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An investigation of novel wood protection methods

Ormondroyd, Graham

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An Investigation of Novel Wood Protection Methods

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Graham A. Ormondroyd

MSc BSc (Hons) MIWSc

School of the Environment and Natural Resources

University of Wales, Bangor

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Abstract

This thesis reports investigations into the use of a biocide and resin system for the prevention of wood decay. The resins were used to modify Corsican pine and European beech. The resins used were urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde. The three resins were used to modify the wood alone, and with the biocide, delivered both sequentially and in a co-delivery system. The resin modified wood was subjected to EN113 type pure culture decay tests which utilised the fungi *Coniophora puteana* (Schumacher ex Fries) Karsten (BAM 15), *Coriolus versicolor* (Linnaeus) Quélet (CTB 863A), and *Phanerochaete chrysosporium* (S179). It was found that the biocide had a significant impact on the decay resistance of the wood when modified to a low resin weight percent gain. However, the biocide did not provide any additional decay resistance at high weight percent gains. Threshold values for the modification of timber with resin were found to be ~30% for Corsican pine and ~22% for beech. The threshold value did not change with increased fungal virulence, indicating that the decay resistance mechanism was a physical and not biocidal. The decay resistance of both acetic and hexanoic anhydride modified wood was investigated as a model for cell wall modification. Threshold values for each modification were found to be 15% for the acetic anhydride and 22% for the hexanoic. The threshold values were found to be independent of wood species, fungal species and virulence again indicating that that the decay resistance is due to a physical mechanism and not a biocidal one. Cell wall swelling due to resin or anhydride modification was determined using helium pycnometry, a technique never before applied in such studies. Cell wall swelling due to modification as determined by helium pycnometry did not correlate with that determined by external dimensions (a new finding). Cell wall accessibility was determined using solute exclusion. Anhydride modification reduced fibre saturation point (as determined by solute exclusion). This reduction correlated with the volume occupied in the cell wall by the bonded adduct. Resin treatment presented a more complex picture due to resin filling the lumen and the cell wall.

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Abbreviations

Abbreviation	Definition
°C	Degrees centigrade
Å	Angstrom
ASE	Anti shrink efficiency
ASTM	American standard testing methods
AWPA	American wood preservers association
BSi	British Standards Institute
CCB	Copper chrome boron preservative
CEN	European committee for Standardisation
cm^3	Cubic centimetres
DP	Degrees of polymerisation
EN	Euro Norm
FSP	Fibre saturation point
g	Grams
h	Height
IMS	Industrial methylated spirits
K	Kelvin
kg	Kilograms
L	Longitudinal
LMWDA	Low molecular weight wood decaying agents
m^3	Cubic metres
MC	Moisture content
MF	Melamine formaldehyde resin
ml	Millilitres
ml g^{-1}	Millilitres per gram
mm	Millimetres
Mol	Molarity

MUF	Melamine urea formaldehyde resin
MV	Molecular volume
OH	Hydroxyl group
PF	Phenol formaldehyde resin
Psi	Pounds per square inch
R	Radial
RH	Relative humidity
T	Tangential
UF	Urea formaldehyde resin
v/v	Volume on volume
V_{rel}	Relative volume
w/v	Weight on volume
w/w	Weight on weight
WL	Weight loss
WPG	Weight percent gain

1 Literature review

1.1 The structure of wood.

Wood can be described as "the hard fibrous substance consisting of xylem tissue that occurs beneath the bark in trees, shrubs and similar plants" (Collins 2003). Desch and Dinwoodie (1996) suggested that the woody part of a tree has three principle functions to perform:

- Support of the crown, which contains the manufacturing and reproductive elements;
- Conduction upwards of dilute mineral solutions;
- Storage of manufactured organic substances.

These three functions are fulfilled by different types of cells in the tree and this will be discussed in Section 1.1.2. The ability of wood to fulfil function one has led man to use it as a material throughout the ages; however the properties which make wood desirable as a material can be traced back to the cellular and sub-cellular levels.

1.1.1 The macrostructure of wood.

1.1.1.1 The growth of a tree.

The growth of a tree is bi-directional; the tree will grow outwards to give a large diameter trunk and upwards to give a tall tree. Both of the directions of growth are to give the tree a competitive edge over its neighbours while it competes for its source of food, the sunlight. The growth upwards will push the crown of the tree high and there for out of the shadow of its neighbours, whereas the outward growth will aid the tree to support a larger crown which will then be able to increase the amount of sunlight intercepted for photosynthesis.

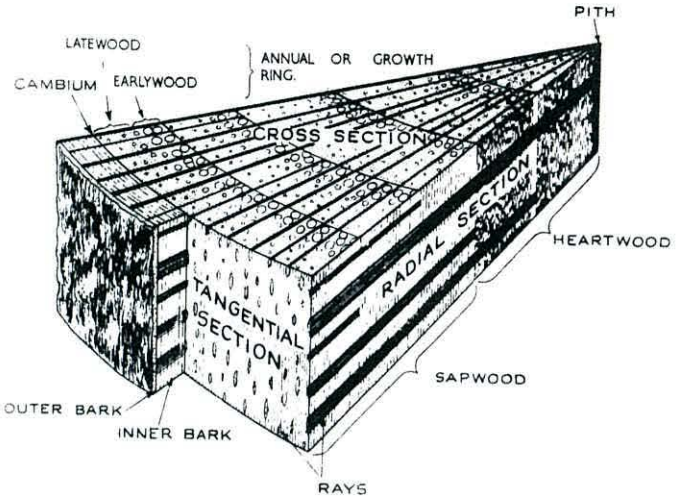


Figure 1.1: A wedge of wood cut from a five year old tree showing the Principle structural features (Desch and Dinwoodie, 1996).

The increase in the height of a tree is due to the subdivision of the cells that form the apical meristem. The cells are produced downwards and therefore the apical meristem is always on top. The new cells that are formed are of two types; one that forms the soft tissue of the pith and the second that form vascular bundles that contain cambial layers that coalesce to form the cambium.

The cambium is a sheath of living tissue around both the trunk and the branches. In the winter the cambium lays dormant and only one cell thick. However, as growth begins in the spring the cells rapidly divide producing a cambial zone between eight and ten cells thick. Some of these cells will remain in the cambial zone and undergo more sub division and produce daughter cells. The cells that are to the outer of the cambial zone will differentiate in to bark cells while the cells on the inner edge of the cambial zone will develop into wood cells and form that season's growth ring. The increase in the circumference of the cambium is accommodated by the occasional development of a cell with a sloping tangential wall and the subsequent elongation of the two new cells to form and overlapping pair of cells.

1.1.1.2 Growth rings.

Temperate wood is grown under seasonal conditions and there for is made up of concentric circular areas of tissue known as growth rings. Each growth ring represents the wood laid down through division of cambial cells towards the pith in a single growth season. The wood is laid down by the cambium (which extends for the full height of the tree) at growing tips still in bundles and one growth ring will extend the full length of the tree, therefore the wood nearest the outside of the tree is the youngest.

The inner part of the growth ring is formed first and is known as earlywood, this is characterised in softwoods by having cells with large lumens and thin cell walls when viewed radially. When the cells are observed in transverse section they are seen to be hexagonal and the cells in adjacent radial files tend to alternate in their positions along the radius (Wilson and White 1986). As the season progresses the type of cells laid down change, this period is called transition period. This transition can be abrupt or gradual and this depends on the type of wood and the environmental condition in which the tree is grown. Latewood is formed late in the growing season and consists of cells with smaller lumens and thicker cell walls. The cells in adjacent files move from their alternative position to nearly opposite their neighbouring cells. Latewood has been found to be 3-4 times denser than earlywood. The properties of earlywood and latewood in softwoods and ring porous hardwoods differ greatly; the earlywood is lighter, softer and weaker than the latewood (Desch and Dinwoodie 1996). These differences of properties have lead to the proportion of latewood in a sample of timber being used to assess how strong that timber will be. Growth rings can be seen in the illustration shown in Figure 1.1. In latewood the tracheids can be over twice as strong as in early wood, they are also thicker walled and the lumens are smaller in diameter than in early wood.

1.1.1.3 Sapwood and Heartwood.

The cross section of a tree can be divided into two distinct regions, the sapwood and the heartwood. The sapwood comprises the outer layer of wood in the trunk and can be said to be the physiologically active part of the tree, it is responsible for the conduction of mineral solutions upwards and the storage of the manufactured products. Conversely, the heartwood has neither storage nor conduction roles in the wood.

The sapwood forms the distinctive outer layer of the wood and will typically range, in temperate species, from 12.5-50mm in width (Desch and Dinwoodie 1996). However, if the tree is plantation grown, in close competition with its neighbours, then the percentage of sapwood will decrease when compared with sapwood from a tree of the same species and age that has been grown in the open. Within the sapwood area some of the cells are still alive; the parenchyma cells of the rays are alive to perform their role of storage.

The onset of heartwood formation is related to the growth in diameter of the tree trunk and the amount of sapwood will remain constant over long periods of time, and thus the amount of sapwood can be used to characterise the species of tree, for example larch has a small amount of sapwood where as maples have much more (Wilson and White 1986).

As the timber changes from sapwood to heartwood several chemical and physiological changes will take place to the inner most sapwood cells. These changes are outlined by (Wilson and White 1986; Desch and Dinwoodie 1996):

- The moisture content of the cells will fall significantly.
- The acidity of the wood will increase (in most cases only slightly but in some such as oak the pH can be as low as 3.0).
- The inter-tracheid pits in softwoods become aspirated.

- Extractives are produced. Extractives are complex organic compounds which gives the heartwood timber its natural durability. The amount and type of extractives that are to be found in timber varies with species and therefore the amount of natural durability varies similarly.
- Various gums and resins are formed in the heartwood of softwoods.

In hardwoods, cell tissue in the transition zone can grow through adjoining pits and produce blockages known as tyloses. The production of gums and tyloses makes the heartwood less permeable to water and thus less hydroscopic.

The stored starch disappears from the cells, perhaps used in the synthesis of the extractives and tyloses.

However, there is generally no change in the density (except with the formation of extractives) or the strength between heartwood and sapwood, when compared at the same moisture content.

Heartwood, with the related hydrophobic cell wall and aspirated pits, is harder to treat with preservatives than sapwood, however, this may not be as concerning as can be first thought as heartwood has the natural durability which is inherent from the extractives and resins. Lightly preserved heartwood can be as durable as heavily preserved sapwood (Forest Products Laboratory 1987).

Sapwood and heartwood are illustrated in Figure 1.1.

1.1.2 The microstructure of Wood.

It was noted in Section 1.1.1 that cells develop and then differentiate in the cambium layer. This differentiation can take up to three weeks (Desch and Dinwoodie 1996). Once the changes have taken place the cell dies, leaving the degenerated cell contents coating the cell walls, and is then ready to take on one of the three cell functions (conduction, support or storage).

This thesis is concerned with the treatment of timber for the building industry within the UK and there for concentrates on the treatment of softwoods, therefore, this section will continue to explore the microstructure of softwoods only.

The cells responsible for support and for conduction in softwoods are tracheids and typically make up approximately 90 percent in softwoods.

1.1.2.1 Tracheids.

Tracheids are hollow needle shaped cell with a length of 2.5-5.0 mm and an aspect ratio (length: breadth) of 100/1. Tracheids are packed close together to give a honeycomb like structure when viewed in the transverse plane. As has been noted earlier (in chapter 1.1.1.2), the cells produced early in the growing season have a larger diameter and a thinner cell wall and therefore it is the tracheids of the early wood that are generally used for conduction. The larger diameter of the tracheid means that rate of flow is greater than it would be if the cells were thinner.

The tracheids also perform a mechanical or support function in softwood. The support function that is imparted to the tree directly relates to the ratio of thick to thin walled tracheids, the higher the proportion of thick walled cells, the denser the timber, the stronger the tree and thus the timber that is harvested from the tree.

1.1.2.2 Rays.

The cells responsible for the storage of sugars in softwoods are mainly orientated horizontally but may also be present vertically. The horizontal storage cells radiate from the centre outwards and these are known as ray parenchyma. The continuation of the ray parenchyma outwards is due to the cambial cells from

which the rays arise being specialist and only produce ray cells. As a tree increases in girth addition groups of cambial cells that produce only ray cells are formed. The number of ray plates per unit of circumference stays approximately the same throughout the tree irrespective of age; however the number of rays per unit of circumference changes dramatically depending on the species of the tree, from less than one to more than ten per millimetre of circumference. Most ray parenchyma cells are uniseriate, or one cell wide, however some rays are biseriate, two cells wide, and these include the rays in *Sequoia* and *Cupressus*. The height of a softwood ray varies from two cells to more than forty; this variation is in part due to the species of the tree but also to it growth rate and its age.

In hardwoods rays are usually visible to the naked eye and appear as horizontal lines between 0.05 and 0.5mm in width on the radial surface, however in softwoods they are very sparse in amount and can only be seem under a microscope. On the transverse surface they can be seen with a low powered lens (x10) and appear as narrow lines crossing the growth rings at right angles. Finally, a ray when looked at on the tangential surface appears as a short boat shaped line. If a ray cell is viewed through a microscope it can be seen that the cell has a length that is 3-7 times greater than the width of the neighbouring tracheids. The end walls of the ray cells are very oblique in both the axial and tangential directions.

Ray cells are mainly parenchyma cells and retain their living protoplasts for several years and only die in the transition from sapwood to heartwood. The cells contain simple pits in both the axial and transverse walls, however, in the upper and lower margins of the rays there are 1-3 rows of ray tracheids which are elongated cells that contain bordered pits and when fully differentiated loose their protoplasts. The bordered pits are small in comparison to those between axial tracheids. The bordered pits connect either the ray tracheids together, a ray tracheid with a ray parenchyma or with an axial tracheid. Ray tracheids are present in species of *Picea*, *Pinus*, *Larix*, and *Tsuga* among others. The walls of the ray cells are thickened when compared with tracheids.

The form of the ray tracheids varies between the different species and this can be used to aid in the microscopic identification of timber. The thickening of the walls of the ray tracheids can take different forms, smooth, dentate or reticulate, the thickening can be seen in Figure 1.2.

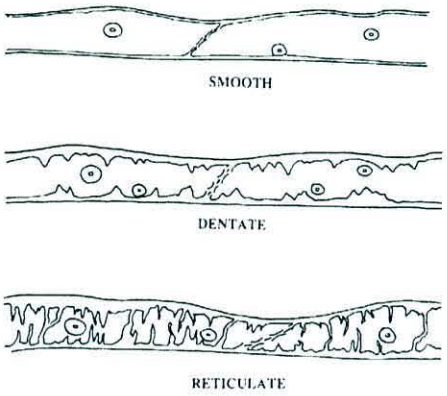


Figure 1.2: Diagrammatical representation of the types of thickening to be found in the horizontal walls of the ray tracheids (Desch and Dinwoodie, 1996).

As well as the ray parenchyma, vertical storage cells can also be found in softwood, these are known as wood parenchyma and can be found around the resin canals.

Both the ray and wood parenchyma, unlike tracheids remain alive for some years after there development, this is due to the fact that the sugars are stored in a form that can not be used by the tree and requires conversion prior to use, this conversion can only take place in a living cell. Once the cell is not needed for storage it dies like any other secondary xylem cell. Parenchyma cells have relatively thin cell walls and transport from cell to cell is through simple pits (see 1.1.2.4).

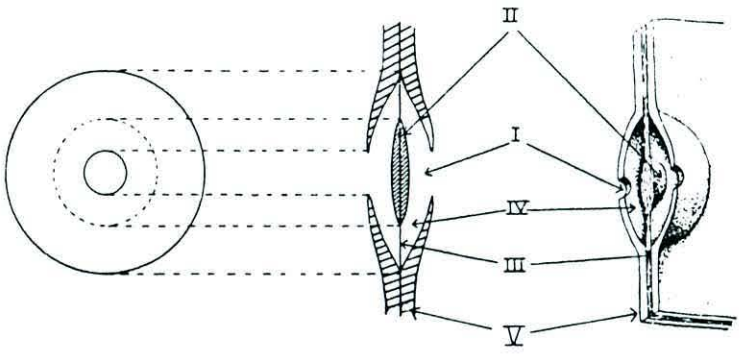
1.1.2.3 Resin Canals.

Resin canals are cavities in the wood which is lined with an epithelium of parenchyma cells which excrete resin into the canals. Resin canals are scattered throughout the growth ring however in some species they are restricted to the late wood. Tangentially orientated resin canals can be found in all types of timber, however these are\due to wounding of the tree. When a tree is wounded it responds by producing traumatic resin canals, which are usually irregular in shape and size and frequently touching one and another.

1.1.2.4 Pits and micropores.

It has been noted that the tracheids are needle shaped and thus closed at either end; however they are responsible for transport. Inter tracheid movement is achieved through valves known as bordered pits (Figure 1.3) which are predominantly concentrated towards the ends of the radial walls of the early wood cells. Although the bordered pits are concentrated in the early wood cells they can also be found in the latewood cells, however they are much smaller in size and there are far fewer (approximately 200 bordered pits in earlywood and 50 in latewood), they can also be found in the tangential wall interconnecting the last row of latewood cells from one years growth to the first row of the earlywood cells in the new years growth.

A bordered pit is about 15-20 μm in diameter and in cross section is analogous to two saucers facing one another with the centres removed and a diaphragm suspended in the centre (Desch and Dinwoodie 1996).

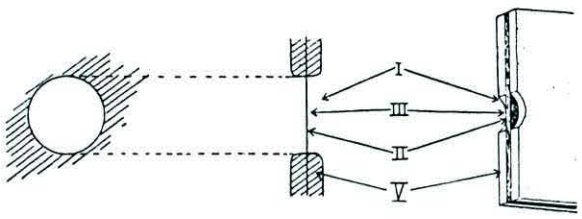


I. Pit opening.
II. Torus.
III. Margo strands.
IV. Pit cavity.
V. Secondary Cell wall.

Figure 1.3: A bordered pit (Desch and Dinwoodie, 1996)

The thickened diaphragm is known as the torus and is suspended on the margo strands. The torus responds to changes in water pressure within the cells, when the cell dries the retreating meniscus causes the torus to move to one side and it will become fixed into the closed state known as aspirated, this is due to hydrogwen bonding which occurs between the torus and the pit cavity. An aspirated pit does not become unaspirated when the cell rewetted therefore pit aspiration causes a reduction in permeability of the wood to preservatives. The exact structure of bordered pits can vary between different species of timber and this, like the structure of ray tracheids, can be used in the identification of timber.

Passage of stored materials from the parenchyma cells is through simple pits which consist of a cylindrical hole in the two secondary walls and the primary wall remaining as a semi permeable membrane (Figure 1.4).



I. Pit opening.
II. Primary wall.
III. Pit cavity.
IV. Secondary wall

Figure 1.4: A simple pit (Desch and Dinwoodie, 1996).

Cross field pits are pits that occur between a ray parenchyma cell and a tracheid. The cross field pits are semi bordered pits. The cross field pits take on one of five different forms and the type of pit can be used to aid the identification of timber. The five different type of cross field pits are shown in Figure 1.5.

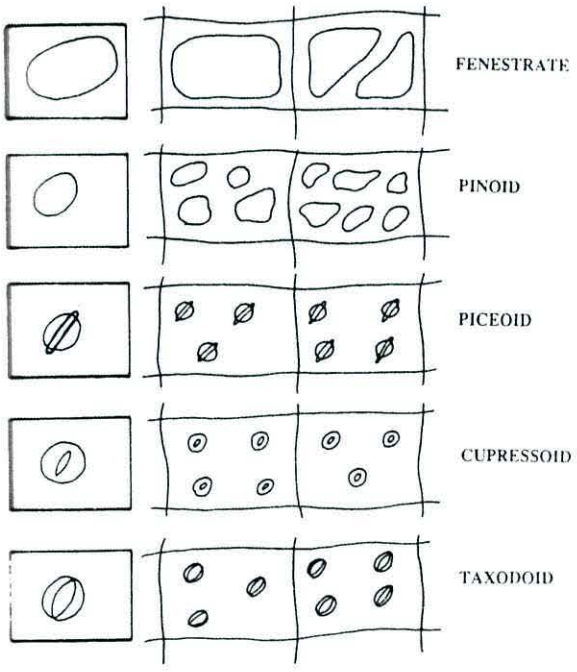


Figure 1.5: Cross field pits (Desch and Dinwoodie, 1996).

The smallest of the pores that can be found in the wood cells are the micropores. The micropores are approximately 2nm in diameter and enter the cell wall and therefore shall be discussed in greater detail in the next chapter.

1.1.3 The molecular and chemical structure of wood.

The principle chemical constituents of wood are cellulose, hemicellulose and lignin. In addition to these principle components there are a number of trace elements that are required for the metabolism of the living cells. Complex organic compounds can be found in the heartwood of many timbers, these are know as extractives, the name derives from the fact that they can be easily extracted from the timber without altering the structure of the wood.

This section will explore each of the principle components of wood and how they affect the physical and treatment properties of softwoods.

1.1.3.1 Cellulose.

Cellulose is the major building block of wood as of most plants, it makes up between 40 and 50% of the dry mass of timber (Desch and Dinwoodie 1996). Glucose ($C_6H_{12}O_6$) is produced in the crown of the tree by the act of photosynthesis. The glucose units are then transported down to the cambial zone where they bond together to form cellulose. Chemically, cellulose is the polymer of the hexose, ß-D-glucopyranose, with the polymer links being between the 4^{th} and the 1^{st} carbons on the molecules (Figure 1.6). This polymer is a crystalline structure (i.e.it is made up of repeating units) therefore it is easier to degrade.

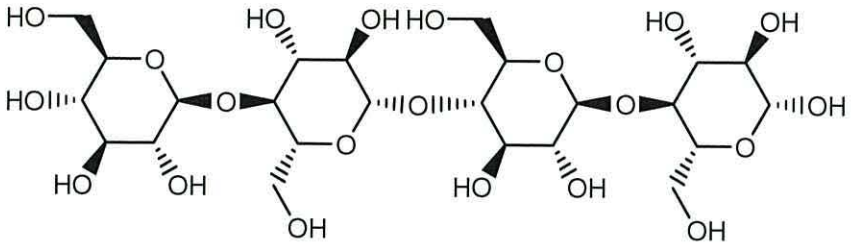


Figure 1.6: ß 1-4 Glucan

The degree of polymerisation (DP) of wood cellulose is between 8000 and 10000 making each cellulose chain approximately 4-5 μm and the molecular weight is in the order of 1.5 x 10^6 (Wilson and White 1986).

Within wood, cellulose molecules over most of there length lay parallel to one another to form a crystalline structure. There has been many attempts to model the crystalline structure of cellulose I, however it was the model proposed by (Gardner and Blackwell 1974) that has gained worldwide acceptance. Gardner and Blackwell proposed an 8 chain structure with all the chains running in the same direction. There are many variants of this model, however this was the first model proposed.

Both primary and secondary bonding is present in the formation of cellulose I, the primary, or covalent, bonding being located in the glucose rings and in the joining of these rings together. The secondary bonding comprising of both hydrogen bonds and Van de Waals forces are present in specific areas, the hydrogen bonds are present within the cellulose molecule and between the molecules linking them into sheets with in a single plane and Van de Waals forces link the sheets together in the opposite plane.

As noted above the length of a cellulose molecule is approximately 5 μm or 5000 nm. This length is a great deal larger than the length of the areas of crystallinity which are approximately 60nm in length (Desch and Dinwoodie 1996). This means that a molecule will pass through areas of high crystallinity as well as regions of low crystallinity, in which molecules are only loosely associated with each other. It has been noted (Desch and Dinwoodie 1996) that the molecules

that pass from one area of crystallinity will pass to another and therefore generate a high degree of longitudinal association to form a unit of undefined length known as a microfibril. The degree of crystallinity will vary but on average 70% of cellulose in wood is crystalline.

1.1.3.2 Hemicellulose.

Hemicelluloses differ greatly to cellulose. The molecules are shorter with a DP of between 150-200 and are built up of different sugar units. As well as glucose hemicellulose can contain primarily the mannose and galactose, but they can also contain the pentoses xylose and arabinose. The hydroxyl groups in the ring structure can also be replaced by methoxyl and acetoxyl groups. The differing sugars may also be present in their uronic acid forms.

In softwoods the majority of the hemicelluloses are known as Galacto-gluco-mannans; these are 1-4 polymers of glucose and mannose, in which the mannose predominate, while the galactose units are borne laterally on this main chain.

It has been noted (Wilson and White 1986) that hemicellulose make up 25%-40% of dry wood mass.

1.1.3.3 Lignin.

Lignin is a highly complex non crystalline molecule comprising of a large number of phenyl-propane units (Desch and Dinwoodie 1996). Unlike cellulose lignin is a three dimensional polymer. Lignin's not susceptible to hydrolysation as cellulose is, however other forms of chemical break down give a range of products which have a common carbon skeletal structure Figure 1.7. The molecular weight of lignin after it is extracted from wood has been estimated at 1100 which means that it contains approximately 60 of the monomer units, however this is the extracted size and is undoubtedly larger within the wood

(Wilson and White 1986). The large number of bonds types in lignin mean that the structure is heard to break down.

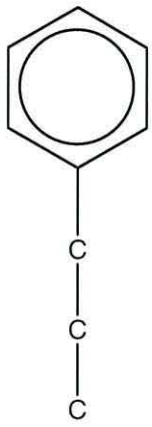


Figure 1.7: The phenol propane structure of the monomer of lignin.

About 25% of all the lignin in wood is found in the middle lamella (Dinwoodie 2000), an intercellular layer that is made of lignin and pectin. The middle lamella is very thin and therefore the concentration of lignin is very high (approximately 70%). The other 75% of lignin that can be found in the wood cell is found in the secondary cell wall and is deposited following the completion of the cellulosic frame work. The lignification of the cell wall begins when the middle lamella is about half formed and it begins to extend across the secondary sell wall (Saka and Thomas 1982).

Hardwood lignin differs appreciably from softwood lignin. The basic building units for hardwood lignin are the phenolic nuclei of both propyl guaiacyl and propyl syringyl, whereas for softwood lignin it appears to be almost all propyl guaiacyl type.

Termination of the lignification process coincides with the death of the cell.

1.1.3.4 The microfibril.

The microfibril, which is of undetermined length is believed to be 10 x 5nm in cross section. It contains the crystalline core which is 5 x 3nm in cross section

and comprises of 48 molecules of cellulose, this number actually varies depending on where the microfibril is found. Surrounding the core of crystalline cellulose is, firstly, an area of non crystalline cellulose and hemicellulose. Outside this layer is a layer of amorphous lignin. The layers of hemicellulose and lignin is analogous to the matrix in a manmade composite.

Preston (in Dinwoodie, 2000) states that the hemicelluloses are intimately associated with the celluloses, binding the microfibrils together. Bundles of cellulose chains are thus seen to have a polycrystalline sheath of hemicellulose material. As noted earlier the lignin is deposited in varying amounts within the cell wall but its primary function is to protect the non-crystalline cellulose and the hemicellulose from the effects of there hydrophilic nature.

The actual structure of the microfibril has been a great debate. However two of the models are illustrated in Figure 1.8(a) and Figure 1.8(b). The model shown in Figure 1.8(a), derived by Fengel in 1970 (Dinwoodie 2000), depicts cellulosic subunits some 3nm in diameter. These units comprising of 40 cellulose chains are known as elementary fibrils or protofibrils. Gaps of 1nm between these units are filled with hemicellulose while more hemicellulose and lignin form a sheath. The model shown in Figure 1.8(b) adopted from Preston in 1974 shows a crystalline core to be about 5nm x 3nm containing about 48 chains in either four or eight chain unit cells. Prestons model has now become the widely accepted model.

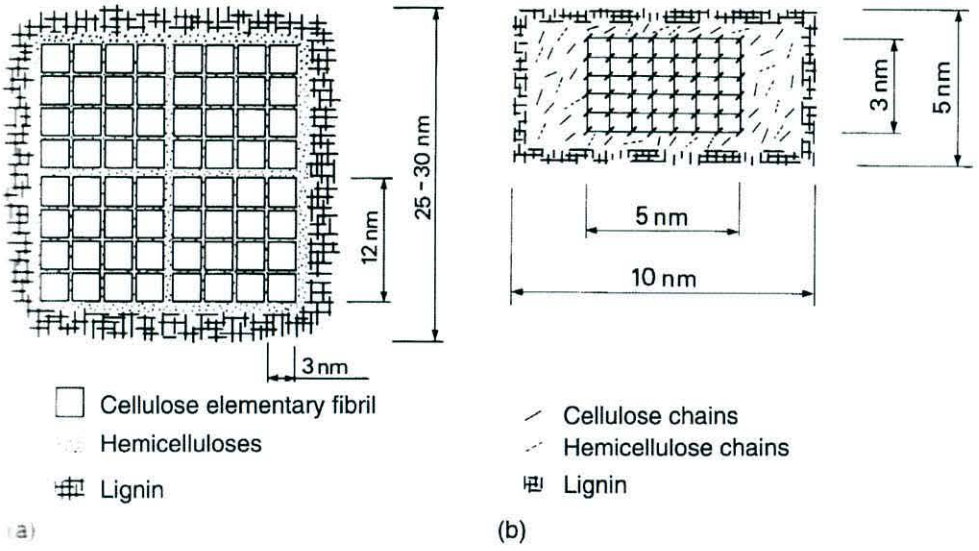


Figure 1.8: Two models of the microfibril, model (a) from Fengel, 1970 and (b) from Preston, 1974 (Desch and Dinwoodie, 1996).

1.1.3.5 The cell wall structure.

The cell wall is made up of millions of microfibrils and can be subdivided into a number of different layers dependent on the arrangement of the microfibrils. The microstructure of the cell wall can be seen in Figure 1.9.

The angle of the microfibrils have been derived using X-ray diffraction analysis, on either the paratropic (002) plane and the diatropic (040) plane. X-ray diffraction can only give the mean microfibril angle for any single layer of the cell wall and an example of these measurements can be seen in Table 1.1.

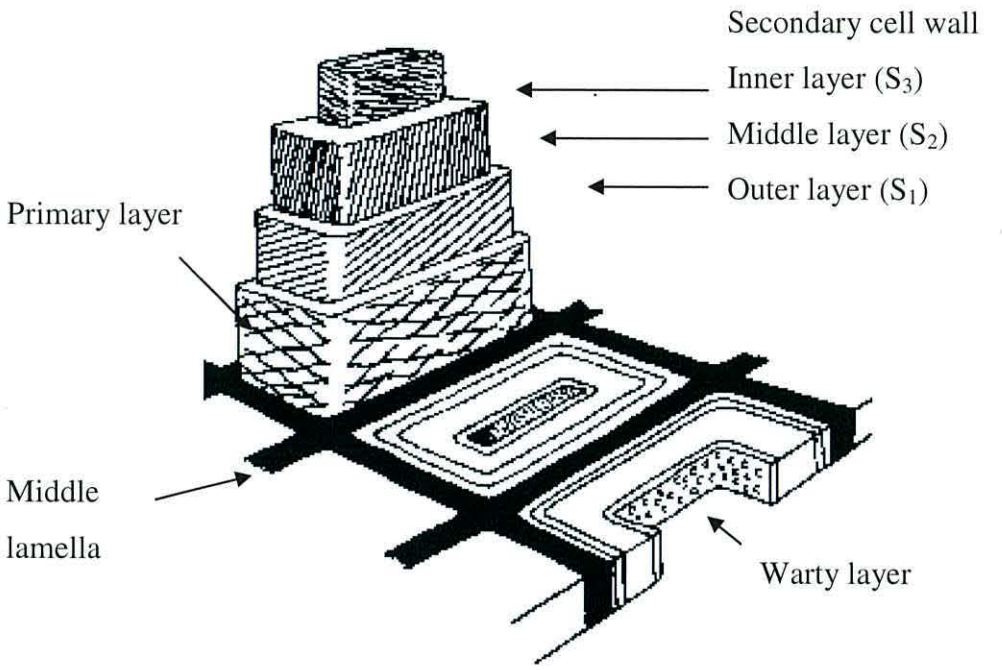


Figure 1.9: Simplified structure of the cell wall, showing the microfibril angles in each of the wall layers (Desch and Dinwoodie, 1996).

Wall Layer	Approximate thickness (%)	Angle to longitudinal axis
P	3	Random
S_1	10	50-70°
S_2	85	10-30°
S_3	2	60-90°

Table 1.1: Microfibril angle and percentage thickness of the cell wall layers in spruce timber (*Picea abies*) (Dinwoodie, 2000).

As mentioned earlier, the middle lamella is devoid of cellulose where as the primary (P) layer has microfibrils loosely packed and interwoven at random and no lamination is present. In the secondary layer of the cell wall the microfibrils are closely packed and parallel to each other. The S_1 layer is again thin and has between 4 and 6 concentric lamellae, the microfibrils of each having alternating spirals (S and Z helix). Both the S and the Z helixes have a pitch of 50° to 70° depending on the species of the timber.

The S_2 layer of the secondary cell wall is, in comparison to the other layers thick. As can be seen in Table 1 the S_2 layer makes up 85% of the cell wall volume and is comprised of 30 to 150 lamellae. All the microfibrils in the S_2 layer exhibit a right hand spiral with a pitch of 10°-30°. The actual angle of the microfibrils can be related to the length of the cell, which can in turn be related to the growth rate of the tree. The ultrastructure of the S_2 layer has a great influence on the properties of the cell wall and thus the timber, anisotropic behaviour in relation to movment with moisture content changes, shrinkage, tensile strength, and failure morphology can all be related to the S_2 layer (Dinwoodie 2000).

The S_3 layer is again a very similar layer to the S_1 layer, it is thin (only 2% of the cell wall volume) and exhibits both S and Z spirals. Generally the S_3 layer is of a more irregular nature than the S_1 and S_2 and is encrusted with extraneous materials. The S_3 layer has been reported to have a higher lignin content than the S_2 layer and acts as a filler between the microfibrils (Saka and Thomas 1982).

Scanning electron microscopy has also shown that the S_3 layer exhibits a warty layer in softwood timbers but not in hardwoods (Dinwoodie 2000).

Dinwoodie (2000) shows that the microfibril angle quoted in Table 1 are only averages over the whole sub layer and a variation can be found through the lamellae. The inner lamellae of the S_1 layer tend to have a smaller angle and the outer lamellae a larger angle than the average. Variation again occurs in the S_3 layer but they are opposite to those in the S_1 layer.

Abe *et al.* (1991) investigated microfibril angles in *Abies sachalinensis* using a field emission electron microscope. As well as confirming the systematic variation across the cell wall layers of the microfibril angle they found that, in the S_1 layer, instead of each lamella containing microfibrils in both the S and Z helix form, the outer lamella contains microfibrils with an angle of 45° in the S helix and as you track in to the layer the angle increases toward 90° and then reverses itself to form the Z helix. The S_3 layer was shown to be a mirror image of the S_1 layer. The changing of the microfibril angle throughout the layers

results in the layers being rather indistinct. The microfibril angle also seems to vary along the length of the cell. The angle of the S_2 layers seem to decrease towards the end of the cell (Dinwoodie 2000).

A number of hypotheses have been put forward to account for the variation in microfibril angle. Rolfsten and Houwink (1935) suggest that the reorientation of the microfibrils after they are laid down is due to the extension of the cell; however, this theory is incompatible with some microfibril arrangements. Boyd (1985) suggested a theory based on strains built up in the cell wall as a consequence of extension and thickening growth. This theory explains the differences in the orientation between the different wall layers.

Booker and Sell (1998) suggest another theory which relates to the mechanical function of the cell wall in the tree and the microfibril angle.

1.1.3.6 Mircropores.

As has been noted earlier wood contains pores of varying sizes. Micropores are the smallest of the pores, which are of molecular scale in dimensions (Siau 1984). Micropores are pores that extend into the cell wall, winding their way between the microfibrils.

The actual determination of the geometry of the micropores is problematic due to the nature of the material. The original experiments that inferred the presence of the micropores were liquid displacement experiments (Stone, *et al.* 1966). It was particularly noted that there was a difference between the densities found using polar and non polar liquids (Stamm 1964). When a non polar liquid is used as the displacement liquid it can be seen that the density values fall between 1.42 g/cm^3 and 1.48 g/cm^3, however when water is used as the displacement liquid the density values are found to be in the region of 1.50 g/cm^3 to 1.55 g/cm^3 (Stamm 1964). Two explanations of this phenomenon have been given, Stamm (1964), suggested that this was due to the water molecules having a stronger cohesive bond with the cellulose than the non polar liquid.

The issue of cell wall collapse is an important one and it has been reported that wood becomes essentially non-porous when water saturated wood is oven dried (Stone *et al.*, 1966b). It was reported by (Stone *et al.*, 1966a) that the surface area of wood when oven dried is about 1 m^2/g. When wood is dried by solvent exchange pa surface area of approximately 5 m^2/g (Stone, *et al.* 1969). Solvent exchange drying involves the removal of water using anhydrous ethanol, the removal of ethanol using anhydrous acetone, the replacement of acetone with anhydrous toluene and finally the removal of toluene in a stream of dry nitrogen (Hill and Papadopoulos 2001). This method has been criticised due to a collapsing force experience on the microvoids due to the surface tension between the toluene and the nitrogen gas (Hill and Papadopoulos 2001). A superior drying method uses carbon dioxide instead of the nitrogen, avoiding the problem of the liquid vapour interface in the mouth of the microvoid. When the final solvent used in the drying is CO_2 a surface area of 144 m^2/g was found. This shows that lignin provides an additional collapsing force. Delignified material exhibits a surface area in the order of 150-200 m^2/g showing that the cell wall no longer collapses.

A study of deligninfied wood by Heaslton in 1954 (Hill and Papadopoulos 2001) showed that, when dried conventionally there was no detectable cell wall porosity, however (Stone and Scallan 1965) showed that *Picea mariana* fibres had microvoids in the cell wall in the region of 2nm to 4nm. (Sawabe, Muri et al. 1973) investigated the cell structure of various woods using nitrogen sorption isotherms and found that the majority of pore sizes ranged between 2.5nm and 5.0nm in diameter and concluded that there was no difference in pore sizes across species.

The properties of the micropores is very dependent on the history of the wood particularly whether it has been dried or not (Stone and Scallan 1967). It has been seen that the total pore volume of a sample of wood decreases dramatically to 1-4 $x10^{-3}$ cm^3/g (from 0.4 cm^3/g) when wood is dried (Flournoy *et al.* 1991;

Flournoy, *et al.* 1993). This reduction in pore volume is a result of the micropore network in the cell wall collapsing when it is dried (Hill, *et al.* 2004).

It has been mentioned earlier that microvoids collapse when wood is dried and that this effects the measurement of cell wall microvoids. One technique that has been used to measure the cell wall microvoids of swollen wood is that of solute exclusion. The method determines pore size by diffusing a series of 'probe' molecules into the cell wall, with the diameter of the probe molecules increasing through the series. If the water in the microvoids is accessible to the probe molecules then there will be a net dilution of the probe solution. As the probe molecules increase in size some of (and eventually all of) the microvoids will become inaccessible and therefore a model of the size distribution of the microvoids can be created. Probe molecules that have been used by researchers are sugars and cross linked dextrans (Stone and Scallan 1968; Farahani 2003; Hill, Forster *et al.* 2004) and polyethyleneglycols (Tarkow, *et al.* 1966).

The solute exclusion technique is widely used, however, it has been shown that although the technique can give comparable results it does not give a definitive microvoid distribution curve. Several problems with solute exclusion have been recognised and a brief outline of these follows;

- This method relies on the concentration of the solution in the accessible pores being equal to that in the bulk solution
- There is no interaction between the cell wall and the solution of probe molecules however the presence of a carboxylic group on the probe molecules causes a negative absorption, or repulsion, from the microvoids and as this alters the measurements from solute exclusion (Allan *et al.* 1991).

The solute exclusion technique also assumes that the probe molecules totally fill pores of larger sizes, however this may not be the case. Day *et al.* (1979) suggests that as the size of the molecule converges with that of the pore the pore is not fully penetrated. Alince (1991) also suggests that the solution in the

micropore will not be the same as that of the bulk solution unless the diameter of the molecule is infinitely smaller than that of the pore.

Walker (1993) suggests that this method actually gives a smaller measurement than the actual microvoid volume. This is due to the hydrogen bonded monolayer of water which may not be accessible to the probe molecules. (Hill and Papadopoulos 2001) suggest that the geometry of the microvoids influence the apparent size as measured by this method.

Other methods have also been used for the, thermoporosimetry, using a differential scanning calorimeter, was used by Maloney and Pauolapuro (1998 and 1999) and provided credible microvoid dimensional results. Thermoporosimetry is based on the decrease in the melting temperature of a probe liquid in small pores, with a certain melting temperature corresponding to a certain pore diameter. The amount of pores with a certain pore diameter can be calculated from the melting enthalpy at a particular temperature in a calorimeter measurement. Nuclear magnetic resonance has also be used to determine the diffusion of water within pulp fibres (Lu *et al.* 1992; 1995 in (Hill and Papadopoulos 2001). Micropore dimensions can be found by determining the NMR relaxation time of the water in the microvoids. Water at or very close to the surface of the microvoids exhibits very different dynamic behaviour compared to water with in the microvoid, which acts as free water and therefore the size of the micropore can be calculated from the ratio of the two types of water.

The determination of the microvoids of the cell wall has proven to be problematic and even the established technique of solute exclusion has its problems. However, it has been shown that the diameter of the microvoids in, on average, in the region of 2 nm.

As has been shown in section 1.2.3 a reduction in Fibre Saturation Point will lead to a reduction in the rate of decay of the wood. Hill *et al.* (2004) stated that the blocking of the cell wall microvoids will have the effect of reducing the FSP of a sample of timber. The paper, which uses acetic anhydride to treat samples of

Corsican pine shows that as the weight percent gain (WPG) increases the fibre saturation point falls. Hill also comments that when the WPG reaches between 20-25% the FSP of Corsican pine will drop to around 20% which, as discussed in section 1.2.3. is the value considered to be the threshold value for fungal decay. The blocking of micropores as a mechanism for decay resistance will be revisited, in more detail in section 1.5.

1.2 The Fungal Decay of Wood.

1.2.1 The taxonomy of wood decaying fungi.

Whitaker, in 1969, produced a classification system for all living organisms in which fungi were given a kingdom of their own. The five kingdoms were Monera, Protista, Fungi, Plantae and Animalia. The kingdom of fungi was then discribed to contain organsims that are, filamentous eukaryotic cells, generally multicellular and heterotrophic. Fungi are seen as a higher life form and it has been suggested that they evolved from the protista along separate lines to the animals and plants (Zabel and Morrell 1992). The fungi kingdom is split into two major divisions, the Myxomycota and the Eumycota. The Myxomycota are generally described as slime moulds however these are out of the remit of this work and therefore will not be discussed any further. The Eumycota are split in to five sub-divisions; Mastigomycotina, Zygommycotina, Ascomycontina, Basidiomycotina and Deuteromycotina. The majority of these fungi, although showing a range of vegetative and somatic cell forms, have filamentous hyphae and are therefore considered more advanced than the Myxomycetes. Of the five sub-divisions of the Eumycota only the basidiomycotina have been used within this study, therefore it is the only sub division to be discussed here.

1.2.1.1 Basidiomycotina.

The Basidiomycotina contains the majority of the wood decaying fungi with over 16,000 species being identified. Of the three classes, Hymenomycetes are the most economically important fungi and contain; mushrooms, bracket fungi, toadstools and jelly fungi. Some Gasteromycetes decay wood but the third class, Teliomycetes, which include the rusts and the smuts are plant pathogens and do not affect wood in service.

The major distinguishing feature between Gasteromycetes and Hymenomycetes is the development of the spores (Eaton and Hale 1993) which is shown in Figure 1.10.

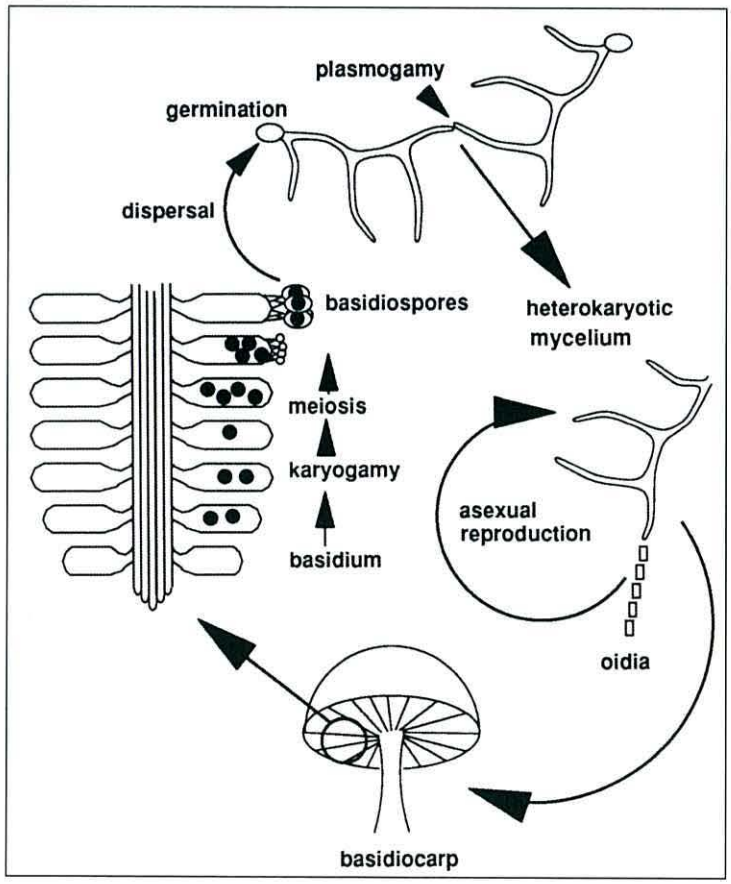


Figure 1.10: The life cycle of a basidiomycete.

In Hymenomycetes the basidiospores are forned on the fertile hymenium which is then exposed when the fruiting body or sporophore is mature, however in the Gasteromycetes (such as puff balls), the hymenium is enclosed in the sporophore even when it reaches maturity.

Once the basidiospores are released from the fruiting body they will germinate on a suitable substrate with the right environmental conditions and produce a mycelium which has simple cross walled septa. Each hyphaeal compartment has a single haploid nucleus and therefore is described as monokaryotic, therefore fusion between two hyphae is required to initiate fruit body development. Once these two hyphae have fused they then contain two nuclei and are therefore described as dikaryotic, the two nuclei are genetically distinct and the mycelium can then be described as heterokaryotic. Once a dikaryotic cell has formed the septa will be modified to keep this pairing together. This modification is characterised by a swelling in the cell which is known as a clamp connection (Figure 1.11).

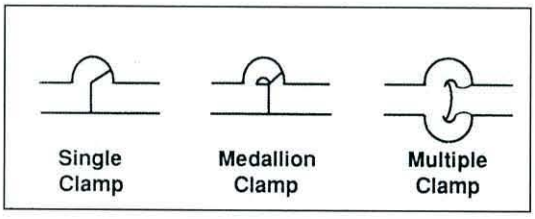


Figure 1.11: The three types of clamp connectors.

The presence and the type of clamp connection are important ways of identifying fungi.

1.2.2 Fungal Nutrition.

Fungi need both organic compounds, which they use as a source of energy, and carbon, which is used in metabolism.

Wood decaying fungi can sequester the organic and in-organics needed to support life in several different ways. The organic compounds are found in the wood structure itself as polysaccharides (see Section 1.1.3), in the immediate environment, and they may also be supplied by other organisms. There is no evidence to suggest that the lignin is a major source of nutrients however some white rot fungi have the ability to degrade the three major components of wood (Section 1.2.4). As well as being able to degrade the free sugars, fungi can utilise the starch, which is the storage medium in the wood, this is mostly found in the ray parenchyma. In addition to the carbohydrates the fungi can break down the proteins that are found in the wood, although these are found in relatively small amounts they do contribute to the total carbon and nitrogen assimilated by the hyphae (Eaton and Hale 1993).

The nitrogen content is of wood is very low compared to cereal crops; the ratio of carbon to nitrogen in wood can range from 300-1200:1. Due to these low amounts of nitrogen the fungi have to conserve and recycle their nitrogen. King (1980) suggests that the fungi can sequester the nitrogen from external sources with the aid of bacteria and it has also been suggested that the fungi can utilise atmospheric nitrogen again with the aid of bacteria (Levy 1974). Fungi also can recycle nitrogen through a process of autolysis (the enzymatic digestion of the fungis own cells when they are dying). The nitrogen is needed for the production of carbohydrates.

1.2.3 Fungal water interactions.

The presence of water is an essential requirement for fungal decay and if wood is kept under a moisture content of around 20%- 22% (Eaton and Hale, 1993, Cartwright and Findley, 1958) the wood is generally safe form fungal decay.

The percentage moisture content of wood needed for decay varies depending on the type of fungus, some fungi, termed as osmophilic, can tolerate very low water contents, the *Aspergillus* fungi can grow in a moisture content as low as 15% (Eaton and Hale 1993). Although it has been mentioned that fungi can not

tolerate low moisture contents there is also an upper threshold which again alter with the type of fungi. Soft rot fungi, such as *Chaetomium globosum*, can tolerate high moisture content growing in areas where there is contact with ground water, sea water or where water accumulates in the edges of joinery, however if the wood is fully water saturated the soft rot fungi lay dormant in the wood with the lack of oxygen being the limiting factor.

The basidiomycotina are less tolerant to high moisture contents that the soft rots. The high moisture content of the wood results in a lower oxygen level and therefore the fungi, which are aerobic cannot respire.

Timbers that are in ground contact exhibit a cone of moisture that moves depending on the moisture content of the soil. The degree of saturation at the point of ground contact has a direct effect on the speed of decay. Although the interaction between fungi and water the main concern of this section it is interesting to note that colonisation of wood at the point of ground contact is not a single entity occurrence. Generally, the wood is first colonised by bacteria, then mould fungi, stain fungi, soft rot fungi and then finally basidiomycetes. These different colonisers have varying tolerances to moisture content and therefore the wood is under attack in a large range of moisture contents. The increased moisture content of the wood swells the pores and micropores to open, this will allow the fungal spores and bacteria to easily enter the cell of the timber.

Viitanen (1991) shows that the optimum moisture content for the growth of brown rot on Scots pine and Norway spruce is between 30 and 70% and the relative humidity above 95%. Viitanen (1991) also notes that the fibre saturation point for the two species is between 28 -30% and therefore it was found that the fungi prefer wood that has free water in the cell lumen. The water content of wood is also important for the germination of fungal spores; the germination of fungal spores needs free water in the wood for its initiation.

As has been mentioned earlier if wood is kept in a totally submerged and anaerobic state the growth of the fungi can be arrested and therefore wood can be

preserved in this state, however if the timber is then dried the fungi will the reactivate as has been seen with the rising of sunken wooden ships such as the Mary Rose. If the timber continues to dry to fungal decay is again arrested, this is due to the fungi drying out …

1.2.4 White Rot Decay of Wood.

Of all the wood decay types, white rot decay of wood by basidiomycetes has been studied with the greatest intensity over the last 25 years (Daniel 2003). The research into the white rot degradation of wood has been spurred by the biotechnological potential of using white rot for pulping and other uses.

In nature white rot fungi are found inhabiting hardwoods in terrestrial environments. However white rot fungi have also been found in marine environments (Leightley, 1980) and have also been found in CCA treated wood in mooring poles and in cooling towers under service conditions (Schmidt *et al.* 1997).

Both simultaneous and non simultaneous decay have been the shown to be the principal ways that both hardwood and softwood are decayed by white rot. Colonisation of the wood substrate occurs via the rays and the hyphae penetrate the cell walls via the pits and by development of bore holes. The fungal hyphae are generally located in the cell lumen during the decay of the wood.

1.2.4.1 Simultaneous white rot.

When simultaneous white rot takes place (as with *Phanerochaete chrysosporium*, which is used in this thesis) all the wood components are degraded at the same time, starting at the cell lumen and working outwards, however decay is quicker along the thinner tangential cell walls than through the thicker radial walls of the cell. As the decay reaches the middle lamella the white rot fungi decays the lignin and thus decay can progress into adjacent cells. At the decay wood

interface simultaneous white rot can be distinguished by a thin advancing zone in which the wood is mineralised. The zone is distinguishable via staining (e.g. with safranin) at the light microscopic level but is only discernable with TEM by a thin electron lucent layer.

Researchers (Daniel 2003) have found, using immunocytochemical techniques and antibodies, many enzymes at the wood decay interface, these include ligninolytic, celluloytic, hemicellulolytic, and glucose oxidising enzymes. It has also be shown that these enzymes originate from the fungal hyphae, and more specifically from the periplasmic space and the intercellular spaces in the hyphae (Daniel 1993). Research has found that the enzymes are transported from the hyphae to the wood via slime material which fills the gap between the fungal hyphae and the cell wall (Daniel 1993). The extra cellular slime produced by *Phanerochaete chrysosporium* has been characterised as a glucan (Messner, *et al.* 2003). Eriksson, *et al.* (1986) suggests that the slime may cover the whole cell wall, which aids the achievement of the optimum moisture level for white rot activity as this is far above fibre saturation point. The water film will contain the slime components and the watery matrix that is formed may decrease the evaporation when the wood is dried. The slime layer has also been attributed to controlling the rate of decay by controlling the amount of glucose in the medium (Eriksson, *et al.* 1986). The production of the glucan polymers is either due to the extra cellular involvement of enzymes located in the extra cellular membrane or due to the metabolisation of carbohydrates and *de novo* synthesis of glucanses. The slime also creates a microenvironment where the H_2O_2 needed for lignin degradation is maintained. Because the glucan polymers are depolymerised by laminarinase as well as glucanse it is likely that the slime fractions have a low enough molecular weight to penetrate the cell wall.

A tripartite membrane has also been found to play a role in the transportation of the enzymes (Palmer *et al.* 1983). The tripartite membrane is also known as the hyphal sheath and is not found on all white rotting fungi, however it has been found on *Trametes versicolor* and *P. chrysosporium* which are both used in these studies. (Foisner *et al.* 1984) found that the extra cellular structures produced by

P. Chrysosporium were composed of equal amounts of carbohydrates, lipids (however, not phospholipids) and proteins, which included five fractions with molecular weights of between 30,000 and 200,000.

It is currently unknown how the products of decay are absorbed into the hyphae wall (Daniel 1993). However it is known that the that the only material remaining after advanced decay are the corners of the middle lamella cells (which are lignin rich), which are usually surrounded by slime. These areas are eventually degraded by ligninolytic enzymes (Daniel 1993). It has been found that the cell walls can only be decayed when they have been 'opened'; this is because the enzymes are unable to penetrate closed (or unmodified) cell walls due to their high molecular weights (40-70,000 Kda). As has been discussed in section 1.2, the micropores of the cell wall are around 2 nm and therefore the enzymes are far too big to get into the cell wall.

Table 1.2 shows an example of the weight loss of *Picea sitchensis* after it has been decayed by *C. versicolor* for varying times, this table gives an indication to the rates of decay from a simultaneous white rot.

Weight loss (%)				
Total (biomass)	Glucan	Mannan	Xylan	Lignin
13	4	13	13	27
22	17	22	21	33
43	43	47	47	52
61	65	68	67	62
83	85	89	89	86

Table 1.2: Weight loss with a simultaneous white rot fungi (Zabel and Morrell 1992).

1.2.4.2 Preferential White Rot Decay.

Preferential attack selectively decays the hemicellulose and the lignin within the cell wall. This type of attack is generally observed in the latewood cells of softwoods and the decay is easily recognisable by the distinct rings progressing across the wood cell walls (Daniel 1993). Preferential white rot is similar to simultaneous white rot in that the decay can pass through the middle lamella, however unlike simultaneous white rot the decay is not localised to the cell wall. The rings can give the location of the attack with in both space and time with regards to the demineralisation of both the lignin and the hemicellulose. As decay progresses the lignin and hemicelluloses are removed and the remaining fibre cell wall is composed of cellulose which swells into the cell lumen (Daniel 2003). Messner and Srebotnik (1994) have observed, after 6 weeks white rot decay, complete dissolution of the wood tissue, however with the aid of TEM microscopy they noted that none of the fibres where damaged. Srebotnik and Messner (1994) confirmed these results by selectively staining lignin and cellulose with safranin and astra blue and noting the selective delignification of both the cell wall and the middle lamella. Blanchette and Reid (1986) showed preferential white rot by *Phlebia tremellosa* by the fixation of wood by OsO_4^- gluta-aldehyde and then staining with uranyl acetate. Blanchette and Reid (1986) found that the delignification of the cell wall began next to the hyphae and then spread though the cell wall and gradually broke down the middle lamella. They also found that this was happening through out the circumference of the cell wall.

The mechanism for preferential white rot is undetermined (Daniel 2003). As was pointed out in Section 1.2.4.1 the enzymes are too big to enter into the cell walls via the micropores. (Daniel 2003) indicates that the mechanism for preferential white rot could be similar to that of proposed for brown rot decay in which there is an involvement of non-enzymatic processes and that low molecular weight oxidising agents can be diffuse into the cell wall. Metals such as Cu, Mn and Fe have been identified as being involved with possible oxidising agents for both white and brown rots. These metals have been observed in complexes with the cellulosic fibres but never observed as free metal ions. However, Mn is the

exception and it was reported as early as 1878 by Hartig (in Daniel (2003)) that Mn was seen as dark flecks in white rotted wood, these dark flecks were found to be MnO_2. This has been confirmed in several papers (Blanchette 1984, Daniel 1993, Daniel and Bergman 1997). MnO_2 was found to be associated with the fungal hyphae, the extra-cellular slime and the penetration into the cell walls. Mn has also found to be associated with the bleaching of the cell walls, which can be put down to lignin attack, and the delamination of the cell wall structure in both the S_2 and middle lamella layers (Daniel and Bergman 1997; Daniel *et al.* 1997). It is not known what levels of Mn, its cofactors (e.g. H_2O_2) and stabilizers (i.e. organic acids, chelators and oxalators) are needed to produce the cell wall modification to allow the ligninolytic and hemicellulolytic enzymes into the wall.

P. chrysosporium produces pyranose 2-oxidase which has been found to be able to break, via a double oxidation reaction, a molecule of glucose to produce 2 H_2O_2 (Volc, *et al.* 1995), which, as said before, is a cofactor in the 'opening' of the cell wall to the enzymes.

It has been found that both types of white rot decay can be produced by the same fungus on the same piece of wood and the determining factors to the type of decay remain obscure. However (Messner, *et al.* 2003) suggested that moisture content may be one of the determining factors for the determination of the type of white rot decay.

1.2.5 Brown Rot Decay of Wood.

Brown rot is considered to be the most important type of decay for wood in service (Daniel 2003) and is characterised by their extensive and rapid depolymerisation of the cellulose which in turn leads to a loss of wood strength in the early stages of the decay process. Strength losses due to brown rot decay have been reported to be as high as 70% for both modulus of elasticity and modulus of rupture in the incipient stages of decay (Wilcox 1978). Curling *et al.* (2001) noted that mass loss from *Geophilum traebium* was not detectable until the strength loss (MOR) had reached 40%. Although it is generally understood

that the rapid depolymerisation of the cellulose leads to loss in strength, it has also been noted by (Winandy and Morrell 1993) that the loss of hemicellulose in the early stages of brown rot decay also adversely effects the strength of the wood.

In general, decay due to brown rot involves the removal of cellulose and hemicellulose leaving the lignin as a weak amorphous skeleton which easily crumbles and fractures cubically (Daniel 2003). The lignin is thought to be largely left unchanged however this hypotheses has changed as will be discussed later. The level of lignin with in the wood does not seem to have an effect on the amount of decay via brown rot, therefore the levels of decay are similar in both hardwoods and softwoods when assessed with standard laboratory tests (Nilsson and Daniel 1987). Although it has been stated that brown rot readily decays the cellulose it has been reported that brown rots are incapable of degrading cellulose in isolation (Highley 1973). It has therefore been suggested that brown rot needs either, components of the lignin or the hemicellulose to allow the degradation to take place, this could be due to the use of modified phenolic groups from the lignin taking part in the Fenton based reactions to give oxidative activity (Goodall *et al.* 1997).

Brown rot generally colonises timber via the rays, then moves out into the axial wood structure penetrating the cells either through the pits or using bore holes. In softwood brown rot generally attacks through the window pits and creates a diamond decay pattern (Daniel 1993).

Micro- and Ultra- structural studies have shown that the hyphae of brown rot fungi do not have to be in close proximity of the wood cell for cellulose and hemicellulose depolymerisation to take place, the decay radiates out across the cell walls in a similar way to the decay of preferential white rot (Section 1.2.4.2). It has also been shown that the agents of decay are able to defuse through the S3 and S2 layer causing initial decay at the S1-S2 interface and that it is likely that the agents of decay are low molecular oxidising agents, which act in the early parts of the decay, this has been deduced due to the rapidity of the decay process

and the apparent tight and complex structure of the S2 layer in softwoods (Daniel 2003). (Daniel *et al.* 1991) suggested that brown rot selectively removes polysaccharides from the middle lamella regions. It has also been suggested by researchers that there is an association with extra cellular components, such as slimes and tripartite membranes, during the decay process (Palmer *et al.* 1983) in a similar way to white rot.

The mechanism for brown rot decay is not fully understood, especially the role of non enzymatic agents. These non enzymatic agents include, oxalic acid (Schmidt *et al.* 1981), low molecular weight chelators (Jellison *et al.* 1991), fenton reagent (Koenings 1974), glycoprotiens (Enoki *et al.* 1989). The difficulties in understanding the roles of these molecules in the degradation of wood arises from the technical difficulties of loss and movement of the molecules while the wood is been fixed on a slide, therefore in many cases it can only be assumed that the agents were present (Daniel 2003). The differences in the physiology of the individual brown rot fungi also hamper our understanding of the decay mechanism, for example some brown rot fungi (such as *Posita* spp.) strongly reduce the pH of the wood substrate while other species, such as *Gloeophyllum trabeum* retain the wood at a slightly acidic pH (Daniel 2003).

Another problem with the analysis of brown rot decay is that there are distinct dissimilarities between decay, caused by the same fungi but in different types of wood. For example the attack on the S2 layer of birch leaves an open structure while the attack on softwoods leaves a denser and compact cell wall matrix (Daniel 1993). However this can be explained by the type of lignification in the cell walls (Daniel 2003). The type of lignin found in Birch is largely guaiacyl however in softwoods there is a 1:1 ration of guaiacyl and syrinzyl lignins.

