decrease in hysteresis in chemically modified wood is also associated with a greater decrease in lignin hysteresis.

3.2 SORPTION ISOTHERMS DETERMINATION PROCEDURE

3.2.1 Experimental

3.2.1.1 Experiment design

The experiment was designed in order to analyze mathematically the sorption behaviour of chemically modified wood and particularly the relative contribution of the deactivation of sorption sites and the bulking effect on its hygroscopicity. Specimens of the two species untreated and treated to five different levels with the four isocyanates (see Table 2.5) comprised the basic matrix of variants. Each complete set of specimens was split into duplicates and taken through one complete sorption cycle from oven dry to saturated and back. Six different relative humidities (RH) within the range from zero to 100 per cent relative humidity were selected. Each duplicate was brought into equilibrium with a particular level of relative humidity first in adsorption and subsequently in desorption. Hence, the duplicates at each WPG gave rise to six points for both adsorption and desorption conditions. By plotting the equilibrium moisture content (EMC) obtained at any given relative humidity separately for each WPG level it was anticipated that a family of curves might be obtained for each species and for each isocyanate, where the unreacted specimens (controls) would show maximum EMC, the highest WPG minimum EMC and the intermediate WPG's would fall between the two according to the influence of treatment. Each set of treatments (comprised of samples of one

species treated to five levels of WPG and controls) is a
factorial design with three variables: WPG, relative
humidity and type of sorption (adsorption and desorption)
with duplicate specimens (Table 3.1)

Table 3.1 Main experiment design.

CORSICAN PINE

Reagent	Variables	Intervals	N° of Classes in variables
n-Bu-NCO	WPG (%)	0 7.5 11.3 19.7 24.1 34.3	6
	Relative humidity (%)	12 23 44 55 76 93	6
	Type of sorption	Adsorption and Desorption	2
		N° of variable combinations	72
		Replications	2
		Total n° of observations	144
Ph-NCO	WPG (%)	0 9.6 17.6 19.3 25.9 29.6	6
	Relative humidity (%)	12 23 44 55 76 93	6
	Type of sorption	Adsorption and Desorption	2
		N° of variable combinations	72
		Replications	2
		Total n° of observations	144
HDI	WPG (%)	0 6.1 12.9 17.5 19.5 22.6	6
	Relative humidity (%)	12 23 44 55 76 93	6
	Type of sorption	Adsorption and Desorption	2
		N° of variable combinations	72
		Replications	2
		Total n° of observations	144
TDI	WPG (%)	0 5.0 6.4 7.0 8.6 10.7	6
	Relative humidity (%)	12 23 44 55 76 93	6
	Type of sorption	Adsorption and desorption	2
		N° of variable combinations	72
		Replications	2
		Total n° of observations	144

3.2.1.2 Control of relative humidity (RH)

An evacuated system for determination of
sorption characteristics has been described on the
literature (Stamm and Woodruff, 1941; Spalt, 1957 and

Table 3.1 (Cont.) Main experiment design.

BEECH

Reagent	Variables	Intervals						N° of classes in variables
n-Bu-NCO	WPG (%)	0	7.9	11.7	18.1	23.3	37.3	6
	Relative humidity (%)	12	23	44	55	76	93	6
	Type of sorption (%)	Adsorption and Desorption						2
		N° of variable combinations						72
		Replications						2
		Total of observations						144
Ph-NCO	WPG (%)	0	7.7	12.9	15.4	22.8	26.3	6
	Relative humidity (%)	12	23	44	55	76	93	6
	Type of sorption	Adsorption and Desorption						2
		N° of variable combinations						72
		Replications						2
		Total n° of observations						144
HDI	WPG (%)	0	9.3	12.3	16.0	19.2	23.1	6
	Relative humidity (%)	12	23	44	55	76	93	6
	Type of sorption	Adsorption and Desorption						2
		N° of variable combinations						72
		Replications						2
		Total n° of observations						144
TDI	WPG (%)	0	4.0	5.9	7.5	9.3	11.0	6
	Relative humidity (%)	12	23	44	55	76	93	6
	Type of sorption	Adsorption and Desorption						2
		N° of variable combinations						72
		Replications						2
		Total n° of observations						144

1958; Wangaard and Granados, 1967). Such apparatus however was not available. A simpler alternative system, producing different RH's in small enclosed atmospheres over saturated salt solutions, similar to that used by Higgins (1957), was adopted. The vapour pressure control was therefore achieved by placing the wood specimens in jars over selected saturated salt solutions and storing them in a controlled temperature room kept at $20+-1^{\circ}C$.

This technique which is described by Stamm (1964) and by McLaren and Rowen (1951), has been widely used and was selected for being simple, rapid, economical and reasonably precise. Six relative humidities were obtained by the use of the saturated salt solutions showed at Table 3.2. They were chosen on the basis of giving minimum RH variation with changes in the temperature (Stamm, 1964 and Young, 1967). According to data published by Kaye and Laby (1966), a variation of +- 5°C causes a maximum variation of +-1% in the nominal RH's produced by the saturated salt solutions used. Since the variation in the controlled temperature room was of the order of +-1°C the variation in the nominal RH's was assumed to be very small causing therefore a negligible variation in the EMC inside the jars. A considerable excess of salt was always present in each desiccator and the volume of the atmosphere was fairly small (approx. 0.025m^{3}) so that a stable RH was quickly reached and maintained. To minimise any vapour pressure gradient within the jars, air was bubbled trough the solution, so keeping the atmosphere well mixed.

3.2.1.3 Measurement of relative humidity

The nominal RH produced by each saturated salt solution used is given in table 3.2. These values were continuously monitored by the use of a wet-and-dry bulb psycrometer placed inside the jars. The wet bulb water reservoir used was very small and only a minimal part of the wick (virtually that which covers the bulb) was

subject to water evaporation. Hence, accurate humidity reading confirming the nominal values was possible in all but the lowest humidity environment. At 12% RH erratic measures were produced due to disturbance caused either by water evaporating from the wet bulb or by the excessive difference in the vapour pressure produced by distilled water in the wick and the salt solution in the jar. Hence in this jar, a check was kept on the RH indirectly, by monitoring the weight of a thin unreacted wood wafer kept alongside the specimens.

Table 3.2 Relation between the saturated salt solution and relative humidity (RH) (after Kaye and Laby, 1966) with the respective equilibrium moisture content (EMC) at 20°C (Rasmussen, 1962).

Salt	RH(%)	EMC (% approx.)
KNO_3	93	21.0
$NaCl$	76	15.0
$Na_2Cr_2O_7$	55	10.0
K_2CO_3	44	8.5
$CH_3.COOK$	23	5.0
$LiCl$	12	3.0

3.2.1.4 Sample conditioning

Duplicate specimens of treated and untreated wood after oven drying and measurement as described in the previous chapter, were stored over phosphorus pentoxide until they were required for the sorption tests. The duplicate specimens were exposed

simultaneously (single-step) to the various levels of RH over the range 12-93%, first in adsorption and subsequently in desorption. Before starting the desorption part of the cycle, the specimens were stored for a period between damp cloths to ensure that they were at or above fibre saturation moisture content.

At each level of RH, samples were weighed periodically, using a four-place analytical balance to assess when equilibrium moisture content was attained. To minimise moisture loss or gain from the surface of the specimens during weighing the specimens were placed in closed weighing bottles. Preliminary investigation showed that if samples being conditioned at high humidities during desorption were exposed repeatedly to lower RH's in the process of weighing, they lost a considerable percentage of moisture. This may cause a gradual shift downwards towards the adsorption values. Conversely, if samples being conditioned at low RH's during adsorption were exposed to often to high RH's they gained moisture producing a shift upwards towards the desorption values (Higgins, 1957). Hence, care was taken to minimise the number of times the specimens were removed from conditioning jars.

Repeated weighing (about ten times) using a weighing bottle showed the reproducibility of the analytical balance used to be within +-0.1mg. This corresponds to +-0.01 percent moisture content or less for all samples. Successive weighing was made initially twice a week and afterwards, once a week, until it was

obvious that no significant weight change was detected over a week interval. The weighing was discontinued when the samples appeared to reach equilibrium with the atmospheric conditions inside the jars. Probably because as equilibrium was approached the rate of sorption was very slow, for each type of sorption any set of specimens needed about six to eight weeks to come into equilibrium at the required level in adsorption or desorption.

3.3 RESULTS

3.3.1 Experimental data and preliminary analysis

For each species and for each level of weight gain (WPG) duplicate determinations of equilibrium moisture content (EMC) (g of moisture per 100g of oven dry sample), were made in adsorption and in desorption at each level of relative humidity (RH). The experimental data shown in Table 3.3 are the average values and standard deviation obtained from the duplicate samples. At this stage, a significance test for analysis of variance (ANOVA) was conducted separately for each group of specimens consisting of six WPG levels and two replications or a total of twelve observations within each level of RH. Cochran's test (according to Kassab, 1989) for homogeneity of variances within each group was also proceeded. There were 48 such groups for each wood species and the differences between the mean EMC produced at each WPG level in adsorption and desorption proved to be significant for all groups (Appendix A, Table A.1). In addition, an analysis of variance 3-factor ANOVA was proceeded for each set of treatments (according to the design in Table 3.1), following the procedure given by Steel & Torrie (1960). Cochran's test for the homogeneity of variances was also applied. In that basis differences in EMC associated with RH, WPG and type of sorption are all significant at the 1 % level of probability. All the first order interactions are also significant at the 1 % level with the exception of that between WPG and type of

sorption for the TDI treated samples (both species). This
indicates that for these samples the variation of the EMC
with the WPG in adsorption is likely to be similar to
this variation in desorption. The second order
interaction (type of sorption x RH x WPG) is not
significant for any of the sets of treatment (Appendix A,
Table A.2).

Without further analysis it can be readily
seen that certain trends are clearly apparent, (Table
3.3). That is, EMC values decrease with decreasing RH
values and with increasing WPG values. The data for TDI
treated C. pine show a departure from this general
trend. Here an increase in WPG does not produce the
corresponding reduction in sorption. This apparent
atypical behaviour is discussed later in this chapter. It
is also evident from Table 3.3 that hysteresis is present
at every level of relative humidity regardless of the
WPG considered.

3.3.2 Analysis of data

The pattern of the wood sorption isotherm is well
known and several equations supported by physical models
for the interpretation of sorption data are described in
the literature (see Skaar, 1972 and 1988). The
experimental data shown in Table 3.3 were analyzed by
means of the Hailwood and Horrobin (1946) single-hydrate
sorption model. The main reason for choosing this model
for this analysis is the fact that it makes possible
partitioning of the total sorbed moisture into

Table 3.3 Experimental equilibrium moisture content (EMC) values obtained at the various levels of relative humidity (RH) for the reacted and unreacted wood of the two species studied. Mean values of duplicate specimens and standard deviations (in parenthesis) are shown.

Reagent	WPG		12	23	Relative humidity (%) 44	55	76	93
					CORSICAN PINE EMC(%)			
Controls	0.0	Ads	2.56(.08)	4.60(.09)	7.73(.08)	9.57(.12)	14.00(.17)	22.79(.21)
		Des	3.20(.10)	5.75(.11)	9.30(.10)	11.49(.12)	16.42(.16)	25.10(.24)
nBu-NCO	7.5	Ads	1.65(.12)	3.04(.12)	5.10(.14)	6.60(.18)	10.01(.20)	16.92(.29)
		Des	2.10(.07)	3.73(.09)	6.00(.18)	7.79(.16)	11.60(.14)	18.60(.30)
	11.3	Ads	1.58(.09)	2.65(.14)	4.54(.08)	5.89(.06)	9.44(.16)	15.03(.28)
		Des	1.92(.04)	3.25(.11)	5.63(.05)	7.06(.08)	10.80(.18)	16.43(.27)
	19.7	Ads	1.33(.04)	2.30(.05)	3.89(.08)	4.92(.16)	7.69(.21)	11.33(.24)
		Des	1.63(.08)	2.81(.05)	4.61(.07)	5.96(.11)	9.00(.25)	12.43(.18)
	24.1	Ads	1.22(.03)	1.96(.06)	3.45(.10)	4.49(.07)	6.94(.16)	10.43(.31)
		Des	1.50(.06)	2.36(.08)	3.99(.06)	5.33(.08)	7.96(.13)	11.50(.24)
	34.3	Ads	0.97(.04)	1.60(.07)	2.86(.09)	3.63(.05)	4.99(.16)	8.66(.23)
		Des	1.15(.03)	1.85(.10)	3.20(.08)	4.01(.06)	6.00(.15)	9.32(.27)
Ph-NCO	9.6	Ads	1.93(.09)	3.47(.11)	5.25(.10)	6.60(.11)	9.50(.19)	15.59(.34)
		Des	2.38(.13)	4.23(.15)	6.32(.13)	7.81(.17)	10.80(.13)	17.17(.41)
	17.6	Ads	1.74(.11)	3.08(.14)	4.67(.12)	5.65(.15)	8.66(.20)	13.87(.36)
		Des	2.13(.08)	3.71(.13)	5.63(.15)	6.72(.21)	10.20(.20)	15.30(.32)
	19.3	Ads	1.61(.08)	2.82(.15)	4.56(.10)	5.40(.18)	8.51(.17)	13.00(.22)
		Des	1.97(.10)	3.45(.15)	5.53(.12)	6.43(.26)	9.84(.33)	14.26(.24)
	25.9	Ads	1.47(.03)	2.64(.11)	4.04(.18)	5.27(.18)	7.58(.22)	11.38(.19)
		Des	1.75(.09)	3.14(.10)	4.85(.11)	6.10(.16)	8.83(.19)	12.46(.23)
	29.6	Ads	1.36(.11)	2.44(.09)	3.89(.15)	4.78(.13)	7.46(.21)	10.67(.38)
		Des	1.63(.14)	2.91(.09)	4.72(.13)	5.73(.18)	8.67(.24)	11.48(.40)
HDI	6.1	Ads	2.33(.06)	4.07(.05)	6.82(.12)	8.35(.14)	12.00(.19)	19.73(.33)
		Des	2.89(.04)	4.86(.06)	7.95(.10)	10.14(.15)	14.02(.26)	21.31(.36)
	12.9	Ads	2.26(.07)	3.97(.09)	6.20(.07)	7.95(.10)	11.55(.12)	16.86(.20)
		Des	2.82(.08)	4.65(.10)	7.17(.09)	9.35(.13)	13.00(.14)	18.39(.25)
	17.5	Ads	2.02(.02)	3.60(.08)	5.70(.11)	7.26(.13)	10.05(.14)	14.20(.29)
		Des	2.48(.05)	4.22(.09)	6.35(.20)	8.56(.15)	11.01(.13)	15.40(.36)
	19.5	Ads	2.02(.04)	3.48(.06)	5.58(.15)	7.08(.07)	9.95(.16)	13.67(.16)
		Des	2.43(.05)	4.14(.05)	6.02(.16)	7.94(.09)	10.90(.12)	14.55(.20)
	22.6	Ads	2.00(.04)	3.33(.08)	5.18(.12)	6.52(.12)	8.80(.21)	12.27(.22)
		Des	2.39(.04)	3.98(.08)	5.62(.10)	7.35(.15)	9.61(.11)	13.05(.25)
TDI	5.0	Ads	2.29(.08)	3.68(.06)	5.40(.10)	6.66(.18)	10.05(.23)	16.00(.50)
		Des	2.79(.06)	4.55(.08)	6.47(.15)	8.23(.28)	12.13(.26)	18.07(.54)
	6.4	Ads	2.34(.06)	3.82(.05)	6.50(.11)	8.05(.25)	12.10(.15)	18.20(.30)
		Des	2.92(.05)	4.72(.08)	7.72(.12)	9.84(.21)	14.25(.17)	21.06(.48)
	7.0	Ads	2.31(.04)	3.73(.10)	5.80(.16)	7.40(.12)	11.20(.35)	17.21(.18)
		Des	2.87(.06)	4.84(.10)	7.60(.15)	9.17(.12)	13.38(.56)	19.98(.35)
	8.6	Ads	2.22(.07)	3.68(.10)	5.60(.11)	7.10(.12)	10.40(.23)	16.20(.38)
		Des	2.73(.08)	4.67(.12)	7.37(.16)	9.02(.19)	13.05(.26)	19.60(.46)
	10.7	Ads	2.15(.06)	3.47(.09)	5.30(.12)	7.05(.14)	10.70(.15)	16.30(.39)
		Des	2.74(.03)	4.51(.06)	7.20(.14)	8.49(.17)	13.31(.18)	20.00(.45)

Table 3.3 (Cont.) Experimental equilibrium moisture content (EMC) values obtained at the various levels of relative humidity (RH) for the reacted and unreacted wood of the two species studied. Mean values of duplicate specimens and standard deviations (in parenthesis) are shown.

Reagent	WPG		12	23	44 BEECH EMC(%)	55	76	93
Controls	0.0	Ads	2.59(.09)	4.40(.06)	7.22(.08)	8.58(.12)	13.56(.19)	23.59(.21)
		Des	3.55(.10)	5.71(.08)	8.70(.10)	10.90(.14)	16.10(.20)	26.60(.19)
n-Bu-NCO	7.9	Ads	1.71(.07)	3.03(.08)	4.71(.15)	6.30(.21)	9.65(.14)	16.99(.20)
		Des	2.18(.04)	3.70(.11)	5.66(.11)	7.83(.22)	11.41(.13)	19.10(.22)
	11.7	Ads	1.44(.03)	2.72(.05)	4.29(.08)	5.70(.14)	9.22(.12)	15.28(.22)
		Des	1.84(.03)	3.24(.10)	5.13(.10)	7.20(.16)	10.91(.19)	17.20(.23)
	18.1	Ads	1.30(.05)	2.20(.09)	4.05(.11)	4.93(.13)	7.94(.23)	12.53(.30)
		Des	1.67(.03)	2.68(.11)	4.83(.13)	6.40(.17)	9.30(.20)	14.02(.30)
	23.3	Ads	1.07(.03)	1.92(.06)	3.59(.09)	4.42(.11)	6.68(.18)	10.71(.21)
		Des	1.40(.05)	2.45(.10)	4.30(.13)	5.39(.15)	8.03(.19)	11.83(.31)
	37.3	Ads	0.77(.05)	1.45(.05)	2.57(.04)	3.25(.10)	5.10(.12)	7.53(.24)
		Des	1.00(.07)	1.78(.06)	3.04(.07)	3.91(.08)	5.80(.15)	8.08(.25)
Ph-NCO	7.7	Ads	2.01(.04)	3.43(.13)	5.40(.09)	6.73(.19)	10.34(.24)	17.16(.44)
		Des	2.57(.09)	4.18(.16)	6.51(.12)	8.70(.26)	12.20(.33)	19.38(.40)
	12.9	Ads	1.86(.07)	3.17(.11)	4.81(.15)	5.64(.19)	8.69(.23)	14.03(.30)
		Des	2.38(.08)	3.82(.12)	5.76(.14)	6.93(.22)	10.30(.29)	15.73(.37)
	15.4	Ads	1.62(.07)	2.93(.10)	4.47(.15)	5.44(.17)	8.24(.26)	13.60(.28)
		Des	2.06(.09)	3.47(.11)	5.23(.15)	6.69(.17)	9.81(.21)	15.28(.40)
	22.8	Ads	1.41(.06)	2.50(.14)	3.96(.18)	4.90(.19)	7.62(.19)	12.08(.37)
		Des	1.79(.09)	2.92(.11)	4.85(.13)	6.07(.23)	8.90(.22)	13.60(.33)
	26.3	Ads	1.32(.04)	2.18(.09)	3.74(.13)	5.19(.44)	7.21(.21)	11.74(.24)
		Des	1.61(.06)	2.67(.07)	4.40(.19)	6.04(.46)	8.40(.25)	13.20(.30)
HDI	9.3	Ads	2.00(.08)	3.40(.09)	5.27(.12)	6.53(.14)	10.81(.22)	17.64(.42)
		Des	2.48(.07)	4.27(.06)	6.40(.09)	8.24(.15)	12.70(.20)	19.50(.45)
	12.3	Ads	1.92(.03)	3.28(.07)	4.98(.13)	6.03(.17)	10.30(.21)	16.57(.26)
		Des	2.35(.05)	4.11(.11)	5.98(.12)	7.63(.12)	12.00(.18)	18.30(.25)
	16.0	Ads	1.90(.03)	3.22(.06)	4.90(.08)	5.66(.10)	10.03(.18)	15.99(.19)
		Des	2.31(.06)	3.84(.09)	5.83(.10)	7.20(.08)	11.60(.17)	17.40(.23)
	19.2	Ads	1.86(.09)	3.08(.04)	4.71(.09)	5.57(.16)	10.00(.13)	14.39(.35)
		Des	2.20(.10)	3.67(.06)	5.41(.07)	6.80(.13)	10.97(.10)	15.53(.34)
	23.1	Ads	1.85(.06)	3.01(.04)	4.61(.08)	5.40(.12)	9.26(.15)	13.21(.22)
		Des	2.13(.04)	3.60(.07)	5.30(.06)	6.62(.10)	10.43(.18)	14.11(.20)
TDI	4.0	Ads	2.28(.06)	3.71(.08)	6.10(.20)	7.55(.13)	11.15(.60)	19.87(.40)
		Des	2.90(.09)	5.15(.06)	7.29(.19)	9.35(.18)	14.30(.28)	22.40(.50)
	5.9	Ads	2.13(.07)	3.51(.11)	5.80(.13)	7.00(.18)	10.32(.49)	18.15(.39)
		Des	2.75(.04)	4.59(.07)	6.90(.11)	8.10(.20)	12.80(.22)	20.60(.32)
	7.5	Ads	2.15(.06)	3.36(.07)	5.50(.09)	6.25(.15)	9.30(.27)	17.00(.59)
		Des	2.75(.04)	4.35(.09)	6.60(.10)	7.55(.17)	12.40(.24)	19.50(.41)
	9.3	Ads	2.10(.04)	3.26(.08)	5.34(.10)	6.00(.15)	8.96(.20)	15.90(.41)
		Des	2.68(.03)	4.25(.10)	6.54(.08)	7.26(.16)	11.60(.23)	19.01(.32)
	11.0	Ads	2.09(.02)	3.30(.06)	5.05(.12)	5.58(.16)	8.41(.17)	15.33(.29)
		Des	2.68(.03)	4.28(.04)	6.33(.10)	7.10(.24)	10.91(.16)	18.35(.25)

monomolecular and polymolecular phases and also provides a measure of the sorptive sites accessibility within the wood structure. This will be shown to be essential for the elucidation of the mechanism of sorption reduction in chemically modified wood. In addition, according to Simpson (1973 and 1979) this model produces one of the best degrees of fitting for wood sorption isotherms (see sections 3.1.4 and 3.1.5) and has been applied before by other workers for the study of wood sorption with considerable success, (see for example, Spalt, 1958; Wangaard and Granados, 1967; Prichananda, 1966; Okoh and Skaar, 1980). Since the present work deals with chemically modified wood, which sorption behaviour is hardly known, the use of a model which has its applicability to wood already well established is essential. An extensive approach however, has not so far been presented to describe even semi-quantitatively the effects of any chemical modification process in wood-water sorptivity.

3.3.2.1 The theoretical model

Derivation of the model is fully explained in the original paper (Hailwood and Horrobin, 1946). It is also extensively discussed by Skaar (1972) and has recently been reviewed (Skaar, 1988). According to the model, the total sorbed water m (g of water per 100 g of sample dry weight) exists in two states: water of hydration (m_h) and water of solution (m_d). The three chemical species present in the cell wall are assumed to

be unhydrated polymer (dry wood), hydrated molecules (hydrated wood) and dissolved water. These are assumed to behave as an ideal solution where the activities of the dry wood, the dissolved water and the hydrated molecules are considered to be proportional to their mole fractions. The total equilibrium results from two sets of individual equilibria: the equilibrium constants of the hydrates formed between dissolved water and certain units of the polymer molecule (K_h) and the equilibrium between the dissolved water and the water vapour (K_d). According to Skaar (1988), K_h is defined as the ratio of the activity (A_h) of the hydrate to the product of the activities (A_dA_o) of the two reactants, respectively, dissolved water and dry wood. K_d expresses the ratio A_d/V_p, i.e. the activity of the dissolved water per unit relative vapour pressure[*]. A third constant (W_o) is defined as the apparent molecular weight of the sorbate (dry wood) per mole of sorption sites and is related to the moisture content (M_o), corresponding to complete polymer hydration. For the wood-water sorptive system the relationship is $M_o = 1800/W_o$ (Skaar, 1988).

The model offers the following equation for the sorption isotherm:

$$m = m_h + m_d = \frac{1800K_hK_dh}{W_o(1+K_hK_dh)} + \frac{1800K_dh}{W_o(1-K_dh)} \qquad (3.1)$$

[*] According to Skaar (1972), the reaction of water and dry wood can be written:
dissolved water (activity A_d) + dry wood (activity A_o) $\overset{K_h}{\rightleftharpoons}$ hydrated wood (activity A_h).
The equilibrium condition between water vapour and dissolved water can be written:
water vapour (activity p/po) $\overset{K_d}{\rightleftharpoons}$ dissolved water (activity A_d).

Where **m** is the total moisture content (g of moisture per 100g of dry wood), the first term corresponds to m_h, the moisture content of the hydrated water and the second term to m_d, that present as the dissolved water at the vapour pressure **h** (h=RH/100, where RH is the relative humidity).

For convenience in fitting to the experimental data, equation 3.1 is transformed to the form:

$$h/m = A + Bh - Ch^2 \qquad (3.2)$$

in which the relationship **h/m** vs **h** is considered. This predicts a parabolic relationship between the ratio **h/m** and the vapour pressure **h** instead of the well known sigmoid relationship existing between **h** and **m** for wood-water sorption at constant temperature. The empirical constants **A B** and **C** are found by fitting the experimental data to equation 3.2. These fitted constants are used to calculate the fundamental constants K_h, K_d, W_o and M_o through the following relationships:

$$K_d = \frac{-B + \sqrt{B^2 + 4AC}}{2A} \qquad (3.3)$$

$$K_h = \frac{1}{1 - K_d(B/C)} \qquad (3.4)$$

$$W_o = AK_d(K_h+1)\,18 \qquad (3.5)$$

$$M_o = 1800/W_o = \frac{100}{AK_d(K_h+1)} \qquad (3.6)$$

As stated above, the model divides total water sorbed into hydrated water, which is monomolecular (sorbed in a layer one molecule thick) (m_h), and dissolved water held in solid solution, which is polymolecular (m_d). Therefore, the additive effect of mono and polymolecular sorption is equal to the total water sorbed (m). The relationships are:

$$m_h = \frac{M_o K_h K_d h}{1 + K_h K_d h} \qquad (3.7)$$

$$m_d = \frac{M_o K_d h}{1 - K_d h} \qquad (3.8)$$

$$m = m_h + m_d \qquad (3.9)$$

Where the parameters are those already defined above.

3.3.2.2 Fitting the isotherms

The experimental mean values of Table 3.3 were transformed by dividing the relative vapour pressure (h) by the equilibrium fractional moisture content (m) and the relationship h/m vs h was determined. The transformed experimental values were fitted by means of the quadratic equation 3.2 by the method of least squares. The relationship h/m vs. h, predicted by Eq. 3.2, was tested by analysis of variance approach applied to regression and all F-ratios were found to be statistically significant (see Table 3.4).

Once the empirical fitted constants A, B and C were determined as stated above, they were used for the calculation of the three fundamental equilibrium constants K_h, K_d and W_O through the relationships shown in equations 3.3, 3.4 and 3.5. The moisture content corresponding to complete polymer hydration M_O was also calculated by means of equation 3.6. The empirical fitted constants (A, B, and C) and the calculated fundamental constants (K_d, K_h, W_O and M_O) for the wood of the two species, untreated and treated at the five levels of weight gain with the four isocyanates are presented in Table 3.4.

The constants K_d, K_h, W_O and M_O obtained for the untreated woods were found to be similar to those previously reported by Spalt (1958) and Wangaard and Granados (1967). For the treated wood, the M_O values decrease as the WPG increases, indicating that the treatment blocks a proportion of sites which are made unavailable for water sorption and this proportion increases with adduct weight increase. The M_O values are also lower for adsorption than for desorption revealing that there are fewer sorption sites available for adsorption than for desorption. As Skaar (1972) pointed out, this is anticipated because, upon drying, some of the hydroxyl groups tend to form hydrogen bonding between each other and are not available to sorb water during the subsequent adsorption until these hydrogen bonds are broken at high moisture contents, due to swelling pressures developing in the cell wall. Consequently,

Table 3.4 Fitted and physical constants of the stable isotherms calculated by the means of the Hailwood and Horrobin (1946) model - for the two species on the untreated conditions and treated with the several isocyanates. The regression coefficient of determination (r^2) and F-ratio for the data fitted to equation 3.2 are also shown.

Reagent	WPG		r^2	F-ratio	A	B	C	K_h	K_d	Wo	Mo
						Corsican pine					
Control	0.0	Ads	0.95	26.63*	3.65	8.5	8.5	4.09	0.755	252.88	7.12
		Des	0.94	23.12*	2.87	7.1	6.5	4.42	0.715	201.00	8.95
n-Bu-NCO	7.5	Ads	0.96	37.53**	5.82	11.9	13.0	3.59	0.790	379.96	4.74
		Des	0.97	40.84**	4.37	11.5	11.5	4.37	0.775	327.59	5.49
	11.3	Ads	0.99	221.61**	6.10	14.8	15.9	4.01	0.806	442.98	4.06
		Des	1.00	6601.17**	5.08	11.2	11.4	3.92	0.756	340.00	5.29
	19.7	Ads	0.92	16.83*	7.17	17.5	17.9	4.14	0.776	515.21	3.49
		Des	0.96	31.57**	6.04	12.5	11.9	3.93	0.709	379.62	4.74
	24.1	Ads	0.96	36.56**	8.24	18.0	18.8	3.83	0.771	552.35	3.26
		Des	0.93	19.80*	6.53	16.4	16.0	4.33	0.752	471.55	3.82
	34.3	Ads	0.97	46.49**	10.12	22.5	23.3	3.90	0.769	686.14	2.62
		Des	0.99	154.54**	8.20	22.4	22.0	4.57	0.766	629.35	2.86
Ph-NCO	9.6	Ads	0.93	19.65*	4.25	15.6	14.6	5.75	0.772	399.10	4.51
		Des	0.92	17.91**	3.36	13.3	11.7	6.33	0.741	328.34	5.48
	17.6	Ads	0.95	31.38**	4.57	18.8	17.6	6.22	0.787	467.35	3.85
		Des	0.96	38.59**	3.78	15.2	13.6	6.32	0.755	376.05	4.79
	19.3	Ads	0.96	39.18**	5.41	17.1	16.4	5.12	0.769	457.93	3.93
		Des	0.96	36.97**	4.46	13.7	12.4	5.23	0.728	364.01	4.94
	25.9	Ads	0.93	20.51*	6.10	17.0	15.8	4.79	0.735	467.37	3.85
		Des	0.95	29.66*	5.20	13.6	12.0	4.76	0.696	374.68	4.80
	29.6	Ads	0.95	29.28*	6.76	17.1	16.3	4.46	0.736	488.57	3.68
		Des	0.95	26.09*	5.92	12.2	10.7	4.11	0.664	361.84	4.97
HDI	6.1	Ads	0.94	23.82*.	3.89	10.6	10.3	4.60	0.757	296.88	6.06
		Des	0.96	36.93**	3.19	08.7	7.9	4.79	0.719	238.87	7.54
	12.9	Ads	0.96	38.01**	4.02	11.0	10.1	4.77	0.724	302.38	5.95
		Des	0.96	39.59**	3.16	10.1	8.6	5.53	0.703	260.90	6.90
	17.5	Ads	0.95	29.13*	4.67	10.5	9.1	4.38	0.666	301.54	5.97
		Des	0.90	13.95*	3.67	10.2	8.2	5.28	0.650	269.64	6.68
	19.5	Ads	0.98	69.02**	4.72	10.9	9.3	4.48	0.663	308.53	5.83
		Des	0.93	21.01*	3.61	11.6	9.3	5.82	0.665	294.63	6.04
	22.6	Ads	0.98	74.13**	4.46	13.7	11.0	5.62	0.662	352.03	5.11
		Des	0.95	29.59*	3.42	13.7	10.4	7.13	0.654	327.50	5.50
TDI	5.0	Ads	0.99	126.12**	3.09	18.7	16.9	8.58	0.800	425.93	4.22
		Des	0.97	53.60**	2.63	14.5	12.8	8.20	0.770	334.58	5.38
	6.4	Ads	1.00	805.86**	4.00	11.0	10.5	4.65	0.752	305.58	5.89
		Des	0.98	94.86**	3.10	9.6	8.8	5.19	0.738	255.14	7.05
	7.0	Ads	0.99	144.92**	3.60	14.7	13.8	6.20	0.785	366.55	4.91
		Des	0.99	99.76**	2.93	10.7	9.5	5.97	0.736	270.52	6.65
	8.6	Ads	0.98	83.41**	3.64	15.4	14.1	6.48	0.774	379.36	4.74
		Des	0.98	75.99**	3.16	10.5	9.4	5.54	0.733	272.53	6.60
	10.7	Ads	0.96	39.84**	3.75	16.2	15.3	6.44	0.797	399.74	4.50
		Des	0.98	90.70**	3.02	12.1	11.2	6.20	0.772	301.99	5.96

**Significant at the 1% level of probability.
*Significant at the 5% level of probability.

Table 3.4.(Cont.) Fitted and physical constants of the stable isotherms calculated by the means of the Hailwood and Horrobin (1946) model - for the two species on the untreated conditions and treated with the several isocyanates. The regression coefficient of determination (r^2) and F-ratio for the data fitted to equation 3.2 are also shown.

Reagent	WPG		r^2	F-ratio	A	B	C	K_h	K_d	Wo	Mo
						Beech					
Control	0.0	Ads	0.97	54.85**	3.18	12.4	12.4	5.74	0.823	317.72	5.66
		Des	0.97	48.82**	2.37	10.2	9.6	6.45	0.794	252.06	7.14
n-Bu-NCO	7.9	Ads	0.96	34.65**	5.06	16.6	17.3	4.96	0.831	450.67	3.99
		Des	0.93	21.00*	3.96	13.8	13.8	5.32	0.809	364.53	4.94
	11.7	Ads	0.94	24.39*	6.46	15.1	16.6	3.86	0.817	461.18	3.90
		Des	0.92	17.52*	5.18	12.3	13.0	3.99	0.793	369.00	4.88
	18.1	Ads	0.99	109.66**	7.75	14.9	16.3	3.45	0.782	485.33	3.71
		Des	0.93	18.81*	6.21	11.5	11.9	3.51	0.739	372.62	4.83
	23.3	Ads	0.97	43.66**	9.79	13.0	15.0	2.79	0.741	494.13	3.64
		Des	1.00	2007.83**	7.28	12.1	12.3	3.33	0.711	403.74	4.46
	37.3	Ads	0.98	65.90**	13.70	15.7	18.4	2.59	0.720	636.83	2.83
		Des	0.98	66.37**	10.30	15.7	15.5	3.22	0.684	535.39	3.36
Ph-NCO	7.7	Ads	0.98	88.30**	4.12	15.9	15.5	5.77	0.806	405.24	4.44
		Des	0.95	28.48*	3.34	12.3	14.6	5.77	0.771	313.86	5.73
	12.9	Ads	0.96	38.65**	4.00	20.2	18.5	7.36	0.794	477.57	3.77
		Des	0.94	23.14*	3.69	15.3	13.7	6.50	0.754	376.01	4.79
	15.4	Ads	0.94	22.79*	4.99	19.0	18.2	5.84	0.790	485.19	3.71
		Des	0.97	55.26**	3.94	16.2	14.9	6.32	0.774	402.41	4.47
	22.8	Ads	0.97	49.46**	6.17	19.5	19.1	5.02	0.786	525.34	3.43
		Des	0.99	139.29**	5.01	16.0	15.1	5.20	0.761	425.17	4.23
	26.3	Ads	0.90	13.11*	7.54	16.1	16.7	3.79	0.765	497.71	3.62
		Des	0.91	15.52*	5.95	14.7	14.5	4.26	0.755	425.33	4.23
HDI	9.3	Ads	0.98	67.12**	4.05	17.0	16.9	6.05	0.831	426.60	4.22
		Des	0.96	38.36**	3.34	12.9	12.2	5.89	0.788	326.52	5.51
	12.3	Ads	0.96	36.02**	4.03	19.0	18.7	6.63	0.836	462.72	3.89
		Des	0.95	26.21*	3.39	14.4	13.5	6.33	0.794	355.45	5.06
	16.0	Ads	0.94	22.10*	3.88	20.7	20.1	7.34	0.841	489.39	3.68
		Des	0.97	51.89**	3.47	15.2	14.3	6.51	0.796	373.63	4.82
	19.2	Ads	0.91	15.36*	4.24	19.8	19.0	6.69	0.818	480.10	3.75
		Des	0.94	24.08*	3.66	15.9	14.6	6.58	0.779	388.92	4.63
	23.1	Ads	0.93	20.95*	4.21	20.4	18.9	7.08	0.797	487.79	3.69
		Des	0.93	20.17*	3.90	15.2	13.5	6.25	0.743	378.14	4.76
TDI	4.0	Ads	0.97	52.38**	3.61	14.8	14.5	6.03	0.817	373.01	4.83
		Des	0.94	21.97*	2.64	12.2	11.4	6.82	0.795	294.98	6.10
	5.9	Ads	0.96	37.26**	3.86	15.6	15.0	6.01	0.806	391.93	4.59
		Des	0.97	49.97**	2.62	14.7	13.6	7.94	0.807	340.03	5.29
	7.5	Ads	0.94	24.43*	3.30	20.0	18.6	8.36	0.822	456.89	3.94
		Des	0.97	49.75**	2.48	16.5	15.1	9.11	0.816	369.08	4.88
	9.3	Ads	0.94	25.24*	3.37	20.6	19.0	8.50	0.813	468.83	3.84
		Des	0.96	35.94**	2.46	17.3	15.7	9.64	0.814	383.10	4.70
	11.0	Ads	0.94	22.92**	2.83	24.3	22.0	11.35	0.827	521.17	3.45
		Des	0.96	36.75**	2.25	18.6	16.6	11.20	0.812	400.69	4.49

**Significant at the 1% level of probability.
*Significant at the 5% level of probability.

more sites are available for monomolecular sorption during desorption than for adsorption and the values obtained for M_O or W_O reflect this variation.

As defined above, the constant K_d 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_d values in Table 3.4 vary approximately between 0.7 and 0.8 indicating that the dissolved water shows a different activity than liquid water.

The constants A, B and C given in Table 3.4 (which are the regression coefficients of equation 3.2 for each fitted curve) were used for the calculation of the sigmoid isotherms, solving equation 3.2 for m by substituting selected values for h. The curve-fitted isothermal data calculated at each 10 percentile level of relative humidity (RH) are presented in Table 3.5 for the whole experiment, in adsorption and desorption.

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 isocyanates. This, however, is not too surprising since the fitting produced by the model used is reported to be one of the best for the sorption of water by cellulosic materials (see Simpson, 1973 and 1979 and the original paper by Hailwood and Horrobin, 1946). The coefficient of determination values (given in Table 3.4) range from 0.90

Table 3.5 Curve-fitted isothermal equilibrium moisture content (EMC) data at 10 percentile levels of relative humidity (RH), calculated by means of equation 3.2.

Reagent	WPG		Relative humidity (%)									
			10	20	30	40	50	60	70	80	90	100
						CORSICAN PINE						
						EMC (%)						
Control	0.0	Ads	2.26	3.99	5.51	7.02	8.65	10.53	12.87	15.96	20.38	27.42
		Des	2.84	4.97	6.81	8.59	10.47	12.60	15.13	18.40	22.82	29.31
n-Bu-NCO	7.5	Ads	1.45	2.60	3.65	4.70	5.87	7.25	9.01	11.41	15.04	21.28
		Ads	1.85	3.22	4.43	5.63	6.93	8.46	10.38	12.98	16.81	23.18
	11.3	Ads	1.35	2.38	3.29	4.22	5.25	6.48	8.08	10.30	13.75	19.97
		Des	1.64	2.91	4.04	5.16	6.38	7.78	9.52	11.82	15.10	20.33
	19.7	Ads	1.14	2.01	2.78	3.54	4.37	5.35	6.58	8.24	10.69	14.78
		Des	1.39	2.48	3.44	4.38	5.36	6.48	7.81	9.49	11.76	15.05
	24.1	Ads	1.01	1.80	2.51	3.22	3.99	4.89	6.02	7.54	9.77	13.43
		Des	1.25	2.18	3.00	3.80	4.66	5.66	6.89	8.51	10.82	14.47
	34.3	Ads	0.82	1.46	2.03	2.60	3.21	3.93	4.83	6.04	7.80	10.68
		Des	0.98	1.69	2.32	2.93	3.60	4.37	5.34	6.64	8.52	11.59
Ph-NCO	9.6	Ads	1.76	2.95	3.94	4.90	5.95	7.18	8.72	10.82	13.90	18.99
		Des	2.19	3.61	4.77	5.88	7.07	8.43	10.10	12.30	15.40	20.19
	17.6	Ads	1.59	2.62	3.48	4.32	5.23	6.32	7.70	9.61	12.48	17.41
		Des	1.94	3.19	4.22	5.21	6.28	7.51	9.05	11.10	14.04	18.72
	19.3	Ads	1.48	2.52	3.40	4.27	5.20	6.29	7.66	9.48	12.14	16.46
		Des	1.80	3.07	4.14	5.16	6.24	7.47	8.96	10.87	13.50	17.42
	25.9	Ads	1.31	2.26	3.07	3.86	4.70	5.66	6.83	8.35	10.47	13.70
		Des	1.55	2.69	3.66	4.59	5.56	6.64	7.92	9.52	11.64	14.67
	29.6	Ads	1.20	2.09	2.87	3.63	4.43	5.35	6.48	7.93	9.97	13.07
		Des	1.42	2.52	3.48	4.40	5.35	6.39	7.59	9.05	10.93	13.48
HDI	6.1	Ads	2.06	3.57	4.88	6.16	7.54	9.15	11.14	13.78	17.57	23.61
		Des	2.51	4.34	5.90	7.41	8.99	10.79	12.95	15.72	19.49	25.09
	12.9	Ads	1.99	3.44	4.68	5.88	7.15	8.59	10.33	12.57	15.64	20.24
		Des	2.45	4.14	5.56	6.89	8.29	9.86	11.72	14.07	17.23	21.79
	17.5	Ads	1.77	3.12	4.28	5.38	6.52	7.77	9.22	10.98	13.34	16.33
		Des	2.17	3.71	4.50	6.20	7.42	8.75	10.27	12.10	14.22	17.52
	19.5	Ads	1.75	3.07	4.20	5.27	6.38	7.59	8.99	10.70	12.88	15.85
		Des	2.14	3.60	4.80	5.92	7.07	8.32	9.78	11.55	13.84	16.96
	22.6	Ads	1.75	2.96	3.97	4.90	5.86	6.90	8.12	9.59	11.49	14.06
		Des	2.13	3.48	4.55	5.53	6.52	7.60	8.85	10.37	12.31	14.93
TDI	5.0	Ads	2.09	3.25	4.18	5.08	6.09	7.30	8.87	11.08	14.49	20.56
		Des	2.53	3.98	5.14	6.25	7.45	8.87	10.67	13.11	16.70	22.62
	6.4	Ads	2.00	3.47	4.73	5.97	7.29	8.83	10.72	13.23	16.79	22.41
		Des	2.52	4.28	5.78	7.22	8.76	10.52	12.67	15.48	19.41	25.45
	7.0	Ads	2.03	3.34	4.43	5.49	6.65	8.03	9.79	12.20	15.82	22.01
		Des	2.56	4.26	5.67	7.02	8.44	10.08	12.09	14.70	18.35	23.94
	8.6	Ads	1.98	3.24	4.28	5.29	6.38	7.67	9.30	11.50	14.76	20.17
		Des	2.43	4.09	5.49	6.83	8.24	9.87	11.84	14.40	17.97	23.40
	10.7	Ads	1.92	3.13	4.14	5.13	6.22	7.52	9.20	11.53	15.10	21.39
		Des	2.43	4.01	5.31	6.58	7.95	9.57	11.60	14.36	18.41	25.13

Table 3.5 (Cont.) Curve-fitted isothermal equilibrium moisture content (EMC) data at 10 percentile levels of relative humidity (RH), calculated by means of equation 3.2.