The research into the decay mechanisms brown rot is still ongoing, however Daniel (2003) points out that research should turn towards the involvement of enzymes in the production of depolymerisation agents, such as in the production of H_2O_2 by the enzymatic decay of glucose and other sugars, which may be the

source of the H_2O_2 for the Fenton reagent and radicals which are involved in the cell wall depolymerisation.

The decay of lignin by brown rots has been much debated. (Goodall 2003) acknowledges that lignin decay has not been recognised in the past however shows that there is much new evidence that supports the idea that some decay of the lignin takes place, and states that there is evidence that suggests that up to 25% of lignin can be removed by brown rot. Lignin specific enzymes are generally not seen with brown rot, however it has been reported that laccase has been produced by brown rot, in artificial media (D'Souza *et al.* 1996). There have also been reports of manganese peroxidase and lignin peroxidase being produced by some brown rot species (Szklarz, *et al.* 1989) which will, as with white rot, decay the lignin. (Goodall, 2003) points out that brown rot will readily penetrate the wood cell wall via bore holes from adjacent cells, therefore passing through the middle lamella which has a high concentration of lignin; therefore the brown rots will need a mechanism for the decay of lignin for this to happen. It has been noted earlier that the residue lignin is found to be demethylated, however it has also been reported that lignin has been found to be dealkylated and demethoxylated as well (Jin *et al.* 1990; Filley *et al.* 2002). As has been mentioned earlier, with respect to white rot, the cell wall micropore are too small to let enzymes into the cell wall and therefore it is once again thought that it is low molecular weight chemical that enter the cell wall and modify the lignin. It has been suggested by Barr and Aust (1994) that hydroxyl radicals can cause rapid depolymerisation and repolymerisation of the lignin.

It has generally been found that the pH of wood that is undergoing decay via brown rot is lower than that of sound wood and that of wood undergoing decay via white rot. Highley (1976) found that if the pH of wood is increase then the activity of brown rot (however, not white rot) is inhibited. This reduction in pH is initiated by the production of oxalate which appears as crystals and is then solubilised to form oxalic acid. This production of oxalic acid by some fungis and the reduction in pH is discussed as a key factor in the decay of wood via some brown rotting fungi (Goodall 2003).

It has been mentioned earlier that Fenton based reactions may be responsible for the degradation of the holocellulose component of the wood cell wall, several hypotheses have been developed to model how the Fenton reactions alone with the low molecular weight metabolites, the metals and radicals may initiate the decay of wood. The most common hypotheses are listed below, however they are not described in any detail as this is out side the remit of this brief introduction to wood decay. A description of each hypothosis can be found in Goodall (2003).

The hypothoses are as follows;

- Glycopeptide degradation.
- Cellobiose Dehydrogenase Iron reduction – Autoxidation.
- Chelator-Mediated Fenton Systems.
- Quinone Redox Cycling.

The theory of decay via brown rot has changed dramatically in recent years. It is now understood that lignin is decayed by brown rot and that this is due to low weight metabolites and not enzymes. It is also understood that the low molecular weight metabolites are involved in the cellulose degradation processes as precursors to the main enzymatic degradation. (Goodall 2003) suggests that further work is still needed to establish the true mechanism for brown rot decay.

1.3 Resins and their role in wood protection.

1.3.1 Resin Chemistry.

The chemistry and formulation of resins varies with manufacturers and the exact requirements of the resin. However, the general chemistry is the same for each type of resin. The chemistry of each of the resins used in this study is described below.

1.3.1.1 Urea Formaldehyde.

Urea formaldehyde resin was developed in the 1930's (Dinwoodie 1979) and is widely used in the composite's industry, 90% of the worlds particleboard is produced using UF resin (Dinwoodie 1979). The advantages of UF resins were listed by (Pizzi 1994) as follows;

1. The initial water solubility renders UF resins suitable for bulk and inexpensive production.
2. The hardness of the resin.
3. The low flammability of the resin.
4. The good thermal properties of the resin.
5. The absence of colour in the cured polymer.
6. The adaptability of the resin to a variety of curing conditions.

However, UF resin has disadvantages, the major problem being that UF resin is subject to hydrolytic degradation when in the presence of moisture and / or acids. This degradation is mainly due to the hydrolysis of the amino plastic and the methylene bridges.

1.3.1.2 The Manufacture of Urea Formaldehyde Resin.

The manufacture of UF resin is complex. Urea is manufactured from carbon dioxide and ammonia at a temperature of 135°C-200°C and at a pressure of 70-230 atmospheres. Formaldehyde is manufactured by the oxidation of methanol which can be produced from the reaction of carbon dioxide with hydrogen or can be derived from petroleum.

The combination of the urea and the formaldehyde gives both branched and linear polymers as well as the 3-dimensional matrix that can be found in the cured resin. These different structures are due to the functionality of the urea and

the formaldehyde. Urea has a functionality of 4 (due to the presence of four replaceable hydrogen atoms) and formaldehyde has a functionality of 2 (Figure 1.12).

Urea *Formaldehyde*

Figure 1.12: Urea and Formaldehyde

The most important factors affecting the properties of the reaction products are;

- The relative molarities or the reactants.
- The reaction temperature.
- The pH at which the condensation reaction takes place.

These factors influence the rate of increase of the molecular weight of the resin (Pizzi and Mittal 1994), therefore the reaction products vary widely with the changes in reaction criteria. Solubility, viscosity, water retention and final rate of cure all vary with molecular weight.

The reaction of urea and formaldehyde is divided into two stages. The first stage is alkaline condensation to form mono-, di-, and trimethylolureas (Figure 1.13). The reaction also produces cyclic derivatives such as uron, monomethyloluron, and dimethyloluron.

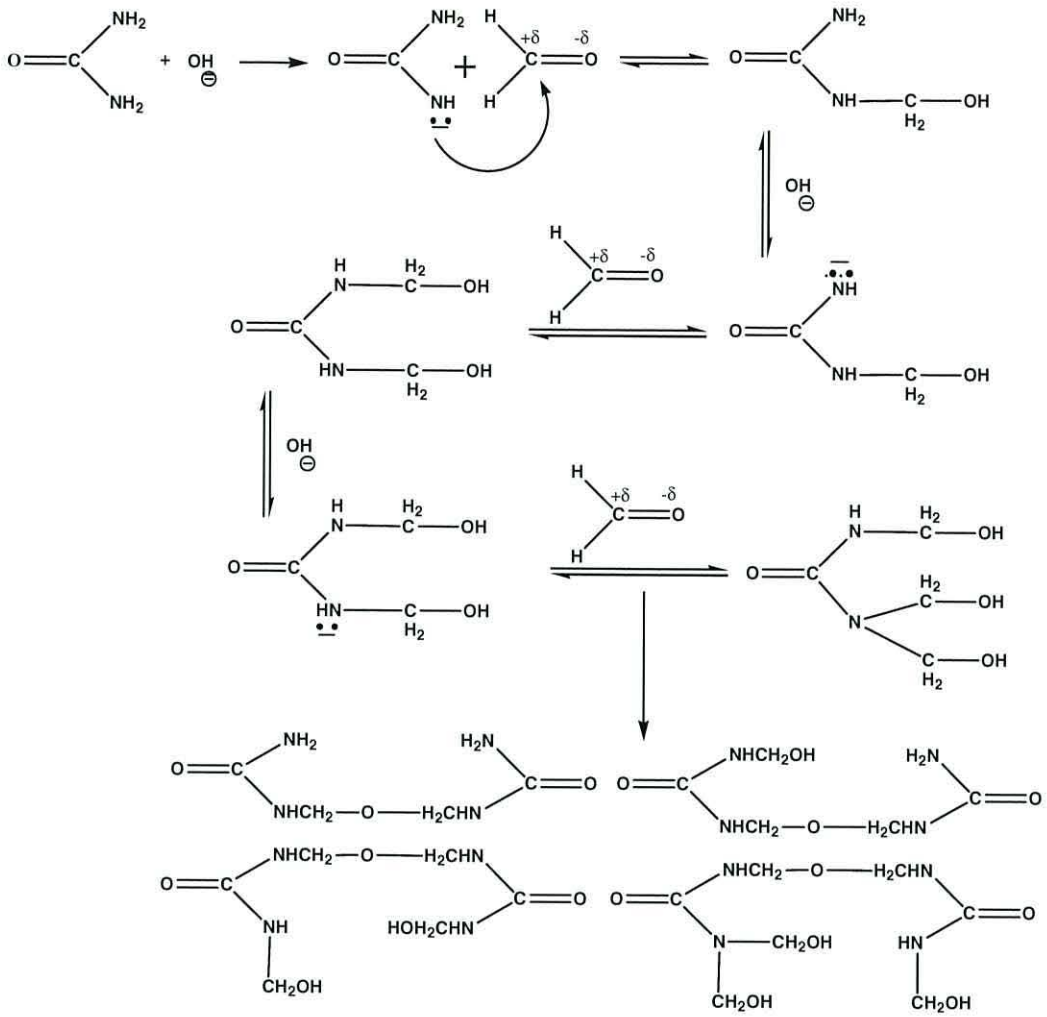


Figure 1.13: Alkaline condensation of Urea and Formaldehyde.

The second stage is an acid condensation of the methylolureas to form firstly soluble and then insoluble cross-linked resins.

When acid condensation takes place, the products that precipitate from an aqueous solution of urea and formaldehyde, or from methylolureas, are low molecular weight methyleneureas (Figure 1.14).

$$H_2NCONH(CH_2NHCONH)_nH$$

Figure 1.14: Low molecular weight Methyleneurea

These contain methylol end groups in some cases, through which it is possible to continue the hardening process. The monomethylolureas copolymerise by acid catalysis and produce polymers and then highly branched and cured networks (Figure 1.15).

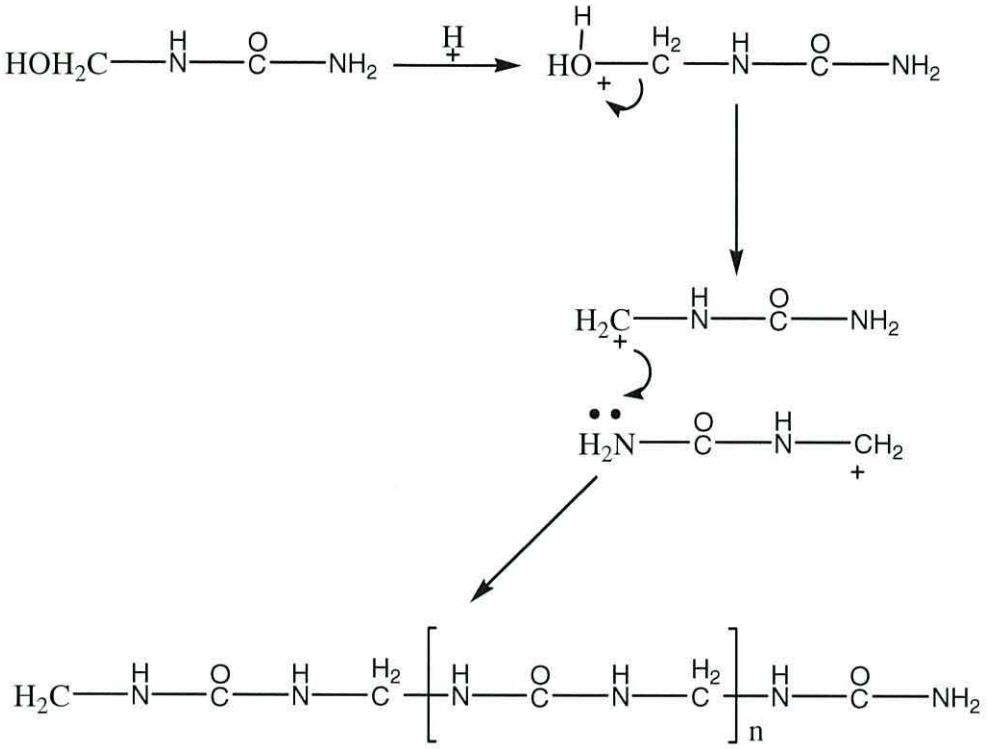


Figure 1.15: Copolymerisation of monomethylolureas.

The kinetics of the formation of mono and dimethylolureas and of the simple condensation products have been studied extensively. The formation of the monomethylolurea molecules in a weak acid or alkaline solutions is characterised by an initial fast phase followed by a slow bimolecular reaction. The rate of reaction varies with the pH of the system. A minimum rate of reaction is achieved with a pH of 5 to 8 for a urea / formaldehyde ratio of 1:1 and a pH value of ±6.5 for a 1:2 molar ratio (Figure 1.16).

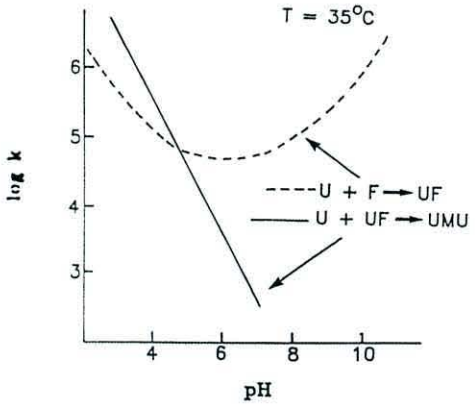


Figure 1.16: Influence of pH on the addition and condensation reactions of urea and formaldehyde (Pizzi and Mittal 1994).

The rate of formation of the methylenebisurea molecules by the condensation of urea with monomethyleneurea is also pH dependent. The rate of reaction decreases exponentially from a pH of 2 to 3 to a neutral pH, the reaction does not take place in alkaline conditions.

The initial addition of formaldehyde to urea is reversible. The rates of introduction of the one, two and three methylol groups have been estimated to be 9:3:1 respectively. The formation of *N,N'*-dimethylolurea to monomethylolurea is three times that of monomethylolurea to urea.

The methylenebisurea and higher oligomers undergo further condensation with formaldehyde and monomethylurea, which behaves like urea (Pizzi and Mittal 1994). The capacity of methylenebisurea to hydrolyse to urea and methylolurea in weak acid solutions (pH 3 to 5) indicates the reversibility of the aminomethylene link and its proness to chemical change in weak acid moisture.

1.3.1.2.1 Commercial production of Urea Formaldehyde Resins.

In the commercial production of UF resin the most important property that has to be controlled is the size of the molecules. As the size of the molecules increases, the properties of the resin change, the most perceptible being the increase in

viscosity (Pizzi and Mittal 1994). The increase in molecular weight is due to water molecules splitting off the resin molecules at random thus presenting reactive groups for further condensation. However the condensation reaction is not favoured in aqueous conditions. Once the viscosity has been established and the pH, concentration and solubility have been determined the resin can be used.

The most common method of preparation for commercial UF resin is the addition of a second amount of urea during the reaction. The ratio of urea to formaldehyde is between 1:2 and 1:2.2 and therefore methylolation can take place at in a short amount of time at temperatures between 90 and 95°C, with a mixture being maintained under reflux. The formation of the resin is completed after the exotherm has subsided. Acid is then added to decrease the pH to allow the polymer building stage to begin (usually with a pH of 5.0 to 5.3). As soon as the correct viscosity, is reached the pH is increased to stop the polymers increasing in size. The second urea is added to mop up any free formaldehyde until a ratio of 1:1.1 to 1:1.7 has been established. The resin is then left to react for another 24 hours at a temperature of 25 to 30°C after which the resin solids content is adjusted appropriately and the pH is altered to give maximum shelf life.

1.3.1.3 Melamine Formaldehyde.

Melamine formaldehyde resins are widely used in applications in which the product may come in to contact with water, such as exterior grade panel products and kitchen furnishings. This is due to its high resistance to water attack which distinguishes it from UF resins. However, melamine formaldehyde is expensive (approximately 2.5 times the price of Urea formaldehyde) and therefore a varying amount of urea is added to the resin so that a compromise between cost and performance is met.

1.3.1.3.1 The Chemistry of Melamine Formaldehyde Resin.

The initial reaction in the formation of MF resin is the condensation of melamine with formaldehyde. The formaldehyde first attacks the amino groups of the melamine, forming methylol compounds. This reaction is similar to the initial reaction of formaldehyde with urea, however, the reaction between formaldehyde and melamine occurs more freely and completely than the reaction with urea. It has been noted by (Pizzi 1983; Pizzi and Mittal 1994) that complete methylolation of melamine is possible which is not the case with urea. The condensation will lead to a series of methylol compounds with between two and six methylol groups attached (Figure 1.17). Due to reduced solubility in water of melamine, when compared to urea, the hydrophilic stage of the reaction proceeds more rapidly in the formation of MF than in the formation of UF, therefore hydrophobic intermediaries appear early in the reaction. An important difference between the condensation of MF resin (and also the curing) and the condensation of UF resin is that the resin condenses not only in acid conditions but also in neutral and alkaline conditions (Pizzi and Mittal 1994). The reaction mechanism continues as with urea formaldehyde (see Section 1.3.2.1.1.), methylene and ether bridges form and the molecular weight of the resin increases rapidly. The intermediates that are formed at this stage of the reaction make up the bulk of commercially available resins. The final curing process transforms the intermediates to the desired insoluble, infusible resins through the reaction of amino and methylol groups which are still available for reaction. Koehler (1941) and Frey (1935) noted that ether bridges formed next to un-reacted methylol groups and methylene bridges. This is because when MF resin is cured at temperatures of up to 100°C no substantial amounts of formaldehyde are liberated whereas UF liberates significant amounts.

1.3.1.3.2 Commercial Production of Melamine Formaldehyde Resin.

Generally the commercial production of MF resin is not difficult and is in fact similar to the production of UF resin. The specifics of the production of the MF resin system depend on the application for which the resin is intended.

Resins that are intended for the impregnation of paper or fibres have to be modified with other compounds such as acetoguonamine and E-caprolactame (Pizzi and Mittal 1994). These modifying compounds are usually added at around 3 – 5% w/w and decrease the cross linking in the cured resin, thus making the resin less brittle. In the manufacture of wood panel products, the additives are not usually needed. Sugars have been used as modifiers in the wood panel adhesive industry but these are added to lessen the cost of the resin. However the addition of sugars means that with age the resin will yellow and crack and has a detrimental effect on long term resin properties.

Resins intended for use on the wood panels industry are generally designed with a higher viscosity than those intended for the infusion of paper, this is to prevent over penetration into the wood substrate. However, this work relied on the penetrability of the resin in to the wood cell wall and therefore the lower viscosity resins were of interest. Low viscosity resins have been used in other industries in which the flow of the resin is of concern.

Resins with good penetration can be created in several ways; a resin with a low level of condensation and high methylol group content will create a low viscosity resin with fast curing rate. A resin with a low level of condensation and a melamine / formaldehyde ratio of 1:1.8 – 2.0 will give the desired resin. A second approach to creating the resin is to form a resin with a higher degree of condensation and a lower methylol group content and add a second batch of melamine to the mix (usually giving a total melamine content of 3 – 5%) towards the end of the reaction. Typical total melamine formaldehyde ratios are in the region of 1:1.5 to 1:1.7 for this system.

1.3.1.4 Melamine Urea Formaldehyde Resins.

It has been noted that a major problem with using melamine is the expense. To negate the expense, copolymers can be formed with urea, these will decrease the cost of the resin system but also create a system with less desirable properties. The production of copolymer resins can be done in two ways, either by the copolymerisation of the two constituents at the resin formation phase or by the mixing of preformed UF and MF resins, however the former has superior properties to the latter. The ratios of melamine to urea generally used in the production of MUF resins usually range from 50:50 (melamine to urea) to 40:60. Although melamine urea formaldehyde resin are the generally available copolymerisation of melamine resins melamine phenol formaldehyde resins have also been produced and have been found to have superior performance than either PF or MF resins, however the MPF resins have a colouring effect and are therefore outside the scope of this thesis.

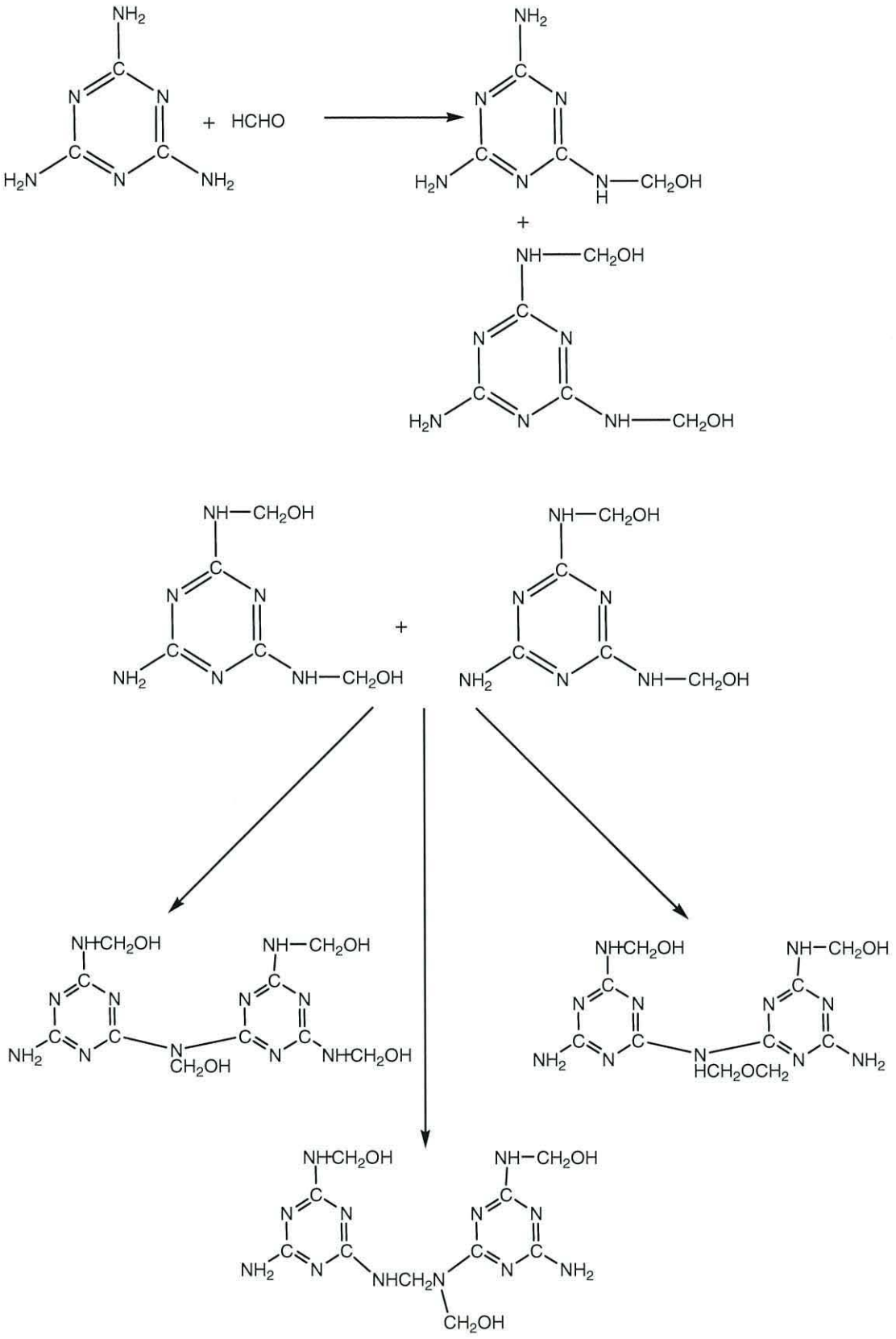


Figure 1.17: Methylolation and subsequent condensation reactions to form MF resin.

1.4 Resin modification of Wood.

1.4.1 Introduction.

The primary use of resins in the wood products industry is as a bonding agent. Resins are generally used in the particleboard industry, and in the joinery industry as adhesives and for repairing cracked timbers, however, it has been found that resins have an effect on the decay resistance of wood.

Resins can impart increased decay resistance in two distinct ways; either by simply blocking the micropores in the wood making the wood cell wall impervious to water and the low molecular weight non enzymatic decay agents or by acting as a toxic chemical barrier that kills the fungi (as traditional preservatives do).

The preliminary work on resin treated solid wood was directed towards increasing dimensional stability, which was done by filling the voids of the wood, both the micro and macrovoids, with resin and therefore stopping the ingress of moisture. As has been mentioned earlier the general reduction in the moisture content of the wood will prevent timber decay. (Stamm and Seborg 1936) suggested that the permanency of resin bonded to the hydroxyl groups of the cellulose would give a far more permanent effect that with other materials such as waxes.

Below can be found a list of three essential criteria that are based on the list produced by (Stamm and Seborg 1939);

- The resin components have to be unpolymerised or only very slightly polymerised so that the molecules are sufficiently small enough to enter the cell wall completely. This therefore means that the monomers and their sphere of solvation have to fit the cell wall micropores that have been calculated to be approximately 2 nm in diameter.

- The resins have to be soluble in polar liquids so the solvents can swell the wood cell wall making it more accessible to the resin components.
- The resins must be sufficiently polar to bond to the cell wall molecular components.
- Resin / co-biocide mixed have also been studies for their preservation performance. Vasishth (1983) studied the interactions of ENVIROLITE^{TM} and pentachlorophenol. Vasishth (1983) found that if a combined treatment was used leaching losses for the PCP were reduced to an average of 1.8% of the initial amount of PCP added to the sample compared with a loss of 28% when timber is treated with just PCP. A study of the application of a post treatment coating was also made, (Vasishth 1983) shows that a post treatment coating of PCP treated timbers is already in operation and states that a building with PCP / polymer treated timbers is now in use.

1.4.2 Phenol formaldehyde.

The use of phenol formaldehyde to modify solid wood has been studied extensively, this is due, in part, due to its use in the plywood industry and the research into the decay and stabilisation of plywood.

(Stamm and Baechler 1960) showed that as the retention of the phenol formaldehyde increases, both the anti shrink efficiency and the decay resistance of the treated timbers increased. (Stamm and Baechler 1960) also gave a theoretical maximum weight increase for cellulose, lignin and spruce when three phenol dialcohols are bonded through the phenol hydroxyl group as follows.

	Theoretical maximum weight increase. (%)
Cellulose	247
Lignin	46.5
Spruce wood	191

Table 1.3: Theoretical weight increase with Phenol formaldehyde modification.

The data given by Stamm and Baechler (1960) is probably imprecise due to the fact that hemicellulose is not taken into consideration. However, it does show the vast difference between the reactivity of cellulose and the reactivity of lignin.

Some of the original work on phenol formaldehyde treated wood was produced by Stamm and Seborg (1936) they treated blocks of white pine, measuring 8.9 cm x 2.2 cm x 2.2 cm with a varying formulations of phenol formaldehyde resin. The treatment regimes were relatively simple and involved the blocks being immersed in the resin solution and a vacuum being applied. Once the blocks were saturated they were left for 24 hours so that the resin molecules could diffuse into the cell wall. The resins were then cured at either 70 °C for three days or 105 °C for a day.

The resin uptake of these blocks was considerable, weight gains of 179 % were reported when the blocks were treated with 250 g phenol, 500 cm^3 of 40 % formaldehyde and 50 cm^3 concentrated ammonia, which is close to the theoretical maximum weight increase shown in Table 1.3. However these blocks were repeat treated five times and thus the blocks built up layers of resin within the cell. The high weight gains were giving good anti-shrink efficiencies when the blocks were subjected to cycling humidity conditions, the 179 % weight gained blocks had an anti-shrink efficiency of 99.8 %, which shows that the blocks were very impervious to the ingress of water from the atmosphere. When single treatment systems were used a WPG of 121 % was achieved using 100 g of phenol and 50 g of formaldehyde. An anti-shrink efficiency of 50 % was achieved with this regime. However Hill (2006) notes that the high WPG will not

be due purely to the ingress of resin into the cell wall especially with the more viscous resins as there is not space within the cell wall, the excess resin was found to be within the lumen of the cell. Stamm and Seborg (1936) found that pre-polymerisation reduced the effect of the resin due to the molecules being too large to fit into the cell wall nanopore structure.

More recently Deka and Saikia (2000) treated small blocks of *Anthocephalus cadamba* (1 x 0.5 x 8 cm) with PF, UF and MF resins. They found that the optimum criteria for treatment were at 75 psi for 1-2 hours at 90-100°C and using a 30% solid content resin and that a maximum anti shrink efficiency (70.6%) was obtained with a PF weight percent gain of 33.7%. The apparently low uptake compared with the work of Stamm and Seborg (1936) is probably due to the high solids content of the resin and therefore the high molecular weight.

The problem of molecular weight and the ingress of resin into the cell wall was examined by Furuno *et al.* (2004) and they concluded that low molecular weight phenol formaldehyde resins enter the cell wall and the resin plays an important role in the stabilisation of the solid wood. They noted that with the medium molecular weight resins, the lower molecular weight fraction still entered the cell wall however the higher molecular weight fraction formed resin granules on the lumen surface and the resin only slightly altered the dimensional stability of the wood. In keeping with the trend the high molecular weight resins did not enter the cell wall but filled the lumen and did not have any significant affect on the dimensional stability of the wood.

Goldstein *et al.* (1959) looked at several different methods for bulking the cell wall and preventing the ingress of water. The research they performed on phenol formaldehyde was of interest as they studied resin of different ages. It is well know that as the age of a resin increases its bonding efficiency decreases, this is due to the self polymerisation that takes place. Goldstein *et al.* (1959) showed that as the age of the resin increased the anti swell properties attributed to the timber by the resin decreased. Goldstein suggested that this was due to the reduction in the simple methylphenols, the work also showed that if the resins are

kept at elevated temperatures the decrease in reduction of swelling increases dramatically.

Treatments of pure phenol with out the formaldehyde component have been researched. Alma *et al.* (1995) treated wood meal of *Betula maximowicziana* Regel with phenol and hydrochloric acid then created moldings by the inclusion of HMTA (curing agent), zinc stearate (lubricating agent) and calcium hydroxide (accelerating agent). It was found that as the amount of combined phenol increases so does the anti-sorption effects of the phenol, however even with 117.8% combined phenol the anti-swelling efficiency of the wood did not reach that of wood treated with commercial Novolak resin.

As was noted earlier the reduction in the moisture content (and thus the increase in the dimensional stability) will have an affect on the resistance to decay of the solid wood. The addition of resin to the wood however also has a coupled effect of the addition of a foreign chemical compound into the cell wall. (Takahashi and Imamura 1990) treated blocks of *Cryptomeria japonica* D. Don, *Tsuga heterophylla* Serg. and *Fagus crenata* Blume with two types of PF resin, one a water soluble resin with a molecule weight of 170 and the second an ethanol soluble resin with a molecular weight of 300. The blocks were then decayed for twelve weeks by the following fungi, *Tyromyces palustris* (Berk et Curt.) Murr. And *Coriolus versicolor* (L. ex Fries) Quel. The researchers found that as the resin retention increased, the weight loss after 12 weeks decreased. Generally it was found that a weight percent gain of 16 % (w/w) gave full protection over the twelve week period. Takahashi and Imamura (1990) reiterated the fact that resin deposited in the lumen does not significantly affect the decay resistance of the wood and it is the resin that is deposited in the cell wall that has an important role to play.

Ryu *et al.* (1991) make the important point that PF resin treated wood has yielded a better biological resistance than that of acetylated wood (which in this thesis will be used as a model for cell wall bulking (see Section 1.5). This implies that the resistance imparted to the wood by the PF resin is not just from

the cell wall bulking effect but some of the resistance is due to the chemical composition of the resin. Ryu *et al.* (1993) showed that the lower the molecular weight of a resin the greater the decay resistance imparted to the wood, this is in concurrence with the work of Furuno *et al.* (2004) mentioned earlier. In Toole and Barnes (1974) the researchers suggest that the low molecular weight PF resins act as a biocide as well as having a blocking effect. However Toole and Barnes (1974) also suggest that the phenol is stripped out of the wood in accelerated leaching tests.

The decay resistance of the particleboard produced using phenol formaldehyde has been studied extensively. Yusaf *et al.* (1999) produced a paper on the biological resistance of PF treated and PF bonded particleboard after natural weathering which is of particular interest. As would have been expected the PF treated wood gave significantly greater decay resistance than the control boards (a 10% resin loading gave a 0.68% loss in a laboratory *C. versicolor* decay test compared with a 12.18% loss in the case of the control samples) however, it was also shown that the increased decay resistance continued after natural weathering tests (Table 1.4).

Resin Loading	*Coriolus versicolor*			*Tyromyces palustris*		
	Percentage WL after weathering (months).			Percentage WL after weathering (months).		
	0	6	12	0	6	12
Control	12.18	14.55	27.27	12.66	14.09	24.09
5%	1.79	5.55	8.18	1.89	2.0	4.91
7.5%	0.87	2.10	3.18	0.34	0.68	2.73
10%	0.68	2.10	2.68	0.25	0.36	2.27

Table 1.4:The weight loss of radiata pine particleboards with low molecular weight PF-resin exposed to decay after weathering.

It can be seen in Table 1.4 that the decay resistance properties of the treated particleboards do decrease with weathering however, the high level of decay

resistance is maintained when compared with the control samples. The increased bio resistance of the PF bonded particleboard is in agreement with other work (Ryu *et al.* 1991) who also show that a simple dipping regime imparts decay resistance and therefore, indicate that an envelope treatment may be enough to protect solid wood.

1.4.3 Urea formaldehyde.

Urea formaldehyde treatment has been found to have beneficial anti-shrink efficiency and anti bio deterioration properties when treating solid wood. However it has been found that urea formaldehyde has a low hydrolysis resistance to long periods of wetting and drying and therefore it has only been recommended for use in low hazard class systems (Desch and Dinwoodie 1996). However the urea formaldehyde resins are much cheaper than other types and are colourless, therefore they were of potential interest to this project.

Urea based compounds can be used as fire retardants in solid wood and therefore there has been an interest in the decay resistance of wood as a by-product of the fire retardancy. Juneja and Shields (1973) modified solid wood with urea formaldehyde and found that it had a decay inhibiting effect. They suggest that the formaldehyde within the resin has an adverse affect on the decay ability of the fungi. It has been noted from the experimentation done by Deka and Saikia (2000) that wood that has been modified to a 33.8 % weight gain with UF resin had an ASE value of 48.5 %. However, once again the cost of the resin must be taken into account if a treatment system were to become viable.

The low ASE value of wood modified with UF resin compared to other resins can be attributed to low resistance to the influence of water and moisture, this is due to the hydrolysis of the aminomethylene link (Dunky 1998). This reaction may also lead to the release of formaldehyde when the wood is in service. It has been shown that the degradation of the UF resin could be initiated by residual acid catalyst left in the wood as well as by the hydrolysis caused by the ingress of

water (Mayer 1983). It has been shown that a neutral glue line has a distinctly improved hydrolysis resistance.

Although urea formaldehyde has been shown to impart some increased dimensional stability to solid wood it has been reported that when low levels of UF resin are impregnated in to timber, fungi will break the UF resin down and it may act as a nutrient source for the fungi (Stolley 1958; Imamura 1993; Curling 1998). However, this may not pose a problem if it is used in conjunction with a biocide.

1.4.4 Melamine formaldehyde and melamine urea formaldehyde

In Section 1.4.3 it was noted that urea formaldehyde is prone to hydrolysis and therefore may not be suitable for preserving timbers in situations above hazard class 2 (without ground contact and protected from weathering), it has also been noted in Section 1.4.3 that urea formaldehyde can be modified with melamine or in fact melamine can replace urea to give a resin with better properties in the presence of water.

In the work of Deka and Saikia (2000) pure MF resin was evaluated along with the PF and UF resins mentioned above. A WPG of 34.1% was achieved with an MF resin. This WPG gave an ASE of 68.23% which was similar to that of PF resin (70.6%). Sailer and Rapp (1997) suggest that out of 4 resin systems tested (fatty acid modified polyurethane emulsion; urea-glyoxal resin; methanol etherificated melamine formaldehyde resin; fatty acid modified alkyd resin emulsion) the melamine resin produced the best ASE and absorption results, an ASE of 25% was reached with samples of *Pinus radiata* regardless of whether the wood was treated to 7.5% or 15% WPG. Rapp and Peek (1999) exposed melamine formaldehyde treated samples to natural weathering and found that, even at low concentrations, this gave good protection against photochemical degradation (due to the blocking of UV light) and staining fungi, however it did

not give protection against cracking and high moisture contents. After a second year of weathering, the pine impregnated with MF resin reached a moisture content of 25% by 160 days which is compared with 166 days for untreated pine. The difference between the untreated and the treated could be due to the ingress of water through the cracking that had taken place over the two years of weathering.

Rapp and Peek (1996) performed decay tests on both *Pinus sylvestris* and the heartwood of *Larix decidua*. They treated 20 x 15 x 15 mm blocks of wood with 7.5%, 15% and 30% resin solution, this resulted in WPGs of 10%, 20% and 40% respectively. The blocks were assessed for decay resistance against *C. puteana* and *C. versicolor* over 16 weeks. It was found that the resin type had a marked effect on the decay of the wood blocks. When the samples were decayed with *C. versicolor* the pine control blocks lost approximately 21% compared to a 2% loss from the blocks treated with a 7.5% (w/w) solution of melamine resin. The resistance to decay with the brown rot *C. puteana* showed similar results; the controls had decayed by 60% whereas the samples that have been treated with the 7.5% solution had a mass loss of only 9% and the blocks treated with a 15% solution had a mass loss after 16 weeks of only 2.5%. These results are in agreement with the work of Sailer *et al.* (1998). Rapp and Peek (1996) note that melamine resin is completely harmless and that it is allowed for the manufacture of children's toys in Germany, therefore they suggest that the mechanism for decay resistance is entirely due to the reduction in the moisture content of the wood.

Pittman, *et al.* (1994) reported that southern yellow pine treated with MF resin had an increased dimensional stability, however they did note that the increase in dimensional stability did not correlate with the WPG. This apparent no correlation between WPG and dimensional stability could be due to where the resin cures in the wood; if the resin is curing in the cell wall (which could happen with lower concentrations and WPG) a high dimensional stability / WPG ratio will be reached compared to the curing of resin in the lumen. This theorem is in agreement with the work of Rapp *et al.* (1999) who suggest that lower

concentrations of MF resins increase the penetration into the cell wall. Rapp suggests in the paper that the resins hamper the spread of fungi through the wood substrate by depositing inert material on to and in to the cell wall and plugging the pit chambers. It is also suggested that the resin prevents the actions of the wood decaying enzymes which are used for the primary breakdown of the cell wall. Sailer, *et al.* (1998) noted that the type of fungi and type of wood did not have much effect on the amount decay resistance imparted to the wood by the resin, this again points to the fact that the resistance imparted to the wood by melamine resin is entirely moisture related.

1.4.5 Other resins.

As has been mentioned earlier (Rapp and Peek 1995) evaluated 30 resins for the treatment of wood and the increase of the anti-shrink efficiency. It has been mentioned that the melamine formaldehyde based resins gave the best anti-shrink efficiencies however there is another resin that should be noted from this paper. Urea-glyoxal resin was impregnated in to wooden blocks (450 x 80 x 25mm) and a retention of 260 Kg/m^3 was achieved which was comparable to the melamine resins. This retention gave a ASE of approximately 22% which again is comparable to the MF resin. However, the Urea-glyoxal will suffer from similar problems as the urea formaldehyde resin in that fungus may use it as a nutrient source.

Work has been performed treating wood with alkyd resin (Smulski and Cote 1984; Sailer, Rapp et al. 1998) it was found to increase the ASE of the timber however, it was noted by Sailer *et al.* (1998) that the alkyd resin promoted decay (compared with control samples) when the wood was subjected to soil bed tests.

1.5 Anhydride modification – A model for cell wall micropore blocking.

1.5.1 Introduction.

The reaction of acetic anhydride and wood has been studied for over 50 years. Ridgeway and Wallington (1946) patented a method catalysed with zinc chloride and just a year after Stamm and Tarklow (1947) patented a process of acetylating wood in the presence of pyridine.

1.5.2 The reaction of Wood and Acetic Anhydride.

The reaction between wood and acetic anhydride is a fairly straightforward one. The anhydride molecule reaction with the hydroxyl group within the wood cell and acetic acid is liberated as a by product (Figure 1.18).

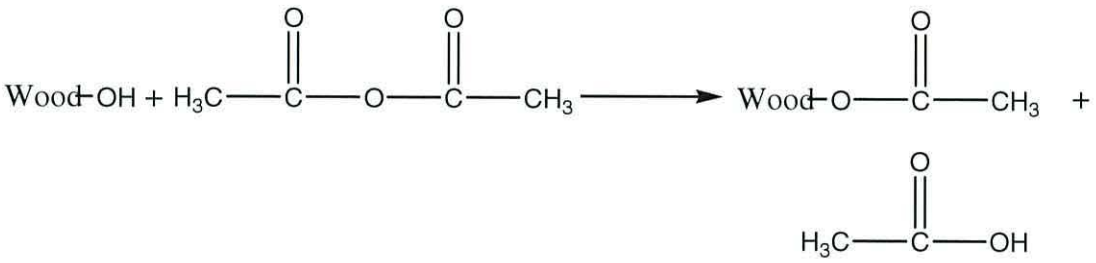


Figure 1.18: Acetic Anhydride modification of wood.

Although the chemical reaction between wood and acetic anhydride is straightforward the actual running of the reaction is complex with many variables affecting the reaction. The variables that affect the reaction are listed below (adapted from Hill (2006));

- Species of timber (density; early wood / late wood ratios).

- Sample preparation (moisture content; extractive content; sample dimensions).
- Reaction chemical. (Neat anhydride or solution; use of catalyst; swelling agent; vapour-phase or liquid-phase reaction; presence of acetic acid).
- Reaction variables (size of reaction; reaction temperature; length of reaction; pre-impregnation of samples; method of applying heat to the reaction medium/vessel; ambient pressure or pressure vessel; quenching of reaction).
- Clean-up procedure (solvent extraction; vacuum with heating; water-soaking; steam stripping; solvent stripping).
- Although there are many reaction variables (Hill 2006) notes that these are generic to all wood / chemical reactions and not just anhydride modification.

The species of wood plays a role in the treatability with any liquids. Kakaras and Phillippou (1996) illustrated this in their 1996 paper in which they treated 24 different Greek timbers with CCB preservative and rated both the sapwood and the heartwood on a scale starting from very permeable to impermeable. The samples were cut to the same size and the moisture content was achieved by air drying and was kept between 15-18%. In their paper Kakaras and Phillippou (1996) rated *Pinus nigra* with a permeable sapwood and a resistant heartwood. (Slahor, Hassler et al. 1997) produced similar results showing differences in permeability between four different Appalachian wood species (yellow poplar, red maple, hickory and beech).

Rowell and Plankett (1988) show that when flakes of wood are treated acetic anhydride does not exhibit differences in treatability between heartwood and sapwood and this is in concurrence with the work of (Rowell, Simonson et al. 1990) who acetylated wood chips, both pure heartwood chips and commercial chips containing sapwood and heartwood and found no difference between the treatability.

However, when the size of the samples is increased the treatability of heartwood and sapwood becomes an issue of permeability rather than reactivity. As has been pointed out earlier there is a difference in the treatability of sapwood and heartwood and the general rule, as shown by Kakaras and Phillippou (1996) is that the heartwood is less permeable than the sapwood. This will be due to the size of the lumen and the laying down of extractive and stored sugars in the heartwood which will inhibit the flow paths in the heartwood. The difference in the treatability of sapwood and heartwood may cause distortion of the modified timber.

1.5.2.1 Sample preparation.

The moisture content plays an important role in determining the extent of reaction of wood with the anhydride molecule. The presence of water in the cell wall will cause the wall to be swollen and therefore it will become more accessible to the anhydride molecules than if the wood was oven dry. However, there will also be a reduction in the amount of anhydride bonding with the cell wall; this is due to the acetic anhydride bonding to the water molecules in the cell and creating acetic acid and acetate bonded to the cell wall. Water in the lumen does not give any advantages to the reaction between wood and anhydride molecules. Beckers and Militz (1994) reacted anhydride with wood of varying moisture contents (from 0%-26%). It was noted that the WPG, when timbers were reacted for 6 hours, decreased as the moisture content increased. However it was noted that even with the moisture content at 20% (which is around fibre saturation point) a reaction still took place and a WPG of 8% was achieved. Rowell *et al.* (1990) reported the reaction of wood at low moisture contents (0%; 4.9% and 7.3%) and it was shown that there was no change in weight gain with the increase in moisture content. However it was shown that there was an increase in the rate of reaction with an increase in moisture content.

The presence of extractives in the wood also has an effect on the reactivity of the wood and the reproducibility of WPGs. In laboratory tests the wood is generally extracted using 4:1:1 (Toluene : Ethanol : IMS) to remove the extractives

(Rowell 1983; Rowell, Simonson et al. 1990; Hill and Hillier 1999; Hill, Forster et al. 2004).

The reaction of the cell wall with an anhydride requires the cell wall to be accessible to the anhydride itself, therefore the sample dimensions have a great impact on the weight percent gain of the wood.

The importance of the influence of the size of the sample needs to be reiterated in the context of anhydride modification. The rate flow of reagent in to a wood sample is determined by the accessibility of the flow pathways and therefore the longer the flow pathways the slower the rate of flow along these pathways. The drying of the wood also has an effect in these pathways, pits become aspirated and thus the rate of flow is less. It is not uncommon in both the preservation field and the chemical treatment field for big samples to be treated with an envelope treatment, i.e. the outer portions of the wood are treated but the inside remains untreated. Although the theory of an envelope treatment is that if the fungi have to go through a barrier of treated wood before reaching untreated wood there will be an increased decay resistance, it may actually lead to a decrease in decay resistance. This is due to an increased MC in the centre of the sample compared with the outer, treated portion; this will lead to a decrease in dimensional stability and thus decay resistance will fall due to the high potential of cracking.

1.5.2.2 Reaction chemical.

The reaction chemical used has a great impact on the rate of reaction and the final WPG.

The use of a catalyst plays an important role in the chemical treatment of wood. As was mentioned at the beginning of the chapter, pyridine was used in the reaction with acetic anhydride. Pyridine has a two fold effect on the reaction. Firstly it swells the wood and therefore makes the cell wall more accessible to the anhydride molecules. Secondly the pyridine is a stronger base than the OH group and therefore it acts as a proton accepter, accepting a proton from the –OH

group making it $-OH^-$ and therefore more readily accepting of the positively charged anhydride group. Although the use of pyridine as a catalyst increases the reaction rates it is very toxic and can cause liver damage as well as affecting renal, neurological pathways (National Safety Council 2005), therefore the commercial use is very unlikely and handling in the laboratory must be done with extreme care. Other catalysts have been used, Ridgeway and Wallington (1946) catalysed the reaction with zinc chloride, trifluoroacetic acid and magnesium perchlorate were used as catalysts to aid in the lowering of the reaction temperature (Arni *et al.* 1961).

If the solution as a whole reaches a certain acidity (this depends on the species of timber) the cell wall may start to degrade, the degradation begins in the region of pH 4. The overall acidity is affected by both the initial solution acidity and the production of acetic acid as the reaction progresses. If the acidity is kept low enough not to degrade the cell wall the acetic acid can act as a swelling agent and therefore increase the rate of the reaction (Hill, 2006) and a slight increase in reaction rate has been found with acetic acid content of up to 15% after which the rate begins to decrease Rowell, *et al.* (1990).

1.5.2.3 Reaction variables.

The temperature is one of the reaction variables which has a major effect on the reactivity of anhydrides with wood. The increase of temperature gives an increase in the rate of the reaction, however an upper temperature of 120°C is generally imposed as this is the temperature at which wood cell degradation starts to occur (Hill 2006).

If when wood is treated with anhydrides the limiting factor is generally the diffusion gradient and the time it takes for the reagent to diffuse into the cell wall, this will lead to a lag phase in which the reagent has not entered the cell wall and therefore there is no reaction taking place. This lag phase is prevented by pre impregnating with anhydride, as it would be with a standard preservative, before the heat is applied to the wood. If pre-impregnation has taken place then the rate of the reaction is fast when compared with non pre impregnated samples.

The rate then trails off as the reaction becomes governed by the diffusion of anhydride in and acid out of the cell wall (Hill *et al.* 2000).

There is a relationship between the length of time the wood is reacted with the reagent and the WPG gained by the end of the reaction. As the reaction time increases the WPG will increase, however, as has been mentioned earlier, the relationship between time and WPG (or OH groups substituted) is not a linear one, it is more fitted to a inverse log curve (1/log), this can be seem in Figure 1.19, recreated from (Hill and Hillier 1999).

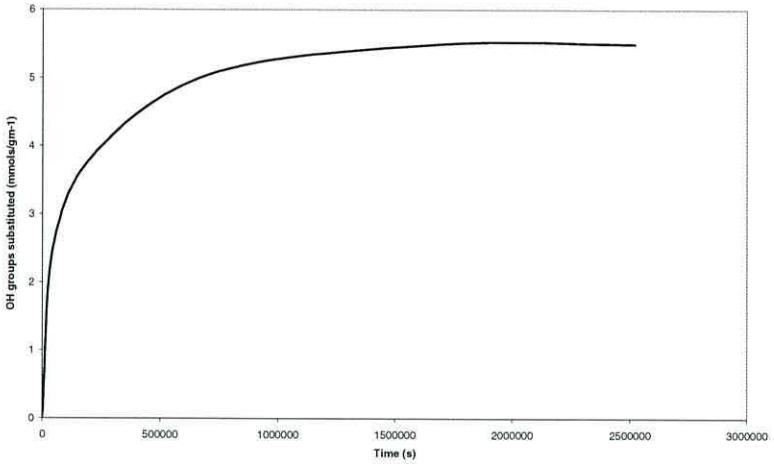


Figure 1.19: The WPG vs. Time for the reaction of *Pinus nigra* and acetic anhydride (Hill and Hillier, 1999).

1.5.2.4 Clean up procedure.

To complete the treatment the blocks must be cleaned of all excess anhydride and also of the acetic acid. This can be done in a variety of ways. The way generally employed in Bangor is to re-extract the blocks with a 4:1:1 solution (Toluene : Ethanol : IMS) and strip out any excess chemicals left in the wood (Hill and Jones 1999; Hill and Jones 2002; Hill and Mallon 2003; Hill, Forster et al. 2004; Hill and Ormondroyd 2004; Hill, Papadopoulos et al. 2004; Hill, Ormondroyd et al. 2005). Other methods of cleaning the wood have been employed, Singh, *et al.* (1992) post-treated the blocks with aniline which mops

up the acetic acid. Goldstein, *et al.* (1961) used a vacuum system at 105°C to 120°C to recover the reagents and by-products from timber; however this system is dependent on the size of the samples being treated. Beckers and Militz (1994) used a system of heating under vacuum then rinsing with water to turn excess acetic anhydride to acetic acid, then drying for ten days using an increasing temperature profile from 40°C to 100°C. More recently Bongers and Beckers (2003) used a steam post treatment to clean the blocks of wood before a final drying regime.

1.5.2.5 Proof of bonding and permanency of acetic anhydride with wood.

Rowell (1983) gave three criteria for accessing the permanency of chemical component s when they have been entered into the cell wall.

- Increase in the volume of the sample.
- Resistance to leaching of the chemical reagent.
- Infrared analysis.

1.5.2.5.1 Increase in volume of sample.

The increase in dry volume is an indication of cell wall bulking. Rowell and Ellis (1978) produced data that shows increased weight gain gives a volume increase, which in turn is approximately the same as the calculated volume of reagent added to the wood (Table 1.5).

Treatment	WPG	Increase in volume of wood	Calculated Volume of Chemical Added.
Acetic Anhydride	17.5	3.0	2.9
	19.5	3.6	3.3
	22.8	3.9	4.0

Table 1.5: Volume change in southern pine upon treatment with acetic anhydride (Rowell and Ellis 1978).

Although this method shows that the chemicals have entered and bulked the cell wall it does not prove the permanency of the chemical and whether it has bonded to the cell wall. Rowell and Ellis (1978) also treated wood with methyl methacrylate. It was found that although the WPG increased significantly the volume did not and therefore it can be determined that the reagent stayed within the cell lumen (Table 1.6).

Treatment	WPG	Increase in volume of wood	Calculated Volume of Chemical Added.
Methyl methacrylate	58.0	0.6	7.6
	91.4	0.9	10.1

Table 1.6: Volume change in southern pine upon treatment with Methyl methacrylate (Rowell and Ellis 1978).

1.5.2.5.2 Resistance to leaching of the chemical agent.

There are two main types of leaching that occur with in the laboratory environment; one is chemical leaching and the second is simulated weathering.

Chemical leaching has already been mentioned as a method for the cleaning up of the timbers after they have been treated (section 1.5.2.5). If the chemical reagent has not bonded to the cell wall then it will leach out under the conditions of a solvent extraction resulting in a high weight loss, just as the non-reacted regents are stripped out of the wood in the clean up procedure.

Another, more realistic test, is the water soak test; there are a variety of standard water soak tests which are appropriate to check that the chemical reagent is bonded to the wood enough to withstand weathering. The British standard BS EN 84:1997 (BSI, 1997) is the UK standard leaching procedure which is undertaken before any biological testing of preserved timbers. The CEN

committee has drafted a leaching standard that replicates more closely real life (CEN, 2004). The standard calls for the wood to be intermittently dipped in water for short lengths of time therefore stimulating rain fall.

The leaching with water will show whether bonds have been made between the wood and the reagent and also whether the bonds are strong enough to withstand weathering, if this was not the case the water would contain anhydride molecules, which can be easily identified with the use of NMR.

1.5.2.5.3 Infrared Analysis.

Infrared analysis can give an indication to whether the reagent has bonded to the wood. Infrared analysis analyses bonds and therefore if the reagent has bonded with the wood the bonds in the wood will have changed. The change in the spectra will occur due to the replacement of –OH groups with the chemical reagent. (Rowell 1982) shows that there is a distinct change in the infrared spectrum at a wave length of approximately 1650 to 1730 cm^{-1}. Carbonyl stretching groups occur in this region of the graph and this observed change is due to the formation of bonded acetyl groups (Figure 1.20).

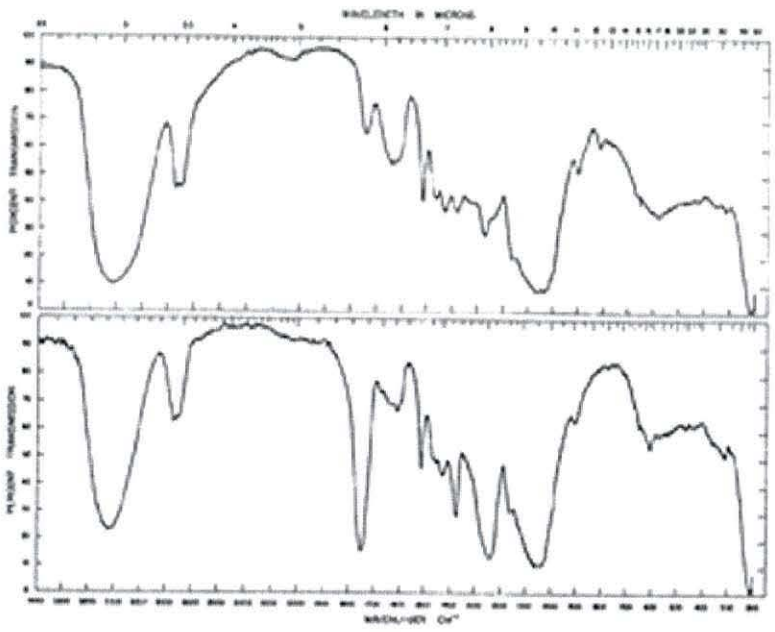


Figure 1.20: Infrared spectra for acetic anhydride treated and non treated southern pine.

1.5.3 Reactivity of the cell wall

Rowell (1982) stated that the three major components of the cell wall have different reactivity rates with lignin being the most reactive, followed by hemicellulose and then cellulose. This was also show by Callow (1951) with cellulose and lignin isolated from jute and cellulose, hemicellulose and lignin isolated from wood Rowell *et al.* (1994). Rowell (1982) reported that lignin is completely reacted at 20% weight gain. Distribution of the anhydride through the cell wall is dependent on the reaction variable mentioned above. If the cell wall is pre-impregnated then it is more likely that all the three components will be reacted (Hill 2006).

1.5.4 The effects of acetylation on the Dimensional stability of wood.

Papadopoulos and Hill (2003) recorded changes in equilibrium moisture contents at various levels of relative humidity after modification with acetic anhydride.

The results, shown in Table 1.7 show that at any given relative humidity the EMC decreases with the increase in the WPG of the reacted wood. (Chang and Chang 2002) show that it is the substitution of the hydrophilic -OH groups with the hydrophobic anhydride groups that give the wood its increased dimensional stability.

Weight Percent Gain	Relative Humidity					
	12%	23%	44%	55%	76%	93%
0	2.59	4.35	7.27	8.49	13.01	19.29
5.2	2.19	3.64	6.01	7.25	10.87	16.01
11.4	1.91	3.07	5.27	6.35	9.62	15.01
15.8	1.63	2.54	4.39	5.16	7.77	12.02
19.6	1.24	2.13	3.74	4.43	6.71	10.37
22.5	0.99	1.73	3.28	3.91	6.05	9.54

Table 1.7: Mean values for experimentally derived EMCs at various levels of RH for acetic anhydride modified Corsican pine.

Baird (1969) shows that as the WPG increases with anhydride modification the anti shrink efficiency of white pine also increases. Baird also noted that volumetric swelling of cross sections of timber were reduced by up to 75% with acetic anhydride. These results are similar to the results from the work of Goethals and Stevens (1994) and Hill and Jones (1996).

Hill and Jones (1996) reacted wood with acetic anhydride and other anhydrides with larger actyl groups. The researchers suggest that the stabilisation that has taken place is purely due to the bulking effect of the anhydride on the cell and not due to the amount of hydroxyl group substitution that takes place. Chang and Chang (2002) show that it is the size and volume of the anhydride molecules that have an effect on the dimensional stability of the treated wood.

1.5.5 Biological resistance of anhydride modifed woods.

The biological resistance of acetylated wood has been assessed for both solid wood and for acetylated wood products.

Chow, *et al.* (1994) acetylated aspen and southern pine chips for the use in composite boards. The chips were acetylated to 23% WPG and then were pressure refined to a fibrous state. Boards were produced containing 3% and 7% phenol formaldehyde resin. The boards were then tested in accordance with ASTM method D2017 (ASTM 1991) with the following fungi; *Gleophyllum trabeum, Poria placenta, Polyporus versicolor.* It was found that the acetylation of the fibres prior to the production of the boards gave an increase in decay resistance to both the 3% and 7% resinated boards (Table 1.8).

Fungus	Wood Species.	3% Resin		7% Resin	
		UT	T	UT	T
G. trabeum	Aspen	47.0	1.7	30.0	1.0
	S. pine	44.6	0.9	36.9	0.4
P. placenta	Aspen	50.8	1.1	40.8	1.1
	S. pine	50.0	2.5	34.3	2.5
P. versicolor	Aspen	80.0	2.2	60.9	2.9
	S. pine	18.1	2.3	21.3	2.2

Table 1.8: Average weight loss for composite boards made with anhydride modified fibres (T) and control fibrers (UT) (chow *et al.* 1994).

It can be seen that the acetylation of the fibres results in a product that is highly resistant to fungal attack, and it was noted by Chow, *et al.* (1994) that the aspen treated blocks were not as resistant as the southern pine.

Hill, *et al.* (1998) acetylated coir fibres, to two weight gains (labelled, high and low). These were then exposed to un-sterile soil bed tests for up to 20 weeks before being subjected to strength tests. It was found that after 8 weeks the unmodified samples were too fragile to be tested. However the treated samples

retained 80% of their strength after 20 weeks exposure, thus showing the significant decay resistance afforded to the fibres by the modification.

Peterson and Thomas (1978) modified small blocks (10mm x 10mm x 5mm) of yellow poplar, loblolly pine and green ash. The blocks were modified for 1,5 and 29 hours. They were washed to eliminate the acetic acid from the blocks dried and then weighed. The blocks were then steam sterilised and transferred into soil bins previously inoculated with *G. trabeum* or *C. versicolor* and stored at 25°C and 70% RH for a period of 6 weeks (in accordance with AWPA M10-74). The results of the decay tests can be seen in Table 1.9.

Treatment	Weight Loss (%)					
	G. Trabeum			*C. versicolor*		
	Poplar	Ash	Pine	Poplar	Ash	Pine
Control	66.8	63.7	61.0	33.6	40.8	28.0
1 hour	10.3	3.7	6.7	3.3	7.9	1.6
5 hour	2.6	2.4	2.6	3.1	6.6	1.4
29 hour	1.6	1.4	1.7	2.9	6.0	1.1

Table 1.9: Average weight losses for brown rotted and white rotted acetylated wood. (Peterson and Thomas 1978).

It can be seen that, as with fibre board made from acetylated fibres, the acetylation creates a vast improvement in decay resistance of all the timbers to all the fungi, even at the low levels of acetylation.

Peterson and Thomas (1978) show that the protection from fungal decay not due to fungitoxic nature of the anhydride. They noted that the fungus grew out of the wood onto the agar on the culture plates. Table 1.10 shows the surface growths and viability of both brown and white rot fungi in acetylated wood. As can be seen from the table only the viability of white rot on pine is diminished and then only at high levels of acetylation.

The conclusions of Peterson *et al.* (1978) are similar to those of Suttie *et al.* (1997). It is noted in this paper that the bio resistance must be, at least in part, due to the lower moisture content of chemically modified wood. Suittie *et al.* modified blocks with actetic, propionic, butyric, hexanoic and succinic and hydrides and found that there is no consistent trend which indicated an advantage in using one anhydride over another. However it was indicated that the smaller molecule anhydrides gave a better final product that the larger molecule anhydrides.

Species	Acetylation level	Fungi	Viability (%)	Surface growth
Poplar	1 hour	White Rot Fungus	100	Sparse
	5 hour		100	Sparse
	29 hour		100	Very Sparse
Ash	1 hour	White Rot Fungus	100	Sparse
	5 hour		100	Sparse
	29 hour		100	Very Sparse
Pine	1 hour	White Rot Fungus	100	Sparse
	5 hour		40	Sparse
	29 hour		0	Very Sparse
Poplar	1 hour	Brown Rot Fungus	100	Moderate to Abundant
	5 hour		60	Moderate to Abundant
	29 hour		40	Moderate to Abundant
Ash	1 hour	Brown Rot Fungus	100	Moderate to Abundant
	5 hour		100	Moderate to Abundant
	29 hour		100	Moderate to Abundant
Pine	1 hour	Brown Rot Fungus	100	Moderate to Abundant
	5 hour		100	Moderate to Abundant
	29 hour		60	Moderate to Abundant

Table 1.10: Surface growth and viability of brown and white rot fungi in acetylated wood.

Once again it has been reported (Suttie *et al.* 1997) that the cyclic anhydride does not perform as well as linear anhydrides. Succinic anhydride gave wood an increased potential for attack by soft rot and suggested that the six membered ring of the succinic can easily be assimilated into the metabolism of soft rot.

Forster *et al.* (1997) discussed the influence of the structure of the anhydride on the properties of the modified wood. It is reported that the cyclic anhydrides do not reduce the number of hydrophilic groups in the modified wood, this is caused by the breaking open of the cyclic ring on modification and it is suggested that this could lead to the encouragement of the bulk flow of water even at low moisture contents.

Forster also notes that high levels of succinic anhydride modification damaged the wood and that treated block were prone to falling apart. Such damage may lead to the exposure of previously unavailable hydroxyl groups.

Within this study acetic anhydride will be used as a model for cell wall blocking as a way to prevent decay and the decay resistance of the resin treated wood will be evaluated against the anhydride treated to show that the resin is acting as a benign agent against decay and not as an active one.

2 Characterisation of biocide

2.1 Introduction

The work described in this thesis looks at the use of a novel biocide as a wood preservative and how to protect this in the timber. The work described in this chapter is the characterisation of the biocide itself. This work is needed to ensure that the biocide will enter the cell wall and to what extent this will occur. It will become apparent in later chapters that it is essential that the biocide and its protection enter the wood cell wall, thus the protection being responsible for an alteration in the FSP of the timber and the biocide protecting the wood from fungal decay that happens due to breaches in the protection.

The biocide is firstly modelled using Chemdraw 3D and the theoretical size of the molecule is assessed. The biocide will then by characterised by diffusing it through different size filter membranes, this will show the size of the molecule within its sphere of salvation and within its complexed state.

2.2 Characterisation of the Biocide

2.2.1 Methods

2.2.1.1 Analysis by computer modelling

The chemical formula for the biocide used in this thesis was supplied by the manufacturers. Chemdraw 3D was used to produce a computer model of the molecule and its sphere of solvation.

2.2.1.2 *Analysis by diffusion and forced diffusion through known pore size membranes*

The two types of biocide supplied by the manufactures, the pure biocide (dissolved in methanol) and the emulsion, were diffused through membranes of known pore sizes. This gave an indication to the size of pores in the wood that the biocide could access.

2.2.1.3 *Diffusion through membranes at ambient pressure*

A closed system of tubes was fabricated in the workshop as illustrated in Figure 2.1.

Figure 2.1: The diffusion system

One half of the system was filled with the appropriate solvent (either distilled water or methanol) and the other half was filled with biocide. The membrane was then placed between the two halves and the system sealed with parafilm and clamped shut. The systems were then left at ambient temperature and moisture content for 4 weeks and then the solvent side was analysed for the presence of the biocide using HPLC.

Table 2.1 shows the systems that were studied.

Biocide	Solvent	Pore Size of membranes used
Biocide solid	Methanol	400nm
		200nm
		100nm
Emulsion supplied by manufacturer	Distilled water	400nm
		200nm
		100nm

Table 2.1: Diffusion systems set up to evaluate the size of pore the biocide will enter at ambient pressures.

2.2.1.4 Analysis of pore size that the biocide will enter while under pressure

A system was set up using a glass syringe and a series of syringe filters. The syringe was depressed using a screw threaded pump to ensure that a constant pressure was been applied to the syringe. The syringe was filled with the biocide and then the screw was turned at a constant rate. The filtrate was collected and analysed via HPLC to ascertain whether the biocide had come through the filter or just the solvent. Table 2.2 shows the filter systems that were used in this experiment. The sizes of the pores in the filter membrane are much larger than that of the biocide molecule, however these were used so that an assessment of size of the complexed biocide molecule could be made.

Biocide	Size of membranes used
Biocide in methanol	200nm
	20nm
	10nm
Emulsion supplied by manufacturer	200nm
	20nm
	10nm

Table 2.2: Size of filter used for the forced diffusion experiment.

2.2.2 Results of characterisation

The properties of the molecular model of the biocide molecule are shown in Table 2.3. Figure 2.2 shows a graphical representation of the biocide from which the dimensions were calculated.

Dimension	Average Size nm
Length	1.01
Width	0.78
Depth	0.43

Table 2.3: The dimensions of the biocide molecule

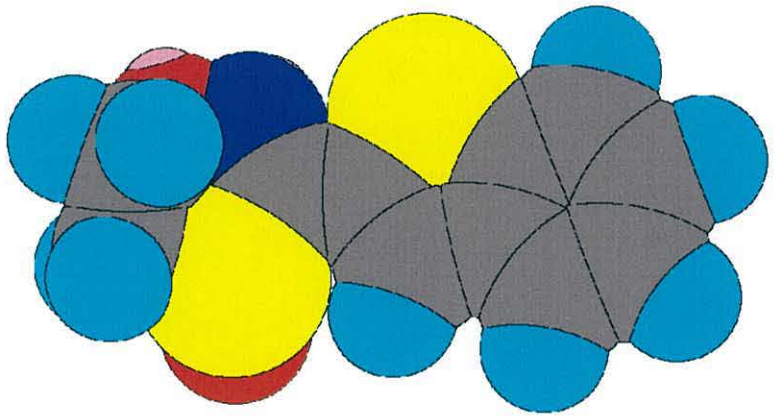


Figure 2.2: The biocide molecule

The sizes shown in Table 2.3 show that the molecule of biocide is small enough to enter the wood cell wall. However, each molecule of biocide will have a sphere of solvation associated with it when it is in a solution and this will increase the apparent size of the molecule.

The ability of the biocide to enter the cell wall when in solution was assessed by the using membrane filters of known porosity to simulate the wood cell wall. Table 2.4 shows results of the membrane filter experiment, it shows that the

biocide delivered in methanol will enter the cell wall, by diffusion; however the stabilised biocide emulsion (as supplied by the manufacturer) is too large to enter the cell wall. The experiment was repeated using a syringe to simulate pressure impregnation. This experiment again found that the biocide emulsion would not enter the cell wall, even when pressure was used to force the biocide to the cell wall quicker.

Type of Filtration	Size of Filter	Biocide in Methanol	Biocide in Emulsion
Diffusion	400 nm	✓	✓
	200 nm	✓	✓ (very slow)
Forced	200 nm	✓	✓
	20 nm	✓	×
	10 nm	✓	×

Table 2.4: The results of the filtration experiments

2.2.3 SEM EDAX analysis of biocide retention

2.2.3.1 Introduction

The location of the biocide within the cell wall is of great importance to the study if the biocide is to be locked in the cell wall then it obviously must be located there in the first place. SEM EDAX was used to determine whether the biocide had entered the cell wall via the microvoids or whether it was to be found solely adjacent to the cell wall. Elemental analysis was possible due to the presence of sulphur in the biocide. Sulphur was found not to be present in the untreated wood and therefore the only sulphur in the treated wood would be from the biocide.

2.2.3.2 Treatment

Small cylinders similar to those used in the helium pycnometry experiments were vacuum impregnated with two variants of the biocide 1, the pure biocide dissolved at 5% in methanol and 2, the ready made emulsion diluted to give 1.5% active ingredient with distilled water. The samples were submerged in the treatment fluid and held in place with weights. They were then held under vacuum for 2 hours to ensure that there was full uptake of the liquid in to the cells. The samples were then placed in a fume hood and were air dried prior to oven drying at 105°C.

2.2.3.3 Preparation of samples for SEM microscopy

After the samples were dried they were impregnated with a slow setting epoxy resin catalysed using hydrogen peroxide. Each sample was fixed to the bottom of a 6cm diameter foil dish using blue tack. 10ml of the epoxy resin was then poured on to the sample and the hardening agent was added (approximately 3 drops to each 10ml). It was ensured that the resin and the hardener were both free of sulphur. The resin was then stirred before the dish was placed in a vacuum desiccator and a vacuum applied. The vacuum was applied for 4 hours to ensure that the resin penetrated the lumen of the sample.

When the vacuum cycle was complete the samples were dried in an oven at 55°C until the resin was set. Once the samples had cooled the wood was cut out of the resin using a dowel cutter. The top surface was then sanded with 4 grades of sand paper, 2 grades of polishing paper and a sheet of diamond paper until the resin was just above the wood and then sanding continued to remove the top millimetre of the sample to ensure that the biocide patterns shown were not surface absorption. The base of the sample was also sanded to provide a smooth even surface.

Once the sanding regime had been completed the sample was fixed to a carbon SEM stub with carbon tape. The stubs were then coated with carbon to increase the surface conductivity of the samples. Carbon was chosen instead of the usual gold coating because gold has a x-ray peak very close to sulphur on an EDAX spectrum and therefore it was thought that a high amount of gold would 'swamp' the spectra and the data for the biocide would not be found.

Once the samples were coated they were kept in a moisture-free environment and viewed using a Hitachi S-520 SEM with an Oxford Instruments ISIS -3 EDAX detector. Several types of images were obtained. A line spectrum was traced across the cell walls to show regions of increased sulphur, also composite images were taken which mapped the concentrations of sulphur onto an image of the cell.

Ten samples were analysed for both types of biocide (emulsion and solution in methanol).

2.2.3.4 Results

The visualisation of the biocide within the wood sample showed that the biocide was entering the cell wall.

Figure 2.3 shows the location of the biocide in the cell wall when the biocide is being delivered using a methanol carrier. The green colouring on the image depicts the sulphur marker within the biocide and it can be clearly seen that there is cell wall penetration.

Both line analysis and spot analysis confirmed that the cell wall was higher in sulphur, and thus biocide, than the lumen. Figure 2.4 shows a typical spot analysis of lumen in a treated sample of wood (treated with biocide in a methanol carrier), as can be seen the sulphur content is within the background of the trace. Figure 2.5 shows a spot analysis of the cell wall in a methanol / biocide treated

piece of timber. It can be clearly seen that the sulphur peak is above the baseline and shows a significant increase in sulphur and thus biocide.

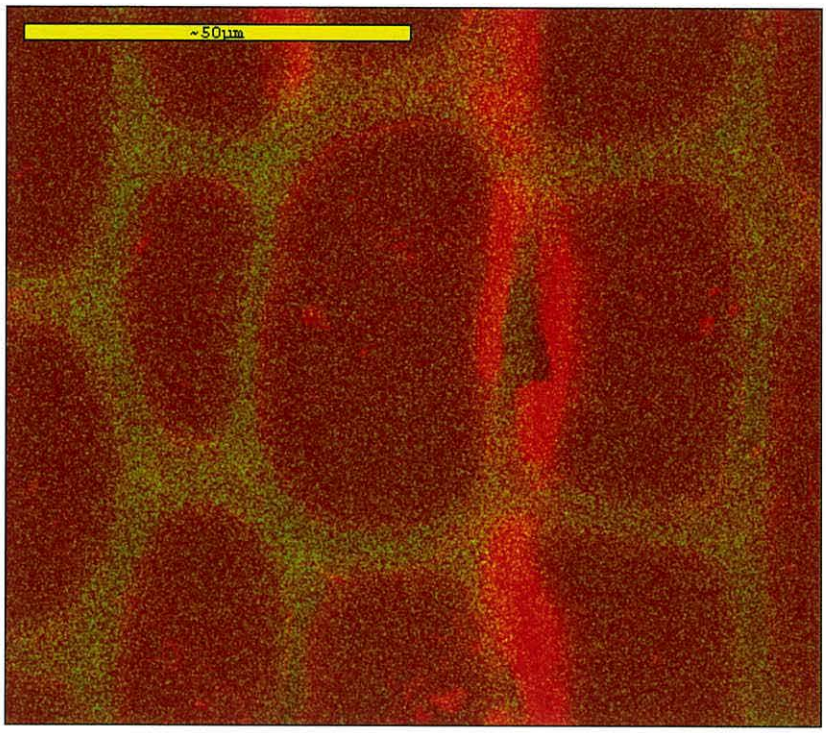


Figure 2.3: The visualization of the biocide within the cell wall after treatment with the biocide in a methanol solution (green dots represent the sulphur).

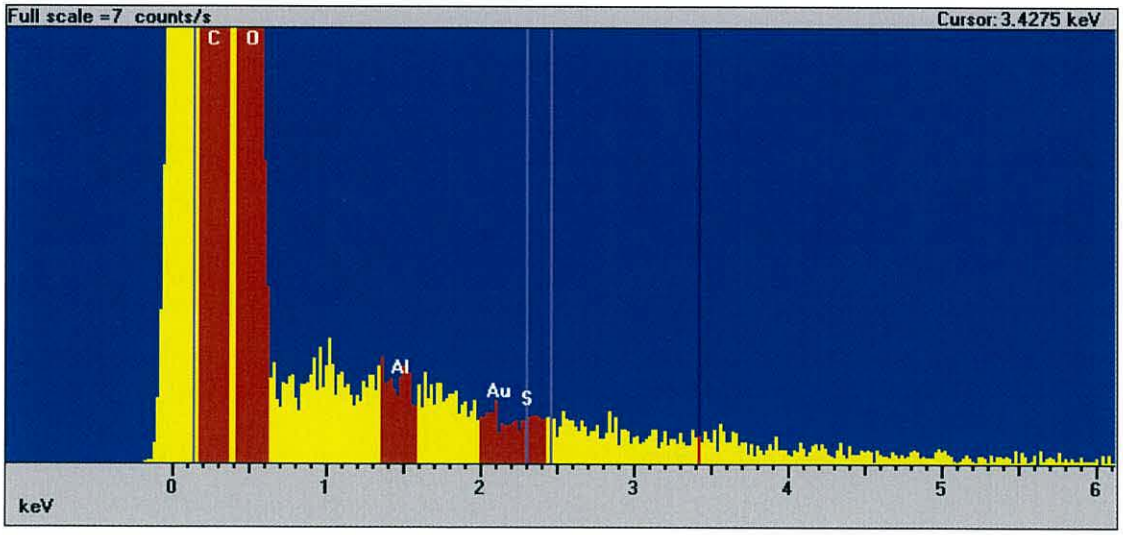


Figure 2.4: Spot analysis of a spot in the lumen of the treated wood

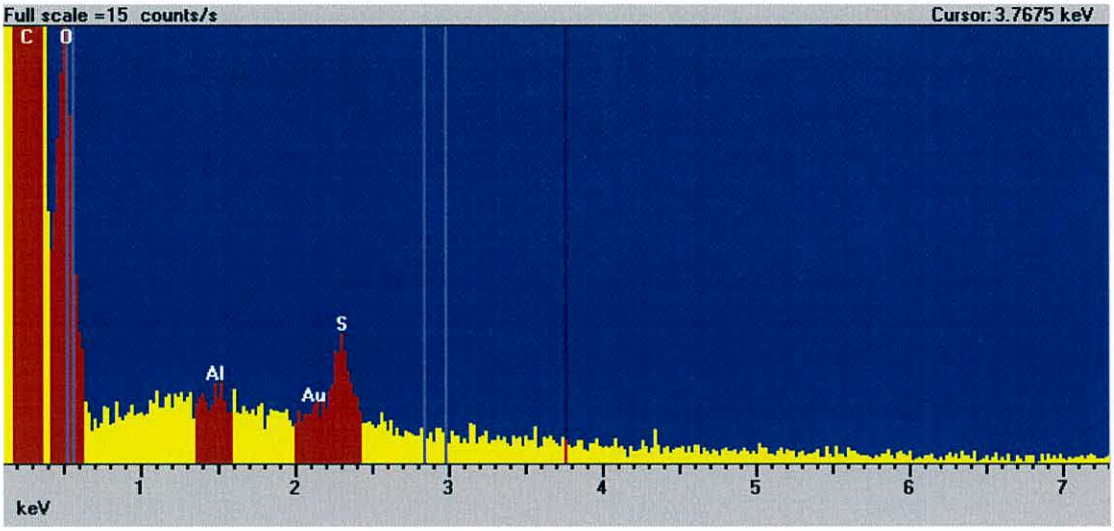


Figure 2.5: Spot analysis of the cell wall of the treated wood

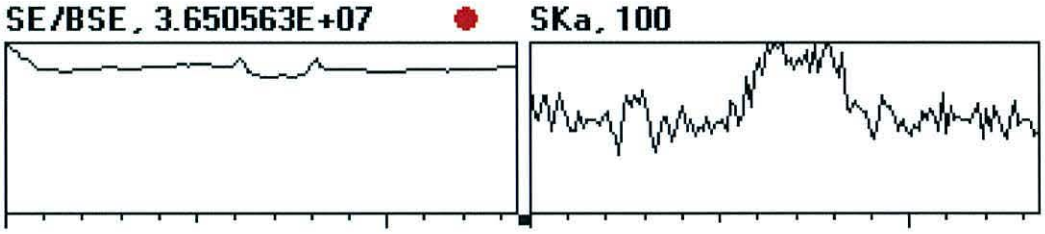


Figure 2.6: [left] A line scan of the sulphur trace in a treated sample of wood & [right] the surface profile of the timber sample.

Figure 2.6 shows the line scan of a piece of biocide treated wood. The biocide was delivered as an emulsion. The right hand graph shows the surface profile of a cell of wood, the rise in the centre of the graph depicts the cell wall. It can be seen in the left hand graph that the sulphur rises in two peaks in the area depicting the edges of the cell wall. This shows that the preservative is located on the cell wall surface but does not penetrate the cell wall; this is due to the biocide molecules being too large to fit through the microvoids.

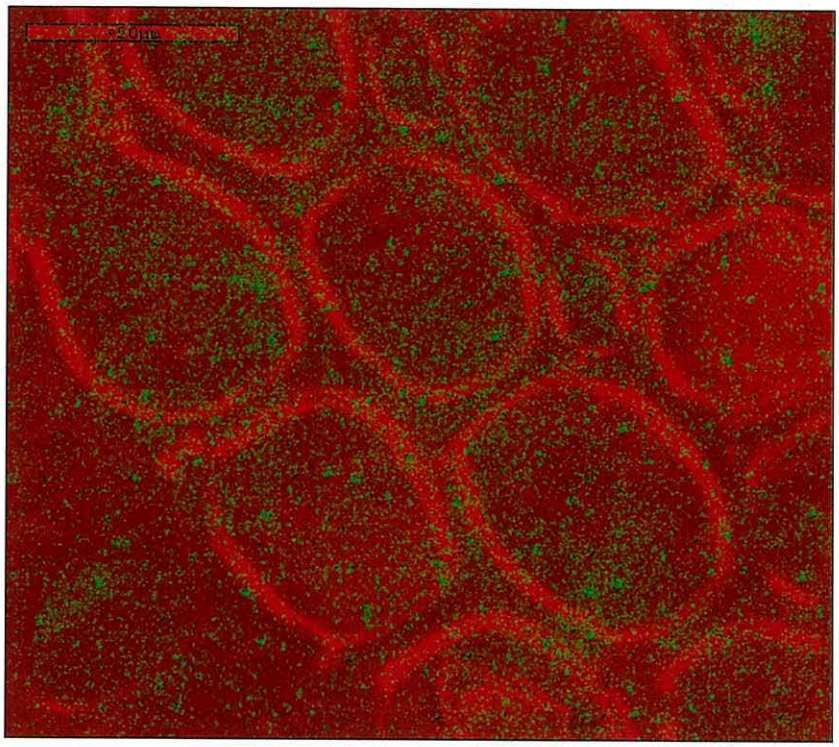


Figure 2.7: The visualization of the biocide within the cell wall after treatment with the biocide in a supplied emulsion.

Figure 2.7 shows that when the biocide was delivered in an emulsion (supplied by the manufacturer) it is not able to penetrate the cell wall. The scatter of the sulphur throughout the sample is probably due to the biocide being pushed out of the lumen as the sample is impregnated with epoxy resin. There is, however no evidence that the biocide has entered the cell wall as shown in Figure 2.3, this was found in all ten samples analysed.

2.2.4 Conclusion of section

The results showed that the biocide when delivered as a solute in methanol will enter the cell wall through the microvoids. This shows that the biocide in this form can be locked into the cell wall. This was seen in both the membrane diffusion experiments and with the SEM EDAX of the treated wood samples.

However the emulsion of the biocide will not enter the cell wall, this is due to the molecules and their sphere of solvation being too large.

The work carried out in this thesis will focus on protecting the biocide with in the cell wall and aid the protection of the wood with the use of resin systems.

3 Decay Resistance Tests of Wood Treated with Resin and Resin Combined with a Biocide in Accordance with EN113 Protocols.

3.1 Introduction

This chapter reports on investigations into the modification of wood with resin and the novel biocide as described in Chapter 2. The chapter will show the effectiveness of the resins alone as a treatment against decay and the implications of the addition of the biocide in two different ways, co-delivery and sequential delivery. The problems with resin systems for decay prevention will also be discussed within this chapter. Finally this chapter will recommend the treatments that should be used in any future scale up trials (which are outside the remit of this work).

3.2 Method

3.2.1 Sample Preparation

Samples of *Pinus nigra var maritima* (Corsican pine) and *Fagus sylvatica* (European beech) were prepared for this experiment. For each species samples were cut with the following dimensions 15 x 25 x 50mm (R,T,L).

- All of the samples were extracted in a Soxhlet extractor using a solvent mix of toluene acetone and methanol (4:1:1 in ratio). All samples were extracted for 6 hours to ensure that all the soluble extractives were removed from the samples. Samples were then air dried for 24 hours and then oven dried at a temperature of 105°C for 8 hours. All samples used in the experiments were selected for the straight orientation of the growth

rings and for the consistency of growth ring spacing. All samples were labelled appropriately using pencil as to avoid the loss of labels when the samples were treated.

3.2.2 Resin preparation

A Brooks viscosimeter was used to determine the viscosity of the resins prior to the treatment of the block samples. The solids content of the resin was also checked. This was achieved by accurately weighing exactly 1g of resin in a dish and then heating it for 4 hours in an oven at 105°C. The resin was then reweighed to give a weight of the solid. A solid content could then be calculated using Equation 3.1. This was repeated three times and a mean value taken.

$$SC = \left[1 - \left(\frac{ww - dw}{dw}\right)\right] \times 100 \qquad (3.1)$$

The viscosities and the solids contents of each resin are recorded in Table 3.1. If the viscosity or resin content varied from the manufacturers stated values it was rejected and a new resin used.

Resin	Viscosity	Solids content
Urea formaldehyde	150	63%
Melamine formaldehyde	127	61%
Melamine urea formaldehyde	184	61%

Table 3.1: Resin characteristics

3.2.3 Sample treatment.

3.2.3.1 Treatment with resin only

Samples were weighed, in grams to 4 DP and measured (in mm) with a micrometer to 3 DP. The samples were treated in the pilot preservation plant at SENR, Bangor University. The samples were immersed in the resin and a vacuum was applied to the samples, using a rotary vacuum pump, for 1 hour and then released. Then 8 bar of pressure was applied for two hours. The blocks were oven dried at 105 °C for 8 hours. The blocks were then re-weighed and re-measured so that weight gain could be calculated.

3.2.3.2 Resin and Biocide in a methanolic solution

As with the resin only samples the EN113 samples were treated in the pilot scale preservation plant. The samples were treated with a 0.05% (w/w) solution of biocide in methanol. A vacuum was applied to the samples, using a rotary vacuum pump for 1 hour and then released. 8 bar of pressure was then applied on to the blocks for two hours. The blocks were then air dried for 24 hours and then subsequently oven dried at 105°C for 8 hours. The blocks were then retreated with the resin. Again, a vacuum was pulled on to the samples for 1 hour and then released and 8 bar of pressure was then applied on to the blocks for two hours.

3.2.3.3 Resin with the biocide in emulsion

The resins were mixed with the biocide emulsion (as described in Chapter 2) to give a 0.05% (w/w) level of active ingredient. Care was taken to ensure that the emulsion did not flocculate when mixed with the resin and that the addition of the emulsion to the resin did not affect the curing of the resin. Gel time tests, at

100 °C, were used to analyse whether there was an adverse effect on the curing of the resin and it was found that they were comparable with the resins alone. The samples were then treated in the pilot scale preservation plant with a vacuum being pulled on the sample for an hour and then released, after which a pressure of 8 bar was applied for two hours.

3.2.4 The decay tests

The European standard BS EN113:1997 is a method for determining the toxicity values of wood preservatives, introduced to wood by impregnation, against basidiomycetes cultured on an agar medium. Three fungi were used to decay the timber, *Coniophora puteana* (Schumacher ex Fries) Karsten (BAM 15), *Coriolus versicolor* (Linnaeus) Quélet (CTB 863A), and *P. chrysosporium* (S179).

The fungi was grown on 75ml of 4% malt agar. The agar was prepared in batches of 400 ml; 8 g of agar and 16 g of malt were added to 400 ml of distilled water, the agar was then microwaved at 500 W for 5 minutes. The agar was shaken half way through the heating and then left in a water bath at 50 °C for 10 minutes to ensure that the agar had melted. The agar was then measured into squat jars (65 ml to each jar) and the lid loosely put on the jar. The jars were then autoclaved at 121 °C for 20 minutes to ensure that the agar was sterile. Once the jars had cooled a pellet of fungus was transferred from the petra dishes to the jar in a laminar flow hood to prevent contamination. The jars were then transferred to a temperature and humidity controlled room (set at 22°C and 65% RH) and the fungus was left to grow for 2 weeks.

The treated samples and their control counterparts were individually bagged and then gamma irradiated (2.5 Mrad) at Isotron Ltd. Once the fungi had grown to cover the agar the jars were returned to the laminar flow cupboard and the blocks placed on a sterilised (via autoclaving) polypropylene mesh inside the jars. The jars were resealed and then returned to the conditioned room for sixteen weeks. After the exposure period the samples were removed from the jars and the fungal mat which had surrounded the blocks was removed. The blocks were then

weighed on a balance to three decimal places before drying. Three decimal places were used to ensure that the slight weight losses between the blocks with higher resin loadings could be detected. They were then dried in an oven for 24 hours at 105 °C (to a constant weight). They were reweighed and the dry mass loss and the water uptake were calculated. The control were oven dried prior to them being sterilised so that the dry mass loss could be calculated.

3.3 Results and Discussion

3.3.1 Results of the decay tests with resin impregnation only

Samples of Corsican pine were treated with three different resins; UF, MUF and MF. The results of the decay tests for the samples when they were subjected to the three fungi *C. puteana* (Schumacher ex Fries) Karsten (BAM 15), *Coriolus versicolor* (Linnaeus) Quélet, and *P. chrysosporium* (S179) are shown in Figure 3.1 to Figure 3.5.

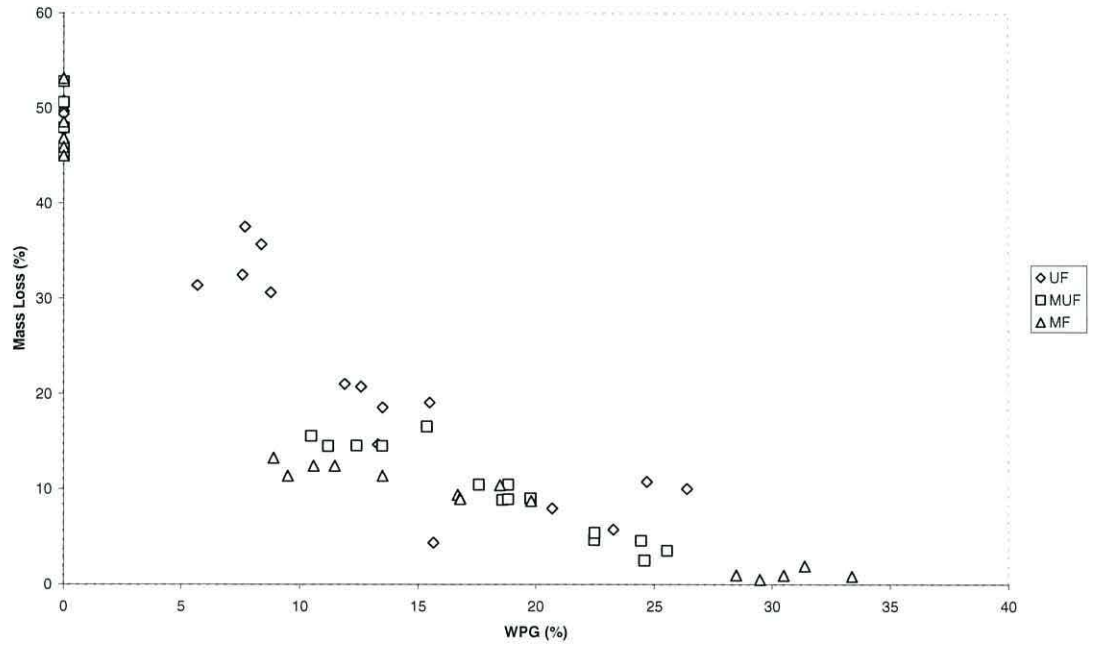


Figure 3.1: Graph to show the decay resistance of Corsican pine untreated and treated with 3 different resins against *C. puteana* (Schumacher ex Fries) Karsten (BAM 15). 0% weight gains are the untreated control samples.

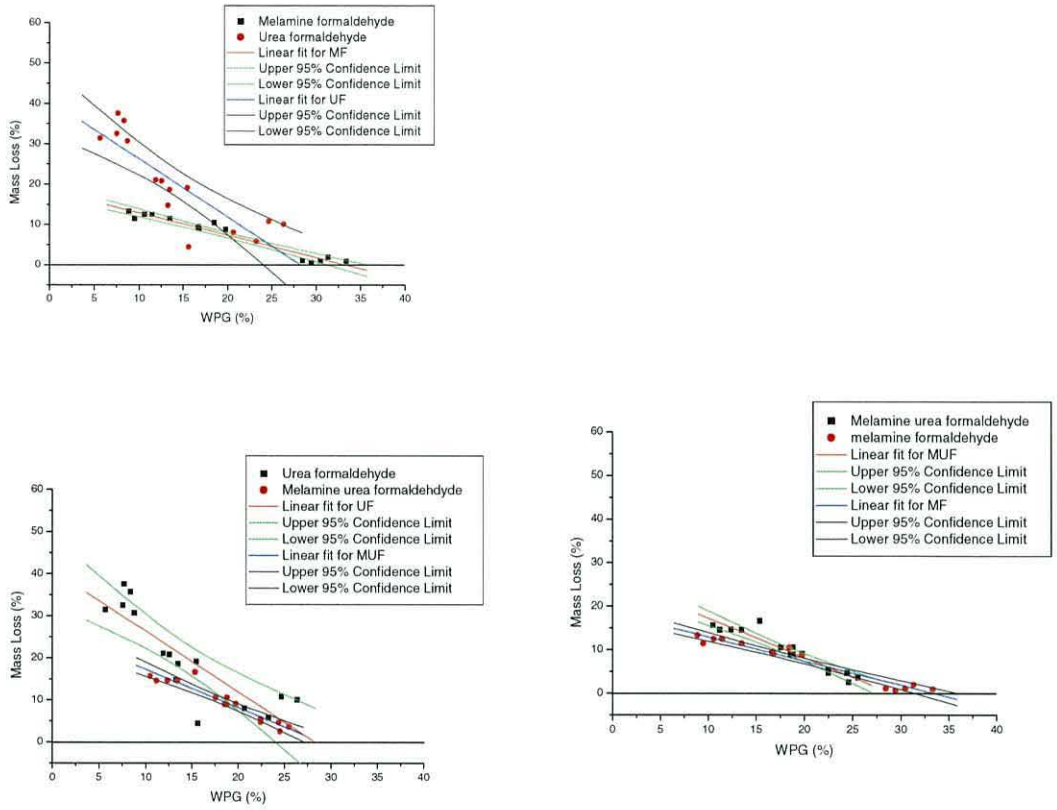


Figure 3.2: Interactions between the linear regressions of the resin only treated Corsican pine (including the 95% confidence intervals) when decayed by *C. puteana*.

The samples were treated to a know time and therefore it can be seen that there is a variation within the WPGs of the treated samples. This variation is due to a variety of considerations, including the variation in the microstructure of the individual blocks and whether they have other blocks laid on top of them in the treatment chamber.

The 95% confidence intervals shows, statistically, where 95% of measured observations will be scattered around the mean.

Treatment	Linear regression equation	SD	P value

MF resin only	y=18.44248+(-0.55354*x)	1.15919	<0.0001
MUF resin only	y=26.32251+(-0.90689*x)	1.497662	<0.0001
UF resin only	y=40.7596+(-1.44004*x)	6.06316	<0.0001

Table 3.2: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.1.

	MUF	MF	UF
MUF		NS	
MF			S
UF	NS		

Table 3.3: Table to show whether the difference between the linear regressions in Figure 3.1 are significent (S) or not significent (NS).

In Figure 3.1 it can be seen that, when the treated wood is exposed to *C. puteana* all the resins improve decay resistance.

It can be seen that there is a mass loss of 0% with melamine formaldehyde at a weight percentage gain of 30%. This is a significant value and this will be discussed later. Unfortunately the urea formaldehyde treatment and the melamine urea formaldehyde treatment did not reach a 30% WPG and therefore it can not be seen whether the 30% threshold holds true for all the resins. However if this data was extrapolated it would indicate that the UF resin would show a mass loss of 0% at 30% WPG.

Table 3.3 shows whether the difference between the linear regressions for the mass loss of the resin modified woods are significantly different or not. It can be seen that only the differences between the urea formaldehyde and the melamine formaldehyde show significant difference. The lack of significant difference adds credence to the postulation that resin treatment is a benign treatment and the resins do not have any biocidal effects. If the differing forms of resin did exhibit

a biocidal effect then there would be a significant difference between the three resins due to the different chemical make ups of the resins.

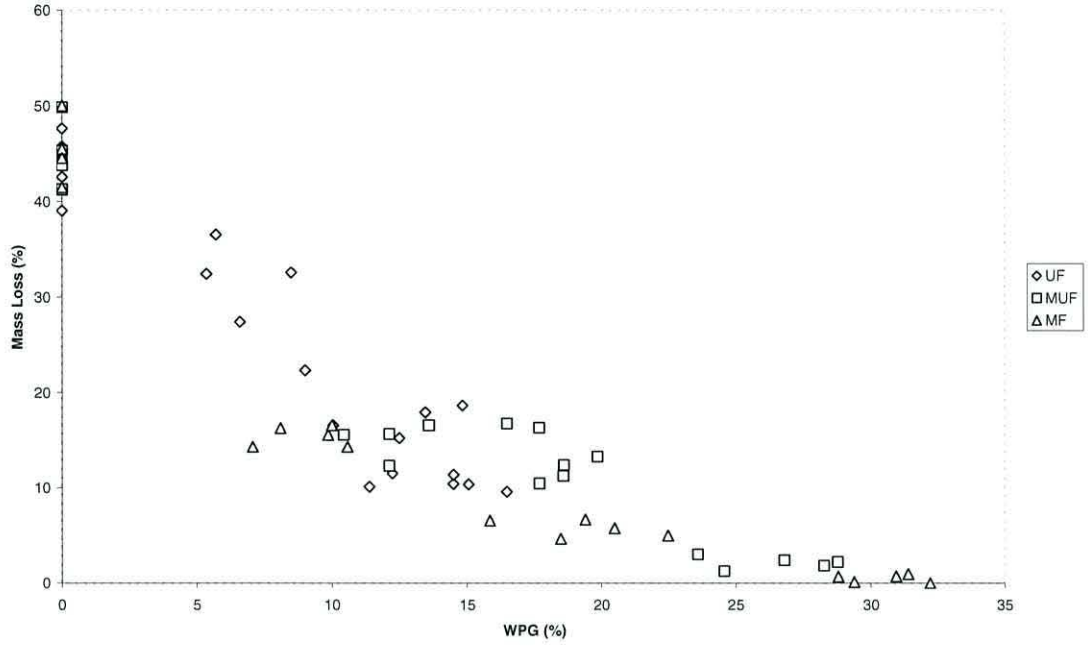
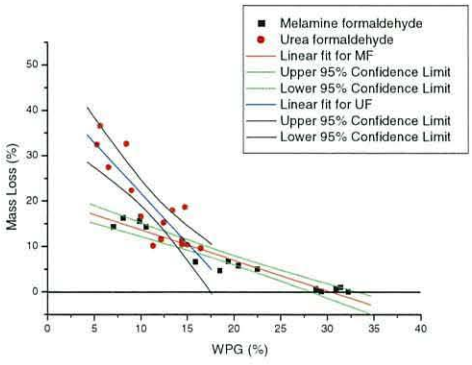


Figure 3.3: Graph to show the decay resistance of Corsican pine treated with 3 different resins against *C. versicolor* (Linnaeus) Quélet

All the fungi used in this study have shown high virulence and therefore it can be seen that the reduction in mass loss is due to the addition of the resin and not to a reduced action of the fungus. The virulence of the fungi has been shown to be greater than that required in the standard EN113, to prove the tests valid.



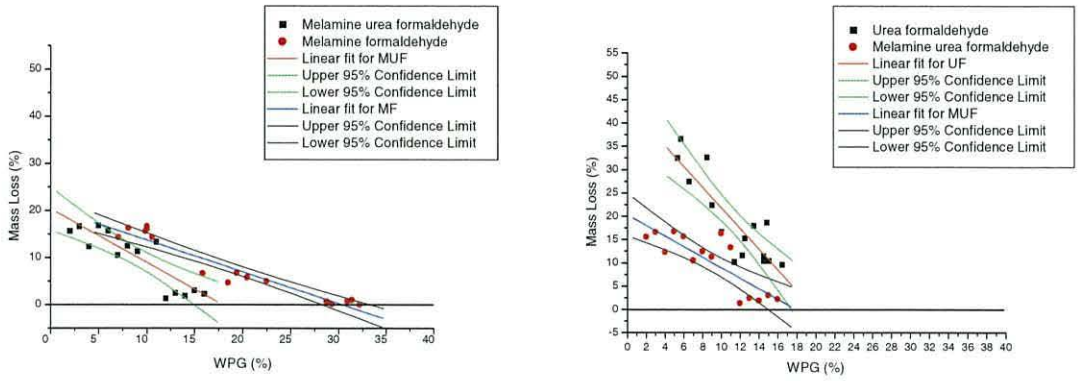


Figure 3.4: Interactions between the linear regressions of the resin only treated Corsican pine (including the 95% confidence intervals) when decayed by *C. versicolor*.

Treatment	Linear regression equation	SD	P value
MF resin only	y=20.43045+(-0.67172*x)	1.85104	<0.0001
UF resin only	y=44.04059+(-2.21835*x)	4.77723	<0.0001
MUF resin only	y=27.60417+(-0.90786*x)	2.94256	<0.0001

Table 3.4: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.4.

	MUF	MF	UF
MUF		S	
MF			S
UF	S		

Table 3.5: Table to show whether the difference between the linear regressions in Figure 3.4 are significent (S) or not significent (NS).

Figure 3.3 shows the decay resistance of Corsican pine treated with the three different resins against *C. versicolor* (Linnaeus) Quélet. Again it can be seen that the threshold WPG is around 30%. It can be seen that there are significant differences between the urea formaldehyde and the two melamine containing resins. This may be because the urea formaldehyde resin is readily hydrolysed thus preventing it from imparting a decay resistance to the timber and that the ingress of moisture plays an important role in the decay of timber by *C. versicolor*.

C. versicolor is known to excrete oxalic acid as a decay agent in the presence of wood and the presence of oxalic acid would speed up the rate of hydrolysis of the urea formaldehyde resin.

It can be seen that there is high virulence (about 50% mass loss) within the tests (this can be noted due to the high decay of the control samples). This shows that the decay resistance is due to the presence of the resin and not due to lack of virulence of the fungi.

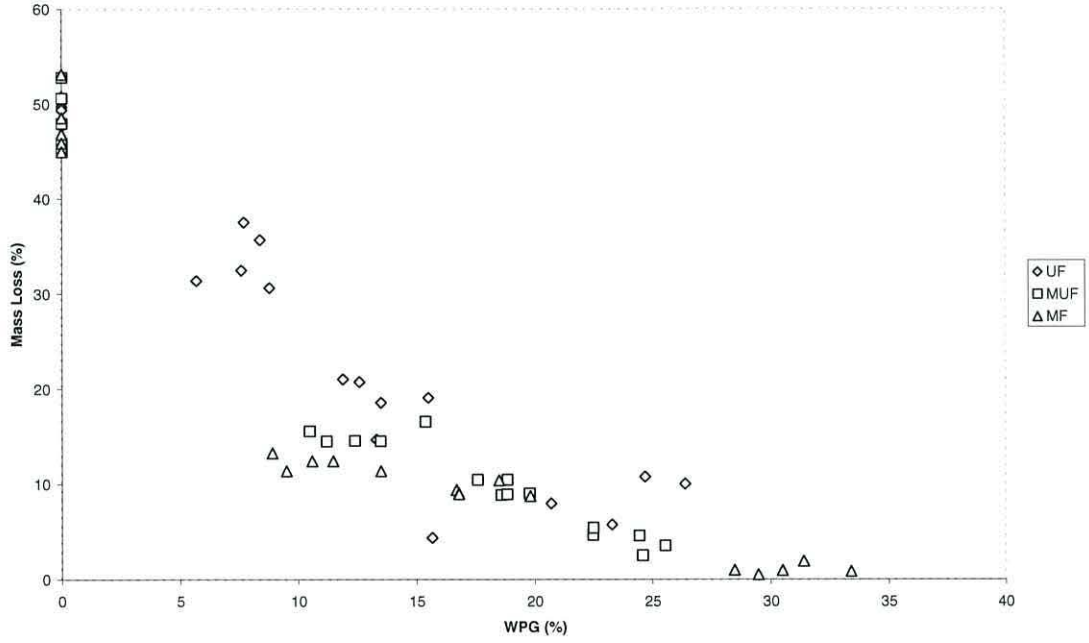


Figure 3.5: Graph to show the decay resistance of Corsican pine treated with 3 different resins against *P. chrysosporium*

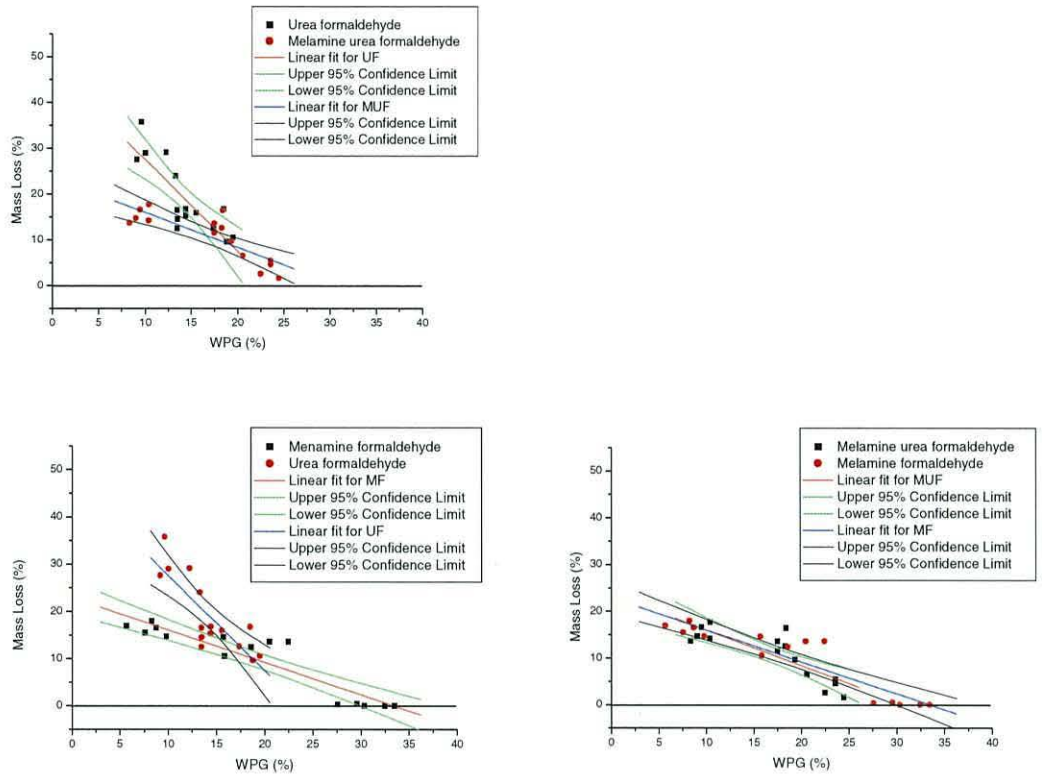


Figure 3.6: Interactions between the linear regressions of the resin only treated Corsican pine (including the 95% confidence intervals) when decayed by *P. chrysosporium*.

Treatment	Linear regression equation	SD	P value
MF resin only	y=22.88455+(-0.68489*x)	2.87458	<0.0001
UF resin only	y=47.55563+(-2.00363*x)	4.66396	0.0002
MUF resin only	y=23.61503+(-0.76189*x)	3.053915	0.0001

Table 3.6: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.6.

	MUF	MF	UF
MUF		NS	
MF			S

UF	Prob S

Table 3.7: Table to show whether the difference between the linear regressions in Figure 3.6 are significent (S) or not significent (NS).

Figure 3.5 shows the decay resistance of resin treated Corsican pine against *P. chrysosporium*. The data exhibits a similar trend to that of resin modification against the two other resins. A threshold value of 30% is found with the MF treated samples. It can again be observed that there are significant differences between the urea formaldehyde resin and the two melamine containing resins. The interaction graphs in Figure 3.6 show that there is a higher mass loss when the timber is modified with low levels of UF resin than with low levels of melamine containing resin. This suggests that when timbers are treated with a low amount of resin they are more susceptible to water ingress and thus the UF resin will suffer from increased hydrolysis leading to increased decay of the timbers.

Again the virulence within this test is high and therefore it can be shown that this test is valid.

It can be seen from figures 3.1, 3.3 and 3.5 that the weight percentage gain needed with the resins to achieve no mass loss in an EN113 test was around 30% for all three resins when modifying Corsican pine. It can also be noted that the samples are not saturated with resin and therefore covered with an envelope treatment. this can be seen when a sample is cut in half, a outer envelope of resinated timber can be see surrounding untreated wood. It can therefore be assumed that a WPG of 30% will give a full envelope treatment that the fungi cannot breach.

Neither the MUF resin nor the UF resin reached the 30% WPG needed to give the wood decay resistance, this is probably due to the large molecule size and the pre-cure of the resins while the treatment was taking place.

The value of 30% is very significant. It will be shown in later work that the threshold value for decay resistance to EN113 specification of timber treated with acetic anhydride, a benign cell wall bulking agent, is around 30%. It should therefore be noted that the threshold value against decay, for the modification of timbers with resin, is what would be expected if the resistance was attributed to cell wall bulking alone and therefore it can be suggested that there is no biocidal effect from the resins.

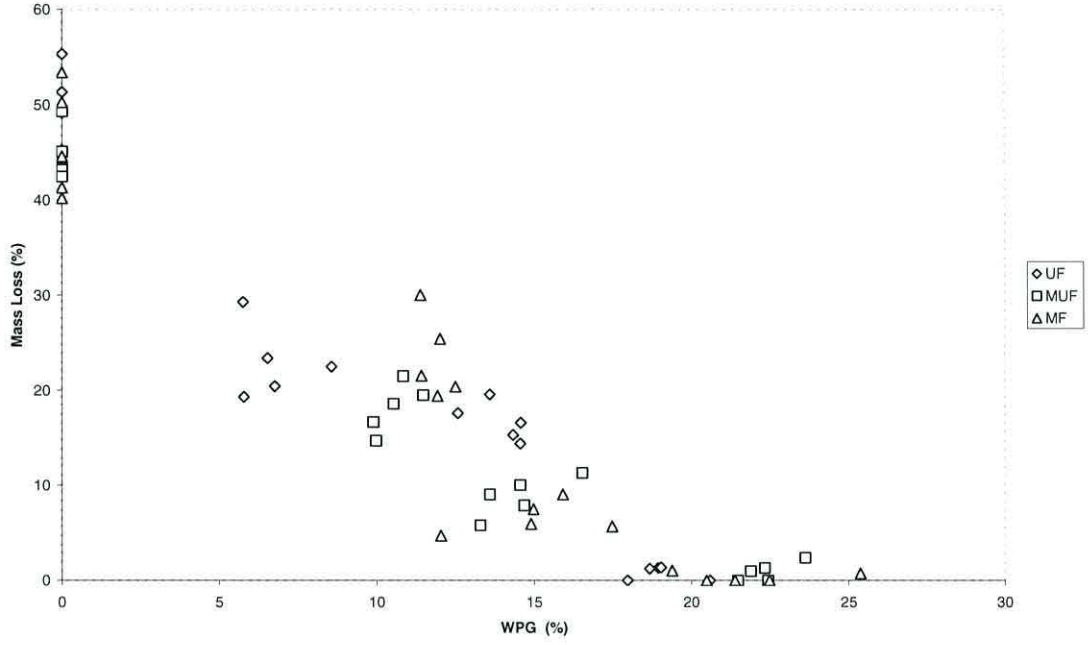
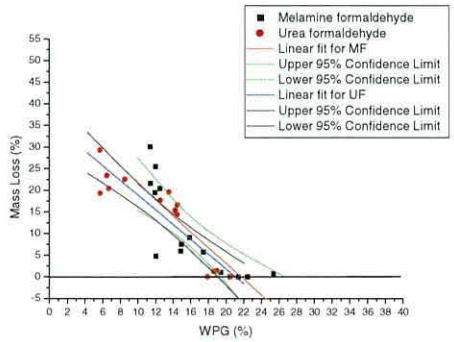


Figure 3.7: Graph to show the decay resistance of beech treated with 3 different resins against *C. versicolor* (Linnaeus) Quélet



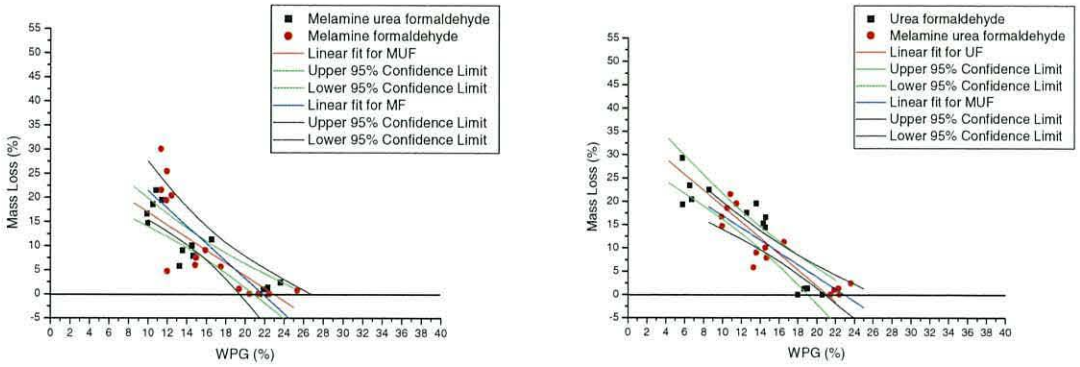


Figure 3.8: Interactions between the linear regressions of the resin only treated beech (including the 95% confidence intervals) when decayed by *C. versicolor*.

Treatment	Linear regression equation	SD	P value
MF resin only	y=39.67647+(-1.82131*x)	6.32259	<0.0001
UF resin only	y=36.02012+(-1.70461*x)	4.2304	<0.0001
MUF reisn only	y=30.06581+(-1.31289*x)	3.43356	<0.0001

Table 3.8: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.8.

	MUF	MF	UF
MUF		NS	
MF			NS
UF	NS		

Table 3.9: Table to show whether the difference between the linear regressions in Figure 3.8 are significent (S) or not significent (NS).

Figure 3.7 shows the decay resistance of beech to *C. versicolor* (Linnaeus) Quélet. It can be seen from the graph that the threshold value for resin treated beech is around 22%. It can be seen from Table 3.9 that there is no significant

difference between the three resins when treated. Again with this investigation the virulence of the fungi was good, giving mass losses of 40 – 50% in untreated controls.

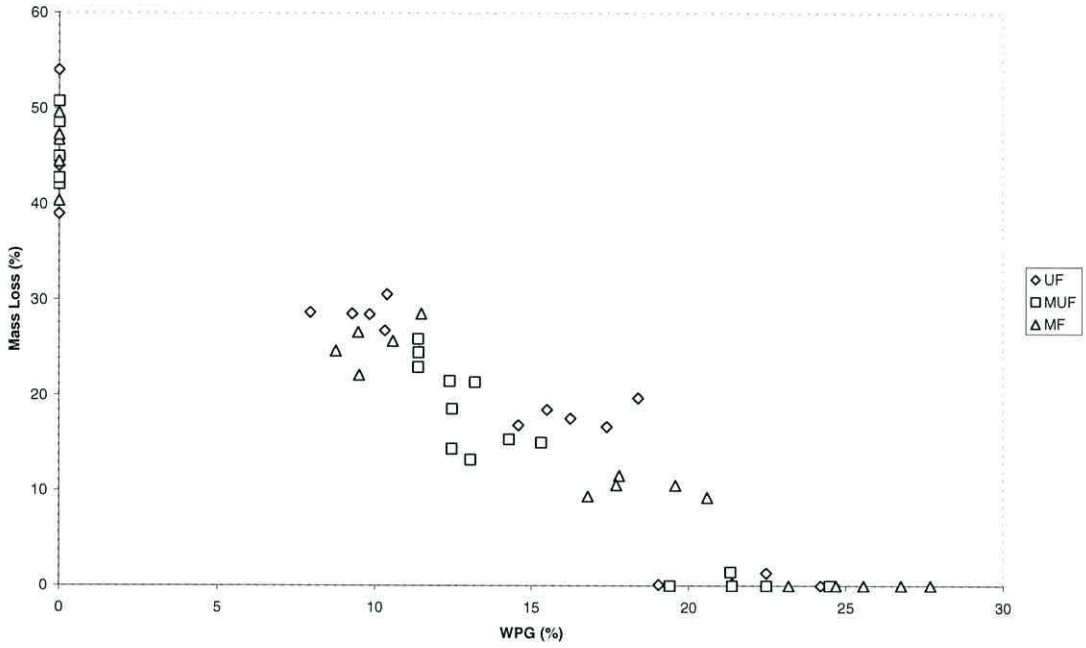


Figure 3.9: Graph to show the decay resistance of beech treated with 3 different resins against *C. puteana* (Schumacher ex Fries) Karsten (BAM 15)

Figure 3.9 shows the decay resistance of beech treated with 3 different resins against *C. puteana.* It can be seen that the threshold value for the beech is around 22%. Table 25 shows that there is no significant difference between the decay resistances imparted to beech by any of the resins.

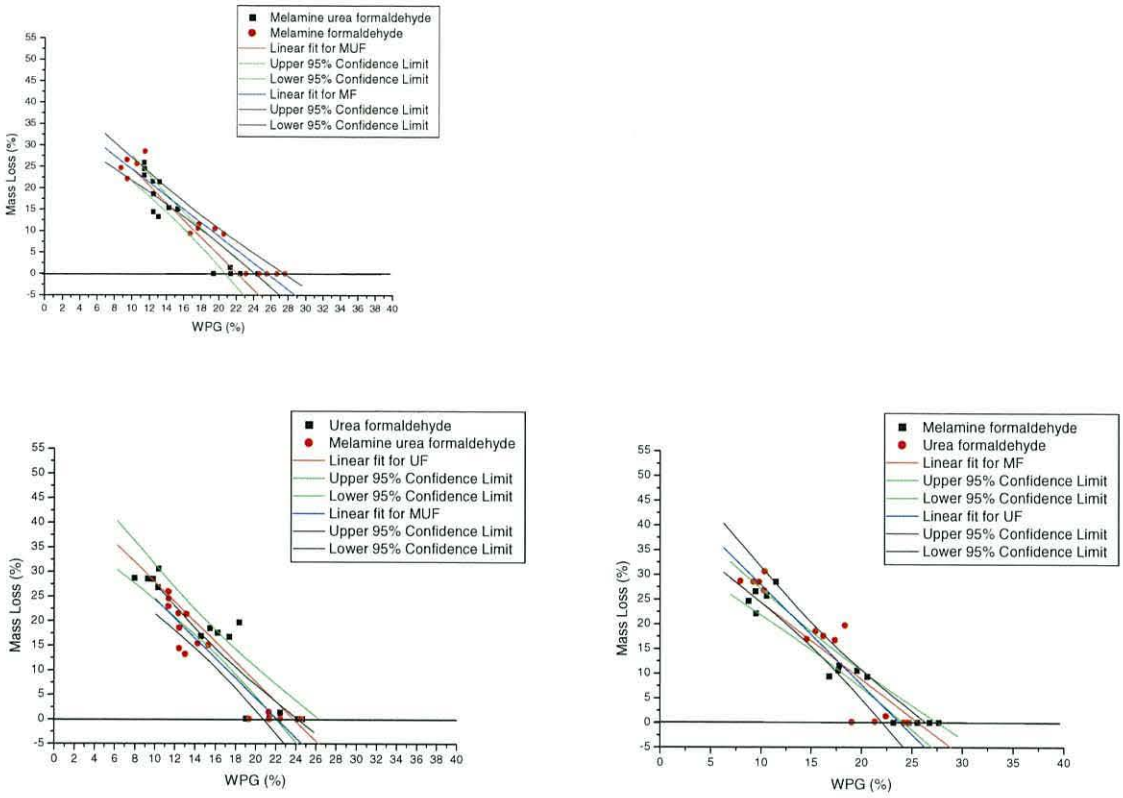


Figure 3.10: Interactions between the linear regressions of the resin only treated beech (including the 95% confidence intervals) when decayed by *C. puteana*.

Treatment	Linear regression equation	SD	P value
MF resin only	y=40.06735+(-1.56214*x)	3.001	<0.0001
UF resin only	y=47.64739+(-1.94456*x)	3.78448	<0.0001
MUF resin only	y=44.7931+(-2.01957*x)	3.42414	<0.0001

Table 3.10: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.10.

	MUF	MF	UF
MUF		NS	
MF			NS
UF	NS		

Table 3.11: Table to show whether the difference between the linear regressions in Figure 3.10 are significent (S) or not significent (NS).

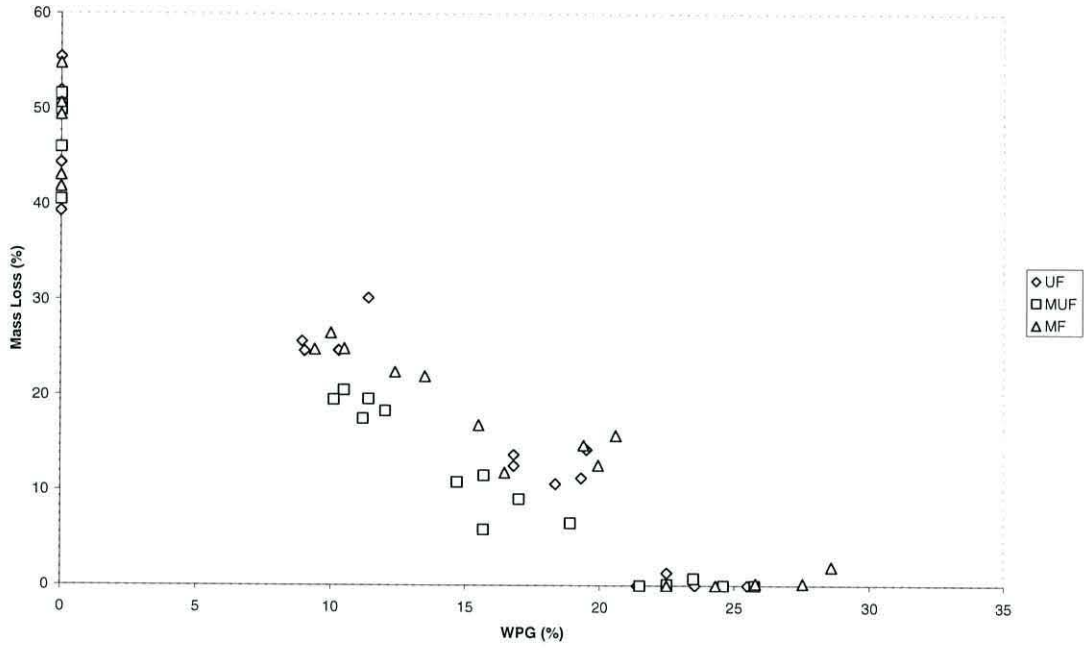


Figure 3.11: Graph to show the decay resistance of beech treated with 3 different resins against *P. chrysosporium*

Figure 3.11 shows the decay resistance imparted to beech when modified with 3 different resins against *P. chrysosporium.* Once again it can be observed that a threshold value of around 22% is achieved. It can also be noted, as with the protection against the other fungi, that the results for the differing resins are not statistically significant.

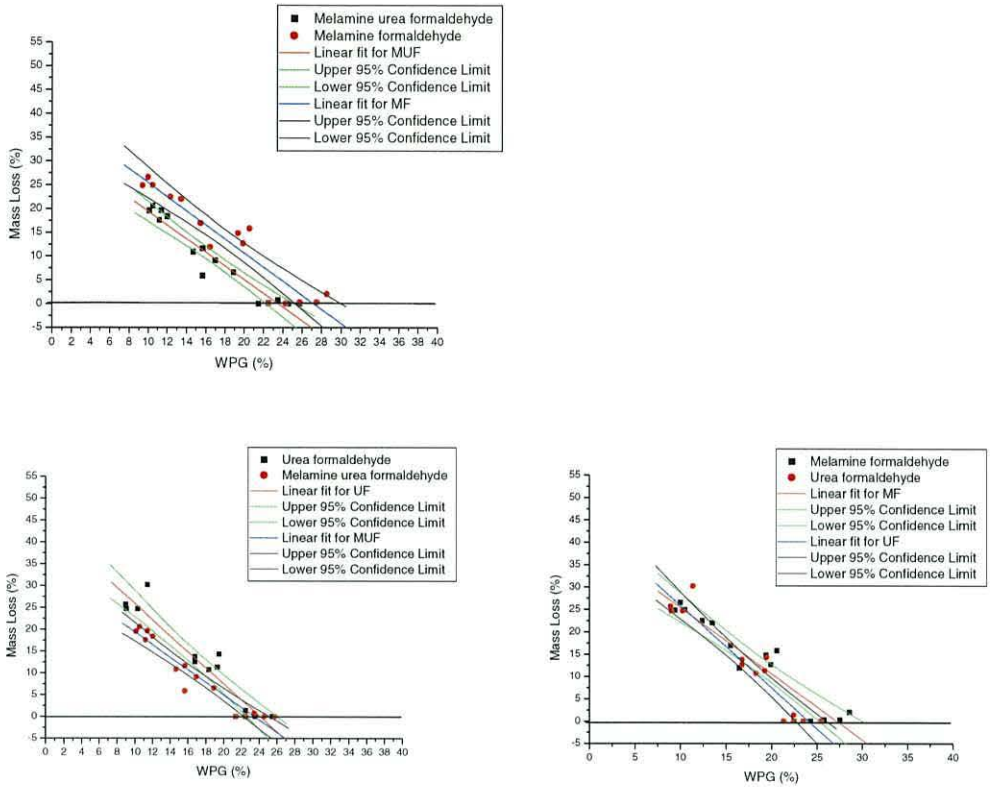


Figure 3.12: Interactions between the linear regressions of the resin only treated beech (including the 95% confidence intervals) when decayed by *P. chrysosporium*.