Reagent	WPG		Relative humidity (%)
			10	20	30	40	50	60	70	80	90	100
							BEECH EMC (%)					
Control	0.0	Ads	2.33	3.87	5.18	6.48	7.94	9.71	12.04	15.38	20.73	30.93
		Des	3.04	4.96	6.56	8.12	9.84	11.89	14.52	18.18	23.75	33.50
n-Bu-NCO	7.9	Ads	1.53	2.60	3.53	4.47	5.53	6.81	8.52	10.98	14.98	22.82
		Des	1.92	3.24	4.37	5.49	6.72	8.21	10.15	12.88	17.13	24.89
	11.7	Ads	1.28	2.27	3.17	4.07	5.09	6.31	7.90	10.17	13.75	20.45
		Des	1.59	2.81	3.90	4.99	6.20	7.63	9.45	11.97	15.78	22.42
	18.1	Ads	1.10	1.99	2.80	3.61	4.51	5.57	6.91	8.73	11.43	15.99
		Des	1.38	2.49	3.49	4.49	5.56	6.70	8.29	10.25	12.98	17.18
	23.3	Ads	0.91	1.70	2.43	3.18	3.99	4.93	6.08	7.57	9.65	12.86
		Des	1.20	2.17	3.06	3.94	4.88	5.94	7.20	8.80	10.96	14.11
	37.3	Ads	0.66	1.24	1.79	2.35	2.95	3.64	4.47	5.53	6.98	9.11
		Des	0.85	1.56	2.21	2.84	3.51	4.25	5.13	6.21	7.61	9.58
Ph-NCO	7.7	Ads	1.80	2.99	4.01	5.00	6.11	7.43	9.16	11.58	15.35	22.17
		Des	2.24	3.75	5.00	6.23	7.55	9.11	11.07	13.71	17.60	24.00
	12.9	Ads	1.71	2.74	3.58	4.39	5.29	6.36	7.74	9.66	12.58	17.70
		Des	1.97	3.22	4.25	5.24	6.30	7.53	9.06	11.10	14.02	18.66
	15.4	Ads	1.49	2.48	3.31	4.12	5.01	6.07	7.42	9.28	12.11	16.98
		Des	1.85	3.03	4.01	4.97	6.00	7.22	8.75	10.84	13.92	19.05
	22.8	Ads	1.26	2.15	2.91	3.67	4.49	5.46	6.70	8.40	10.95	15.30
		Des	1.55	2.63	3.55	4.45	5.41	6.53	7.93	9.80	14.30	16.84
	26.3	Ads	1.11	1.98	2.76	3.54	4.38	5.37	6.60	8.24	10.62	14.47
		Des	1.37	2.41	3.31	4.21	5.17	6.28	7.66	9.48	12.10	16.26
HDI	9.3	Ads	1.79	2.96	3.94	4.92	6.02	7.36	9.15	11.74	15.95	24.22
		Des	2.21	3.69	4.92	6.12	7.44	9.00	11.00	13.76	17.91	25.07
	12.3	Ads	1.74	2.83	3.73	4.63	5.65	6.90	8.58	11.02	15.05	23.09
		Des	2.13	3.50	4.63	5.74	6.96	8.41	10.26	12.88	16.84	23.78
	16.0	Ads	1.74	2.78	3.63	4.48	5.44	6.64	8.24	10.61	14.54	22.55
		·Des	2.06	3.37	4.44	5.50	6.66	8.05	9.83	12.32	16.11	22.79
	19.2	Ads	1.66	2.69	3.55	4.40	5.34	6.48	7.99	10.14	13.56	19.97
		Des	1.96	3.20	4.21	5.20	6.28	7.55	9.17	11.37	14.65	20.17
	23.1	Ads	1.65	2.66	3.48	4.28	5.17	6.23	7.60	9.50	12.43	17.58
		Des	1.89	3.12	4.14	5.11	6.14	7.33	8.80	10.72	13.44	17.67
TDI	4.0	Ads	2.02	3.34	4.44	5.54	6.76	8.24	10.18	12.95	17.33	25.53
		Des	2.67	4.33	5.69	7.02	8.48	10.23	12.48	15.61	20.39	28.78
	5.9	Ads	1.90	3.14	4.18	5.21	6.35	7.71	9.49	11.98	15.85	22.86
		Des	2.53	3.99	5.17	6.33	7.61	9.17	11.20	14.07	18.54	26.68
	7.5	Ads	1.96	3.07	3.94	4.82	5.80	7.01	8.60	10.91	14.61	21.66
		Des	2.51	3.87	4.95	6.01	7.21	8.66	10.59	13.35	17.73	25.94
	9.3	Ads	1.91	2.97	3.83	4.67	5.61	6.75	8.26	10.40	13.79	20.08
		Des	2.48	3.78	4.81	5.83	6.97	8.36	10.19	12.82	16.98	24.70
	11.0	Ads	1.98	2.94	3.69	4.44	5.28	6.34	7.75	9.80	13.15	19.64
		Des	2.54	3.77	4.73	5.69	6.75	8.07	9.80	12.28	16.21	23.47

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to 1.00 indicating that the experimental values are all close to the corresponding fitted values. Fig. 3.1 shows selected typical adsorption-desorption isotherms obtained from the fitted data of Table 3.5. Also plotted are the related mean equilibrium moisture content points from the experimental data of Table 3.3. The graphs in Fig. 3.1 show clearly that the mathematically fitted curves represented the trends shown by the experimental data in a very satisfactory way, since for the most part, deviation of specific data points from the curves are almost undetectable.

According to Kassab, (1989), r^2 measures the goodness of fit of the regression line to the data, and the lower the r^2 value the lower the proportion of total variation explained or accounted for by the fitted regression line. Therefore, an example representing the worst overall variation in EMC attained through the model in this work was chosen to assess the sensitivity of the equilibrium moisture content obtained by means of equation 3.2 to the degree of fitting. The example in Table 3.6, (HDI treated Corsican pine at 17.5 WPG), shows deviations between actual and fitted data of about 0.5% moisture content or less, that is, of the same magnitude as the experimental standard deviations (Table 3.3). This result is in good agreement with work of Simpson, (1979) who analysing the Hailwood-Horrobin model fitted with experimental sorption data from the USDA Wood Handbook (1974), found that the worst deviation between actual

data and fitted isotherms was about 0.8% moisture content.

Table 3.6 Example showing the sensitivity of the EMC calculated by means of Equation 3.2 to the degree of fit, for the lowest coefficient of determination (r^2) value (0.90)[*].

RH(%)	EMC(%)		Deviation from exp. value
	Exp.	Calc.	(% of moisture content)
12	2.48	2.51	+0.03
23	4.22	4.11	-0.11
44	6.35	6.69	+0.34
55	8.56	8.06	-0.50
76	11.01	11.33	+0.32
93	15.40	15.25	-0.15

[*]Data for HDI Corsican pine treated at 17.5 WPG with HDI, in desorption;

The isotherms in Fig. 3.1 are extrapolated to a common intersection point at 0% relative humidity. This is reasonable since under this condition no moisture can be sorbed, irrespective of substrate hygroscopic properties. It has been shown in earlier work by Spalt, (1958) and Wangaard and Granados, (1967), that extrapolation to the saturation limit at 100% relative humidity (from equation 3.2) is consistently lower for adsorption than for desorption, producing open hysteresis loops at the upper end. This is to be expected since these are values extrapolated from lower relative humidities and, according to Stamm (1964), EMC values found through the extrapolation to 100% relative humidity represent roughly the fiber-saturation-points of the materials at a relative vapour pressure of about 0.995
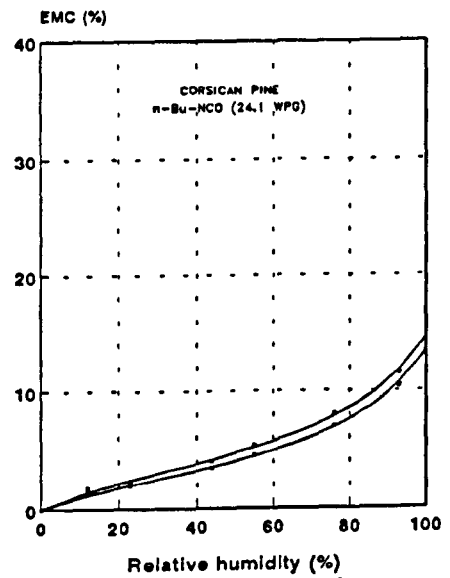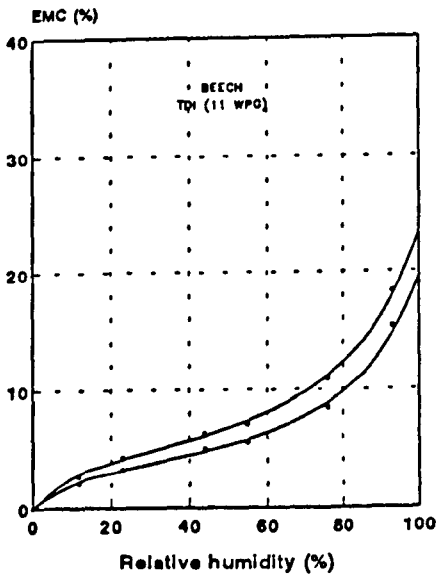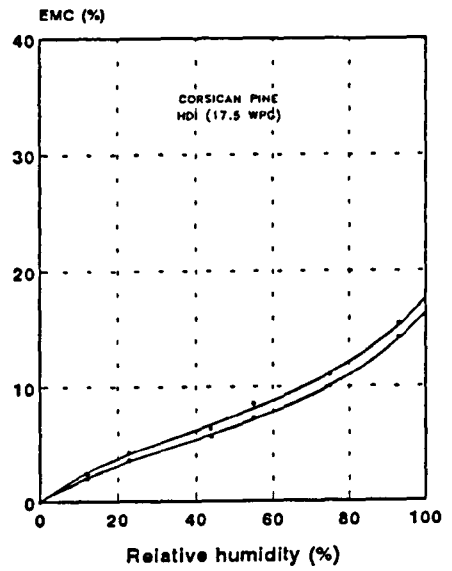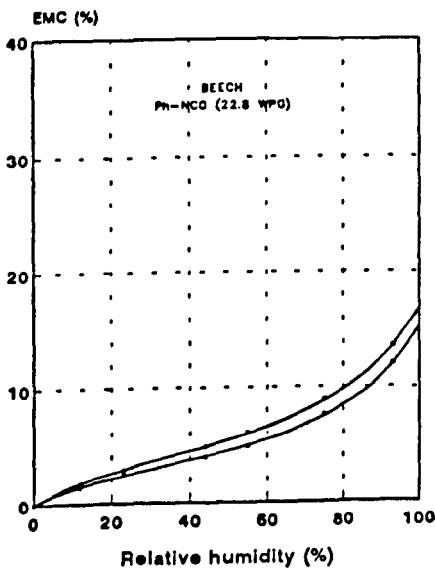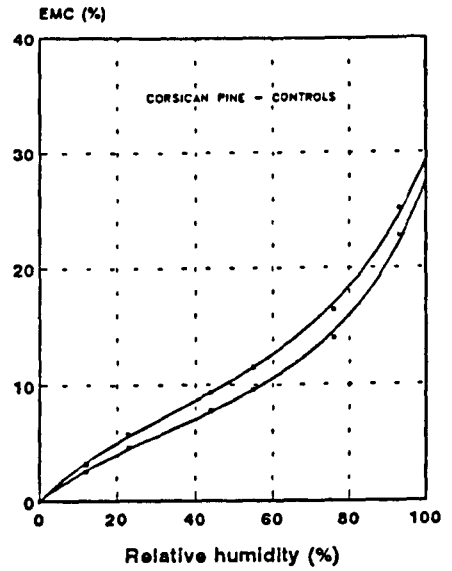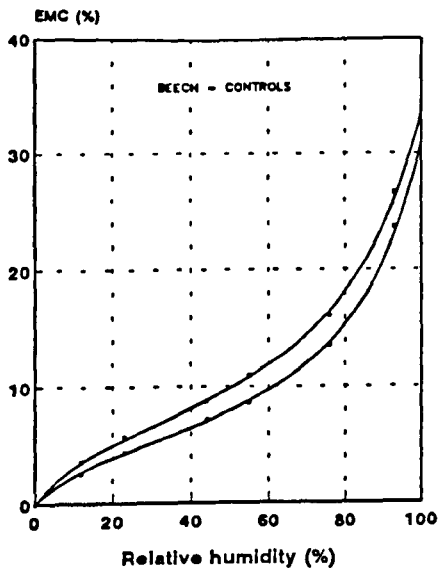
Fig 3.1 Adsorption and desorption isotherms - experimetal points and fitted curves are shown for untreated wood (controls) and for wood treated to selected weith gains (WPG).

and not the moisture content at which the relative humidity becomes unity. At the upper end a sharp upward break must occur in the adsorption curves at a relative vapour pressure about 0.995 due to capillary condensation (Stamm, 1964). Therefore it seems that the upper end of these curves remains open simply because extrapolation from lower values cannot adequately account for this sharp increase caused by condensation. This question will be considered again in the section concerning hysteresis.

3.4 DISCUSSION

3.4.1 General

Figures 3.2.a and 3.2.b show typical sigmoid adsorption isotherms drawn from data of Table 3.5 for the controls and for selected levels of weight gains (WPG). It is apparent from Fig. 3.2 that the effect of the treatment is to depress the isotherms at each reaction level and also, that the isotherms of modified and unmodified wood are of similar general sigmoid shape. Since the sigmoid shape of the isotherms reflects the physical processes involved in sorption (see section 3.1.2), the phenomenon suggests that similar sorption mechanisms apply in both modified and unmodified wood. Hence it may be that the modification reaction occurs initially with the most reactive and sterically available hydroxyls and subsequently with those of decreasing reactivity and/or reduced accessibility to the reagents. The shape of the treated wood isotherms indicates that at each level of treatment there remains a population of sorptive sites (probably hydroxyl groups) which are able to sorb water in the fashion predicted by the Hailwood and Horrobin model (and also by other classical sorption theories) with zones corresponding to monomolecular and polymolecular sorption. As shown later, ultimately it appears that a situation is reached where no further hydroxyl sites are available to the reagent without damage occurring to the specimens at the ultrastructural or macromolecular level. The extent of reaction at which
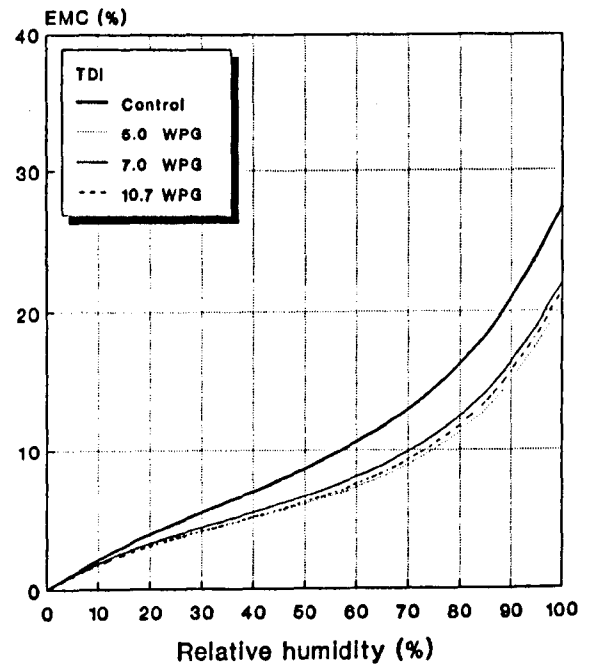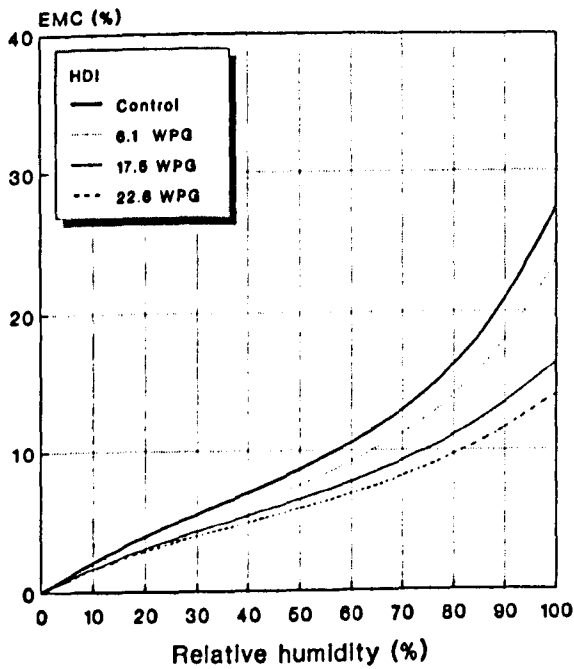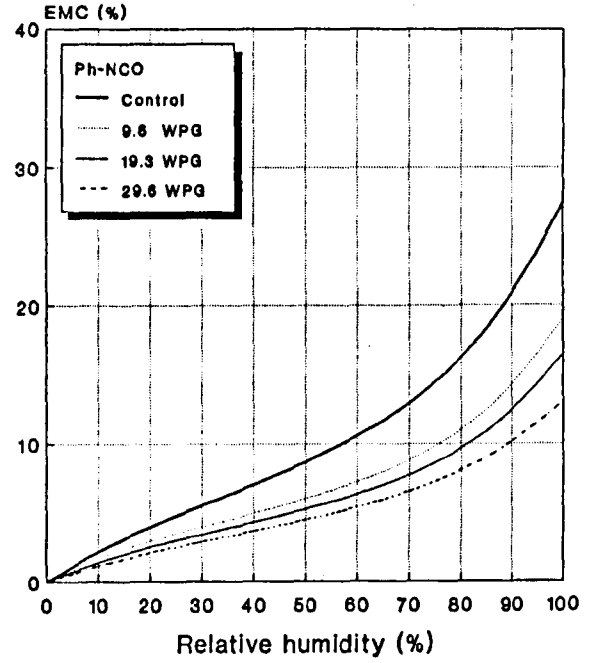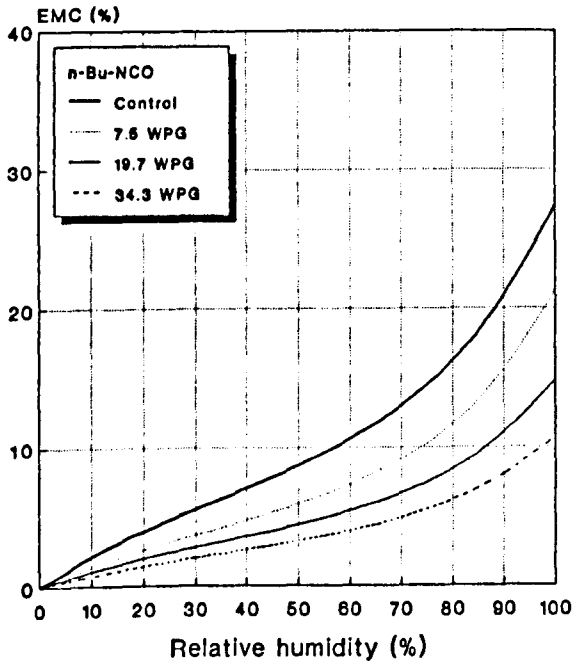
Fig. 3.2.a Typical adsorption isotherms for Corsican pine wood untreated (controls) and treated with the four isocyanates to selected weight gains (WPG's).
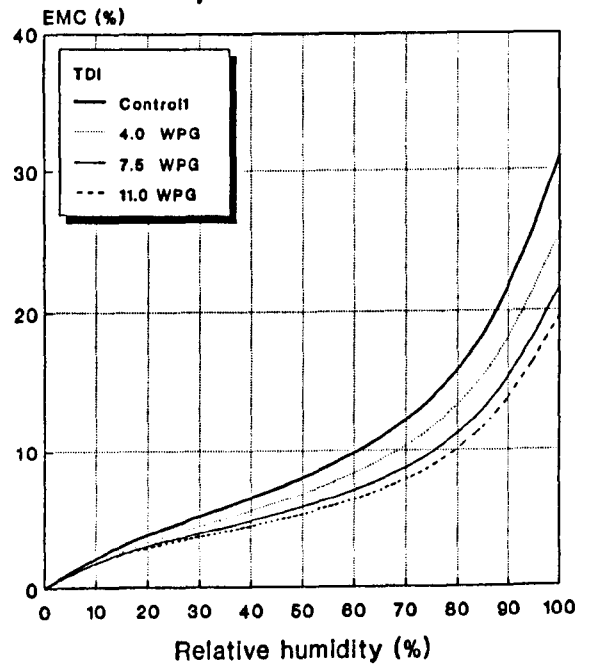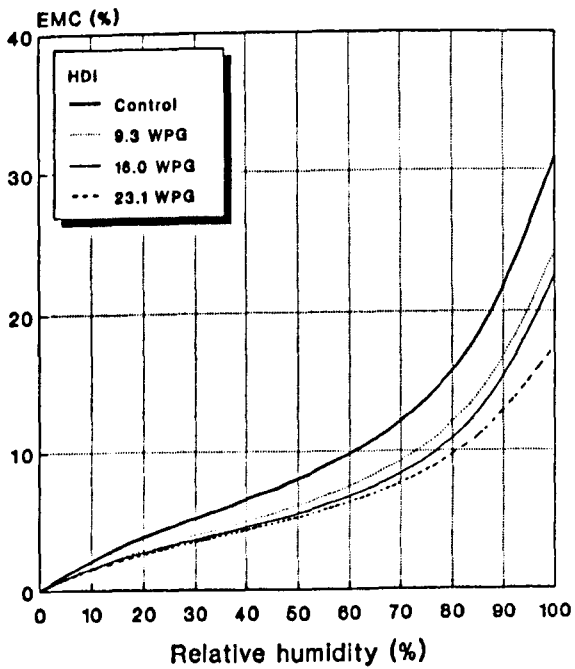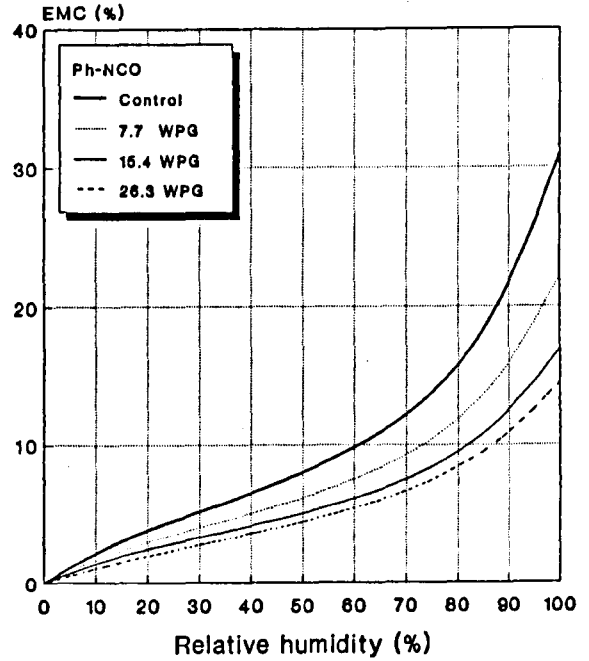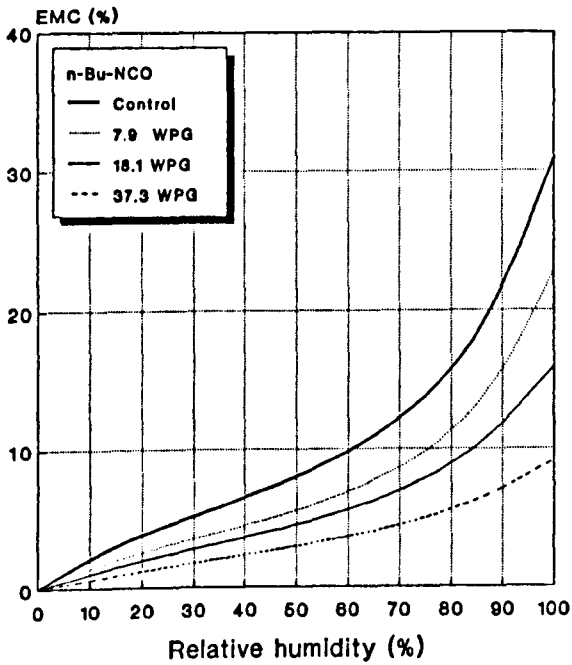
Fig 3.2.b Typical adsorption isotherms for beech wood untreated (controls) and treated with the four isocyanates to selected weight gains (WPG's).

this situation is reached appears to be dependent on the characteristics of the reagent used and it seems to be reached earlier with the phenyl reagent (see next section). However, even at this stage of treatment the population of sorptive sites which remains unavailable to reaction is accessible to water molecules, and they behave as predicted by the sorption model.

3.4.2 Reduction in hygroscopicity

The effect on hygroscopicity has been quantified by calculating the percentage reduction in the treated wood equilibrium moisture content (EMC) in relation to the controls equilibrium moisture content EMC at the same relative humidity (RH), by means of equation 3.10, as suggested by Stamm and Tarkow (1947), Stamm and Harris (1954) and Skaar (1988).

$$HR = 100(EMC_c - EMC_t)/EMC_c \qquad (3.10)$$

Where HR is the percent hygroscopicity reduction, EMC_c and EMC_t are respectively the equilibrium moisture content of the controls and of the treated specimens.

By the same principle the integral reduction in hygroscopicity was obtained by integrating equation 3.2 within the limits from 0% to 100% RH and calculating the reduction in hygroscopicity based on the areas below the sorption curves of the treated samples and the controls. The integral reduction in hygroscopicity therefore, represents the overall effect of the treatment on

Table 3.7 - Hygroscopicity reduction calculated from the data of Table 3.5 at 20 percentile levels of relative humidity, and integral hygroscopicity reduction (IRH) derived from the areas below the curves.

Reagent	WPG		20	40	60	80	100	IRH	WPG		20	40	60	80	100	IRH
					RELATIVE	HUMIDITY	(%)									
					PERCENT	REDUCTION	IN	HYGROSCOPICITY								
			CORSICAN	PINE						BEECH						
nBuNCO	7.5	Ads.	35	33	31	29	22	32	7.9	Ads	33	31	30	29	26	31
		Des.	35	34	33	29	20	32		Des	35	32	31	29	26	32
	11.3	Ads.	41	40	38	35	27	38	11.7	Ads	41	37	35	34	34	41
		Des.	41	40	38	46	31	39		Des	43	39	36	34	33	39
	19.7	Ads.	50	51	51	52	54	49	18.1	Ads	49	44	43	43	48	46
		Des.	50	51	52	52	51	49		Des	50	45	43	44	49	47
	24.1	Ads.	55	54	54	53	51	54	23.3	Ads	56	51	49	51	58	53
		Des.	56	56	55	54	51	55		Des	56	51	50	52	58	54
	34.3	Ads.	63	63	63	62	61	63	37.3	Ads	68	64	63	64	71	66
		Des.	66	66	65	64	60	65		Des	69	65	64	66	71	67
PhNCO	9.6	Ads.	26	30	32	32	31	29	7.7	Ads	23	23	23	25	28	24
		Des.	27	32	33	33	31	31		Des	24	23	23	25	28	24
	17.6	Ads.	34	38	40	40	37	37	12.9	Ads	29	32	35	37	43	33
		Des.	36	39	40	40	36	38		Des	35	35	37	39	44	37
	19.3	Ads.	37	39	40	41	40	40	15.4	Ads	36	36	37	40	45·	38
		Des.	38	40	41	41	41	41		Des	39	39	39	40	43	40
	25.9	Ads.	36	45	46	48	50	46	22.8	Ads	44	43	44	45	51	45
		Des.	46	47	47	48	50	47		Des	47	45	45	46	50	46
	29.6	Ads.	48	48	49	50	52	49	26.3	Ads	49	45	45	46	53	47
		Des.	49	49	49	51	54	50		Des	52	48	46	47	52	49
HDI	6.1	Ads.	11	12	13	14	14	12	9.3	Ads	24	24	24	24	22	24
		Des.	13	14	14	15	14	14		Des	26	24	24	25	28	24
	12.9	Ads.	14	16	18	21	26	18	12.9	Ads	27	29	29	28	25	28
		Des.	17	20	22	23	25	20		Des	29	29	29	30	31	29
	17.5	Ads.	22	23	26	31	40	27	16.0	Ads	28	31	32	31	27	30
		Des.	25	27	30	34	40	30		Des	32	32	32	33	35	32
	19.5	Ads.	23	25	28	33	42	28	19.2	Ads	30	32	33	34	35	32
		Des.	28	31	34	37	42	33		Des	35	36	37	38	41	37
	22.6	Ads.	26	31	34	39	45	33	23.1	Ads	31	34	36	38	44	35
		Des.	30	36	40	46	53	38		Des	37	37	38	41	48	39
TDI	5.0	Ads.	19	28	31	31	25	25	4.0	Ads	14	15	15	16	17	15
		Des.	20	27	30	29	23	24		Des	13	14	14	14	14	14
	6.0	Ads.	13	15	16	17	18	15	5.9	Ads	19	20	21	22	26	20
		Des.	14	16	17	16	13	15		Des	20	22	23	23	20	21
	7.0	Ads.	16	22	24	24	20	20	7.5	Ads	21	26	28	29	30	25
		Des.	14	18	20	20	18	18		Des	22	26	27	27	23	25
	8.6	Ads.	19	25	27	28	26	24	9.3	Ads	23	28	30	32	35	28
		Des.	18	21	22	22	20	20		Des	24	28	30	29	26	27
	10.7	Ads.	22	27	29	28	22	25	11.0	Ads	24	32	35	36	37	31
		Des.	19	23	24	22	14	21		Des	24	30	32	32	30	29

sorption over the entire range of relative humidity. The integral reduction values in adsorption are plotted against the WPG values in Fig. 3.3 and are also included in Table 3.7 together with the calculated values at twenty percentile RH levels in adsorption and desorption.

The data show clearly that all levels of chemical modification cause reduction in hygroscopicity. It can be seen in Table 3.7 that, within the limits of experimental accuracy, at all extents of reaction, the effect on hygroscopic properties is roughly similar for all RH levels in the case of the monofunctional isocyanates. The difunctionals reagents appear to produce higher reduction at high RH's. This is particularly noticeable with HDI for the two species. This higher reduction at high RH's when difunctional reagents are used has been reported as to be caused by crosslinking which restricts swelling and reduces the accessible spaces into which water molecules may enter (Zeronian and Kim, 1988).

As can be seen in Fig. 3.3, the integral reduction increases with increasing levels of chemical reaction. TDI treated Corsican pine shows an atypical result in which the highest reduction in hygroscopicity was obtained with the lowest level of reaction (5% WPG). During the treatment with TDI it was found 'that the WPG achieved did not cause the expected cell wall volume increase and therefore part of the chemical product is
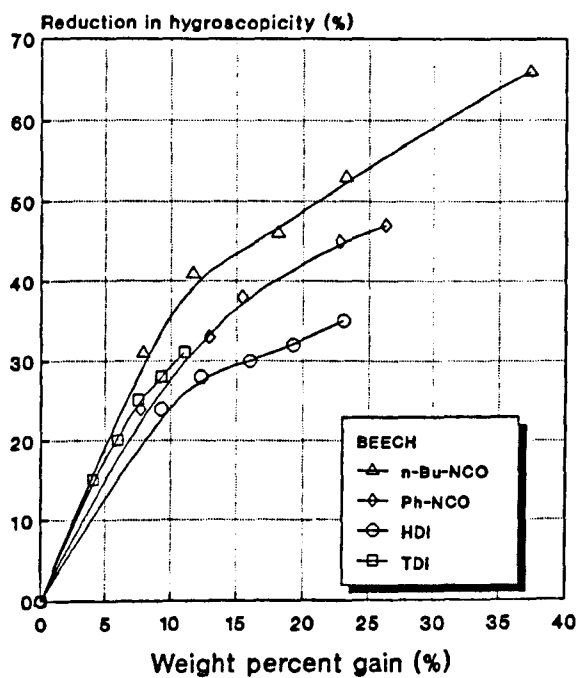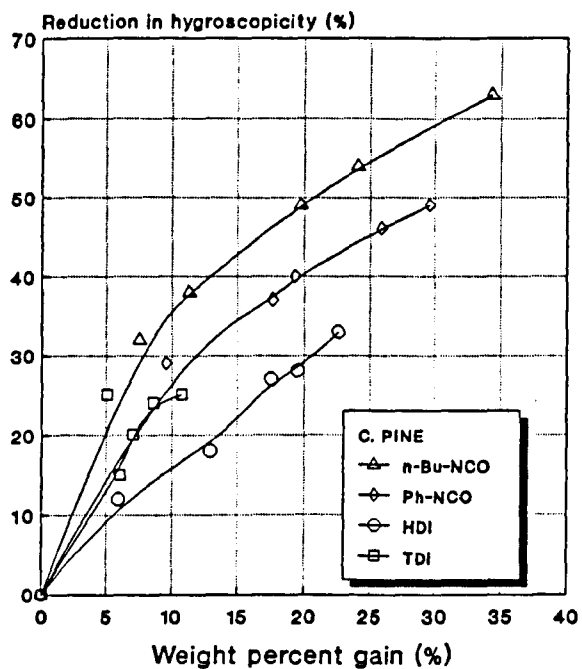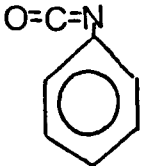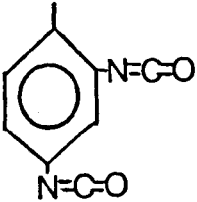
Fig. 3.3 Hygroscopicity reduction in adsorption as a function of weight percent gain (WPG) for Corsican pine and beech reacted with the four isocyantes.

probably located outside the cell walls. At least part of the apparent discrepancy may arise from this fact as the 5% WPG level also shows the highest proportion and the highest absolute mass of chemical within the cell wall of the five TDI treatment levels with this species (see Figure 2.3). No reasonable explanation was found for this higher proportion of chemical in the cell walls at this level. The reduction obtained at the other WPG levels with TDI treated Corsican pine and TDI treated beech follow the general trend, i.e. it increases with increase in WPG.

Fig. 3.3 also shows that at any chosen level of modification the reduction in hygroscopicity caused by the adducts vary in magnitude with type of reagent. For both species the butyl reagent appears to produce the greatest reduction, HDI the lowest and phenyl and TDI lie in between (the atypical TDI result at 5% WPG with C. pine is not considered in this instance). These differences in behaviour may be associated with dissimilarities in molecular size, molecular weight, molecular geometry and functionality. Between the monofunctionals the butyl reagent is of lower molecular weight and hence for a given weight increase substitutes more hydroxyl groups. The butyl reagent shows also higher specific volume and therefore at the same WPG is able to produce higher degree of bulking in the cell walls (see Table 3.8). Furthermore, the butyl group is also much more free to bend and flex than is the relatively rigid phenyl molecule. The extra rigidity may cause the phenyl

Table 3.8 Some molecular properties of the isocyanates (NCO) used.

NCO	Molar mass g	Molar vol. cc	Density g/cc	Specific vol. cc/g	Functionality	Structure
n-Bu-NCO	99.13	112.6	0.88	1.136	monofunctional	
Ph-NCO	119.12	108.7	1.096	0.912	"	
HDI	168.2	161.7	1.04	0.962	difunctional	
TDI	174.16	142.2	1.225	0.82	"	

adduct to force the cell wall polymer chains apart so that sorptive sites are uncovered and made available to water molecules. This is in line with the observations that at higher WPG's this reagent appeared to produce damage to the samples. The lack of a sharp break at higher WPG's in the curves for Ph-NCO treated samples in Fig. 3.3 suggests that this uncovering of new sorption sites is more likely to be gradual than abrupt but it appears that only at the higher WPG is the damage of enough magnitude to become visible.

It can be seen in Figure 3.3 that reduction in hygroscopicity with butyl isocyanate extends to weight gains of around 35%. With phenyl isocyanate the effect is not illustrated for reaction levels greater than 25-30% weight gain. This is because at these higher reaction levels, micro splitting was observed in the specimens and this was accompanied by somewhat erratic sorption behaviour. This may be because the micro splitting exposes a new population of sorption sites which requires an even higher level of reaction to bring about sorption control. Hence the system is unstable, since the further reaction needed will in turn cause further micro splitting and so on. This explanation is in line with finding of Rowell and Ellis (1979) who reported loss in anti-swelling efficiency at high weight gains in southern pine treated with methyl isocyanate. This was believed to be due to cell wall splitting.

Bearing in mind the explanations given above, regarding the difunctional isocyanates, at a given

weight gain HDI was expected to produce higher reduction in hygroscopicity than TDI since the first shows slightly lower molecular weight (substitutes more hydroxyl groups at a given WPG) and higher specific volume (produces higher degree of bulking). According to Figure 3.3 however, within the range of WPG obtained, TDI appears to be more efficient than HDI with the two species used despite the lower range of loading and volume increase achieved. TDI performance may be even more efficient than at first apparent when it is considered that a significant part of the WPG attained is located outside the cell walls. In contrast, despite some indication of crosslinking effectiveness from data of Table 3.7, the results produced by HDI seem to fall below the expectations considering its combined potential for bulking, hydroxyl deactivation and crosslinking.

Concerning differences between species, Fig. 3.4 shows clearly that there is practically no difference between the reduction in hygroscopicity obtained with the monofunctional reagents. This is not surprising. It is anticipated that, since the hardwood is denser and swells more, it requires a higher amount of hydroxyls blocked and also more bulking than the softwood to achieve the same reduction in hygroscopicity with the same reagent. On the assumption of carbamate formation only, the percent of hydroxyl groups reacted is directly proportional to the amount of adduct taken up by the cell walls, and since the take up of chemical is expressed on weight percent basis, the same weight gain
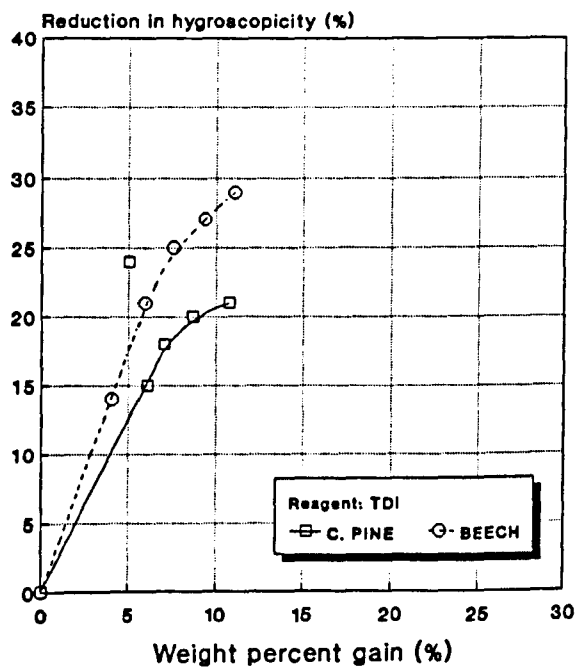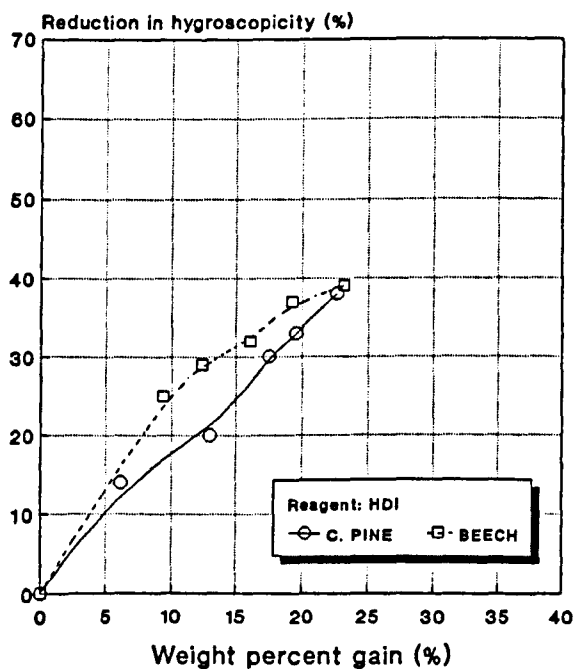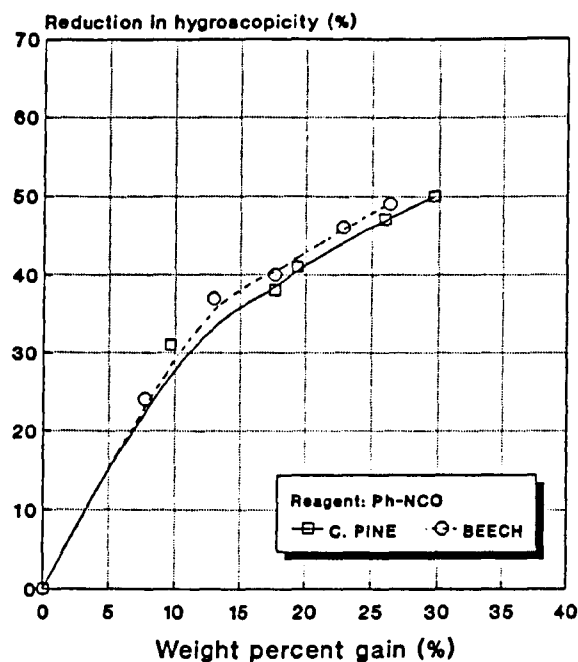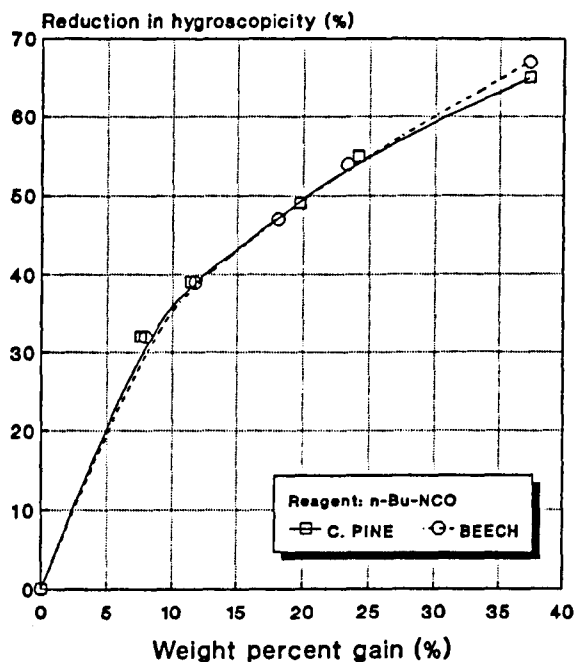
Fig. 3.4 Hygroscopicity reduction obtained for the two wood species in function of the weight percent gain achieved with each isocyanate, in desorption.

means higher bulking for the heavier wood. With the diisocyanates however, hardwood hygroscopicity seems to be more affected than that of softwood. This may be explained on the basis of crosslinking influence. Since the volumetric swelling of beech is larger than that of Corsican pine, the hardwood may be more likely to be affected by any swelling restriction caused by the crosslinkages.