Treatment	Linear regression equation	SD	P value
MF resin only	Y=40.23401+(-1.47804*x)	3.50851	<0.0001
UF resin only	Y=44.25498+(-1.83527*x)	3.36092	<0.0001
MUF resin only	Y=33.76378+(-1.43541x)	2.28034	<0.0001

Figure 3.13: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.12

	MUF	MF	UF
MUF		NS	
MF			NS
UF	NS		

Table 3.12: Table to show whether the difference between the linear regressions in Figure 3.12 are significent (S) or not significent (NS)

It should be noted that throughout this work there is no significant difference between the mass loss due to decay between any of the modifications on beech. It is possible that the lack of difference in resins is due to the difference in decay mechanisms of the three fungi when decaying hardwoods compared with softwoods and therefore it can be assumed that the mechanisms for the decay of hardwoods are not as reliant on the ingress of water to the timber as the decay of softwoods.

It should also be noted that when beech is modified with the urea formaldehyde resin and then decayed with *C. versicolor* the decay does not seem to be accelerated by the presence of the oxalic acid. The reason for this is currently unknown.

Throughout the work evaluating the decay resistance, it has been constantly found that the threshold value for Corsican pine is a 30% weight gain with modification and a 22% weight gain for beech. It has been found that this does not vary with the resin used or the fungi that is decaying the wood. The lack of constant large significant differences between the resin treatments does indicate that modification of timber with urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde offers a non-active form of wood protection and suggests a common mechanism for the prevention of decay.

3.3.2 The Moisture Content Tests

Literature states that for decay to occur a wood cell moisture content of approximately 20% is needed and for the wood cells to be around FSP (Eaton and Hale, 1993).

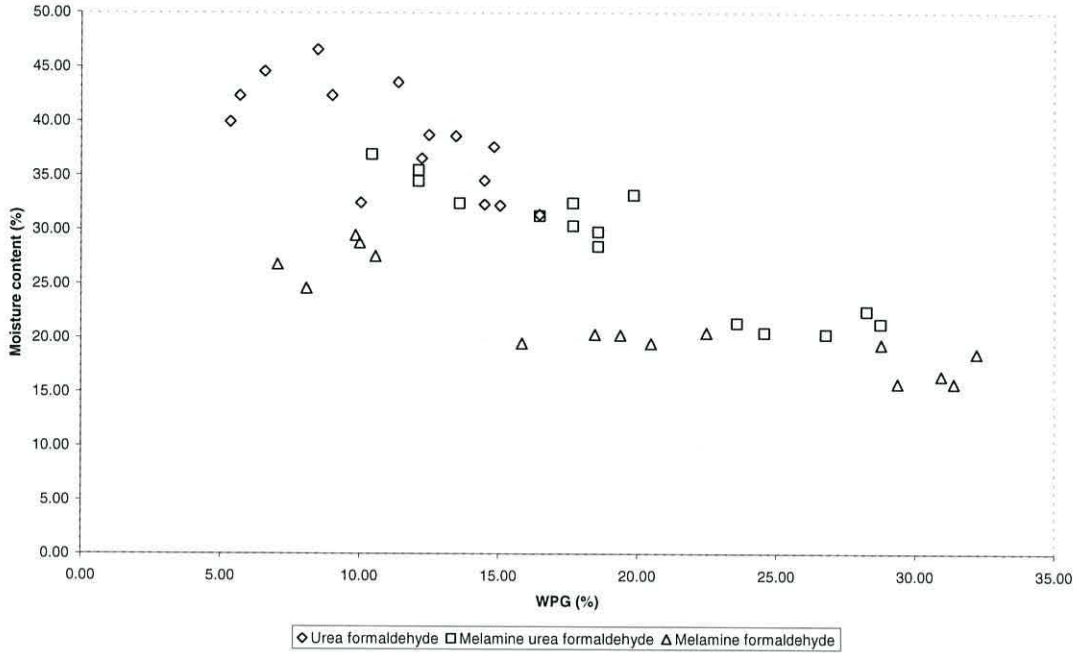


Figure 3.14: Post decay Moisture content decrease with the increase in WPG of resin impregnated Corsican pine (in a decay test with *C. versicolor*)

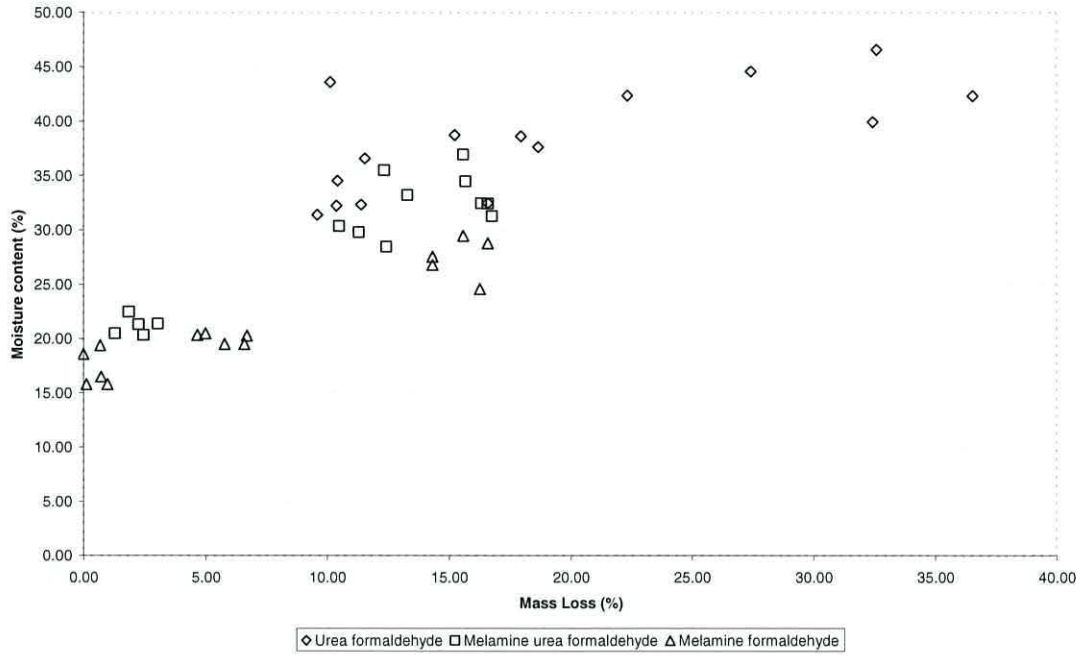


Figure 3.15: Mass loss vs. post decay moisture content of resin modified Corsican pine when decayed with *C. versicolor*

Figure 3.14 shows that as the WPG increases due to modification with resin, the final moisture content at the end of the decay test decreases. It can be seen that there is no difference between the three resins. Figure 3.15 shows that as the final moisture content is reduced, the amount of decay is also reduced. It can be seen that as the moisture content decreases to around 20% the amount of decay approaches 0% (between 5% and 0% as shown in Figure 3.15), this is in agreement with the 20% threshold value given by Eaton and Hale (1993). The data shown here is for Corsican pine treated with three resins in decay tests against *C. versicolor,* however this is indicative of all the resins tested with the three fungi. The mass loss at 20% moisture content is due to there being sufficient moisture in the wood to allow decay to take place (this is discussed in Chapter 1).

Figure 3.16 shows the reduction of moisture content at the end of decay with the increase of resin modification. It can be seen that the threshold value of 20% is reached with a WPG of 22%. It can be seen in Figure 3.17 that as the moisture content reaches 20% the mass loss due to decay reaches 0%.

The moisture content of the treated blocks and the fibre saturation point will be investigated further in Section 6.

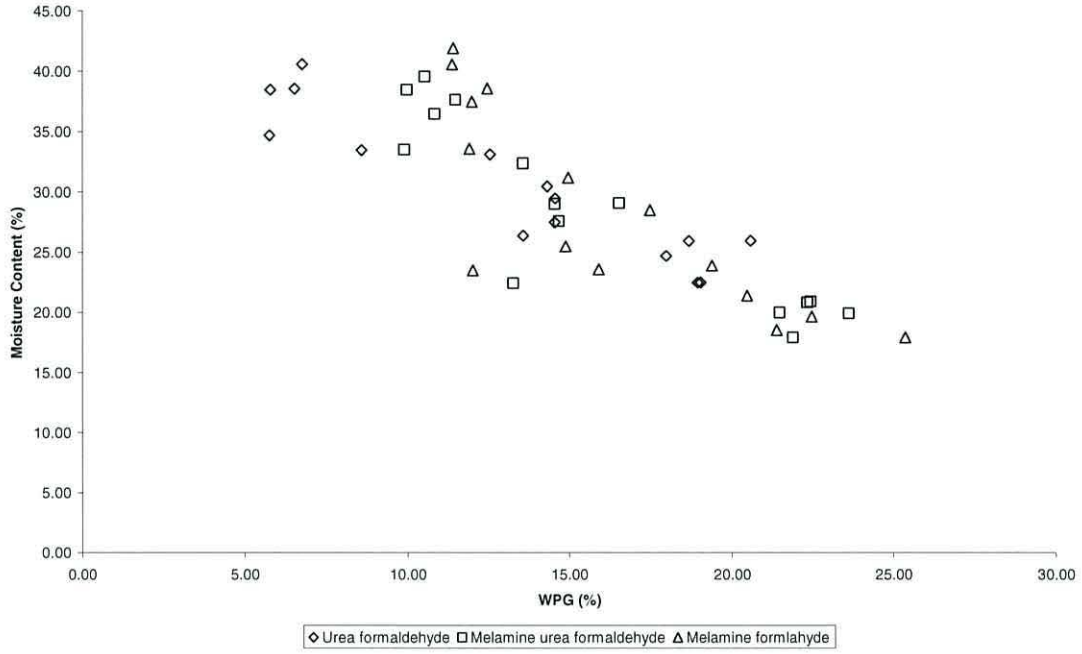


Figure 3.16: Moisture content decrease with the increase in WPG of resin impregnated beech (in a decay test with *C. versicolor*)

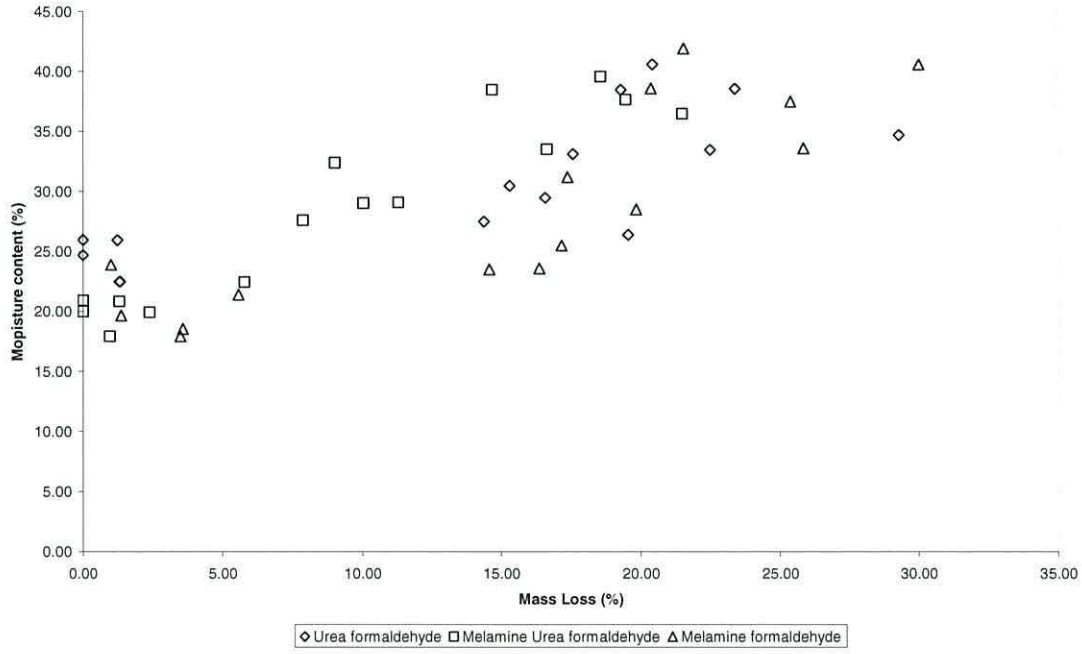


Figure 3.17: Mass loss vs. moisture content of resin modified beech when decayed with *C. versicolor*

3.3.3 Results of resin and biocide impregnations

The biocide was used to improve the resistance to biological decay of the timber. The delivery of the biocide into the samples was done in two ways, the first was a sequential delivery system and the second was a co-delivery system (the resin and biocide was mixed together).

Samples were treated with biocide only, however the biocide leached from the samples and contaminated the growth medium therefore the tests were deemed invalid. However, it should be noted that the fungi was killed in the areas hat the biocide leached and therefore the biocide can be deemed active against the fungi.

Figure 3.18 shows the decay resistance of melamine formaldehyde treated Corsican pine and MF / biocide treated Corsican pine. It can be seen that as the WPG increases so does the decay resistance. However Figure 3.19 and Table 3.14 shows that there is no statistical difference between the MF treated samples and the MF and biocide treated samples. This indicates that the decay resistance imparted in these systems, in an EN113 situation is due the presence of the resin alone and not to the action of the biocide.

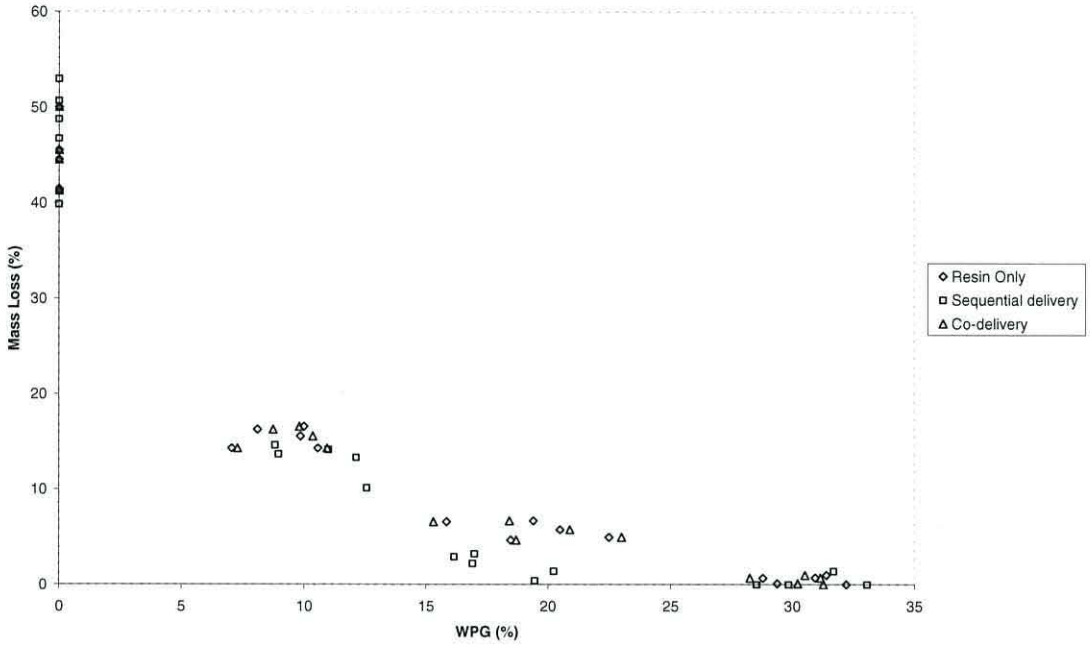


Figure 3.18: Graph to show the comparison of the *C. versicolor* decay resistance of MF only treated timber against timber treated with MF resin and biocide (also shown are the untreated control samples)

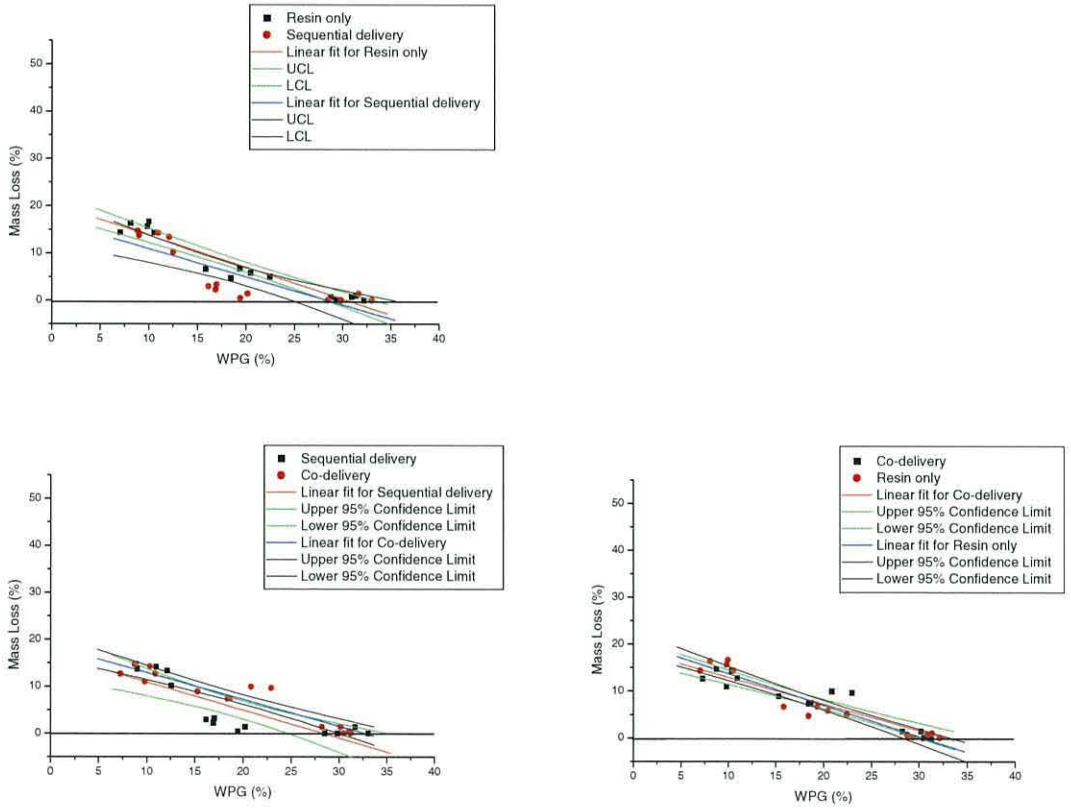


Figure 3.19: Interaction between the linear regressions for Corsican pine treated with MF resin decayed with *C. versicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MF resin only	Y=20.43045+(-0.67172*x)	1.85104	<0.0001
MF resin sequential	Y=16.80314+(-0.59174*x)	3.40511	<0.0001
MF resin co-delivery	Y=18.60472+(-0.56819*x)	3.40511	<0.0001

Table 3.13: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.19.

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.14: Table to show whether the difference between the linear regressions in Figure 3.19 are significent (S) or not significent (NS).

Figure 3.20 shows the decay resistance of MF and biocide treated Corsican pine against *C. puteana*. Again, the treated timber exhibits the same trends as when being decayed with *C. versicolor*. Again there is no statistical difference between the resin only modification and the modification with the biocides.

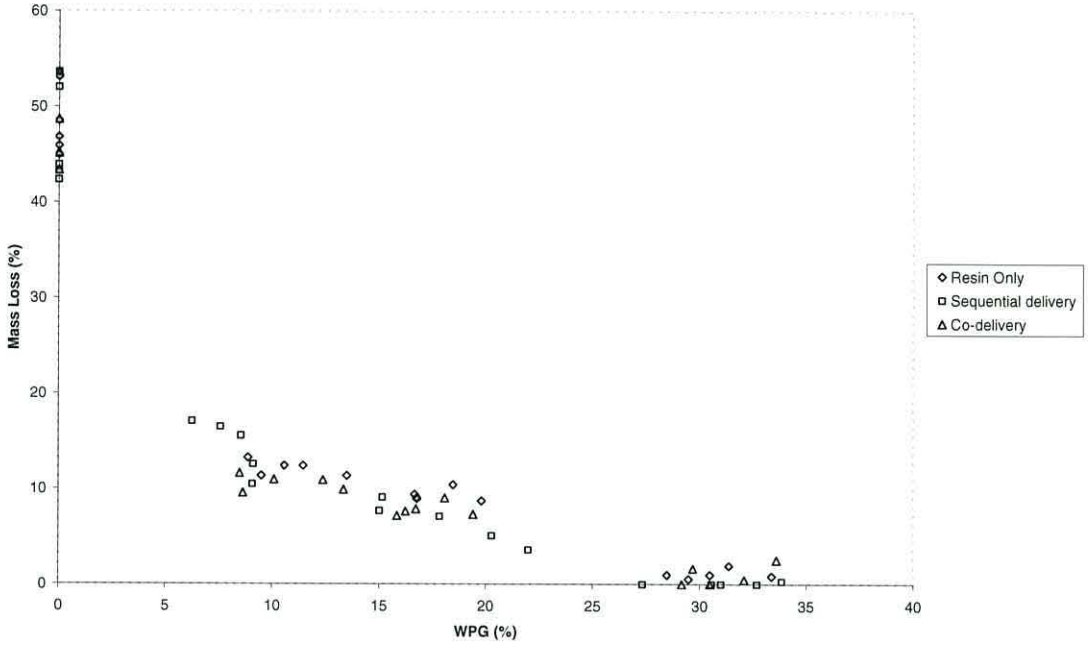


Figure 3.20: Graph to show the comparison of the *C. puteana* decay resistance of MF only treated Corsican pine against timber treated with MF resin and biocide (also shown are the untreated control samples)

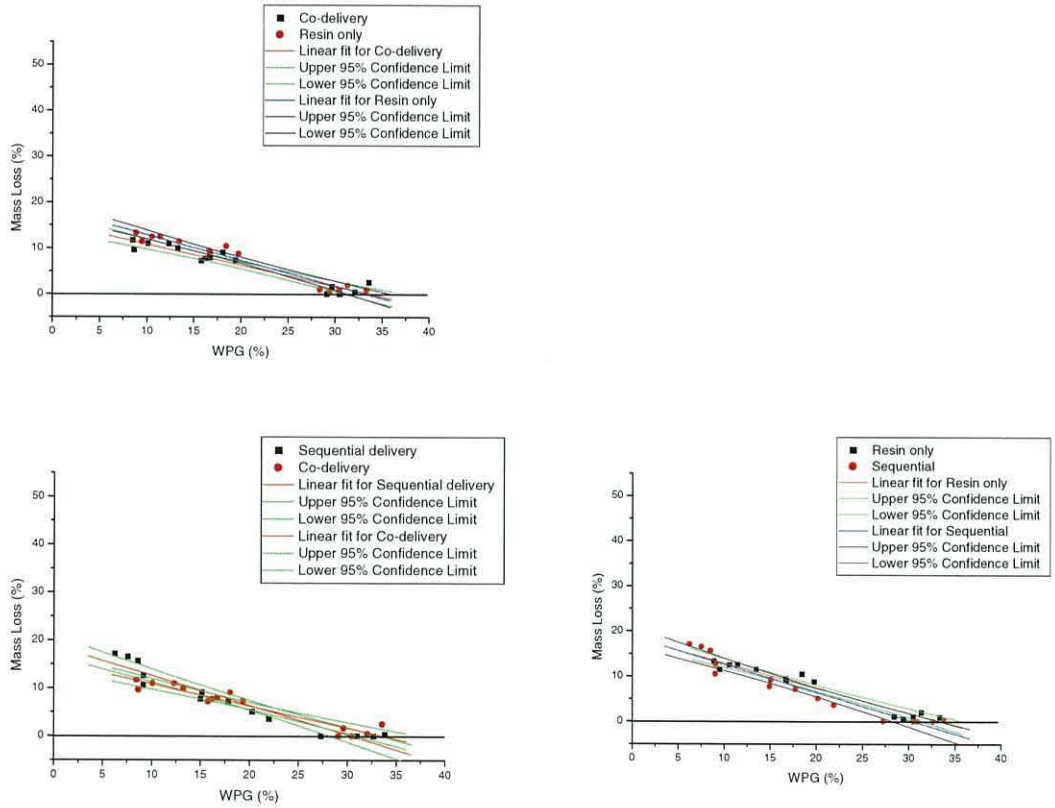


Figure 3.21: Interaction between the linear regressions for Corsican pine treated with MF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MF resin only	y=18.44248+(-0.55354*x)	1.15919	<0.0001
MF reisn sequential	y=18.781112+(-0.61609*x)	1.79161	<0.0001
MF reisn co-delivery	y=15.44891+(-0.45801*x)	1.34399	<0.0001

Table 3.15: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.21.

	Resin only	Sequential	Co-delivery
Resin only	-	NS	-
Sequential	-	-	NS
Co-delivery	NS	-	-

Table 3.16: Table to show whether the difference between the linear regressions in Figure 3.21 are significent (S) or not significent (NS).

Figure 3.22 shows the decay resistance of the MF and biocide treated Corsican pine against *P. chrysosporium*. Table 3.18 shows that there are significant differences between the resin and biocide modification and the resin only modification. It is apparent that lower WPG the resin only treatment appears to exhibit better decay protection than the modification with the biocide and resin. The reason for this is not understood and requires further study.

It can be seen that as the WPG reaches 15% the mass losses of the three treatments converge to show no significant differences.

There is a threshold value of around 30% WPG as seen with all the MF treated samples.

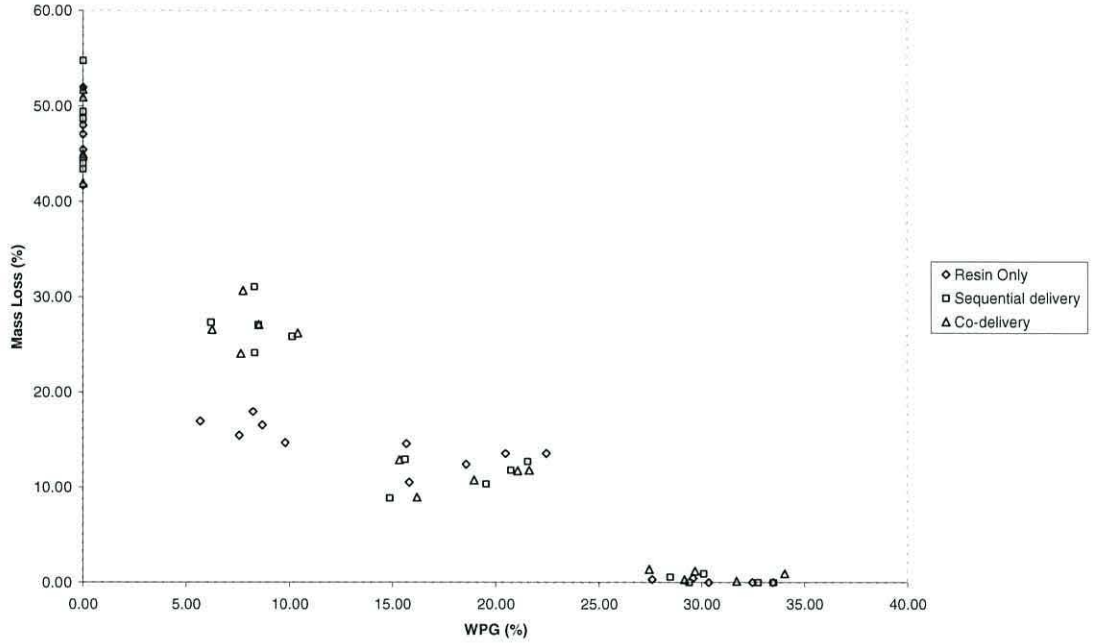


Figure 3.22: Graph to show the comparison of the *P. chrysosporium* decay resistance of MF only treated Corsican pine against timber treated with MF resin and biocide (also shown are the untreated control samples)

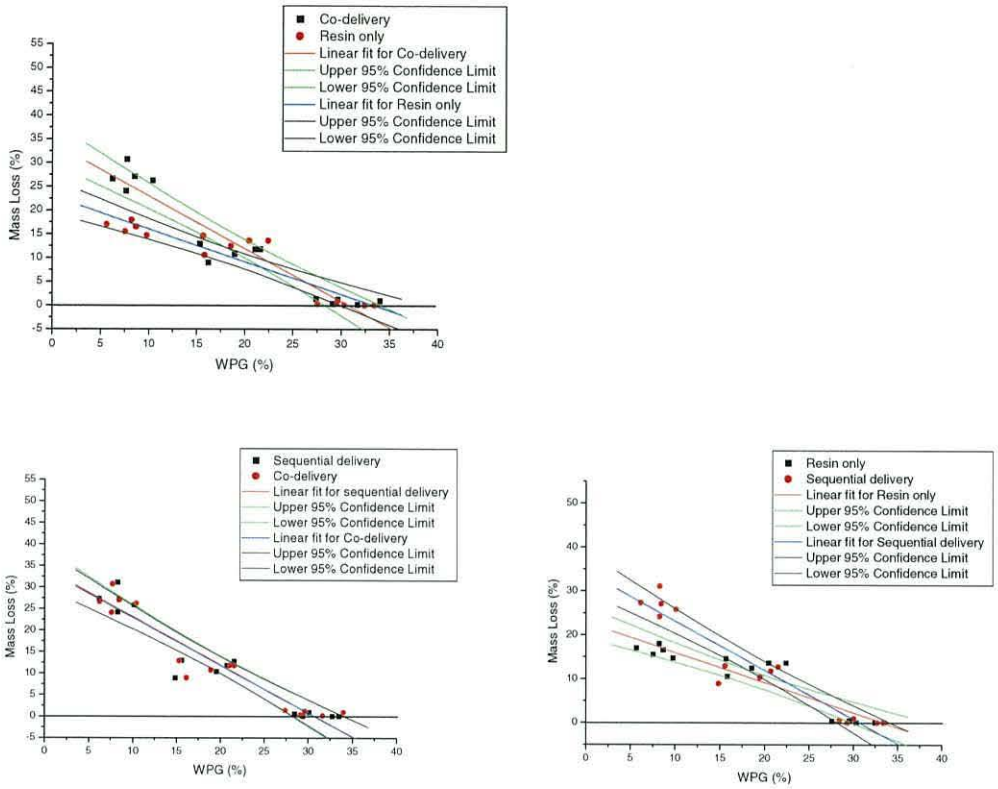


Figure 3.23: Interaction between the linear regressions for Corsican pine treated with MF resin decayed with *P. chrysosporium*(and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
Resin only	y=22.88455+(-0.68489*x)	2.87458	<0.0001
Sequential	y=34.38559+(-1.11852*x)	3.66971	<0.0001
Co-delivery	y=34.09034+(-1.10744*x)	3.46931	<0.0001

Table 3.17: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.23

	Resin only	Sequential	Co-delivery
Resin only	-	S	-
Sequential	-	-	NS
Co-delivery	S	-	-

Table 3.18: Table to show whether the difference between the linear regressions in Figure 3.23 are significent (S) or not significent (NS).

Figure 3.24, Figure 3.26 and Figure 3.28 show the decay resistance of melamine urea formaldehyde treated Corsican pine against *C. puteana*, *P. chrysosporium* and *C. versicolor* respectively. It can be seen that there is no statistical difference between any of the treatments. This again is a good indication that the decay resistance is due to the reduction in moisture content and the reduction in FSP (as discussed in Section 2.4).

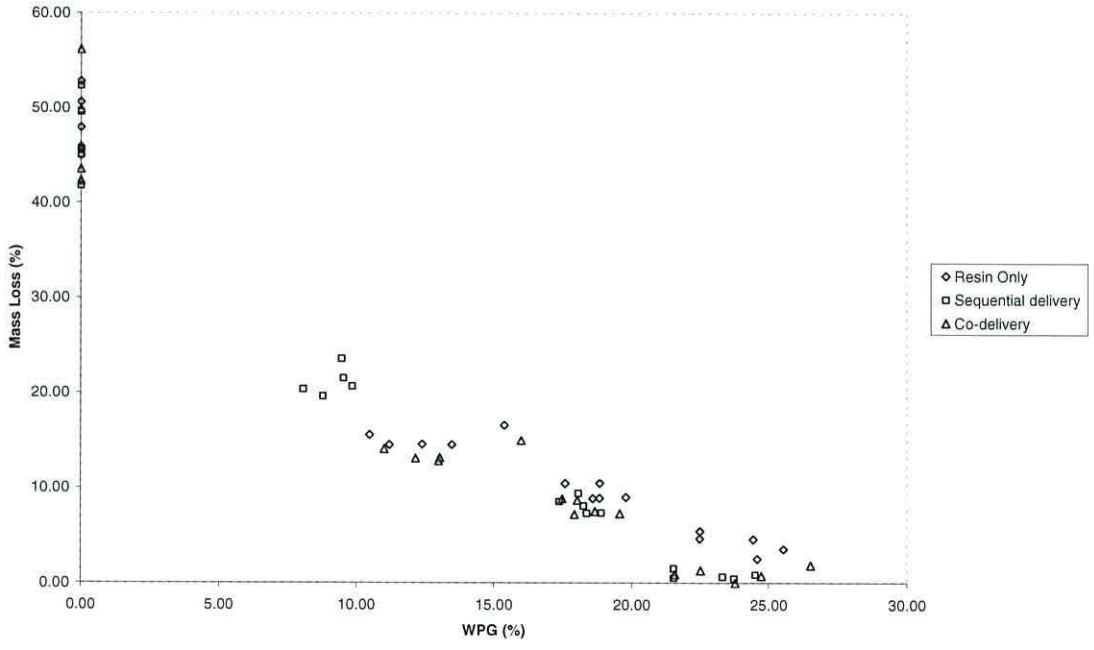


Figure 3.24: Graph to show the comparison of the *C. puteana* decay resistance of MUF only treated Corsican pine against timber treated with MUF resin and biocide (also shown are the untreated control samples)

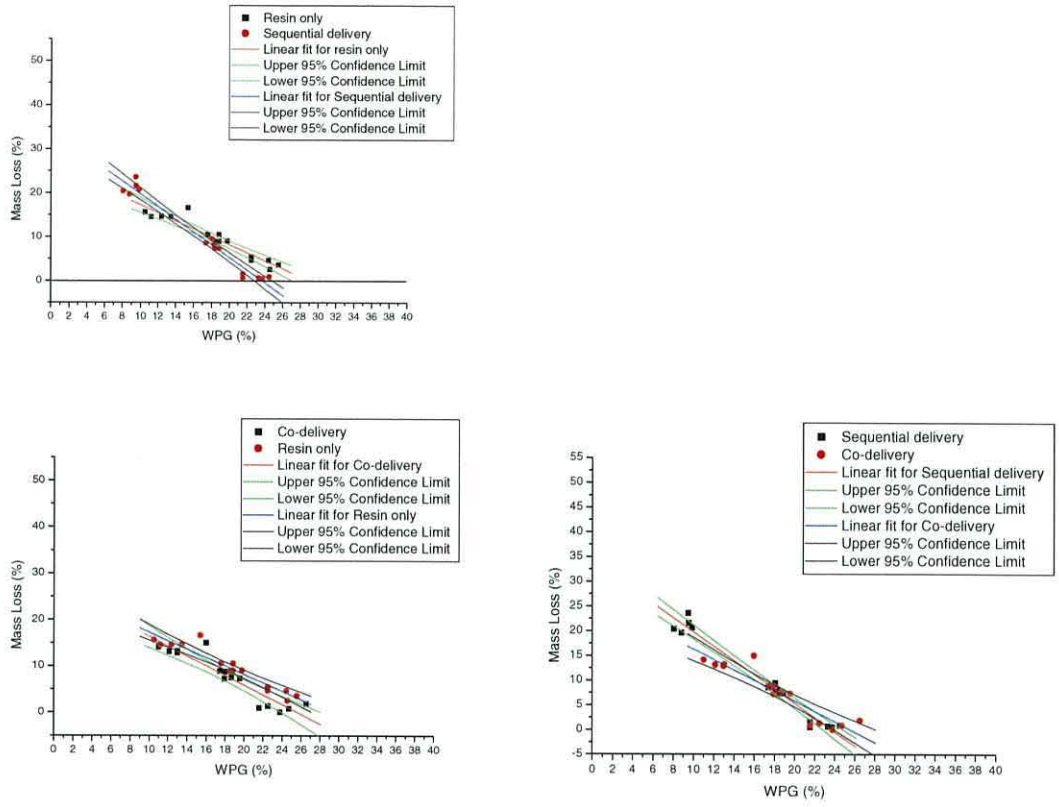


Figure 3.25: Interaction between the linear regressions for Corsican pine treated with MUF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF reisn only	y=26.32251+(-0.90689*x)	1.497662	<0.0001
MUF resin sequential	y=34.22221+(-1.44266*x)	1.64847	<0.0001
MUF resin co-delivery	y=26.8104+(-1.04901*x)	2.06598	<0.0001

Table 3.19: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.25

	Resin only	Sequential	Co-delivery
Resin only	-	Prob NS	-
Sequential	-	-	NS
Co-delivery	NS	-	-

Table 3.20: Table to show whether the difference between the linear regressions in Figure 3.25 are significent (S) or not significent (NS).

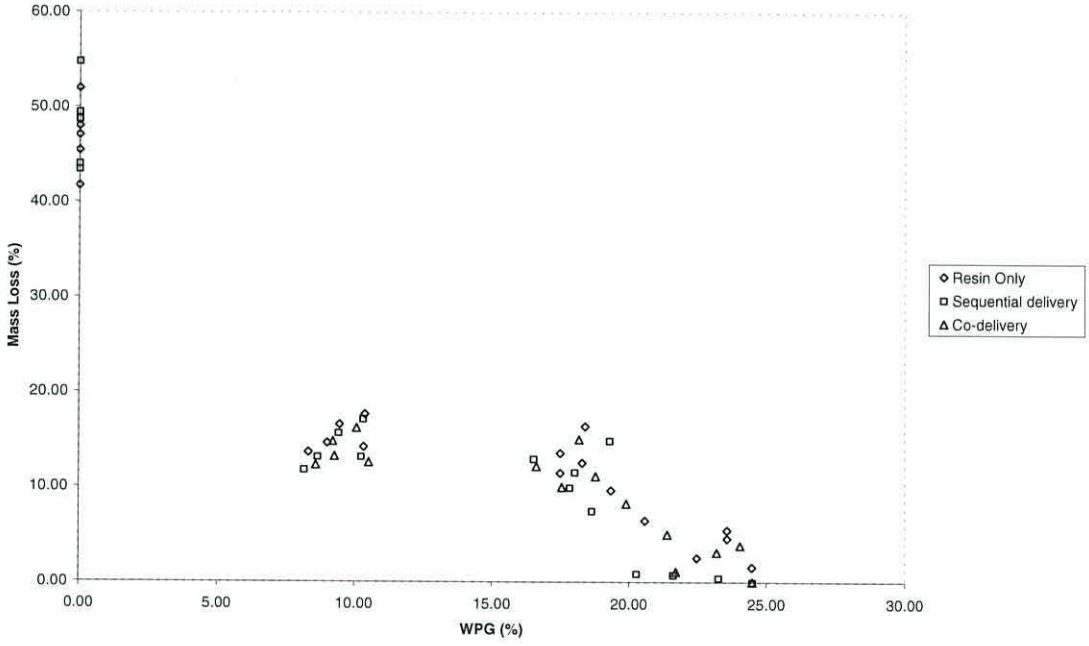


Figure 3.26: Graph to show the comparison of the *P. chrysosporium* decay resistance of MUF only treated Corsican pine against timber treated with MUF resin and biocide (also shown are the untreated control samples)

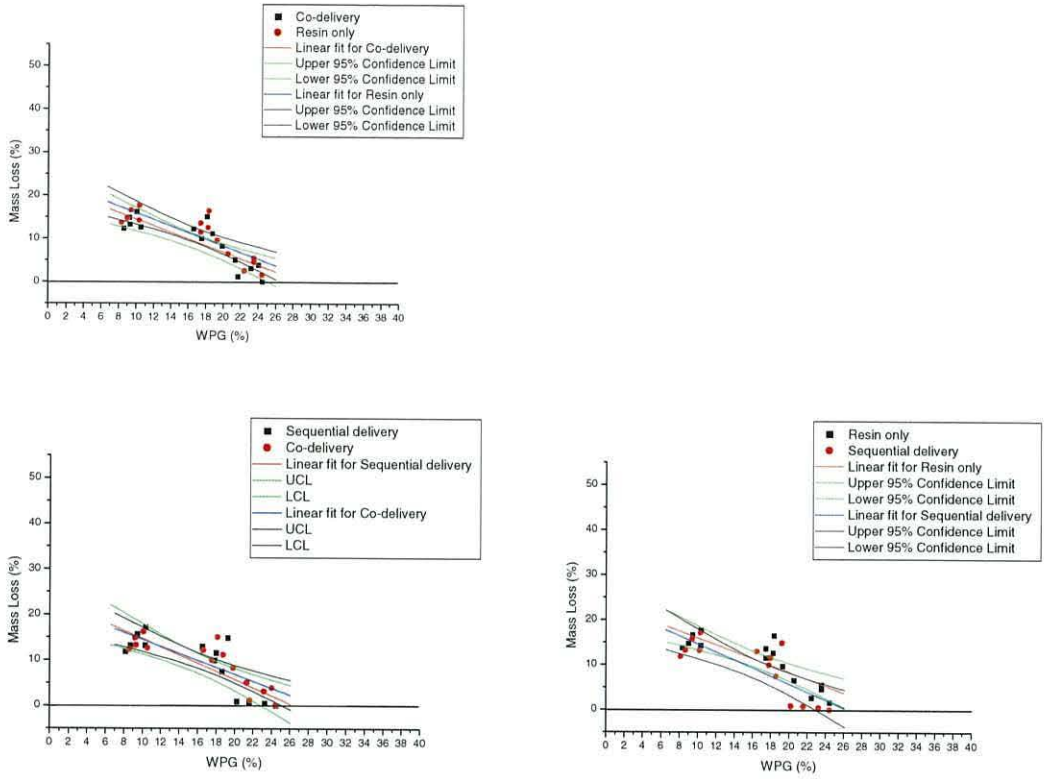


Figure 3.27: Interaction between the linear regressions for Corsican pine treated with MUF resin decayed with *P.chrysosprium* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF reisn only	y=23.61503+(-0.76189*x)	3.053915	0.0001
MUF resin sequential	y=23.58831+(-0.89144*x)	3.89144	0.0002
MUF resin co-delivery	y=22.16146+(-0.06233*x)	3.04604	0.0001

Table 3.21: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.27

	Resin only	Sequential	Co-delivery
Resin only	-	NS	-
Sequential	-	-	NS
Co-delivery	NS	-	-

Table 3.22: Table to show whether the difference between the linear regressions in Figure 3.27 are significent (S) or not significent (NS).

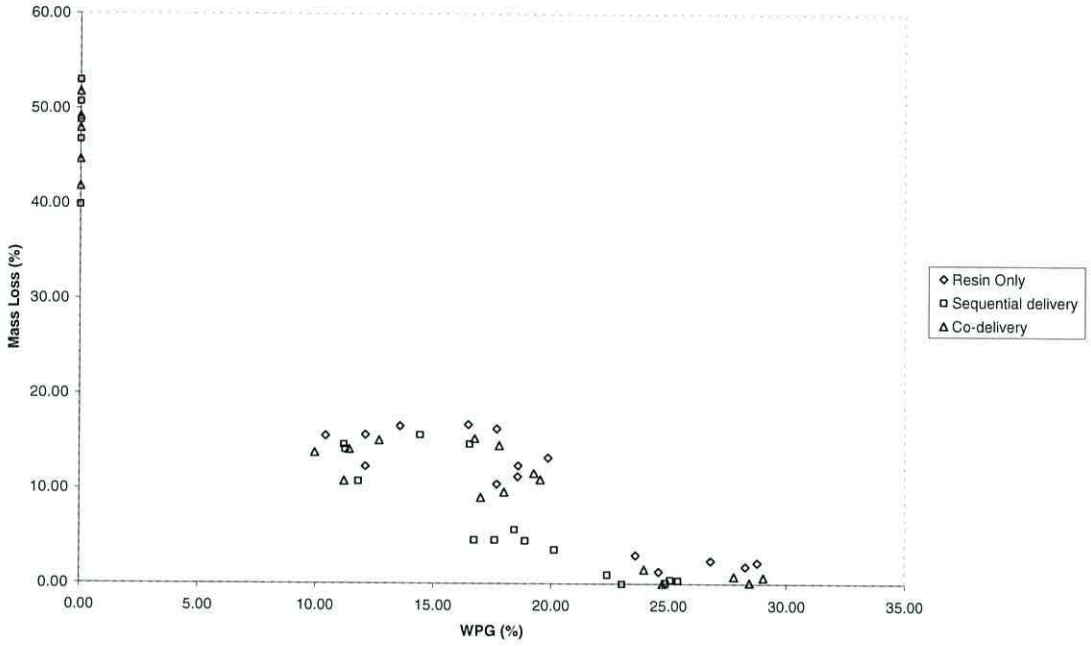


Figure 3.28: Graph to show the comparison of the *C. versicolor* decay resistance of MUF only treated Corsican pine against timber treated with MUF resin and biocide (also shown are the untreated control samples)

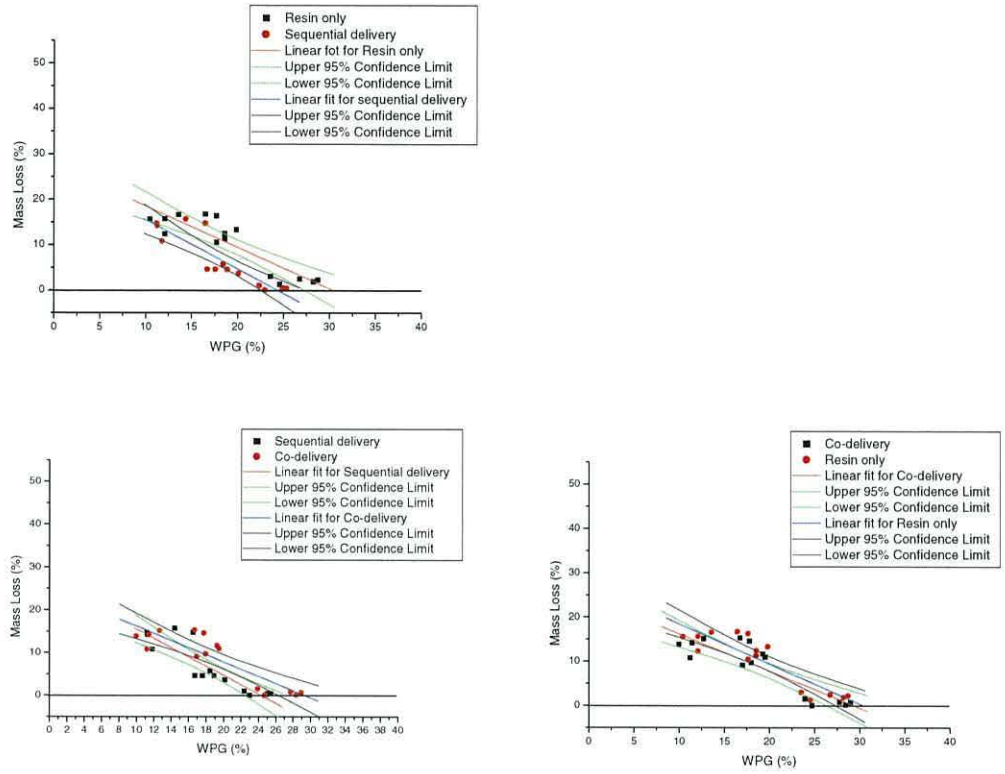


Figure 3.29: Interaction between the linear regressions for Corsican pine treated with MUF resin decayed with *C. versicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF reisn only	y=27.60417+(-0.90786*x)	2.94256	<0.0001
MUF resin sequential	y=26.30772+(-1.07884*x)	2.81251	<0.0001
MUF resin co-delivery	y=24.63865+(-0.83884*x)	3.00264	<0.0001

Table 3.23: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.29

	Resin only	Sequential	Co-delivery
Resin only	-	NS	-
Sequential	-	-	NS
Co-delivery	NS	-	-

Table 3.24: Table to show whether the difference between the linear regressions in Figure 3.29 are significent (S) or not significent (NS).

Figure 3.30, Figure 3.32 and Figure 3.34 show the decay resistance of UF treated timber and UF and biocide treated Corsican pine against *C. puteana*, and *C. versicolor* and *P. chrysosporium*.

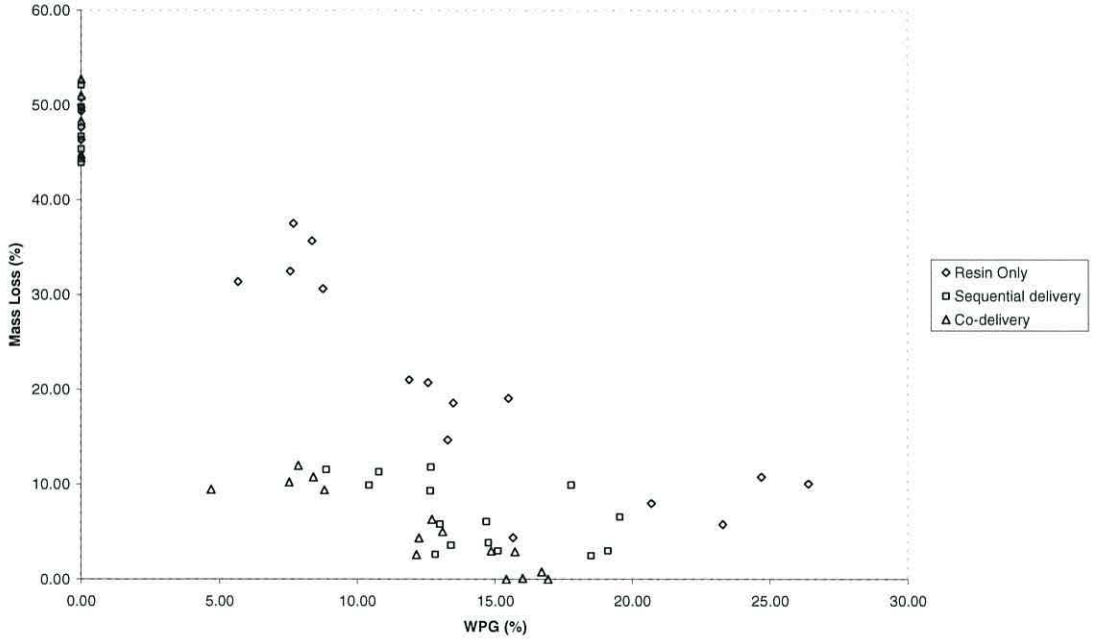


Figure 3.30: Graph to show the comparison of the *C. puteana* decay resistance of UF only treated Corsican pine against timber treated with UF resin and biocide (also shown are the untreated control samples)

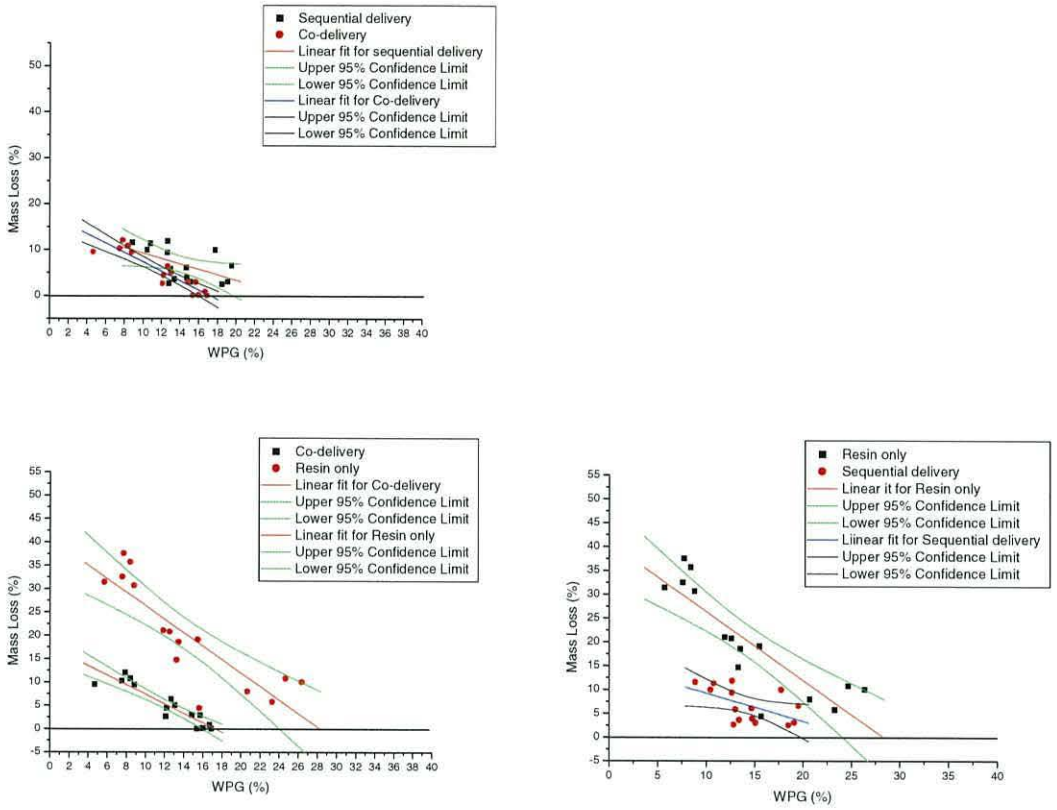


Figure 3.31: Interaction between the linear regressions for Corsican pine treated with UF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=40.7596+(-1.44004*x)	6.06316	<0.0001
UF resin sequential	y=15.13486+(-0.58842*x)	3.13971	0.04015
UF resin co-delivery	y=17.57089+(-1.011852*x)	1.73283	<0.0001

Table 3.25: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.31

	Resin only	Sequential	Co-delivery
Resin only	-	S	-
Sequential	-	-	NS
Co-delivery	S	-	-

Table 3.26: Table to show whether the difference between the linear regressions in Figure 3.31 are significent (S) or not significent (NS).

Figure 3.30 shows the mass loss of wood modified with UF timber and UF timber and biocides. It can be seen that there is a significant difference between the resin only modified samples and the resin and biocide treated samples. It can be seen that there is no significant difference between the two biocide modifications. It is likely that the reduction in mass loss is due to the effect of the biocide being 'released' as the UF resin is hydrolysed by the moisture transported into the timber by the fungi.

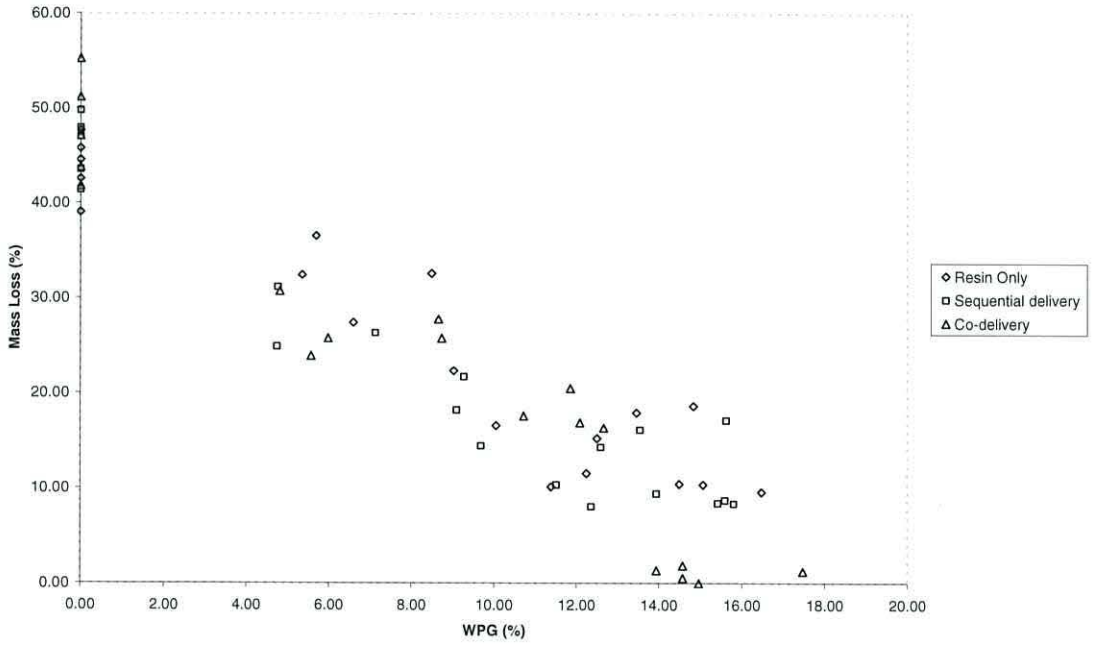


Figure 3.32: Graph to show the comparison of the *C. versicolor* decay resistance of UF only treated Corsican pine against timber treated with UF resin and biocide (also shown are the untreated control samples)

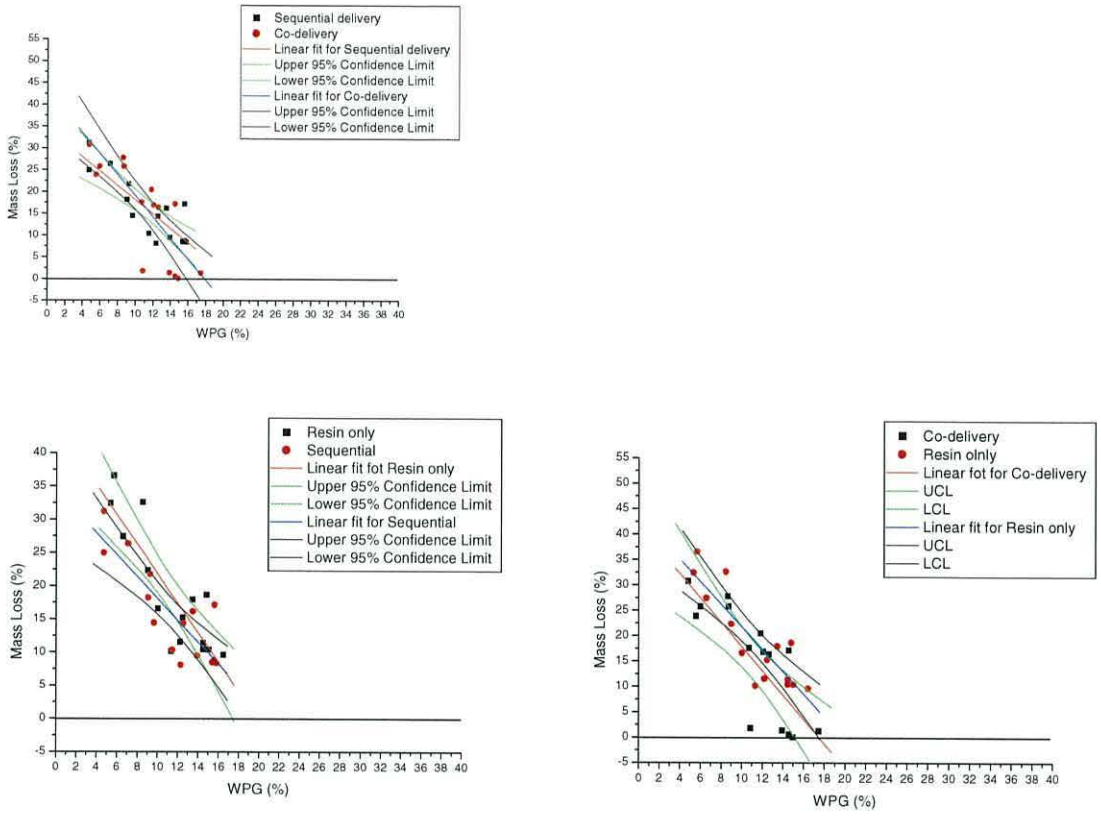


Figure 3.33: Interaction between the linear regressions for Corsican pine treated with UF resin decayed with *C. vesicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=44.04059+(-2.21835*x)	4.77723	<0.0001
UF resin sequential	y=44.04059+(-2.21835*x)	4.77723	<0.0001
UF resin co-delivery	y=43.20058+(-2.41443*x)	5.55648	<0.0001

Table 3.27: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.33

	Resin only	Sequential	Co-delivery
Resin only	-	NS	-
Sequential	-	-	NS
Co-delivery	NS	-	-

Table 3.28: Table to show whether the difference between the linear regressions in Figure 3.33 are significent (S) or not significent (NS).

Figure 3.32 shows the mass loss of the Corsican pine when decayed by *C. versicolor*. It can be seen that there is no significant difference between the mass loss of the timber modified with just resin and modified with resin and biocide.

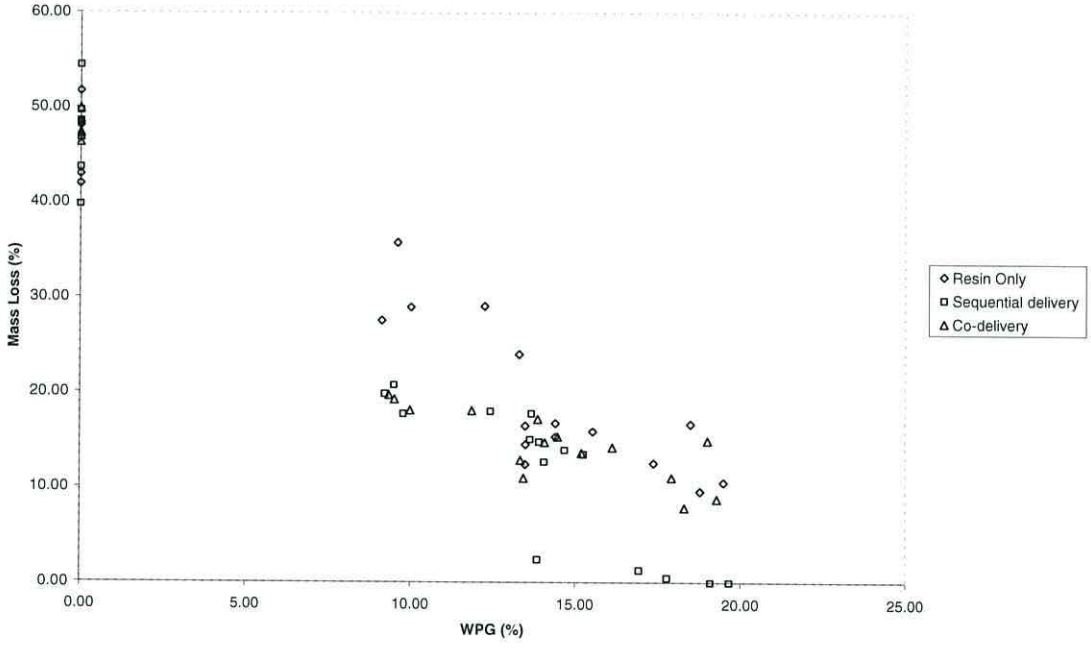


Figure 3.34: Graph to show the comparison of the *P. chrysosporium* decay resistance of UF only treated Corsican pine against timber treated with UF resin and biocide (also shown are the untreated control samples)

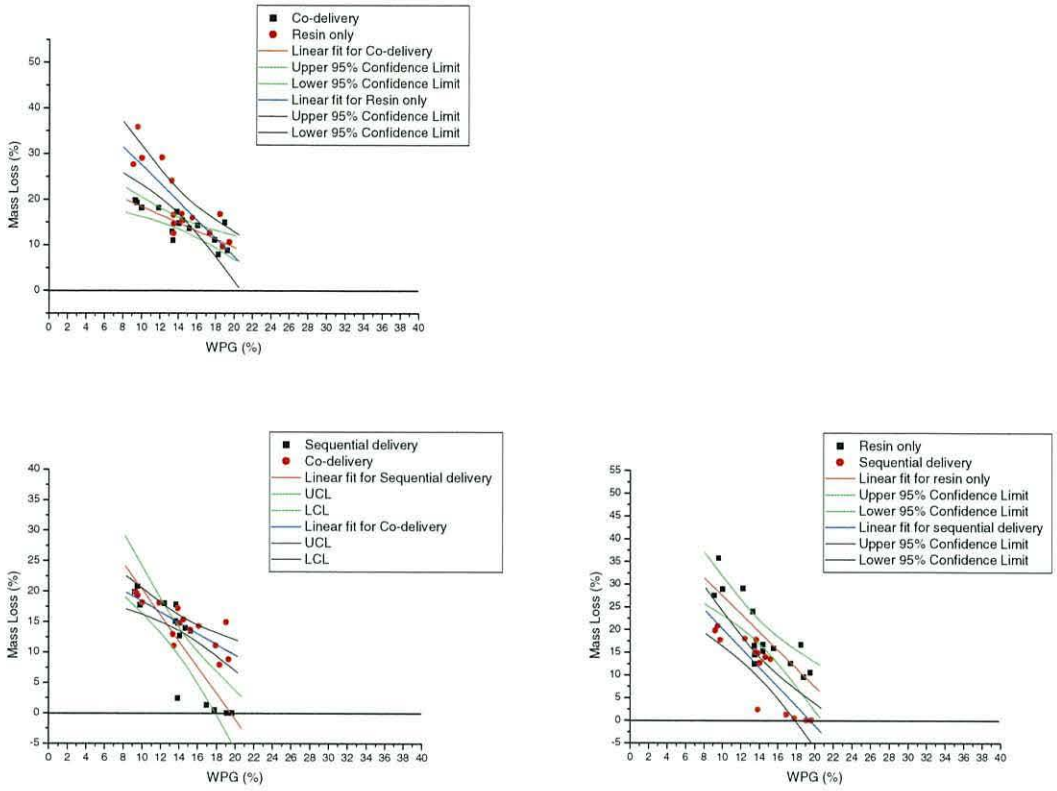


Figure 3.35: Interaction between the linear regressions for Corsican pine treated with UF resin decayed with *P. chrysosporium* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=47.55563+(-2.00363*x)	4.66396	0.0002
UF resin sequential	y=41.53619+(-2.13061*x)	4.12443	<0.0001
UF resin co-delivery	y=27.16845+(-0.88395*x)	2.28411	0.0003

Table 3.29: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.34

	Resin only	Sequential	Co-delivery
Resin only	-	NS	-
Sequential	-	-	Prob S
Co-delivery	Prob S	-	-

Table 3.30: Table to show whether the difference between the linear regressions in Figure 3.34 are significent (S) or not significent (NS).

Figure 3.34 shows the decay of the UF and UF and biocide modified timber by *P. chrysosporium*. It can be seen that there is significant difference between the co-delivery and the resin only modified timber. It can be seen that at low weight percent gain the resin and biocide has a lower weight loss than just resin. This is likely to be due to the hydrolysis of the resin and the release of the biocide. There is no significant difference between the resin only and the sequential delivery, however this is likely to be due to the spread of the data.

There is also a significant difference between the sequential and the co-delivery system. It can be seen that the sequential delivery system appears to give a lower mass loss at a higher WPG than the co-delivery system. It is likely that as the resin is hydrolysed the co-delivery system will release a limited amount of biocide, whereas in the sequential delivery system the resin is hydrolysed and a larger amount of biocide is released to prevent decay.

Figure 3.36, Figure 3.38 and Figure 3.40 shows the decay resistance of melamine formaldehyde treated beech against *C. puteana, C. versicolor* and *P. chrysosporium* respectively. It can be seen that the decay resistance of the samples against the three species of fungi all display a similar threshold value of 22% and they also show that there is no statistical difference between the resin only treated samples and the resin and biocide treated samples. The lack of significant difference can be attributed to the MF resins resistance to hydrolysis; it is likely that at lower concentrations of resin modification a similar pattern will

be found to those seen with the UF resin, however this will require further experimentation.

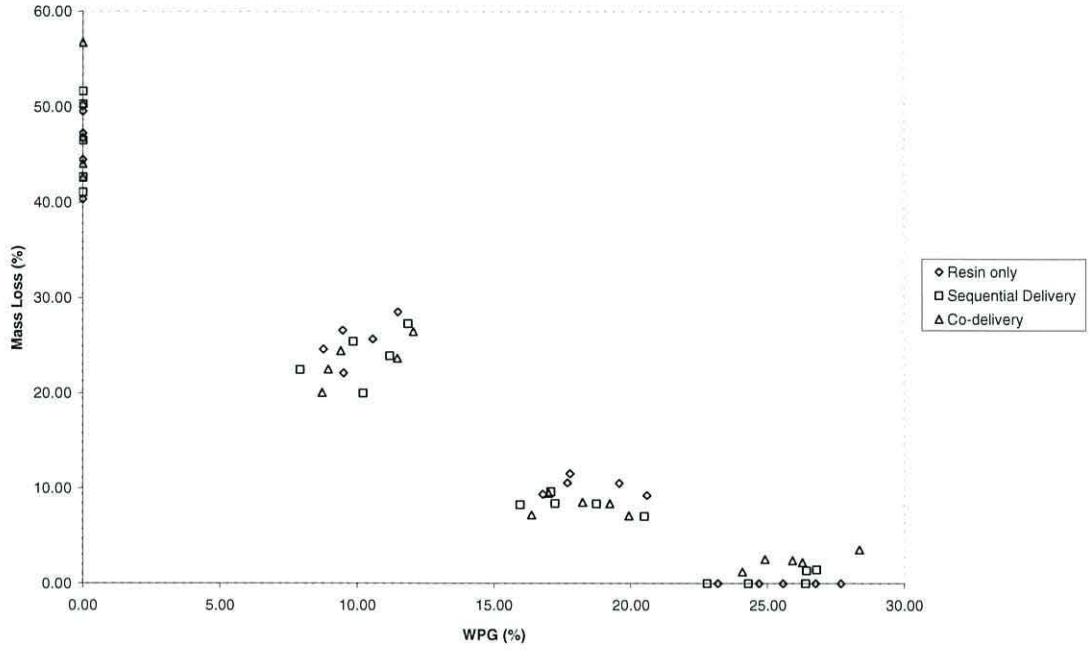


Figure 3.36: Graph to show the comparison of the *C. puteana* decay resistance of MF only treated beech against timber treated with MF resin and biocide (also shown are the untreated control samples)

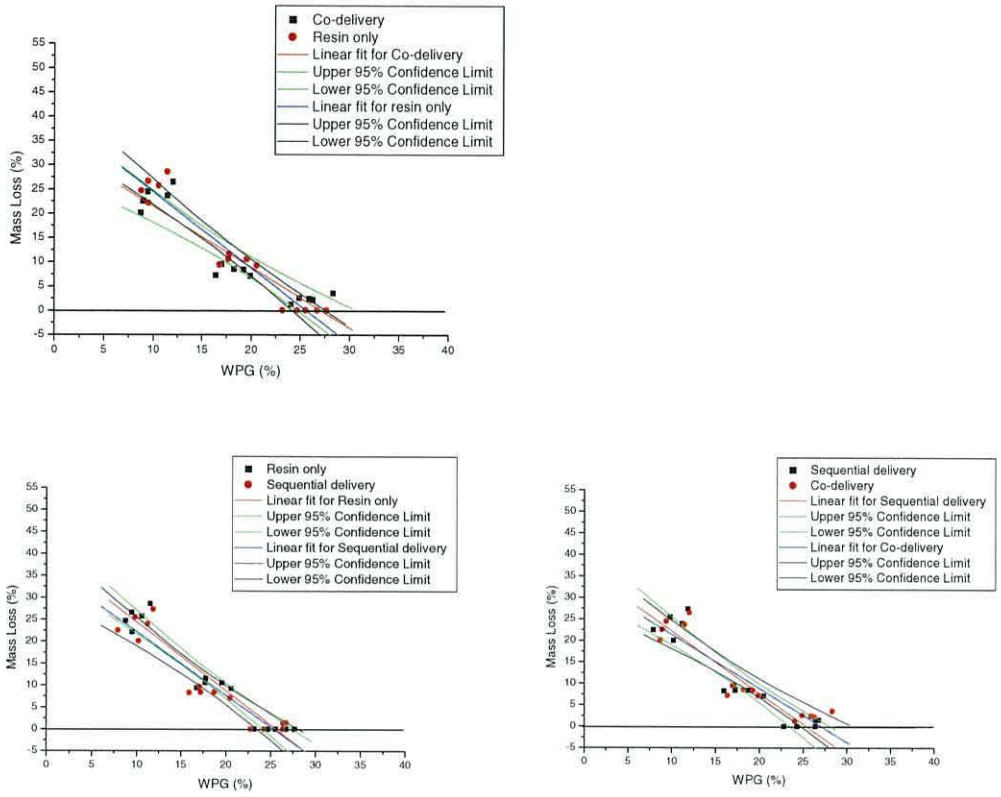


Figure 3.37: Interaction between the linear regressions for beech treated with MF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MF resin only	y=40.06735+(-1.56214*x)	3.001	<0.0001
MF resin sequential	y=36.65291+(-1.44389*x)	3.703229	<0.0001
MF resin co-delivery	y=33.99399+(-1.25426*x)	3.76633	<0.0001

Table 3.31: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.37

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.32: Table to show whether the difference between the linear regressions in Figure 3.37 are significent (S) or not significent (NS).

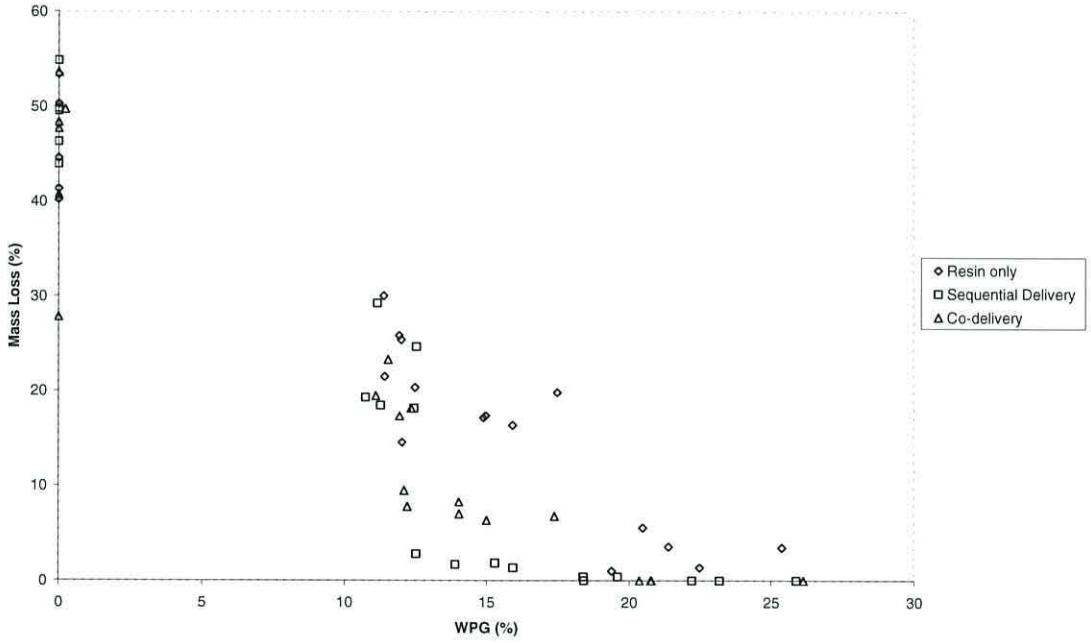


Figure 3.38: Graph to show the comparison of the *C. versicolor* decay resistance of MF only treated beech against timber treated with MF resin and biocide (also shown are the untreated control samples)

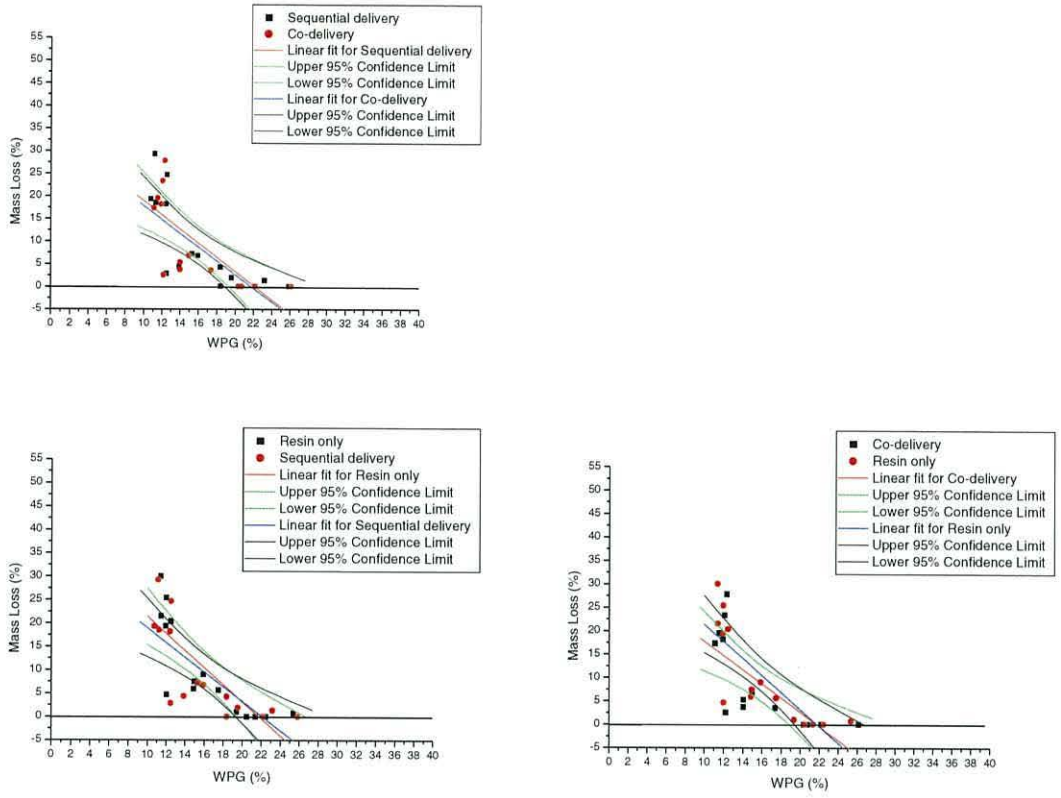


Figure 3.39: Interaction between the linear regressions for beech treated with MUF resin decayed with *C. versicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MF resin only	y=39.67647+(-1.82131*x)	6.32259	<0.0001
MF reisn sequential	y=34.65318+(-1.56546*x)	6.67722	<0.0001
MF reisn co-delivery	y=32.99102+(-1.51597*x)	6.84576	<0.0001

Table 3.33: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.39.

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.34: Table to show whether the difference between the linear regressions in Figure 3.39 are significent (S) or not significent (NS).

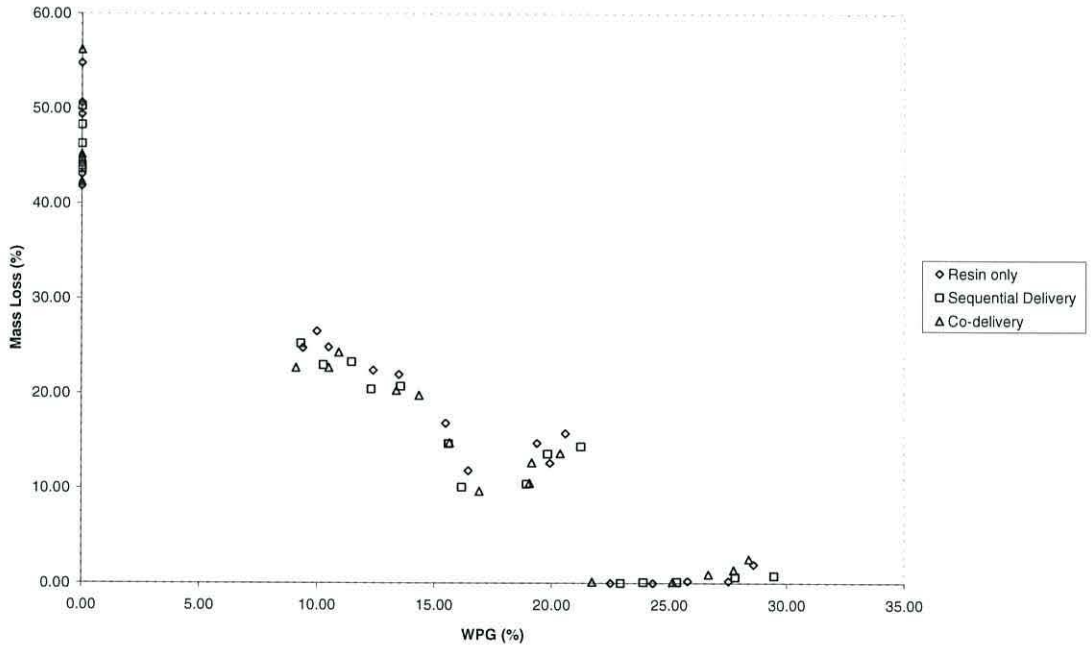


Figure 3.40: Graph to show the comparison of the *P. chrysosporium* decay resistance of MF only treated beech against timber treated with MF resin and biocide (also shown are the untreated control samples)

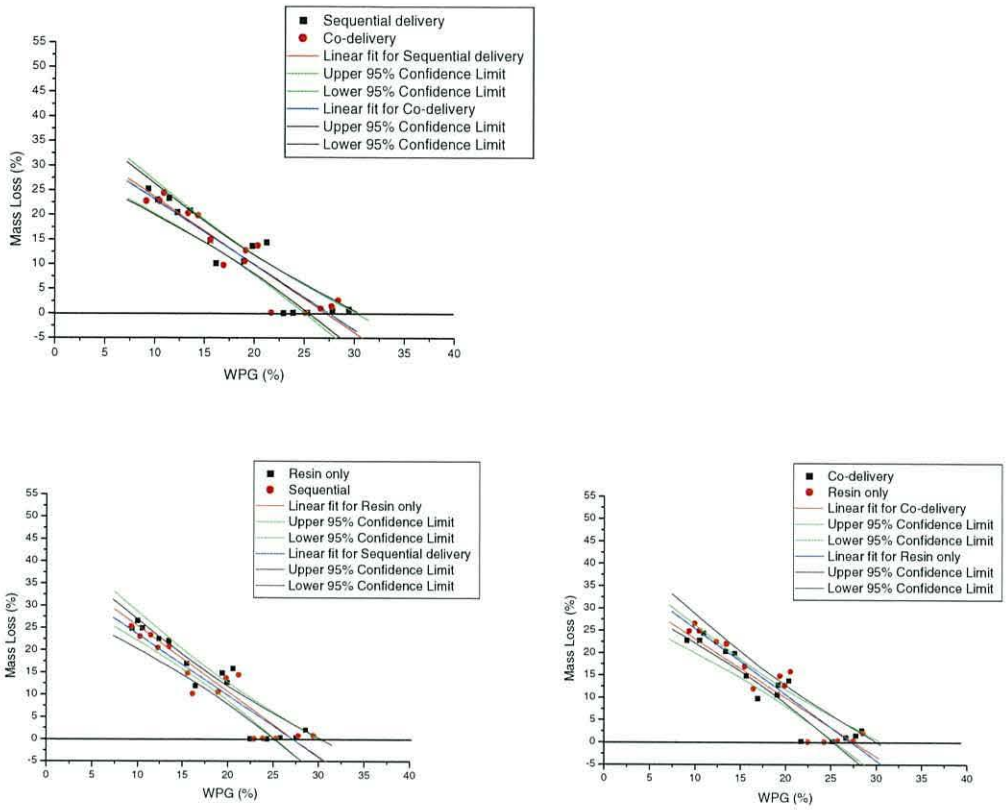


Figure 3.41: Interaction between the linear regressions for beech treated with MF resin decayed with *P. chrysosporium* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MF resin only	y=40.23401+(-1.47804*x)	3.50851	<0.0001
MF reisn sequential	y=37.31638+(-1.3727*x)	3.54619	<0.0001
MF reisn co-delivery	y=36.29467+(-1.31806*x)	3.28174	<0.0001

Table 3.35: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.41

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.36: Table to show whether the difference between the linear regressions in Figure 3.41 are significent (S) or not significent (NS).

Again no statistical difference is seen between the MUF modified beech and the beech modified with the resin and biocide systems. The 22% threshold value is again apparent with the MUF treated samples.

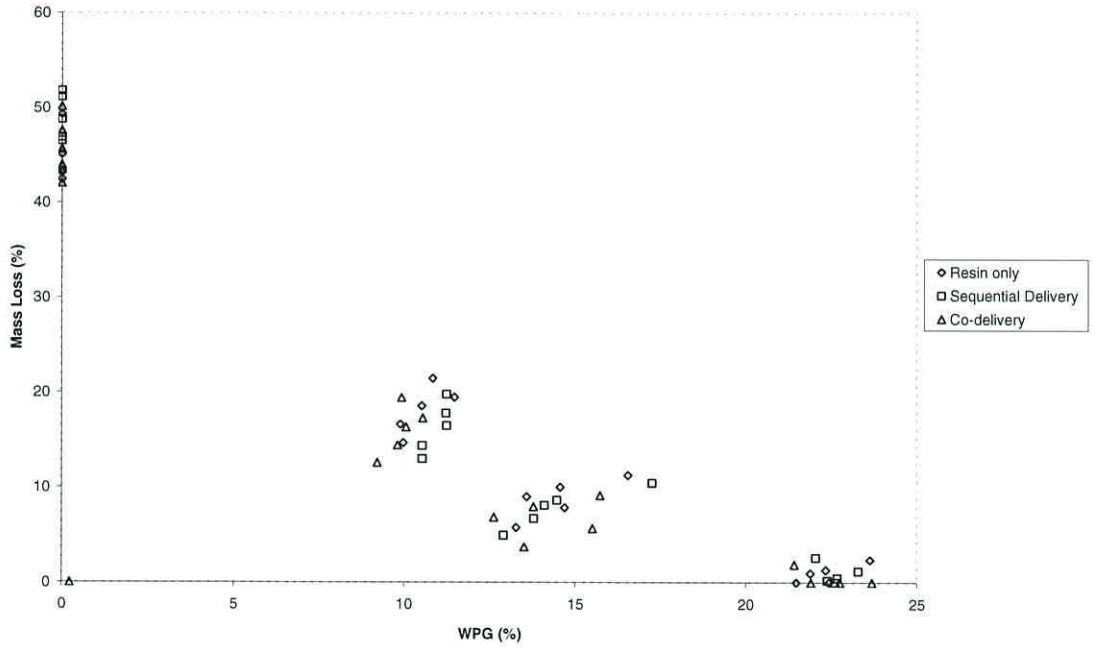


Figure 3.42: Graph to show the comparison of the *C. puteana* decay resistance of MUF only treated beech against timber treated with MUF resin and biocide.

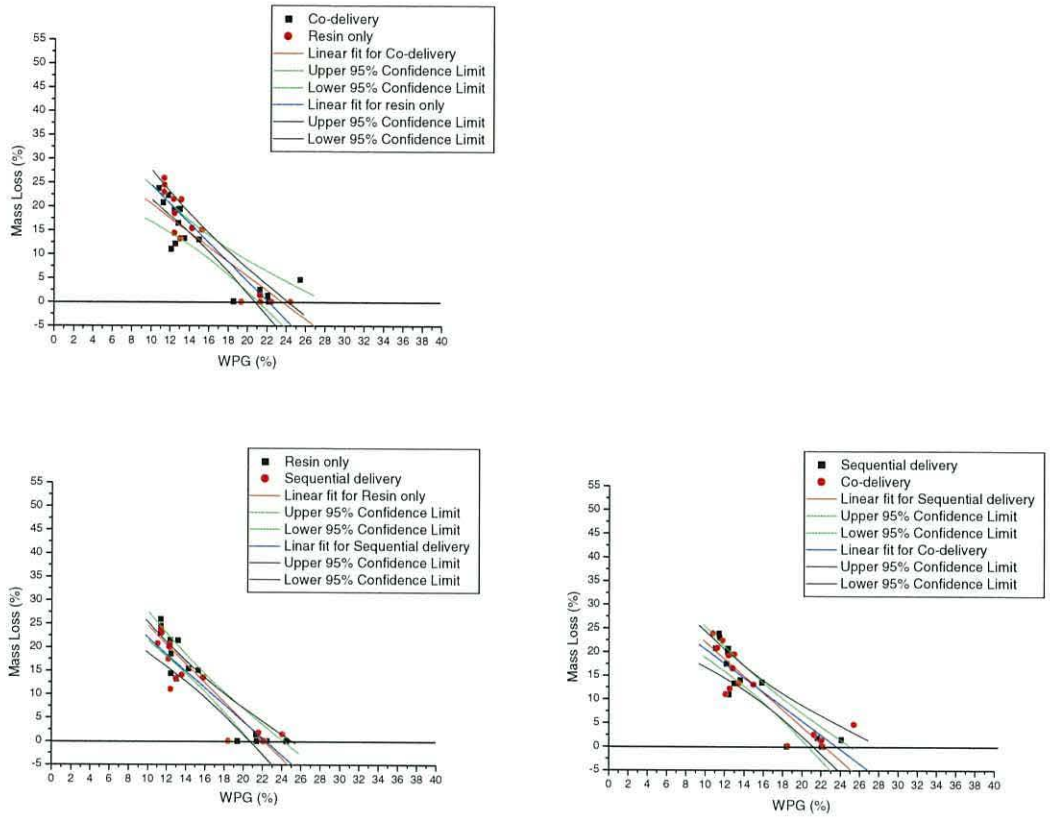


Figure 3.43: Interaction between the linear regressions for Beech treated with MUF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF reisn only	y=44.7931+(-2.01957*x)	3.42414	<0.0001
MUF resin sequential	y=39.889+(-1.78225*x)	3.69881	<0.0001
MUF resin co-delivery	y=35.65053+(-1.50887*x)	4.33063	<0.0001

Table 3.37: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.43

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.38: Table to show whether the difference between the linear regressions in Figure 3.43 are significent (S) or not significent (NS).

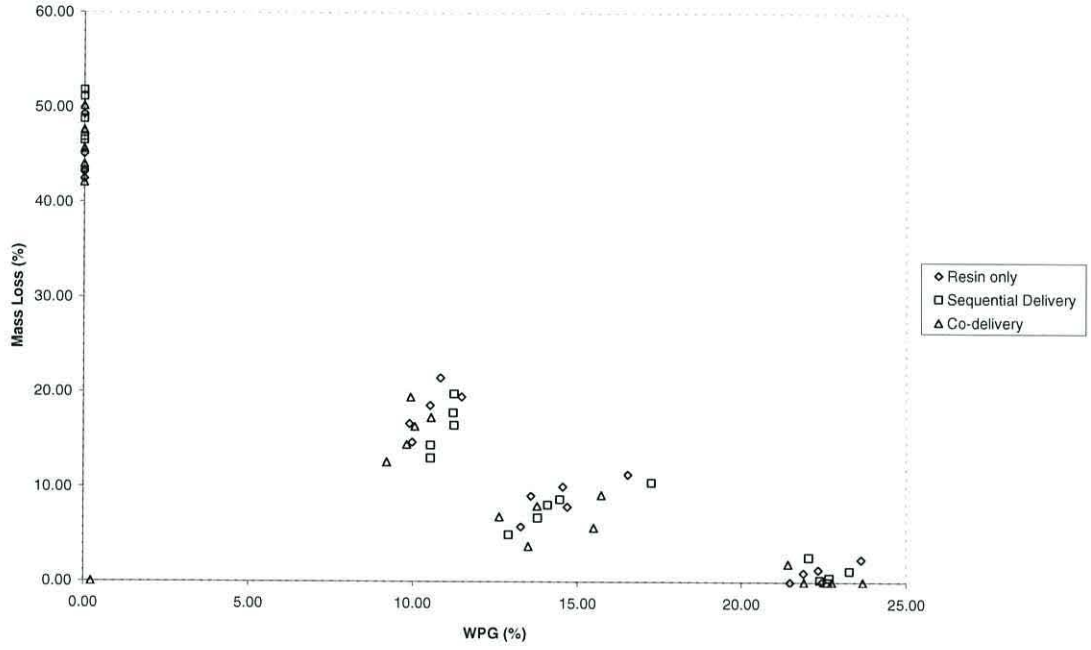


Figure 3.44: Graph to show the comparison of the *C. versicolor* decay resistance of MUF only treated beech against timber treated with MUF resin and biocide. (also shown are the untreated control samples)

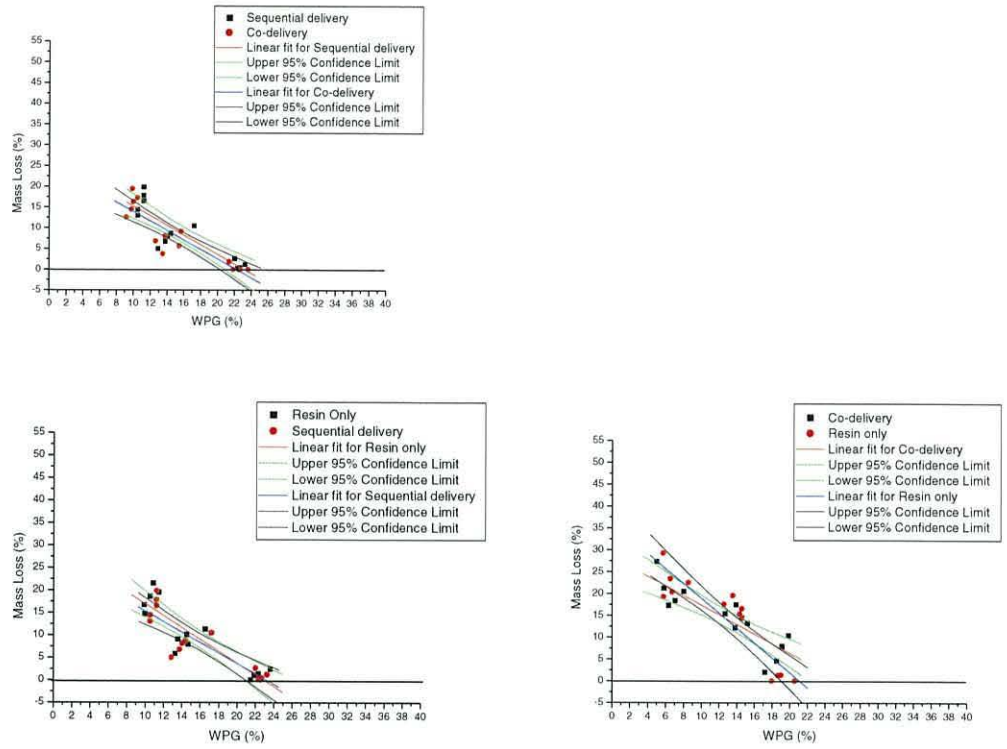


Figure 3.45: Interaction between the linear regressions for Beech treated with MUF resin decayed with *C. versicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF resin only	y=30.06581+(-1.31289*x)	3.43356	<0.0001
MUF resin sequential	y=26.89626+(-1.15845*x)	3.41931	<0.0001
MUF resin co-delivery	y=25.34949+(-1.13492*x)	3.11301	<0.0001

Table 3.39: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.45

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.40: Table to show whether the difference between the linear regressions in Figure 3.45 are significent (S) or not significent (NS).

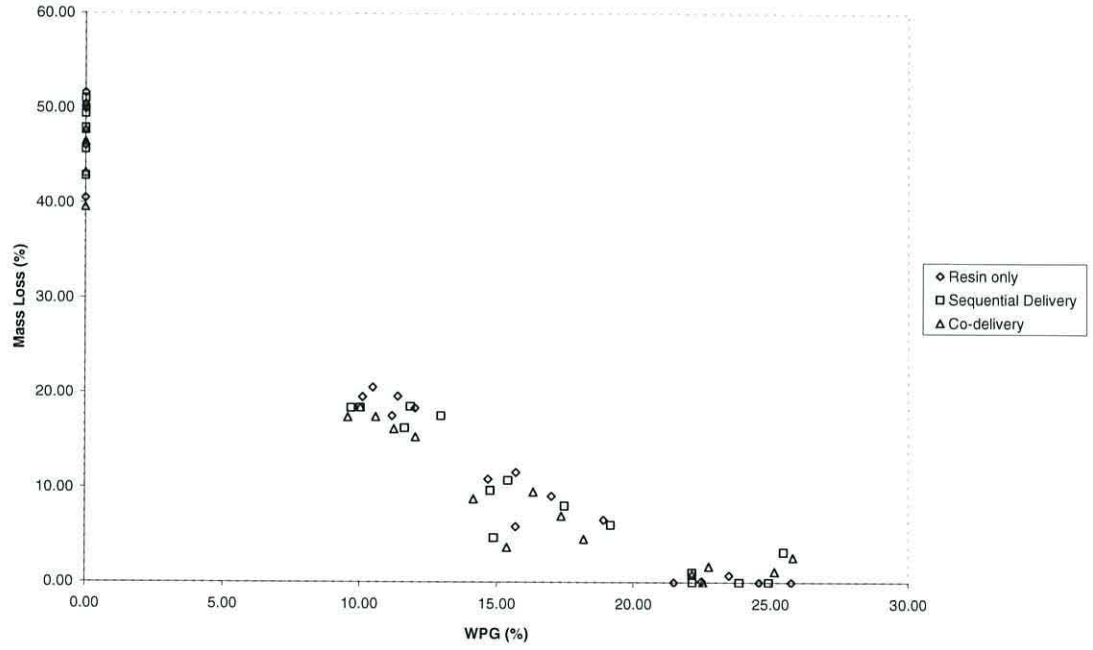


Figure 3.46: Graph to show the comparison of the *P. chrysosporium* decay resistance of MUF only treated beech against timber treated with MUF resin and biocide. (also shown are the untreated control samples)

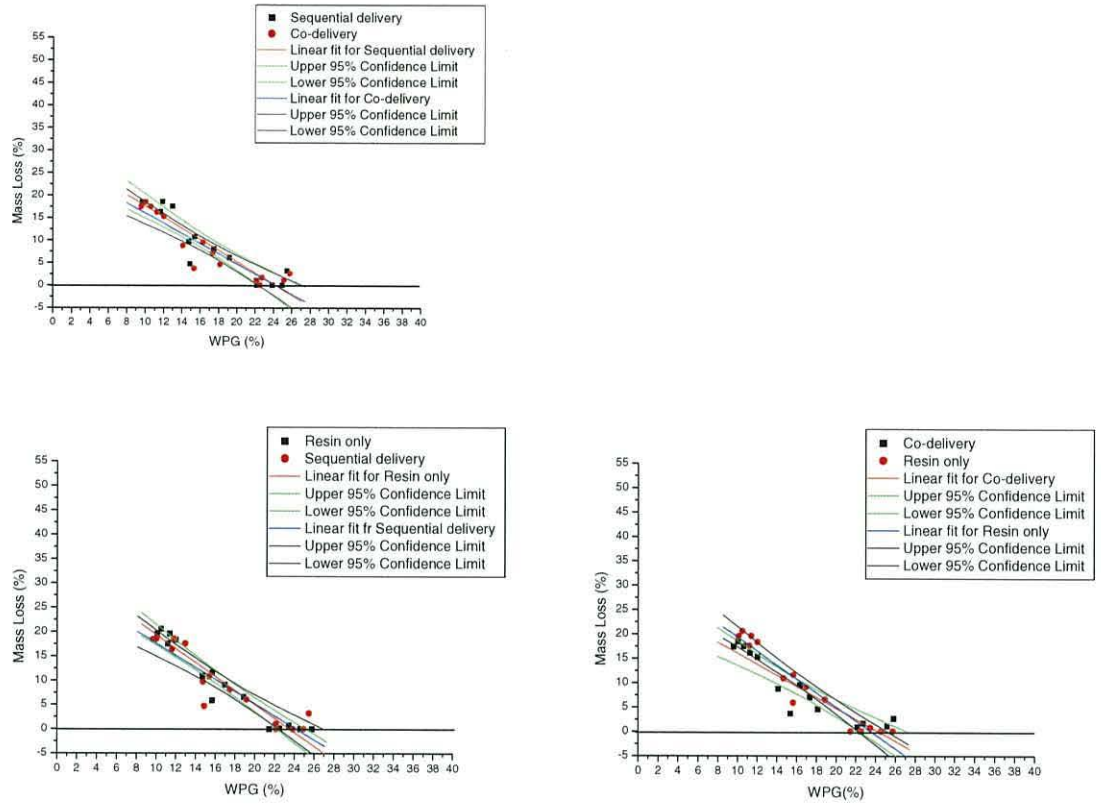


Figure 3.47: Interaction between the linear regressions for beech treated with MUF resin decayed with *P. chrysosporium* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
MUF resin only	y=33.76378+(-1.43541x)	2.28034	<0.0001
MUF resin sequential	y=30.07943+(-1.24178*x)	2.89149	<0.0001
MUF resin co-delivery	y=27.35794+(-1.12822*x)	2.7584	<0.0001

Table 3.41: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.47

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.42: Table to show whether the difference between the linear regressions in Figure 3.47 are significent (S) or not significent (NS).

Figure 3.48, Figure 3.50 and Figure 3.52 show the decay resistance of urea formaldehyde modified beech and UF and biocide modified beech. It can be seen that there is no statistical difference between the resin only treatment and the resin and biocide treatments. It would have been expected that the decay of the UF modified timber would be influenced by the presence of the biocide as with the other fungi trialled.

It can be seen that the threshold value of around 22% is achieved with all three treatments.

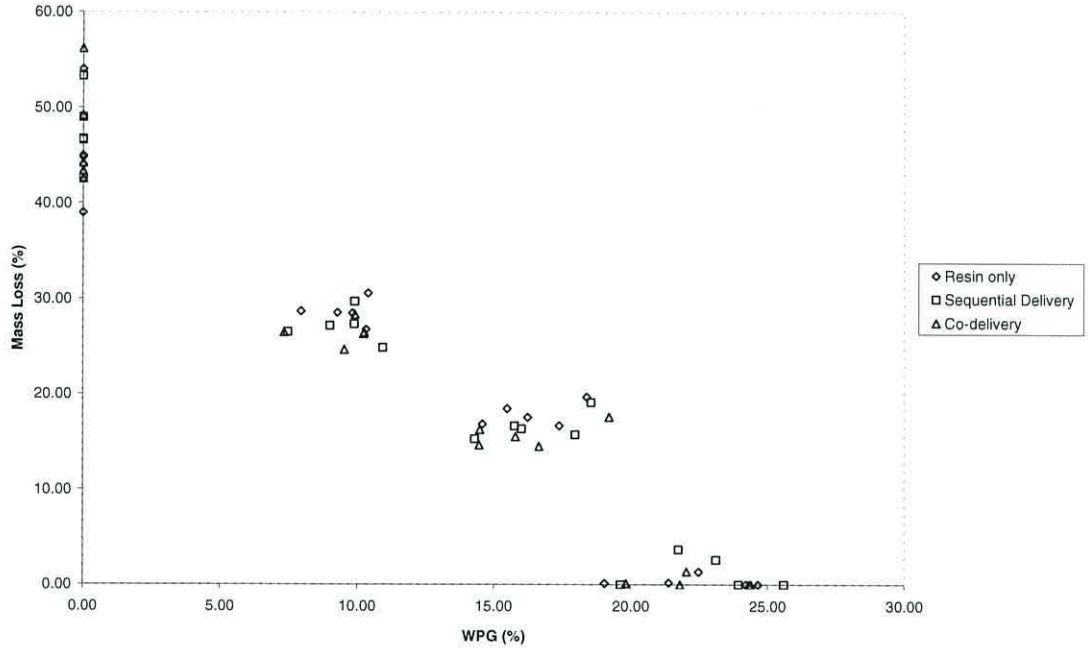


Figure 3.48: Graph to show the comparison of the *C. puteana* decay resistance of UF only treated beech against timber treated with UF resin and biocide. (also shown are the untreated control samples)

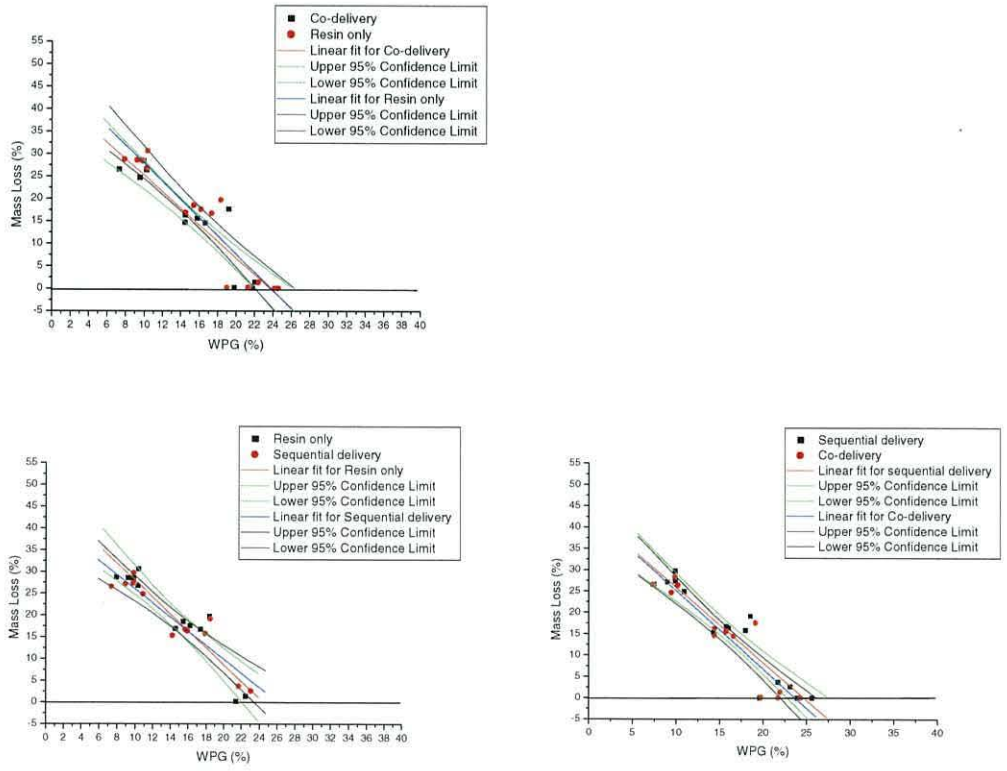


Figure 3.49: Interaction between the linear regressions for beech treated with UF resin decayed with *C. puteana* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=47.64739+(-1.94456*x)	3.78448	<0.0001
UF resin sequential	y=42.33302+(-1.61907*x)	3.34649	<0.0001
UF resin co-delivery	y=43.59620+(-1.83721*x)	3.85333	<0.0001

Table 3.43: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.49

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.44: Table to show whether the difference between the linear regressions in Figure 3.49 are significent (S) or not significent (NS).

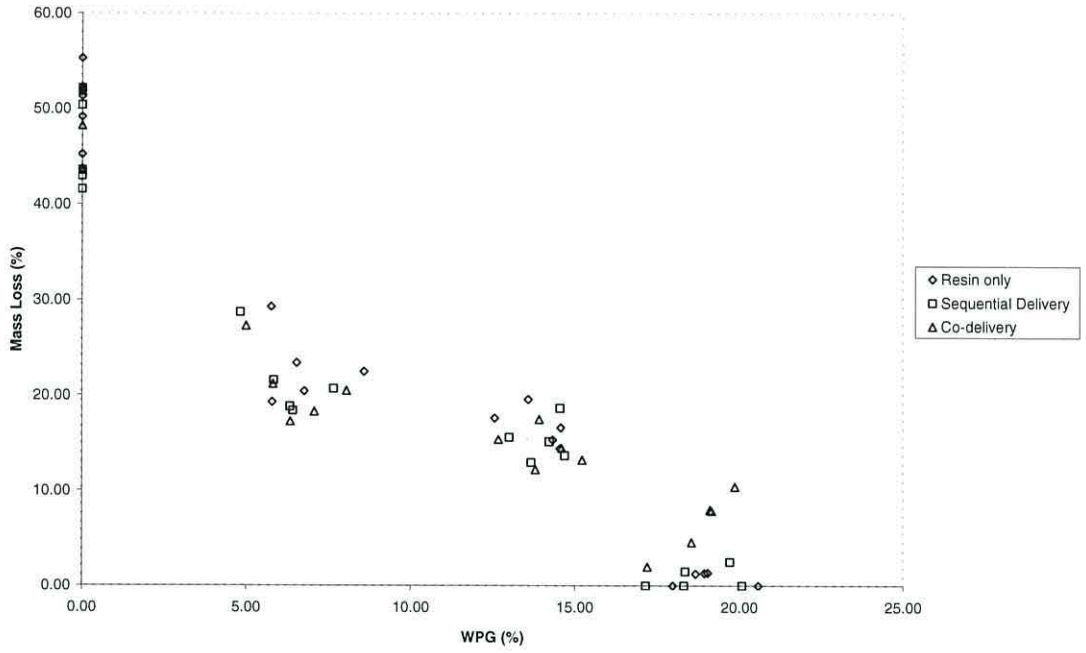


Figure 3.50: Graph to show the comparison of the *C. versicolor* decay resistance of UF only treated beech against timber treated with UF resin and biocide (also shown are the untreated control samples)

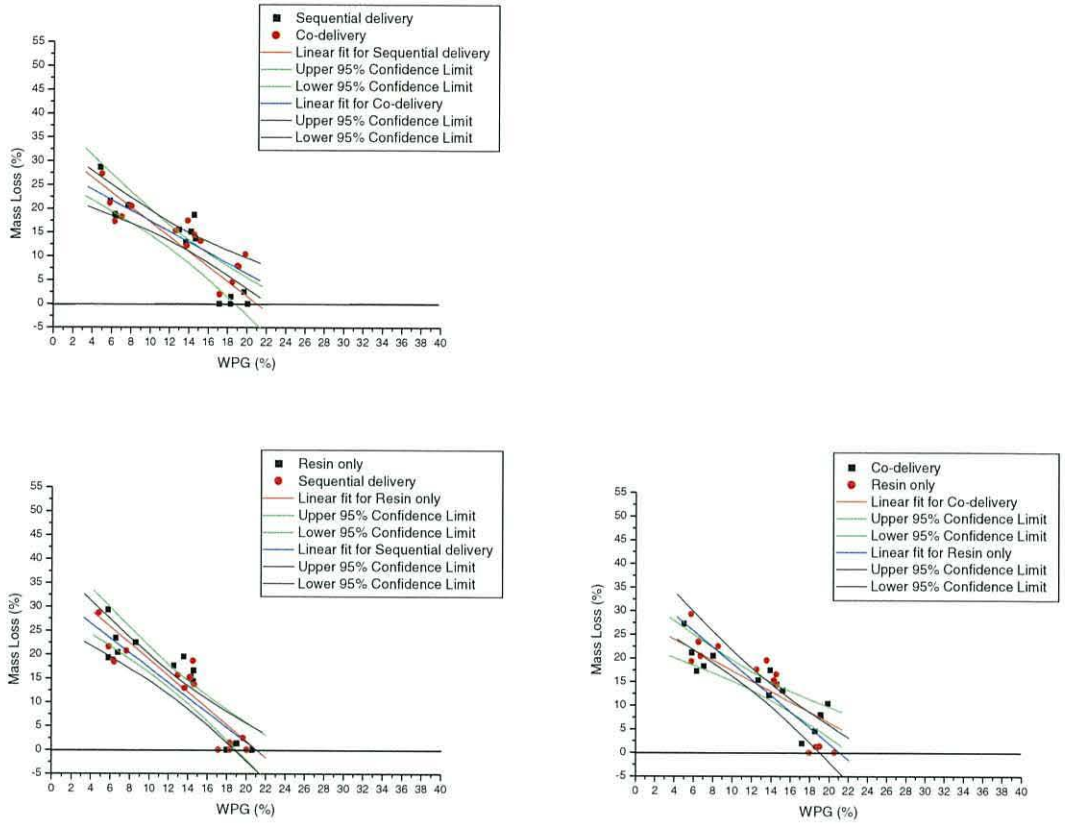


Figure 3.51: Interaction between the linear regressions for beech treated with UF resin decayed with *C. versicolor* (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=36.02012+(-1.70461*x)	4.2304	<0.0001
UF resin sequential	y=32.76142+(-1.55576*x)	4.26247	<0.0001
UF resin co-delivery	y=28.39366+(-1.09935*x)	3.4578	<0.0001

Table 3.45: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.51

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.46: Table to show whether the difference between the linear regressions in Figure 3.51 are significent (S) or not significent (NS).

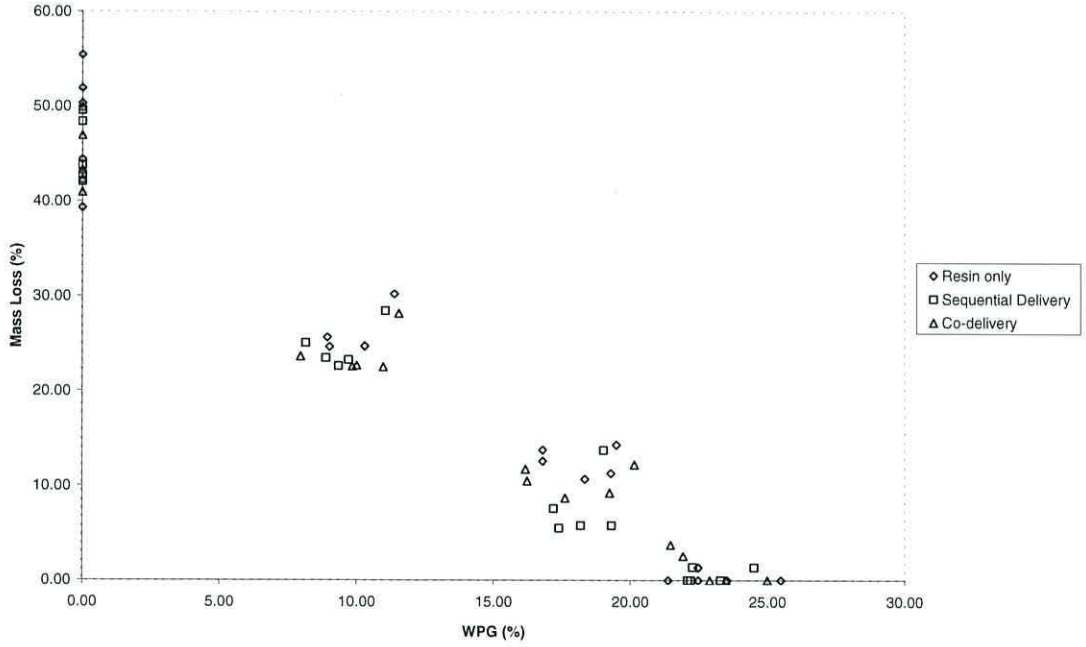


Figure 3.52: Graph to show the comparison of the *P. chrysosporium* decay resistance of UF only treated beech against timber treated with UF resin and biocide. (also shown are the untreated control samples)

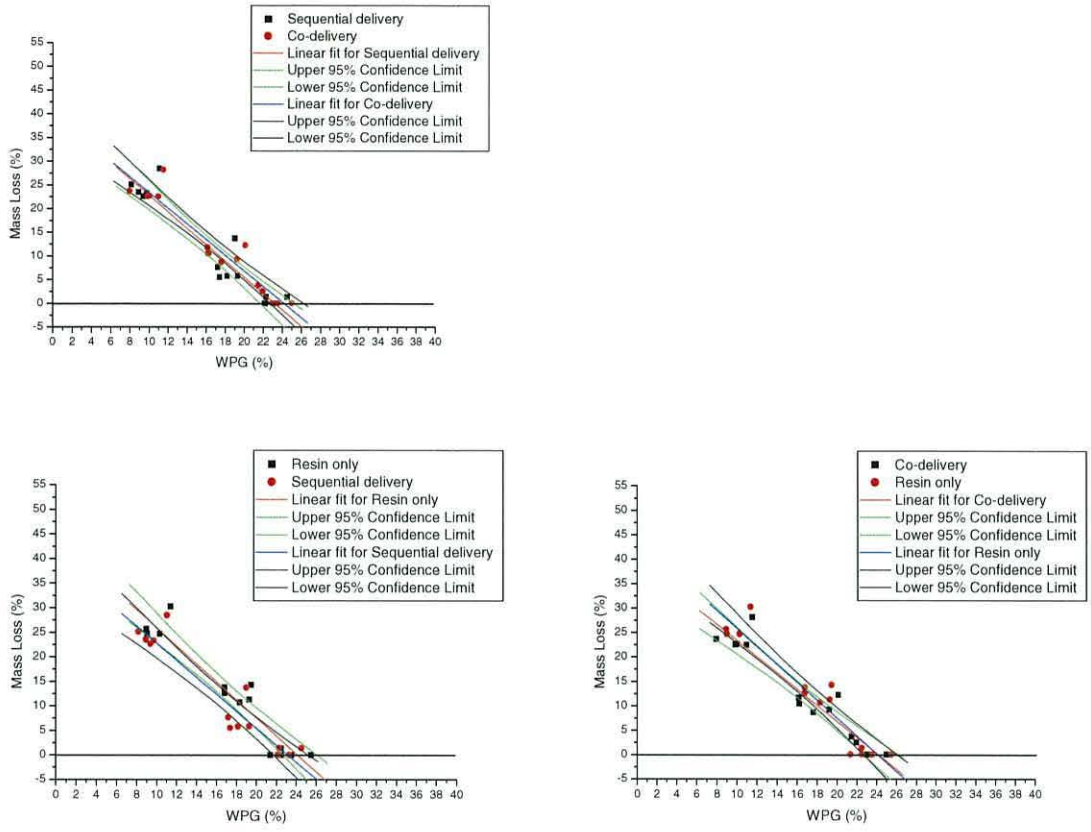


Figure 3.53: Interaction between the linear regressions for beech treated with UF resin decayed with P. chrysosporium (and the 95% confidence intervals)

Treatment	Linear regression equation	SD	P value
UF resin only	y=44.25498+(-1.83527*x)	3.36092	<0.0001
UF resin sequential	y=40.0818+(-1.73x)	3.50174	<0.0001
UF resin co-delivery	y=39.86449+(-1.64897*x)	3.0465	<0.0001

Table 3.47: Equations for linear regressions, standard deviations and P-values for the interactions shown in Figure 3.53

	Resin only	Sequential	Co-delivery
Resin only		NS	
Sequential			NS
Co-delivery	NS		

Table 3.48: Table to show whether the difference between the linear regressions in Figure 3.53 are significent (S) or not significent (NS).

3.4 Chapter Summary

This chapter reports an investigation into the use of resin coupled with a novel biocide to protect wood from fungal decay.

The work here was carried out in accordance with BS EN 113:1997 9with leaching carried out in accordance with BS EN 84. BS EN 113 determines decay resistance over a 16 week period.

Three resins were trialled in the investigation; urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde.

Table 3.49 shows a summary of the resin decay trial run with resin only modified samples. In the case of the Corsican pine, it can be seen that, with exception to the MUF modified samples decayed with *C. puteana*, all the timbers modified with melamine containing resins are have a linear regression that is significantly different to that of the UF containing resins. it should also be noted that the all the linear regressions for the timbers decayed with *C. versicolor* are all significantly different to one another. It can be seen that there are no significant differences between the mass losses of the resin modified beech samples.

Timber species	Fungal species	Significant differences	Non significant differences
Corsican pine	*C. puteana*	MF/UF MF/UF	MUF/UF MF/MUF
	C. versicolor	MF/MUF MUF/UF	-
	P. chrysosporium	MUF/UF MF/UF	MUF/MF
Beech	*C. puteana*	-	MF/UF MF/MUF MUF/UF
	C. versicolor	-	MF/UF MF/MUF MUF/UF
	P. chrysosporium	-	MF/UF MF/MUF MUF/UF

Table 3.49: Summary of the significant differences in the resin only modification decay tests

Table 3.50 shows the threshold values for the resin treated Corsican pine have an average of 28.33% and resin treated beech has an average threshold value of 22.56%

Timber Species	Resin type	Fungal species	Threshold value (rounded to 0dp)
Corsican Pine	Melamine Formaldehyde	*C. puteana*	30%
		C. versicolor	30%
		P. chrysosporium	30%
	Melamine Urea Formaldehyde	*C. puteana*	30%
		C. versicolor	30%
		P. chrysosporium	27%
	Urea Formaldehyde	*C. puteana*	30%
		C. versicolor	23%
		P. chrysosporium	25%
Beech	Melamine Formaldehyde	*C. puteana*	24%
		C. versicolor	21%
		P. chrysosporium	22%
	Melamine Urea Formaldehyde	*C. puteana*	22%
		C. versicolor	22%
		P. chrysosporium	22%
	Urea Formaldehyde	*C. puteana*	26%
		C. versicolor	21%
		P. chrysosporium	23%

Table 3.50: Summary of threshold values for the resin treated timber

Table 3.51 shows a summary of the significant differences of the mass losses of the biocide and resin treated Corsican pine. When MF treated timbers are subjected to decay by *P. chrysosporium* it can be seen that there is a significant difference between the resin only treatment and the two treatments that include biocide, however it has been found that the resin only treatment gives better protection than the treatment containing the biocide. The most probable cause for this anomalous result is experimental error.

Resin Type	Fungal species	Significant differences	Non significant differences
Melamine Formaldehyde	*C. puteana*	-	RO/S RO/CD S/CD
	C. versicolor	-	RO/S RO/CD S/CD
	P. chrysosporium	RO/S RO/CD	S/CD
Melamine Urea Formaldehyde	*C. puteana*		RO/S RO/CD S/CD
	C. versicolor		RO/S RO/CD S/CD
	P. chrysosporium		RO/S RO/CD S/CD
Urea Formaldehyde	*C. puteana*	RO/S RO/CD	S/CD
	C. versicolor		RO/S RO/CD S/CD
	P. chrysosporium	RO/CD S/CD	RO/S

Table 3.51: Summary of the significance of the differences between the decay results of the treated Corsican pine

The decay results for the UF treated Corsican pine is of great interest. It can be seen that there are significant differences between the resin only treated and the resin and biocide treated samples when being decayed with *C. puteana* and *P. chrysosporium* (however not with sequential delivery but this was deemed due to the spread of the data). These significant differences showed the resin and biocide providing greater decay resistance than the resin alone. This was deemed

due to the biocide being released by the resin when it was broken down by hydrolysis. It is also interesting to note that in the case of the UF and biocide treated Corsican pine decayed with *P. chrysosporium* the sequential delivery exhibits better decay resistance than the co-delivery. This was attributed to the sequential delivery causing the release of a greater amount of biocide on hydrolysis than the co-delivered system in which the biocide is locked in the resin. This could be demonstrated in further studies by addressing the leaching properties of the biocide when coupled with the resins.

Due to the hydrolytic properties of the urea formaldehyde resin it can be used as a model for how the timbers modified with the melamine containing resins will perform in longer decay tests or in service. It is expected that the resin will eventually break down, as the UF resin did in this test, and release the biocide to aid the decay prevention. However this theory should be tested in further experimentation.

The differences between the decay resistance given to beech by the different modifications were not significant for any of the fungi or resin types.

3.5 Conclusion of this chapter

It was found that the resins themselves give decay protection to the wood; this is in agreement with the work of Stamm and Baechler (1960). This protection is due to the physical blocking of the OH groups in the cell wall and the inhibition of moisture ingress into the cell wall thus making it unsuitable as a substrate for decay.

This investigation showed that when Corsican pine was treated with the three resins the threshold value for the prevention of the decay by *C. puteana, C. versicolor* and *P. chrysosporium* had an average of 28.33% WPG and this did not vary significantly with the type of resin used. It has shown that significant

differences were found between UF resin modified timbers and timbers modified with UF and biocide.

It has been noted that the urea formaldehyde modified Corsican pine can be used as a model for longer term decay of modified timbers due to the fact that the urea formaldehyde breaks down due to hydrolysis. This investigation has shown that as the urea formaldehyde breaks down there is a release of biocide that aids the prevention of decay. It can be postulated that even when modified with resins that do not hydrolyse over time the barrier created by the resin will eventually break down and therefore the biocide will be needed to aid decay resistance. In further studies this can be tested by running long term soil burial tests.

It has also been shown that the average threshold value for the prevention of the decay of beech by *C. puteana, C. versicolor* and *P. chrysosporium* was 22.55% WPG and this did not vary significantly with the type of resin used. However with beech no significant differences were found in the decay resistance of the difference modifications used.