3.4.3 Mechanisms of reduction in hygroscopicity

3.4.3.1 General

It is generally accepted that the reduced sorptive capacity of wood chemically modified with monofunctional compounds is a consequence of the conversion of hydroxyl groups to less hydrophylic groups and of the bulking resulting from the introduction of these groups into the cell walls (Stamm and Tarkow, 1947; Risi and Arsenau, 1957; Spalt, 1958; Goldstein, 1961; Stamm, 1964 and 1977a). Difunctional compounds, in addition, are believed to form crosslinkages preventing the chains from being pulled apart upon sorption (Sato et al, 1978; Rowland, 1978; Rowell & Youngs, 1981; Nakagami and Yokota, 1983; Zeronian and Kim, 1988). As a first approach in order to assess the mechanisms involved in the process, the integral values for the hygroscopicity reduction obtained for the four isocyanates were separately plotted against the percentage of hydroxyls depleted and against the respective bulking effect produced at each level of reaction (Fig. 3.5). The percentage of hydroxyls depleted was calculated by the same assumptions described in section 2.3.4 for the reaction rates, i.e. based on the theoretical maximum WPG assuming 100% accessibility of all hydroxyl groups, including those in the cellulose fraction. Also, the volume of adducts in the cell walls, which is an expression of the degree of bulking achieved, was calculated based on the specific volume of the
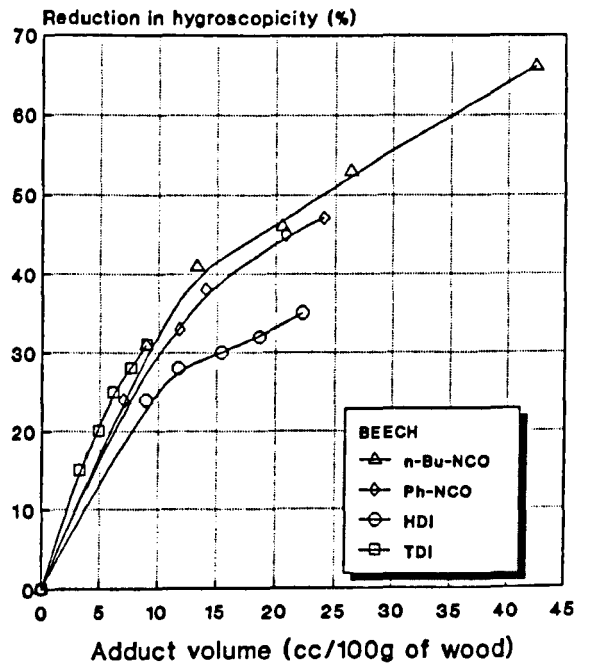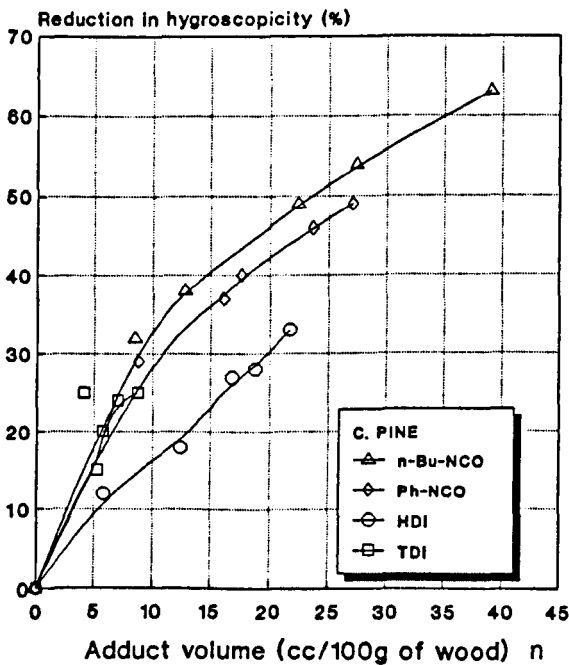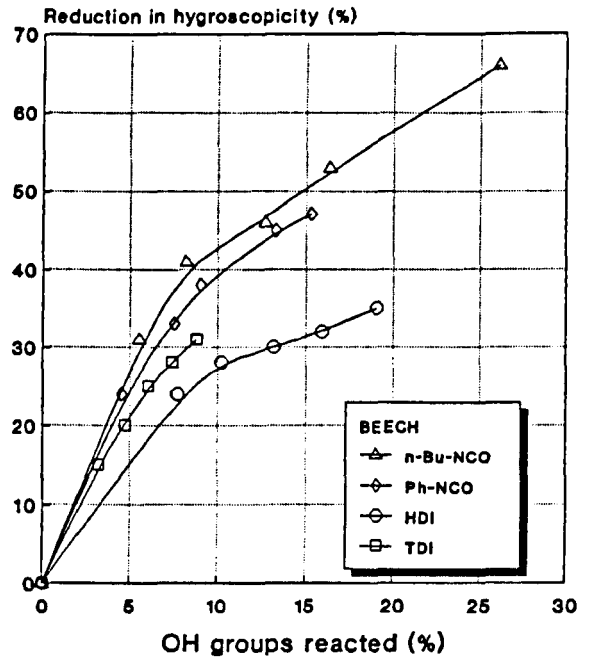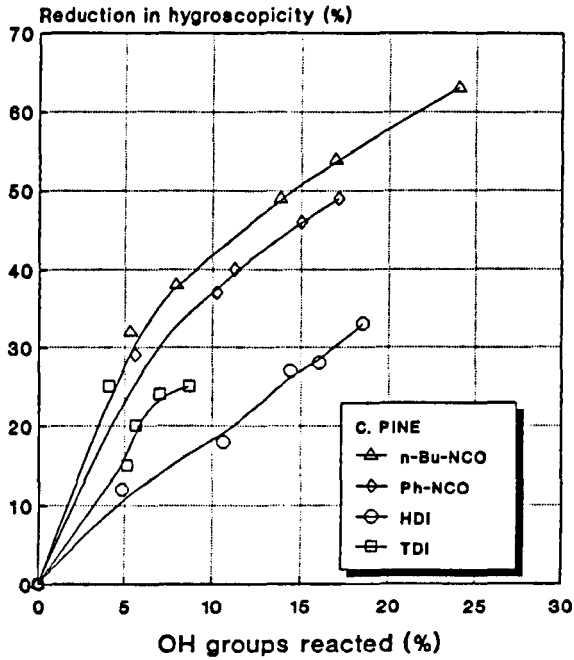
Fig. 3.5 Hygroscopicity reduction as a function of the percentage of total hydroxyl groups reacted and as a function of adduct volume (adsorption).

free isocyanates assuming that all adducts are in the cell walls. The four isocyanates produce four individual curves when either of the two mechanisms is separately considered. This indicates that reduction over the entire range of relative humidity cannot be satisfactorily explained on the basis of one of these factors alone. This may be because the hygroscopicity reduction achieved is the result of a combination of these two effects with variable relative influence along the range of relative humidities. This is in agreement with suggestions made by Spalt (1958) for acetylated spruce wood. For the difunctional reagents, in addition, this may also indicate that effects other than reduced polarity and bulking effect (e.g. crosslinking) may be present in the process.

Following this preliminary consideration the study of the mechanisms was dealt with using data provided by the Hailwood and Horrobin model analysis .

3.4.3.2 Monofunctional reagents

EMC values at saturation for monomolecular, polymolecular and total sorption were calculated by means of equations 3.7, 3.8 and 3.9 respectively. The contribution of each type of sorption to total water sorbed at saturation is presented in Table 3.9.

Table 3.9 shows decreasing monomolecular, polymolecular and total sorption EMC values as the WPG increases, implying that the treatment is effective towards the two types of sorption described by the model

Table 3.9 Distribution of sorbed water at saturation in unmodified and modified wood to several levels of reaction (WPG) according to the Hailwood and Horrobin (1946) model – Monofunctional isocyanates.

Reagent	WPG (%)	[1]Vol. (cc/g)		[2]Wo	Water sorbed (%) Mono	Poly	Total
				Corsican pine			
Control	0	0.0	Ads	253	5.38	22.04	27.42
			Des	201	6.81	22.50	29.31
n-Bu-NCO	7.5	0.085	Ads	380	3.50	17.78	21.28
			Des	328	4.24	18.94	23.18
	11.3	0.128	Ads	443	3.10	16.87	19.97
			Des	340	3.96	16.37	20.33
	19.7	0.224	Ads	515	2.66	12.12	14.78
			Des	380	3.49	11.56	15.05
	24.1	0.273	Ads	552	2.43	11.00	13.43
			Des	472	2.92	11.55	14.47
	34.3	0.390	Ads	686	1.97	8.71	10.68
			Des	629	2.22	9.37	11.59
Ph-NCO	9.6	0.088	Ads	399	3.68	15.31	18.99
			Des	328	4.52	15.67	20.19
	17.6	0.161	Ads	467	3.20	14.21	17.41
			Des	377	3.96	14.76	18.72
	19.3	0.176	Ads	457	3.13	13.06	16.46
			Des	364	3.92	13.21	17.43
	25.9	0.236	Ads	467	3.00	10.70	13.70
			Des	375	3.69	10.99	14.67
	29.6	0.270	Ads	489	2.82	10.25	13.07
			Des	362	3.64	9.84	13.48

[1] Volume of adducts in the cell wall calculated based on the density of the free isocyanate and on the respective WPG.
[2] Apparent molecular weight of the polymer associated to one mole of water.

Table 3.9 (Cont.) Distribution of sorbed water at saturation in unmodified and modified wood to several levels of reaction (WPG) according to the Hailwood and Horrobin (1946) model — Monofunctional isocyanates.

Reagent	WPG (%)	[1]Vol. (cc/g)		[2]Wo	Water sorbed (%) Mono	Poly	Total
					Beech		
Controls	0.0	0.0	Ads	318	4.67	26.26	30.93
			Des	252	5.98	27.52	33.50
nBu-NCO	7.8	0.089	Ads	451	3.22	19.60	22.82
			Des	365	4.01	20.88	24.89
	11.7	0.133	Ads	461	2.97	17.48	20.45
			Des	369	3.71	18.71	22.42
	18.1	0.206	Ads	485	2.71	13.28	15.99
			Des	373	3.49	13.69	17.18
	23.3	0.265	Ads	494	2.45	10.41	12.86
			Des	404	3.13	10.98	14.11
	37.3	0.424	Ads	637	1.84	7.27	9.11
			Des	526	2.31	7.27	9.58
Ph-NCO	7.7	0.070	Ads	405	3.66	18.51	22.17
			Des	314	4.68	19.32	24.00
	12.9	0.118	Ads	478	3.22	14.48	17.70
			Des	376	3.98	14.68	18.66
	15.4	0.141	Ads	485	3.05	13.93	16.98
			Des	402	3.71	15.34	19.05
	22.8	0.208	Ads	525	2.73	12.57	15.30
			Des	425	3.38	13.46	16.84
	26.3	0.240	Ads	498	2.69	11.78	14.47
			Des	425	3.23	13.04	16.26

[1] Volume of adducts in the cell wall calculated based on the density of the free isocyanate and on the respective WPG.
[2] Apparent molecular weight of the polymer associated to one mole of water.

as well as towards the total water sorbed (the additive effect of mono and polymolecular sorption). From these tables it is evident that the treated woods are less hygroscopic in both monomolecular and polymolecular sorption and also, that the hygroscopicity tends to decrease with increasing WPG.

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 treated woods from Table 3.9. As the effect of the treatment has been shown to be similar for both adsorption and desorption equilibria, these analyses were carried out on combined absorption and desorption data. The results of these analyses (Table 3.10) show clearly that as expected, the variation in total water sorbed is dependent on both monomolecular and polymolecular sorption. However, the higher r^2 and F-ratios 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 implies that the mechanism responsible for the reduction in polymolecular sorption must be also the main mechanism causing the reduction in total water sorbed at saturation. The decrease at the monomolecular level seems to affect total sorption in a secondary way.

In the Hailwood and Horrobin model, W_O is the molecular weight of sorptive substance associated with one mole of water at saturation. Accordingly, sorption

Table 3.10 Regression analysis of the relation between types of sorption and total sorption at saturation - Monofunctional isocyanates.

SOURCE	DF	Sum of Squares	Mean Squares	F-ratio

Corsican pine reacted with n-Bu-NCO

Monomolecular vs. Total sorption

REGRES.	1	137.13	137.13	32.62**
ERROR	8	33.63	4.20	
TOTAL	9	170.76		
r^2x100		80.3		

Polymolecular vs. Total sorption

REGRES.	1	169.38	169.38	982.55**
ERROR	8	1.38	0.17	
TOTAL	9	170.76		
r^2x100		99.2		

Corsican pine reacted with Ph-NCO

Monomolecular vs. Total sorption

REGRES.	1	28.943	28.943	7.85*
ERROR	8	29.493	3.687	
TOTAL	9	58.436		
r^2x100		49.5		

Polymolecular vs. Total sorption

REGRES.	1	56.769	56.769	272.36**
ERROR	8	1.667	0.208	
TOTAL	9	58.436		
r^2x100		97.1		

**Significant at 99 percent level of probability
* Significant at 95 percent level of probability

Table 3.10 (Cont.) Regression analysis of the relation between types of sorption and total sorption at saturation - Monofunctional isocyantes.

SOURCE	DF	Sum of Squares	Mean Squares	F-ratio

Beech reacted with n-Bu-NCO

Monomolecular vs. Total sorption

REGRES.	1	216.18	216.18	26.59**
ERROR	8	65.04	8.13	
TOTAL	9	281.22		
r^2x100		76.9		

Polymolecular vs. Total sorption

REGRES.	1	280.06	280.06	1930.37**
ERROR	8	1.16	0.15	
TOTAL	9	281.22		
r^2x100		99.6		

Beech reacted with Ph-NCO

Monomolecular vs. Total sorption

REGRES.	1	64.138	64.138	32.40**
ERROR	8	15.839	1.980	
Total	9	79.977		
r^2x100		80.2		

Polymolecular vs. Total sorption

REGRES.	1	79.028	79.028	666.22**
ERROR	8	0.949	0.119	
TOTAL	9	79.977		
r^2x100		98.8		

**Significant at 99 percent level of probability

site accessibility decreases with increasing W_O values. As the WPG increases, the increasing values shown for W_O in Table 3.9 indicate that the availability of bonding sites is progressively reduced causing the consequent decline in monomolecular sorption. This is because as the WPG increases the proportion of sorption sites occupied by the isocyanates forming butyl and phenyl carbamates also increases and therefore less free hydroxyl sites are left available for hydrogen bonding to water molecules. As the WPG increases, polymolecular and total sorption are also reduced. A relation between site accessibility, polymolecular and total sorption is apparent in Table 3.9. However, the presence of the adducts in the cell walls not only reduces monomolecular sorption by decreasing sites accessibility but also causes a great degree of bulking in the cell wall as is shown by the increasing volume of adducts laid down in the cell walls (Table 3.9). The reduction in site accessibility is therefore accompanied by cell wall bulking and it is unwise to assume that the correlation observed may be interpreted as if the reduction in polymolecular and in total sorption were primarily a consequence of the reduction in site accessibility. Hence, regression analysis of the data shown for the treated woods in Table 3.9 was conducted in order to verify the effect of declining W_O on the moisture sorbed as monomolecular, polymolecular and total water at saturation. Also, the effect of increasing volume of adducts in the cell walls

on the mentioned types of sorption was assessed by regression analysis.

The results of these analyses are presented in Table 3.11 where all meaningful trends shown are negative. It is apparent that better correlations for W_O are found when this factor is related to monomolecular sorption. Conversely, the volume of adducts in the cell walls clearly correlates better to polymolecular and total water sorbed. This is indicated by the higher coefficients of correlation (r^2) and F-ratios in all relationships considered and it is particularly evident for Corsican pine treated with phenyl isocyanate where the regressions for W_O vs. polymolecular sorption, W_O vs. total sorption and volume vs. monomolecular sorption are nonsignificant statistically. It seems therefore that only the decrease in monomolecular sorption can be primarily attributed to the decrease in site accessibility. Polymolecular sorption and total sorption appear to be much more strongly influenced by bulking. This conclusion is supported by the works of Spalt (1958) and by Wangaard and Granados (1967) in relation to the effects of extractives on these types of sorption. It was evident in the above workers analyses that the presence of the extractives in the cell walls, although causing à slight increase in monomolecular sorption, greatly decreased polymolecular and total sorption. These effects were interpreted by Wangaard and Granados as due to the extractives, being themselves hygroscopic and some of them slightly more hygroscopic than the skeletal cell

Table 3.11 Regression analysis of the relations between the types of water sorbed at saturation and sites accessibility (expressed as Wo) and volume of adducts in the cell wall - Monofunctional isocyanates.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio	Sum Squares	Mean Squares	F-ratio

Corsican pine reacted with n-Bu-NCO

		Monomolecular vs. Wo			Monomolecular vs. Volume		
REGRES.	1	4.7851	4.7851	143.71**	3.8881	3.8881	26.74**
ERROR	8	0.2664	0.0333		1.1634	0.1454	
TOTAL	9	5.0515			5.0515		
r^2x100		94.7			77.0		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	86.258	86.258	18.69**	114.15	114.15	101.18**
ERROR	8	36.916	4.614		9.03	1.13	
TOTAL	9	123.174			123.17		
r^2x100		70.0			92.7		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	131.68	131.68	26.95**	160.17	160.17	120.98**
ERROR	8	39.09	4.89		10.59	1.32	
TOTAL	9	170.76			170.76		
r^2x100		77.1			93.8		

Corsican pine reacted with Ph-NCO

		Monomolecular vs. Wo			Monomolecular vs. Volume		
REGRES.	1	2.1814	2.1814	71.81**	0.8427	0.8427	4.26NS
ERROR	8	0.2430	0.0304		1.5817	0.1977	
TOTAL	9	2.4244			2.4244		
r^2x100		90.0			34.8		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	4.793	4.793	0.99NS	40.974	40.974	127.13**
ERROR	8	38.760	4.845		2.578	0.322	
TOTAL	9	43.553			43.553		
r^2x100		11.0			94.1		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	13.438	13.438	2.39NS	54.034	54.034	98.20**
ERROR	8	44.998	5.625		4.402	0.550	
TOTAL	9	58.436			58.436.		
r^2x100		23.0			92.5		

** Significant at 99 percent level of probability
NS Not significant

Table 3.11 (Cont.) Regression analysis of the relations between the types of water sorbed at saturation and sites accessibility (expressed as Wo) and the assumed volume of adducts in the cell wall — Monofunctional isocyanates.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio	Sum Squares	Mean Squares	F-ratio

Beech reacted with n-Bu-NCO

		Monomolecular vs. Wo			Monomolecular vs. Volume		
REGRES.	1	3.6862	3.6862	84.25**	2.7950	2.7950	18.01**
ERROR	8	0.3500	0.0438		1.2412	0.1552	
TOTAL	9	4.0362			4.0362		
r^2x100		91.3			65.4		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	115.32	115.32	8.32*	210.84	210.84	106.94**
ERROR	8	110.86	13.86		15.34	1.92	
TOTAL	9	226.18			226.18		
r^2x100		51.0			93.2		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	160.24	160.24	10.60*	262.18	262.18	110.18**
ERROR	8	120.98	15.12		19.04	2.38	
TOTAL	9	281.22			281.22		
r^2x100		57.0			93.2		

Beech reacted with Ph-NCO

		Monomolecular vs.Wo			Monomolecular vs. Volume		
REGRES.	1	3.0568	3.0568	117.55**	1.7496	1.7496	9.24*
ERROR	8	0.2080	0.0260		1.5152	0.1894	
TOTAL	9	3.2648			3.2648		
r^2x100		93.6			47.8		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	32.236	32.236	11.71**	43.100	43.100	30.88**
ERROR	8	22.031	2.754		11.167	1.396	
TOTAL	9	54.267			54.267		
r^2x100		59.4			79.4		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	55.140	55.140	17.76**	62.286	62.286	28.17**
ERROR	8	24.837	3.105		17.691	2.211	
TOTAL	9	79.977			79.977		
r^2x100		68.9			77.9		

* Significant at 95 percent level of probability
** Significant at 99 percent level of probability
DF Degrees of freedon

wall. Hence the hygroscopicity of the surfaces is slightly increased causing an increase in accessibility and consequently, in sorption at the monomolecular level. The marked decline observed in polymolecular and in total sorption even when more sorption sites are available is clear evidence that the bulking effect of the extractives, precluding water from occupying the same space in the cell wall, offsets the sites accessibility influence in polymolecular and in total sorption. In the case of the chemically modified wood presented in this study the two effects (site accessibility and polymolecular sorption) are complementary to each other, i.e. the presence of the adducts in the cell walls causes a decrease in the hygroscopicity of the internal surfaces, decreasing sites accessibility and monomolecular sorption. Simultaneously, it decreases polymolecular sorption by bulking the cell walls. These combined effects strongly suggest that in the case of wood treated with monofunctional isocyanates the reduction in moisture sorbed at the monomolecular level is chiefly governed by the decrease in availability of sorption sites. The reduction attained at the polymolecular level and in total water sorbed at saturation, where polymolecular sorption clearly predominates (see Table 3.10), seems to be highly influenced by the degree of bulking brought about by the presence of the adducts in the cell walls.

The influence of the reduction in site accessibility (expressed by the decline in monomolecular

sorption) and of bulking, (expressed by the reduction in polymolecular sorption) in total sorption, within the entire range of RH is revealed by splitting the isotherms for total water sorbed in its two components predicted by the model. The effect of these mechanisms along the entire range of relative humidity is represented graphically in Fig. 3.6 where isotherms for the two types of sorption and for total sorption are separately depicted for the controls and for the treated woods, in desorption. For the untreated woods the isotherms produced by monomolecular sorption rise rapidly in the range of low RH levelling off asymptotically at higher RH's showing the characteristic shape of the Type I isotherm (Langmuir sorption). 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 summation of mono and polymolecular types of sorption) are the Type II, exhibiting the well known sigmoid shape (see section 3.1.2). Fig. 3.6 shows clearly that polymolecular sorption predominates at the higher relative humidities while monomolecular sorption predominates at the lower ones. As far as the isotherms for the treated wood are concerned, it can also be seen in Fig. 3.6 that the two types of sorption, and consequently the total sorption isotherms, are affected by the treatment, since the two complementary isotherms are clearly depressed when compared to those produced by the controls (unreacted
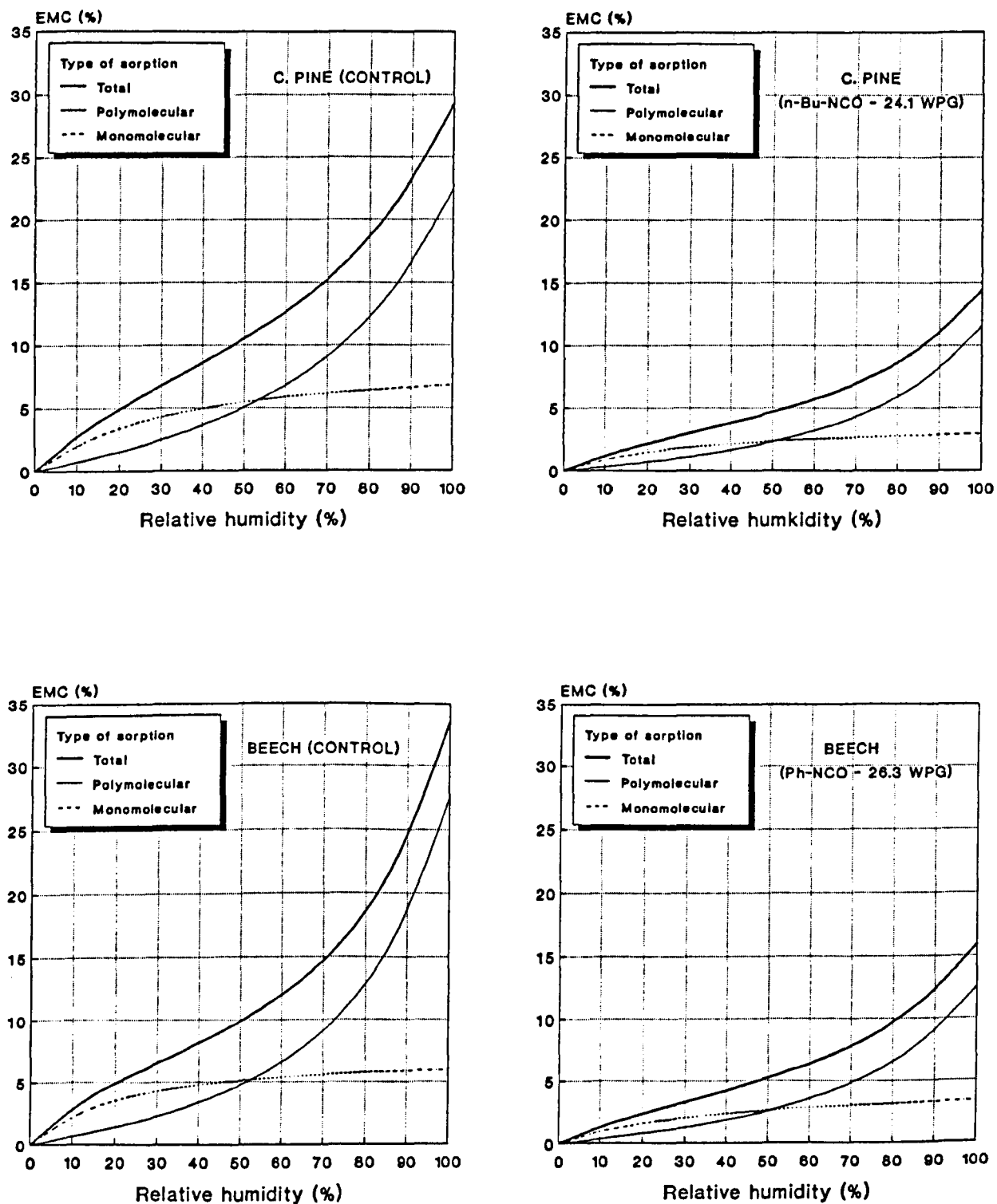
Fig. 3.6 Contribution of polymolecular and monomolecular sorption to total sorption over the entire range of relative humidity (desorption curves).
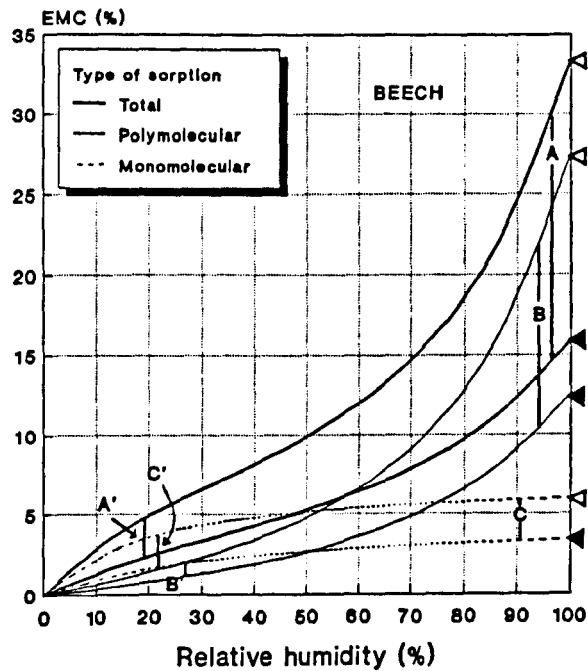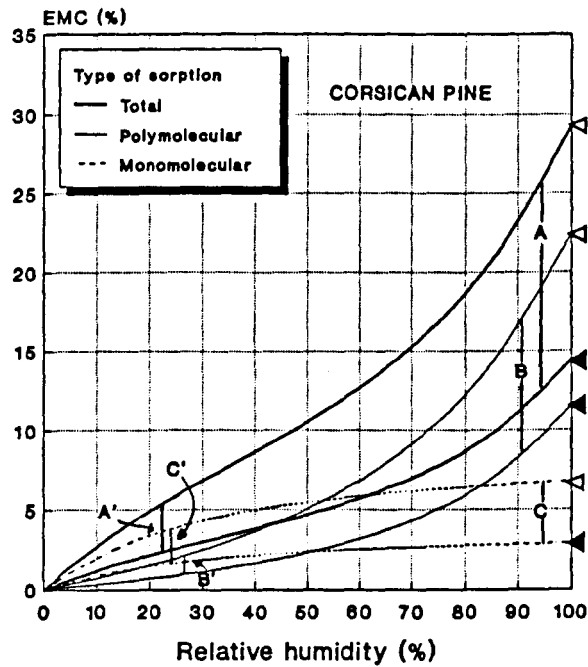
Fig. 3.7 Superposition of the graphs in Fig. 3.6 showing the shift in the relative contribution of the reduction in monomolecular and polymolecular sorption to the reduction in total water sorbed. A, B and C and A', B' and C' represent the reduction in total, polymolecular and monomolecular sorption, respectively, at a high and a low relative humidity.
◁Control specimens curves. ◀Treated specimens curves.

wood). This is more apparent when the isotherms for the controls and for the treated woods shown in Fig. 3.6 are superposed (Fig. 3.7). Lines A B and C in Fig. 3.7 illustrate, respectively, the reduction in total, polymolecular and monomolecular sorption at the high RH level, and A' B' and C', at the lower RH level. As the relative contribution of polymolecular sorption 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 treated woods. This reflects the moisture exclusion caused by the bulking effect (lines B & B'). At saturation this contribution reaches a maximum. Conversely, the relative participation of monomolecular sorption in 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 & C') making clear that the decline in total sorption achieved at lower ranges is chiefly due to a reduction in site accessibility.

These relationships are shown numerically at saturation and at 10% relative humidity in Table 3.12. It can for instance be seen in the case of beech treated with phenyl isocyanate that at a WPG of 34.3, 77% of the total reduction in hygroscopicity at saturation is caused by the bulking of the cell walls by the ester. At 10% RH however, 75% of the total reduction is brought about by the reduction in site accessibility.

Table 3.12 Contribution of the reduction in monomolecular and polymolecular sorption to the reduction in total water sorbed at 10 percent and at 100 percent relative humidity (RH) - Monofunctional isocyanates.

Reagent	WPG (%)	Type of sorption	10% RH			100% RH		
			Percent of total reducton					
			Ads.	Des.	Mean	Ads.	Des.	Mean

CORSICAN PINE

Reagent	WPG (%)	Type of sorption	Ads.	Des.	Mean	Ads.	Des.	Mean
n-Bu-NCO	7.5	Mono	78	77	78	31	42	37
		Poly	22	23	23	69	58	63
		Total	100	100	100	100	100	100
	11.3	Mono	76	78	77	30	32	31
		Poly	24	22	23	70	68	69
		Total	100	100	100	100	100	100
	19.7	Mono	74	77	76	22	23	23
		Poly	26	23	24	78	76	77
		Total	100	100	100	100	100	100
	24.1	Mono	75	76	76	21	26	24
		Poly	25	24	24	79	74	76
		Total	100	100	100	100	100	100
	34.3	Mono	74	76	75	20	26	23
		Poly	26	24	25	80	74	77
		Total	100	100	100	100	100	100
Ph-NCO	9.6	Mono	58	62	60	20	25	23
		Poly	42	38	40	80	75	77
		Total	100	100	100	100	100	100
	17.6	Mono	63	67	65	26	27	27
		Poly	37	33	35	74	73	73
		Total	100	1001	100	100	100	100
	19.3	Mono	73	76	74	21	24	23
		Poly	27	24	26	79	76	77
		Total	100	100	100	100	100	100
	25.9	Mono	72	74	73	17	21	19
		Poly	28	26	27	83	79	81
		Total	100	100	100	100	100	100
	29.6	Mono	73	76	74	18	20	19
		Poly	27	24	26	82	80	81
		Total	100	100	100	100	100	100

Table 3.12 (Cont.) Contribution of the reduction in monomolecular and polymolecular sorption to the reduction in total water sorbed at 10 percent and at 100 percent relative humidity (RH) – Monofunctional isocyanates.

Reagent	WPG (%)	Type of sorption	10% RH			100% RH		
			Ads.	Des.	Mean	Ads.	Des.	Mean

Percent of total reducton

BEECH

Reagent	WPG (%)	Type	Ads.	Des.	Mean	Ads.	Des.	Mean
n-Bu-NCO	7.8	Mono	81	83	82	18	23	21
		Poly	19	17	18	82	77	79
		Total	100	100	100	100	100	100
	11.7	Mono	83	86	85	16	20	18
		Poly	17	14	15	84	80	82
		Total	100	100	100	100	100	100
	18.1	Mono	84	86	85	13	15	14
		Poly	16	14	15	87	85	86
		Total	100	100	100	100	100	100
	23.3	Mono	85	85	85	12	15	14
		Poly	15	15	15	88	85	86
		Total	100	100	100	100	100	100
	37.3	Mono	83	83	83	13	15	14
		Poly	17	17	17	87	85	86
		Total	100	100	100	100	100	100
Ph-NCO	7.7	Mono	77	81	79	12	14	13
		Poly	23	19	21	88	86	87
		Total	100	100	100	100	100	100
	12.9	Mono	69	79	74	11	13	12
		Poly	31	21	26	89	87	88
		Total	100	100	100	100	100	100
	15.4	Mono	77	80	79	12	16	14
		Poly	23	20	21	88	84	86
		Total	100	100	100	100	100	100
	22.8	Mono	79	82	81	12	16	14
		Poly	21	18	19	88	84	86
		Total	100	100	100	100	100	100
	26.3	Mono	83	84	83	12	15	14
		Poly	17	16	17	88	85	86
		Total	100	100	100	100	100	100

This shift in predominance shown by each effect along the range of relative humidity is shown in Table 3.12 to be very consistent over the entire range of weight gains produced by the two isocyanates for the two species used. However, the relative contribution of the reduction in monomolecular sorption shown by the phenyl isocyanate treated samples is somewhat lower at the lower level of reaction. This may be related to the rigidity of the phenyl group forcing the polymer chains apart and uncovering a new population of sorptive sites, (see section 3.4.2). As these uncovered sites become operative in sorption the reduction at the monomolecular level may be partially offset. This, however, should not affect the reduction caused by bulking "providing the volume of adduct is not sufficient to cause disruption or change in the polymorphic configuration of the cellulose unit cell" (Stamm and Tarkow, 1947). This peculiarity may also explain the lack of significance in the regression analysis of the relationships between sites accessibility and polymolecular sorption and sites accessibility and total sorption shown by phenyl isocyanate treated Corsican pine. That is, the overall effect on hygroscopicity may be that when some sites are blocked others are simultaneously made available by the effect of the penetration of the phenyl / adduct between the polymer chains. This then offsets the relationship between monomolecular sorption and adduct volume. Similar counter effects may occur with the difunctional reagents. Here, the restraining effects of the cross linkages may be

obscured by uncovering of extra sorption sites as the (relatively long) cross linkage molecular chains are extended upon swelling (see section 3.4.3.3).

3.4.3.2.1 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 achieved by comparing the effect on water sorption produced by two adducts with significant difference in molecular size. This allows different degrees of bulking to be achieved with similar levels of hydroxyl groups reacted. The two monofunctional isocyanates used so far in this work are insufficiently different in molecular size to show this effect satisfactorily (see Table 3.8). In addition, the problem of the formation of a new population of sites caused by the penetration of Ph-NCO molecules into the cell wall and the possibility that the two difunctional NCO's produce some parallel effects such as crosslinking, make interpretation of the results uncertain. Octadecyl isocyanate (OCDC-NCO), a long carbon chain aliphatic monofunctional isocyanate was chosen to be compared with the other aliphatic monofunctional reagent used in this study - n-Bu-NCO. OCDC-NCO has characteristics which make it particularly suitable for this comparison (Table 3.13). It is about three times the molecular weight and molecular volume of n-Bu-NCO, with similar density. Therefore, OCDC-NCO may react with an equivalent amount

Table 3.13 Some characteristics of n-Bu-NCO and OCDC-NCO, percentage of total hydroxyl groups reacted and respective amount of bulking produced at selected weight gains (WPG's).

Reagent	MW (g)	MV (cc)	D (g/cc)	WPG	Percent of total OH[1]		Bulking[3]
					A	B	
CORSICAN PINE							
n-Bu-NCO	99.13	112.6	0.88	7.5	5.3	7.8	0.085
"	"	"	"	24.1	16.9	25.1	0.274
OCDC-NCO	295.1	348.4	0.847	24.5	5.8	8.6	0.289
BEECH							
n-BU-NCO	99.13	112.6	0.88	7.5	5.3	7.9	0.085
"	"	"	"	23.3	16.3	24.6	0.265
OCDC-NCO	295.1	348.4	0.847	21.0	4.9	7.4	0.248

[1]A and B - Assuming, respectively, total accessibility and 65% crystallinity for the cellulose fraction.

[3]cc/g of oven-dry wood (based on the WPG and on the density of the respective reagent).

MW - Molar mass

MV - Molar volume

D - Density

of hydroxyls but bringing about three times as much bulking. Conversely, at a similar degree of bulking, OCDC-NCO will have reacted with about one-third of the OH groups substituted by n-Bu-NCO.

With this in mind, samples of Corsican pine and beech taken from the same stock as that used throughout this work, were chosen and treated to the selected weight gains shown in Table 3.13, using the methodology previously described in Chapter 2. The treated samples were then taken through an adsorption and desorption cycle under the conditions described above (Section 3.2). The experimental EMC's obtained are shown in Table 3.14 together with the experimental values for n-Bu-NCO (taken from Table 3.3). The experimental EMC data obtained for OCDC-NCO treated samples were analysed by employing the Hailwood-Horrobin model. The empirical and physical calculated constants, the fitted-curve EMC values and the reduction in hygroscopicity data have been calculated as explained in section 3.3.2.2. and 3.4.2. The calculated values are shown respectively in Table 3.15, 3.16 and 3.17 together with the values for n-Bu-NCO at the relevant weight gains, taken from Tables 3.4, 3.5 and 3.7.

The results show that at equivalent WPG's the effect of the bulkier OCDC-NCO in decreasing sorption is similar to that caused by n-Bu-NCO. Yet to achieve this only one-third of the hydroxyl groups replaced by n-Bu-NCO are replaced by OCDC-NCO. Where similar proportions of OH groups are chemically replaced by each of the

Table 3.14 Experimental equilibrium moisture content (EMC) values for OCDC-NCO treated samples, compared to those obtained for the controls and for n-Bu-NCO (from Table 3.3) at selected WPG's. Mean values and standard deviations are shown.

Reagent	WPG		Relative humidity (%)					
			12	23	44	55	76	93
					CORSICAN PINE EMC (%)			
Controls	0.0	Ads	2.56(.08)	4.60(.09)	7.37(.08)	9.57(.12)	14.00(.17)	22.79(.21)
		Des	3.20(.10)	5.75(.11)	9.30(.10)	11.49(.12)	16.42(.16)	25.10(.24)
n-Bu-NCO	7.5	Ads	1.65(.12)	3.04(.12)	5.10(.14)	6.60(.18)	10.01(.20)	16.92(.29)
		Des	2.10(.07)	3.73(.09)	6.00(.18)	7.79(.16)	11.60(.14)	18.60(.30)
	24.1	Ads	1.22(.03)	1.96(.06)	3.45(.10)	4.49(.07)	6.94(.16)	10.43(.31)
		Des	1.50(.06)	2.36(.08)	3.99(.06)	5.33(.08)	7.96(.13)	11.50(.24)
OCDC-NCO	24.5	Ads	1.14(.01)	1.89(.08)	3.31(.14)	4.40(.07)	6.78(.09)	10.32(.56)
		Des	1.63(.03)	2.65(.03)	4.47(.17)	5.56(.08)	8.28(.07)	12.80(.52)
					BEECH (EMC)			
Controls	0.0	Ads	2.59(.09)	4.40(.06)	7.22(.08)	8.58(.12)	13.56(.19)	23.59(.21)
		Des	3.55(.10)	5.71(.08)	8.70(.10)	10.90(.14)	16.10(.20)	26.60(.19)
	7.9	Ads	1.71(.07)	3.03(.08)	4.71(.15)	6.30(.21)	9.65(.14)	16.99(.20)
		Des	2.18(.04)	3.70(.11)	5.66(.11)	7.83(.22)	11.41(.13)	19.10(.22)
	23.3	Ads	1.07(.03)	1.92(.06)	3.59(.09)	4.42(.11)	6.68(.18)	10.71(.21)
		Des	1.40(.05)	2.45(.10)	4.30(.13)	5.39(.15)	8.03(.19)	11.83(.31)
OCDC-NCO	21.0	Ads	1.04(.05)	1.96(.06)	3.66(.07)	4.40(.09)	6.94(.23)	11.13(.15)
		Des	1.66(.05)	2.88(.06)	4.66(.08)	6.01(.09)	9.00(.29)	13.00(.16)

Table 3.15 Fitted and physical constants of the stable isotherms calculated by means of the Hailwwod and Horrobin (1946) model, for the controls and treated wood with OCDC-NCOand n-Bu-NCO at selected WPG's. The regression coefficient of determination (r^2) and F-ratio for the data fitted to equation 3.2 are also shown.

Reagent	WPG		r^2	F-ratio	A	B	C	K_h	K_d	Wo	Mo
				CORSICAN PINE							
Controls	0.0	Ads	0.95	26.63*	3.63	8.5	8.5	4.09	0.755	252.88	7.12
		Des	0.94	23.12*	2.87	7.1	6.5	4.42	0.715	201.00	8.95
n-Bu-NCO	7.5	Ads	0.96	37.53**	5.82	11.9	13.0	3.59	0.790	379.96	4.74
		Des	0.97	40.84**	4.37	11.5	11.5	4.37	0.775	327.59	5.49
	24.1	Ads	0.96	36.56**	8.24	18.0	18.8	3.83	0.771	552.35	3.26
		Des	0.93	19.80*	6.53	16.4	16.0	4.33	0.752	471.55	3.82
OCDC-NCO	24.5	Ads	0.97	49.50**	8.91	17.5	18.9	3.55	0.773	563.16	3.20
		Des	0.99	452.52**	5.60	16.8	16.1	4.93	0.764	456.41	3.94
				BEECH							
	0.0	Ads	0.97	54.85**	3.18	12.4	12.4	5.74	0.823	317.72	5.66
		Des	0.97	48.82**	2.37	10.2	09.6	6.45	0.794	252.06	7.14
n-Bu-NCO	7.9	Ads	0.96	34.65**	5.06	16.6	17.3	4.96	0.931	450.67	3.99
		Des	0.93	21.00*	3.96	13.8	13.8	5.32	0.809	364.53	4.94
	23.3	Ads	0.97	43.66**	9.79	13.0	15.0	2.79	0.741	494.13	3.64
		Des	1.00	2007.83**	7.28	12.1	12.3	3.33	0.711	403.74	4.46
OCDC-NCO	21.0	Ads	0.95	28.66*	10.89	11.6	14.3	2.55	0.745	479.69	3.75
		Des	0.97	54.77**	5.79	13.4	12.9	4.20	0.727	394.79	4.56

**Significant at the 1% level of probability.
* Significant at the 5% level of probability>

Table 3.16 Curve-fitted isothermal equilibrium moisture content (EMC) data at 10 percentile levels of relative humidity (RH) calculated by means of equation 3.2, obtained for OCDC-NCO treated samples compared to those obtained for the controls and for n-Bu-NCO at selected WPG's from Table 3.5.