It is thought by the investigator that the inclusion of the biocide will aid the long term decay resistance of the resin modified timber and it will also aid the decay resistance of timber in hazard class 2 and 3.

Chapter 4 will show the decay resistance of the known benign modification and the results of this investigation into the decay of anhydride modified timber will be compared with those of the resin treated timber.

4 The decay of Anhydride treated timber.

4.1 Introduction

Chapter 3 has shown that the presence of resin within the wood improves the decay resistance of the wood. It has been postulated that this could be due to the reduction in the cell wall moisture content. However this can be directly attributed to the resin weight percent gain because the distribution of the resin within the wood is unknown.

It is widely known that the reactions of anhydride modification take place within the cell wall and therefore a link between the WPG, moisture content reduction and the decay resistance of the modified timber can be investigated. The mechanism for the decay resistance of the resin modified wood can then be compared.

This chapter reports an investigation into the decay resistance of two timbers (Corsican pine and beech) modified with two anhydrides (acetic and hexanoic). The mechanism for decay resistance of anhydride treated timbers will also be investigated and two competing theories will be compared, namely cell wall bulking and hydroxyl substitution. Cell wall bulking prevents decay by blocking the micropores to the ingress of water and decay enzymes and excreted chemicals (such as oxalic acid) into the cell wall. The second route for decay resistance is the substitution of the hydroxyl groups with the acetyl groups which will prevent the enzymatic attack of the cell wall. It has been suggested that this prevention is due to the enzymes not being able to recognise the substrate.

4.2 Method

4.2.1 Sample Preparation

Samples of *Pinus nigra var maritima* (Corsican pine) and *Fagus sylvatica* (European beech) were prepared for experimentation. The following sample size was prepared for this investigation:

- Square 20 x 20 x 5mm, (R, T, L) used to obtain maximum penetration of the cell wall due to the longitudinal direction only being 5mm and thus only two cells long (assuming a minimum cell length of 2.5 mm).

All the samples were extracted in a Soxhlet extractor using a solvent mix of toluene acetone and methanol (4:1:1 by volume). All samples were extracted for 6 hours to ensure that all the soluble extractives were removed from the samples (it was ensured that the solvent was running clear through the Soxhlet extractor after 6 hours to show that the all extractable extractives were extracted). Samples were then air dried for 24 hours, in a fume hood and then oven dried at a temperature of 105°C. All samples used in the experiments were selected for the straight orientation of the growth rings and for the consistency of growth ring spacing to try to minimise variation of density throughout the sample set. All samples were labelled appropriately using pencil as to avoid the loss of labels when the samples are treated.

4.2.2 Sample treatment.

For the acetylation of samples the following method was followed.

Square samples were selected with four growth rings that were straight across the sample. The samples were then weighed to 4 d.p. and the mass was recorded. The samples were vacuum impregnated with acetic anhydride and 20 replicates

were added at various time intervals (see Table 4.1) to a vessel containing acetic anhydride at 100°C to give a range of WPG's.

Addition times for the Acetic and Hexanoic Anhydride Modification (min)
1575
405
285
165
105
75
60
45
30
15

Table 4.1: Sample addition times for the Acetic Anhydride modification

After the reaction was completed, the reaction vessel was quenched in ice and the cooled reagent was then decanted off. The samples were then thoroughly washed with acetone to remove any non-reacted acetic anhydride, followed by extraction in a Soxhlet apparatus for 8 h, using a solvent system composed of toluene, methanol and acetone (4:1:1 by volume). These samples were then air dried for 24 hours in a fume hood and then dried for 8 hours in an oven.

The samples were then weighed so that a weight percent gain could be calculated as shown in Equation 4.1.

For the hexanoylation of samples the following method was followed.

The samples were vacuum impregnated, at room temperature with a solution of hexanoic anhydride in pyridine for 1 h. The samples were then added to the reaction vessel containing a 1 M solution of hexanoic anhydride in pyridine, and at a temperature of 100 °C. 20 replicate samples were added to the reaction

vessel at varying intervals as shown in Table 4.1. Following the reaction the reaction was quenched in ice and the samples were washed through with acetone to remove any unreacted hexanoic anhydride solution. The samples were then extracted in a Soxhlet with a solution of of toluene, methanol and acetone (4:1:1 by volume). The samples were extracted for 8 hours and if the samples still smelt of pyridine they were re extracted until the smell of pyridine had left the samples.

The samples were air dried for 24 hours and then oven dried at 105 °C for 8 hours after which they were cooled in a dessicator and the masses of the samples were measured.

4.2.3 Calculations

Weight percentage gain (WPG) was calculated according to:

$$WPG\ (\%) = [(W_{mod} - W_{unmod}) / W_{unmod}] \times 100 \qquad (4.1)$$

where: W_{mod} is the mass of the acetylated wood sample and W_{unmod} is the mass of the unmodified wood sample.

Molar volume of adduct was calculated thus:

$$\text{Molar volume } (cm^3\ mol^{-1}) = MW / D \qquad (4.2)$$

where: MW is the molecular weight in g mol^{-1} and D is the density in g cm^{-3}.

The ratio of theoretical to measured volume change due to modification (V_{rel}) was calculated from:

$$V_{rel} = V_{theor} / V_{meas} \qquad (4.3)$$

where: V_{theor} is the theoretical volume increase (density of acetic acid / wt. gain of wood sample due to modification) and V_{meas} is the measured volume increase due to modification.

Volume change (VC) due to acetylation was calculated according to:

$$VC\ (\%) = [(V_{mod} - V_{unmod}) / V_{unmod}] \times 100 \qquad (4.4)$$

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

Molar volumes (cm^3 per mol) were calculated as follows:

$$(V_m - V_u)/M \qquad (4.5)$$

where: M = number of moles of acetic anhydride, V_m = volume of modified wood (in cm^3), and V_u = volume of unmodified wood (in cm^3).

Degree of hydroxyl substitution (in millimoles per gram of oven dry wood) was calculated according to Equation 6.

$$OH\ groups\ substituted = (((W_m - W_u)/W_u)/(MW-1))x1000 \qquad (4.6)$$

4.2.4 Decay resistance tests.

Prior to the decay resistance tests being performed all samples were subjected to leaching in deionised water for 2 weeks (as described in EN84), these were then oven dried at 105 °C for 24 hours.

After leaching samples were randomly placed into bags holding four treated samples and one untreated virulence sample. Samples were picked at random to avoid an entire range of weigh percent gain data being lost if a jar became

contaminated. Once the samples were sorted they were sterilised via gamma irradiation (2.5 Mrad) by Isotron Ltd.

Squat mycology jars were prepared with 60ml of 4% malt agar and then autoclaved for sterilisation. After cooling the jars were inoculated with the following fungi.

Corniophora puteana (Schumacher ex Fries) Karsten (BAM 15)
Trametes versicolor (Linnaeus) Quélet (CTB 863A)
Phanerochaete chrysosporium (Burdsall) (FPRL S179)

After inoculation the jars were sealed with pierced lids plugged with non absorbent cotton wool and then incubated at 22 °C and 65% RH for 2 weeks.

After the two week growth period any jars that did not exhibit good fungal growth were rejected. The remainder had blocks arranged within the jars as shown in Figure 4.1. The central block in each jar was an unmodified control block, although the control block was in contact with the old mycelium the controls showed similar mass losses to those of the virulence samples. The samples were arranged on a polypropylene mesh, the mesh was used to prevent possible water logging of the samples. The jars were then sealed and incubated for 16 weeks at 22 °C and 65% RH.

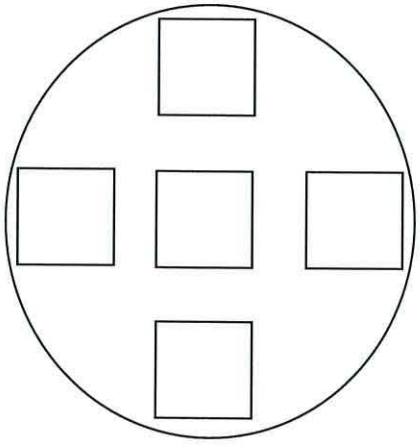


Figure 4.1: Schematic of block placement in the decay jars

For each species of fungi, 5 jars were prepared for each timber species (10 in total) with 5 unmodified samples of timber. This was to ensure that the presence of modified wood did not have an adverse effect on fungal growth.

At the end of this period the samples were removed from the jars and the mycelial mat was removed from the samples the blocks were then weighed, oven dried at 105 °C for 24 hours and then reweighed.

4.3 Results and Discussion

4.3.1 Acetic anhydride modified Corsican pine

Figure 4.2 shows the mass loss of acetic anhydride modified Corsican pine when decayed with *C. puteana.* It can be seen that the threshold value (or the WPG at which no mass loss can be seen) for acetic anhydride modified Corsican pine against *C. puteana* is approximately 18%. The shape of the graph shown in Figure 4.2 should be noted. It can be seen that the rate of decay between 7% and approximately 18% is relatively linear with a steep gradient, however, below 7% it can be seen that the gradient is relatively shallow. It can be seen that the mass loss of the unmodified samples range between 35% and 75%, the higher mass losses of the range being considered to be total degradation of the cellulose and hemicelluloses within the cell wall. It can be seen that the mass loss decreases significantly (to around 55%) with a low amount of modification (~ 2%). This suggests that the even at low WPG the acetic anhydride gives decay resistance to the Corsican pine. The reason for this is unclear however it can be hypothesised that this is due to the lignin being preferentially modified by the anhydride, however this will need further studies to verify this.

It should be also noted that at around 17% WPG there is an increase in the mass loss of the acetic anhydride modified Corsican pine. Although this can be taken as an artefact in this single graph, it has been seen through out this

experimentation, and also by other investigators (Farahini, 2003). This anomaly can be attributed to damage been caused by the large amount of modification being applied to the timber opening up new sites for decay. When the modification is increased again the new sites for decay are blocked again allowing a 0% mass loss to be attained again.

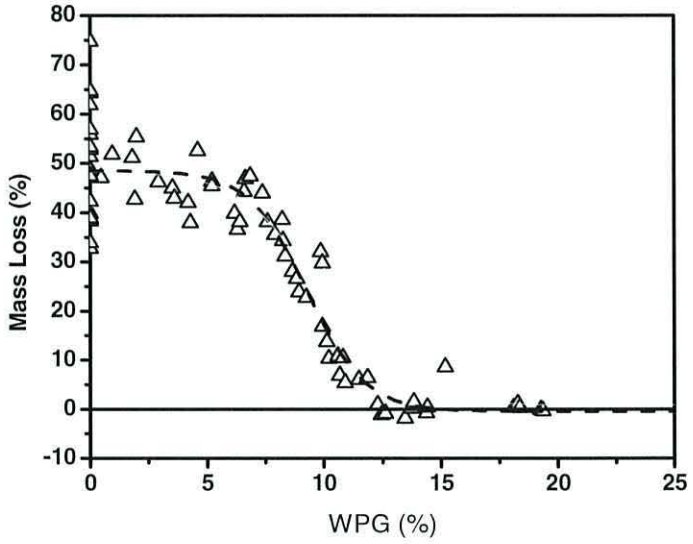


Figure 4.2: The decay resistance of acetic anhydride modified Corsican pine against *C. puteana*

Figure 4.3 shows the OH substitution that occurs when Corsican pine is modified with acetic anhydride and the effect that it has on the decay of the timber by *C. puteana*.

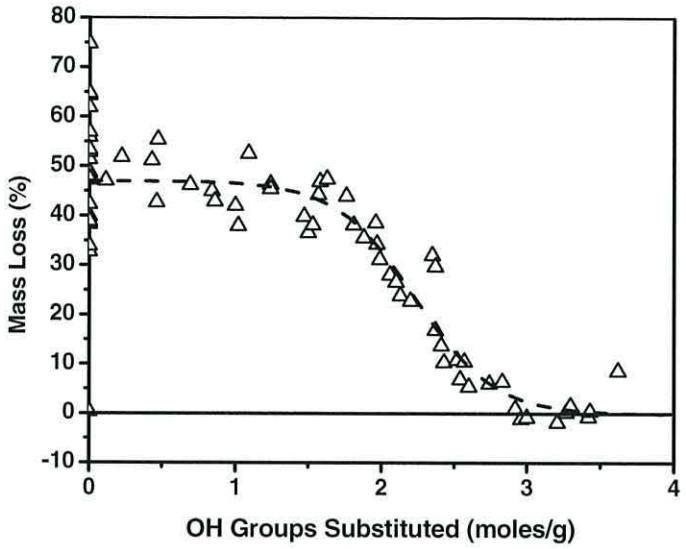


Figure 4.3: Mass loss on decay with *C. puteana* plotted against OH group substitution when Corsican pine is modified with acetic anhydride

Figure 4.4 shows the decay of acetic anhydride modified Corsican pine by *P. chrysosporium.* It can be seen that the profile of the decay vs WPG exhibits a similar shape to that of the decay of Corsican pine by *C. puteana.* However, it should be noted that the mass loss at the lower end of the WPG are considerably lower than those when the modified timber was decayed by *C. puteana.* This is due to the virulence of the fungi used in this investigation, mass loss for the virulence test samples was recorded at between 20% and 35%.

It can be seen that the threshold value for the prevention of decay by *P. chrysosporium* is around 15%. This is in agreement with the threshold for *C. puteana.*

Figure 4.5 shows the OH substitution that occurs during modification of Corsican pine vs the decay of the modified timber by *P. chrysosporium.*

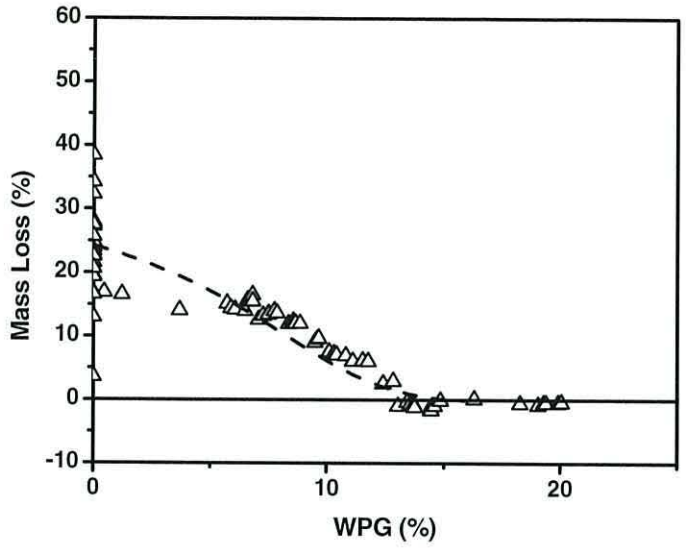


Figure 4.4: The decay resistance of acetic anhydride modified Corsican pine against *P. chrysosporium*

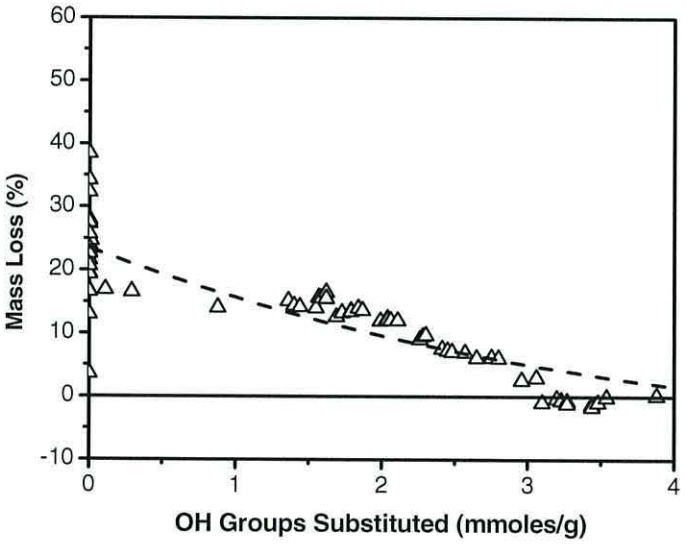


Figure 4.5: Mass loss on decay with *P. chrysosporium* plotted against OH group substitution when Corsican pine is modified with acetic anhydride

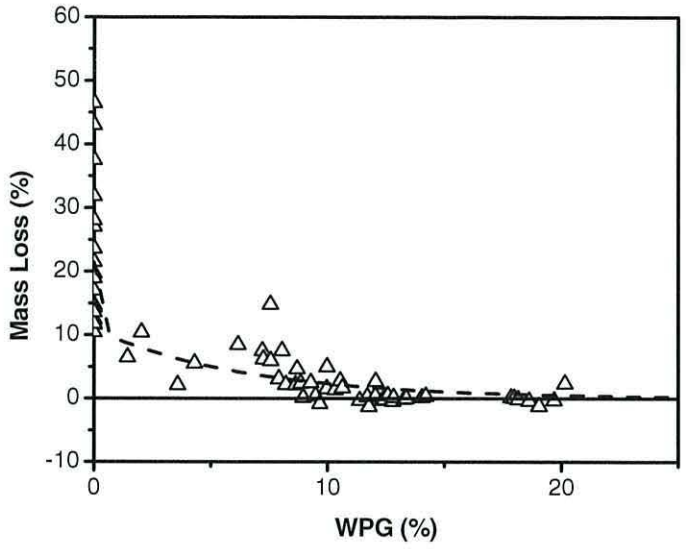


Figure 4.6: The decay resistance of acetic anhydride modified Corsican pine against *C. versicolor*

Figure 4.6 shows the decay resistance of acetic anhydride modified Corsican pine against *C. versicolor*. It can be seen that the mass loss is rather low compared with the other two fungi and this was seen to be a product of the virulence of the fungi. The range of mass loss for the unmodified samples was between 10% and 50%. It should be noted that although there is a wide range of mass losses for the untreated samples the mass loss of the modified wood is very constant. However it still can be noted that the threshold value lies between 15% and 20%.

Figure 4.7 shows the OH substitution by the acetic anhydride in the Corsican pine decayed by *C. versicolor.*

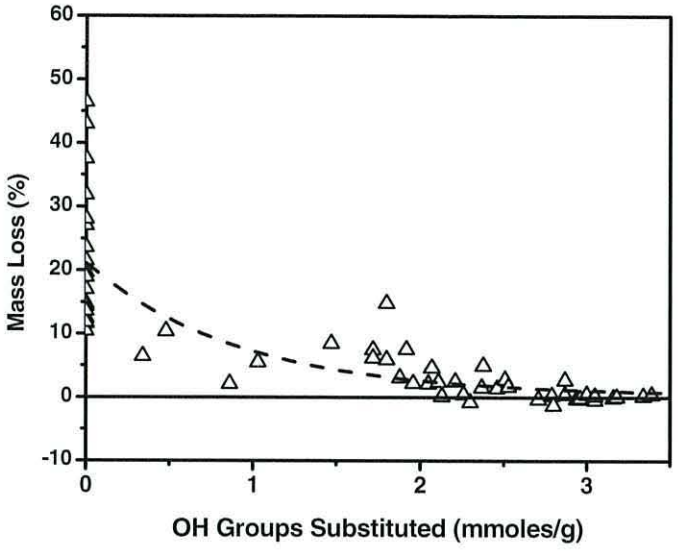


Figure 4.7: Mass loss on decay with *C. versicolor* plotted against OH group substitution when Corsican pine is modified with acetic anhydride

It can generally be seen that the decay threshold for Corsican pine modified with acetic anhydride is between 15% and 20% WPG. It can be seen in Figure 4.8 that although the virulence of the three fungi were different, the threshold value remained in the range of 15% to 20%. With standard preservation techniques a lack of virulence of the fungi would lead to less biocide being needed to protect the wood and thus a lower threshold value being recorded. However, as has been noted earlier, anhydride modification is a benign preservative technique, not employing a biocide to prevent the decay. It can therefore be hypothesised that if the micropores are not fully blocked a low virulence fungi may decay the timber as well as a high virulence fungi due to the fact that there are still active sites for decay within the cell wall. It is not until the WPG reaches 15% that the micropores are sufficiently blocked to prevent decay.

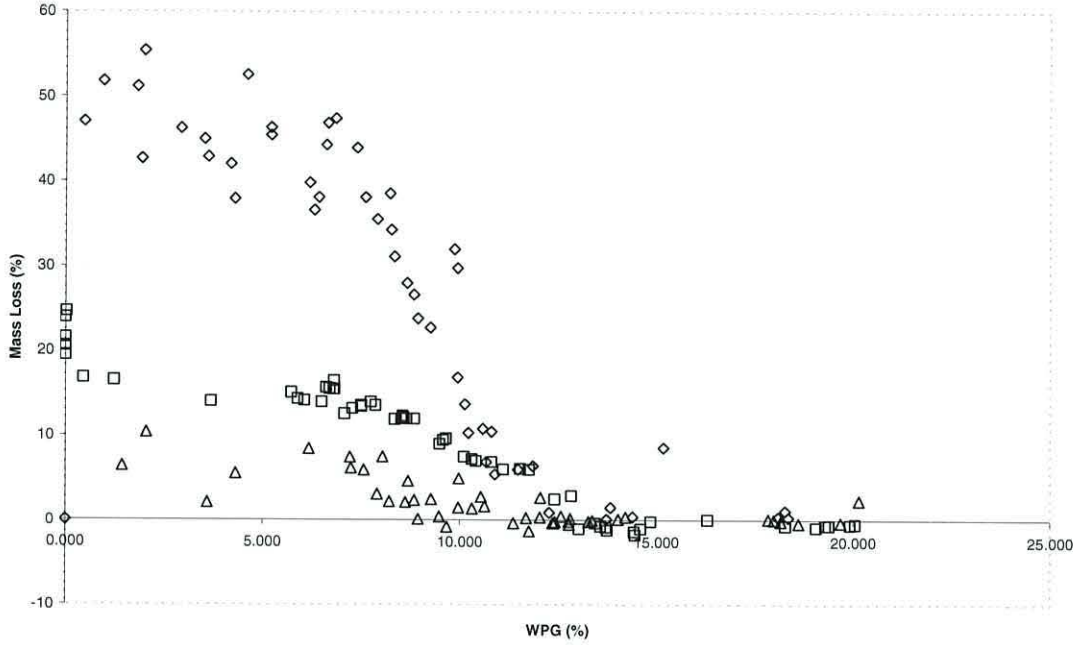


Figure 4.8: Decay resistance of acetic anhydride modified Corsican pine to *C. puteana* (diamonds), *P. chrysosporium* (squares) and *C. versicolor* (triangles)

Figure 4.8 shows that the threshold values against all three fungi investigated here are approximately 15%. This suggests that the mechanism for decay prevention is one that is not preferential to a particular fungus. This fact, along with the suggestion that virulence does not have an effect on the final threshold value for the prevention of decay points to cell wall micropore blocking as the mechanism for decay prevention and not any biocidal properties of the treatment. If biocidal properties were causing the decay prevention the threshold values would be different for each of the fungi (the more virulent the fungi, the higher the threshold value would be) however this is not the case here. Anhydride modification has shown that the definite threshold values is needed for both high and low virulence fungi, showing that although a low virulence the fungi is not decaying the timber as fast it is still decaying the timber to some degree until there threshold value of 15% is reached.

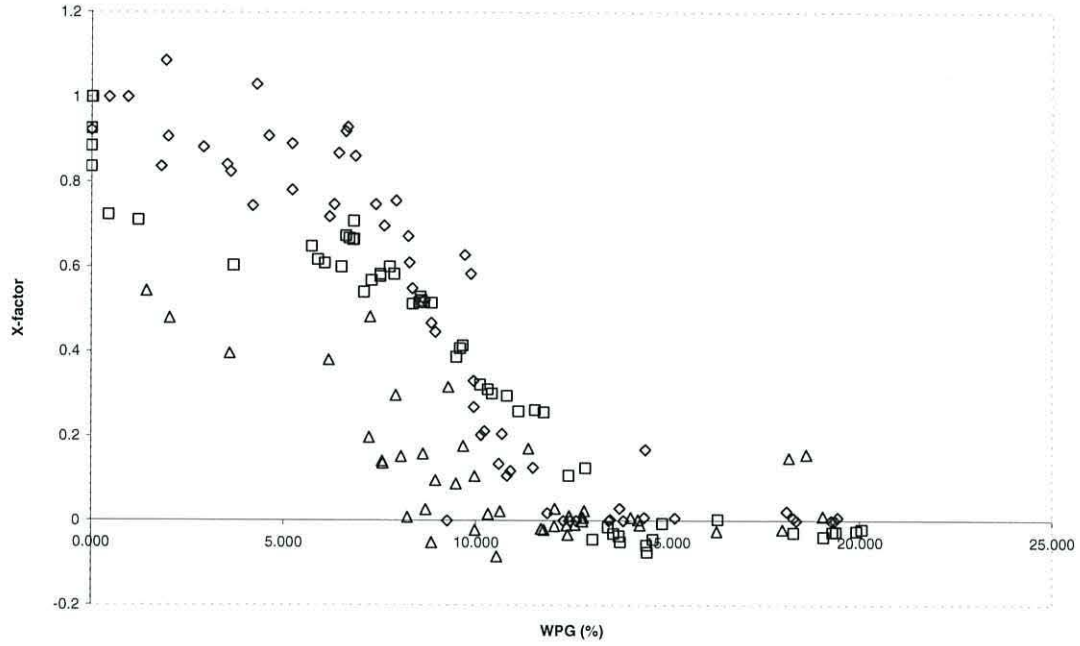


Figure 4.9: the X-factors for the decay resistance of acetic anhydride modified Corsican pine to *C. puteana* (diamonds), *P. chrysosporium* (squares) and *C. versicolor* (triangles)

Figure 4.9 shows the decay data for the acetic anhydride modified wood as a percentage of the mass loss for the unmodified virulence test samples, this is known as the x-factor. This simple calculation removes the influence of the inherent virulence of the fungi on the decay data of the modified wood. It can be seen that there is no significant differences between the decay of the modified Corsican pine by the three fungi.

4.3.2 Hexanoic anhydride modified Corsican pine

Figure 4.10 shows the decay resistance of hexanoic anhydride modified Corsican pine against *C. puteana*. It can be seen that the graph follows a similar profile to that of the decay of acetic anhydride modified Corsican pine. However the threshold value is slightly higher at around 22% WPG.

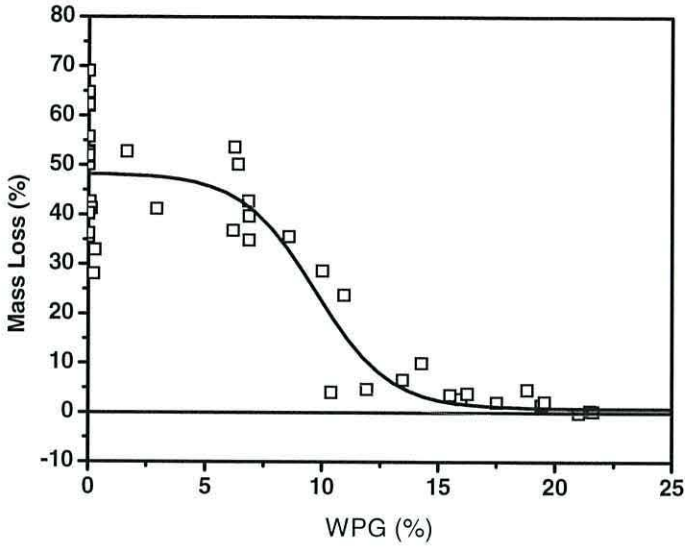


Figure 4.10: The decay resistance of hexanoic anhydride modified Corsican pine against *C. puteana*

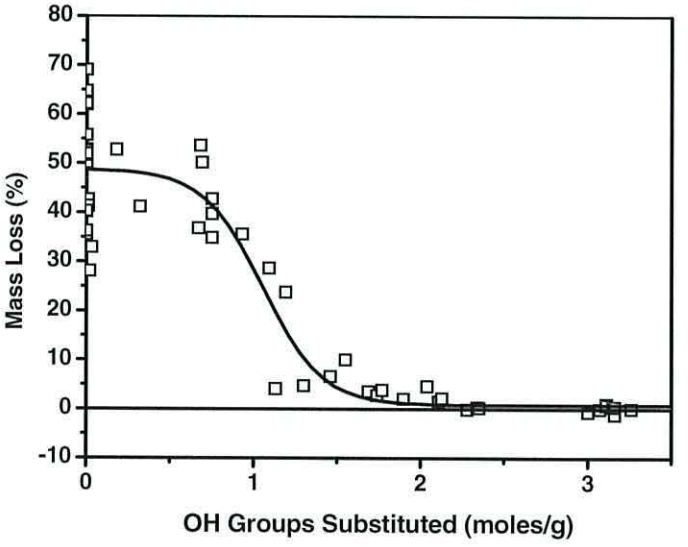


Figure 4.11: Mass loss on decay with *C. puteana* plotted against OH group substitution when Corsican pine is modified with hexanoic anhydride

Figure 4.11 shows the mass loss of the hexanoic anhydride modified Corsican pine against the OH group substitution.

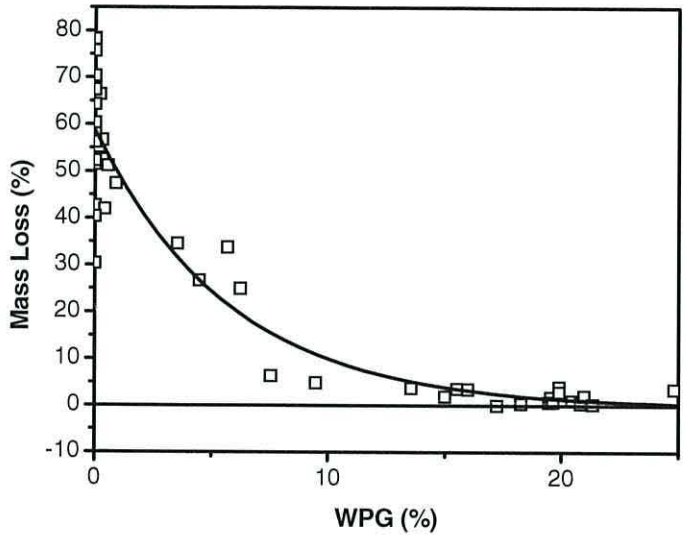


Figure 4.12: The decay resistance of hexanoic anhydride modified Corsican pine against *C. versicolor*

Figure 4.12 shows the decay resistance of the hexanoic anhydride modified Corsican pine against *C. versicolor.* It can be seen that although the mass loss decreases rapidly between 0% WPG and 10% WPG the threshold value is around 22%. It can be seen that there is a good virulence within this experiment.

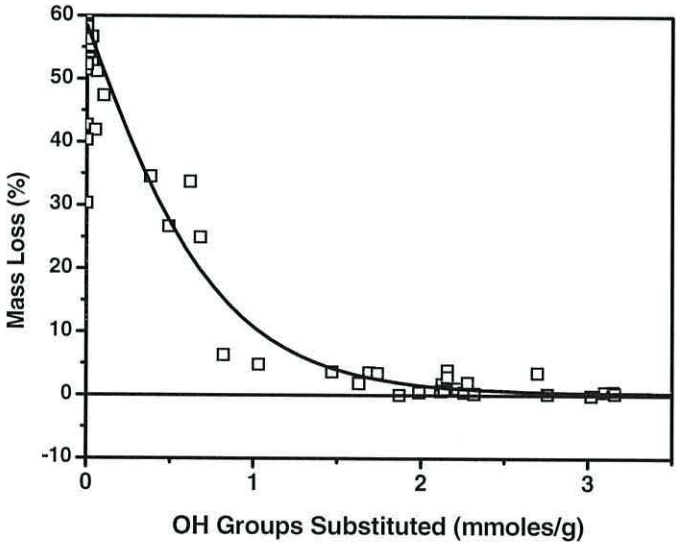


Figure 4.13: Mass loss on decay with *C. versicolor* plotted against OH group substitution when Corsican pine is modified with hexanoic anhydride

Figure 4.13 shows the mass loss plotted against the amount OH substitution by hexanoic anhydride in the Corsican pine samples.

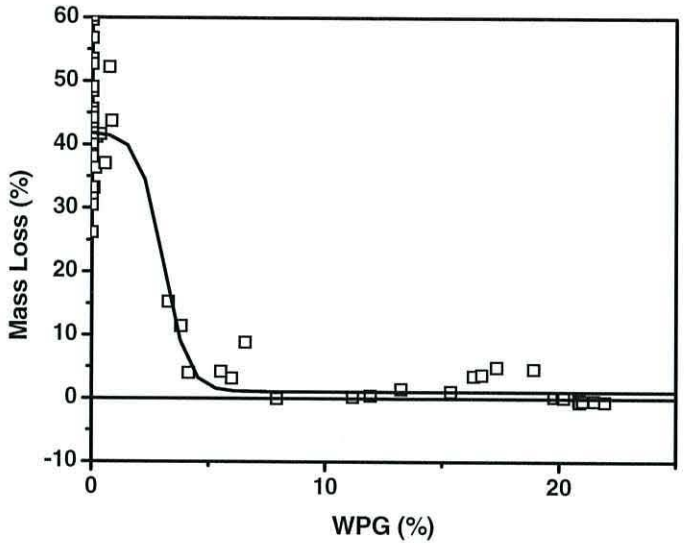


Figure 4.14: The decay resistance of hexanoic anhydride modified Corsican pine against *P. chrysosporium*

Figure 4.14 shows the decay resistance of hexanoic anhydride modified Corsican pine against *P. chrysosporium*. It can be seen that the threshold value for this particular fungi is approximately the same as with the first two and lies between 25% and 30%. Again the mass loss of the modified timbers has been plotted against the amount of OH group substitution and this can be seen in Figure 4.15. It can be seen in Figure 4.14 that there is again an increase in mass loss after 15%, again this can be accredited to cell wall damage when the timber is being modified.

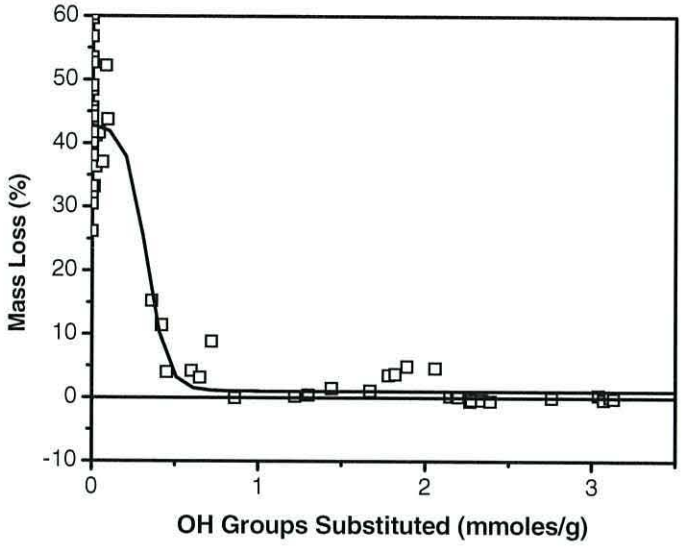


Figure 4.15: Mass loss on decay with *P. chrysosporium* plotted against OH group substitution when Corsican pine is modified with hexanoic anhydride

It can be seen from both the acetic anhydride modified Corsican pine and the hexanoic anhydride modified Corsican pine that the threshold value for all three of the fungi was approximately the same for each modification. It was found that the threshold value was approximately 17% WPG modification for the acetic anhydride modified samples and approximately 22% for the hexanoic anhydride modified samples. It should be again noted that the threshold values shown for both acetic anhydride modified Corsican pine and hexanoic anhydride modified, whilst being different in themselves, are the same within the set and are independent of fungal type or the virulence of the fungi.

It is difficult to compare threshold values between different investigations as there are many factors affecting the decay of timber, including, the decay protocol, the virulence of the fungi and the strain of the fungi used. Table 67 shows the threshold values of decay resistance from experimentation run by different investigators. Although the threshold values differ from investigation to investigation it can be seen that many of the values fall between 15% and 20% WPG and the threshold values found in this investigation fall with in this spectrum of values.

Fungus	Wood Species	Threshold [WPG (%)]	Virulence (%)
C. puteana (Mad 515)	Ponderosa pine	17	37
C. puteana (BAM 15)	Beech (Fagus sylvatica)	17	27
C. puteana (BAM 15)	Poplar (Populus spp)	17	40
C. puteana (BAM 15)	Scots pine (Pinus sylvestris)	>20	25
C. puteana (FPRL 11E)	Corsican pine (*Pinus nigra*)	24	58
C. puteana (FPRL 11E)	Corsican pine (*Pinus nigra*)	18	62
C. puteana	Radiata pine (*Pinus radiata*)	20 to >20	22 to 57
P. chrysosporium (FPRL S179)	Corsican pine (Pinus nigra)	10	46
C. (Polyporus) versicolor (Mad 697)	Ponderosa pine	17	25
C. (Coriolus) versicolor	Hondo spruce (Picea jezoensis)	6	31
C. (Coriolus) versicolor	Japanese beech (Fagus crenata)	16	72
C. (Coriolus) versicolor	Japanese cedar (Cryptomeria japonica)	6	46
C. (Coriolus) versicolor	Albizzia (Albizia falcata)	16	47
C. (Coriolus) versicolor	Albizzia (Albizia falcata)	15	29
C. (Coriolus) versicolor (CTB 863A)	Beech (Fagus sylvatica)	12	34
C. (Coriolus) versicolor (CTB 863A)	Poplar (Populus spp)	12	38
C. versicolor (CTB 863A)	Corsican pine (Pinus nigra)	17	47
C. (Coriolus) versicolor (FFPRI 1030)	Makamba (Betula maximowiczii)	12	22
C. (Coriolus) versicolor (CTB 863A)	Corsican pine (Pinus nigra)	10	45
C. versicolor (CTB 863A)	Beech (Fagus sylvatica)	20	18

Table 4.2: Decay threshold data of acetic anhydride modified timber from previous studies by different investigators (Hill, 2006).

Anhydride modification offers two possible routes for decay resistance; the first is cell wall bulking / micropore blocking. Cell wall bulking will prevent decay by blocking the micropores to the ingress of water and fungal metabolites (such as

enzymes and fungally produced decay chemicals such as oxalic acid) into the cell wall. The second route for decay resistance is the substitution of the hydroxyl groups with the acetyl groups which will prevent the enzymatic attack of the cell wall. It has been suggested that this prevention is due to the enzymes not being able to recognise the substrate.

Analysis of data from this investigation suggests that the decay resistance afforded to the timber by anhydride modification is due to cell wall bulking rather than OH substitution. Figure 4.16 shows the mass loss of both hexanoic and acetic anhydride modified Corsican pine when decayed by *C. puteana*. It can be seen that when the mass loss is plotted against WPG the hexanoic anhydride and acetic anhydride decay profiles are very similar, whereas the decay profiles when graphed against the OH substitution of the two anhydride modifications can be seen to be very different.

(a) (b)

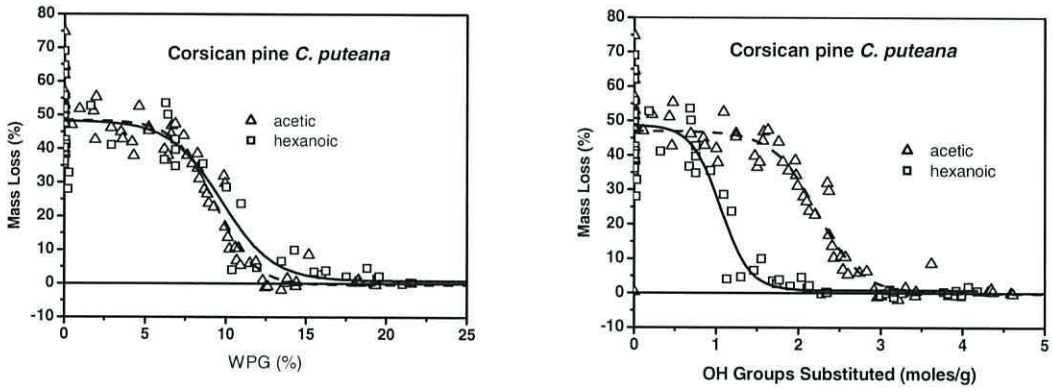


Figure 4.16: The mass loss of Corsican pine (when decayed with *C. puteana*) modified with both acetic and hexanoic anhydride graphed against (a) WGP and (b) OH substitution

If the decay resistance was due to the OH substitution the WPG required to attain the mass loss of 0% would be greater with the hexanoic anhydride (due to the increased molecular weight of hexanoic over acetic anhydride). These graphs

indicate that for decay prevention against *C. puteana* is due to the WPG of the timber modified with anhydride rather than the OH group substitution.

Similar conclusions can not be drawn for the decay resistance of Corsican pine modified with acetic and hexanoic anhydride against *P. chrysosporium* and *C. versicolor* due to the vast difference in virulence of the decay fungi in the investigation into the decay of acetic anhydride and hexanoic anhydride modified wood. If this experiment was to be repeated it is suggested that the acetic anhydride modified samples and the hexanoic anhydride modified samples should be randomised throughout a single decay test and therefore it will negate any effects of the virulence of the fungi on one particular set of samples, as has happened here.

4.3.3 Acetic anhydride modified Beech

Figure 4.17 shows the decay resistance of acetic anhydride modified beech. It can be seen that the threshold value for acetic anhydride modified beech against *C. puteana* is approximately 15%, which is slightly lower than the 18% that has been found for Corsican pine modified with acetic anhydride. It should be noted that the mass losses of the non treated samples are between 55% to 62%. It can be seen that there is a distinct levelling off of the slope between 5% and 10% and then an increase in gradient after 10% however this has not been found in subsequent experimentation and therefore is believed to be anomalous to this experiment.

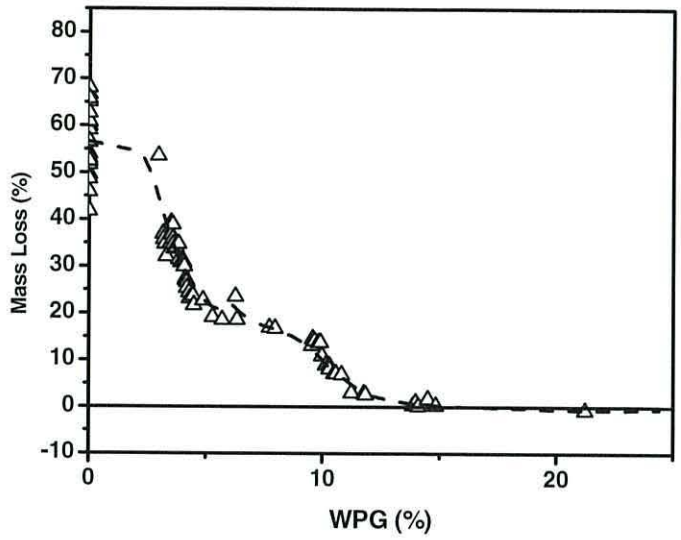


Figure 4.17: The decay resistance of acetic anhydride modified Beech against *C. puteana*

Figure 4.18 shows the OH substitution that occurs when Corsican pine is modified with acetic anhydride and the effect that it has on the decay of the timber by *C. puteana*.

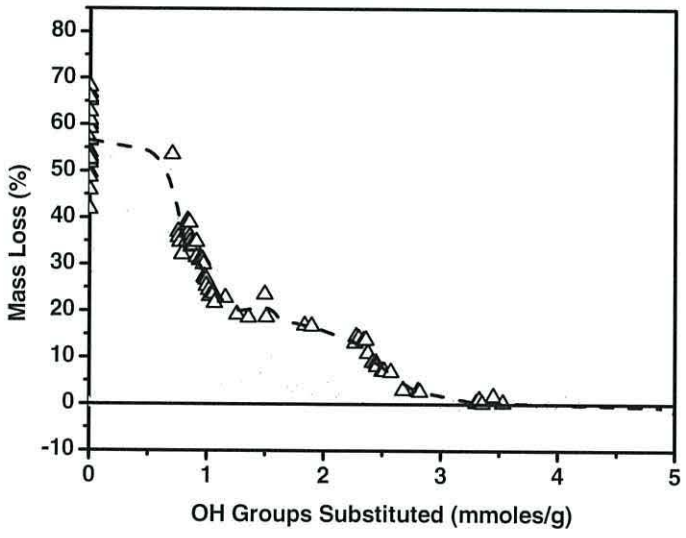


Figure 4.18: Mass loss with decay with *C. puteana* plotted against OH group substitution when Beech is modified with acetic anhydride

Figure 4.19 shows the mass loss of beech modified with acetic anhydride when decayed with *C. versicolor*. It can be seen that the threshold value for beech modified with acetic anhydride against the decay of *C. versicolor* is around 15%. This is similar to the threshold value as that found for acetic anhydride modified beech decayed with *C. puteana* and is similar to that of the acetic anhydride modified Corsican pine decayed with *C. versicolor*. However it should also be noted that the mass loss has a large spread, this is similar to the mass loss of the acetic anhydride modified Corsican pine. The virulence of the non-treated samples of beech was lower than that of the beech decay by *C. puteana* at between 40% and 75%.

Figure 4.20 shows the mass loss of acetic anhydride treated beech graphed against the amount of hydroxyl substitution that has taken place.

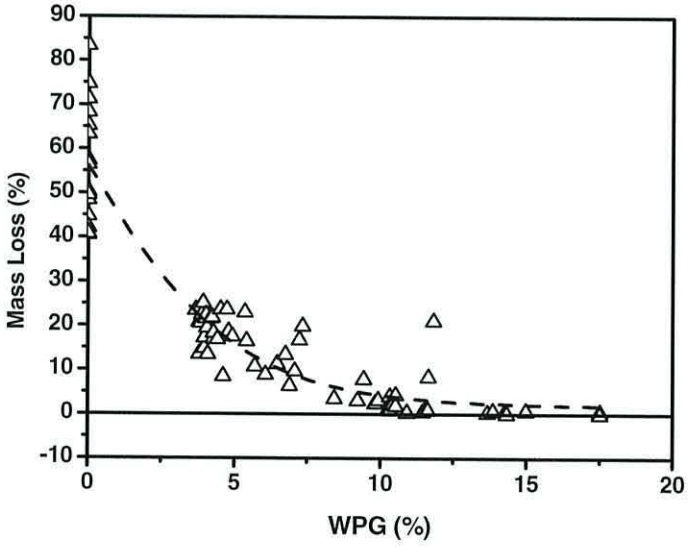


Figure 4.19: The decay resistance of acetic anhydride modified beech against *C. versicolor*

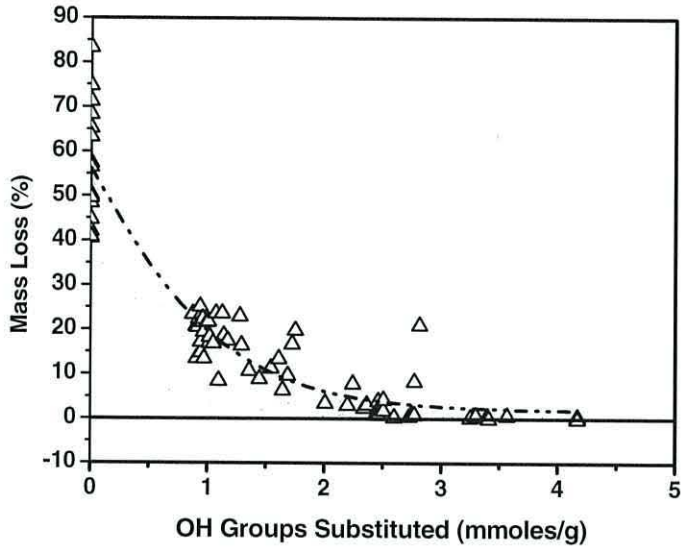


Figure 4.20: Mass loss on decay with *C. versicolor* plotted against OH group substitution when beech is modified with acetic anhydride

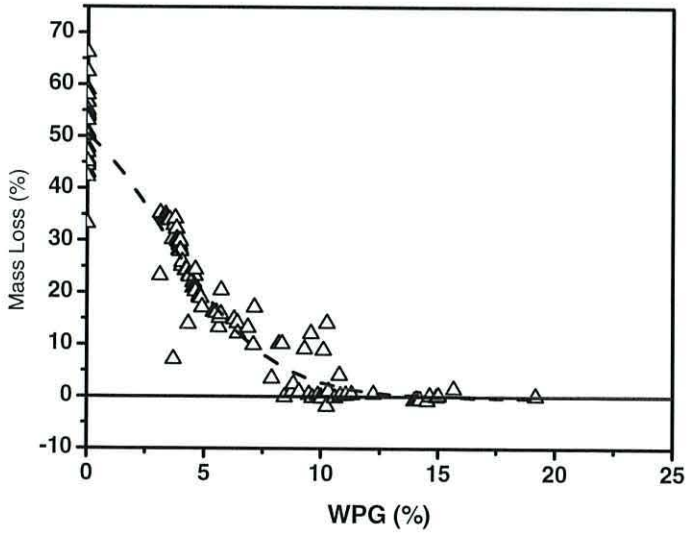


Figure 4.21: The decay resistance of acetic anhydride modified beech against *P. chrysosporium*

Figure 4.21 shows the mass loss of acetic anhydride modified beech when decayed with *P. chrysosporium*. It can be seen that the threshold value for the

acetic anhydride modified beech is around 15%. It should be noted that the mass loss of the unmodified samples was between 40% and 68%, these are similar to the mass loss of the untreated samples of Corsican pine when decayed with *P. chrysosporium*.

Figure 4.22 shows the mass loss of acetic anhydride modified beech versus the hydroxyl substitution.

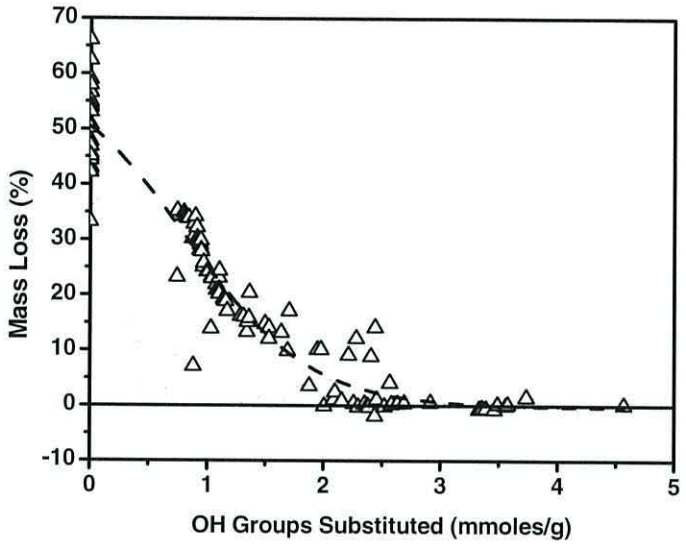


Figure 4.22: Mass loss due to decay with *P. chrysosporium* plotted against OH group substitution when beech is modified with acetic anhydride

It can be seen that the decay threshold values for beech modified with hexanoic anhydride is around 15% independent of the fungi that has been used to decay the timber. This is the same threshold value as found for acetic anhydride modified Corsican pine. It is interesting to note to that the threshold value for both Corsican pine and beech appear to be the same; this suggests a decay prevention mechanism that is independent of the species of timber as well as the species of fungi.

4.3.4 Hexanoic anhydride modified beech

Figure 4.23 shows the mass loss of the hexanoic anhydride modified beech when decayed with *C. puteana*. It can be seen that the threshold value is around 22%, this is much higher than the threshold values found for the acetic anhydride modified beech (threshold = 15% WPG). The threshold value for the hexanoic anhydride modified beech is similar to that of the hexanoic anhydride modified Corsican pine when decayed by *C. puteana*. It should also be noted that the non-treated samples have mass losses between 30% and 70%.

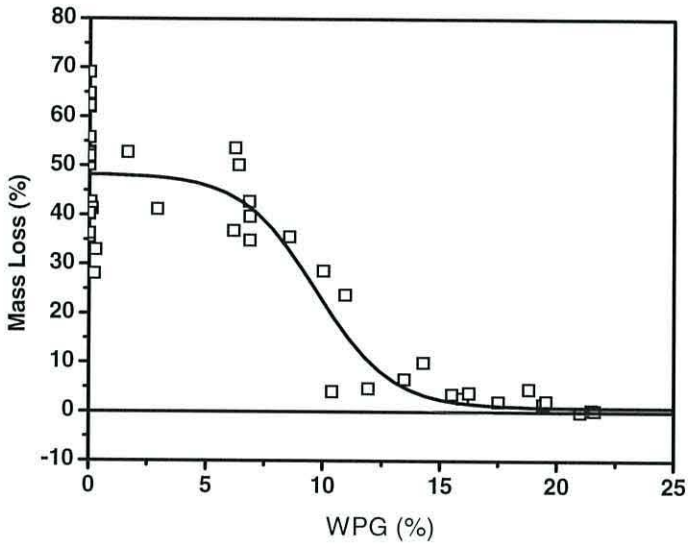


Figure 4.23: The decay resistance of hexanoic anhydride modified beech against *C. puteana*

Figure 4.24 shows the mass loss of hexanoic anhydride modified beech against the hydroxyl group substitution.

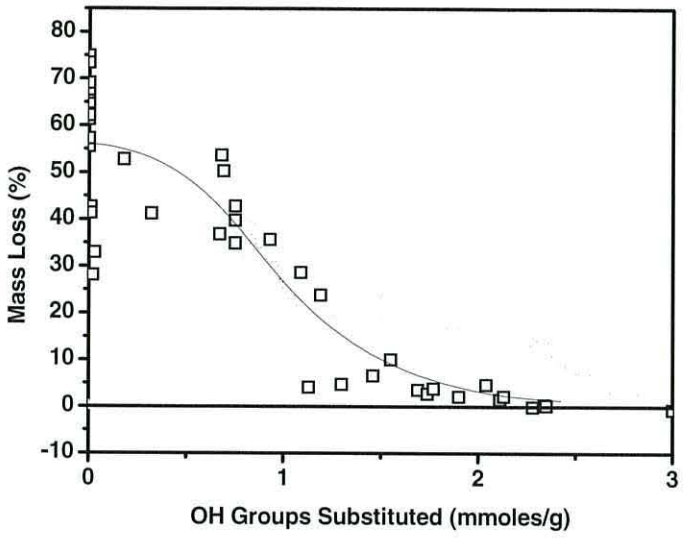


Figure 4.24: Mass loss with decay with *C. puteana* plotted against OH group substitution when beech is modified with hexanoic anhydride

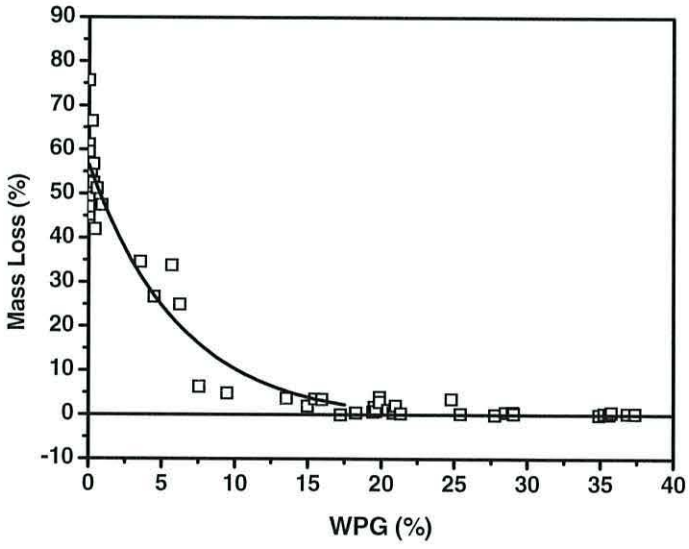


Figure 4.25: The decay resistance of hexanoic anhydride modified beech against *C. versicolor*

Figure 4.25 shows the mass loss of hexanoic anhydride modified beech. It can be seen that the threshold value for hexanoic anhydride modified beech against *C. versicolor* is around 20%, again this is similar to the threshold value reported

here for the hexanoic anhydride modified Corsican pine. The virulence samples all suffered mass losses between 45% and 75%.

Figure 4.26 shows the mass loss of hexanoic anhydride modified beech when decayed with *C. versicolor* plotted against the hydroxyl substitution within the wood.

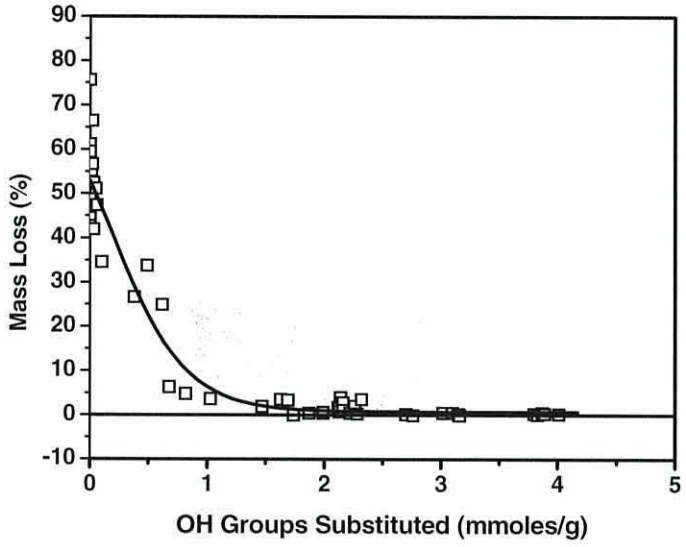


Figure 4.26: Mass loss due to decay with *C. versicolor* plotted against OH group substitution when beech is modified with hexanoic anhydride

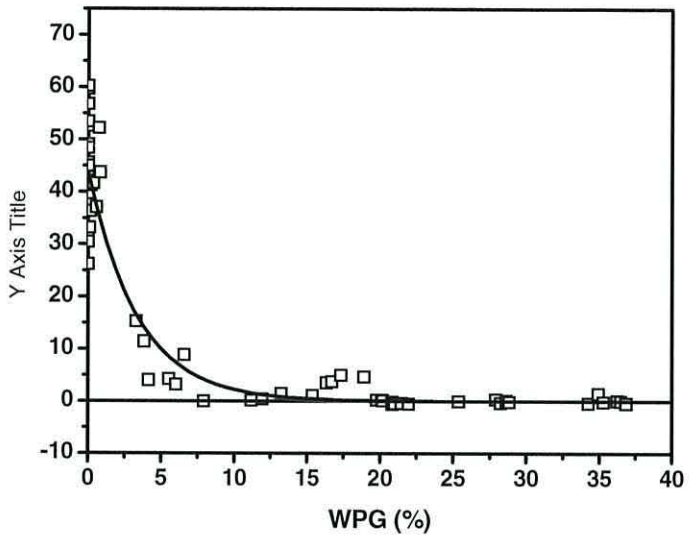


Figure 4.27: The decay resistance of hexanoic anhydride modified beech against *P. chrysosporium*

Figure 4.27 shows the mass loss of the hexanoic anhydride modified beech against *P. chrysosporium*. It can be seen that the threshold value is around 20% which is similar to that of other hexanoic anhydride modified beech but less than the threshold value for hexanoic modified Corsican pine when decayed with *P. chrysosporium*. It should be noted that the decay of the non-treated samples ranged between 30% and 60%.

The decay profile of the hexanoic anhydride treated beech exhibits the same increase in decay between 15% and 20% WPG that has been seen in earlier experimentation. Again it is likely that this is due to cell wall damage occurring when modification is taking place.

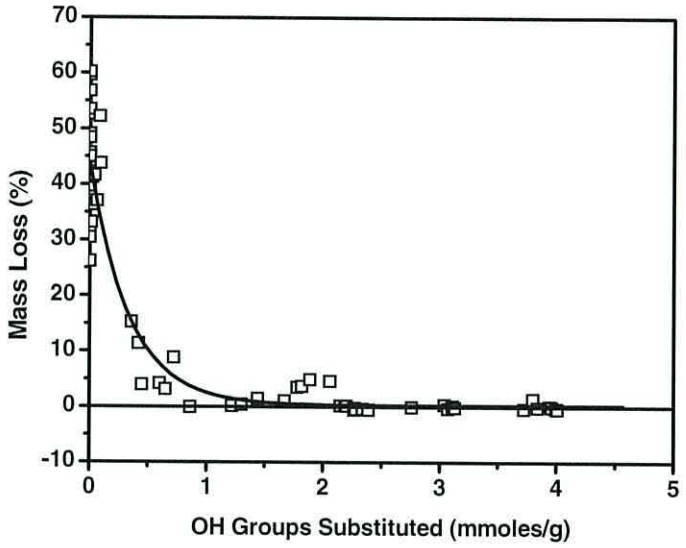


Figure 4.28: Mass loss on decay with *P. chrysosporium* plotted against OH group substitution when beech is modified with hexanoic anhydride

Figure 4.28 shows the mass loss of hexanoic anhydride modified beech plotted against the hydroxyl substitution in the wood cell wall of the modified beech.

It should be noted that throughout the decay trials involving the modification of beech the range of values of mass loss exhibited by the virulence samples was larger than that of the virulence tests for the modified Corsican pine.

It is interesting to note that the threshold value for beech modified with hexanoic anhydride is similar to that of Corsican pine modified with hexanoic anhydride (~22%). Again this suggests that the threshold values are independent of the species of timber.

It can be seen that throughout this experiment there is no significant difference between the mass loss of acetic anhydride modified beech and that of the hexanoic anhydride modified beech when graphed as mass loss against weight percent gain, however, there is significant difference when the mass loss is graphed against the amount of hydroxyl substitution. This leads to the conclusion that the decay resistance of the anhydride modified beech is due to the weight

percent gain and not the hydroxyl substitution within the cell wall, which is in agreement with the work on the anhydride modification of Corsican pine reported earlier in this section.

4.4 Conclusions to Chapter 4

The experimentation reported in this section, show the decay resistance of anhydride modified Corsican pine and beech. Two anhydrides were used, hexanoic and acetic and these were decayed with three fungi, *P. chrysosporium*, *C. puteana* and *C. versicolor*.

This investigation has shown that even with a small amount of modification the mass loss of timber is reduced significantly. Table 4.3 shows the mass loss due to decay of the virulence samples and the mass loss at a 5% WPG for each of the trials that have been run. Although there is a significant reduction on the mass loss with a 5% WPG the mass losses reported will lower the mechanical properties (such as MOE and MOR) of the timber.