Reagent	WPG		Relative humidity (%)									
			10	20	30	40	50	60	70	80	90	100
			CORSICAN PINE									
			EMC (%)									
Controls	0.0	Ads	2.26	3.99	5.51	7.02	8.65	10.53	12.87	15.96	20.38	27.42
		Des	2.84	4.97	6.81	8.59	10.47	12.60	15.13	18.40	22.82	29.31
n-Bu-NCO	7.5	Ads	1.45	2.60	3.65	4.70	5.87	7.25	9.01	11.41	15.04	21.28
		Des	1.85	3.22	4.43	5.63	6.93	8.46	10.38	12.98	16.81	23.28
	24.1	Ads	1.01	1.80	2.51	3.22	3.99	4.89	6.02	7.54	9.77	13.43
		Des	1.25	2.18	3.00	3.80	4.66	5.66	6.89	8.51	10.82	14.47
OCDC-NCO	24.5	Ads	0.96	1.72	2.41	3.10	3.86	4.75	5.87	7.37	9.57	13.20
		Des	1.40	2.40	3.26	4.10	5.01	6.07	7.39	9.15	11.71	15.85
			BEECH									
			EMC (%)									
Controls	0.0	Ads	2.33	3.87	5.18	6.48	7.94	9.71	12.04	15.38	20.73	30.93
		Des	3.04	4.96	6.56	8.12	9.84	11.89	14.52	18.18	23.75	33.50
n-Bu-NCO	7.9	Ads	1.53	2.60	3.53	4.47	5.53	6.81	8.52	10.98	14.98	22.82
		Des	1.92	3.24	4.37	5.49	6.72	8.21	10.15	12.88	17.13	24.89
	23.3	Ads	0.91	1.70	2.43	3.18	3.99	4.93	6.08	7.57	9.65	12.86
		Des	1.20	2.17	3.06	3.94	4.88	5.94	7.20	8.80	10.96	14.11
OCDC-NCO	21.0	Ads	0.90	1.69	2.44	3.21	4.06	5.03	6.23	7.80	10.01	13.44
		Des	1.43	2.51	3.46	4.38	5.37	6.49	7.85	9.59	12.00	15.63

Table 3.17 Reduction in hygroscopicity calculated from the data of Table 3.16 at 20 percentile levels of relative humidity, and integral hygroscopicity reduction reduction (IHR) derived from de areas below the curves for OCDC-NCO treated samples, compared to those for n-Bu-NCO from Table 3.7, at the relevant weight gains.

Reagent	WPG		RELATIVE HUMIDITY					
			20	40	60	80	100	IHR

PERCENT REDUCTION IN HYGROSCOPICITY
CORSICAN PINE

Reagent	WPG		20	40	60	80	100	IHR
n-Bu-NCO	7.5	Ads	35	33	31	29	22	32
		Des	35	34	33	29	20	32
n-Bu-NCO	24.1	Ads	55	54	54	53	51	54
		Des	56	56	55	54	51	55
OCDC-NCO	24.5	Ads	57	56	55	54	52	55
		Des	52	52	52	50	46	52

BEECH

Reagent	WPG		20	40	60	80	100	IHR
n-Bu-NCO	7.9	Ads	33	31	30	29	26	31
		Des	35	32	31	29	26	32
n-Bu-NCO	23.3	Ads	56	51	49	51	58	53
		Des	56	51	50	52	58	54
OCDC-NCO	21.0	Ads	56	50	48	49	52	52
		Des	49	46	45	47	52	48

reagents (and therefore, enabling n-Bu-NCO to induce one-third of the bulking caused by OCDC-NCO), n-Bu-NCO is clearly less effective. This observation appears to be valid for both species in adsorption and in desorption. Nevertheless the effectiveness of OCDC-NCO in desorption appears to be slightly lower.

Fig. 3.8 shows a plot of the curve-fitted isotherms from Table 3.16 (OCDC-NCO) and table 3.5 (n-Bu-NCO) as well as the experimental points from Table 3.14 (OCDC-NCO) and Table 3.3 (n-Bu-NCO). It is evident from these curves that the sorption reduction imparted by OCDC-NCO is comparable to that produced by n-Bu-NCO at similar WPG's, despite the substantial difference in the proportion of OH groups chemically reacted. However, the isotherms for the equivalent WPG's coincide better in adsorption than in desorption, where the samples treated with OCDC-NCO show slightly higher EMC values than those treated with n-Bu-NCO. This can also be seen in Table 3.17 where the reduction in hygroscopicity for OCDC-NCO treated samples is somewhatlower in desorption than in adsorption. The same effect is not observed in the n-Bu-NCO treated samples where the hygroscopicity reduction values are shown to be essentially equivalent.

The total sorption isotherms from Fig. 3.8 were then split into monomolecular and polymolecular sorption according to the Hailwood-Horrobin model. These curves are depicted separately in Fig. 3.9.a (adsorption) and 3.9.b (desorption). At the two comparable WPG's, the adsorption curves shown in Fig. 3.9.a for OCDC-NCO and
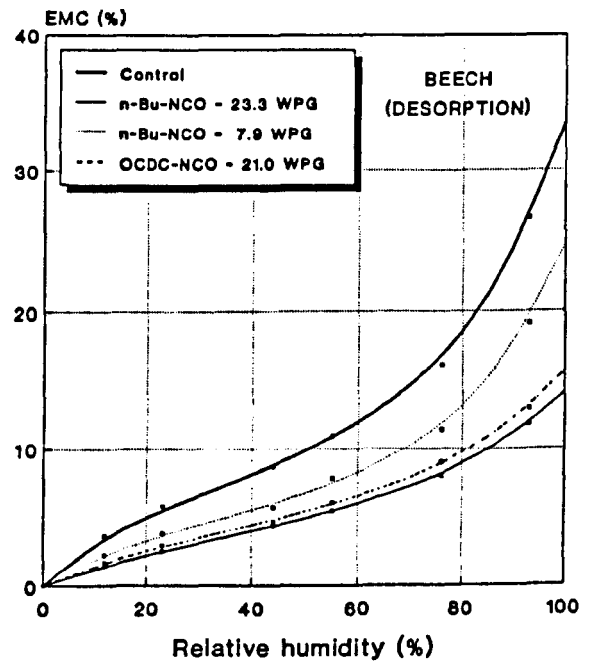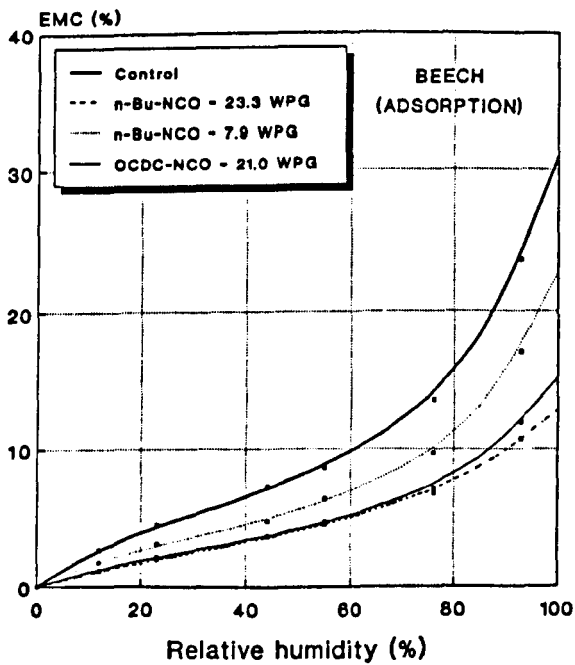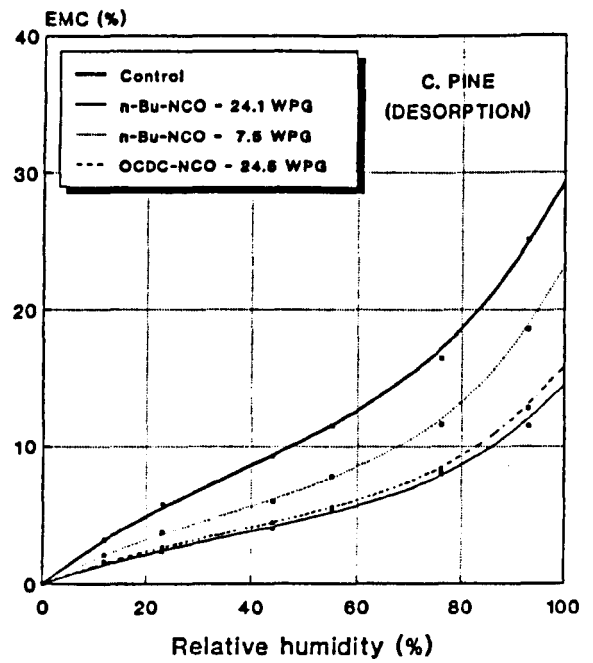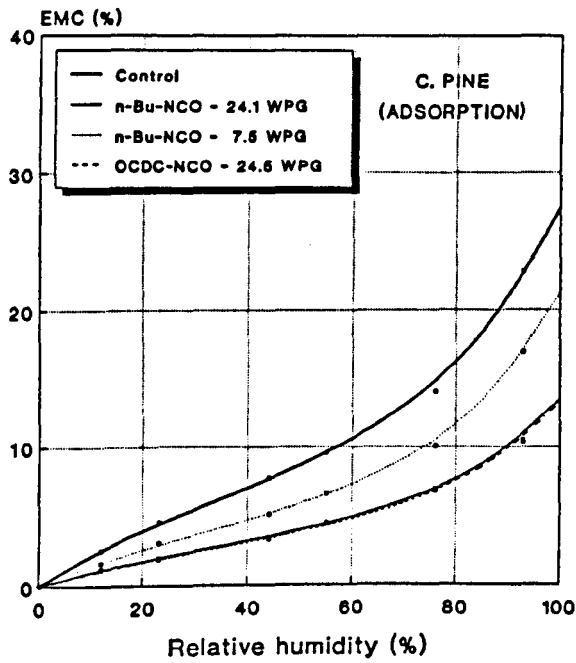
Fig. 3.8 Total sorption isotherms for the two wood species untreated (controls) and treated with n-butyl (n-Bu-NCO) and octadecyl (OCDC-NCO) isocyanates, at selected weight gains (WPG's).

EMC (%)

C. PINE MONOMOLECULAR ADSORPTION

- Control
- n-Bu-NCO - 7.5 WPG
- n-Bu-NCO -24.1 WPG
- OCDC-NCO -24.5 WPG

Relative humidity (%)

EMC (%)

C. PINE POLYMOLECULAR ADSORPTION

- Control
- n-Bu-NCO - 7.5 WPG
- N-Bu-NCO -24.1 WPG
- OCDC-NCO -24.5 WPG)

Relative humidity (%)

EMC (%)

BEECH MONOMOLECULAR ADSORPTION

- Control
- n-Bu-NCO - 7.9 WPG
- n-Bu-NCO -23.3 WPG
- OCDC-nco -21.0 WPG

Relative humidity (%)

EMC (%)

BEECH POLYMOLECULAR ADSORPTION

- Control
- n-Bu-NCO - 7.9 WPG
- n-Bu-NCO -23.3 WPG
- OCDC-NCO -21.0 WPG

Relative humidity (%)

Fig. 3.9.a Monomolecular and polymolecular adsorption isotherms for the two wood species untreated (controls) and treated with n-Bu-NCO and OCDC-NCO at selected weight gains.
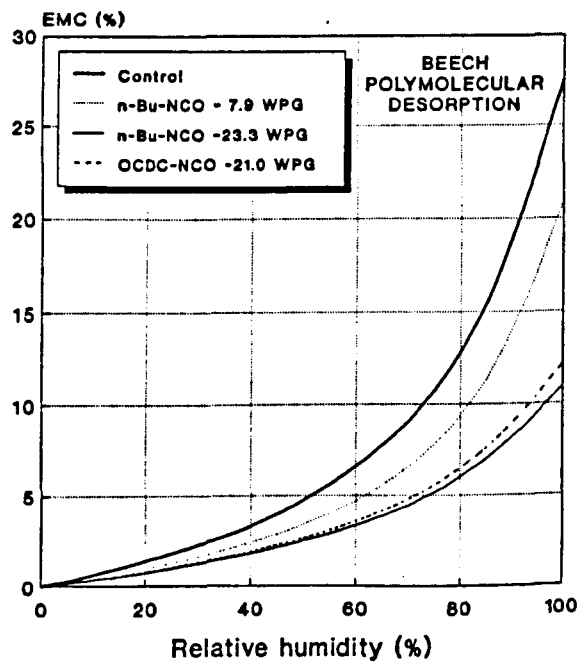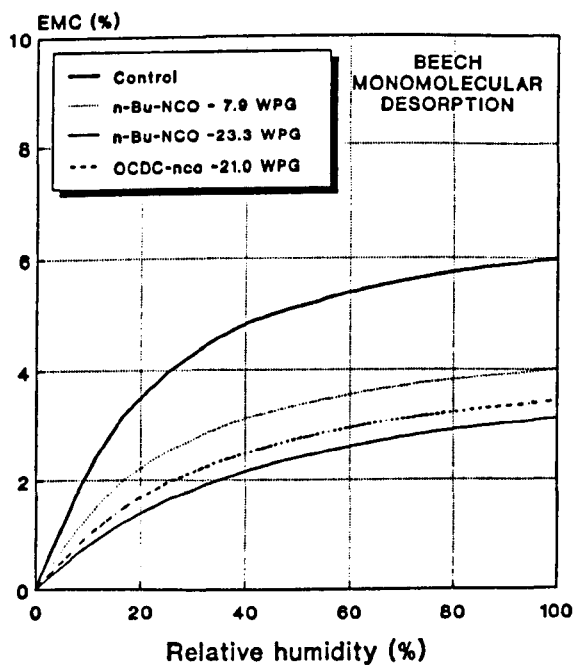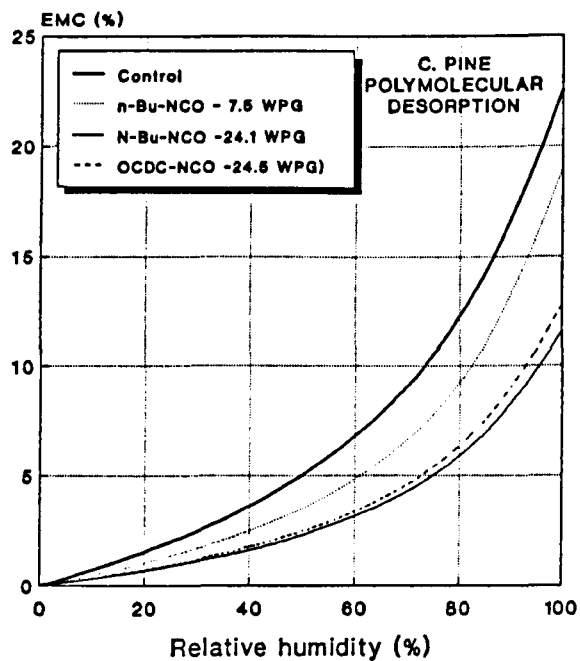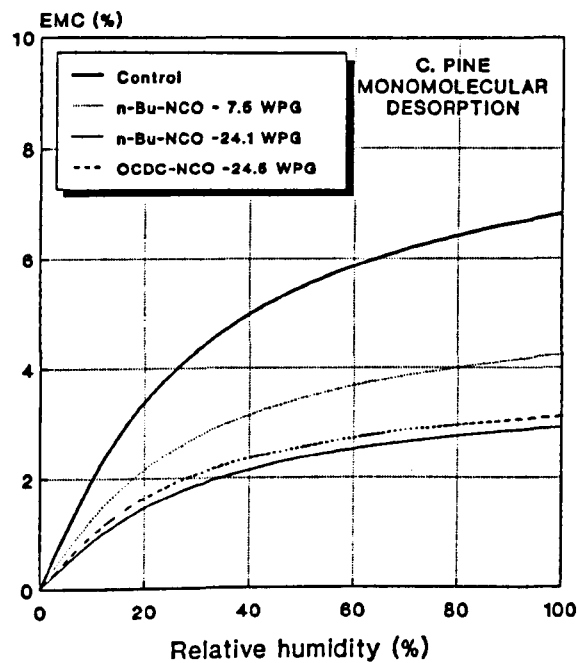
Fig. 3.9.b Monomolecular and polymolecular desorptiom isotherms for the two wood species untreated and treated with n-Bu-NCO and OCDC-NCO at selected weith gains.

n-Bu-NCO treated samples are virtually superimposable revealing that the two isocyanates show similar effectiveness in adsorption not only at the polymolecular level but also at the monomolecular level. For polymolecular sorption, this similarity was anticipated based on the evidences shown that this type of sorption is governed by the bulking effect and, according to Table 3.13, at similar WPG's the two isocyanates also produce similar bulking. Monomolecular sorption however, as discussed previously, is primarily a function of the availability of sorption sites. The fact that OCDC-NCO, which chemically blocks only one-third of the amount of OH groups reacted by n-Bu-NCO at similar WPG, produces similar effect in monomolecular adsorption, strongly suggests that is the amount of adduct laid down in the cell wall that determines the reduction obtained at the monomolecular level. This is substantiated by the values for W_O and M_O, shown in Table 3.15, which according to the Hailwood-Horrobin model reflect sites accessibility. It is clear that these values are closer when similar WPG's are considered denoting similar accessibility for the wood samples with substantial different proportions of hydroxyl groups chemically reacted but with comparable levels of bulking. Hence it is likely that the effect on site accessibility is not only chemical but also physical.

The desorption curves in Fig. 3.9.b show similar reduction at the polymolecular level for the two comparable WPG's with the two isocyanates. However,

differences can be readily seen at the monomolecular level where OCDC-NCO is seen to be less effective in desorption than is n-Bu-NCO at the monomolecular level.

Combining these observations it appears that the reduction in sorption produced by the OCDC-NCO and n-Bu-NCO adducts is partially due to simple physical blocking reducing the accessibility of the internal surfaces. Due to the relatively large molecular size, when the adduct reacts with one OH group it might cover some of the adjacent ones, providing a physical barrier which makes it difficult for water vapour molecules to reach some of the unreacted sites. Although reacting with substantially less OH groups, the presence of the bulkier OCDC-NCO molecule may be able to produce this physical barrier to a greater extent than the smaller n-Bu-NCO molecule. At similar weight gains, this results in a similar overall proportion of sites shielded by the two adducts, thus producing equivalent reduction in hygroscopicity. However, the 'shielding effect' caused by OCDC-NCO appears to be less effective in desorption. This is indicated by the slightly lower hygroscopicity reduction values in desorption than in adsorption shown by OCDC-NCO treated samples. It is suggested therefore that some of the unreacted sites hindered by the OCDC-NCO adduct became accessible to water molecules before the start of the desorption isotherm cycle when the samples are fibre saturated (by storage between damp cloths). This may be because under these conditions, the concentration of water molecules is higher leading to the

attainment of the full water swelling effect. The swelling stresses imposed at saturation render the hindered sites gradually accessible to water molecules. Hence, some of these water molecules are retained in desorption producing higher moisture content values at equilibrium with each relative humidity level than in adsorption. When departing from dryness however, these sites are kept unavailable by the shielding effect, probably until close to saturation. This explanation has some similarity to the interpretation of the hysteresis phenomenon in water sorption by cellulosic materials given by Urquhart and Williams (1924). According to these workers, more sites are available for water molecules during desorption than in adsorption, thus producing the hysteresis loop.

It should not be overlooked that due to the large difference in molecular size of the two adducts there may be differences in the topochemistry of the two differently modified cell walls (mainly as a result of steric hindrance effects). Hence, it is possible that the OCDC-NCO adduct is confined mainly to the outer part of the microfibrils and/or reacted chiefly to the surface of the molecular bundles of cellulose affecting a different population of sites than does n-Bu-NCO. The fact that OCDC-NCO molecule is much larger than the n-Bu-NCO and may not penetrate into all the spaces and reach the same population of sites as n-Bu-NCO, implies that similar arguments are valid when comparing accessibility of the two adducts with that of the much smaller water

molecules. This is suggested by previous workers; i.e. in order to occupy all sites accessible to moisture, the cell wall bulking chemical must be as small as the water molecules. (Spalt, 1958; Goldstein *et al*, 1960; Rowell and Rowell 1988;). Nevertheless, it still appears that, compared to n-Bu-NCO, some of the unreacted sites are prevented from hydrogen bonding to water molecules by OCDC-NCO. Since this adduct cannot occupy these sites by reacting with then, (apart from being unable to reach some sites, at the same WPG as n-BU-NCO, OCDC-NCO can have reacted with only about 1/3 the number of hydroxyls reacted with n-Bu-NCO), the only logical explanation for the observed effects seems to be that the shielding effect of the bulkier OCDC-NCO reduces the sorption forces.

However, since the effectiveness of n-Bu-NCO does not seem to drop in desorption (as it is shown above in the case of OCDC-NCO), it is suggested that, because the physical effect produced by this adduct is accompanied by a much more substantial chemical blocking (about three times higher that produced by OCDC-NCO), it may be that the shielding effect produced by the n-Bu-NCO adduct is less susceptible to the uncovering of hindered sites produced upon swelling.

Support for physical blocking of hydroxyl groups by isocyanate adducts is provided by molecular modelling studies. The figures derived below (Fig. 3.10 and 3.11) respectively of n-Bu-NCO and OCDC-NCO adducts, have been produced using a standard molecular modelling

program with optimisation of the structures by free energy minimisation (ChemMod II Molecular Modelling System). In agreement with the results obtained from sorption data, this different approach shows clearly that the coverage of more than one sorption site by each adduct molecule is perfectly plausible. There is also clear indication in Fig. 3.11 that the OCDC-NCO adduct physically covers a larger proportion of hydroxyl sites than does the n-Bu-NCO adduct, in line with the suggestions based on the sorption analysis.

The shielding effect may be also associated with differences in the hydrophobic character of the adducts, since longer carbon chains must render the isocyanate molecule more hydrophobic and improve the capacity for moisture exclusion presented by the OCDC-NCO adduct. This possibility, although extremely interesting, extends beyond the scope of this work, and no further exploration along this line has been conducted.
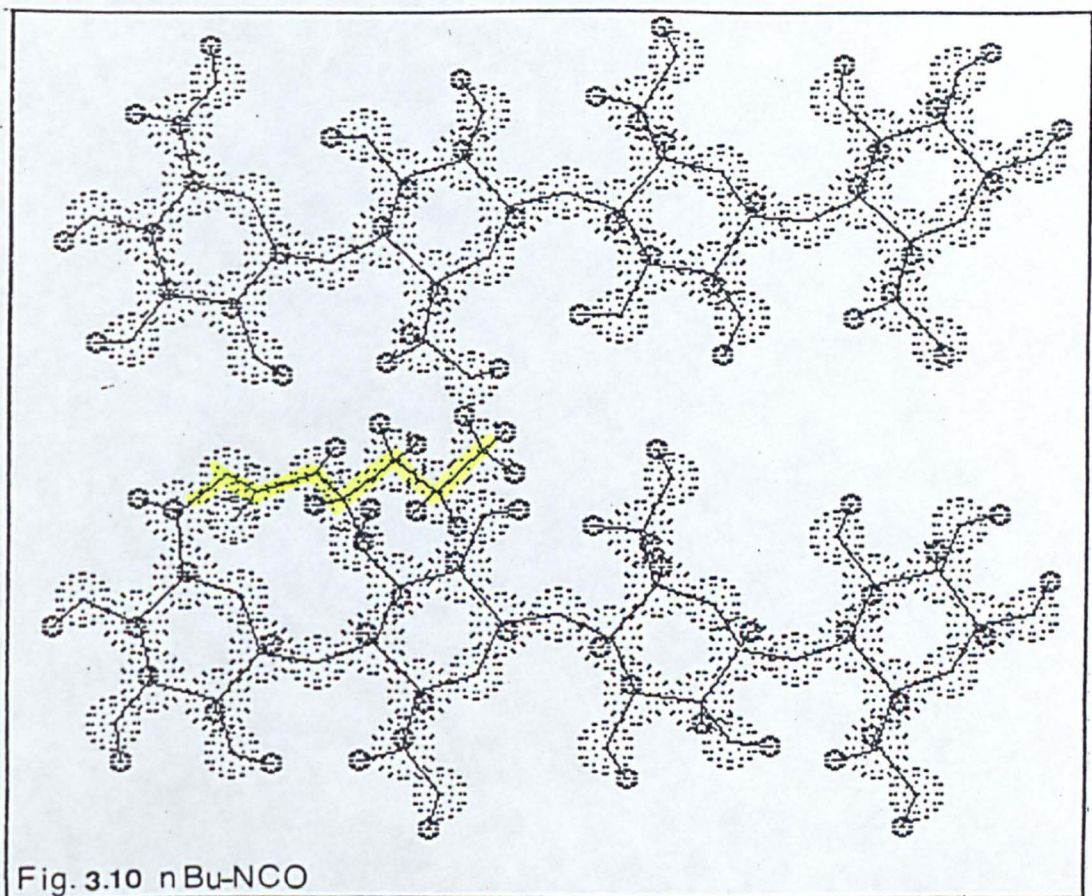
Fig. 3.10 n Bu–NCO
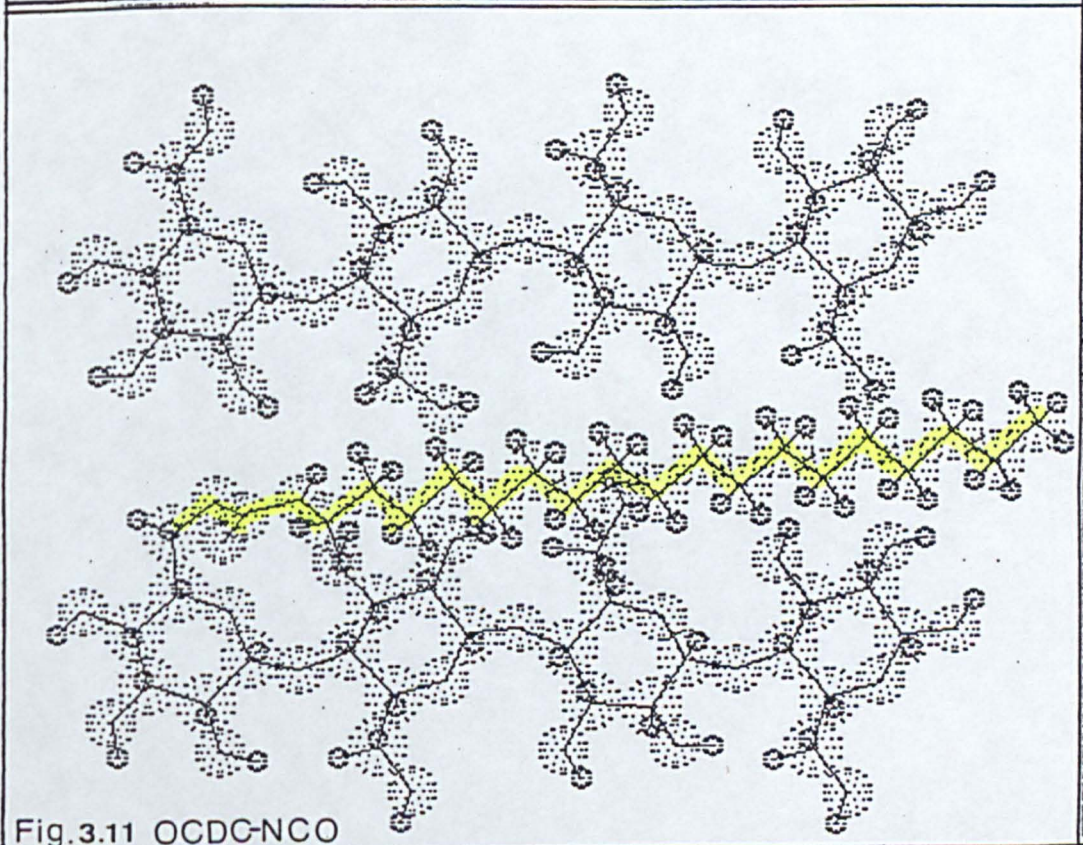
Fig. 3.11 OCDC-NCO

Figures 3.10 & 3.11 Adduct molecule between two adjacent cellulose chains as shown by a standard molecular modelling program with optimisation of the structures by free energy minimisation (ChemMod II - Molecular Modelling System). The cloud of points represents an approximation of the covalent radius.

3.4.3.3 Difunctional reagents

The analysis of the mechanisms involved in sorption reduction in wood treated with the difunctional isocyanates was conducted in a similar way to that described for the monofunctional ones. Table 3.18 shows the contribution of the various types of sorption to total sorption at saturation, calculated according to the Hailwood-Horrobin model. In general, apart from the previously mentioned exception of TDI treated Corsican pine, the sorption values for monomolecular, polymolecular and total sorption decrease with increasing reaction level. It should be noted however, that for HDI treated wood both monomolecular and polymolecular sorption decrease as the WPG increases but the latter does so far more rapidly. This effect is illustrated by the lower reduction in hygroscopicity observed at the lower range of RH where monomolecular sorption predominates. Regression analysis carried out (Table 3.19), using sorption data for modified woods from Table 3.18 shows that, as for the wood modified with the monofunctional reagents, the majority of the variation in total water sorbed is accounted for by variations in polymolecular sorption. The relationship between monomolecular sorption and total water sorbed shows consistently lower correlation. For HDI treated beech, this relationship is nonsignificant statistically. It appears therefore that the same general inferences concerning the reduction in total water sorbed made for

Table 3.18 Distribution of sorbed water at saturation in unmodified and modified wood to several levels of reaction according to the Hailwood and Horrobin (1946) model. Difunctional isocyanates.

Reagent	WPG (%)	[1]Volume (cc/g)		[2]Wo	Water sorbed (%) Mono	Poly	Total
			Corsican pine				
Controls	0.0	0.0	Ads	253	5.38	22.04	27.42
			Des	201	6.81	22.50	29.31
HDI	6.1	0.059	Ads	297	4.71	18.90	23.61
			Des	234	5.84	19.25	25.09
	12.9	0.124	Ads	302	4.61	15.63	20.24
			Des	261	5.49	16.30	21.79
	17.5	0.168	Ads	302	4.44	11.89	16.33
			Des	270	5.17	12.35	17.52
	19.5	0.188	Ads	309	4.37	11.48	15.85
			Des	295	4.85	12.11	16.96
	22.6	0.217	Ads	352	4.03	10.03	14.06
			Des	327	4.53	10.40	14.93
TDI	5.0	0.039	Ads	426	3.69	16.87	20.56
			Des	335	4.64	17.98	22.62
	6.4	0.022	Ads	306	4.58	17.84	22.42
			Des	255	5.59	19.86	25.45
	7.0	0.033	Ads	367	4.08	17.93	22.01
			Des	271	5.42	18.52	23.94
	8.6	0.035	Ads	379	3.95	16.22	20.17
			Des	273	5.30	18.10	23.40
	10.7	0.037	Ads	400	3.76	17.63	21.39
			Des	302	4.93	20.20	25.13

[1] HDI - volume of adducts in the cell wall calculated based on the density of the free disocyanate and on the respective WPG. TDI - measured volume increase.

[2] Apparent molecular weight of the polymer associated to one mole of water.

Table 3.18 (Cont.) Distribution of sorbed water at saturation in unmodified and modified wood to several levels of reaction according to the Hailwood and Horrobin (1946) model. Difunctional isocyanates.

Reagent	WPG (%)	[1]Volume (cc/g)		[2]Wo	Water sorbed (%) Mono	Poly	Total
			Beech				
Controls	0.0	0.0	Ads	318	4.67	22.26	30.93
			Des	252	5.98	27.52	33.50
HDI	9.3	0.089	Ads	427	3.52	20.70	24.22
			Des	327	4.54	20.53	25.07
	12.3	0.118	Ads	463	3.29	19.80	23.09
			Des	355	4.23	19.55	23.78
	16.0	0.154	Ads	489	4.16	19.39	23.55
			Des	374	4.04	18.75	22.79
	19.2	0.185	Ads	480	3.17	16.80	19.97
			Des	389	3.87	16.30	20.17
	23.1	0.222	Ads	488	3.13	14.45	17.58
			Des	378	3.92	13.75	17.67
TDI	4.0	0.019	Ads	373	3.81	21.52	25.53
			Des	295	5.15	23.63	28.78
	5.9	0.037	Ads	392	3.81	19.05	22.86
			Des	340	4.58	22.10	26.68
	7.5	0.040	Ads	457	3.44	18.22	21.66
			Des	369	4.30	21.64	25.94
	9.3	0.057	Ads	469	3.35	16.73	20.08
			Des	383	4.17	20.53	24.70
	11.0	0.065	Ads	521	3.12	16.52	19.64
			Des	401	4.05	19.42	23.47

[1] HDI - volume of adducts in the cell wall calculated based on the density of the free disocyanate and on the respective WPG. TDI - measured volume increase.

[2] Apparent molecular weight of the polymer associated to one mole of water.

Table 3.19 Regression analysis of the relation between the types of sorption and the total water sorbed at saturation.-Difunctional isocyantes.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio

Corsican pine reacted with HDI

Monomolecular vs. Total sorption

REGRES.	1	74.004	74.004	10.44**
ERROR	8	56.719	7.090	
TOTAL	9	130.723		
r^2x100		56.6		

Polymolecular vs. Total sorption

REGRES.	1	129.25	129.25	703.80**
ERROR	8	1.47	0.18	
TOTAL	9	130.72		
r^2x100		98.9		

Corsican pine reacted with TDI

Monomolecular vs. Total sorption

REGRES.	1	22.705	22.705	30.04**
ERROR	8	6.046	0.756	
TOTAL	9	28.752		
r^2x100		79.0		

Polymolecular vs. Total sorption

REGRES.	1	26.678	26.678	102.92**
ERROR	8	2.074	0.259	
TOTAL	9	28.752		
r^2x100		92.8		

** Significant at the 99 percent level of probability
DF Degrees of freedom

Table 3.19 (Cont.) Regression analysis of the relation between the types of sorption and the total water sorbed at saturation - Difunctional isocyantes.

SOURCE	DF	Sum squares	Mean squares	F-ratio

Beech reacted with HDI

Monomolecular vs. Total sorption

REGRES.	1	17.958	17.958	2.93^{NS}
ERROR	8	49.089	6.136	
TOTAL	9	67.046		
r^2		26.8		

Polymolecular vs. Total sorption

REGRES.	1	65.213	65.213	284.65^{**}
ERROR	8	1.833	0.229	
TOTAL	9	67.046		
r^2x100		97.3		

Beech reacted with TDI

Monomolecular vs. Total sorption

REGRES.	1	70.311	70.311	79.22^{**}
ERROR	8	7.100	7.100	
TOTAL	9	77.411		
r^2x100		90.8		

Polymolecular vs. Total sorption

REGRES.	1	76.935	76.935	1291.62^{**}
ERROR	8	0.477	0.600	
TOTAL	9	77.411		
r^2x100		99.4		

** Significant at the 99 percent level of probability
NS Not significant
DF Degrees of freedom

the monofunctionally modified specimens are valid for those reacted with the difunctional reagents; i.e. the decrease in total moisture sorption at saturation is primarily explained by a decrease in polymolecular sorption and the decrease in monomolecular moisture is of smaller importance. It cannot be overlooked however that, in the TDI treated samples, the variation in monomolecular sorption contributes more to the variation in total sorption than in the case of those treated with HDI. As already pointed out, this reflects the lower effectiveness presented by HDI treated samples at the low levels of relative humidity (Table 3.7) where monomolecular sorption effects are dominant.

Table 3.20 shows the result of a regression analysis carried out using the data from treated wood from Table 3.18. As before, the objective is to ascertain the influence of site accessibility (W_o) and the volume of adduct in the cell wall on monomolecular, polymolecular and total water sorbed at saturation. Due to the poor correlation between theoretical and measured volume increases shown by the TDI adduct (Table 2.6 and Fig. 2.3) the TDI chemical volume presented in Table 3.18 is that derived from the volume increase measured at each WPG. The results of this analysis for HDI are comparable to those presented for the specimens modified with monofunctional reagents shown in Table 3.11. The variation in W_o accounts for the most of the variation in monomolecular sorption. The relationships between W_o and polymolecular and W_o and total sorption are either of

Table 3.20 Regression analysis of the relations between the types of water at saturation and sites accessibility (expressed as Wo) and the volume of adducts in the cell wall- Difunctional isocyanates.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio	Sum Squares	Mean Squares	F-ratio

Corsican pine reacted with HDI

		Monomolecular vs. Wo			Monomolecular vs. Volume		
REGRES.	1	2.5012	2.5012	90.84**	1.1064	1.1064	5.48NS
ERROR	8	0.2203	0.0275		1.6150	0.2019	
TOTAL	9	2.7214			2.7214		
r^2x100		91.9			40.7		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	52.571	52.571	8.01*	102.58	102.58	330.42**
ERROR	8	52.491	6.561		2.48	0.31	
TOTAL	9	105.062			105.06		
r^2x100		59.7			97.6		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	78.006	78.006	11.84**	124.99	124.99	174.44**
ERROR	8	52.718	6.590		5.73	0.72	
TOTAL	9	130.723			130.72		
r^2x100		59.7			95.6		

Corsican pine reacted with TDI

		Monomolecular vs. Wo			Monomolecular vs. Volume		
REGRES.	1	4.2907	4.2907	181.64**	0.0263	0.0263	2.01NS
ERROR	8	0.1890	0.0236		4.4534	0.5567	
TOTAL	9	4.4796			4.4796		
r^2x100		95.8			20.0		

		Polymolecular vs. Wo			Polymolecular vs. Volume		
REGRES.	1	6.6815	6.6815	8.38*	0.332	0.332	0.92NS
ERROR	8	6.3794	0.7974		12.729	1.591	
TOTAL	9	13.0609			13.061		
r^2x100		51.2			10.4		

		Total sorption vs. Wo			Total sorption vs. Volume		
REGRES.	1	21.681	21.681	24.53**	0.545	0.545	1.47NS
ERROR	8	7.071	0.884		28.206	3.526	
TOTAL	9	28.752			28.752		
r^2x100		75.4			15.5		

** Significant at 99 percent level of probability
* Significant at 95 percent level of probability
NS Not significant
DF Degrees of freedom

Table 3.20 (Cont.) Regression analysis of the relations between the types of water at saturation and sites accessibility (expressed as Wo) and the volume of adducts in the cell wall- Difunctional isocyanates.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio	Sum Squares	Mean Squares	F-ratio

Beech reacted with HDI

		Monomolecular vs. Wo				Monomolecular vs. Volume	
REGRES.	1	1.2038	1.2038	10.49^{*}	0.3015	0.3015	1.33^{NS}
ERROR	8	0.9178	0.1147		1.8201	0.2275	
TOTAL	9	2.1216			2.1216		
r^2x100		56.7			14.2		

		Polymolecular vs. Wo				Polymolecular vs. Volume	
REGRES.	1	2.087	2.087	0.31^{NS}	52.598	52.598	99.59^{**}
ERROR	8	54.736	6.842		4.225	0.528	
TOTAL	9	56.823			56.823		
r^2x100		3.7			92.6		

		Total sorption vs. Wo				Total sorption vs. Volume	
REGRES.	1	6.461	6.461	0.85^{NS}	60.864	60.864	78.76^{**}
ERROR	8	60.585	7.573		6.182	0.773	
TOTAL	9	67.046			67.046		
r^2x100		9.6			90.8		

Beech reacted with TDI

		Monomolecular vs. Wo				Monomolecular vs. Volume	
REGRES.	1	3.0146	3.0146	70.21^{**}	0.9865	0.9865	3.11^{NS}
ERROR	8	0.3435	0.0429		2.3716	0.2965	
TOTAL	9	3.3582			3.3582		
r^2x100		89.8			28.0		

		Polymolecular vs. Wo				Polymolecular vs. Volume	
REGRES.	1	46.295	46.395	98.96^{**}	25.003	25.003	8.31^{*}
ERROR	8	3.743	0.468		25.034	3.129	
TOTAL	9	50.037			50.037		
r^2x100		92.5			50.9		

		Total sorption vs. Wo				Total sorption vs. Wo	
REGRES.	1	72.937	72.937	130.40^{**}	35.923	35.923	7.37^{*}
ERROR	8	4.475	0.559		41.488	5.186	
TOTAL	9	77.411			77.411		
r^2x100		94.2			47.9		

** Significant at 99 percent level of probability
* Significant at 95 percent level of probability
NS Not significant
DF Degrees of freedom

lower significance (Corsican pine) or nonsignificant statistically (beech). Conversely, for the two species, polymolecular and total sorption are strongly correlated to the volume of adducts in the cell wall while monomolecular sorption appears to be independent of the volume added.

Concerning the TDI treated samples, Corsican pine shows relationships between the three types of sorption and W_O which are analogous to those found for those treated with HDI i.e., they are all significant and the best correlation is shown by the monomolecular vs. W_O relationship. Beech treated samples also shows high correlation between W_O and monomolecular sorption but the values are somewhat higher for W_O vs. polymolecular and Wo vs. total sorption relationships. No meaningful trend is found for any of the correlations between volume & type of sorption in the case of Corsican pine treated samples (even when the values at 5% WPG are excluded, these correlations are still nonsignificant). For beech treated samples the regressions for volume vs. polymolecular and volume vs. total sorption are found to be significant but the correlations are much lower than for HDI treated wood. As in the case of HDI reacted wood, the monomolecular sorption vs. volume correlation is nonsignificant.

On the basis of this analysis it is suggested that as in the case of wood modified with monofunctional reagents, the reduction in water sorbed shown by HDI and TDI treated samples at the monomolecular level is brought
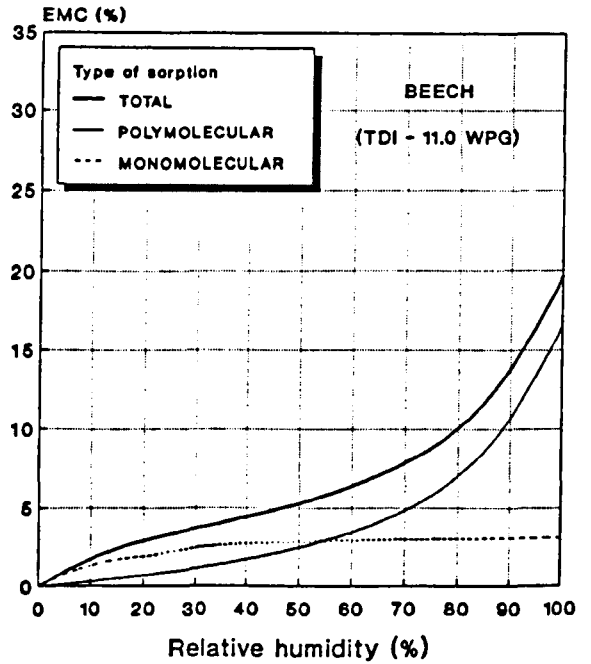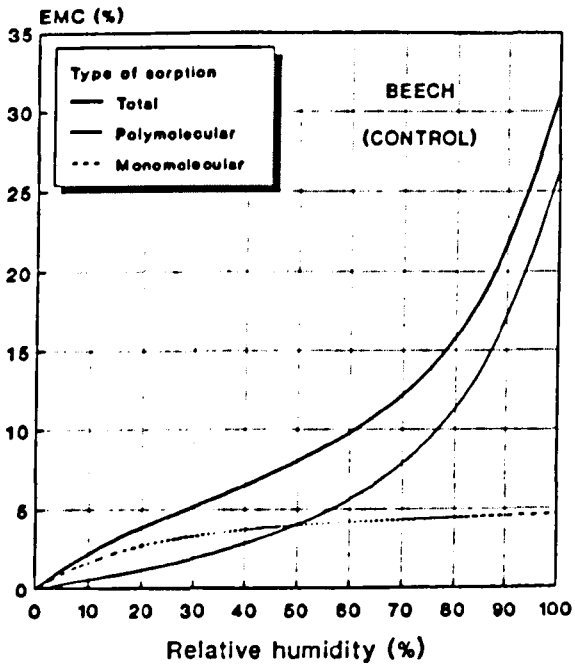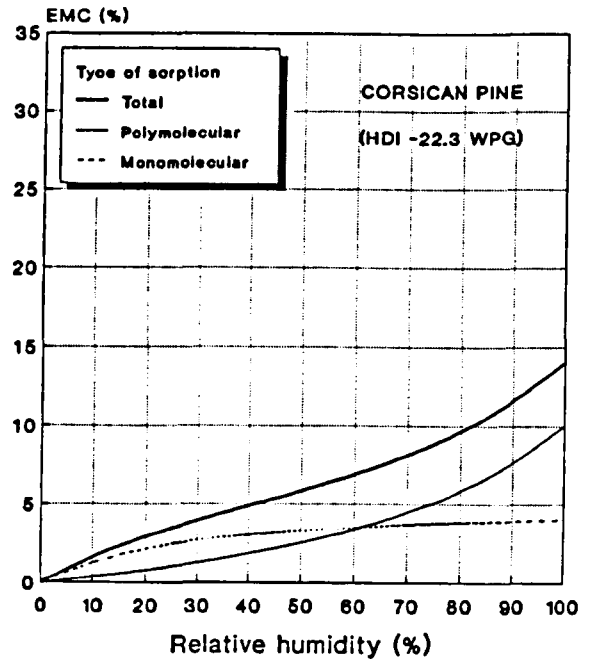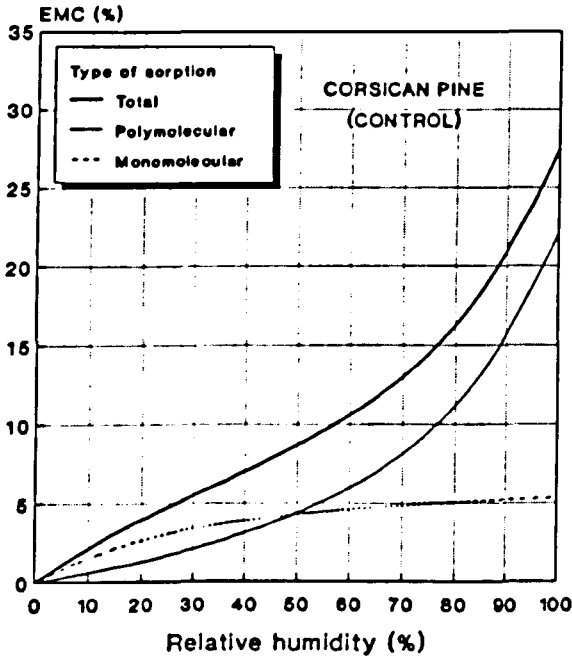
Fig. 3.12 Contribution of monomolecular and polymolecular sorption to total sorption over the entire range of relative humidity - desorption isotherms. (difunctional isocyanates).
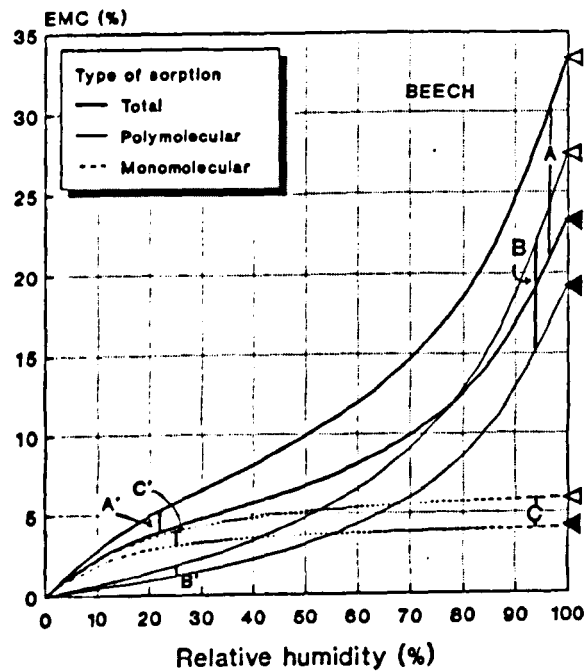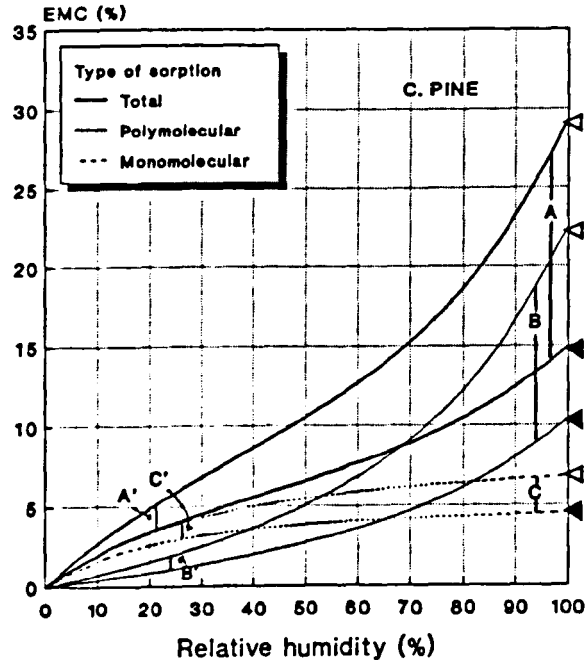
Fig. 3.13 Superposition of the graphs in figure 3.12 showing the relative contribution of the reduction in monomolecular sorption to the reduction in total water sorbed - desorption curves (difunctional isocyanates). A, B and C and A', B' and C' represent the reduction in total, polymolecular and monomolecular sorption, respectively, at a high and a low relative humidity. ◁Control specimens curves.◀Treated specimens curves.

about by a decrease in the availability of bonding sites represented by W_O. At the polymolecular level, only in the case of HDI does the reduction appear to be satisfactorily explained by the volume of adducts in the cell wall. With TDI, the volume does not adequately account for this reduction. It appears that part the reason for this is associated with the overall volume increase at each level of reaction being far too low when compared with HDI (Table 3.18), to account for the variation observed at the polymolecular and total sorption levels, where the bulking dominates. This observation suggests the participation of an additional effect improving the TDI adduct effectiveness against moisture sorption under vapour sorption conditions (see next section).

Figs. 3.12 and 3.13 show the contribution of each type of sorption to total sorption over the entire range of RH. It can be seen that the interchange in the participation of each type of sorption along the RH range shown for the wood treated with the monofunctional reagents is also apparent for that treated with difunctionals. However, the predominance of monomolecularly sorption effects are not so marked in wood treated with difunctional reagents. Although at the lower RH values the reduction in monomolecular sorption shows some dominance, the contribution of the reduction in monomolecular (C') and polymolecular sorption (B') to the total reduction (A') appears to be more evenly balanced than in the case of the monofunctionally

Table 3.21 Contribution of the reduction in Monomolecular and in Polymolecular sorption to the reduction in total water sorbed at 10 percent and at 100 percent relative humidity (RH)- Difunctional isocyanates.

Reagent	WPG (%)	Type of sorption	10% RH Percent of total reduction			100% RH		
			Ads.	Des.	Mean	Ads.	Des.	Mean

CORSICAN PINE

Reagent	WPG (%)	Type	Ads.	Des.	Mean	Ads.	Des.	Mean
HDI	6.1	Mono	60	67	64	18	24	21
		Poly	40	33	36	82	76	79
		Total	100	100	100	100	100	100
	12.9	Mono	56	56	56	11	18	15
		Poly	44	44	44	89	82	85
		Total	100	100	100	100	100	100
	17.5	Mono	69	66	67	8	14	11
		Poly	31	34	33	92	86	89
		Total	100	100	100	100	100	100
	19.5	Mono	67	63	65	9	16	12
		Poly	33	37	35	91	84	88
		Total	100	100	100	100	100	100
	22.6	Mono	57	56	57	10	16	14
		Poly	43	44	43	90	84	86
		Total	100	100	100	100	100	100
TDI	5.0	Mono	81	77	79	25	32	28
		Poly	19	23	21	75	68	72
		Total	100	100	100	100	100	100
	6.4	Mono	62	59	61	16	32	24
		Poly	38	41	39	84	68	76
		Total	100	100	100	100	100	100
	7.0	Mono	30	43	37	24	26	25
		Poly	70	57	63	76	74	75
		Total	100	100	100	100	100	100
	8.6	Mono	36	59	48	20	26	23
		Poly	64	41	52	80	74	77
		Total	100	100	100	100	100	100
	10.7	Mono	44	54	49	27	45	36
		Poly	56	46	51	73	55	64
		Total	100	100	100	100	100	100

Table 3.21 (Cont.) Contribution of the reduction in Monomolecular and in Polymolecular sorption to the reduction in total water sorbed at 10 percent and at 100 percent relative humidity (RH)- Difunctional isocyanates.

Reagent	WPG (%)	Type of sorption	10% RH Percent of total reduction			100% RH		
			Ads.	Des.	Mean	Ads.	Des.	Mean
		BEECH						
HDI	9.3	Mono	76	82	79	17	17	17
		Poly	24	18	21	83	83	83
		Total	100	100	100	100	100	100
	12.3	Mono	73	80	77	18	18	18
		Poly	27	20	23	82	82	82
		Total	100	100	100	100	100	100
	16.0	Mono	71	80	76	8	18	82
		Poly	29	20	24	92	82	88
		Total	100	100	100	100	100	100
	19.2	Mono	73	79	76	14	16	15
		Poly	27	21	24	86	84	85
		Total	100	100	100	100	100	100
	23.1	Mono	72	75	74	12	13	13
		Poly	28	25	26	88	87	87
		Total	100	100	100	100	100	100
TDI	4.0	Mono	74	76	75	12	18	15
		Poly	26	24	25	88	82	85
		Total	100	100	100	100	100	100
	5.9	Mono	74	69	72	11	21	16
		Poly	26	31	28	89	79	84
		Total	100	100	100	100	100	100
	7.5	Mono	57	64	61	13	22	17
		Poly	43	36	39	87	78	83
		Total	100	100	100	100	100	100
	9.3	Mono	60	64	62	12	21	16
		Poly	40	36	38	88	79	84
		Total	100	100	100	100	100	100
	11.0	Mono	69	56	63	14	19	17
		Poly	31	44	37	86	81	83
		Total	100	100	100	100	100	100

modified wood (see Fig. 3.7). This is illustrated in Table 3.21 where, at saturation, the contribution of polymolecular sorption reduction is seem to be highly predominant for the two diisocyanates for both two species. At the low RH levels however, more comparable values for the reduction in the two types sorption are achieved, except for HDI treated beech. The reason for this difference, in comparison to the results shown for the monofunctionally modified wood, may be related to some extent to crosslinking effect caused by reaction with difunctional reagents (see below).

3.4.3.3.1 Effect of crosslinking

The introduction of crosslinkages into wood is dependent upon reactions of both functionalities of the crosslinking agent with wood component hydroxyl groups. According to Rowland (1978), the probabilities for reaction of the terminal functionality of the crosslinking agent can be assumed to be subject to the same limitations that apply to the first functionality. Presumably, the two hydroxyls involved should be in adjacent chains in order to produce the desired reduction in moisture sorption. Rowell and Youngs (1981) state that, if the inner carbon chain of the crosslinking agent is relatively long (4 to 10 carbon atoms), the formed crosslinkages (assumed to be monomeric) would be more flexible than those produced by formaldehyde (presumed to be the inflexible crosslinking unit of the -O-C-O- type). These longer carbon chains would allow some

expansion of the crosslinked wood structural units causing less embrittlement but also reducing the dimensional stability that might be accomplished with the treatment.

The question that arises is whether or not these crosslinkages play any role in the wood moisture sorption control and in the associated dimensional stability and, if such is the case, at which part of the RH range they exert their influence. In the reaction conditions used (one mole of the diisocyanate in pyridine) the concentration of pyridine is of about 84% vol:vol (HDI treatment) and 86% vol:vol (TDI treatment). According to West (1988), such a concentration should cause a degree of swelling relative to water of about 75% at 100 ^{o}C. Swelling in pyridine has been shown to occur rapidly at the reaction temperature used in this work (approx. 120 ^{o}C) (West, 1988). Hence, any crosslinkage formed should have been established with the wood swollen at least 75% that occurring in water. In these conditions, the monomeric crosslinking formed would allow expansion of the wood structure network upon sorption, until a degree of swelling is achieved, at least similar to that in which these crosslinkages were set up. That is, although the total amount of hydroxyl groups capable of acting as active sorption centres may be limited by the restriction of swelling caused by these crosslinkages limiting further developing of wood-vapour interfacial area, the effectiveness of these crosslinkages against moisture sorption is likely to be mainly accomplished at

the higher range of relative humidities (beyond the 75% swelling relative to water). Therefore, the moisture exclusion visualized by this mechanism should be reflected mostly as a decrease in polymolecular sorption. On the basis of this explanation the reduction in moisture sorption which may be caused by crosslinking formed under the conditions described is expected to be of very limited efficacy at the lower range of RH's.

In the case of HDI treated samples, the crosslinkages seem not to improve the reduction in sorption at the higher ranges of RH any more than should be expected from the bulking effect of this adduct in the cell wall. This is indicated by the highly significant correlation shown by the HDI adduct volume in the regression analysis with polymolecular and total sorption (Table 3.20). At the lower ranges of RH the reduction in sorption is lower (Table 3.7). This is anticipated from the crosslinking mechanism described above by which enhancement in sorption reduction due to swelling restriction by crosslinkages formed under the present conditions is not expected at the lower RH's. However, as pointed out, TDI treated samples show higher reduction in sorption than would be expected from the lower volume of adduct laid down in the cell walls when compared to those treated with HDI. This is particularly evident for Corsican pine treated samples. The apparent higher effectiveness imparted by that fraction of TDI laid down within the cell wall apparently might be explained on the basis of differences in molecular shape

and lower flexibility of the aromatic group which forms the bulk of the TDI molecule. As expressed above, the crosslinkages formed from HDI and TDI should allow the wood component chains to swell to a given extent. It is tentativelly suggested that as water is absorbed and the wood starts to swell, these crosslinkages begin to expand towards their extended conformation, exposing some sites on the internal surfaces where the water molecules are able to enter and attach themselves to available hydroxyl groups left uncovered as swelling gradually occurs. The better performance against moisture sorption shown by TDI, mainly at the lower RH ranges, implies that this presumed uncovering of sites due to crosslinkages expansion occurs to a lesser extent with TDI. This may be associated with higher rigidity of the crosslinkages formed from TDI. It seems reasonable to expect that expansion of crosslinkages might occur more readily with the much more flexible alkane chain associated with the HDI crosslinkages. This would then decrease its efficiency against moisture sorption at the higher RH ranges, by allowing the wood polymers to be pulled apart upon wetting and at the lower ranges, by the uncovering of some physically hindered hydroxyl sites which should result from this expansion.

Some insight of the sorption process in difunctionally modified wood is provided by the Hailwood-Horrobin model analysis. The apparent complexity of the mechanisms of hygroscopicity reduction in this modified wood, involving crosslinking as well as a chemical and

physical blocking of sites and bulking, requires further experimentation to test the validity of some of the hypothesis made.

<u>Swelling in water:</u>

It has been reported that the crosslinking of wood is associated with a decrease in total swelling in the wet state (Tarkow and Stamm, 1953; Kollman at al, 1975; Nakagami and Yokota, 1983; Zeronian and Kim, 1988). Hence it is necessary to examine if the HDI and TDI cross linkages are able to produce this effect. This was investigated by means of the experiment described below.

Corsican pine and beech samples (20 x 20 x 5 mm - radial x tangential x longitudinal) prepared from the common stock used throughout this study, were extracted by refluxing in toluene/acetone/ethanol (4:1:1 vol.:vol.), oven dried and carefully measured with vernier calliper (accurate to 0.02 mm) in the principle orthogonal directions. They were than water swollen by storing between damp cloths at room temperature for seven days when maximum swelling appeared to be reached. Once the untreated swollen volumes were measured, the samples were left to dry slowly in a conditioning room (20+-1 ^{o}C, approx. 65% RH) for about a week and then oven dried and kept in a desiccator over silica gel self-indicator until required for the tests. Batches of ten samples (5 Corsican pine and 5 beech samples) were reacted with HDI and with TDI under the conditions previously described in Chapter 2. After treatment the oven-dry treated samples

were again measured in order to find the swelling caused

by chemical addition and then placed between

damp cloths again for seven days at room temperature.

Finally the wet volumes of the treated blocks were

determined. The same experiment was repeated with the

monofunctional reagent n-Bu-NCO for comparison. Control

specimens boiled in pyridine only, showed negligible

weight gain and virtually no volume increase due to this

treatment. The results are shown in Table 3.22 where it

can be seem that the three isocyanates caused significant

increase in the oven-dry volume due to chemical addition.

However, the wet swollen volume is not reduced by any of

the chemicals used. Actually, the overall swelling is

slightly but consistently higher after than before

treatment. Baird (1969) also reported increase in the

total volume change of the same order to that found in

the present work for n-Bu-NCO treated samples. Wadsworth

and Cuculo (1978) reported that the attachment of methyl

and acetate groups appears to open up cellulose

structure, facilitating penetration of water molecules

and increasing water sorption at saturation. Swelling

in water above green volume for acetylated wood has been

reported by Rowell (1982). Nakagami and Yokota (1983)

also noticed that wood sample dimensions in the wet state

is invariably increased by methacrylation. All these data

provide evidence that the higher overall swollen volume

shown by the treated samples can be readily explained on

the basis that the wood structure is propped open by the

introduction of the adducts in the cell wall in such way

Table 3.22 Investigation of crosslinking effectiveness based on wood volumetric changes in water - mean values and standard deviations (in parenthesis) are shown.

Wood species	Reagent	Reaction time(hs)	WPG (%)	A (%)	B (%)	C (%)	D (%)	ASE (%)
C. pine	n-Bu-NCO	2.0	20.4(0.5)	11.3(0.3).	5.9(0.7)	17.2	15.0(0.9)	65
Beech		3.0	23.4(0.6)	14.0(0.5)	8.3(0.4)	22.3	19.9(0.6)	63
C. pine	HDI	3.0	21.8(0.6)	8.8(0.3)	7.6(0.7)	16.4	14.7(0.8)	53
Beech		3.0	19.7(0.1)	10.9(0.4)	10.9(0.6)	21.8	19.0(0.4)	47
C. pine	TDI	4.0	10.5(0.7)	3.2(0.2)	12.5(0.3)	15.7	14.8(0.9)	18
Beech		4.0	13.3(0.4)	3.8(0.9)	15.2(0.8)	19.0	18.8(0.6)	22
C. pine	None*	2.0	0.3(0.1)	0.0	15.0(0.1)	15.0	15.0(0.1)	0
Beech		2.0	0.7(0.1)	0.0	19.4().3)	19.4	19.4(0.3)	0

A = Swelling caused by chemical addition
B = Subsequent swelling addition at saturation
C = A+B (Overall swelling at saturation)
D = Swelling at saturation before the treatment
ASE = Antiswelling efficiency (percent swelling untreated minus percent swelling treated divided by percent swelling untreated)
* Boiled in anhydrous pyridine only.
All swelling data expressed on oven-dry untreated volume basis
All data are average of 5 replicates.

that some sites which are not accessible to water
molecules in the untreated samples (probably those
hydroxyls involved in stronger self-bonding in the
amorphous zones of cellulose (Stamm, 1977b) are made
available for the chemical during reaction or/and for
water molecules in the subsequent swelling after
treatment. The increase in overall treated wet volume,
indicates that, although the adducts bulk the cell wall
and also block some sites, reducing the subsequent
swelling in water, the overall number of sites involved
in the process (reaction plus water sorption) is higher
than those involved in water sorption only, in untreated
wood. This may be also a result of bulking caused by the
adduct, i.e., some of the original sites give rise to
extra swelling by reacting with bulky reagent.

In line with published work of Stamm and Tarkow
(1947) concerning acetylated wood, the anti-swelling
efficiency (ASE) values found for n-Bu-NCO and HDI
treated samples (Table 3.22) are higher than those found
for the reduction in hygroscopicity at saturation at
similar WPG's (see Table 3.7). The ASE values found for
TDI treated samples however, are substantially lower than
the values for the reduction in hygroscopicity. This may
indicate that the TDI adduct is more effective in vapour
conditions that in liquid water. A possible explanation
for this is that the reduction in EMC obtained with TDI
samples in vapour conditions is partially improved by the
higher rigidity of the TDI crosslinkages causing a lag in
the EMC attained at each vapour pressure. At

saturation, the considerable stresses developed upon swelling (Barkas, 1949; Stamm, 1964), forces the polymer structure apart and the flexibility of the crosslinkages allows the reacted wood to swell to its normal swollen state. The higher EMC values attained in desorption than in adsorption by the TDI treated samples suggest that some of the sites made available at saturation retain water molecules when undergoing desorption. This effect appears to be similar to that described for OCDC-NCO treated samples (Section 3.4.3.2.1) with the difference that with TDI, the uncovering of hindered sites is increased by the extension of the crosslinkages under swelling stresses. It is observed that the ASE at saturation in liquid water produced by HDI treated samples (Table 3.22) is of similar magnitude to the hygroscopicity reduction extrapolated to saturation, at equivalent weight gains (Table 3.7). This is in good agreement with the proposal that lower crosslinking effectiveness in vapour conditions is due to the higher flexibility of the HDI formed crosslinkages. That is, approaching saturation, most of the sites physically hindered by the HDI crosslinkages might be already uncovered, thus, no significant extra decrease in ASE in liquid water due to crosslinking is observed.

Concerning the crosslinking effectiveness in water, there is no evidence from the data of Table 3.22 that this mechanism is effectively increasing the ASE achieved under the conditions of the experiment. The ASE shown in Table 3.22 is clearly caused by an increase in

the oven dry volume due to the cell wall bulking caused by the adducts rather than to any decrease in the wet swollen volume, i.e., the higher stability shown by the treated wood appears to be the result of a reduction in the degree to which the wood can shrink rather than the degree to which it can swell. The converse would be the case if a significant crosslinking effect is developed.

Swelling in pyridine:

It has been explained above that the potential crosslinking treatments were applied to wood swollen to at least 75% that occurring in liquid water. It may be therefore, that any crosslinks are formed with wood already substantially swollen. Flexibility of the crosslink 'chains' may allow the reacted wood to swell under the considerable stresses developed by water sorption (Barkas, 1949; Stamm, 1964) to the normal water swollen state. Pyridine swells wood about 20-25% more than water (Ashton, 1973). Hence it may be that any crosslinking effect will become more apparent by swelling in pyridine than in water.

The same samples used for the previous water-swelling experiment were carefully dried in a conditioning room, at 20°, 65% RH, then oven dried and kept in anhydrous pyridine (previously stored over KOH) in a sealed glass jar for five days. During the course of the experiment the samples were quickly removed only in order to have their dimensions measured with a vernier calliper (+-0.02 mm). The results are shown in Table 3.23

where they are compared to those obtained from the
swelling experiment in water described above. According
to Table 3.23, the samples modified with HDI and TDI
undergo super-swelling (i.e. to levels greater that those
caused by water) to a similar degree as the controls.
However, the n-Bu-NCO treated samples show substantially
higher super-swelling. This is particularly evident in
the columns concerning the subsequent swelling after
chemical treatment where the ratio, swelling in
pyridine:swelling in water, is twice as high for the n-
Bu-NCO treated samples. For monofunctionally modified
wood, it may be that the structure, already propped open
by the treatment as indicated by the higher overall
swelling in water (Table 3.22), in the presence of the
more powerful and larger swelling molecule, pyridine,
allows the ordered regions of wood cellulose gradually to
become accessible, facilitating solvent penetration and
subsequent super-swelling. Gradual opening of ordered
regions of wood cellulose which are made available for
water molecules has been reported by Nakagami and Yokota
(1983) working with methacrylated wood. They report that
"the dimensions in the wet state invariably is increased
by methacrylation and the magnitude of the increase is
related to the extent of methacrylation".

The high degree of super-swelling shown by n-
Bu-NCO treated samples in Table 3.23 was not observed in
a parallel experiment using samples treated to lower
levels of reaction (10 and 15 WPG) prepared under similar
reaction conditions. This indicates that the opening of

Table 3.23 Comparison between volumetric swelling in water and in pyridine with the purpose of crosslinking effectiveness investigation - mean values and standard deviations (in parenthesis) are shown.

Wood species	Reagent	Reaction Time (hs.)	WPG (%)	Swelling due to reaction (%)	Subsequent swelling			Total swelling		
					in water (%)	in pyridine (%)	Ratio	in water (%)	in pyridine (%)	Ratio
C. pine	n-Bu-NCO	2.0	20.4(0.5)	10.1(0.2)	5.3(0.7)	14.9(1.5)	2.81	15.4	25.0	1.62
Beech		3.0	23.4(0.6)	12.3(0.4)	7.3(0.4)	17.6(0.9)	2.41	19.6	29.9	1.53
C. pine	HDI	3.0	21.8(0.6)	8.3(0.6)	6.9(0.7)	9.1(0.8)	1.32	15.2	17.4	1.14
Beech		3.0	19.7(0.1)	9.0(0.8)	10.0(0.6)	13.5(0.7)	1.35	19.0	22.5	1.18
C. pine	TDI	4.0	10.5(0.7)	3.1(0.2)	12.1(0.3)	15.9(0.6)	1.31	15.1	19.0	1.25
Beech		4.0	13.3(0.4)	3.7(0.8)	14.6(0.8)	20.0(0.3)	1.38	18.2	23.7	1.30
C. pine	None[*]	2.0	0.3(0.1)	0.0	15.0(0.1)	18.5(0.5)	1.23	15.0	18.5	1.23
Beech		2.0	0.7(0.7)	0.0	19.4(0.3)	24.9(0.4)	1.28	19.4	24.9	1.28

[*] Boiled in pyridine only.

All swelling data expressed in oven-dry treated volume basis.

All data are average of 5 replicates.

the structure allowing the super-swelling shown by n-Bu-NCO treated samples in Table 3.23 occurs at weight gains somewhere between 15 and 20-23%. This does not necessarily mean that the crystal lattice structure is opened at this level of reaction by the introduction of the adducts. West and Banks (1987) have shown that in the reaction with n-Bu-NCO catalysed by pyridine, the polysacharide wood fraction reacted to a degree of substitution (DS) 0.2, related to the theoretical maximum weight gain ($\approx$143%, according to Table 2.4)), presented no changes in the X ray diffractogram. Significant changes were observed only at higher degrees of substitution. According to Krassig (1985), in the course of heterogeneous reaction (acetylation) on cellulose fibres, in the early stages, the reaction takes place at the surface of the fibrils and at the less ordered regions interlinking the crystallites. As the reaction progresses it gradually penetrates from there into crystalline zones by a hydrogen bond 'unzipping' process. This forces and open the elementary crystallites from both ends, thus increasing molecular spacing (Fig. 3.14). Therefore, at the level of reaction shown in Table 3.23, the n-Bu-NCO adducts may have opened the fibrillar interstices and entered the interlinking regions between the crystallites propping the structure open. When the treated samples are subsequently exposed to pure pyridine this facilitates penetration of pyridine molecules from both ends of the crystallites causing super-swelling by gradually exposing the more ordered regions. Sato and co-
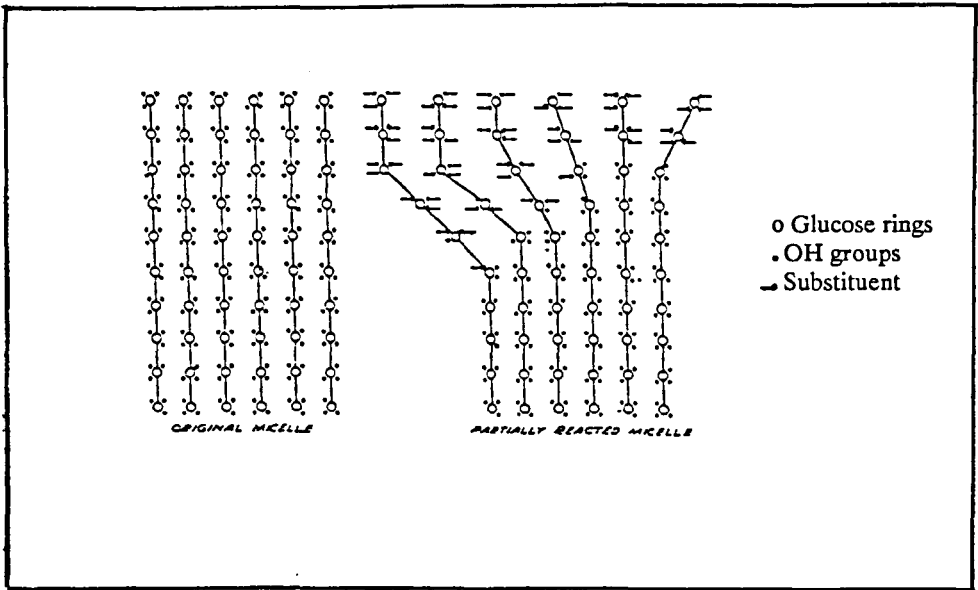
Fig. 3.14 Schematic illustration of the "unzipping" process of hydrogen bonds, showing the reaction zone progressing along the crystalline region (after Krassig, 1985).

workers (1978) reported that "the crosslinking of cotton cellulose with hexamethylene diisocyanate in dimethylformamide (DMF) started in the amorphous regions and proceeded to the crystalline regions at a later stage". Although under different reaction conditions, this observation indicates that crosslinking formation does not preclude difunctional adducts from penetrating the crystalline regions of cellulose. It seems possible however that crosslinkages introduced by reaction with difunctional reagents act to prevent the opening up of more ordered regions upon swelling by pyridine.

3.4.4 Effect on hysteresis

The effect of chemical modification on hysteresis was assessed by calculating the hysteresis ratios of the areas below the adsorption and desorption curves for monomolecular, polymolecular and total sorption hysteresis. These areas were obtained by integrating respectively equations 3.2, 3.7 and 3.8 within the limits from 0% to 100% RH. The results are shown in Table 3.24. The values found for the untreated wood total hysteresis fall within the limits generally reported in the literature for hardwoods and softwoods (Spalt, 1958; Skaar, 1988). With the exception of TDI treated samples, the ratio values appear to increase slightly with increasing weight gain in modified wood, indicating that hysteresis tend to decrease as the level of reaction increases. The departure from this general trend shown by TDI treated samples was expected on the basis of its relationship to the lower reduction in hygroscopicity produced in desorption than in adsorption discussed previously.

Regression analysis was carried out by combining the four series of data for each species shown in Table 3.24. A significant positive correlation between WPG and total hysteresis ratio was obtained for the two species (Table 3.25) confirming that the wood hysteresis phenomenon is significantly affected by the treatment. The regressions however, account for only about 36 and 32 percent of the variation observed with Corsican pine and beech respectively. Although the variation shown is very

small, the slight increase in hysteresis ratios observed
are similar to those reported by Spalt (1958) for spruce
wood acetylated to 32% weight gain and is likely to be
causal rather than purely coincidental.

The variation in monomolecular and
polymolecular sorption hysteresis was compared to that
in total hysteresis. The results shown in Table 3.26
reveal that for the two species, total sorption
hysteresis appears to be influenced by hysteresis in both
mono and polymolecular sorption. The significant
correlation found between monomolecular sorption
hysteresis and total sorption hysteresis is in line with
Urquhart's (1960) explanation of hysteresis (see section
3.1.3), since the reaction and consequent deactivation of
the hydroxyl groups is expected to reduce lateral
hydroxyl-to-hydroxyl bonding upon drying. Also, the
bulking effect of the adducts keeping the cell wall in a
partially swollen state reduces the aggregation of the
cellulosic gel upon drying and consequently decreases
lateral hydroxyl bonding. As a result, a smaller number
of sorption sites satisfy each other by forming
interstructural hydrogen bonds. Therefore, more sites
remain available to water molecules in adsorption, thus
reducing hysteresis. However, the significant
relationship found between polymolecular sorption
hysteresis and total sorption hysteresis indicates that
the variation in total hysteresis is not merely
dependent on the reduced number of sorption sites in
adsorption as postulated by Urquhart's hypothesis. It is

evident from Table 3.26 that polymolecular sorption also exerts a marked influence on total hysteresis. This is in agreement with published work of Spalt (1958) and Chen and Wangaard (1968). Spalt found that total hysteresis is strongly influenced by polymolecular sorption over the entire range of relative humidity (RH). Chen and Wangaard established that at the upper range of RH, a significant positive relationship exists not only between polymolecular and total hysteresis but also between sorption hysteresis and wettability hysteresis, in line with the theory developed by Zsigmondy *at al* (1912) (Section 3.1.3). Stamm (1964) has rejected this explanation of sorption hysteresis for cellulose and wood on the basis that wetting angle is meaningless due to the lack of solid-vapour interfaces in a capillary system consisting almost entirely of solid-solid and solid-liquid-solid interfaces. According to Stamm (1971) and Skaar (1988), when a contact angle of zero degrees is assumed, the Kelvin equation predicts condensation taking place at vapour pressures only slightly lower than unity. This applies for capillaries radii of 0.1 micron and larger. In this case condensation may take place at vapour pressures between 0.9 and 0.99-0.995 in the small capillaries (up to 0.2 micron) in the cell wall. At vapour pressures between 0.995 and unity, condensation should occur in larger cell wall capillaries, and ultimately in bulk outside the cell walls.

If however, the concept of contact angle is applied, the advancing contact angle (in adsorption) should be different from the receding contact angle (in desorption). According to the Kelvin equation in its complete form including cosine of the contact angle:

ln 1/h = 2VJcosA/rRT   (3.11)

where:

h is the relative vapour pressure

V, the molar volume of water

J, the surface tension of the liquid

A, the contact angle

r, the capillary radius

R, the gas constant

and ln is the natural logarithm of what follows, condensation takes place at a lower vapour pressure in desorption than in adsorption producing the phenomenon known as wettability hysteresis (Zsigmondy *at al*, 1912). Zsigmondy's *at al* theory and the work of Weichert (1963) suggest the presence of a substantial volume of voids in the cell walls at high RH's and it is this which supports the concept of capillary condensation. Based on this idea, Chen and Wangaard (1968) observed that polymolecular and total sorption hysteresis above 60-70% RH are significantly correlated with wettability hysteresis. This was interpreted as evidence that capillary condensation may occur in the RH range from 60-70% upwards. According to these workers, sorption hysteresis in the upper range of RH is at least to a

considerable degree a capillary condensation phenomenon explainable by the Kelvin equation in its complete form.

In the present work, the significant correlation found between polymolecular sorption hysteresis and total sorption hysteresis (Table 3.26) seems to corroborate the findings of Spalt (1958) and Chen and Wangaard (1968) in that hysteresis is also a capillary condensation phenomenon. Based on this evidence, the reduced magnitude of hysteresis in the chemically modified wood is proposed to be in part a result of the bulking action of the ester formed within the cell wall reducing any pre-existing void volume and consequently decreasing the likelihood of condensation which could take place within the cell walls at the upper range of relative humidities.

The phenomenon of capillary condensation also explains the fact that the sigmoid hysteresis loop remains open at its upper limit when these curves are extrapolated to 100 percent RH or unit relative vapour pressure. According to Skaar (1988), this extrapolation is subject to error because it is based on the assumption that water will not condense in the cell wall cavities at vapour pressures lower than unity. Stamm (1971) states that this extrapolation is justifiable, as graphically there is no distinction between moisture content at 0.995 and unit relative vapour pressure provided that the nature of the relationship does not change drastically at vapour pressures very close to unity. According to the above discussion concerning

hysteresis, the extrapolation may account for some of the condensation that, according to Chen and Wangaard (1968), occurs in the cell wall between 60 and 90% RH. It seems evident that the sharp increase in moisture content that takes place at vapour pressures close to unity where the bulk of condensation occurs, (Stamm, 1964 and 1971), cannot be accounted for by extrapolation from lower values. On the basis of this reasoning the hysteresis loop probably remains open at its upper end until closure is attained very close to saturation vapour pressure through the condensation of liquid water in the largest available capillaries in the cell wall.

Table 3.24 Sorption hysteresis ratios based on the areas under the adsorption and desorption isotherms for monomolecular, polymolecular and total sorption.

Reagent	WPG	Sorption hysteresis ratio		
		MONO	POLY	TOTAL
CORSICAN PINE				
Controls	0.0	0.788	0.909	0.834
n-Bu-NCO	7.5	0.805	0.907	0.842
	11.3	0.794	0.918	0.841
	19.7	0.780	0.923	0.837
	24.1	0.822	0.914	0.856
	34.3	0.865	0.925	0.886
Ph-NCO	9.6	0.809	0.917	0.849
	17.6	0.811	0.899	0.844
	19.3	0.804	0.913	0.846
	25.9	0.820	0.912	0.857
	29.6	0.796	0.931	0.852
HDI	6.1	0.808	0.915	0.849
	12.9	0.827	0.925	0.863
	17.5	0.841	0.942	0.876
	19.5	0.866	0.950	0.892
	22.6	0.863	0.954	0.893
TDI	5.0	0.802	0.875	0.830
	6.4	0.808	0.875	0.833
	7.0	0.762	0.875	0.806
	8.6	0.767	0.826	0.794
	10.7	0.771	0.824	0.792

Table 3.24 (Cont.) Sorption hysteresis ratios based on the areas under the adsorption and desorption isotherms for monomolecular, polymolecular and total sorption.

Reagent	WPG	Sorption hysteresis ratio		
		MONO	POLY	TOTAL
		BEECH		
Control	0.0	0.774	0.883	0.812
n-Bu-NCO	7.9	0.797	0.881	0.827
	11.7	0.799	0.876	0.827
	18.1	0.781	0.888	0.823
	23.3	0.767	0.900	0.819
	37.3	0.776	0.945	0.841
Ph-NCO	7.7	0.786	0.880	0.821
	12.9	0.828	0.904	0.859
	15.4	0.814	0.877	0.837
	22.8	0.809	0.883	0.837
	26.3	0.811	0.871	0.846
HDI	9.3	0.784	0.898	0.826
	12.3	0.790	0.900	0.830
	16.0	0.801	0.908	0.841
	19.2	0.826	0.934	0.866
	23.1	0.821	0.935	0.867
TDI	4.0	0.769	0.769	0.800
	5.9	0.802	0.869	0.821
	7.5	0.793	0.802	0.804
	9.3	0.793	0.818	0.800
	11.0	0.774	0.754	0.789

Table 3.25 Regression analysis of the relation between total sorption hysteresis and weight percent gain (WPG).

SOURCE	DF	Sum Squares	Mean Squares	F-ratio
		CORSICAN PINE		
REGRES.	1	0.005427	0.005427	10.44**
ERROR	19	0.009875	0.000520	
TOTAL	20	0.015302		
r^2x100		35.5		
		BEECH		
REGRES.	1	0.002820	0.002820	8.84**
ERROR	19	0.006064	0.000319	
TOTAL	20	0.008884		
r^2x100		31.7		

DF - Degrees of freedom
** - Significant at the 99 percent level of probability

Table 3.26 Regression analysis of the relation between monomolecular, polymolecular and total sorption hysteresis.

SOURCE	DF	Sum Squares	Mean Squares	F-ratio

CORSICAN PINE

Monomolecular vs. Total sorption

SOURCE	DF	Sum Squares	Mean Squares	F-ratio
REGRES.	1	0.013562	0.013562	148.04**
ERROR	19	0.001741	0.000092	
TOTAL	20	0.015302		
r^2x100		88.6		

Polymolecular vs. Total sorption

REGRES.	1	0.012591	0.012591	88.22**
ERROR	19	0.002712	0.000143	
TOTAL	20	0.015302		
r^2X100		82.3		

BEECH

Monomolecular vs. Total sorption

REGRES.	1	0.005241	0.005241	27.33**
ERROR	19	0.003643		
TOTAL	20	0.008884		
r^2x100		59.0		

Polymolecular vs. Total sorption

REGRES.	1	0.006029	0.006029	40.12**
ERROR	19	0.002855		
TOTAL	20	0.008884		
r^2x100		67.9		

DF - Degrees of freedom
** - Significant at the 99 percent level of probability.

CHAPTER FOUR

SWELLING AND EQUILIBRIUM MOISTURE CONTENT RELATIONS

4.1 GENERAL CONCEPTS

It is generally established that wood swelling varies linearly with moisture content in the hygroscopic range. Skaar (1988) cites the work of Keylwerth (1964) where it is shown that slight variations occur at the lower and at the upper parts of the hygroscopic range. The deviations at the lower relative humidities are believed to be caused by the first water molecules sorbed which may do not contribute their full volume to the cell wall as they find their way into interstices in the cell wall matrix. At the upper part of the relative humidity range, swelling stresses and capillary condensation may account for the deviations (Skaar, 1988). Kelsey (1957) believes these variations may be also associated with moisture gradients and/or drying stresses.

When wood takes up moisture into the cell wall the walls swell volumetrically in proportion to the volume of water absorbed (Skaar, 1972). This is based on the assumptions that there are virtually no voids in the dry cell wall (and therefore water simply adds its volume to that of the dry wood) and that the lumens of the cell walls do not change in size as moisture is sorbed. According to the literature, the question of the incidence of pre-existent voids in the dry cell wall rather than water filled spaces developed through the sorption-swelling processes has not been resolved. Stamm

(1971) based on observed differences between cell wall densities obtained by water displacement ($\approx$1.53) and by non-polar fluid displacement ($\approx$1.46) established that the void volume in dry wood cell walls lies between zero and 4.5 % of the oven-dry cell wall volume. Part of this difference may be accounted for by the apparent compression of sorbed water, and the void volume may be even smaller than this (Stamm, 1964). Weatherwax and Tarkow (1968) believe that only 15% of this calculated void volume should be attributed to the compression of sorbed water. On the other hand, evidence of substantial void volume has been provided by Jayme and Krause (1963) and Weichert (1963) respectively by microscopic measurements and moisture content-swelling relationships.