Anhydride Type	Timber Spp.	Fungal Spp.	Virulance mass loss	Mass loss at 5% WPG
Acetic	Beech	*C. puteana*	40-70%	20%
		C. versicolor	40-80%	20%
		P. chrysosporium	40-70%	20%
	Corsican pine	*C. puteana*	35-75%	47%
		C. versicolor	20-40%	15%
		P. chrysosporium	10-50%	9%
Hexanoic	Beech	*C. puteana*	30-70%	47%
		C. versicolor	40-75%	27%
		P. chrysosporium	30-60%	5%
	Corsican pine	*C. puteana*	35-70%	50%
		C. versicolor	40-80%	27%
		P. chrysosporium	30-60%	5%

Table 4.3: Summary of the changes in mass loss with 5% anhydride modification

As can be seen there is a significant drop in the mass loss from unmodified samples to samples modified to 5% WPG. This shows that there anhydride modification has a significant effect on the decay rates of timber, even at low WPG. The mechanism that can be attributed for this apparent increase is currently not know, however work in further chapters may suggest a possible mechanism.

Threshold values were calculated for each of the modified timber with regards to the decay with the three fungi. It had been found that the threshold values are independent of both fungi and timber species. The anhydride modified timber was found to have a 15% threshold value while the hexanoic modified timber has a 22% threshold value. Table 4.2 shows decay thresholds and virulence's from different investigations.

It can be hypothesised that the difference in the threshold values attributed to the two anhydrides is due to the cell wall being more accessible to the acetic anhydride due to the size of the molecule. However it should be noted that the hexanoic anhydride treated samples were pre-treated with pyridine, which is used to pre swell the timber prior to modification. This in turn will lead to a greater amount of hexanoic anhydride being needed to prevent decay. The experiment could be repeated without the use of pyridine, however this would result in low WPGs being achieved and thus the treatment would not be comparable with the acetic anhydride modification.

Anhydride modification offers two possible routes for decay resistance; the first is cell wall bulking and micropore blocking. Cell wall bulking will prevent decay by blocking the micropores to the ingress of water and decay metabolites (such as oxalic acid) into the cell wall. The second route for decay resistance is the substitution of the hydroxyl groups with the acetyl groups which will prevent the enzymatic attack of the cell wall. It has been suggested that this prevention is due to the enzymes not being able to recognise the substrate. This section concludes that the decay resistance afforded to timber by the modification by anhydride is due to the cell wall bulking and not by hydroxyl substitution. In every case shown in this experiment there is no significant difference between the mass losses of acetic and hexanoic anhydride treated timbers when graphed against WPG whilst there is when plotted against hydroxyl substitution. If hydroxyl substitution played a role in the decay prevention the WPG of the hexanoic anhydride treated samples would have to be higher than that of the acetic anhydride treated samples as hexanoic anhydride has a higher molecular weight than acetic anhydride and thus a greater mass weight of hexanoic anhydride would have to be used for the substitution of the same amount of hydroxiyls. It should also be noted that the difference in the two threshold values for acetic and hexanoic anhydride modified timbers do not correspond with an agreement in the amount of hydroxyl substitution that takes place.

It should be noted that between 15 – 20% weight percent gain some of the decay profiles have exhibited a rise in decay and tend a second threshold at around

22%. It can be hypothesised that cell wall damage taking place due to the long reaction time needed to achieve the 15%. It is not until a WPG of 22% is reached that the damaged cells are modified sufficiently to prevent decay in the newly exposed sites. This phenomenon has also been observed in other investigations. In further work this should be observed with the aid of a scanning electron microscope.

It should be noted that although the virulence associated with the different trials were different the threshold value remained the same. This is an indication that the decay resistance is due to a benign mechanism and not to any biocide activity on the part of the modification. It the decay resistance was due to an active biocide the decay profiles of the fungi with a lower virulence would reach a lower threshold value. However as the threshold values for the modifications remain the same this implies that although the fungus is a less effective decayer it can still find sites in the cell wall to attack and therefore decay will still take place.

The previous two chapters have dealt with the decay of timbers modified in several different ways. Resin modification and resin with biocide modification were investigated in an attempt to prevent decay. It was found that the major contributor, at high resin loadings, to the decay resistance of both Corsican pine and beech was the resin modification. However, at low resin loadings it was seen that the biocide did have a significant effect on the decay of the timber. The lowering of decay is due to the resin barrier being breeched and the biocide becoming accessible to the fungi.

The decay experimentation of anhydride modified woods went on to investigate the mechanism for increased decay resistance. Anhydride modification offers two possible routes for decay resistance; the first is cell wall bulking and micropore blocking. Cell wall bulking will prevent decay by blocking the micropores to the ingress of water and decay metabolites into the cell wall. The second route for decay resistance is the substitution of the hydroxyl groups with the acetyl groups which will prevent the enzymatic attack of the cell wall. It has

been suggested that this prevention is due to the enzymes not being able to recognise the substrate. This section concludes that the decay resistance afforded to timber by the modification by anhydride is due to the cell wall bulking and not by hydroxyl substitution. In every case shown in this experiment there is no significant difference between the mass losses of acetic and hexanoic anhydride treated timbers when graphed against WPG whilst there is when graphed against hydroxyl substitution. If hydroxyl substitution played a role in the decay prevention the WPG of the hexanoic anhydride treated samples would have to be high as hexanoic anhydride has a higher molecular weight than acetic anhydride.

Chapters 5 and 6 will investigate the reasons for the increased decay resistance of the resin treated wood and of the anhydride modified wood. The investigation will follow two routes, the first will be an investigation in to the cell wall bulking of the timber by the two modifications and the second will be the change in fibre saturation point of the timber as it is modified.

5 Analysis of Dimensional Change of Resin and Anhydride Modified Samples Using Helium Pycnometry

5.1 Introduction

It has been established by previous investigators that the reaction of wood with acetic anhydride will cause bulking of the cell wall (Hill and Jones 1996). This bulking effect has been shown to be the cause of increased dimensional stability and decay resistance in treated wood (Hill, 2006). The amount of bulking attributed to the inclusion of the adduct has been of some dispute, Stamm and Taklow (1947) reported a proportional relationship between the degree of swelling and the amount of acetyl substitution that had taken place and this concurred with the work of Rowell and Ellis (1978). However, Hill and Jones (1996) found that the increase in cell wall volume was greater than the theoretical increase of the modified wood, which was calculated from the weight percentage gain. Hill and Jones attributed this 'over-swelling' to the formation of voids around the anhydride molecules; furthermore it was found that the volume occupied by each molecule of adduct was greater at low WPG than at higher WPG (Hill and Jones, 1999).

The traditional method of calculating volume increase is to measure the change in external dimensions of a sample. This will then give an indication of the gross volume change of the sample. However, as was discussed in Section 1.1.2 timber is not a solid object and a sample of timber contains lumen and micropores. Theoretically, significant swelling of the wood cell wall could take place, outwards towards the surface and also into the lumen, which will not be accounted for using traditional measuring techniques.

This chapter describes work in which the dimensional changes of treated samples, both anhydride treated and resin treated, have been assessed using a helium pycnometer. A helium pycnometer accurately measures the volume of a

sample of known weight by measuring the difference in the amount of helium which is able to be injected into a chamber at a known pressure, when a sample is present and when it is not. The dimensional changes measured by helium pycnometry will be compared to the traditional methods to investigate whether there is a relationship between the gross volume change of the samples and the change in the wood cell volume due to the presence of the adduct or resin.

5.2 Method

Samples of *Pinus nigra var maritima* (Corsican pine) were prepared for all the experimentation as well as *Fagus sylvatica* (European beech) when needed.

For all the treatment regimes used in this chapter the following sample dimensions were used;

Circular 14mm in diameter by 5mm (longitudinal) for use in the helium pycnometer.

All the samples were extracted in a Soxhlet extractor using a solvent mix of toluene acetone and methanol (4:1:1 in ratio). All samples were extracted for 6 hours to ensure that all the soluble extractives were removed from the samples. Samples were then air dried for 24 hours and then oven dried at a temperature of 105°C. All samples used in the experiments were selected for the straight orientation of the growth rings and for the regularity of growth ring spacing. All samples were labelled appropriately using pencil to avoid the loss of labels when the samples were treated.

Prior to treatment the samples were dried for 12 hours at 105°C to ensure that all moisture was removed from the samples. The samples were then cooled in a desiccator. The samples were measured accurately using a micro calliper (accurate to 0.001mm) and weighed on an accurate balance (accurate to 4dp). The volume of each sample was calculated on the presumption that the sample

was cylindrical and an average of the two transverse dimensions was calculated. The blocks were then gathered into groups of seven, as this is the maximum number of samples that will fit in to the helium pycnometer. The helium pycnometer is more accurate when the chamber is filled to its maximum capacity. Each set of seven was weighed (to 4 d.p.). The volume of each set of seven samples was then measured using a Micromeritics AccuPyc 1330. After the samples were measured they were treated as follows;

5.2.1 Resin only.

The samples were weighed, in grams to 4 DP and measured (in mm) with a micrometer to 3 DP. The small samples were treated by vacuum impregnation methods. The samples were added to the resins (the resins used here were the same as in Chapter 3) and a vacuum applied for four hours. After the vacuum treatment the samples were wiped clean of residue resin and then heated to 105°C for 8 hours to cure the resin. The treatment was repeated for the helium pycnometry samples for varying time scales. Samples were treated for 60, 120, 180 and 240 minutes.

5.2.2 Acetic and Hexanoic Anhydride Treatment

5.2.2.1 Sample treatment.

Corsican pine samples were prepared as cylinders with a nominal diameter of 14 mm and a longitudinal dimension of 5 mm. These were subjected to a Soxhlet extraction for 8 hours using a solvent system composed of toluene, methanol and acetone (4:1:1 by volume). Samples were then selected with four growth rings that were straight across the sample, labelled and used in groups of seven replicates (since the helium pycnometer can only hold samples of 35 mm in height). The sample geometry was chosen in order to obtain an efficient fit into the helium pycnometry measurement chamber to obtain the most accurate volume determinations. Following measurement, the samples (in batches of 7) were vacuum impregnated with acetic anhydride and then added at various time

intervals (see Table 63) to a vessel containing acetic anhydride at 100°C to give a range of WPG's. After the reaction was completed, the reaction vessel was quenched in ice and the cooled reagent was then decanted off. The samples were then thoroughly washed with acetone to remove any non-reacted acetic anhydride, followed by extraction in a Soxhlet apparatus for 8 hrs, using a solvent system composed of toluene, methanol and acetone (4:1:1 by volume). A set of control samples (7 replicates) was subjected to Soxhlet extraction, oven-drying and a further period of solvent extraction using the methods as detailed for the acetylation procedure.

5.2.3 Calculations

Weight percentage gain (WPG) was calculated according to:

$$WPG\ (\%) = [(W_{mod} - W_{unmod}) / W_{unmod}] \times 100 \qquad (5.1)$$

where: W_{mod} is the mass of the acetylated wood sample and W_{unmod} is the mass of the unmodified wood sample.

Molar volume of adduct was calculated thus:

$$\text{Molar volume } (cm^3\ mol^{-1}) = MW / D \qquad (5.2)$$

where: MW is the molecular weight in g mol^{-1} and D is the density in g cm^{-3}.

The ratio of theoretical to measured volume change due to modification (V_{rel}) was calculated from:

$$V_{rel} = V_{theor} / V_{meas} \qquad (5.3)$$

where: V_{theor} is the theoretical volume increase (density of acetic acid / wt. gain of wood sample due to modification) and V_{meas} is the measured volume increase due to modification.

Volume change (VC) due to acetylation was calculated according to:

$$VC\ (\%) = [(V_{mod} - V_{unmod}) / V_{unmod}] \times 100 \quad (5.4)$$

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

Molar volumes (cm^3 per mol) were calculated as follows:

$$(V_m - V_u)/M \quad (5.5)$$

where: M = number of moles of acetic anhydride, V_m = volume of modified wood (in cm^3), and V_u = volume of unmodified wood (in cm^3).

Addition times Acetic Anhydride Modification (min)
1575
405
285
165
105
75
60
45
30
15

Table 5.1: Addition times for the Acetic Anhydride modification

Samples were treated with hexanoic anhydride. The procedure was much the same as with acetic anhydride however the wood was pre-swollen with a solution

of hexanoic anhydride in pyridine. In the clean up stage of the reaction the blocks were re-extracted until the smell of pyridine had ceased. This took up to 4 cycles of extraction for the high WPG blocks.

Post treatment samples were then dried for 12 hours at 105 °C to ensure that they were dry and then re-measured both with the helium pycnometer and the micro callipers.

5.3 Results and discussion

5.3.1.1 Acetic Anhydride Modification

The figures in this section compare the helium pycnometry data of three timber species modified with acetic anhydride and the dimensional change measured by conventional methods, namely with micrometers.

Figure 5.1 shows the relationship between the two methods of measuring the dimensional changes of acetic anhydride modified wood. It can be seen that the relationship between the WPG and the volume change (calculated from external dimensions) is curvilinear, which is in agreement with the work of Hill and Jones (1998), but, as mentioned in the introduction to this section, is differing from the work of other investigators, e.g. Stamm and Taklow (1947).

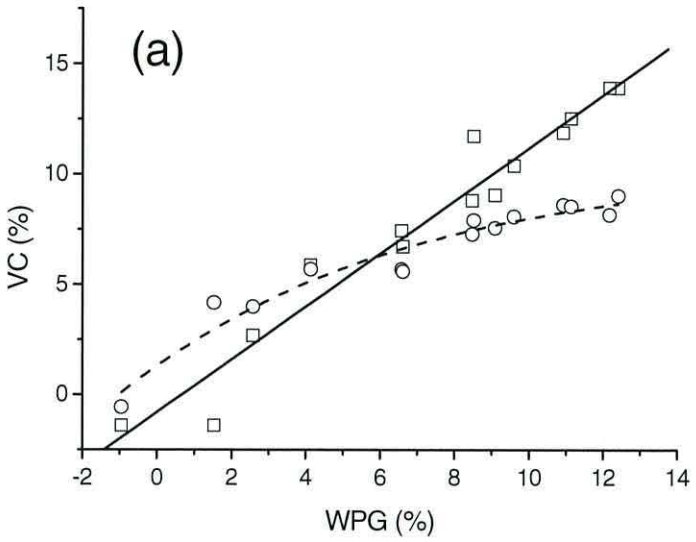


Figure 5.1: Volume change, with acetic anhydride modification, of Corsican pine measured by helium pycnometry (squares) and micro callipers (circles)

The volume changes determined via helium pycnometry can be best described by a linear fit. It should also be noted that the lines of best fit cross. It could be hypothesised that this indicates that the external measurement over-estimates the volume changes at low WPG's and under-estimates them at high WPG's however it has to be noted that measurement of external dimensions gives a much larger volume than the volume measurements with helium pycnometry and therefore the comparison of these two graphs may not be valid. The under and over estimations can be attributed to the expansion of the cell wall, at high WPG's, in to the lumen, this can be shown in Figure 5.2.

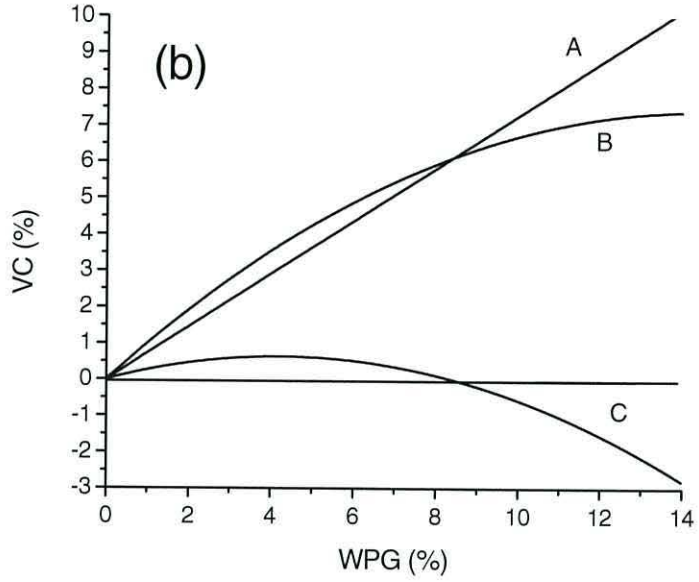


Figure 5.2: Graph to illustrate the relationship between percentage change in cell wall volume (a), total wood volume (b), and lumen volume [a-b}] (c) at different weight percentage gains

The actual percentage change in lumen volume is not determined by subtraction of the two sets of percentage volume change data, but from actual lumen volume changes.

It can be seen from Figure 5.2 that after a WPG of approximately 9% the lumen volume change becomes negative and therefore becomes a volume decrease, which is likely to be due to the swelling of the cell wall into the lumen. Expansion of the cell wall into the lumen at 10% and 15% WPG has been observed in scanning electron microscope studies of acetylated wood (Evans et al. 2000, Sander et al. 2003). Stamm (1964) noted that microtomed sections of wood showed an initial increase in lumen diameter, and then a decrease as the wood cell wall swelled upon exposure to water.

The amount of cell wall swelling when wood is treated with an adduct was theoretically predicted using the method of Rowell and Ellis (1979). This method uses the density of acetic acid (1.049 gcm^{-3}) and the molecular weight of the acyl group when attached to the wood cell wall (the actual molecular weight of an

acetyl group is 43 however the molecule looses a hydrogen molecule when it bonds to the wood and therefore has a molecular weight used in calculations is 42) to calculate the theoretical cell wall swelling from the WPG.

The relationship between the ratio of theoretical measured volume increase against WPG is shown in Figure 5.3. Where the data was calculated from dimensional measurements V_{rel} values are consistently below 1.0, increasing from a value of approximately 0.3 at around 3% WPG, to about 0.6 at 13% WPG.

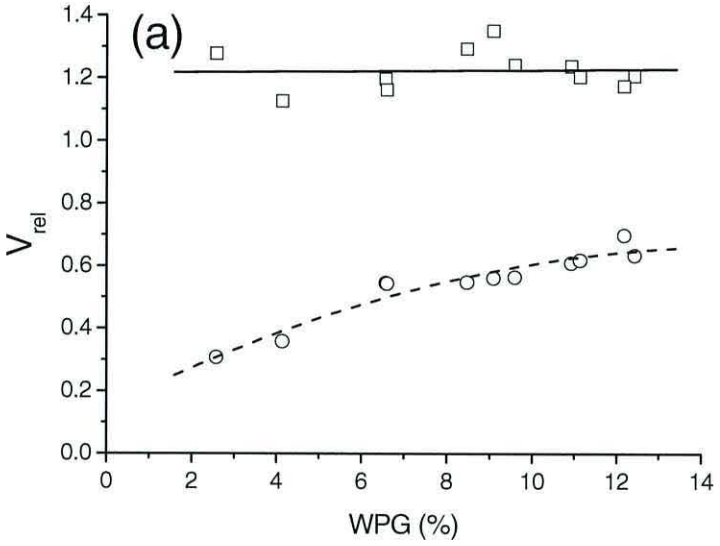


Figure 5.3: Variation in the ratio of theoretical volume increase to experimentally determined volume increase (Vrel) as a function of weight percentage gain (WPG), derived from determination of external dimensions (circles, dashed line) and from helium pycnometry (squares and a solid line)

These values indicate that the wood following modification has swollen to a greater extent than would be theoretically predicted, as has been reported previously for Corsican pine modified with various anhydrides (Hill and Jones 1996; Hill and Jones 1999; Çetin 1999; Çetin and Ozmen 2001).

However, the data obtained from helium displacement measurements are very different, in that V_{rel} values are consistently greater than 1.0 and there is no

significant variation with WPG. Logically, there should be no change in V_{rel} with WPG, since it would be expected that the bonded acyl group should occupy the same volume in the cell wall irrespective of level of substitution. The value for V_{rel} obtained from helium pycnometry is about 1.2, indicating that the true cell wall swelling is less than theoretically predicted. However, the method for obtaining the theoretical swelling volume is open to criticism (Hill and Jones 1996) and little importance is attached to the absolute value of V_{rel}. Hill and Jones (1996) questioned how appropriate the use of acetic acid density was in calculating the theoretical volume change of the cell wall when it has been acetylated. The arguments put forward by Hill and Jones (1996) were whether acetic acid occupies the same volume when bonded to the cell wall as when it is in a liquid state.

Significant differences in values for molar volume (MV) are also observed depending on the method of volume determination (Figure 112).

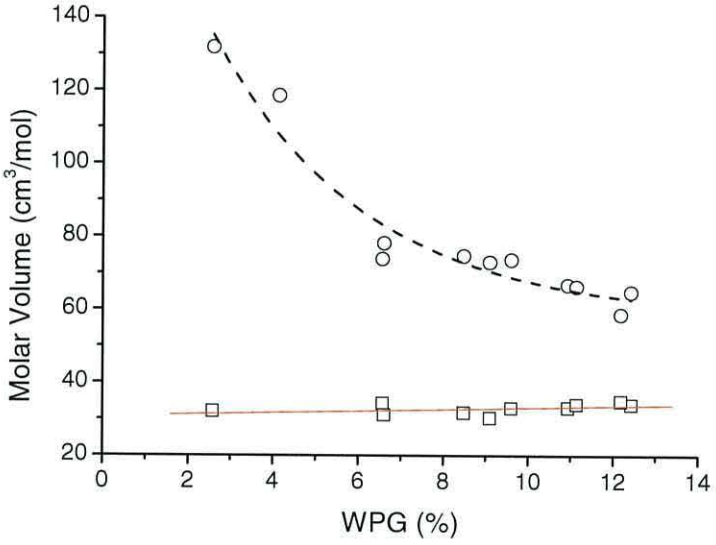


Figure 5.4: Variation in molar volume as a function of weight percentage gain (WPG), derived from determination of external dimensions (circles, dashed line) and from helium pycnometry data (squares, solid line)

With the MV data derived from external dimensional measurement determination, the MV is of the order of 120 cm^3 mol^{-1} at low WPG's, falling to around 60 cm^3 mol^{-1} at about 12% WPG. This phenomenon has been reported previously and described in some detail, relating the observations to the concept of void volume around the acyl adduct in the cell wall (Hill and Jones 1999). Again, the He pycnometry derived data is substantially different, with no evidence of a significant relationship between WPG and MV and a value of approximately 33 cm^3 mol^{-1} being found for MV. It would appear that the apparently large values of MV obtained from dimensional measurement determinations is an artefact which does not truly reflect the changes occurring in the cell wall. Çetin and Ozmen (2001) and Çetin (2000), using determinations of external dimensions, found that on modification of Corsican pine with crotonic anhydride, the values of MV were high at low WPG's and reduced to a constant value as WPG increased, as found with the present study. This apparent high MV at low WPG's is a consequence of neglecting changes in lumen volume as WPG increases.

Cell wall density of the unmodified extracted wood was found to be 1.4200 (+/- 0.0060) g cm^{-3}, which is slightly lower than values reported by other workers (1.44 to 1.47 g cm^{-3}) who have used helium displacement, non-swelling solvents displacement, or mercury porosimetry to determine density (Kellogg and Wangaard 1969; Siau 1984). This compares with values in the range of 1.5 to 1.55 g cm^{-3} found when water is used as the displacement medium. Such differences are generally attributed to the existence of cell wall micropores, which are inaccessible to displacement media when the cell wall is not swollen (Kellogg and Wangaard 1969; Siau 1984). Acetylation resulted in an increase in cell wall density to 1.4410 (+/- 0.0160) g cm^{-3}, but little significance is attached to this since the control samples also exhibited an increase in density (to 1.4484 (+/- 0.0023) g cm^{-3}). The reason is therefore not attributed to the acetylation process, but is considered to be a consequence of the heating process followed by solvent extraction, where it is assumed that degradation products, produced as a result of oven-drying, are removed from the cell wall. The removal of the low

density components from the cell wall will cause an overall increase in density of the cell wall system.

Figure 5.6 shows the volume change of acetic anhydride modified beech when assessed by the standard method and by helium pycnometry. It can be seen that the helium pycnometry and the micro calliper volumes change and that the over-estimation of the external measurements at low WPG does not occur. However it should be noted that the lowest weight percentage gain achieved in this study was 8% and therefore higher than the 6% WPG threshold value found for the onset of lumen shrinkage with modification.

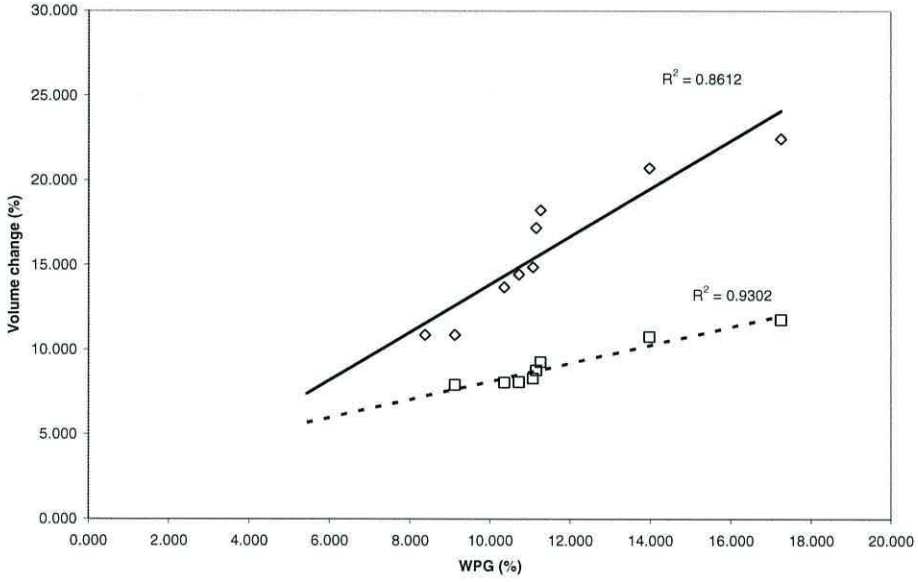


Figure 5.5: Volume change, with acetic anhydride modification, of beech measured by helium pycnometry (Diamonds) and micro callipers (Squares)

It can be seen that the two line cross at around 4% suggesting that lumen shrinkage begins earlier in beech than it does in Corsican pine. However it must be noted that this is a model and further experimental work is needed to ascertain whether this is correct.

The average molar volume of beech has been calculated at 41.71 cm^3mol^{-1} which is considerably higher than that for Corsican pine (33 cm^3mol^{-1}),

5.3.2 Hexanoic Anhydride Modification

The figures in this section compare the helium pycnometry of Corsican pine and beech timber treated with hexanoic anhydride and the dimensional change measured with micrometers.

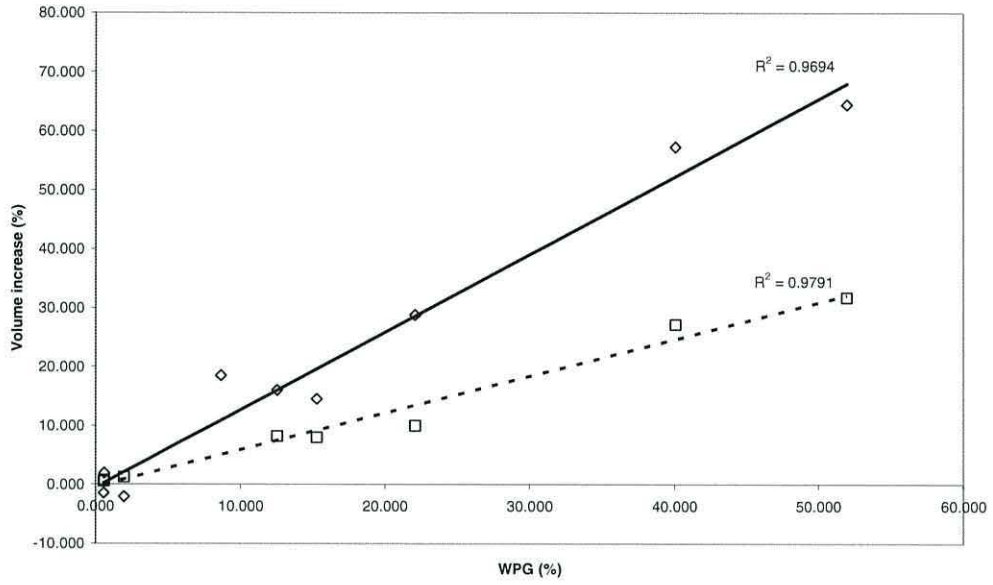


Figure 5.6: Volume change, with hexnoic anhydride modification, of Corsican pine measured by helium pycnometry (diamonds) and micro callipers (squares)

Figure 5.7 shows the relationship between the two methods of measuring the dimensional changes of hexanoic modified Corsican pine. It can be seen that the volume change calculated from the standard method of measurement is best represented by a linear fit. This is also true for the volume change calculated from the helium pycnometry. It can be seen that the two linear fits diverge from each other in a similar way to the acetic anhydride treated beech. It can be seen that the helium pycnometry data shows a large volume change at high weight percent gains; volume changes of 60% at 50% WPG can be seen. The very high weight percent gains and high volume increases suggest that cell wall damage has taken place.

The percentage increase in volume shown by the helium pycnometry shows a swelling in the cell wall, if this swelling was only in the outward direction the percentage volume change would be similar to that calculated from the external measurements. However, the volume change graphs diverge drastically and therefore this shows that a greater volume change is measured by the helium pycnometry than calculated from the external measurements.

The larger percentage volume changes can be attributed to several reasons. The blocking of the cell wall micropores will cause an increase in the cell wall volume without causing an increase in the volume calculated from external dimensions. It can also be hypothesised that larger percentage volume change is due to the swelling of the cell wall into the lumen and thus filling the lumen void, as well as in the radial direction.

Figure 5.8 shows the volume change for the hexanoic anhydride modified beech. Again a large volume change are shown when the helium pycnometer is used to measure the volume of the cell wall; a volume change of 50% has been shown for a weight percent gain of 30%. The percentage volume change of the cell wall is much greater than when it is calculated from the external measurements. It can be again hypothesised that this is due to the cell wall swelling inward into the lumen as well as outward.

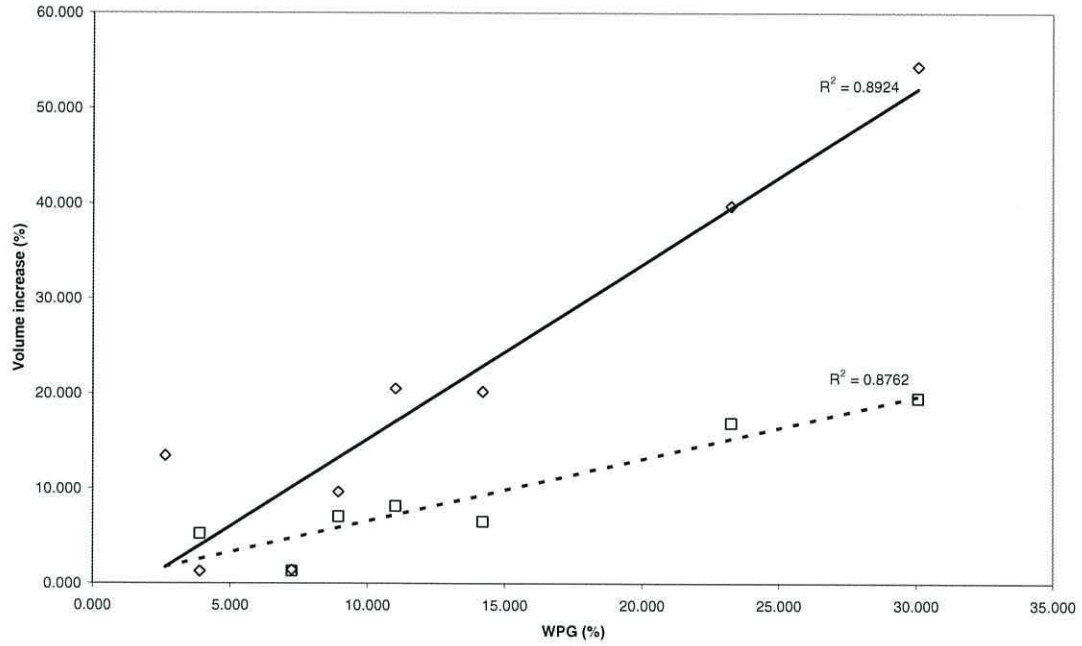


Figure 5.7: Volume change, with hexanoic anhydride modification, of beech measured by helium pycnometry (diamonds) and micro callipers (squares)

5.3.3 Resin Modification

This section of work is concerned with the measurement of the volume change of wood modified with three resins; urea formaldehyde, melamine formaldehyde and urea melamine formaldehyde.

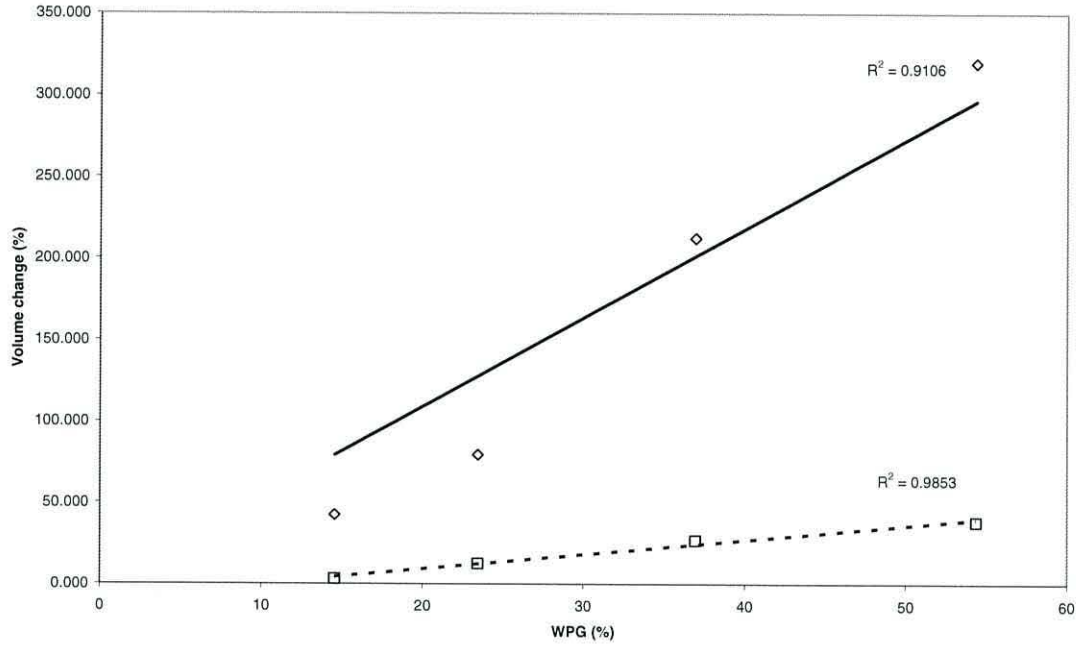


Figure 5.8: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of urea formaldehyde treated Corsican pine.

Figure 5.9 shows the volume change of Corsican pine when impregnated with urea formaldehyde. As mentioned in the method, the shortest treatment time for the timber was 60 minutes and therefore low weight percent gains were not achieved.

It can be seen with all the resins that the percentage volume changes as measured by helium pycnometry are very high. Percentage volume changes of 300 - 400% have been calculated. It is known that modification with an anhydride leads to modification of the cell wall and the adduct entering the cell wall. In the case of anhydride modification percentage volume increases of around 30 – 40% (at 30% WPG) were recorded.

Figure 5.10 shows the actual volume change measured by the two techniques. It has been noted that the increase in volume of the resin modified wood approaches the theoretical volume of a solid cylinder of the same dimensions as the sample (7.14 cm^3). This indicates that the voids in the timber, whether micropores or lumen are being blocked or filled by the resin. At a weight percent

gain of 50% the total volume measured by the helium pycnometry was ~5.8 cm^3 (the volume change plus the original volume of the cell wall). This can be seen in Figure 5.10.

The very large percentage volume change of the sample when measured by helium pycnometry suggests that the lumen is being filled with resin and the resin curing in the lumen. However because swelling can also be seen by measuring the external dimensions it can also be concluded that the resin has entered the cell wall and caused cell wall swelling prior to it curing.

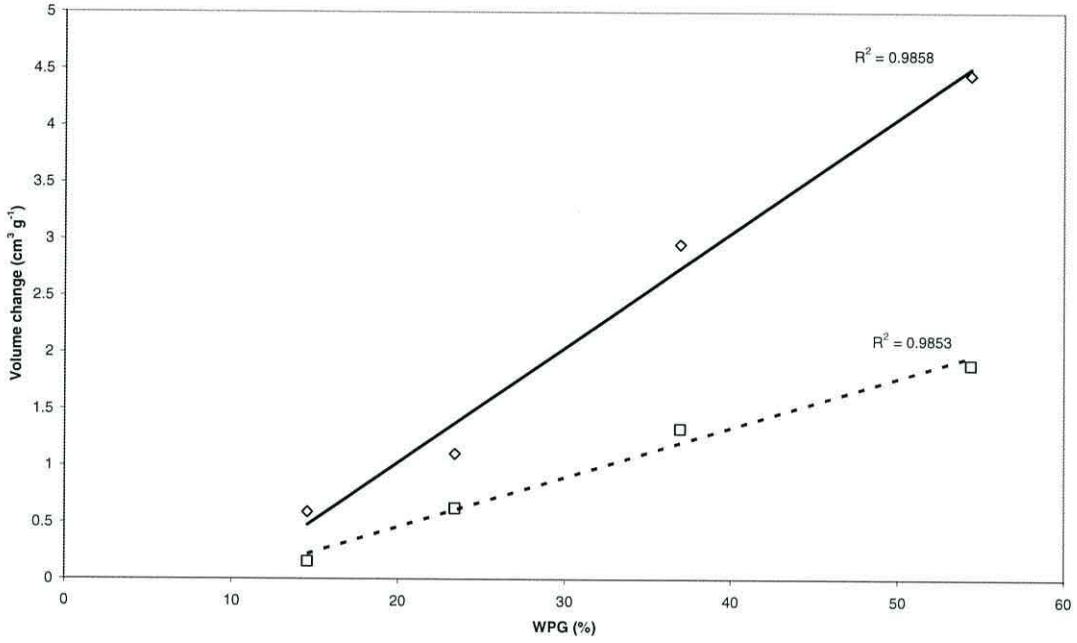


Figure 5.9: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of urea formaldehyde treated Corsican pine.

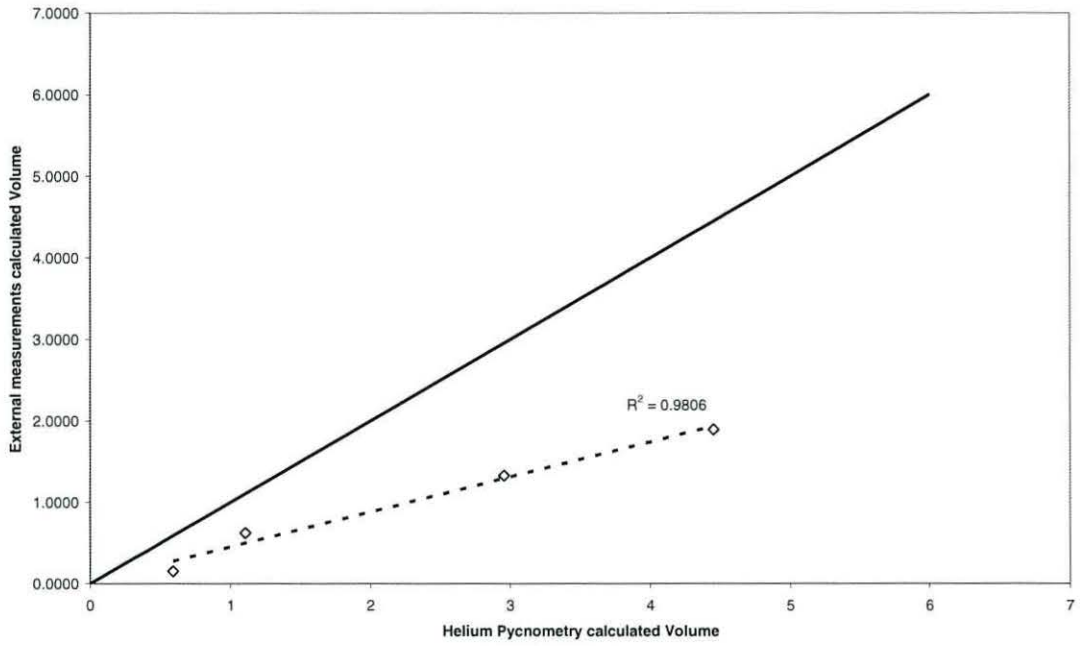


Figure 5.10: Graph of volume change calculated from external dimensions and helium pycnometry for urea formaldehyde treated Corsican pine.

Figure 5.10 show the volume change measured by the helium pycnometry graphed against the volume change calculated from the external measurements. If this graph had a 1:1 ratio it would show that the helium pycnometry volumes and the calculated volumes were increasing at the same rate and therefore no internal volume changes were taking place, however the graph in Figure 5.10 lies below the 1:1 ratio line and diverging away form it, therefore it is shown that the dimensions measured by Helium pycnometry are increasing faster than those calculated by external dimensions, therefore it can be shown that the lumen dimensions are decreasing. The decrease in lumen dimensions can be attributed to the curing of the resin within the lumen before it enters the cell wall and the lumen then filling with resin. It can be postulated that the micropores will begin to fill with resin prior to resin precure then, as the resin precures it will stay in the lumen and not enter due to blockage of the cell micropores and the increased cross linking within the resin.

Similar trends were seen for all three of the resins and both species of timber. The results for these are shown below.

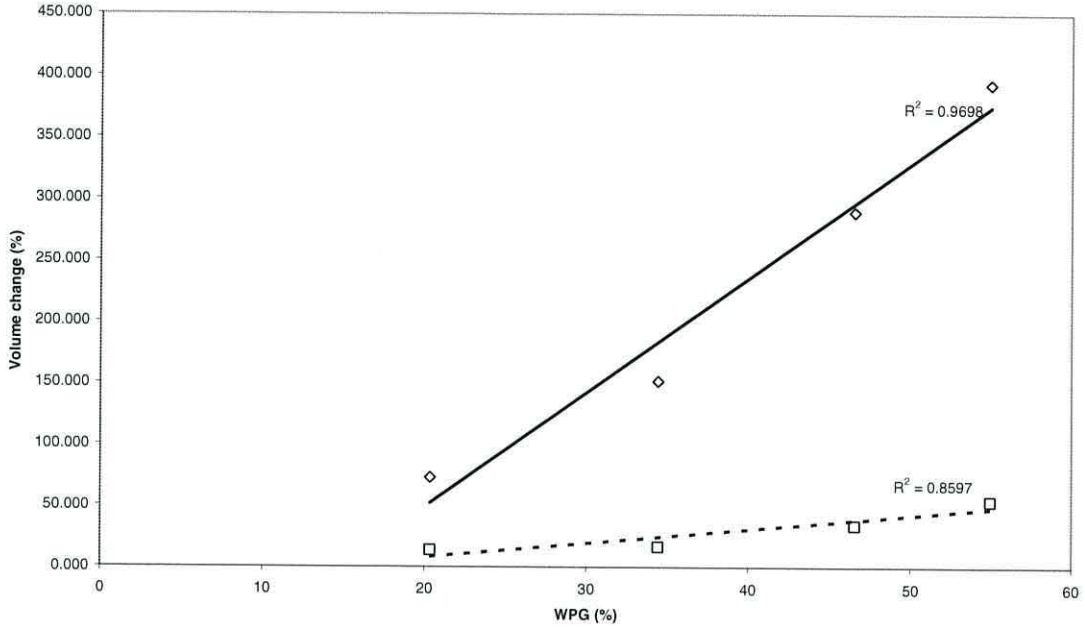


Figure 5.11: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine formaldehyde treated Corsican pine.

It can be seen in Figure 5.11 that the percentage volume changes (both measured by helium pycnometry and calculated by external measurements) are higher with the melamine urea formaldehyde than with the urea formaldehyde. It can be suggested that the increased volume change due to the addition of melamine formaldehyde over urea formaldehyde is due to the lower viscosity of the melamine formaldehyde. The lower viscosity will cause the initial uptake of resin, prior to the onset of curing to be at a greater rate than that of the more viscous resins. The increased rate of ingress of the resin into the samples can also be seen when a comparison is drawn between the first data points on the graphs. As has been noted in the methodology the samples were vacuum impregnated with resin for set amounts of time and it can be seen that the samples modified with the urea formaldehyde attained a WPG of 15% whereas the modified with melamine formaldehyde attained a 20% WPG when treated for 60 minutes.

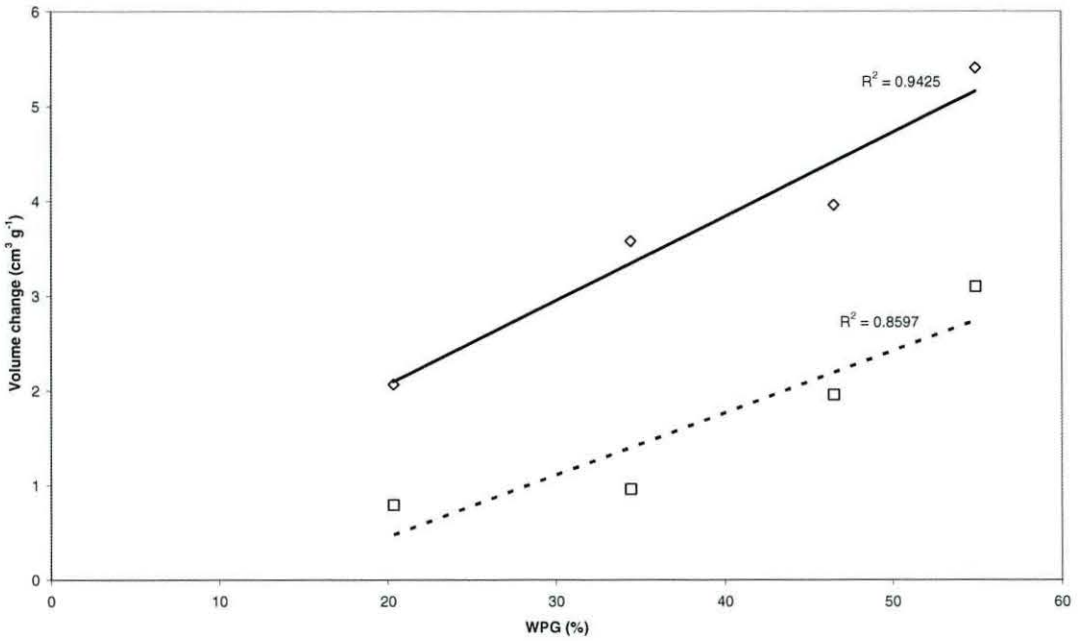


Figure 5.12: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine formaldehyde treated Corsican pine.

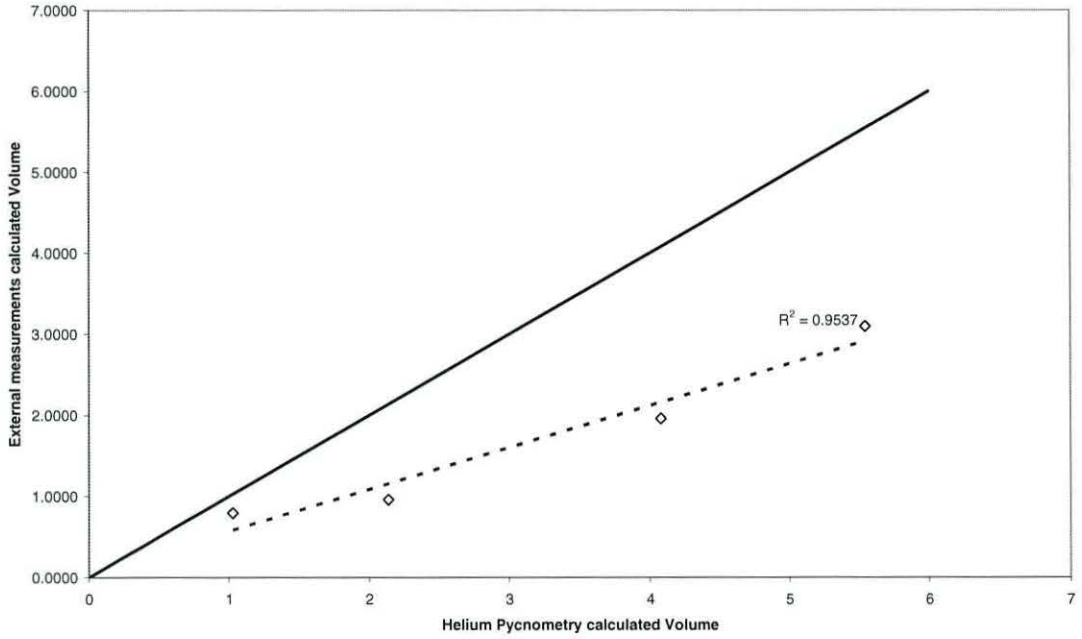


Figure 5.13: Graph of volume change calculated from external dimensions and helium pycnometry for melamine formaldehyde treated Corsican pine.

The graph shown in Figure 5.13, for the treatment of Corsican pine with melamine formaldehyde, again shows the helium pycnometer exhibiting a bigger volume change than that calculated using external dimensions (this is denoted by the graph being below the 1:1 ratio line) .

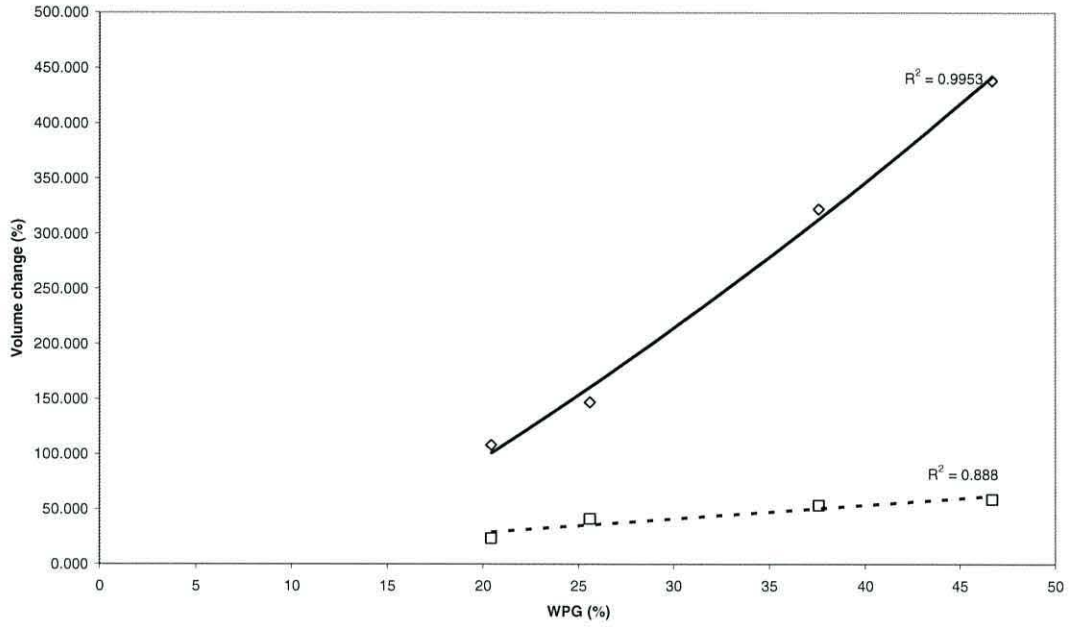


Figure 5.14: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine urea formaldehyde treated Corsican pine.

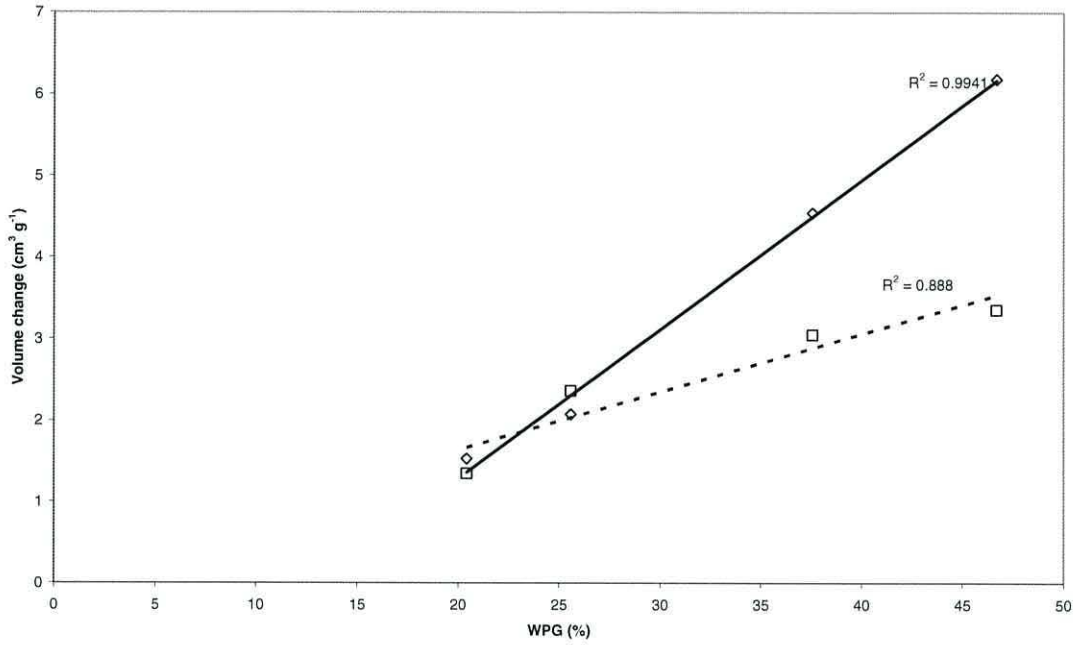


Figure 5.15: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine urea formaldehyde treated Corsican pine.

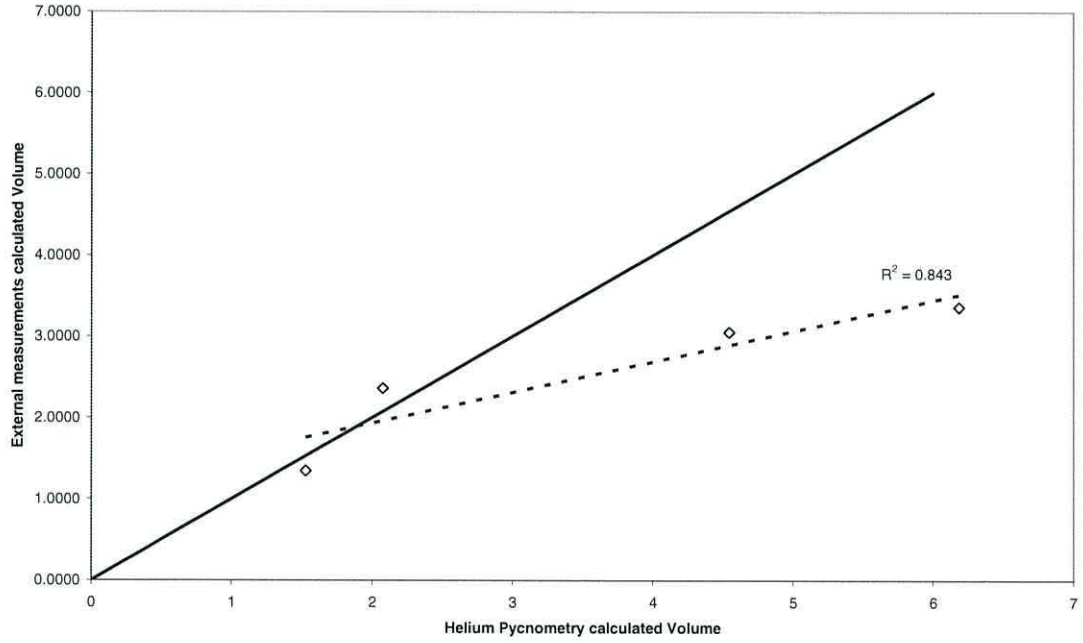


Figure 5.16: Graph of volume change calculated from external dimensions and helium pycnometry for melamine urea formaldehyde treated Corsican pine.

It can be seen in Figure 5.16 that the graph showing the interaction between the two ways to calculate the volume change cross the 1:1 ratio line, indicating that the external measurements are over-estimating the volume change below 23%. However due to the experimental design this is insufficient data to prove this and therefore more work should be undertaken, as it is possible that the lowest data point on this graph is erroneous.

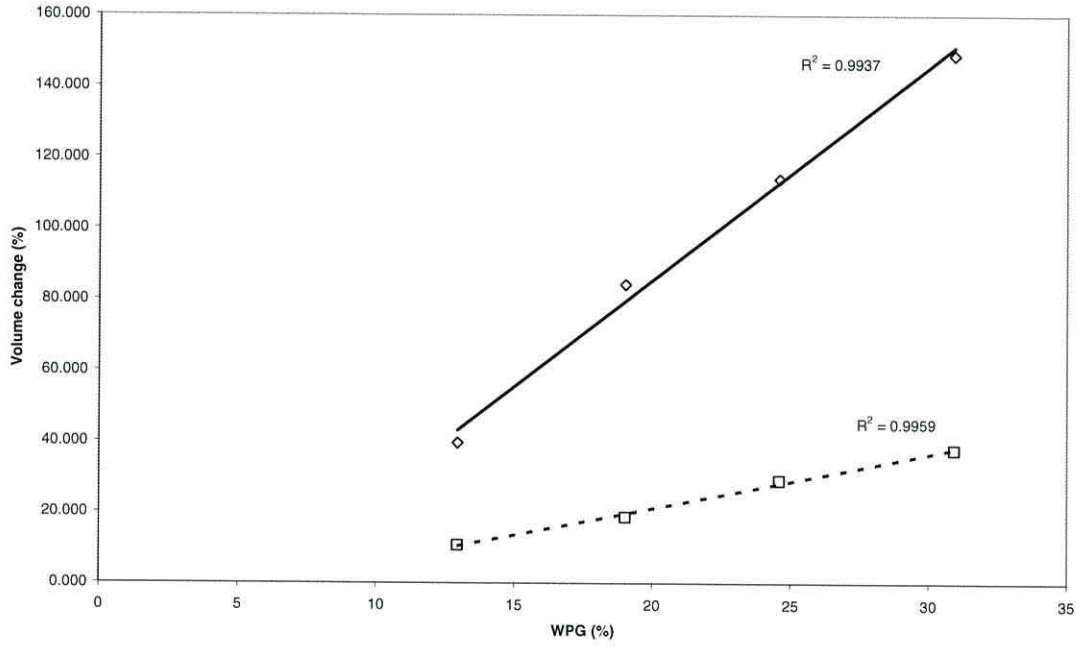


Figure 5.17: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of urea formaldehyde treated beech.

It should be noted that the volume change, when measured by helium pycnometry, for the beech modified with urea formaldehyde (150% VC) does not reach the same large volume changes that the urea formaldehyde modified Corsican pine does (290% VC). However the volume changes when calculated from external measurements are comparable with the volumes calculated form the external measurements of Corsican pine modified with urea formaldehyde resin.

It is also evident from the graphs that the actual volume changes recorded by the helium pycnometer and calculated form the external measurements are similar. It

can be seen from Figure 5.19 that the graph comparing the 2 types of volume measurement is close to a 1:1 ratio. This indicates that the resin is entering the cell wall and curing in the cell wall and not having any significant build up of resin within the lumen.

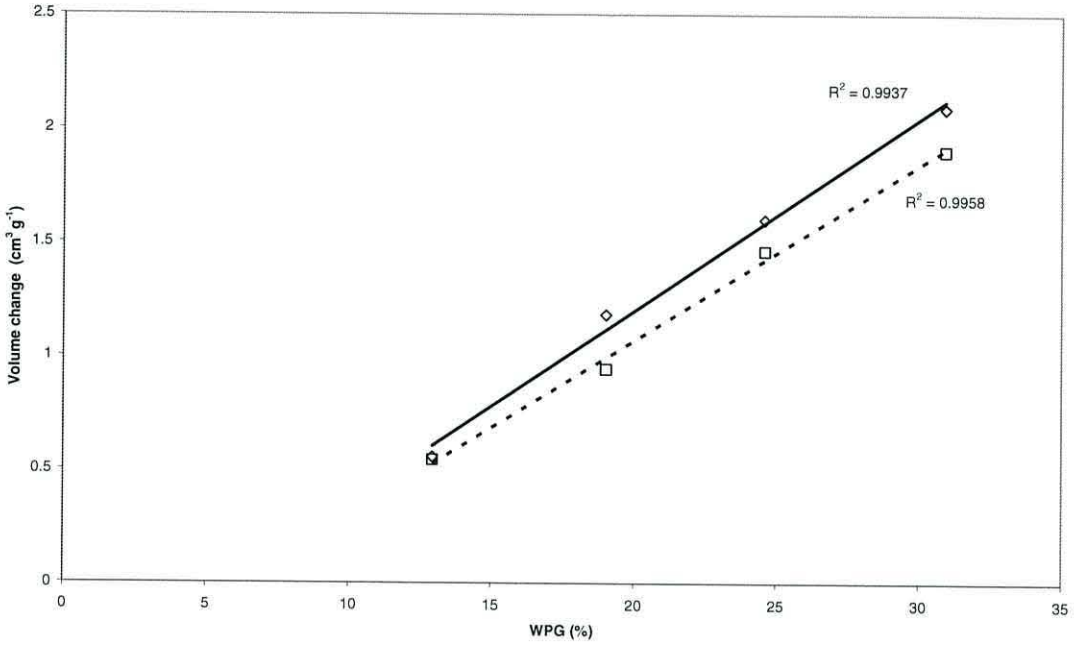


Figure 5.18: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of urea formaldehyde treated beech.