The assumption of constant lumem size does not hold precisely for all species. In some the lumens decrease in size and for others, increase in size with moisture content (Siau, 1984). According to Skaar (1972), in some woods the lumen appears to swell, in others it appears to shrink and in others to remain essentially constant. However, Siau (1984) and Skaar (1972) agree that the assumption of constant lumen size upon adsorption or desorption is a reasonable approximation since as a general rule, the cell wall cavity appears to change only to a small extent during moisture changes. Stamm (1964) also states that the lumen tends to remain fairly constant in size as wood shrinks or swells, due to fibril wrapping restraints. Complete

reviews of this mechanisms are given by Stamm (1964) andSkaar (1972 & 1988).

If it is assumed that the cell wall cavity remains constant in size with moisture change, the relationship between total hygroscopic swelling (S_f) and dry specific gravity (G_o) from dry condition to fibre saturation (M_f) can be expressed:

$$S_f = M_f G_o \hspace{4cm} (4.1)$$

Equation 4.1, which is also valid for shrinkage as long as the swollen volume specific gravity is used, predicts that swelling is greater in denser woods and is directly proportional to specific gravity or the quantity of cell-wall substance present. The fibre saturation point (M_f) is expressed as volume of water per unit dry weight of wood. Choong and Barnes (1968) cited by Skaar (1988), reported that volumetric swelling between dry and water soaked conditions increased essentially linearly with G_o for four southern hard pines. M_f values calculated by means of equation 4.1 gives an average of 27 for 107 American hardwoods and 26 for 52 different species of softwood. Variation from these mean values however was found to be considerable (Skaar, 1972). Vorreiter (1963) and Kellog and Wangaard (1969) observed that woods of lower specific gravity tend to have higher fibre saturation points. Wangaard and Granados (1967) working with tropical woods from Central America, reported that species with high extractive contents show

lower M_f values. They produced evidence that the extractives in the cell wall reduce M_f through a bulking effect. Similar results have been reported recently by Choong and Achmadi (1991). They found that upon extraction, significant increase in M_f was observed on 16 species from Indonesia. According to Choong (1969) the removal of extractives improved the correlation between volumetric shrinkage and specific gravity in southern pine. Chafe, (1986), analysing shrinkage data fo 69 eucalypt species found no positive correlation between volumetric shrinkage and specific gravity. He reports a negative correlation between initial shrinkage and specific gravity for the species, presumably due to initial higher shrinkage or collapse, so common in eucalypt wood. In the work of Choong and Achmadi (1991) the removal of extractives from the tropical woods was shown to increase shrinkage by making available additional moisture sorption sites. In some cases the shrinkage was excessive and caused collapse producing a negative correlation between shrinkage and specific gravity. In cases where this occurs, the use of equation 4.1 for M_f estimation is invalid. Stamm (1964) has previously reported that development of stresses upon drying and bulking of cell wall by extraneous substances may cause deviation from M_f values predicted by equation 4.1.

4.2 MATERIAL AND METHODS

The relationship between EMC and swelling is assessed by measuring the volume of matched duplicate samples (treated and untreated) at the moisture content achieved in equilibrium with each relative humidity during the sorption tests described in section 3.2.1.4. The volume of the oven-dry and swollen samples are derived from the product of the three principal block dimensions (radial x tangential x longitudinal - originally 20 x 20 x 5 mm) quickly measured (with vernier callipers to the nearest 0.02 mm) immediately after the weight in equilibrium with each relative humidity had been taken. This made it possible to determine the volumetric swelling to 0.1 percent. Swelling at saturation after the samples had been stored between damp cloths was also recorded.

The dry-volume specific gravity derived from oven-dry weight and volume of the blocks was determined for the controls and for each set of treated specimens (ten replicates each) at the relevant weight gains, according to a simple method described by Stamm (1964). This consisted of determining the oven-dry weight of the samples to four decimal places and the volume (product of the three main blocks dimensions) with micrometer calliper to about 0.1 percent accuracy.

4.3 RESULTS AND DISCUSSION

4.3.1 EMC and swelling

The percent volumetric swelling values (mean of two samples) in equilibrium with each relative humidity obtained for the controls and for three selected levels of weight gain (the lowest, the highest and the mid value of the five produced with each isocyanate for both wood species from Table 3.3) are shown in Table 4.1. Also included are the respective experimental EMC values taken from Table 3.3 together with the swelling values obtained at saturation (mean of ten samples).

It is at once evident from Table 4.1 that decrease in EMC is accompanied by a decrease in swelling of the controls and treated samples. A separated analysis of variance 2-factor ANOVA was made for each group of specimens consisting of four treatment levels (controls and three weight gains) and six levels of relative humidity (RH), for each isocyanate, following the procedure given by Steel and Torrie (1960). Cochran's test for homogeneity of variances (Kassab, 1989) was proceeded within each group. Despite the possibility of experimental error associated with the difficulties of measuring volumes in equilibrium with very low relative humidities, all the groups show decreasing swelling accompanying the decrease in moisture content with WPG and RH. On the basis of this analysis, these variations are all significant at the 1% level of probability (Appendix B, Table B.1).

Table 4.1 Volumetric swelling for the controls and for the treated samples at saturation and at the equilibrium moisture content (EMC) with the respective relative humidity, taken from Table 3.3.

Reagent	WPG	RELATIVE HUMIDITY (%)												Swelling at saturation (%)
		12		23		44		55		76		93		
		EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	
							CORSICAN PINE							
Control	0	2.56	1.2(.1)	4.60	2.2(.2)	7.73	3.7(.3)	9.57	4.5(.2)	14.00	7.0(.3)	22.79	11.0(.4)	15.0(.4)
nBu-NCO	7.5	1.65	0.6(.1)	3.04	1.2(.1)	5.10	2.2(.2)	6.60	2.8(.3)	10.01	4.4(.3)	16.92	7.7(.3)	9.8(.4)
	19.7	1.33	.5(.0)	2.30	1.0(.1)	3.89	1.5(.0)	4.92	2.0(.1)	7.69	3.0(.1)	11.33	4.9(.2)	6.2(.2)
	34.3	0.97	0.4(.0)	1.60	0.7(.0)	2.86	1.0(.1)	3.63	1.4(.1)	4.99	1.8(.1)	8.66	3.3(.2)	4.0(.3)
Ph-NCO	9.6	1.93	0.8(.0)	3.47	1.5(.0)	5.25	2.4(.0)	6.60	2.9(.3)	9.50	4.3(.4)	15.59	7.0(.4)	10.1(.5)
	19.3	1.61	0.7(.1)	2.82	1.3(.1)	4.56	1.9(.2)	5.40	2.3(.2)	8.51	3.5(.3)	13.00	5.6(.4)	7.9(.4)
	29.6	1.36	0.7(.1)	2.44	0.9(.1)	3.89	1.6(.1)	4.78	2.0(.1)	7.46	3.0(.1)	10.67	4.3(.3)	5.7(.3)
HDI	6.1	2.33	1.1(.1)	4.07	1.8(.2)	6.82	3.0(.2)	8.35	3.8(.4)	12.00	5.6(.3)	19.73	8.9(.5)	12.1(.5)
	17.5	2.02	0.9(.0)	3.60	1.5(.0)	5.70	2.3(.2)	7.26	3.0(.2)	10.05	4.1(.2)	14.20	5.9(.2)	8.4(.4)
	22.6	2.00	0.8(.1)	3.33	1.3(.1)	5.18	2.0(.1)	6.52	2.6(.0)	8.80	3.5(.1)	12.27	4.7(.0)	6.6(.3)
TDI	5.0	2.29	1.0(.1)	3.68	1.5(.1)	5.40	2.6(.2)	6.66	2.9(.0)	10.05	4.4(.3)	16.00	7.0(.3)	12.6(.7)
	7.0	2.31	1.1(.1)	3.73	1.6(.2)	5.80	2.7(.1)	7.40	3.2(.3)	11.20	4.7(.4)	17.21	8.0(.2)	13.0(.6)
	10.7	2.15	0.8(.0)	3.47	1.4(.0)	5.30	2.3(.2)	7.05	3.1(.2)	10.70	4.3(.4)	16.30	6.7(.2)	12.8(.4)

- All data expressed in oven-dry basis.
- Data for hygroscopic swelling are average of two samples and data for swelling at saturation are average of 10 samples (standard deviation in parenthesis).

Table 4.1 (Cont.) Volumetric swelling for the controls and for the treated samples at saturation and at the equilibrium moisture content (EMC) with the respective relative humidity, taken from Table 3.3.

Reagent	WPG	RELATIVE HUMIDITY											Swelling at saturation (%)
		12		23		44		55		76		93		
		EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	EMC	Swell. (%)	

<center>BEECH</center>

Reagent	WPG	12 EMC	12 Swell.	23 EMC	23 Swell.	44 EMC	44 Swell.	55 EMC	55 Swell.	76 EMC	76 Swell.	93 EMC	93 Swell.	Swelling at saturation
Control	0	2.59	1.7(.2)	4.40	3.0(.3)	7.22	5.4(.2)	8.58	6.7(.3)	13.56	10.3(.4)	23.59	16.5(.5)	19.5(.5)
n-Bu-NCO	7.9	1.71	1.0(.1)	3.03	1.9(.2)	4.71	3.2(.2)	6.30	4.5(.2)	9.65	6.9(.1)	16.99	10.9(.4)	14.0(.6)
	18.1	1.30	0.8(.1)	2.20	1.4(.0)	4.05	2.7(.3)	4.93	3.3(.3)	7.94	5.3(.3)	12.53	8.0(.1)	9.8(.5)
	37.3	0.77	0.4(.1)	1.45	0.7(.1)	2.57	1.6(.1)	3.25	2.0(.2)	5.10	3.1(.4)	7.53	4.2(.1)	4.3(.3)
Ph-NCO	7.7	2.01	1.3(.1)	3.43	2.2(.2)	5.40	3.7(.2)	6.73	5.0(.3)	10.34	7.7(.5)	17.16	11.0(.3)	15.2(.4)
	15.4	1.62	1.0(.0)	2.93	1.9(.0)	4.47	3.0(.0)	5.44	3.7(.2)	8.24	5.9(.2)	13.30	8.2(.5)	11.5(.5)
	26.3	1.32	0.7(.0)	2.18	1.2(.1)	3.74	2.2(.2)	5.19	3.1(.0)	7.21	4.6(.0)	11.74	6.9(.4)	7.8(.3)
HDI	9.3	2.00	1.2(.2)	3.40	2.2(.0)	5.27	3.7(.0)	6.53	5.0(.0)	10.81	7.8(.4)	17.64	11.7(.3)	16.2(.6)
	16.0	1.90	1.1(.2)	3.22	2.0(.2)	4.90	3.4(.3)	5.66	4.2(.3)	10.03	7.1(.3)	15.99	10.2(.6)	13.0(.5)
	23.1	1.85	1.0(.1)	3.01	1.7(.1)	4.61	3.0(2)	5.40	3.8(.1)	9.26	6.0(.2)	13.21.	7.4(.1)	8.7(.5)
TDI	4.0	2.28	1.4(.1)	3.71	2.4(.1)	6.10	4.2(.2)	7.55	5.7(.2)	11.15	8.2(.3)	19.87	13.3(.3)	17.5(.7)
	7.5	2.15	1.3(.0)	3.36	2.1(.1)	5.50	3.6(.3)	6.25	4.8(.4)	9.30	7.0(.5)	17.00	11.0(.5)	16.3(.6)
	11.5	2.09	1.2(.1)	3.30	2.0(.2)	5.05	3.1(.0)	5.58	4.0(.1)	8.41	5.9(.5)	15.33	9.4(.3)	15.6(.4)

- All data expressed in oven-dry basis.

- Data for hygroscopic swelling are average of two samples and data for swelling at saturation are average of 10 samples (standard deviation in parenthesis).

The variation of volumetric swelling over the relative humidity range is illustrated in Fig. 4.1. The values plotted are not extrapolated beyond the experimental range. The curves are of somewhat similar shape to the sorption isotherms presented in Chapter 3, suggesting a close relationship between EMC and swelling over the entire relative humidity range studied. Risi and Arsenau (1957) describe sigmoid curves for tangential swelling of acetylated balsam fir wood conditioned to several relative humidities. The results shown in Fig. 4.1 clearly indicate that the volumetric swelling of beech and Corsican pine woods modified with the four isocyanates used in the present work approximately parallels the swelling of the controls. That is, as for the sorption isotherms, the curves are depressed evenly over the entire experimental range, as the weight gain increases.

Fig. 4.2 shows how swelling and EMC vary over the RH range for the controls and samples treated to selected WPG's. These curves show clearly that a reduction in EMC is accompanied by a reduction in swelling and also that for each addition of moisture the treated wood specimens apparently swell correspondingly.

Following these preliminary considerations, the relationship between swelling and EMC data from Table 4.1 was verified by regression analysis. The swelling equations obtained are shown in Table 4.2 and typical examples of the relationship found are illustrated on Fig. 4.3. Within the accuracy of the experiment the
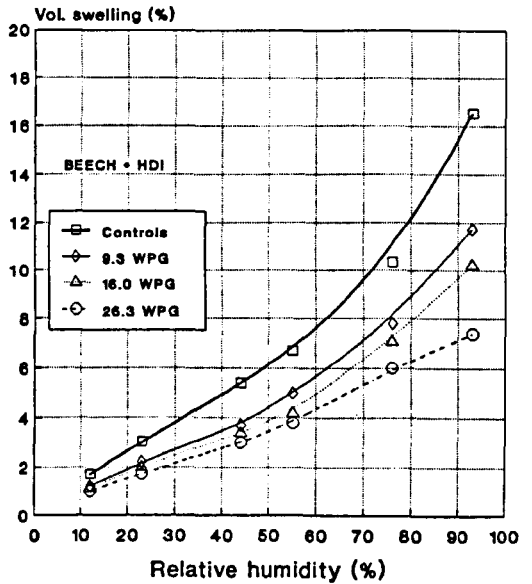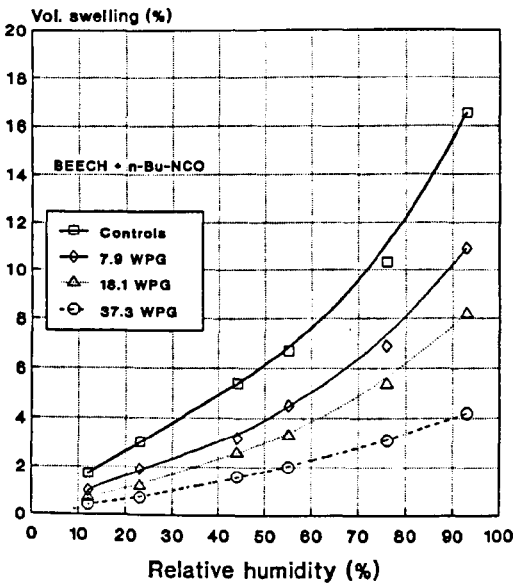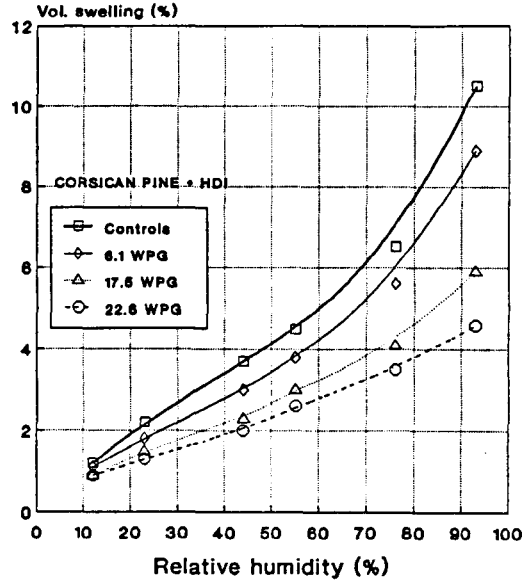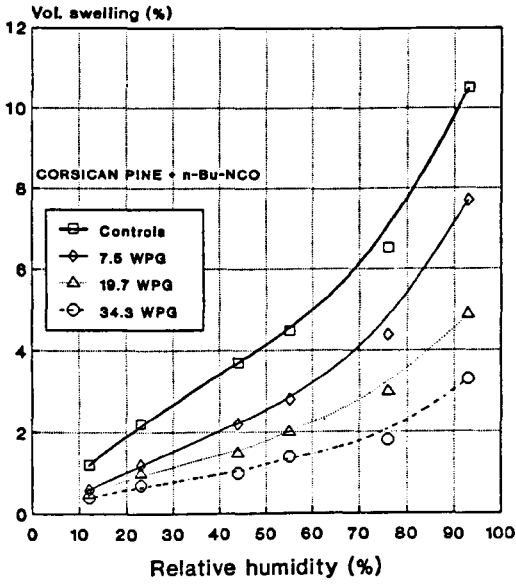
Fig. 4.1 Volumetric swelling at equilibrium with each relative humidity- general trends and plotted experimental points.
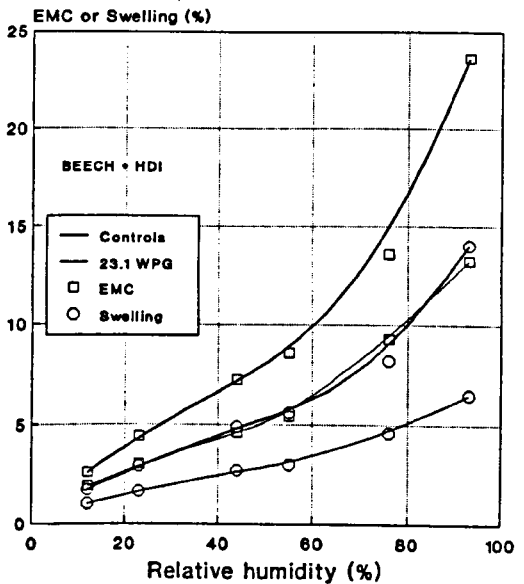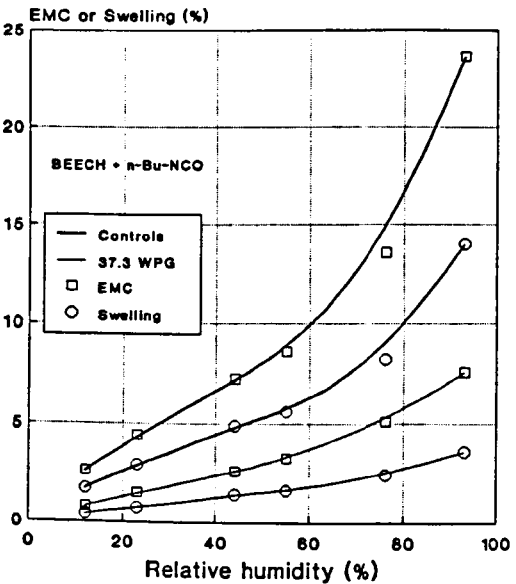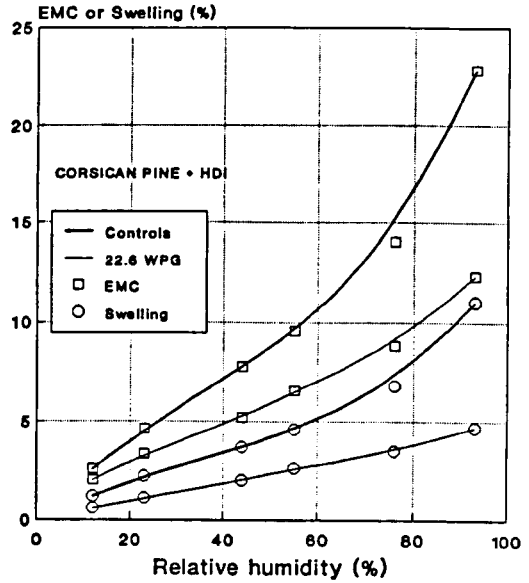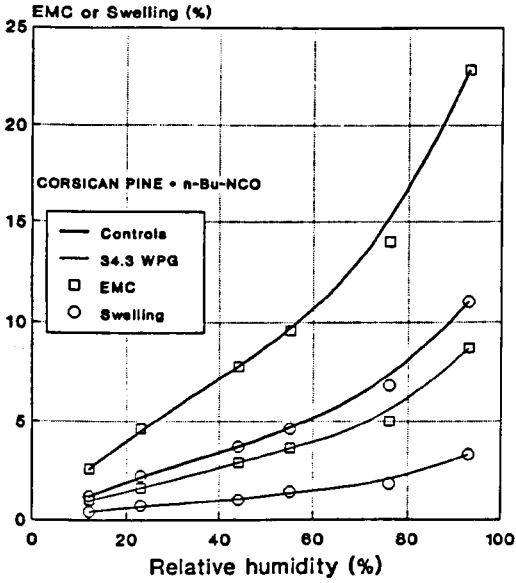
Fig. 4.2 Variation of equilibrium moisture content (EMC) and volumetric swelling over the relative humidity range - general trends and plotted experimental points.

relation is shown to be linear since for each WPG, the points representing averages of two samples lie almost precisely on a straight line with coefficient of correlation values (r^2) varying between 0.97 and 1.00 all significant at 1 percent probability level. These correlations are very high. This means that variation produced by condensation or by other effects suggested by Skaar (1988) (see section 4.1) are minimal and some of them, probably lie beyond the limit of detection by the swelling determination technique used. The linear relationship appears to be valid for the controls and for the treated samples. These results are in agreement with published work of Risi and Arsenau (1957). Working with acetylated wood they found a general linear trend between EMC and tangential swelling for balsam fir wood treated to several acetyl contents.

The slopes of the straight lines representing the regression lines in Fig. 4.3 appear to be reduced with increasing weight gain. This is confirmed in the data of Table 4.2 where it can be seen that the treatment changes the slope of the regression equations considerably. This indicates that as the weight gain increases, the samples swell proportionally less at each EMC attained. The apparent reduction in slope of theses curves is observed when swelling of species showing decreasing densities are plotted together shown by Keylwerth (1964). It is shown in section 4.3.3 however, that the specific gravity of the treated woods increases with the WPG. Hence, a negative

Table 4.2 Volumetric swelling equations for the controls ant treated woods obtained from the correlation EMC vs. volumetric swelling (S_V).

Reagent	WPG	CORSICAN PINE Swelling equation[1]	WPG	BEECH Swelling equation[1]
Controls	0	$S_V=-0.0492+0.488(EMC)$	0	$S_V= 0.204+0.709(EMC)$
n-Bu-NCO	7.5	$S_V=-0.208+0.465(EMC)$	7.9	$S_V= 0.063+0.657(EMC)$
	19.7	$S_V=-0.100+0.420(EMC)$	18.1	$S_V= 0.481+0.644(EMC)$
	34.3	$S_V= 0.0227+0.373(EMC)$	37.3	$S_V= 0.020+0.575(EMC)$
Ph-NCO	9.6	$S_V=-0.0525+0.454(EMC)$	7.7	$S_V= 0.243+0.653(EMC)$
	19.3	$S_V= 0.0145+0.424(EMC)$	15.4	$S_V= 0.185+0.627(EMC)$
	29.6	$S_V= 0.0646+0.396(EMC)$	26.3	$S_V=-0.047+0.605(EMC)$
HDI	6.1	$S_V= 0.0004+0.454(EMC)$	9.3	$S_V= 0.140+0.674(EMC)$
	17.5	$S_V= 0.0165+0.411(EMC)$	16.0	$S_V= 0.151+0.650(EMC)$
	22.6	$S_V= 0.0984+0.378(EMC)$	23.1	$S_V= 0.243+0.574(EMC)$
TDI	5.0	$S_V= 0.0592+0.434(EMC)$	4.0	$S_V= 0.120+0.681(EMC)$
	7.0	$S_V=-0.129+0.461(EMC)$	7.5	$S_V= 0.172+0.660(EMC)$
	10.7	$S_V= 0.026+0.410(EMC)$	11.5	$S_V= 0.136+0.623(EMC)$

[1]- The linear regressions are all significant at the 1 percent level of probability; r^2 ranges from 0.994 to 1.0 for Corsican pine and from 0.975 to 0.998 for beech.
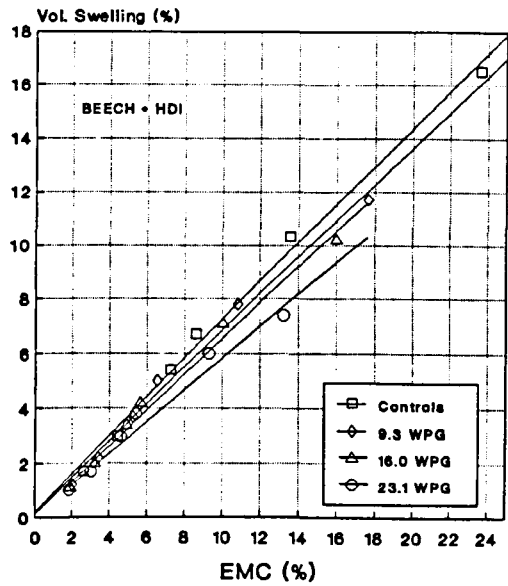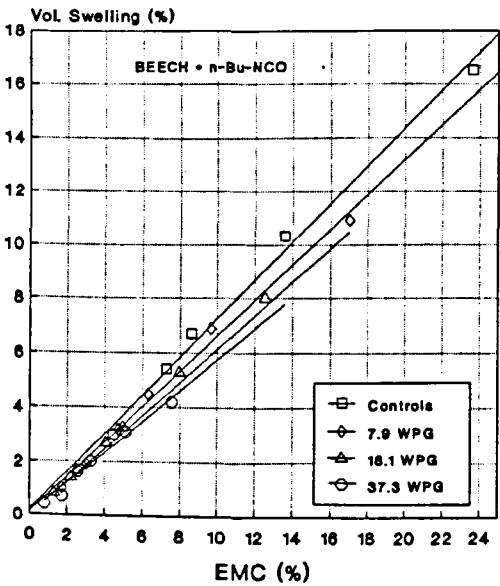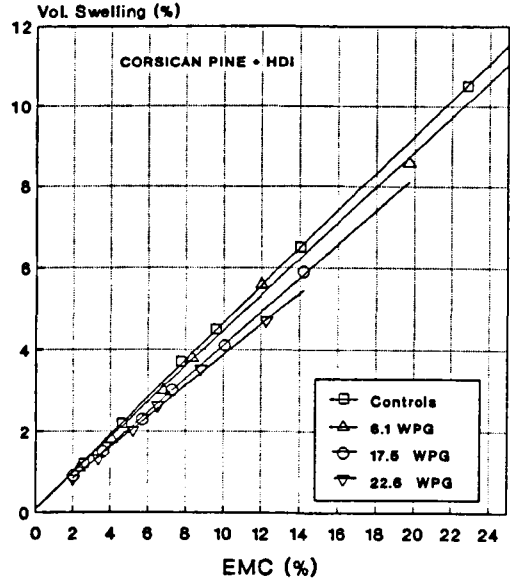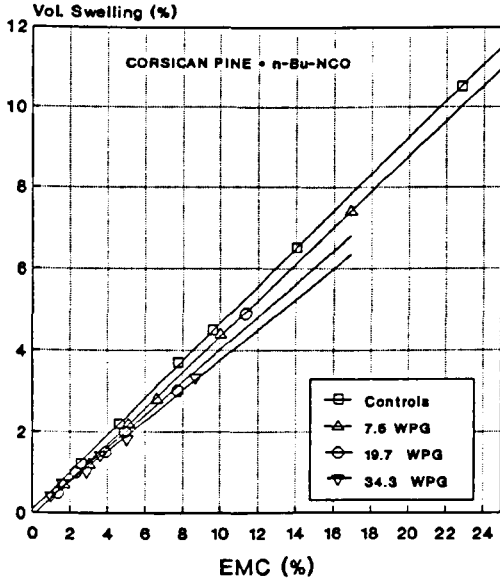
Fig. 4.3 Equilibrium moisture content vs. swelling relationship - plotted points and regression lines.

relationship between swelling and specific gravity is clearly indicated for the treated woods (see Fig. 4.5, section 4.3.3). This is the converse of what is well established for unmodified wood.

4.3.2 Hygroscopicity reduction (HR) and anti-swelling efficiency (ASE)

In the present work the effectiveness of the various dimensional stabilization treatments is assessed based on the reduction in hygroscopicity (see Table 3.7). Skaar (1988) states that the reduction in swelling may be defined in terms of the reduction in hygroscopicity calculated by means of equation 3.10 (section 3.4.2). Stamm and Harris (1954) observed that for some systems ASE is equivalent to HR while for others, HR is somewhat lower. For example, Stamm and Tarkow (1947) found lower values for hygroscopicity reduction than for ASE in the case of acetylated spruce. Lower HR than ASE values are also reported by Risi and Arsenau (1957) for acetylated balsam fir.

HR and ASE were calculated using respectively the experimental EMC and swelling values from Table 4.1 by means of equation 3.10. For the calculation of ASE, equation 3.10 was modified to:

$$ASE = 100(S_c - S_t)/S_c \qquad (4.2)$$

Table 4.3 Hygroscopicity reduction (HR) and anti-swelling efficiency (ASE) obtained from the experimental data of Table 4.1

Reagent	WPG	Relative humidities (%)												ASE at
		12		23		44		55		76		93		
		HR	ASE	HR	ASE	HR	ASE	HR	ASE	HR	ASE	HR	ASE	Saturation
		(%)		(%)		(%)		(%)		(%)		(%)		(%)
CORSICAN PINE														
n-Bu-NCO	7.5	36	50	34	45	34	41	31	38	29	32	26	30	35
	19.7	48	58	50	55	50	59	49	56	45	54	50	55	59
	34.3	62	67	65	68	63	73	62	69	64	72	62	70	75
Ph-NCO	9.6	25	33	25	32	32	35	31	36	32	34	32	32	33
	19.3	37	50	39	41	41	49	44	49	39	46	42	49	47
	29.6	47	50	47	59	50	57	50	56	47	54	53	61	62
HDI	6.1	9	10	12	18	12	19	13	16	14	14	13	19	19
	17.5	21	25	22	32	25	28	24	33	28	37	38	46	44
	22.6	22	33	28	41	33	42	32	48	37	46	46	57	51
TDI	5.0	11	17	20	27	32	30	30	36	28	32	30	36	15
	7.0	10	17	19	27	25	27	23	29	20	28	24	27	13
	10.7	16	33	25	36	31	38	25	31	24	34	28	39	18
BEECH														
n-Bu-NCO	7.9	34	41	31	38	35	41	27	33	29	34	28	32	28
	18.1	50	53	50	53	44	50	43	51	41	49	47	50	50
	37.3	70	76	67	76	64	71	62	70	62	71	68	74	78
Ph-NCO	7.7	22	24	22	28	25	31	22	26	24	27	27	31	22
	15.4	37	41	33	37	38	44	37	45	39	43	42	49	41
	26.3	49	59	50	59	48	59	40	53	47	56	50	57	59
HDI	9.3	23	29	23	28	27	31	24	26	20	26	24	29	16
	16.0	27	35	27	34	32	37	34	37	26	32	32	36	33
	23.1	29	41	32	45	36	44	37	44	32	43	44	54	55
TDI	4.0	12	18	16	21	16	22	12	15	18	22	16	19	10
	7.5	17	24	24	31	24	33	27	30	31	33	28	33	16
	11.0	19	29	25	34	30	43	35	41	38	44	35	41	20

Data for ASE in vapour conditions are average of duplicates and data for ASE at saturation (liquid water) are average of 10 samples.

Where the swelling values for the controls (S_c) and for the treated samples (S_t) are used instead of the EMC values in equation 3.10.

The results are shown in Table 4.3 including ASE at saturation. The ASE values observed for the wood treated with the four isocyanates are somewhat higher than the corresponding HR's. It seems therefore that the isocyanate modified wood system behave similarly to those reported by Stamm and Harris (1954) showing lower values for hygroscopicity reduction than for anti-swelling efficiency. Skaar (1988) pointed out that equations 3.10 and 4.2 only produce similar results over a given humidity range if the moisture expansion coefficient over this given humidity range is the same for untreated and treated wood. According to Skaar (1972 and 1988), the moisture expansion coefficient (X_{VS}) (based on the volumetric expansion coefficient) is defined as follows:

$$X_{VS} = (1/vo)(dv/dm) \qquad\qquad (4.3)$$

where vo is the oven-dry volume and dv/dm is the change in volume per unit change in fractional moisture content. X_{VS} measures the variation in wood volumetric swelling with changes in moisture content. Hence, according to equation 4.3, it is evident that X_{VS} is simply the slope dv/dm of the EMC vs. swelling regression curves shown in Fig. 4.3. From the fitted equations of these curves (Table 4.2) it can be readily seen that, as anticipated in section 4.3.1, for the two species, the treated

samples show lower X_{VS} than the controls, i.e. the slope of the curves decreases with increasing WPG. This indicates that the treatment not only reduces the total swelling caused by moisture sorption but also reduces the dimensional change produced over a given humidity range (represented by X_{VS}). Fig. 4.4 illustrates schematically that the difference between HR and ASE shown in Table 4.3 is due to the decrease in X_{VS} (or of the slope of the EMC vs. swelling curves) of the treated compared to control samples. The decrease in the slopes of the curves appears to be caused by the negative correlation between specific gravity and swelling found for the treated wood. This phenomenon is discussed in the next section.
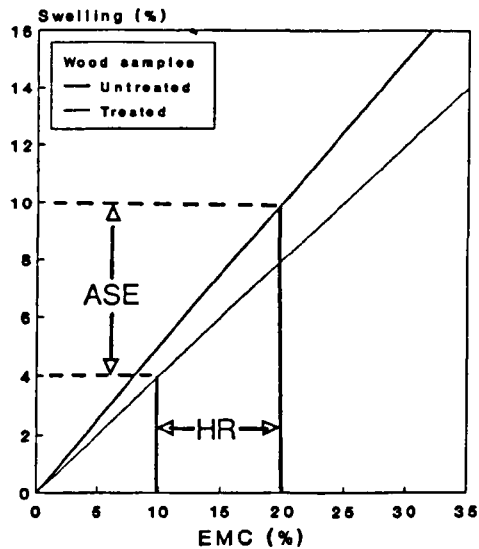
Fig 4.4 Illustration showing the effect of decreasing slope producing the difference between HR and ASE. Example: HR = 100(20-10)/20 = 50%; ASE = 100(10-4)/10 = 60%.

4.3.3 Swelling, Specific Gravity, and Fibre Saturation
Point

The determined dry-volume specific gravity values for the controls and for the treated specimens at the relevant WPG's are shown in Table 4.4 together with the volumetric swelling at saturation taken from Table 4.1 and the fibre saturation points (FSP), obtained from extrapolation to 100% relative humidity, taken from Table 3.5 and those obtained by means of the swelling equations from Table 4.2.

Since the reagents used are denser than the two wood species (section 2.2.1) the specific gravity of the treated wood increases proportionally to the WPG (significant at the 1 percent level of probability - see Appendix B, Tables B.2 and B.3). This is because when the cell wall takes up the reagent, both its mass and volume increase, the former proportionally more than the latter.

According to the literature (Stamm, 1964 and 1971; Skaar, 1972 and 1988) volumetric swelling is proportional to the wood dry-volume specific gravity (G_O) and the relationship is given by equation 4.1. Table 4.4 shows clearly that this relationship does not hold for the chemically modified woods in this work since G_O increases as swelling decreases with increasing WPG. The swelling and G_O data from Table 4.4 are correlated in Fig. 4.5. It is evident that swelling is highly negatively correlated with G_O (r^2 = 0.57 and 0.81 for the correlations with C. pine and beech respectively). This is to be expected since the presence of the adducts in

the cell wall increases G_O and simultaneously, as it is shown in the previous chapter, it blocks some of the sorption sites and bulks the cell wall reducing its swelling capacity.

Stamm (1971) suggests that the fibre saturation point M_f (expressed as volume of water per unit weight of oven-dry wood) can be estimated from equation 4.1. The method therefore assumes that volumetric swelling (at FSP) is proportional to the dry-volume specific gravity (G_O). As Skaar (1988) pointed out, this means that a constant ratio between percent volumetric swelling and G_O is assumed. The negative correlation between swelling (at FSP) and G_O shown by the chemically modified woods is an evident violation of this assumption and therefore, estimation of M_f by this method is inapplicable.

Table 4.4 shows fibre saturation points values obtained from the extrapolation of the adsorption isotherms to 100 percent RH and from the extrapolation of the swelling equations from Table 4.2 to the swelling at saturation (two other methods also given by Stamm, 1971). The agreement between the values is reasonable; the observed discrepancies being no more than expected when extrapolation techniques are used. However, in the case of TDI treated samples this variation is likely to be caused at least in part, by the higher swelling in water presented by the TDI treated samples, discussed in the previous chapter, which increases the FSP values derived from the swelling equations. Despite these distortions, it can be seen in Table 4.4 that the FSP

Table 4.4 Oven-dry specific gravity (G_O), fibre saturation point (FSP) and volumetric swelling at saturation at each weight percent gain (WPG) for the two wood species.

Reagent	CORSICAN PINE WPG	G_O	SWELLING (%)	FSP[1] (%)	FSP[2] (%)	BEECH WPG	G_O	SWELLING (%)	FSP[1] (%)	FSP[2] (%)
Controls	0	.54(.02)	15.0	27.4	30.6	0	.72(.02)	19.5	30.9	27.3
n-Bu-NCO	7.5	.56(.02)	9.8	21.3	20.6	7.9	.75(.02)	14.0	22.8	21.2
	19.7	.59(.03)	6.2	14.8	14.2	18.1	.78(.01)	9.8	16.0	15.3
	34.3	.61(.02)	4.0	10.7	10.7	37.3	.81(.01)	4.3	9.6	7.4
Ph-NCO	9.6	.56(.02)	10.1	19.0	22.4	7.7	.77(.01)	15.2	24.0	22.9
	19.3	.59(.02)	7.9	16.5	18.6	15.4	.79(.02)	11.5	17.0	18.6
	29.6	.64(.02)	5.7	13.1	14.3	26.3	.81(.01)	7.8	14.5	13.0
HDI	6.1	.55(.02)	12.1	23.6	26.7	9.3	.75(.01)	16.2	24.2	23.8
	17.5	.58(.03)	8.4	15.3	20.4	16.0	.77(.01)	13.0	22.6	19.8
	22.6	.60(.01)	6.6	14.1	17.2	23.1	.79(.01)	8.7	17.6	14.7
TDI	5.0	.55(.02)	12.6	20.6	28.9	4.0	.74(.01)	17.5	25.5	25.5
	7.0	.57(.01)	13.0	22.0	27.9	7.5	.76(.01)	16.3	21.7	24.4
	10.7	.60(.01)	12.3	21.4	29.4	11.0	.78(.01)	15.6	19.6	25.3

All data, (except FSP's), are average of ten samples
FSP[1]- Fibre saturation point derived from extrapolation of sorption isotherms to 100% RH (Table 3.5).
FSP[2]- Fibre saturation point derived from the swelling equations (Table 4.2).

values obtained by both methods decrease with increasing G_O. These values are expressed as weight of water per unit weight of oven-dry wood and theoretically, they deviate from M_f (the fibre saturation point expressed as percentage volume of water per unit weight of oven-dry wood) by a factor related to the average specific gravity of the adsorbed water, (reported to be 1.115 by Stamm, 1964). The relationship between G_O and the FSP values obtained through the two techniques (transformed to M_f by dividing by 1.115) have been assessed. G_O was found to be negatively correlated with M_f determined by both methods and the relationships were all found to be significant at the 1 percent level of probability ($r^2 =$ 0.64 and 0.49 for Corsican pine and 0.88 and 0.72 for beech - derived respectively from the sorption isotherms and from the swelling equations - Appendix B, Table B.3). These figures indicate that G_O correlates somewhat better with the M_f values derived from the sorption isotherms. Fig. 4.6, where M_f values derived from the extrapolation of the sorption isotherms are plotted against G_O, illustrates this relationship. As expected, the treated woods show decreasing M_f with increasing G_O. This is in agreement with the findings of Vorreiter, (1963) cited by Skaar, (1972). According to Skaar (1972) this reduction in M_f with increasing G_O in Vorreiter's work is at least in part caused by the bulking effect of extractives in the cell walls of the denser woods. Therefore, for the chemically modified woods in the present work, it seems
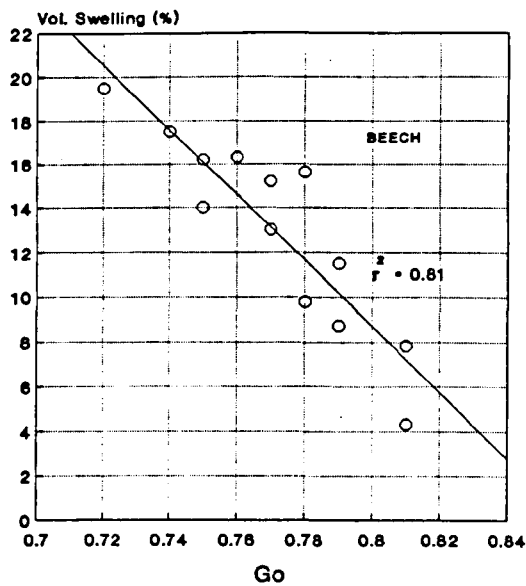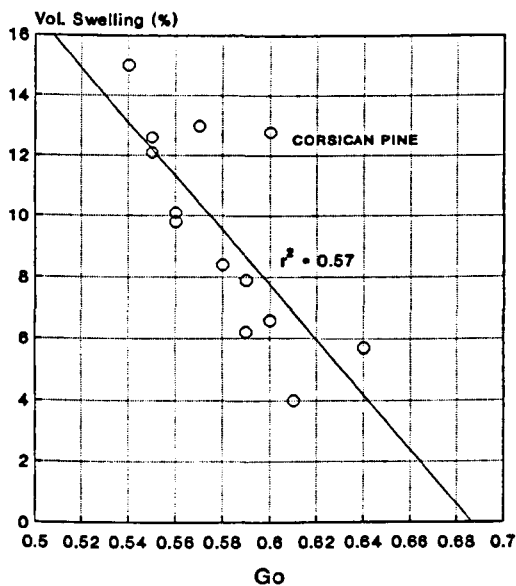
Fig. 4.5 Relationship between oven-dry specific gravity (Go) and volumetric swelling at saturation.
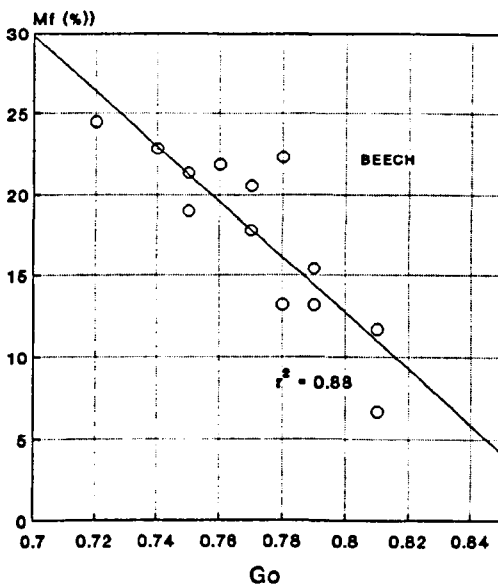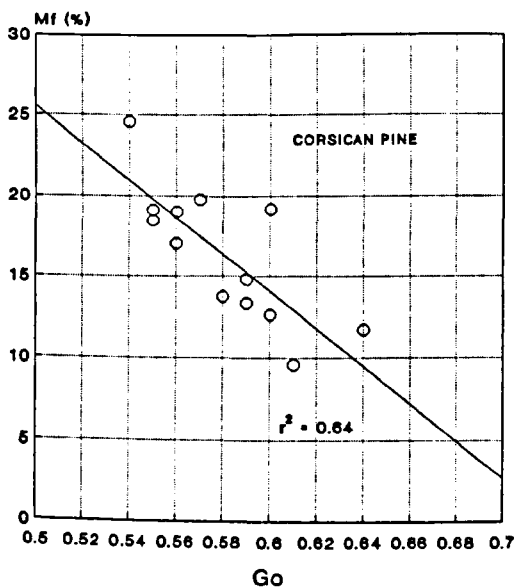
Fig. 4.6 Relationship between oven-dry specific gravity (Go) and the fibre saturation point (Mf) derived from the isotherms.

reasonable to assume a similar explanation for the observed reduction in M_f.

4.3.4 Effective specific gravity

The discussion above suggests that when wood is modified with the reagents used in the present work, the specific gravity G_0 cannot be used for swelling or fibre saturation point prediction through eq. 4.1. Deviation from the general trend predicted by eq. 4.1 has been reported to be caused in non modified woods by the presence of high extractive content in the cell walls and by the development of stresses and moisture gradients upon moisture changes (Stamm, 1964; Skaar, 1972 and 1988; Choong, 1969; Choong and Achmadi, 1991). In the present work the reason for the deviation seems to be that for the chemically modified wood, specific gravity is not a reliable indication of the amount of wood substance present. Even though the specific gravity apparently increases with the WPG, as far as swelling is concerned the treated wood behaves as if the specific gravity were decreasing. This is because the amount of wood substance present in the samples has its swelling capacity reduced, as the WPG increases. If it is considered that theoretically the same amount of wood substance is present in every sample (untreated and treated to any given WPG), the fact that this wood substance swells less as the WPG increases is a clear evidence that the treatment affects the wood substance capacity for sorption and swelling, causing deviation from the

relations predicted by equation 4.1. A similar conclusion was shown by Choong (1969) concerning the presence of extractives in wood cell walls. Comparing the results produced by equations 4.1 applied to extracted and unextracted woods of ten southern pines he stated that unless the extractives are removed from the wood, G_O cannot be used satisfactorily to predict shrinkage or fibre saturation point.

It seems reasonable therefore to assume that for the chemical modified wood, swelling and sorption are proportional to the amount of wood substance which remains active (i.e. able to sorb moisture and produce swelling) at each level of reaction. That is, on the basis of equation 4.1, at each WPG there must exist an "effective specific gravity" which should be proportional to the swelling observed in the treated samples. According to Skaar (1988) the increase in wood volume per unit volume of liquid water added is given by the ratio X_{VS}/G_O (the volumetric expansion coefficient divided by the dry-volume specific gravity). On the assumption that the cell wall cavity remains constant in size upon swelling the magnitude of this ratio is unity, meaning that the amount of swelling of the cell wall is equal to the volume of liquid water added. Thus,

$$X_{VS}/G_O = 1 \quad -> \quad X_{VS} = G_O \qquad\qquad (4.4)$$

For the untreated samples, this relationship shows only a modest small variation from unity, i.e.,

0.90   (0.488/0.54)   for   Corsican   pine   and   0.98 (0.709/0.72) for beech. Since X_{VS} decreases with increasing G_O due to the effects of the treatment discussed above (see section 4.3.2), it is evident that the relationship shown by equation 4.4 is not valid for the treated wood. However, if it is assumed that the treated samples behave as the controls as far as changes in the cell wall cavity upon swelling are concerned, the "effective specific gravity" (G_{oe}) referred to above may be estimated from equation 4.4. In this case:

$G_{oe} = X_{VS}/0.9$ (for Corsican pine treated samples)   (4.5)

$G_{oe} = X_{VS}/0.98$ (for beech treated samples)   (4.6)

Values based on these relationships are shown in Table 4.5. The nature of the correlation between G_{oe} and swelling does not need to be verified through regression analysis. This is because X_{VS} is itself a function of swelling (X_{VS} is the slope dv/dm of the regression swelling equations on Table 4.2 - see section 4.3.2), and therefore, the G_{oe} values found are evidently proportional to the respective volumetric swelling values. This relationship is in agreement with equation 4.1 and clearly indicates that, as anticipated above, the amount of swelling accomplished by the treated samples simply reflects the amount of wood substance per unit volume (G_{oe}) which remains active in the treated wood at each level of reaction.

Table 4.5 Effective specific gravity (G_{oe}) values obtained for treated Corsican pine and beech woods from Eq. 4.5 and 4.6 respectively.

| Reagent | CORSICAN PINE | | BEECH | |
	WPG	G_{oe}	WPG	G_{oe}
n-Bu-NCO	7.5	0.52	7.9	0.67
	19.7	0.47	18.1	0.65
	34.3	0.41	37.3	0.59
Ph-NCO	9.6	0.50	7.7	0.67
	19.3	0.47	15.4	0.64
	29.6	0.44	26.3	0.62
HDI	6.1	0.50	9.3	0.69
	17.5	0.46	16.0	0.66
	22.6	0.42	23.1	0.59
TDI	5.0	0.48	4.0	0.69
	7.0	0.51	7.5	0.67
	10.7	0.45	11.0	0.63

CHAPTER FIVE

GENERAL DISCUSSION, CONCLUSIONS

AND RECOMMENDATIONS FOR FUTURE WORK

5.1 CHEMICAL MODIFICATION STUDIES

5.1.1 Reaction with wood blocks for sorption studies

The present study shows that typical permeable hardwood (beech) and softwood (Corsican pine) thin wafers can be chemically modified using ordinary laboratory glassware, under relatively mild conditions. Both monofunctional and difunctional aromatic and aliphatic isocyanates undergo easy reaction using pyridine as solvent/catalyst and swelling agent. The methodology described, applied to small thin wood specimens, was suitable to produce levels of chemical addition causing substantial reduction in hygroscopicity and greatly improving the associated dimensional stability. The observed volume increase and the infra-red spectra recorded seem to establish beyond any reasonable doubt that most of the adducts ended up within the cell walls and that reaction took place with wood hydroxyl groups forming carbamate esters.

Contrarily to what it might be expected, higher reactivity measured under homogeneous conditions seems not to be necessarily a good guide to reaction rate under heterogeneous conditions. This is evident from the results with TDI, since this very reactive aromatic diisocyanate reacted slower and to a lessen extent than the other reagents used. This poor performance may be

associated with steric hindrance produced by the first TDI molecules to react preventing the subsequent molecules from reaching the remaining sites. Furthermore, as an apparent consequence of this high reactivity, TDI produced a high proportion of insoluble by-product, presumably homopolymer, outside the cell wall. These drawbacks however appear not to prevent TDI from producing a relatively good reduction in hygroscopicity despite the low levels of addition achieved.

In order to assess the relative reaction rate it was necessary to transform the weight gains achieved to the percentage of total theoretical hydroxyls depleted by the adducts. On this basis, the reaction rate orders obtained were 1,6 diisocyanatehexane (HDI) > phenyl isocyanate (Ph-NCO) > n-butyl isocyanate (n-Bu-NCO) > tolylene-2,4 diisocyanate (TDI) for beech, and phenyl isocyanate (Ph-NCO) > n-butyl isocyanate (n-Bu-NCO) > 1,6 diisocyanatehexane (HDI) > tolylene 2,4-diisocyanate (TDI) for Corsican pine. These data suggest that reaction rate is not totally predictable from molecular properties of the reagent alone. The orders also reflect some dependence upon wood species differences. According to the curves shown in Fig. 5.1 the monofunctional adducts seem to react faster with Corsican pine than with beech while the difunctional ones react faster with beech. It is suggested therefore that the overall rate of reaction for each isocyanate is the result of the interaction of several factors such as the

chemical reactivity of the N=C=O group due to inductive effects of neighbouring functional groups, molecular size, shape and flexibility and also of some intrinsic characteristics of the species being treated. It is not among the aims of this work to investigate these factors.

While the purpose of chemical modification with any reagent is to improve certain properties of wood, it must not diminish significantly its already advantageous properties such as appearance, finishability, gluability and strength. As discussed previously, the treated specimens look very similar to the controls. Apparent damage to the wood caused by the treatment could be observed only on the specimens treated with Ph-NCO which showed a somewhat rough surface and micro splitting at the highest weight gains achieved. These effects are more apparent with beech samples where at the highest weight gain the splits were very marked. These splits are believed to upset the hygroscopicity reduction achieved with this adduct to a substantial degree and may restrict the useful upper limit for treatment with Ph-NCO under the reaction conditions used, to a weight increase of not more than about 25%.

Even though damage at least at the superficial level, was not observed on the samples treated with the other reagents, in view of the fact that damage may occur, it appears important to assess how wood strength is affected by the treatments.
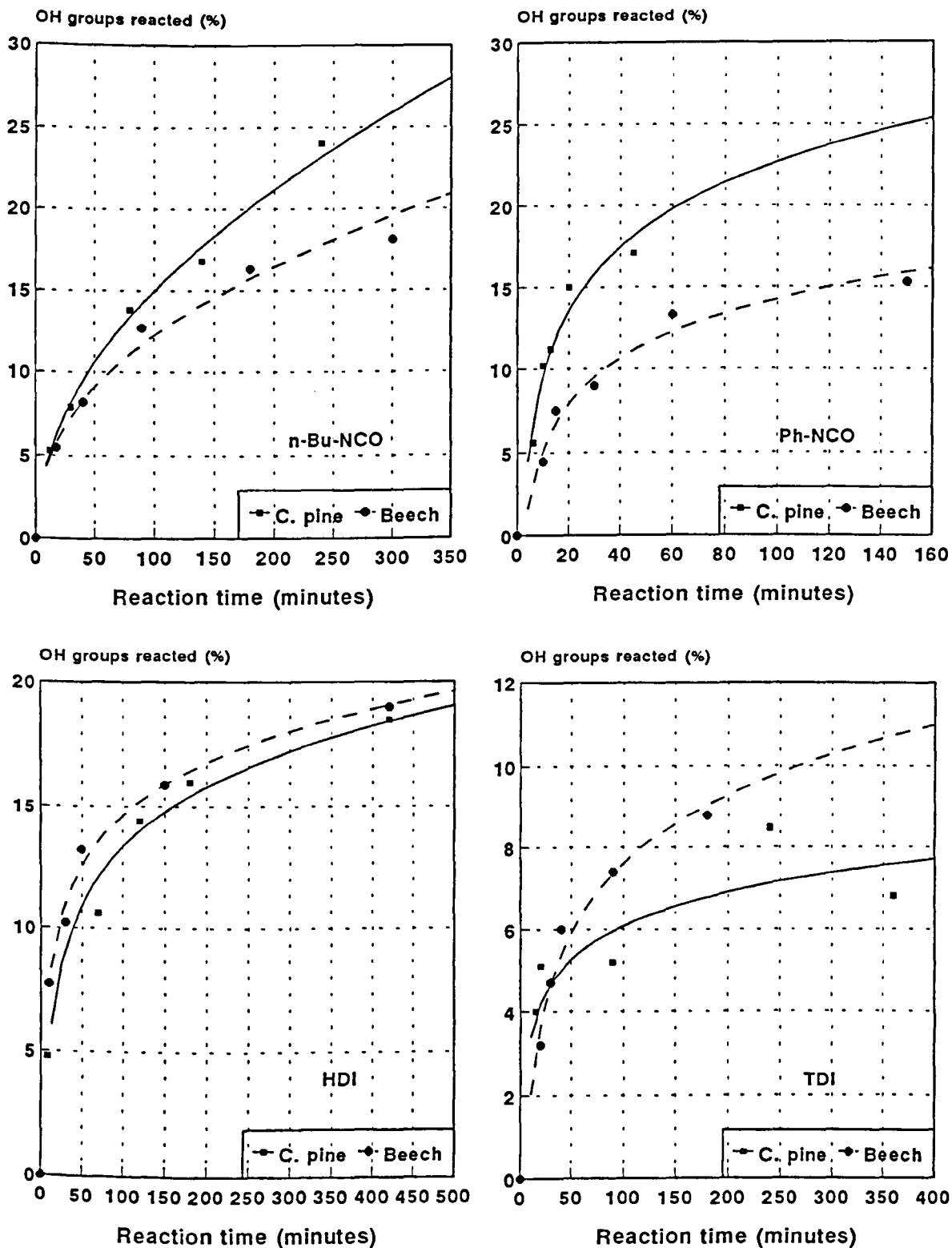
Fig 5.1 Reaction rate based on the percentage reacted of total (theoretical) hydroxyl groups for the two wood species with each isocyanate. Experimental points (average of ten replicates) and general trends.

5.1.2 Effect on wood strength

The effect of the treatments on the strength of the two wood species used is shown in Table 5.1. They are the results of tensile strength tests carried out on strips (50 mm x 10 mm x 100 µm - longitudinal x radial x tangential) microtomed from the longitudinal-radial surface of wood blocks (50 x 30 x 10 mm - longitudinal x tangential x radial). The wood blocks were cut for each species from a straight grained, defect free single stick. The strips were cut from the blocks with an inclination of ≈ 15° to the tangential surface producing a small off set from truly radial orientation in order to avoid ray cells which could form weak points on the surface of the strips. It is well known that strength properties of umatched specimens, from the same species, can vary more than 100% (Biblis, 1969). Hence, strips prepared from a single block were used for the tests with each isocyanate, i.e. each set of samples (composed of controls and treated strips to five WPG levels, with 10 replicates each) originated from the same wood block. The strips were reacted using the same methodology used to prepare the wafers for the sorption tests described in Chapter 2. The strips untreated and treated to the several weight gains were tensile tested (parallel to the grain) using an Instron testing machine (model 4301), over a 25 mm span, with a speed of 1.0 mm/min, at oven-dry condition, at approximately 20°C. The oven-dry condition forthe tests was chosen because most of

Table 5.1- Oven-dry tensile strength   of Corsican Pine ant Beech samples untreated and treated to several weight gains (WPG's) with four isocyanates.

reagent	WPG[a]	SD[b]	Tensile Strength[a] Force[c] SD[b] (N)		WPG[a]	SD[b]	Tensile Strength[a] Force[c] SD[b] (N)	
		CORSICAN PINE				BEECH		
None	0	-	44.1	4.0	0	-	42.9	7.1
n-Bu-NCO	9.6	0.8	32.9	7.6	9.1	0.6	35.9	6.6
	13.0	0.5	33.7	7.7	10.5	0.8	37.5	6.3
	16.0	0.8	29.0	6.2	16.2	1.0	40.4	5.8
	19.5	0.9	41.9	10.1	20.6	1.2	39.9	5.2
	28.1	0.9	34.8	7.0	23.8	1.8	42.1	9.5
None	0	-	31.5	4.5	0		39.9	6.2
Ph-NCO	11.1	1.1	29.4	5.3	9.3	0.7	34.7	4.4
	23.0	1.6	28.2	5.8	12.5	1.5	30.8	4.6
	27.8	1.9	27.6	5.5	15.0	1.0	30.3	4.2
	32.2	1.4	23.3	4.9	19.1	0.7	29.9	3.9
	39.0	1.5	21.8	1.6	24.0	1.7	31.4	4.4
None	0	-	40.7	4.7	0	-	51.7	9.6
HDI	9.0	1.1	36.4	5.8	8.0	0.8	40.7	5.4
	13.2	1.1	35.0	8.4	13.7	1.1	34.4	5.2
	16.1	1.2	36.6	5.3	16.7	1.4	31.7	5.0
	17.8	1.9	31.2	3.2	18.1	2.0	38.7	5.8
	19.8	1.5	25.7	4.1	21.9	2.1	32.4	4.3
None	0	-	34.7	5.2	0	-	54.8	11.8
TDI	2.6	0.8	29.9	6.7	8.7	1.0	36.9	8.0
	5.4	1.0	26.4	4.4	12.7	1.2	35.7	7.3
	7.4	1.2	24.5	5.5	14.8	1.4	34.1	9.2
	8.5	1.7	27.9	6.0	17.3	2.3	33.1	9.0
	9.3	1.9	26.8	3.6	20.2	2.4	26.1	6.5

[a] Average of 10 specimens.
[b] Standard deviation.
[c] Force required to break the strip. Significant at 95 level of probability except n-Bu-NCO treated beech (see text).

mechanical properties of wood are sensitive to moisture i.e., in general the lower the moisture content the higher the strength (Dreher et al, 1964). Since moisture content decreases with the weight gain (see Chapter 3), if the specimens were conditioned to any moisture content different from oven-dry, the lower moisture content that would be achieved for the treated specimens could compensate any loss in strength due to the treatment.

Tensile strength is expressed as the force necessary to cause the strips to fail. Since the untreated and treated strips have different thickness (due to the volume increase cause by the treatment) but essentially the same number of fibres and quantity of wood cell wall material per specimen, a force per unit area was not calculated. In this case, the actual force to cause failure is a better measure of relative strength (Rowell and Banks, 1987).

Table 5.1 includes the standard error of the respective mean values. Despite the careful selection of test specimens, the standard deviation values are quite high. As observed by Henningson (1967), when making strength tests on wood it is impossible to avoid some variation between similarly treated samples. However, analysis of variance (ANOVA) applied to the data show that the differences in strength caused by the increase in WPG are all significant statistically, with the exception of n-Bu-NCO treated beech. Regression analysis of the data of Table 5.1 are represented graphically in Fig. 5.2 (see Appendix C for details). They show that

tensile strength decreases with WPG for all the treatments with the two species. No significant trend however is found for the n-Bu-NCO treated samples relationship with either species. Although the variation in strength shown by sets of Corsican pine strips treated with n-Bu-NCO to several levels of weight gain is statistically significant, in the absence of a unidirectional trend this fails to be meaningful.

Even though the strips treated with Ph-NCO were very brittle, they do not show the largest decrease in strength. The highest loss in strength is shown by TDI treated samples which did not show any obvious visual damage such as the micro splits observed in Ph-NCO treated samples. This points to the fact that strength loss is not related exclusively to visible micro splitting as seen in the treated blocks used for sorption tests. The reduction in strength on chemically modified wood may also be associated with a reduction in the lateral hydrogen bonding between cellulose and hemicellulose chains causing the phenomenon of slippage. When a finite span strength testing is employed, this phenomenon seems to be an important contributor to the development of ultimate tensile strength. According to Ifju (1964) the energy necessary to overcome these lateral hydroxyl bonding is less than that required for breaking the primary valences forces along the chains. Therefore, when aforce is applied, the molecules in each adjacent chain can begin to slide over each other, a process known as slippage. The same effect should be
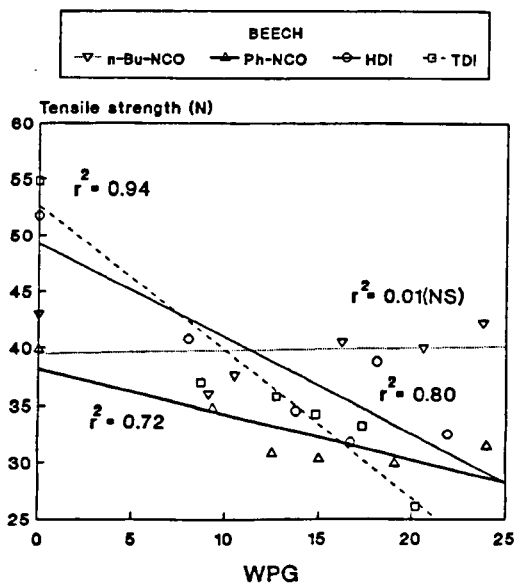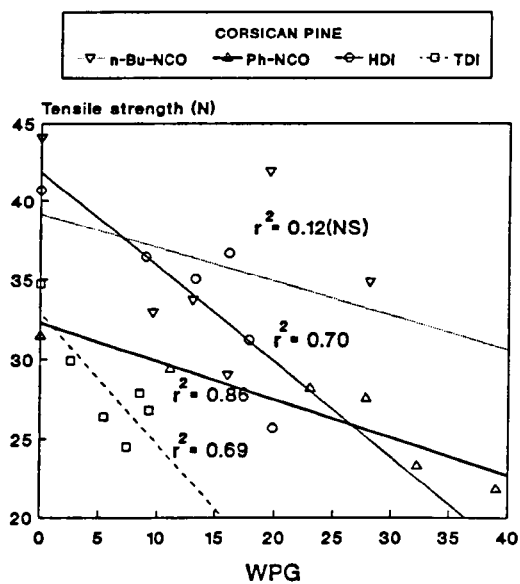
Fig 5.2 Effect of chemical modification on wood strength. Experimental points and calculated fitted lines.
NS = nonsignificant statistically.

produced between micelles or whole fibrils that are held together relatively "loosely" by amorphous cellulose or hemicelluloses, rather than between individual molecules (Ifju, 1964). Since the treated wood is kept in a partially swollen state through the bulking effect it seems logical to expect that the oven-dry treated samples contain less hydroxyl bonding between chains than do the controls. This may facilitate the incidence of the slippage effect. That is, in the treated wood a condition exists in which the number of lateral bonds is no longer enough to resist high tensile stresses and therefore slippage occurs and strength decreases. It also appears that the formation of any ester crosslinkages between adjacent chains in the case of the difunctional reagents does not fully compensate the strength loss by the mechanism referred to above (and possibly by other effects such as damage caused by the chemical treatment), since the strength of the strips treated with the difunctionals reagents is also reduced.

The slippage mechanism should affect only the less rigidly bonded zones such as the amorphous regions of cellulose. This is precisely where the chemical modification treatment is meant to work. In addition, according to published work of Ifju (1964), the strength behaviour of wood in tension depends mostly on its cellulose content and it can be conveniently explained on the basis of secondary valence bond deformation mainly in the amorphous zones of the cellulose fraction. Law and Koran (1979) however, claim that fibre slippage can be

eliminated by employing a zero-span tensile testing method. With the reduction or elimination of the fibre slippage mechanism other effects of chemical modification which affect the wood strength may be assessed. No further insight into the effects of chemical modification in strength is visualised within the scope of this work. Details of the mechanisms involved in wood strength formation are discussed by Ifju (1964), Law and Koran (1979) and Winandy and Rowell (1984).

The results of this study show that there is significant loss in tensile strength in very thin strips modified to several weight gains with Ph-NCO, HDI and TDI. No evidence of significant reduction in strength on strips modified with n-Bu-NCO is shown. The strips are specimens containing essentially just two surface layers of cells. This improves the contact of the reagent with the reactive groups in wood and any effect on strength resulting from the chemical modification by the process used may be greatly magnified by using such a test specimen. Hence, although more practical, the results obtained with the strips should be treated cautiously as they may not reflect perfectly the effect of the treatment on the relatively thicker blocks used for the sorption tests.

5.2 SORPTION STUDIES

5.2.1 The sorption model

5.2.1.1 Hysteresis

Application of the theoretical model derived by Hailwood and Horrobin (1946) for the analysis of experimental wood sorption data has provided a validated description of the sorption process confirming the apparent applicability of the solid-solution model for the evaluation of sorption phenomena in wood. As Spalt (1958) pointed out, such a technique has obvious limitations. Nevertheless, in view of the insight gained, which may lead to a better understanding of the mechanisms involved in dimensional stabilization of wood by chemical modification, the treatment has considerable merit.

It has been shown by other workers (Prichananda, 1966; Spalt, 1958; Wangaard and Granados, 1967; Simpson 1973 and 1979) and it is definitely evident in the present work that the Hailwood & Horrobin (HH) sorption model fits the experimental wood sorption data quite well giving an excellent representation of the sorption isotherm. The criterion of goodness-of-fit of experimental isotherms indicates that a model is suitable for correlating and interpolating experimental data. However, it is not sufficient simply to prove the validity of a model, because it incorporates simplifying assumptions that are necessary in order to make its mathematical derivation feasible. For example, the HH

model (as well as other theories such as the classical BET) cannot account explicitly for the hysteresis phenomenon. As pointed out in the original paper, this is because 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 RH range. However, Hailwood and Horrobin (1946) suggest that the fraction of inaccessible groups is not constant throughout the sorption process since the wood structure is gradually opened as adsorption 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 (Howsman, 1954; Spalt, 1958; Browning, 1963; Morrison et al, 1959; Stamm, 1952 and 1964). It is possible that introducing variable values for W_O in adsorption for example, would help in the assessment of the hysteresis phenomenon. Unfortunately, it is likely that the improvement in precision due to extra constants would not compensate for the increased mathematical complexity required to handle the model. Nevertheless, although the M_O value (the moisture content correspondent to complete polymer hydration) does not vary for a given sorption isotherm, W_O (and consequently, M_O) is always lower for adsorption from the dry condition compared to desorption. As explained by Skaar (1988), this is because after

rewetting, some extra sorption sites become available, possibly because of the swelling forces induced by water sorption. However, it is unlikely that the HH model would be able to reveal the hysteresis phenomenon explicitly even if it could show, for example, increasing values for W_O in adsorption. This is because, as it is shown in the Section 3.4.4, in line with the findings of Spalt, (1958) and Wangaard and Granados (1967), the hysteresis phenomenon is not only influenced by site accessibility but also by polymolecular sorption phenomena. Nevertheless, the analysis presented in section 3.4.4 clearly indicates that the insight into the wood sorption behaviour provided by the HH model allows a comparison between the adsorption and desorption isotherms to be made in terms of total sorption and of the two types of water sorbed described. This permits a reasonable partial description of the phenomenon.

5.2.1.2 Solid solution & Surface sorption theory

Another point that needs to be addressed is the theoretical physical approach taken in the development of the model used. The HH theory has been criticised because of some of the assumptions used in its derivation. In the development of the solid solution theory, it has been found necessary to treat the system as an ideal solution, whereas in fact, the process of solution of water into disordered regions deviates from simple solution theory because of restrictions on the swelling of the system by the insoluble ordered regions (Browning, 1963). The

surface-sorption theory, represented by the classical Brunauer-Emmett-Teller-BET (1938) theory has also been object of criticism, mainly because of its assumption that the thermodynamic properties of the secondary layers of water are essentially the same as those of liquid water (Barkas, 1949), and also, probably a consequence of this assumption, because the correlation with real data beyond a vapour pressure of about 0.4 is not strong (Dent, 1977 and Skaar, 1988).

It has already been mentioned (Chapter 3, section 3.1.4) that the two classes of theory, surface sorption and solution theory, paint the same general picture of the sorption phenomena concerning the way water is held by wood. In both, part of the water sorbed is intimately associated with the polymer (wood) molecules (monolayer, water of hydration) and part is considerably less intimately associated (multilayer, dissolved water) and therefore these two classes of theory are not so different as they may appear. For example, the Dent (1977) surface sorption model, extensively discussed by Skaar (1988), seems to provide a link between the two classes of theory. Both, the Dent (1977) and the HH (1946) models offer the same equation for the sorption isotherm (Eq. 3.2) predicting therefore the same parabolic relationship between relative vapour pressure h and the ratio h/m, where m is the fractional moisture content. Although the two models predict the same sorption isotherm they are quite different in its interpretation. The HH model considers the sorption

process as one of hydration of the polymer and establishment of an equilibrium solid-solution in the cell wall. The Dent model on the other hand, is based on a multilayer theory which is an extension of the BET surface theory model. Like the BET model, it postulates the existence of primary and secondary sorption sites where the water molecules are sorbed with higher energy in the former than in the latter. Differently from the BET model however, it assumes that the water molecules sorbed above the monolayer are thermodynamically different from ordinary liquid water. This assumption requires a third constant (to account for the secondary water) additionally to the two BET constants in order to describe the sorption isotherm (Skaar, 1988).

The Dent model predicts the same empirical constants A, B, and C (from Eq. 3.2) and also three fundamental constants K_1, K_2 and M_0'. However, in agreement with the postulates of the surface-sorption theories, K_1 and K_2 are defined as the ratio of attachment rate to the escape rate per unit relative vapour pressure, of the water molecules respectively in the primary and secondary sorption sites in the cell wall (Dent, 1977). M_0' in the Dent model is the moisture content corresponding to complete monolayer coverage of all available sorption sites, similar to M_0 (the moisture content correspondent to complete polymer hydration) in the HH model. Two of the three fundamental constants (K_2 and M_0') are numerically identical to the two corresponding constants K_d and M_0 in the HH model. The

third constant K_1 is somewhat lower than the equivalent constant K_h in the HH model. According to Okoh and Skaar, (1980), K_1 can be readily related to K_d and K_h in the HH model through the relationship:

$$K_1 = K_d(K_h+1) \tag{5.1}$$

Dent developed two equations for the calculation of the two types of water in which his model splits total water sorbed, namely primary water (m_1) and secondary water (m_2):

$$m_1 = \frac{M_0'K_1h}{1+(K_1-K_2)h} \tag{5.2}$$

$$m_2 = \frac{M_0'K_1K_2h^2}{(1-K_2h)\{1+(K_1-K_2)h\}} \tag{5.3}$$

$$m = m_1 + m_2 \tag{5.4}$$

Since the two models predict the same equation for the isotherm, the total water sorbed m is also the same.

Okoh and Skaar, (1980) applied these two models to their own sorption data obtained for wood and inner bark of 10 hardwoods. They report that although the two types of water vary with the moisture content, they vary in the same proportion for the two models.

Examples of the sorption isotherms obtained in the present work with the two models are plotted in Fig. 5.3 for Corsican pine and beech wood, untreated and treated to selected weight gains. For this example, K_1,

m_1 and m_2 values were found respectively through the equations 5.1, 5.2 and 5.3 above using the fundamental constants from Table 3.4 at the applicable weight gains. Although the Dent model produces slightly higher values for monomolecular sorption and slightly lower values for polymolecular sorption than the respective ones in the HH model, it is evident that in line with the work of Okoh and Skaar (1980), the two types of water sorbed vary within the range of RH in approximately the same proportion for the two models. Yet the same shift in predominance is observed in both models since polymolecular sorption (m_d and m_2) predominates at the higher ranges and monomolecular sorption (m_h and m_1) predominates at the lower ones. Both models predict the same equation for the isotherms and therefore, the integral reduction in hygroscopicity (Table 3.7) remains unaltered.

This analysis indicates that the general conclusions concerning the mechanisms of reduction in hygroscopicity derived from the HH model in the present work appears to be also valid when a surface sorption model, derived from a complete different set of assumptions is applied.
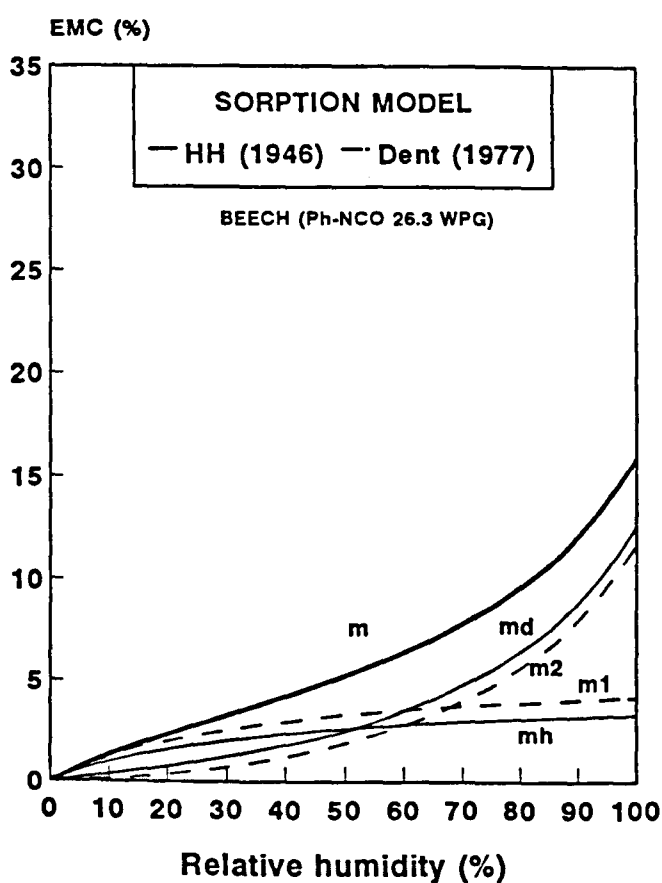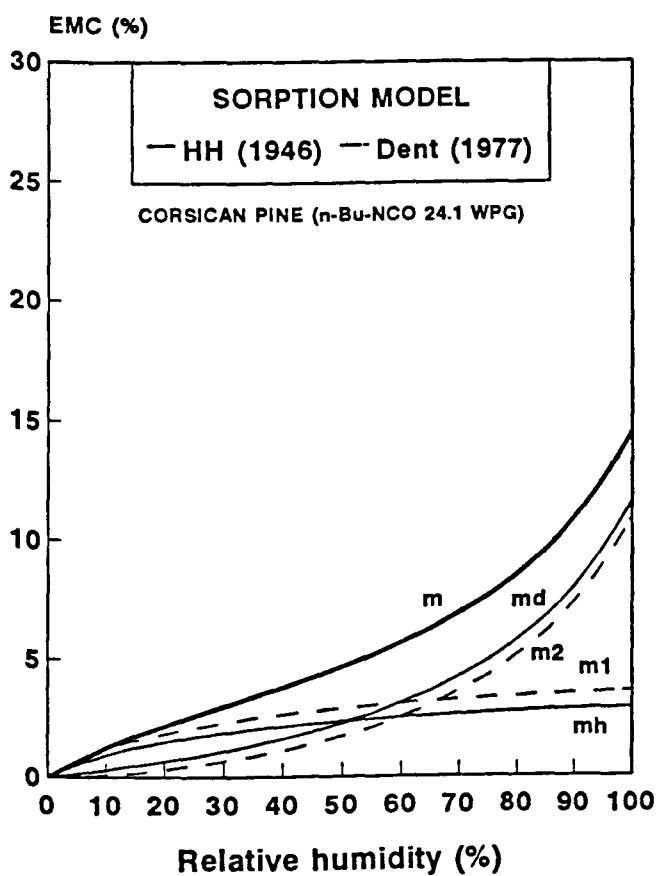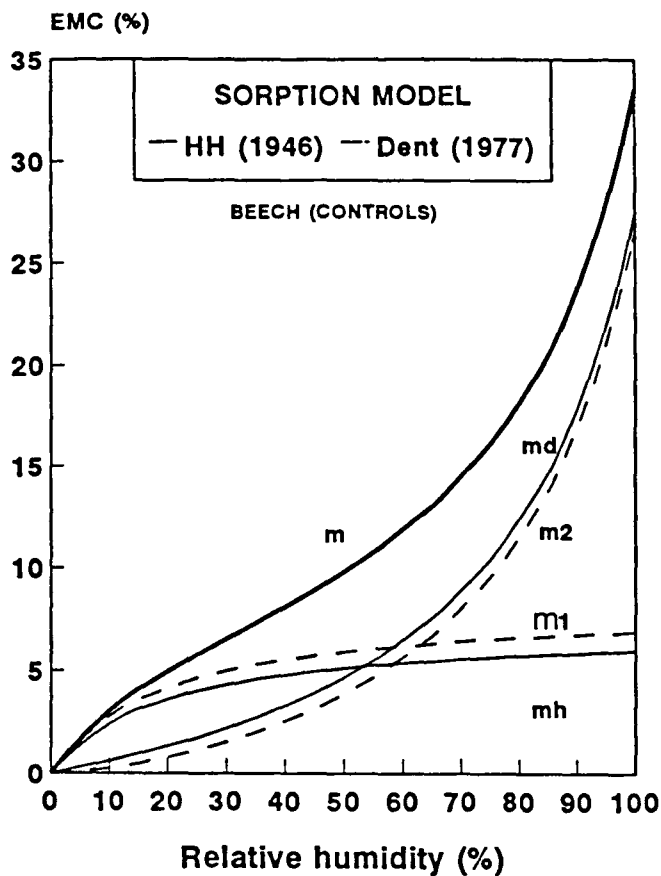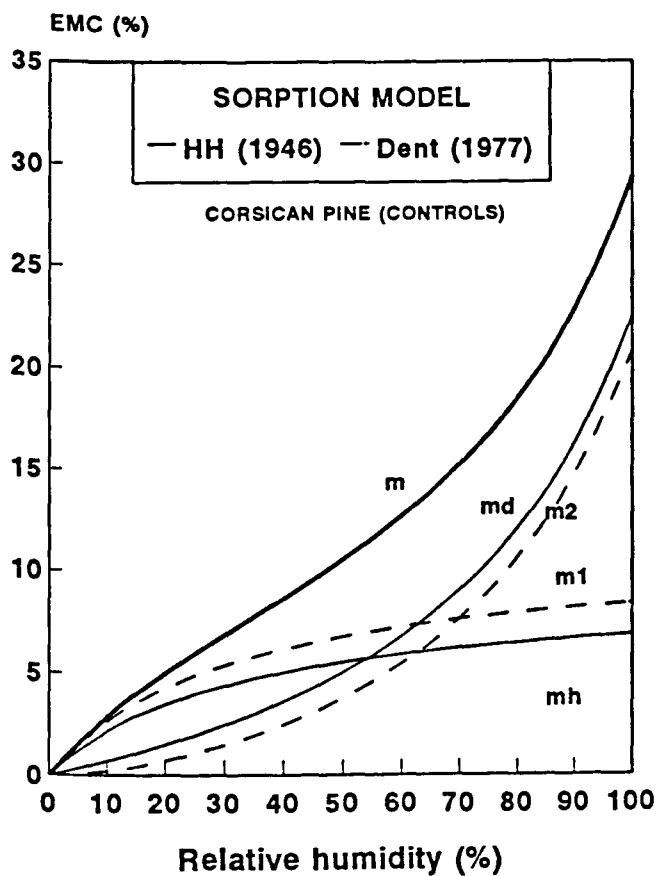
Fig 5.3 Desorption isotherms for untreated and treated woods of Corsican pine and beech, obtained by means of the solution model of Hailwood-Horrobin (1946) and the surface-sorption model of Dent (1977). (The thick line is the total sorption isotherm with both models - see text).

5.2.2 Dimensional stability of chemically modified wood and its mechanisms

The analysis shown in Chapter 4, concerning the relation between EMC and swelling, indicates that the reduction in hygroscopicity of the chemically modified woods is accompanied by a proportional reduction in swelling. When plotted against relative humidity the swelling curves are of somewhat similar sigmoid shape to the sorption curves over the entire range of relative humidity. Regression analysis confirms the close relationship between EMC and swelling, showing that for each weight gain the experimental points lie almost on the regression lines. The relationships above suggests that discussion of the mechanisms of stabilisation based on the effects of the chemical modification process on the hygroscopic properties of the treated wood is valid. Consideration of the sorption vs dimensional stabilisation relationship under saturated conditions is also included.

The hygroscopicity of the treated samples of the two wood species studied is reduced proportionally to the weight gain of adduct for the four isocyanates used. For a given reaction level, the treatment with the monofunctional reagents (n-Bu-NCO and Ph-NCO) affected the samples hygroscopicity in a similar way throughout the hygroscopic range. With the difunctional ones (HDI and TDI) however, the reduction appears to be slightly higher at the upper end of the relative humidity range. A plot of the integral reduction in hygroscopicity

(estimated from the areas below the isotherms produced by the treated and untreated samples) against the WPG shows that the reduction is of different magnitude for each reagent (Fig. 3.3). This indicates that the reduction in hygroscopicty is dependent on the molecular properties of the reagent used. For example, at a given weight gain, reagents with lower molecular weight substitute a higher proportion of hydroxyl groups whereas those with higher specific volume produce a higher degree of bulking in the cell wall. For the monofunctional reagents, apart from the possibility already suggested that the reduction in hygroscopicity obtained with Ph-NCO is partially offset by the mechanical damage to the treated specimens, the better performance presented by n-Bu-NCO at a given weight gain is readily explained on the basis of its lower molecular weight and higher specific volume. These properties may be expected to influence the mechanisms responsible for hygroscopicity reduction, viz, reduction in site accessibility and bulking. This simple explanation does not seem to be valid for the difunctional reagents however, since TDI (relatively higher molecular weight and lower specific volume) is more efficient than HDI, whereas HDI might be expected to perform the better on the basis of the above argument (see Table 3.8).

The effectiveness of the two monofunctional reagents seems to be similar with the two wood species examined whereas for the difunctional ones, a slightly higher reduction in hygroscopicity is achieved with the

hardwood (Fig. 3.4). Since the swelling of beech is larger it seems reasonable to expect that any swelling restriction due to crosslinking effect might be more apparent with this species. In the case of Ph-NCO treated samples, the reduction in hygroscopicity appears to be offset by damage to fine structure caused by the deposition of this rigid adduct in the cell wall. The lack of a sharp increase in hygroscopicity at the higher weight gains (see Fig. 3.3) indicates that this offset is likely to be gradual rather than abrupt. Hence, this effect is possibly caused by localized cell wall disruption which only approaches visible magnitudes at higher weight gains. Further support for this suggestion is provided by the reasonable agreement between the fibre saturation points (FSP) derived from the sorption isotherms and those derived from swelling equations for the Ph-NCO treated samples of each of the two species at the highest weight gain (Table 4.4). That is, substantially higher degrees of swelling at saturation would certainly increase the FSP calculated through the swelling equations.

When the reduction in hygroscopicity is plotted against the percent of total (theoretical) hydroxyl groups reacted and against the volume of adducts in the cell wall it becomes apparent that neither of these two factors alone explains the reduction achieved with the four isocyanates. In line with suggestion made by Spalt (1958), working with acetylated wood, this is believed to be because the reduction in hygroscopicity

obtained is the result of an interaction of these two effects, the extent of which varies over the hygroscopic range. Furthermore, the process may be affected by effects other than the blocking of hydroxyl groups and bulking effects, e.g. crosslinking, in the case of the diisocyanates.

Further insight into the sorption phenomena is required in order to understand fully the effects of the reduction in site accessibility and space available for polymolecular sorption within the cell wall, on the reduction in hygroscopicity.

5.2.2.1 Monofunctional reagents

Analysis by the Hailwood-Horrobin (1946) model suggests that for the two species treated with the monofunctional isocyanates, the reduction in total sorption at saturation is chiefly due to the reduction in polymolecular sorption, reduction in monomolecular sorption being of secondary importance. This relationship tends to invert gradually with decreasing relative humidity as the predominance shown by the reduction in polymolecular sorption decreases. A complete shift in predominance is shown at the lower relative humidities (Table 3.12 and Fig. 3.7).

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 over the hygroscopic range, the next step is 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 confirm that the availability of bonding sites is reduced by modification. This is as expected on the basis of the evidence of carbamate formation (Chapter 2). 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 with the weight gain (a measure of the degree of bulking) was shown to be the primary reason for the decrease in polymolecular sorption.

Since it has been shown that the relative contribution of each type of sorption to total sorption varies with relative humidity (Fig 3.7), the reduction in total hygroscopicity at a given relative humidity is primarily a function of either the availability of bonding sites or of the bulking achieved, depending on the type of sorption that predominates at that particular relative humidity (Fig. 3.7 and Table 3.12).

The insight provided by the model has proven to be of great help in describing the mechanisms involved in site accessibility and bulking effect. However, from these data, the cause of the reduction in site accessibility was obscure and further experimental investigation was required in order to clarify this point.

Site accessibility

The results obtained with the bulkier isocyanate (octadecyl isocyanate), when compared to n-Bu-NCO, showed clearly that when these two adducts are reacted with wood to the same degree of substitution, the bulkier one is more effective in terms of the reduction in hygroscopicity achieved. Conversely, when the two reagents are reacted to give similar degree of bulking, reduction in hygroscopicity is also similar, despite the substantially different proportion of hydroxyl groups reacted, (at similar weight gain, the degree of substitution with octadecyl is only 1/3 that achieved with n-Bu-NCO). These general observations are valid over the entire range of relative humidity, in adsorption and desorption, and with both species studied. However, in desorption, the bulkier isocyanate seems to be somewhat less effective.

When the isotherms were fitted to the Hailwood-Horrobin model, it was seen that in adsorption, the curves from samples treated with the two isocyanates showing similar bulking, matched each other closely, at the mono and polymolecular levels. The fact that the isotherms for monomolecular sorption coincide when samples treated with the two adducts at similar weight gain are considered, and are significantly different when the same proportion of hydroxyl groups are reacted, strongly suggests that it is the amount of adduct laid down in the cell wall rather than the fraction of hydroxyl groups substituted that determines the

reduction in monomolecular sorption. In addition, the accessibility to the sites measured by the W_O an M_O values, indicates closer values for similar weight gains than for similar fractions of hydroxyl groups reacted. Due to the relatively larger molecular size of the adducts in relation to the water molecule (assuming that molecular volume is approximately proportional to molecular weight, n-Bu-NCO and octadecyl are respectively about 6 and 19 times larger than water) when the reagent reacts with one hydroxyl it is likely to cover some of the adjacent ones. Hence, the effect of the adduct covering reacted and unreacted sites (here designated "shielding effect") seems to be a major effect which may overshadow the effect of direct chemical bonding to the sites and hence determine the reduction in monomolecular sorption. The slightly lower reduction in monomolecular sorption in desorption when compared to adsorption for the octadecyl treated specimens (see Figs. 3.9.a and 3.9.b) indicates that the shielding effect may be less effective in desorption. This may be explained on the basis of the swelling forces developed as the wood takes up moisture reducing the shielding effect by partially exposing some of the unreacted hindered sites. That is, some of those sites with water sorbed at saturation retain this water during desorption. The fact that the samples treated with n-Bu-NCO do not show lower effectiveness in desorption may be because the shielding effect produced by this adduct is accompanied by much more substantial site blocking (approximately three times

higher than that produced with octadecyl). As opposed to physically blocked sites, chemically blocked sites are not made accessible by swelling forces at saturation, and therefore, do not have water molecules for retention in desorption.

Monofunctional reagents - summary of the proposed dimensional stabilisation mechanisms

According to the analysis above the most likely mechanisms for the reduction in hygroscopicity for wood treated with the monofunctional reagents used may be summarised as follows.

1) The reagent enters the cell wall, reacts with some of the hydroxyl sorption sites of the wood components, reduces site accessibility and bulks the cell wall.

2) The reduction in site accessibility decreases sorption at the monomolecular level (which predominates at the lower relative humidities).

3) Polymolecular sorption (which predominates at the higher ranges of relative humidity), is primarily reduced by the bulking effect.

4) The accessibility of the internal surfaces to water molecules is reduced by chemical reaction and simultaneously by a physical "shielding" effect when the adduct physically covers some of the adjacent unreacted sorption sites (Fig. 5.4).

5) The proposed "shielding effect", a result of the substituting groups covering reacted and unreacted sites, takes on an increasingly dominant role as adduct molecular size is increased and in some cases may largely determine the reduction in monomolecular sorption.

6) When the adduct is of relatively large molecular size, this shielding effect seems to be slightly less effective in desorption from saturation than in adsorption. This is probably because the low proportion of sites reacted, in comparison to the total amount shielded, produces insufficient chemical blocking, allowing a substantial proportion of the physically hindered sites to become accessible at saturation due to the swelling developed. With the lower molecular size adducts such as n-Bu-NCO, the physical effect is accompanied by a much more significant proportion of chemically reacted blocked sites and a similar loss in effectiveness is not observed.
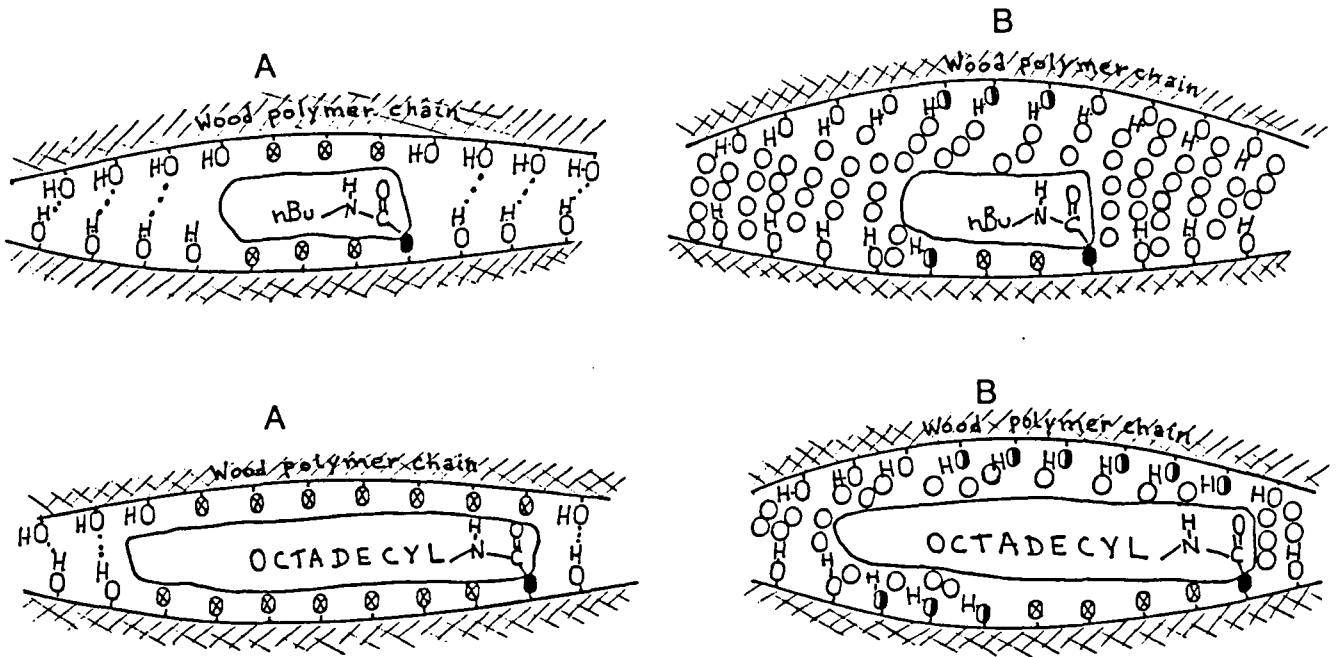
LEGEND:

OH Active sites
● Reacted sites
⊗ Physically blocked sites
OH Sites uncovered upon swelling
O Water molecules.

Fig. 5.4 Schematic one-dimensional illustration of the mechanism of reduction in hygroscopicity in wood reacted with monofunctional isocyanates.

A - Dry condition: reacted and some unreacted sites are covered by the adducts.

B - Swollen condition: as swelling proceeds some of the unreacted sites are uncovered. At a given weight gain, this process of uncovering sites appears to be more severe with the octadecyl than with the butyl adduct due to the higher proportion of physically blocked sites resulting from the octadecyl larger molecular size (see text).

5.2.2.2. Difunctional reagents

The analysis of the data fitted to the Hailwood-Horrobin model indicates that the reduction in hygroscopicity obtained with samples of the two wood species modified with the difunctional reagents follows a similar mechanism to that for monofunctional modification. Therefore, the conclusions drawn above are generally also valid for the difunctionally modified wood. Nevertheless, with the difunctional reagents, the hygroscopicity reduction tends to be slightly lower at low relative humidities (Table 3.6). Hence, although the participation of the reduction in monomolecular sorption increases with decreasing relative humidity, with difunctionally modified wood this increase appears to be less pronounced than in wood treated with monofunctional reagents. The reduction in the two types of sorption (monolayer & multilayer) at low relative humidities tends to be of similar magnitude. This is in contrast to wood modified with monofunctional reagents where the effect on monomolecular sorption is dominant (Fig. 3.8 and Table 3.21). This characteristic, along with the fact that in TDI treated samples, the reduction observed in polymolecular and total sorption is higher than expected from the low added volume, (Table 3.20), points to the participation of a crosslinking mechanism in the process of sorption reduction.

Crosslinking effect

Under the reaction conditions used, any crosslinkages will form with the samples already substantially swollen (about 75% swelling relative to water saturation value). It is reasonable to suppose that below this level of swelling, these crosslinkages are unable to prevent the treated wood from swelling. Hence, crosslink effectiveness against moisture sorption should be greater at high relative humidities and consequently, should be reflected mostly as a decrease in polymolecular sorption, working complementarily to the bulking effect. This seems reasonable since the crosslinking effect preventing the polymer chains from being pulled apart upon sorption, from the point of view of the limitation of the space potentially available for polymolecular sorption development, is essentially similar to the bulking effect. Any reduction in monomolecular sorption due to crosslinking, based on the inhibition of formation of new sorption centres upon swelling, will more probably occur at higher relative humidities. That is, at the relative humidities beyond the point at which the crosslinkage effect upon swelling starts to be effective.

Of the two difunctional reagents used in the present work, only TDI seems to show some improvement in the reduction in hygroscopicity attributable to a crosslinking effect. This becomes apparent as a higher reduction in sorption than can be explained by a bulking

effect. It is ascribed to the lower flexibility of the aromatic TDI molecule.

A carefully designed experiment for the investigation of crosslinking effectiveness under saturated conditions showed no evidence that this mechanism effectively increases the anti-swelling efficiency (ASE). Under the condition of the experiment, wood specimens treated with TDI and HDI swelled to approximately the same extent as the specimens treated with the monofunctional n-Bu-NCO (treated to approximately 20% weight gain) used for comparison, showing no reduction in the water swollen volume. In addition, contrary to what it is expected when significant crosslinking effect is developed, the ASE achieved is roughly of the magnitude expected from the bulking properties alone of the three adducts under discussion (Table 3.22). It seems likely therefore, that under the considerable stress imparted by water sorption, approaching saturation, the flexibility of the crosslinkages allows the reacted wood to swell to a degree similar to the normal water swollen state. This is also indicated by the data on Table 4.3 where for the TDI treated samples, with the two wood species, the ASE at saturation is shown to be substantially lower than under high water vapour pressure conditions.

Bearing the above in mind, it is tentatively suggested that, due to the higher rigidity of the TDI adduct, the expansion of the crosslinkages upon swelling occurs more readily with the more flexible HDI than with

TDI. Thus, the sorption developed by the TDI treated specimens simply lags behind that observed with the more flexible adduct causing the apparent higher effectiveness observed in high vapour pressure conditions.

Proceeding along this line, the crosslinking effectiveness was investigated on samples exposed to a more powerful swelling agent, pyridine, which is known to swell wood 20-25% more than water (Ashton, 1973). The results show that the samples modified with the difunctional reagents undergo swelling in pyridine similar in degree to the control (untreated wood). However, the n-Bu-NCO (monofunctional) treated samples used for comparison swelled substantially more than this (Table 3.23).

All wood specimens showed slightly but consistently higher water swollen volume after the modification treatment than before (Table 3.22). It is suggested that the wood cell walls are kept slightly open (at ultrastructural level) by the bulking treatments. In the case of n-Bu-NCO treated samples, in the presence of the more powerful and larger swelling molecule, pyridine, the bulked wood structure allows the ordered regions of wood cellulose gradually to become accessible, facilitating solvent penetration and subsequent "super-swelling" to the higher degree observed. In the case of the specimens treated with HDI and TDI substantial super-swelling in pyridine beyond the degree shown by the controls is not observed (Table 3.23). It seems possible that this gradual exposure of more ordered regions upon

swelling in pure pyridine <u>after the modification treatment</u> is prevented by the presence of the crosslinkages which prevent the pyridine molecules from penetrating into the more ordered regions of the crystallites.

<u>Difunctional reagents - summary of the proposed dimensional stabilisation mechanisms</u>

On the basis of this discussion, the role played by the crosslinking is summarised below.

1) Similarly to the monofunctional reagents, the difunctional reagents enter the cell wall, react with some of the sites, give rise to bulking and reduce site accessibility.

2) Intra and inter-polymer chain crosslinkages are randomly formed with the cell wall substantially swollen.

3) As water is absorbed and the wood starts to swell from the dry condition, the crosslinkages begin to expand towards their extended conformation.

4) This expansion produces some 'gaps' on the internal surfaces where the water molecules are able to enter and attach themselves to available sites left uncovered as swelling gradually proceeds (Fig. 5.5). This partially offsets the reduction in hygroscopicity at low relative humidities.

5) This expansion is likely to occur more readily with the more flexible alkane chain of the HDI

crosslinkages than with the rigid aromatic group which forms the main part of the TDI crosslinkages.

6) The lower flexibility of the TDI crosslinkages may induce a lag in the swelling of the samples upon sorption. This effect causes the apparent improvement in hygroscopicity reduction observed in the TDI treated samples under vapour (up to near saturation) conditions compared to those treated with HDI, by delaying the formation of the gaps in the internal surfaces which lead to increase in monomolecular sorption.

7) Upon full saturation in water, the stresses developed by swelling cause further extension in the crosslinkages, providing room for polymolecular sorption build up and uncovering further unreacted sorption sites where monomolecular sorption may then occur. This permits the swelling units to separate by about their normal amount (that is, up to the point at which further swelling is prevented by the strongly crystalline regions). Thus, no significant enhancement in ASE due to crosslinking is observed.

8) Substantial "super-swelling" in pyridine, beyond the degree shown by the untreated samples appears to be prevented by the crosslinkages. Whereas, samples treated to similar levels of bulking with a monofunctional reagent (e.g. n-Bu-NCO) are "super swollen" in pyridine significantly more than is unreacted wood.
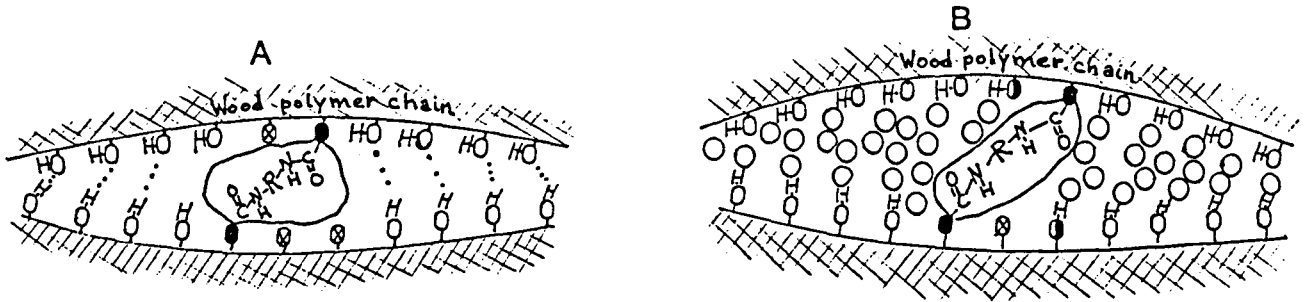
LEGEND:

OHActive sites
● Reacted sites
0 Physically blocked sites
OHSites uncovered upon swelling
O Water molecules.

Fig. 5.5 Schematic one-dimensional illustration of the mechanism of reduction in hygroscopicity in wood reacted with difunctional isocyanates.

A - Dry condition: part of the sorptive sites are physically covered by the crosslinkages, constricted upon drying.

B - Swollen condition; the crosslinkages are pulled apart upon swelling and unreacted sorption sites are uncovered. Since the crosslinkages are extended, it is likely that most of the physically blocked sites become available for water molecules at saturation.

5.3 RECOMMENDATIONS FOR FUTURE WORK

There are some indications of crosslinking effect in water vapour conditions and when soaked in a more powerful swelling agent (pyridine), shown by the samples modified with TDI. However, mechanism of sorption reduction in wood modified with this difunctional isocyanate still needs some explanation. It seems reasonable to expect that an increase in the amount of crosslinkages would make their effects more apparent. Further experimental work is suggested including a modification in the chemical treatment in order to increase the weight gain range for the sorption tests. In terms of a practical treatment system, increase in the length of reaction time should be avoided. However, changing some of the treatment variables such as the temperature of reaction and the catalyst used may achieve this goal.

Application of the Hailwood-Horrobin sorption model proved to be a very useful method to assess the effect of chemical modification in the sorption properties of wood. It would be of interest to employ this technique to assess for example how the accessibility to water molecules is affected in modified wood fibres and modified separated cell wall polymers, hemicelluloses & lignin. It would be useful to employ the model to analyse the effect of non leachable but non bonded cell wall treatments (e.g. phenol-formadehyde resin-forming compounds) on site accessibility. Since these chemicals are not attached or bonded to the cell wall polymers,

analysis of sorption data produced for such treated wood may be useful for further investigation of the suggested shielding effect.

Since the two difunctional reagents used allow the cell wall polymer to swell to full extent in water, and the dimensional stability achieved with formaldehyde treated wood (where only one carbon remains between the crosslinked structural units) has been reported to be accompanied by a definite embrittlement, it seems that the optimum conditions for crosslinking effectiveness may lie between these two limits. Therefore, investigation using aliphatic diisocyanates with four carbon chain (1,4 diisocyanate butane) and two carbon chain (1,2 diisocyanate ethane) which might achieve the desired increase in dimensional stability through crosslinking, is suggested. Similar results might be also obtained through wood reaction with a shorter carbon chain epoxide such as 1,3 butadiene diiepoxide, or by conducting the reaction with the wood in a less swollen state than in the current studies.

In view of the indications that physical blocking of sites and bulking seem to be more important for moisture exclusion than OH site depletion, it might be useful to repeat the reactions with the difunctional reagents used in this work, with the wood samples containing variable percentage of moisture rather than in oven-dry condition. The reaction of the diisocyanates with the water in wood may lead to polymerization "in situ" in the cell wall, producing bulking and therefore,

improving dimensional stability. Polymeric chains bonded to a OH group or physically entrapped in the cell wall would not be leached out upon wetting. Considering the obvious technical difficulties and high costs associated to the need to pre-dry wood to very low moisture content in industrial scale, this approach seems to be more suited to commercial development than those involving chemical reaction systems which have to be conducted under total anhydrous conditions.

The validity of the tensile tests proceed with a finite span gives information about inter fibre slippage but little about change in fibre strength *per se*. It is suggested that the effect of the treatment on strength should be redetermined by employing the zero-span tensile testing method described by Law & Koran (1979).

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APPENDIX A

Table A.1 Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

C. pine reacted with n-Bu-NCO

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	3.049	0.609	55.44**	4.999	1.000	94.04**
	ERROR	6	0.066	0.011		0.064	0.011	
	TOTAL	11	3.115			5.064		
23	WPG	5	11.291	2.258	127.58**	18.831	3.766	220.68**
	ERROR	6	0.106	0.018		0.102	0.017	
	TOTAL	11	11.397			18.934		
44	WPG	5	29.809	5.962	314.33**	46.114	9.223	462.68**
	ERROR	6	0.114	0.019		0.120	0.020	
	TOTAL	11	29.923			46.234		
55	WPG	5	44.091	8.818	317.20**	67.154	13.431	588.21**
	ERROR	6	0.167	0.028		0.137	0.023	
	TOTAL	11	44.258			67.291		
76	WPG	5	100.445	20.089	215.39**	130.100	20.020	434.87**
	ERROR	6	0.560	0.093		0.359	0.060	
	TOTAL	11	101.005			130.459		
93	WPG	5	268.435	53.687	461.89**	332.456	66.491	520.28**
	ERROR	6	0.697	0.116		0.767	0.128	
	TOTAL	11	269.132			333.223		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

C. pine reacted with Ph-NCO

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	1.891	0.378	23.19**	3.229	0.646	27.28**
	ERROR	6	0.098	0.016		0.142	0.024	
	TOTAL	11	1.989			3.371		
23	WPG	5	6.155	1.231	46.28**	10.641	2.128	69.32**
	ERROR	6	0.160	0.027		0.184	0.031	
	TOTAL	11	6.314			10.825		
44	WPG	5	19.937	3.987	124.99**	28.373	5.674	237.10**
	ERROR	6	0.191	0.032		0.144	0.024	
	TOTAL	11	20.128			28.516		
55	WPG	5	30.680	6.136	140.84**	45.552	9.110	128.32**
	ERROR	6	0.261	0.044		0.426	0.070	
	TOTAL	11	30.941			45.978		
76	WPG	5	59.013	11.803	156.39**	82.567	16.513	173.76**
	ERROR	6	0.453	0.075		0.570	0.095	
	TOTAL	11	59.465			83.137		
93	WPG	5	193.69	38.738	238.78**	209.75	41.95	128.87**
	ERROR	6	0.97	0.162		1.95	0.326	
	TOTAL	11	194.66			211.71		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

C. pine reacted with HDI

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	0.511	0.1022	15.95**	1.036	0.207	25.26**
	ERROR	6	0.038	0.0064		0.049	0.008	
	TOTAL	11	0.549			1.085		
23	WPG	5	2.219	0.4438	46.56**	4.266	0.853	59.94**
	ERROR	6	0.057	0.0095		0.085	0.014	
	TOTAL	11	2.276			4.351		
44	WPG	5	8.730	1.7460	99.39**	18.961	3.792	109.71**
	ERROR	6	0.105	0.0176		0.207	0.035	
	TOTAL	11	8.835			10.167		
55	WPG	5	11.811	2.362	88.36**	22.898	4.579	145.54**
	ERROR	6	0.160	0.026		0.189	0.031	
	TOTAL	11	11.971			23.087		
76	WPG	5	34.254	6.851	121.83**	62.117	12.423	238.61**
	ERROR	6	0.337	0.056		0.312	0.052	
	TOTAL	11	34.592			62.430		
93	WPG	5	162.547	32.509	277.78**	185.023	37.005	129.12**
	ERROR	6	0.702	0.117		1.720	0.287	
	TOTAL	11	163.249			186.743		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

C. pine reacted with TDI

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	0.1945	0.3899	4.41*	1.0376	0.2075	24.41**
	ERROR	6	0.0530	0.0088		0.0510	0.0085	
	TOTAL	11	0.2480			1.0886		
23	WPG	5	1.6299	0.3260	9.56**	2.1288	0.4258	24.15**
	ERROR	6	0.2046	0.0341		0.1058	0.0176	
	TOTAL	11	1.8345			2.2346		
44	WPG	5	8.5495	1.7099	63.64**	8.6639	1.7328	58.02**
	ERROR	6	0.1612	0.0269		0.1792	0.0299	
	TOTAL	11	8.7107			8.8431		
55	WPG	5	11.2203	2.2441	45.55**	13.9035	2.7807	38.57**
	ERROR	6	0.2956	0.0493		0.4326	0.0721	
	TOTAL	11	11.5159			14.3361		
76	WPG	5	21.2042	4.2408	42.10**	21.6471	4.3294	24.25**
	ERROR	6	0.6044	0.1007		1.0714	0.1786	
	TOTAL	11	21.8086			22.7185		
93	WPG	5	66.913	13.383	56.31**	42.4751	8.4950	17.06**
	ERROR	6	1.426	0.238		2.9884	0.4981	
	TOTAL	11	68.339			45.4635		

* Significant at the 5% level of probability
** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

Beech reacted with n-Bu-NCO

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	3.9824	0.7965	120.68**	7.8156	1.5631	225.45**
	ERROR	6	0.03960	0.00660		0.0416	0.0069	
	TOTAL	11	4.02200			7.8572		
23	WPG	5	10.7598	2.1520	232.23**	18.7588	3.7518	207.66**
	ERROR	6	0.0556	0.0093		0.1084	0.0181	
	TOTAL	11	10.8154			18.8672		
44	WPG	5	24.3759	4.8752	256.14**	35.8255	7.1651	291.26**
	ERROR	6	0.1142	0.0190		0.1476	0.0246	
	TOTAL	11	24.4901			35.9731		
55	WPG	5	33.4296	6.6859	171.29**	57.322	11.464	221.32**
	ERROR	6	0.2342	0.0390		0.311	0.052	
	TOTAL	11	33.6638			57.633		
76	WPG	5	84.222	16.884	328.28**	123.318	24.664	389.99**
	ERROR	6	0.309	0.0514		0.379	0.063	
	TOTAL	11	84.731			123.697		
93	WPG	5	310.487	62.097	650.92**	414.662	88.932	644.55**
	ERROR	6	0.572	0.095		0.772	0.129	
	TOTAL	11	311.060			415.434		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

Beech reacted with Ph-NCO

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	2.17337	0.4347	52.79**	4.8770	0.9754	66.92**
	ERROR	6	0.04940	0.0082		0.0875	0.1458	
	TOTAL	11	2.22277			4.9645		
23	WPG	5	5.9620	1.1924	60.84**	11.7351	2.3470	105.09**
	ERROR	6	0.1176	0.0196		0.1340	0.0223	
	TOTAL	11	6.0796			11.8691		
44	WPG	5	16.0959	3.2192	88.76**	24.0567	4.8113	113.21**
	ERROR	6	0.2176	0.0363		0.2550	0.0425	
	TOTAL	11	16.3135			24.3117		
55	WPG	5	18.8267	3.7653	33.42**	34.9255	6.9851	47.04**
	ERROR	6	0.6760	0.1127		0.8910	0.1485	
	TOTAL	11	19.5027			35.8165		
76	WPG	5	55.951	11.190	118.57**	81.024	16.205	125.30**
	ERROR	6	0.566	0.094		0.776	0.129	
	TOTAL	11	56.518			81.800		
93	WPG	5	197.763	39.553	203.84**	255.723	51.145	221.76**
	ERROR	5	1.164	0.194		1.384	0.231	
	TOTAL	11	198.928			257.107		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

Beech reacted with HDI

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	0.81044	0.16209	17.17**	2.77667	0.55533	51.10**
	ERROR	6	0.05665	0.00944		0.06520	0.01087	
	TOTAL	11	0.86709			2.84187		
23	WPG	5	2.24257	0.44851	5.76*	6.1272	1.1154	95.00**
	ERROR	6	0.46680	0.07780		0.0774	0.0129	
	TOTAL	11	2.70937			6.2046		
44	WPG	5	9.4816	1.8963	105.64**	15.7835	3.1567	208.W59**
	ERROR	6	0.1077	0.0179		0.0908	0.0151	
	TOTAL	11	9.5893			15.8743		
55	WPG	5	14.1531	2.8306	75.22**	25.6583	5.1317	144.83**
	ERROR	6	0.2258	0.0376		0.2126	0.0354	
	TOTAL	11	14.3789			25.8709		
76	WPG	5	22.7092	4.5418	67.99**	40.8916	8.1783	133.56**
	ERROR	6	0.4008	0.0668		0.3674	0.0612	
	TOTLA	11	23.1100			41.2590		
93	WPG	5	130.696	26.139	194.78**	191.841	38.368	225.87**
	ERROR	6	0.805	0.134		1.019	0.170	
	TOTAL	11	131.501			192.861		

** Significant at the 1% level of probability

Table A.1 (Cont.) Summary of the analysis of variance for the EMC data in Table 3.3 at each RH level.

Beech reacted with TDI

RH(%)	SOURCE	DF	ADSORPTION			DESORPTION		
			SS	MS	F	SS	MS	F
12	WPG	5	0.37334	0.07467	9.45**	1.12590	0.22518	29.24**
	ERROR	6	0.04740	0.00790		0.04620	0.00770	
	TOTAL	11	0.42077			1.17210		
23	WPG	5	1.84324	0.36865	30.53**	3.37640	0.67528	74.75**
	ERROR	6	0.07245	0.01207		0.05420	0.00903	
	TOTAL	11	1.91569			3.43060		
44	WPG	5	9.5730	1.9146	6.41*	9.0227	1.8045	21.26**
	ERROR	6	1.7916	0.2986		0.5092	0.0849	
	TOTAL	11	11.3646			9.5319		
55	WPG	5	12.3951	2.4790	55.38**	22.6078	4.5216	66.56**
	ERROR	6	0.2686	0.0448		0.4076	0.0679	
	TOTAL	11	12.6637			23.0154		
76	WPG	5	35.2639	7.0528	29.37**	36.0552	7.2104	71.41**
	ERROR	6	1.4410	0.2402		0.6058	0.0349	
	TOTAL	11	36.7049			36.6580		
93	WPG	5	92.432	18.486	59.12**	93.355	18.671	77.63**
	ERROR	6	1.876	0.313		1.443	0.240	
	TOTAL	11	94.308			94.798		

* Significant at the 5% level of probability
** Significant at the 1% level of probability

Table A-2 Summary of the analysis of variance (3-factor ANOVA) for the EMC data in Table 3.3, considering each whole set of treatment.

CORSICAN PINE

REAGENT	SOURCE	DF	SS	MS	F-RATIO
n-Bu-NCO	Sorption	1	37.210	37.210	325.20**
	RH	5	2793.516	558.703	4882.82**
	WPG	5	718.919	143.784	1256.61**
	Sorption x RH	5	6.106	1.221	10.67**
	Sorption x WPG	5	7.270	1.454	12.71**
	RH x WPG	25	313.057	12.522	109.44**
	Sorption x RH x WPG	25	2.469	0.099	0.86NS
	Error	72	8.238	0.114	
	Total	143	3886.785		
Ph-NCO	Sorption	1	36.956	36.956	478.95**
	RH	5	2768.492	553.698	7175.81**
	WPG	5	480.357	96.071	1245.06**
	Sorption x RH	5	4.965	0.993	12.87**
	Sorption x WPG	5	2.258	0.452	5.85**
	RH x WPG	25	208.102	8.324	107.88**
	Sorption x RH x WPG	25	0.761	0.030	0.39NS
	Error	72	5.556	0.077	
	Total	143	3507.447		
HDI	Sorption	1	38.560	38.560	610.94**
	RH	5	3483.446	696.689	11000.00**
	WPG	5	306.321	61.264	970.66**
	Sorption x RH	5	3.865	0.773	12.25**
	Sorption x WPG	25	203.066	8.123	128.69**
	Sorption x RH x WPG	25	1.375	0.055	0.87**
	Error	72	4.544	0.063	
	Total	143	4044.868		
TDI	Sorption	1	97.022	97.022	937.26**
	RH	5	4411.148	882.230	8522.58**
	WPG	5	134.164	26.833	259.21**
	Sorption x RH	5	20.339	4.068	39.30**
	Sorption x WPG	5	1.099	0.220	2.12NS
	RH x WPG	25	60.286	2.411	23.30**
	Sorption x RH x WPG	25	3.944	0.158	1.52NS
	Error	72	7.453	0.104	
	Total	143	4735.456		

** Significant at the 1% level of probability.
NS Nonsignificant statistically.

Table A-2 (Cont.) Summary of the analysis of variance (3-factor ANOVA) for the EMC data in Table 3.3 considering each whole set of treatment.

BEECH

REAGENT	SOURCE	DF	SS	MS	F-RATIO
n-Bu-NCO	Sorption	1	44.522	44.522	1039.28**
	RH	5	2976.804	595.361	14000.00**
	WPG	5	746.894	149.379	3486.93**
	Sorption x RH	5	8.197	1.639	38.27**
	Sorption x WPG	5	7.200	1.440	33.62**
	RH x WPG	25	369.463	14.779	344.97**
	Sorption x RH x WPG	25	1.601	0.064	1.49NS
	Error	72	3.084	0.043	
	Total	143	4157.766		
Ph-NCO	Sorption	1	52.986	52.986	541.72**
	RH	5	3254.941	650.988	6655.51**
	WPG	5	469.577	93.915	960.16**
	Sorption x RH	5	10.404	2.081	21.27**
	Sorption x WPG	5	5.054	1.011	10.33**
	RH x WPG	25	234.673	9.387	95.97**
	Sorption x RH x WPG	25	0.852	0.034	0.35NS
	Error	72	7.042	0.098	
	Total	143	4035.530		
HDI	Sorption	1	50.944	50.944	938.88**
	RH	5	3902.980	780.596	14000.00**
	WPG	5	284.529	56.906	1048.75**
	Sorption x RH	5	8.423	1.685	31.05**
	Sorption x WPG	5	5.808	1.162	21.41**
	RH x WPG	25	171.668	6.867	126.55**
	Sorption x RH x WPG	25	1.144	0.046	0.84NS
	Error	72	3.907	0.054	
	Total	143	4429.401		
TDI	Sorption	1	103.751	103.751	872.36**
	RH	5	4671.678	934.336	7856.10**
	WPG	5	207.771	41.554	349.40**
	Sorption x RH	5	22.884	4.577	38.48**
	Sorption x WPG	5	0.827	0.165	1.39NS
	RH x WPG	25	106.951	4.278	35.97**
	Sorption x RH x WPG	25	1.871	0.075	0.63NS
	Error	72	8.563	0.119	
	Total	143	5124.296		

** Significant at the 1% level of probability.
NS Nonsignificant statistically.

APPENDIX B

Table B.1 Summary of the analysis of variance (2-factor ANOVA) for the swelling data in Table 4.1

REAGENT	SOURCE	DF	SS	MS	F-RATIO
			C. PINE		
n-Bu-nco	RH	5	193.867	38.773	516.98**
	WPG	3	82.913	27.638	268.50**
	RHxWPG	15	38.087	2.539	33.85**
	ERROR	24	1.800	0.075	
	TOTAL	47	316.667		
Ph-nco	RH	5	200.246	40.049	368.98**
	WPG	3	56.102	18.701	172.29**
	RHxWPG	15	28.191	1.879	17.32**
	ERROR	24	2.605	0.109	
	TOTAL	47	287.145		
HDI	RH	5	235.671	47.134	462.67**
	WPG	3	43.751	14.584	143.15**
	RHxWPG	15	29.083	1.939	19.03**
	ERROR	24	2.445	0.102	
	TOTAL	47	310.950		
TDI	RH	5	272.664	54.553	515.27**
	WPG	3	25.456	8.435	80.18**
	RHxWPG	15	13.819	0.921	8.70**
	ERROR	24	2.540	0.106	
	TOTAL	47	314.479		

** Significant at the 1% level of probability.

Table B.1 (Cont.) Summary of the analysis of variance (2-factor ANOVA) for the swelling data in Table 4.1.

REAGENT	SOURCE	DF	SS	MS	F-RATIO
			BEECH		
n-Bu-NCO	RH	5	235.671	47.134	462.67**
	WPG	3	43.751	14.584	143.15**
	RHxWPG	15	29.083	1.939	10.03**
	ERROR	24	2.445	0.102	
	TOTAL	47	310.950		
Ph-NCO	RH	5	500.566	100.113	641.58**
	WPG	3	110.672	36.891	236.42**
	RHxWPG	15	63.571	4.238	27.16**
	ERROR	24	3.745	0.156	
	TOTAL	47	678.555		
HDI	RH	5	576.714	115.343	756.35**
	WPG	3	77.542	25.847	169.49**
	RHxWPG	15	48.502	3.234	21.20**
	ERROR	24	3.600	0.152	
	TOTAL	47	706.419		
TDI	RH	5	671.254	134.251	821.94**
	WPG	3	61.642	20.547	125.80**
	RHxWPG	15	33.522	2.235	13.68**
	ERROR	24	3.920	0.163	
	TOTAL	47	770.339		

**Significant at the 1% level of probability.

Table B.2 Summary of the analysis of variance for the Go
data in Table 4.4.

REAGENT	SOURCE	DF	SS	MS	F-RATIO
		C. PINE			
n-Bu-NCO	WPG	3	0.034828	0.011609	29.54**
	ERROR	36	0.014150	0.000393	
	TOTAL	39	0.048978		
Ph-NCO	WPG	3	0.060948	0.020316	60.00**
	ERROR	36	0.012190	0.000339	
	TOTAL	39	0.073138		
HDI	WPG	3	0.021960	0.007320	17.11**
	ERROR	36	0.015400	0.000428	
	TOTAL	39	0.037360		
TDI	WPG	3	0.014988	0.004996	16.48**
	ERROR	36	0.010910	0.000303	
	TOTAL	39	0.025897		
		BEECH			
n-Bu-NCO	WPG	3	0.043887	0.014629	40.98**
	ERROR	36	0.012850	0.000357	
	TOTAL	39	0.056787		
Ph-NCO	WPG	3	0.051068	0.017023	47.84**
	ERROR	36	0.012810	0.000356	
	TOTAL	39	0.063878		
HDI	WPG	3	0.025330	0.008443	26.71**
	ERROR	36	0.011380	0.000316	
	TOTAL	39	0.036710		
TDI	WPG	3	0.022407	0.012690	21.19**
	ERROR	36	0.012690	0.000352	
	TOTAL	39	0.035097		

**Significant at the 1% level of probability.

Table B.3 Summary of the regression analyzes of the relationships for Go and the variables in Table 4.4.

C. PINE

Go vs. WPG:
The regression equation is: Go = 0.544 + 0.00247 WPG
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.007709	0.007709	40.56**
Error	11	0.002091	0.000190	
Total	12	0.009800		
r^2		78.7%		

Go vs. Vol. swelling at saturation
The regression equations is: Go = 0.643 - 0.00658 Swelling
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.005845	0.005845	16.25**
Error	11	0.003955	0.000360	
Total	12	0.009800		
r^2		59.6%		

Go vs.FSP1 (Fibre sat. point derived from the isotherms equations):
The regression equation is: Go = 0.668 - 0.00478 FSP1
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.006302	0.006302	19.82**
Error	11	0.003498	0.000318	
Total	12	0.009800		
r^2		64.3%		

Go vs. FSP2 (Fibre sat. point derived from the swelling equations)
The regression equation is: Go = 0.647 - 0.00307 FSP2
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.004883	0.004883	10.92**
Error	11	0.004917	0.000447	
Total	12	0.009800		
r^2		49.8%		

** Significant at the 1% level of probability.

Table B.3 (Cont.) Summary of the regression analyzes of the relationships for Go and the variables in Table 4.4.

BEECH

Go vs WPG:
The regression equation is: Go = 0.738 + 0.00235 WPG
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.006866	0.006866	46.46**
Error	11	0.001626	0.000148	
Total	12	0.008492		
r^2		80.9%		

Go vs. Vol. swelling at saturation:
The regression equation is: Go = 0.842 - 0.00546 Swelling
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.006853	0.006853	46.00**
Error	11	0.001639	0.000149	
Total	12	0.008492		
r^2		80.7%		

Go vs. FSP1 (Fibre sat. point derived from the isotherms equations):
The regression equation is: Go = 0.863 - 0.00453 FSP1
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.007510	0.007510	84.10**
Error	11	0.000982	0.000089	
Total	12	0.008492		
r^2		88.4%		

Go vs FSP2 (Fibre saturation point derived from the swelling equations):
The regression equation is: Go = 0.847 - 0.00382 FSP2
Analysis of variance:

SOURCE	DF	SS	MS	F
Regress.	1	0.006054	0.006054	27.31**
Error	11	0.002438	0.000228	
Total	12	0.008492		
r^2		71.3%		

** Significant at the 1% level of probability.

Obs. The relationships between Go and MF1 and Go and MF2 (the Fibre sat. points derived, respectively, from the isotherms and from the swelling equations expressed as percentage volume of water per unit weight of oven-dry wood) are the same as those shown for Go vs FSP1 and Go vs FSP2.

APPENDIX C

Table C.1 Summary of the analysis of variance for the tensile strength data in Table 5.1.

REAGENT	SOURCE	DF	SS	MS	F-RATIO
		C. PINE			
n-Bu-NCO	WPG	5	1658.03	331.61	5.56**
	Error	54	3219.36	59.62	
	Total	59	4877.39		
Ph-NCO	WPG	5	793.34	158.67	6.26**
	Error	54	1368.97	25.35	
	Total	59	2162.31		
HDI	WPG	5	1339.97	267.99	8.00**
	Error	54	1808.36	33.49	
	Total	59	3148.33		
TDI	WPG	5	424.76	84.95	2.54*
	Error	54	1806.81	33.46	
	Total	59	2231.57		
		BEECH			
n-Bu-NCO	WPG	5	350.05	70.01	1.33NS
	Error	54	2840.73	52.61	
	Total	59	3190.78		
Ph-NCO	WPG	5	679.31	135.86	5.19**
	Error	54	1414.47	26.19	
	Total	59	2093.78		
HDI	WPG	5	2828.57	565.71	13.27**
	Error	54	2301.99	42.63	
	Total	59	5130.56		
TDI	WPG	5	4573.37	914.67	10.99**
	Error	54	4495.71	83.25	
	Total	59	9069.07		

** Significant at the 1% level of probability.
* Significant at the 1% level of probability.
NS Nonsignificant statistically.

Table C.2 Summary of the regression analysis between the WPG and tensile strength data in Table 5.1.

REAGENT	SOURCE	DF	SS	MS	F-RATIO

C. PINE

n-Bu-NCO: the regression equation is: TS = 39.1 − 0.214 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	20.58	20.58	0.57 NS
	Error	4	145.16	36.29	
	Total	5	165.73		
	r^2x100		12.4%		

Ph-NCO: the regression equations is: TS = 32.3 − 0.239 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	59.016	59.016	24.80**
	Error	4	9.517	2.379	
	Total	5	68.533		
	r^2x100		86.1%		

HDI: The regression equation is: TS = 41.8 − 0.599 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	94.56	94.56	9.42*
	Error	4	40.15	10.04	
	Total	5	134.71		
	r^2x100		70.2%		

TDI: the regression equation is: TD = 33.3 − 0.938 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	48.893	48.893	12.99*
	Error	4	15.060	3.765	
	Total	5	63.953		
	r^2x100		76.5%		

TS = Tensile strength (N) (force to break the strips).
** Significant at the 1% level of probability.
* Significant at the 5% level of probability.
NS Nonsignificant statistically.

Table C.2 (Cont.) Summary of the regression analysis between the WPG and tensile strength data in Table 5.1.

REAGENT	SOURCE	DF	SS	MS	F-RATIO

BEECH

n-Bu-NCO: the regression equations is: TS = 395 + 0.022 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	0.180	0.180	0.02 NS
	Error	4	35.588	8.897	
	Total	5	35.768		
	r^2x100		0.5%		

Ph-NCO: the regression equation is: TS = 38.1 - 0.396 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	54.064	54.064	10.51*
	Error	4	20.569	5.142	
	Total	5	74.633		
	r^2x100		72.4%		

HDI the regression equation is: TS = 49.3 - 0.842 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	222.08	222.08	15.59*
	Error	4	56.97	14.24	
	Total	5	279.05		
	r^2x100		79.6%		

TDI: the regression equation is: TS = 52.7 -1.30 WPG

	SOURCE	DF	SS	MS	F-RATIO
	Regress.	1	430.53	430.53	57.10**
	Error	4	30.16	7.54	
	Total	5	460.69		
	r^2x100		93.5%		

TS = Tensile strength (N) (force to break the strips).
** Significant at the 1% level of probability.
* Significant at the 5% level of probability.
NS Nonsignificant statistically.