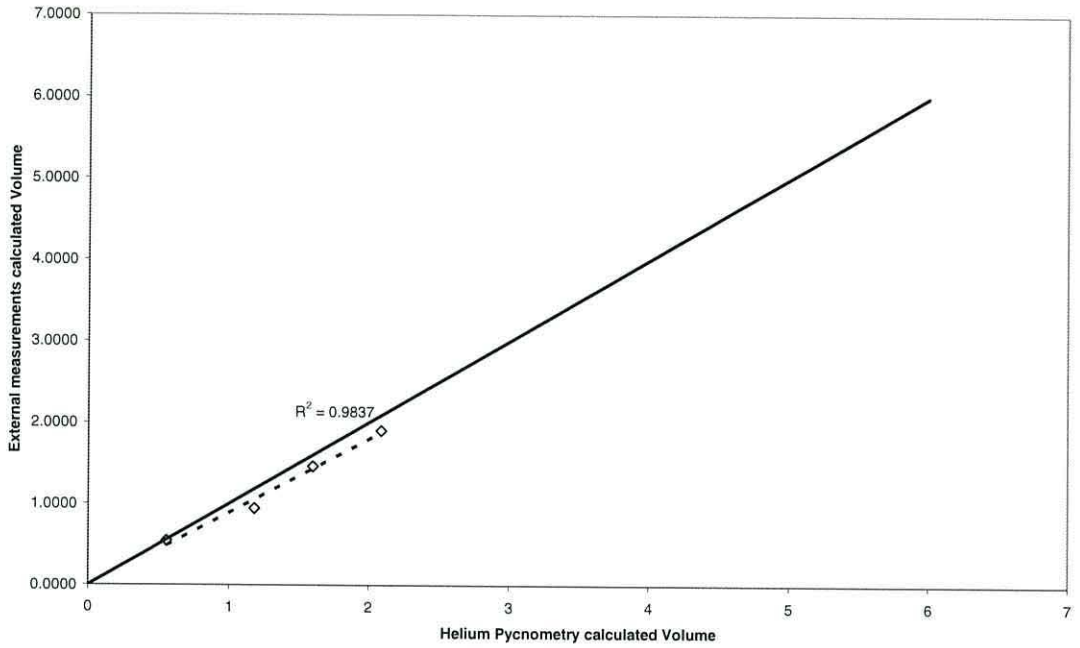


Figure 5.19: Graph of volume change calculated from external dimensions and helium pycnometry for urea formaldehyde treated beech.

Figure 5.20 shows the percentage volume change of beech when modified with melamine formaldehyde resin. It can be seen that the percentage volume change as measured by the helium pycnometer is greater than the volume change of urea formaldehyde modified beech. The percentage volume changes reported here are greater than those reported for urea formaldehyde treated beech and similar to those reported for melamine formaldehyde modified Corsican pine. It can be hypothesised that the resin has begun to procure in the lumen and cause the lumen to be blocked, therefore giving large percentage volume change when measured by helium pycnometry. It can be noted that the increase in volume when calculated from the external dimensions is similar to the volume changes noted throughout this investigation of all the resin / wood combinations.

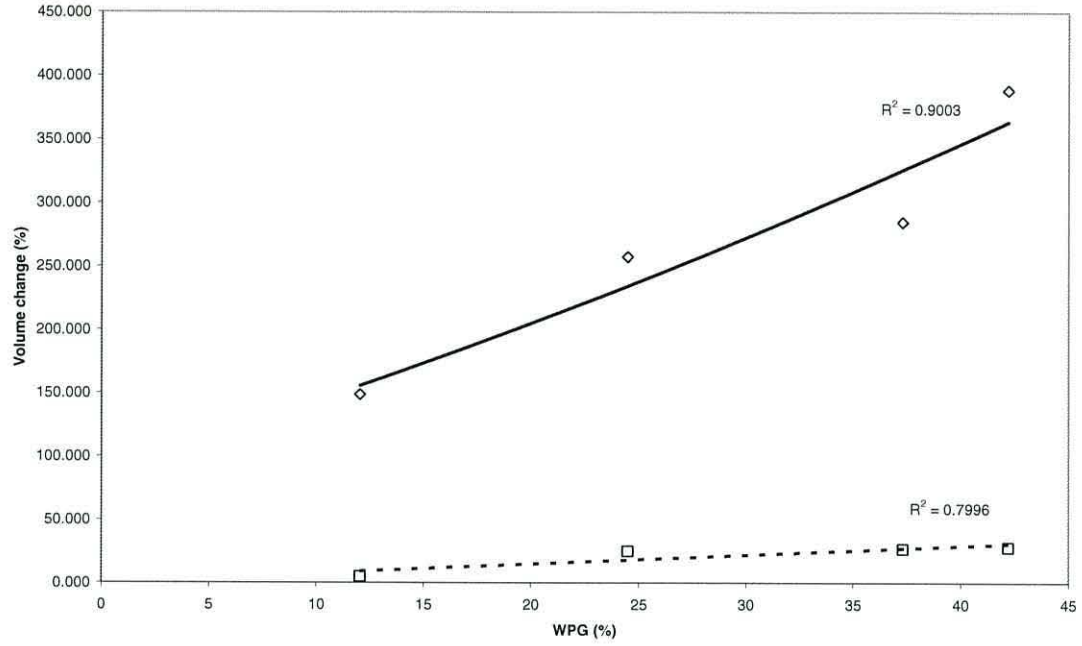


Figure 5.20: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine formaldehyde treated beech.

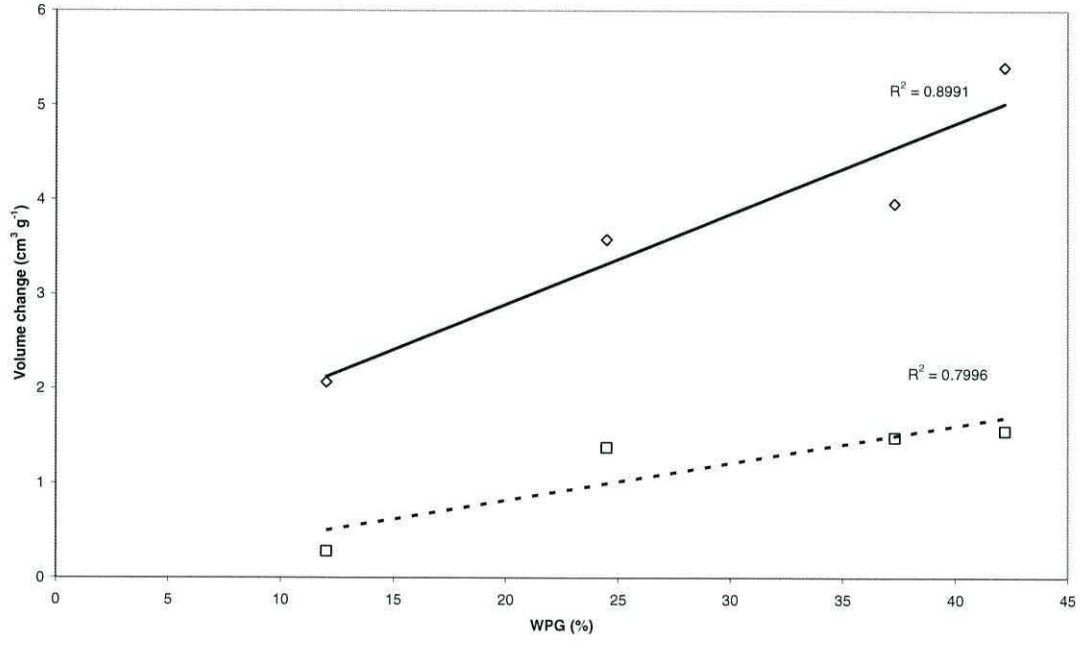


Figure 5.21: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine formaldehyde treated beech.

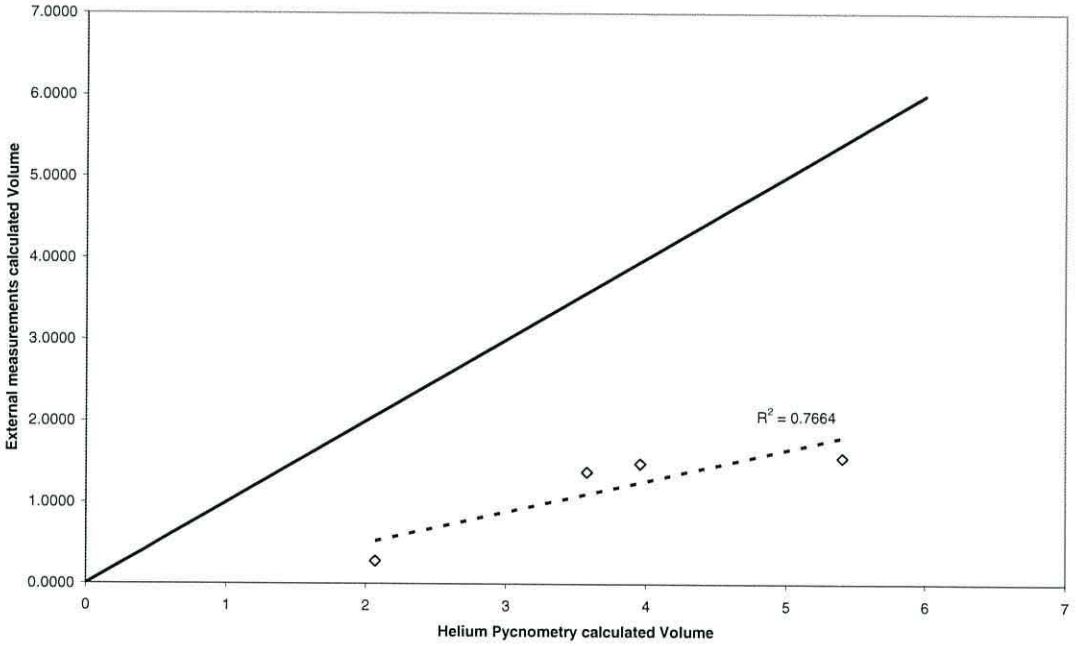


Figure 5.22: Graph of volume change calculated from external dimensions and helium pycnometry for melamine formaldehyde treated beech.

Figure 5.23 shows the percentage volume change for the MUF resin modified beech calculated by two methods. It can be seen that the percentage volume change as measured by helium pycnometry is similar to that reported for Corsican pine modified with MUF resin and of beech modified with MF resin. Again it should be noted from Figure 5.24 that the volume measured by the helium pycnometry is approaching that of a solid cylinder of the same dimensions. Again this indicates that the lumen are being filled with cured resin.

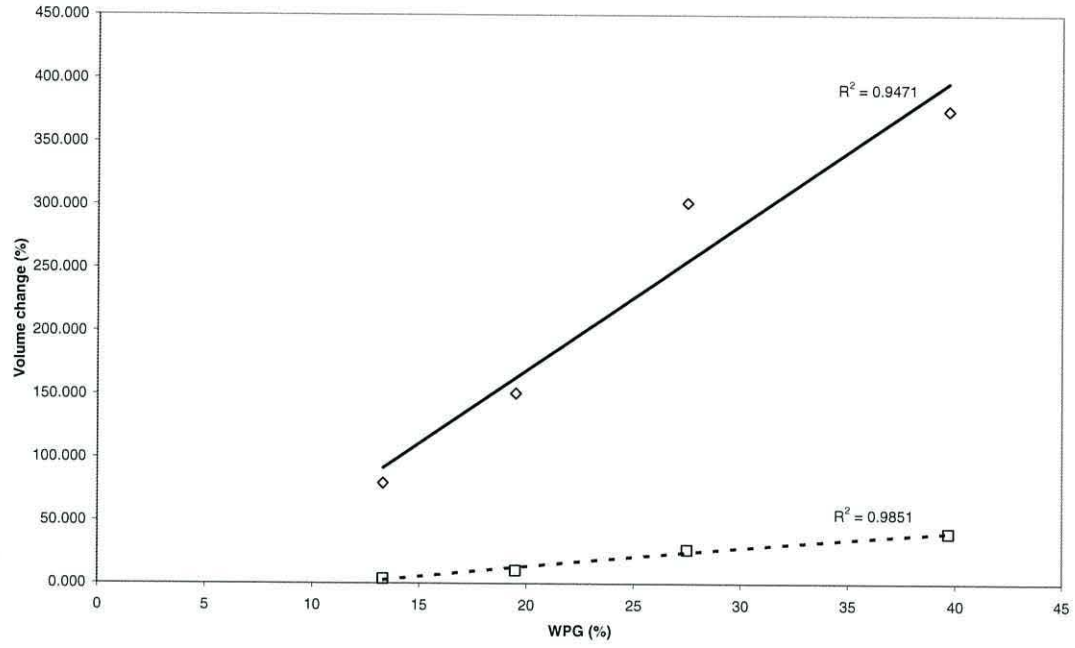


Figure 5.23: Percentage volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine urea formaldehyde treated beech.

Figure 5.25 shows the graph comparing the 2 different techniques for the calculation of volume change. It can again be seen that the graph falls below the 1:1 ratio line (which indicates that the volume change calculated form external dimensions is equal to the volume change measured by helium pycnometry). This indicates that the helium pycnometer is measuring a larger volume change than is calculated from the external dimensions.

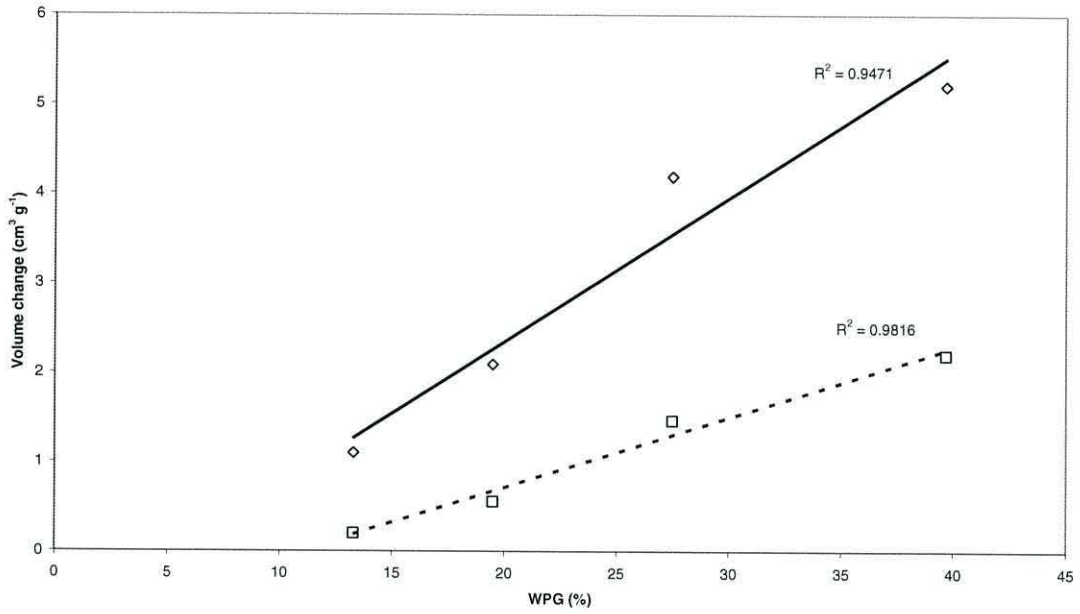


Figure 5.24: Volume change as measured by standard methods (dashed line and squares) and helium pycnometry (solid line and diamonds) of melamine urea formaldehyde treated beech.

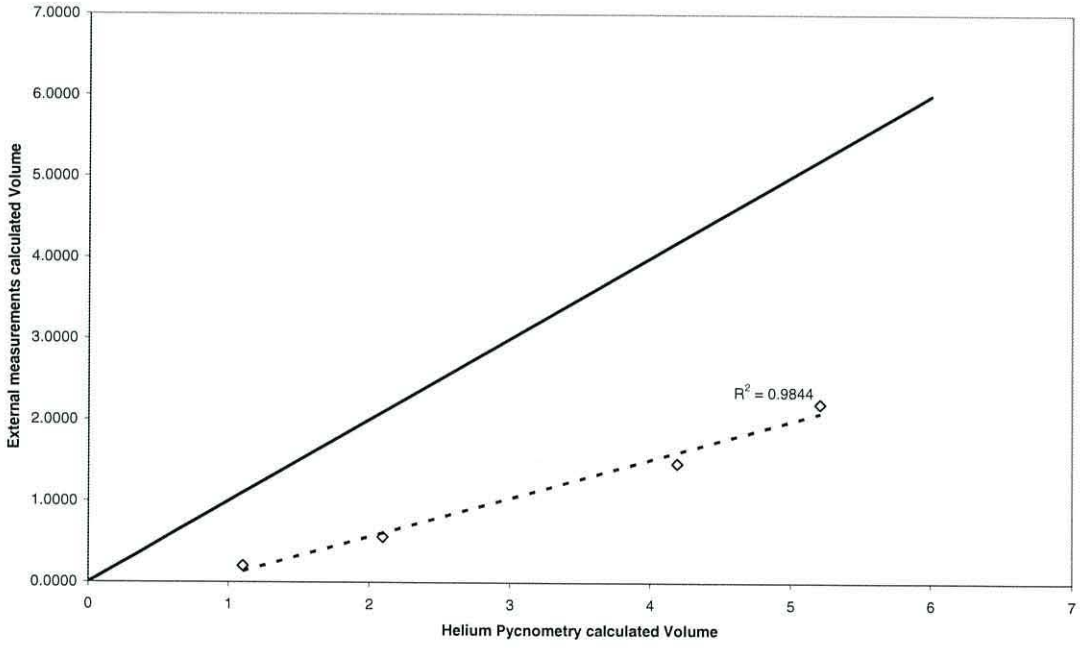


Figure 5.25: Graph of volume change calculated from external dimensions and helium pycnometry for melamine urea formaldehyde treated beech.

The percentage volume change as shown by the helium pycnometry technique gives extremely high changes in volume, within the region of a 400% increase in the volume, this can only be attributed to the resin filling the lumen and blocking the entrances to the micropores. It can be hypothesised that, because all of the treatments exhibit some degree of external swelling, there is some cell wall penetration taking place, it is however unknown whether this takes place during the initial phase of modification (as with anhydride modification) or whether it takes place as the lumen fills with resin. A further study has to be undertaken to assess the destination of the resin at low WPG as the investigation here does not show WPG's under 20% and therefore low WPG can not be assessed.

5.3.4 Conclusion

Two timber species, beech and Corsican Pine have been modified with two anhydrides and three resins. The resultant treated samples were then analysed using a helium pycnometer. It was found that the two types of treatment were vastly different. The anhydride treatments (both acetic and hexanoic) are shown to be cell wall modifications. However, due to their differing molecular weights they have different rate of reaction is different between the two modifications.

The use of helium pycnometry to assess the cell wall volume swelling has been investigated here and compared with the usual method of measuring external dimensions. It has been found that measurement of the external dimensions of wood specimens does not give true information regarding changes in cell wall volume. This is due to the swelling of the cell wall into the lumen. For the external measurements to give a true indication to the amount of volume change it would have to be assumed that the lumen size was not altered and the cell wall only swelled in one direction, namely outwards. However the use of helium pycnometry has show that the actual volume change is larger than calculated from the external dimensions indicating that the cell wall must swell inwards as well as outwards.

By comparing differences in volume determinations from external dimensions and by helium pycnometry on the same samples, it is possible to determine how the lumen volume varies at different levels of swelling.

Acetic anhydride reacts more readily with the cell wall due to its small molecular size and the fact that it can enter the wood cell wall micropores. As it has been established that the acetic anhydride will penetrate the cell wall, it was used to illustrate that measurement of the external dimensions of wood specimens does not give information regarding changes in cell wall volume. This shows that it cannot be assumed that changes in wood volume and changes in the volume of the lumens will show the same behaviour.

The hexanoic anhydride is a larger molecule than the acetic anhydride and thus will not enter an unswollen cell wall, thus the use of pyridine as a swelling agent. The hexanoic anhydride was used in this investigation to show how larger molecules reacted with the cell wall.

The mechanism for the reaction of the resins with the wood is different to that of the anhydrides. The resins do enter the cell wall but generally suffer from precure blocking the micropores towards the surface of the cell wall. The resin then begins to fill and cure within the lumen. This is seen as a large increase in helium pycnometry measured volume which begins to approach the volume of a solid cylinder of the same dimensions. There is bonding with the cell wall but this comprises generally of hydrogen bonds and van de waals forces, as mentioned in section 1.3.2.

Chapter 6 will investigate the effects of the volume changes due to modification on the accessibility of the timber to molecules of differing sizes and how this effects the decay resistance of the timbers.

6 Determination of Pore Size and Accessibility of the Cell Wall of Treated Woods

6.1 Introduction

It has been noted in Chapter 3 that treatment with resin offers a physical barrier to the ingress of fungi, which is a benign form of protection and not an active form (such as that achieved with the use of the biocides). The investigation reported in this chapter studied the effects of resin in blocking accessibility to the cell wall. The method used here was solute exclusion, in which sugars of increasing molecular weight are diffused into the wood, and the dilution of the solution is measured indicates the accessibility of the cell wall related to the size of the sugar molecules.

Also in this chapter the fibre saturation point of the treated timber will be reported. As mentioned in Section 1.2 if the fibre saturation point is low enough it will prevent the decay of timber by not allowing enough moisture into the timber for decay to take place. The FSP of both resin and anhydride treated wood are going to be presented in this chapter.

6.2 Methods

6.2.1 Sample preparation

The following sample dimensions was cut for this investigation form bith Corsican pine and European beech:

- Circular 14mm in diameter by 5mm (longitudinal)

All the samples were extracted in a Soxhlet extractor using a solvent mix of toluene acetone and methanol (4:1:1 by volume). All samples were extracted for 6 hours to ensure that all the soluble extractives were removed from the samples. Samples were then air dried for 24 hours and then oven dried at a temperature of 105°C. All samples used in the experiments were selected for the straight orientation of the growth rings and for the consistency of growth ring spacing. All samples were labelled appropriately using pencil as to avoid the loss of labels when the samples were treated.

6.2.2 Sample treatment

The samples were then modified with acetic anhydride, hexanoic anhydride, UF resin, MF resin and MUF resin in the same manner as shown in Chapter 5. For each of the anhydride treatments 3 different treatment times were used (1575, 105, 30 minutes) and for each different resin treatment 3 different WPGs were attained as seen in Table 1.1. For each of the treatments 3 replicate sets of blocks were treated.

After volume determination the same samples were oven dried to ensure that all moisture has been excluded from the samples. The samples were then vacuum impregnated with a 0.05% solution of sodium azide and then left soaking in the sodium azide solution for 3 months. The samples were kept in a closed desiccator that had had nitrogen blown over the surface to exclude the air. The samples were soaked for three months to ensure that all the leachable components of the treated wood had been leached. The sodium azide was changed on a monthly basis.

Modification	Treatment Time (min)	Average WPG (%)
Acetic Anhydride	1575	23.64
	105	15.64
	30	2.33
Hexanoic Anhydride	1575	50.66
	105	15.96
	30	4.98
Melamine Urea formaldehyde resin	180	19.08
	120	12.52
	60	7.76
Melamine formaldhyde resin	180	23.35
	120	16.94
	60	10.39

Table 6.1: Weight percent gain of the modified samples used in chapter 6.

The probes selected were identical to those used by Flournoy *et al.* (1991) and Hill *et al.* (2005) and are listed, along with their molecular weights and diameters, in Table 6.2. Of the six (non-water) probes, three were sugars and three (the three largest probes) were dextrans.

Probe	Molecular weight	Probe diameter (Å)
Water	18	4
Glucose	180	8
Maltose	342	10
Raffinose	504	12
Fluka AG	6000	38
Pharmacia T10	11200	51
Polysciences 15-20K	17500	61

Table 6.2: Molecular weights and diameters of probes.

Stone and Scallon (1968b) lists three properties of probes necessary for the applicability of the solute exclusion technique:

Probes act as spheres of a particular diameter. For linear dextrans of the type used in this study, this has been found to be the case (Grotte, 1956).

The range of molecular diameters for a probe (governed by the molecular weight range for a given dextran) should be small compared to the range of pore sizes within the porous body being examined. Farahani (2003) notes that the dextrans used in this study were not expected to be able to penetrate the modified wood cell wall to any significant extent. Flournoy *et al.* (1991) found that the same three dextrans did not penetrate unmodified undecayed wood.

Probe molecules should not be adsorbed onto the surface of the wood, as this would cause a reduction in the concentration of the solution and an apparent increase in accessibility. Stone and Scallon (1968b) found adsorption to be negligible for wood and pulp fibre, and in this study it is also assumed, as with the work of Farahani (2003) and Forster (1996) also to be negligible for modified wood samples.

A stock solution of 3% (w/w) glucose was made up using the 0.05% (w/w) sodium azide. Oven dry sample tubes and their lids weighed to 4 d.p.

The samples were taken from the sodium azide solution that they had been conditioned in and the surfaces were dabbed dry. These were added to the sample tubes and again weighed to 4 d.p. Finally the tubes were filled with the probe solution and again weighed to 4 d.p. the weights of the probe solution and the wet blocks of wood could then be determined. The tubes were then sealed using parafilm and then they were stored at 20°C and 65% RH for 2 weeks.

After the two week period the probe solution was decanted off and stored for analysis. The surface of the blocks was then dabbed dry and the weight measured to 4 d.p. The blocks were then soaked in 0.05% sodium azide solution to leach

out any of the probes that had entered the wood. The leaching water was changed every 3 days to ensure that all of the probe solution had leached out of the wood.

This procedure was then repeated for each probe in turn.

The amount of water within each sample was calculated by subtracting the dry weight from the wet weight of the blocks.

The amount of the water within the block of wood accessible to the probes was calculated using the change in concentration of the probe solution. This was found using a Knauer differential refractometer.

The refractometer was initially set up with a 3% solution of the probe in the reference cell. The solutions were analysed by very slowly injecting the solution into the chamber, the solution was hand injected at approximately 1 ml per minute and 3 ml was injected. This ensured that the chamber was full of the solution that was to be analysed and the speed at which the solutions were injected ensured that no turbulence was created within the instrument as this would affect the refraction of the light through the solution. Once the reading had become stable (approximately 1 minute after the end of the injection) a reading was taken. Standards were analysed ranging from 0% to 3% in 0.5% (v/v) intervals. These were then used to produce a calibration curve for that particular probe.

This was repeated for all the probes.

6.2.3 Calculations

The following calculation was used to determine the inaccessible water within the sample;

$$\delta = \frac{w+q}{p}\left[1 - \frac{w}{w+q} \times \frac{C_i}{C_t}\right] \qquad (6.1)$$

Where:

δ = inaccessible water in grams per gram of dry sample.

p = dry weight of sample

q = weight of water in sample

w = weight of solution of solute molecules

c_i = initial concentration of solution of solute molecules

c_t = final concentration of solution of solute molecules

The amount of inaccessible water was then used to calculate the amount of accessible water within the cell wall using the following calculation:

Accessible water = fibre saturation point – inaccessible water

6.2.4 The principle of Solute exclusion as a measure of cell wall porosity

This method of solute exclusion is based on that of Stone *et al.* (1968) and can be described as follows.

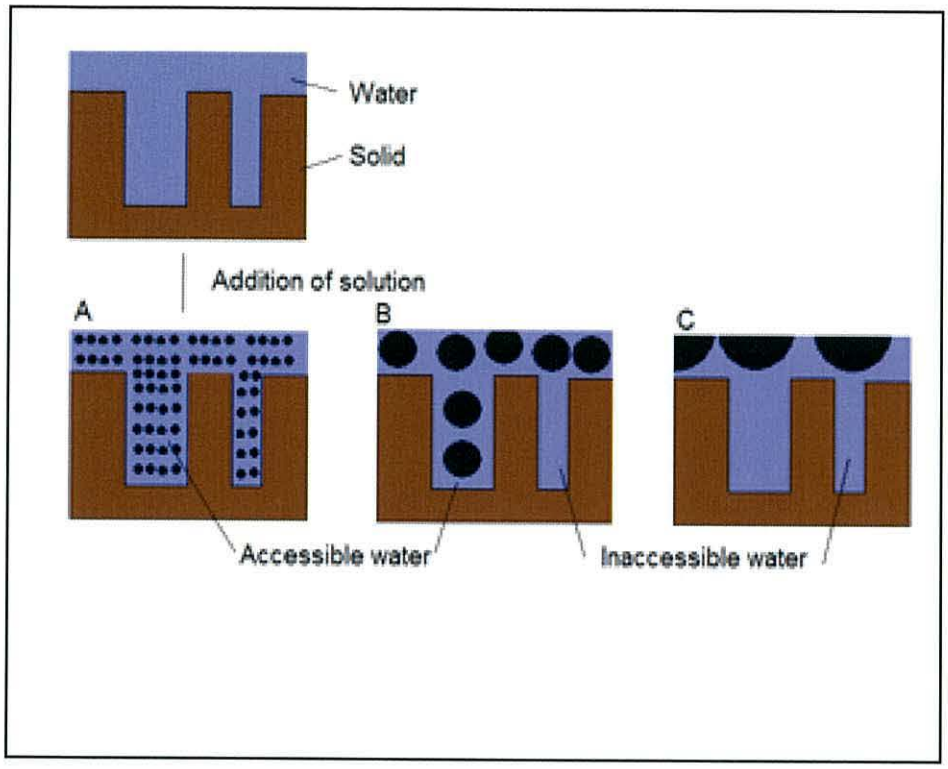


Figure 6.1: Diagram illustrating the principle of solute exclusion.

This method begins with a porous body, which is swollen with water and immersed in an excess of water, which has a known weight of a certain solution added to it (whether, in this case it be a sugar solution or a dextran solution). The solution is then thoroughly mixed. If all the water in the sample is accessible to the solute molecules then this water will contribute to the dilution of the solution (Figure 6.1a). If a solution of larger molecules is used (Figure 6.1b), smaller pores become inaccessible to the solute molecules and therefore the water in these pores is unavailable for the dilution of the solution, therefore after mixing the solution will be less dilute than the solution from Figure 6.1a. This difference in solution is the basis for the calculation to determine the amount of inaccessible water for a particular solute within a system. When the solute molecules are so large that they do not fit into any of the micropores (Figure 6.1c) the inaccessible water is equal to the total water of swelling.

The comparison of the refracted index of the diluted solution with a calibration curve will give a dilution factor which can in turn be used (with the known volume of solution) to calculate the accessible water for that given probe. This

again in turn can be divided by the mass of the original sample weight to give the volume of accessible water per gram of sample (ml g^{-1}). This method relies on the assumption that the water in the cell wall micropores has a specific gravity of 1. The accessibility of the water within the cell wall is calculated by subtracting the accessibility of the largest probes (which do not enter the cell wall) from the accessibility of the smaller probes.

6.3 Results

6.3.1 Cell wall accessibility

Appendix b (Table 9.) shows the results for the accessibility of the whole of the wood cell voids, both macropores (such as lumen) and cell wall micropores.

Appendix b (Table 9.) shows the volume of the cell voids in the modified and resinated woods. These were calculated by assuming that the three largest probes will not have entered the wood cell wall (in accordance with the work of Farahani (2003)). The amount of accessible water for the three largest probes was averaged to give the volume of the lumen. This was then subtracted from the results for the other probes to give a cell wall micropore volume.

The data shown in Table 9. can be seen graphically represented in Figure 6.2 to Figure 6.15. The data is grouped according to, for example the three low level urea formaldehyde resin modified batches are grouped together.

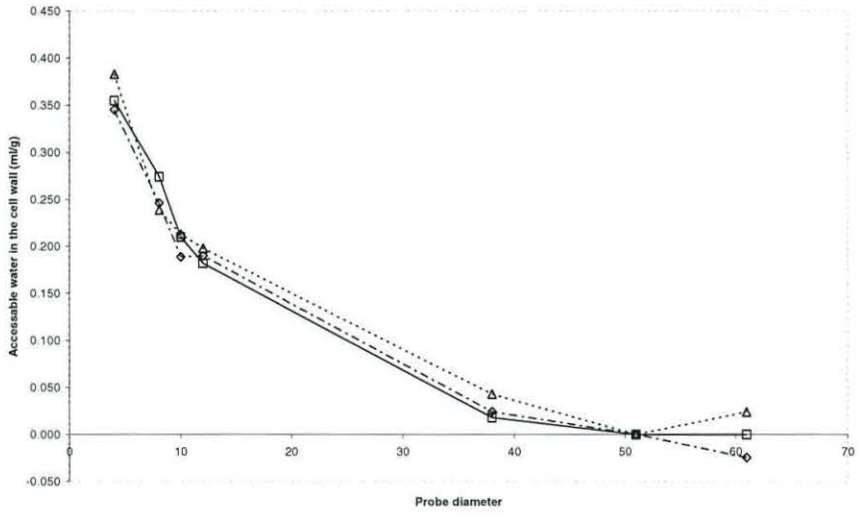


Figure 6.2: Graph to show the volume of accessible cell wall micropores to different sized probes (measured in Å) in Corsican pine control samples.

It is interesting to note that the three replicates shown in Figure 6.2 exhibit excellent reproducibility. It has been found that the fibre saturation point of Corsican pine is around 35%-38% and this is in agreement of the work carried out by Forster (1996), Farahani (2003) and Stone and Scallen (1968) all of which used a similar technique to calculate FSP. However this method shows the FSP to be higher than is conventionally accepted. The data here also shows a maximum micropore diameter of 40-50 Å which again is in agreement with the work of Forster (1996) and Farahani (2003).

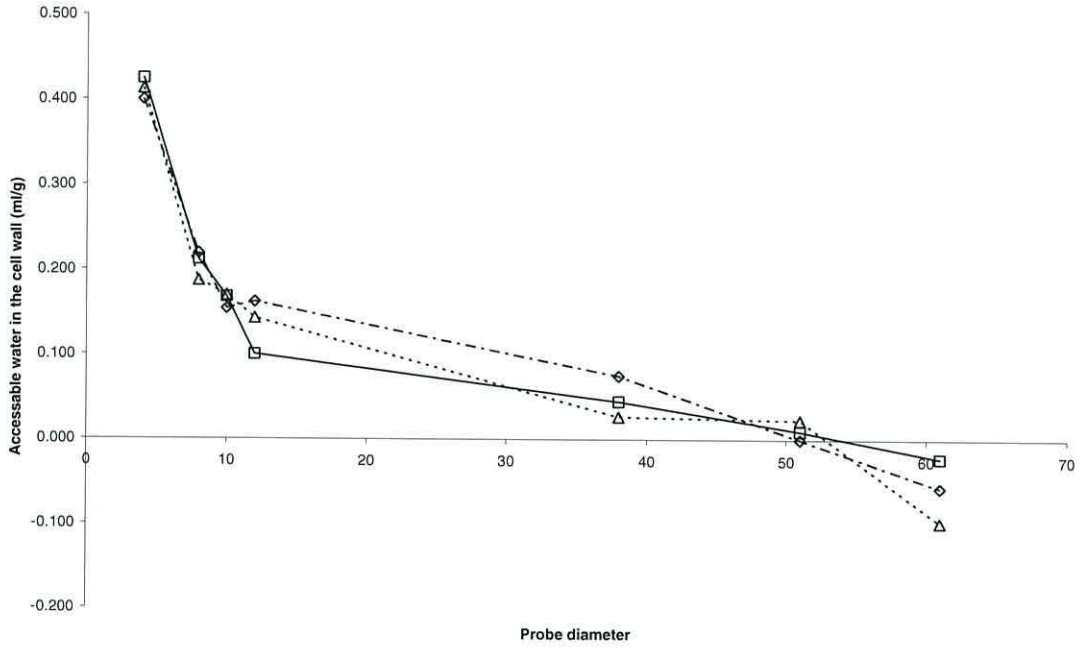


Figure 6.3: Graph to show the volume of accessible cell wall micropores to different sized probes (Å) in Corsican pine modified to an average WPG of 2.33% acetic anhydride.

Figure 6.3 shows the volume of the accessible cell wall micropores. It can be seen that with a 2.33% acetic anhydride modification the FSP of the timber is approximately the same as with the unmodified samples, however the accessibility to the 10Å probe reduced from ~0.2 ml/g to ~0.16 ml/g or by approximately 20%. It was noted in Chapter 3 that the mass loss due to decay of acetic anhydride samples was reduced significantly between 0% WPG and 5%. It can be hypothesised that this is due to the reduction in accessibility to the 10Å and greater sized low molecular weight decaying agents and not the reduction in FSP.

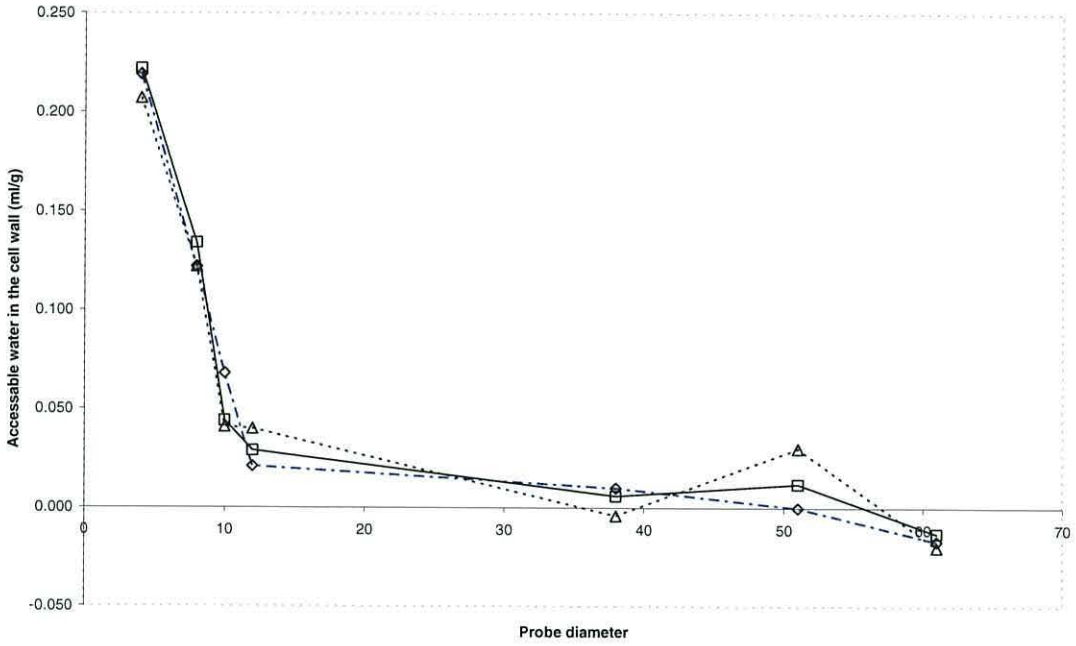


Figure 6.4: Graph to show the volume of accessible cell wall micropores to different sized probes (Å) in Corsican pine modified to an average WPG of 15.64% acetic anhydride.

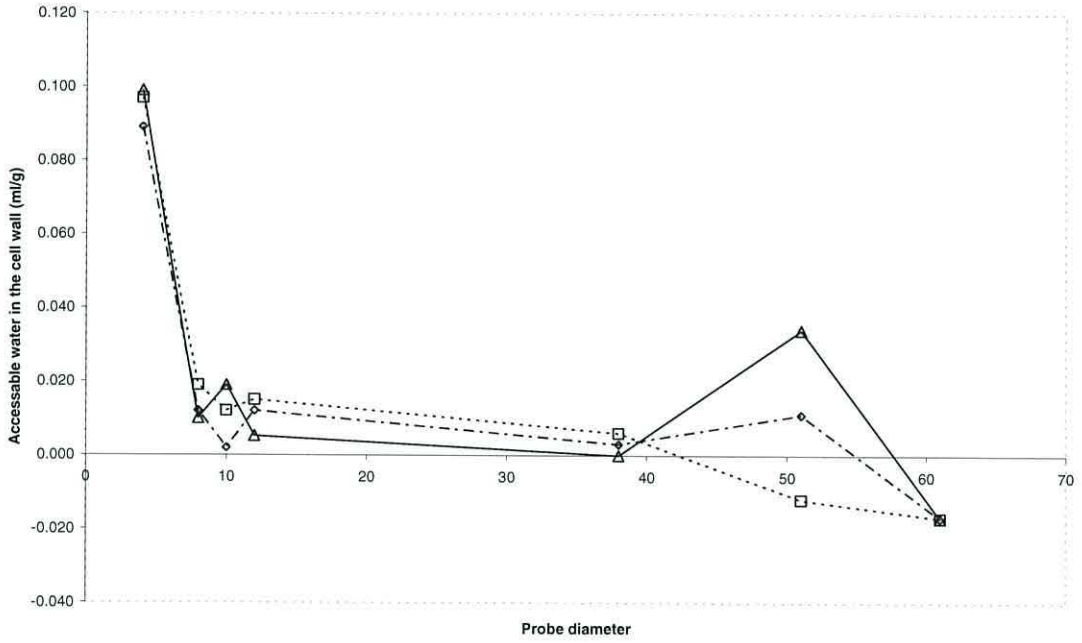


Figure 6.5: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 32.64% acetic anhydride.

Figure 6.6 shows the average cell wall micropore accessibility of acetic anhydride modified wood. It can be seen that accessibility to the cell wall is reduced with the increase in modification. The reduction of the accessibility with the acetic anhydride modification is greater than that shown in other studies (Forster, 1998) and Farahini (2003). It was reported that the cell wall accessibility fell by 50% with a modification of around 20% whereas it has been found in this investigation that there is a fall in accessibility of about 75% for the 10Å molecules. It should be noted that as the WPG due to modification increases the scatter of data between replicates when the accessibility is assessed using a 51Å probe also increases. The reason for this is unknown however it is likely to be due the refractometry methodology being incompatible with the particular dextran being used.

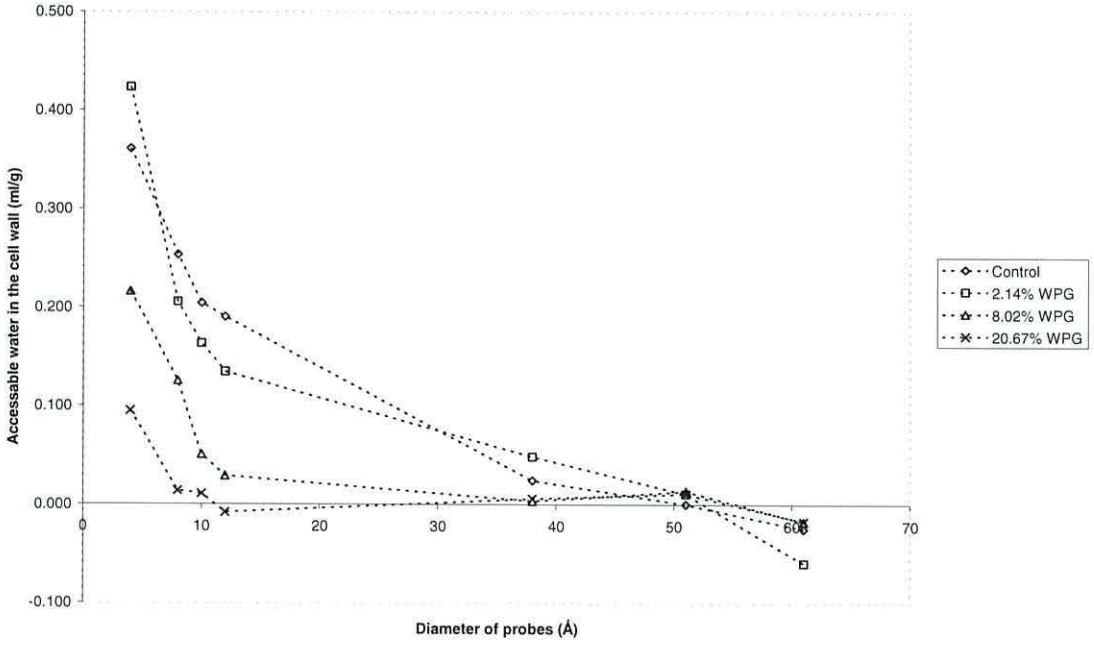


Figure 6.6: Average cell wall micropore accessibility for acetic anhydride modified Corsican pine

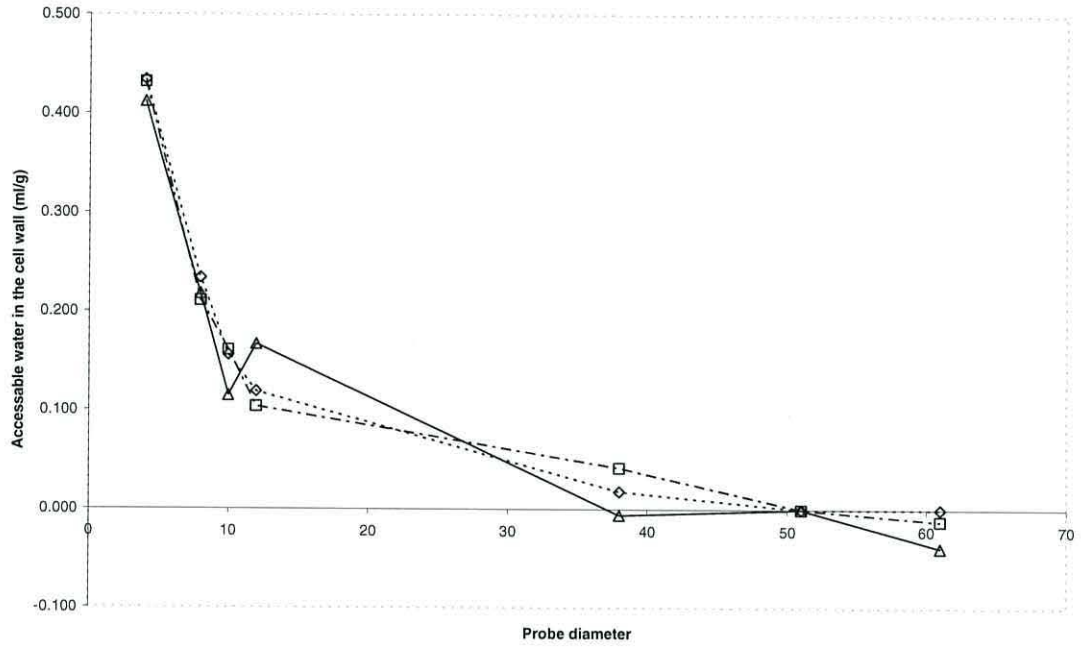


Figure 6.7: Graph to show the volume of accessible cell wall pores to different sized probes (Å) in Corsican pine modified to an average WPG of 4.98% hexanoic anhydride.

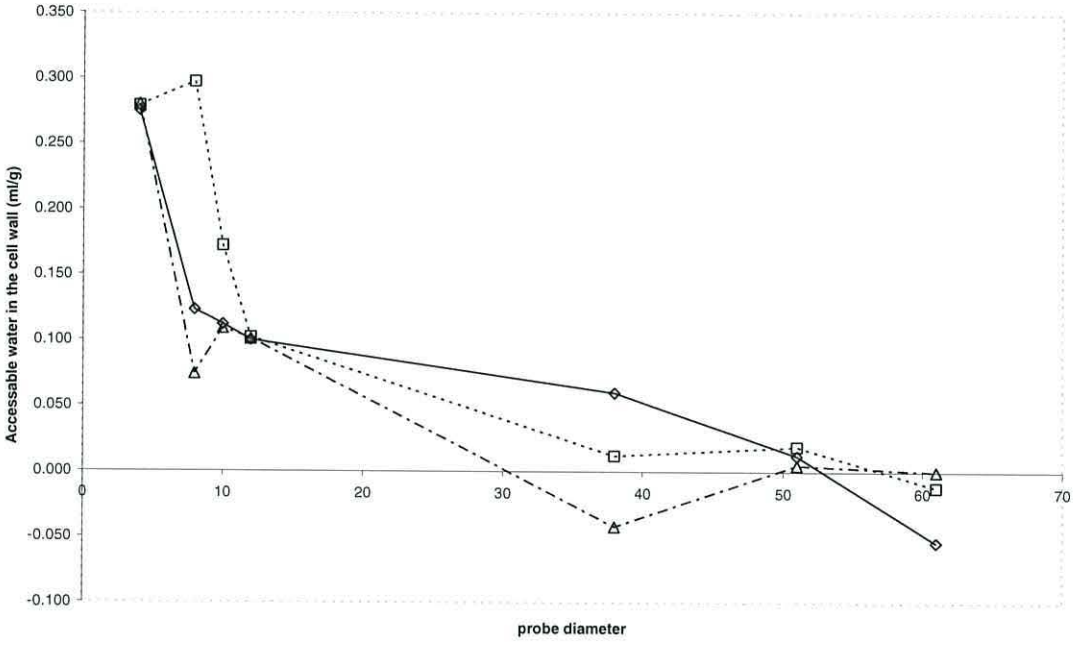


Figure 6.8: Graph to show the volume of accessible cell wall micropores to different sized probes (Å) in Corsican pine modified to an average WPG of 15.96% hexanoic anhydride.

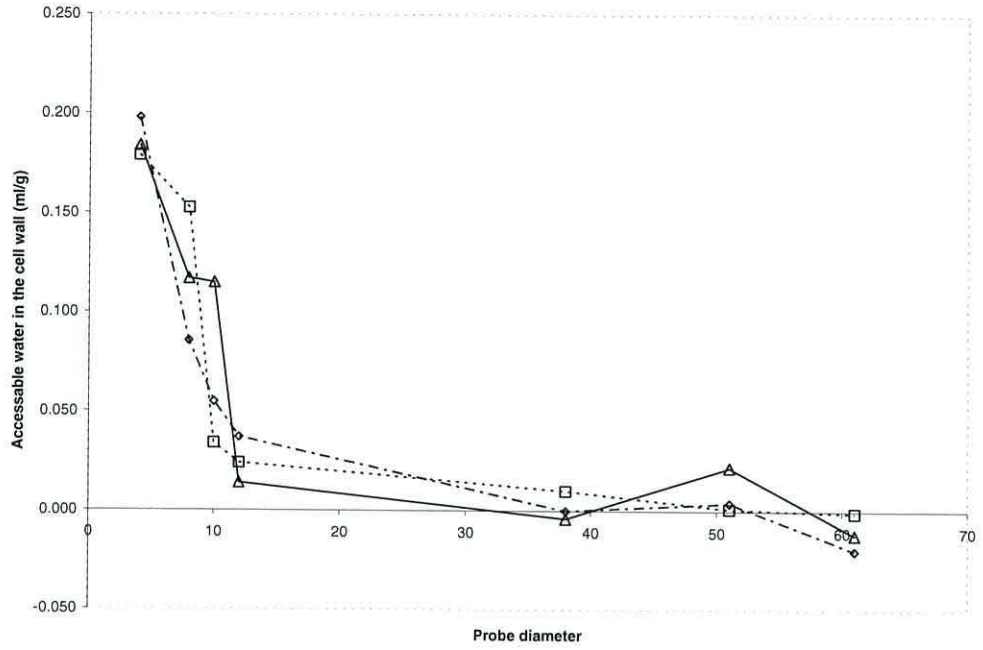


Figure 6.9: Graph to show the volume of accessible cell wall micropores to different sized probes (Å) in Corsican pine modified to an average WPG of 50.66% hexanoic anhydride.

Figure 6.7 to Figure 6.9 show the cell wall micropore accessibility for Corsican pine modified with hexanoic anhydride.. The increased variation between the sample sets should be noticed. This is probably due to the use of pyridine in the treatment of the samples with hexanoic anhydride. The pyridine is used to increase the porosity of the timber to make it easier to treat, unfortunately a sample of pyridine treated timber was not analysed here and therefore the extent of this is unknown. However, some increase must have taken place as the samples treated with the low level of hexanoic anhydride have a greater accessible volume to water (the 4 Å probe) than that of unmodified Corsican pine.

Figure 6.10 to Figure 6.15 show the cell wall accessibility of Corsican pine modified with the two resins MF and MUF.

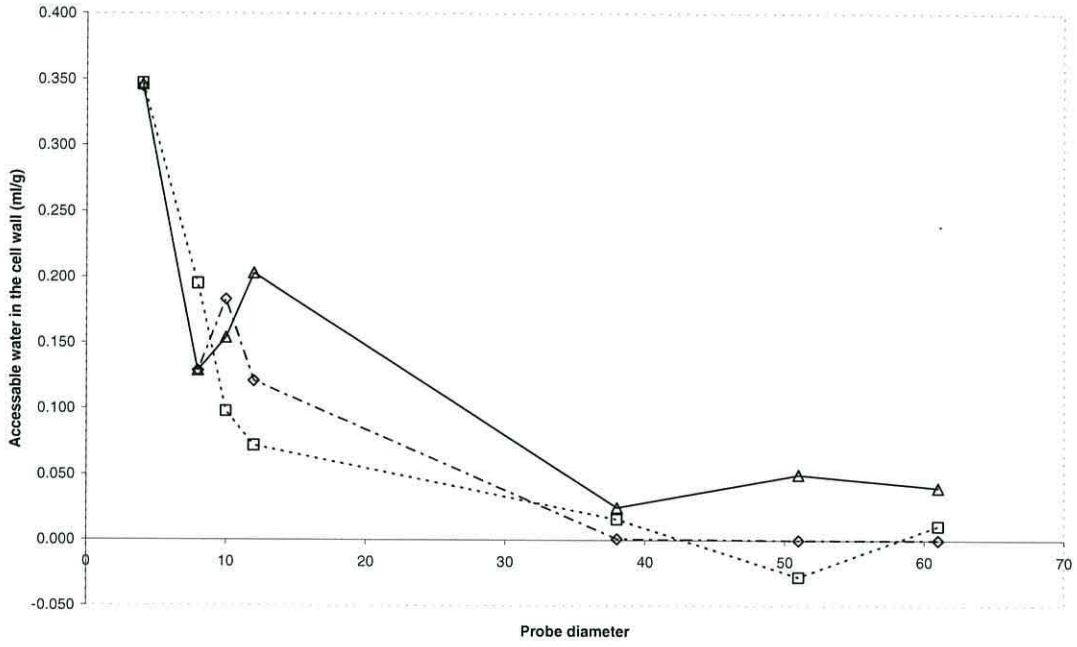


Figure 6.10: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 10.39% melamine formaldehyde resin.

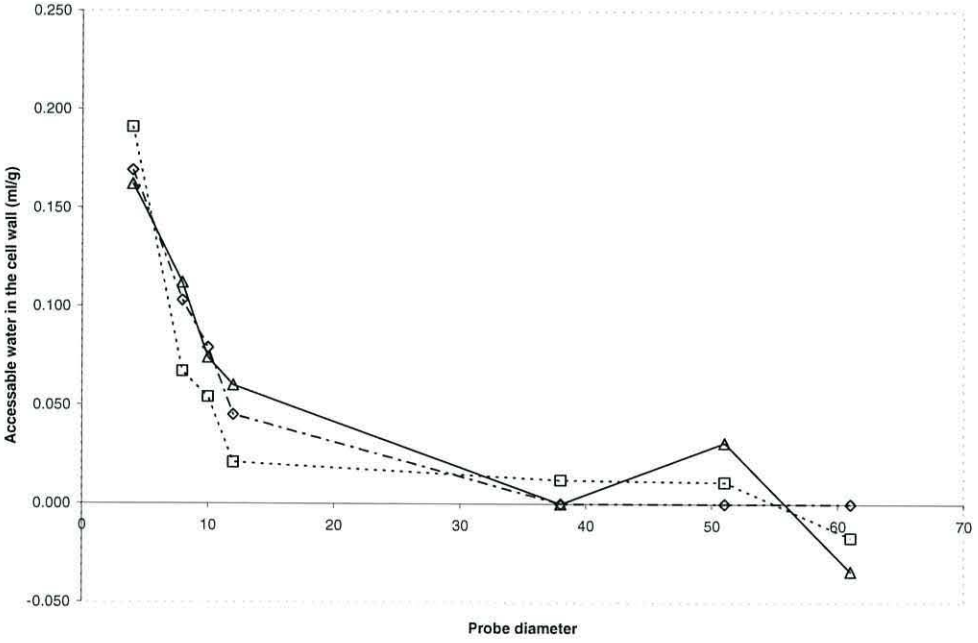


Figure 6.11: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 16.94% melamine formaldehyde resin.

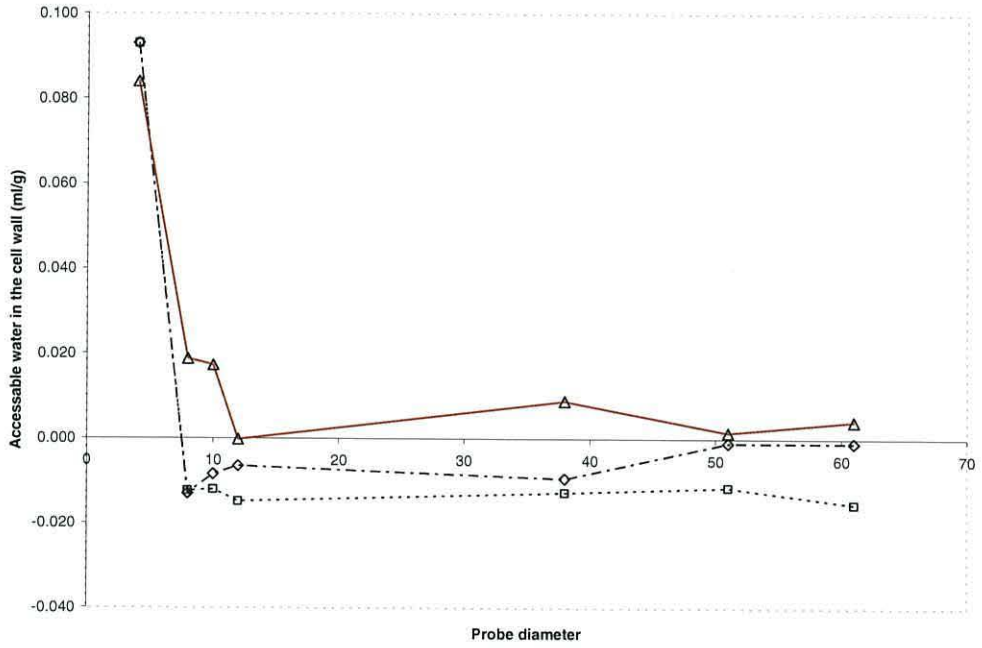


Figure 6.12: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 23.35% melamine formaldehyde resin.

It can be seen with the MF and the MUF modified samples that the accessibility to the cell wall is reduced as the amount of modification is increase. Chapter 5 has shown that there is an enormous change in the volume of the samples when measured by helium pycnometry; this was shown to be due to the lumen being filled with cured resin as opposed to just the cell wall micropores being blocked by the resin (as is the case with anhydride modification). The investigation here has shown that the accessibility of the sample is reduced and therefore the micropores blocked. The blocking of the micropores will be due to a different mechanism than that of the anhydride modification. The anhydride modification enters the cell wall micropores and blocks them internally whereas the resin modified timbers will have there micropores blocked on the surface of the cell wall. This will account for the reduction of cell wall accessibility at relatively low rates of modification.

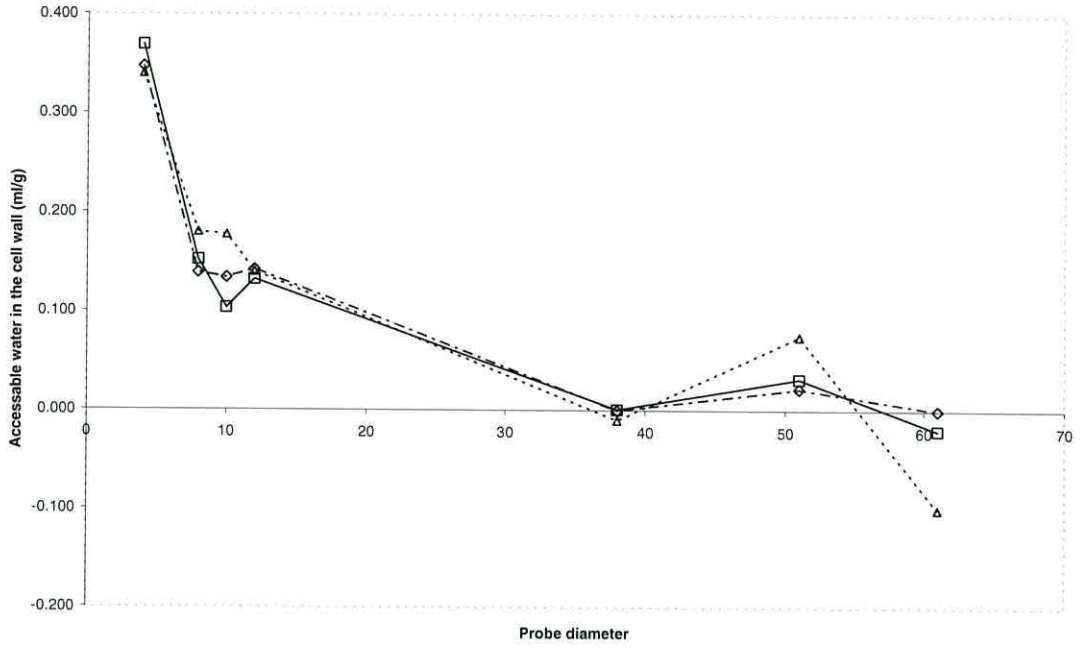


Figure 6.13: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 7.76% melamine urea formaldehyde resin.

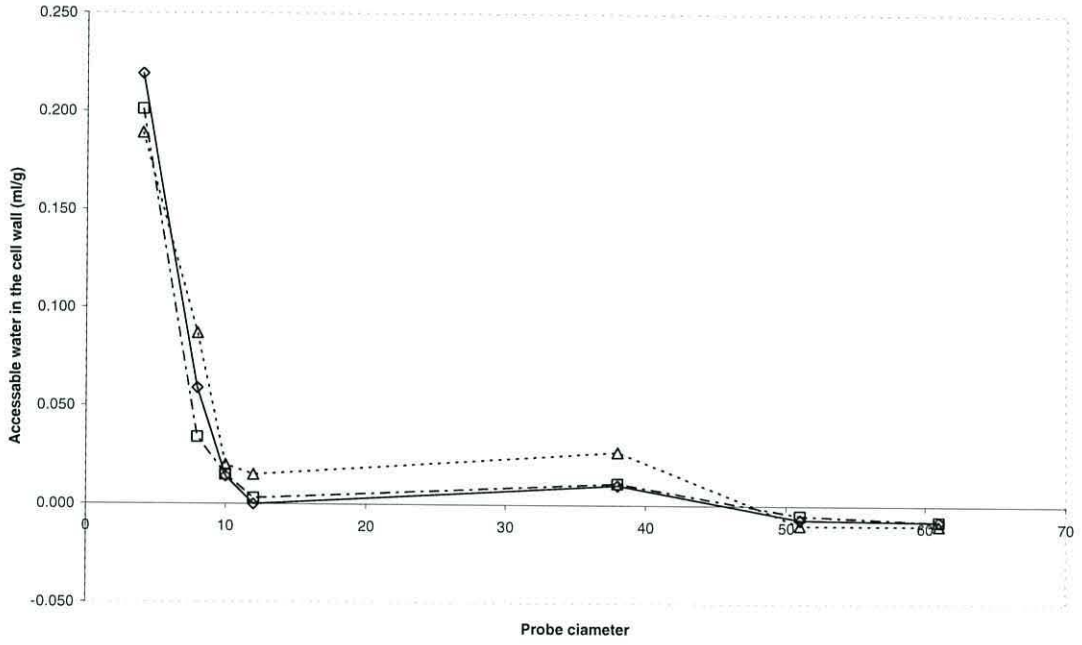


Figure 6.14: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 12.52% melamine urea formaldehyde resin.

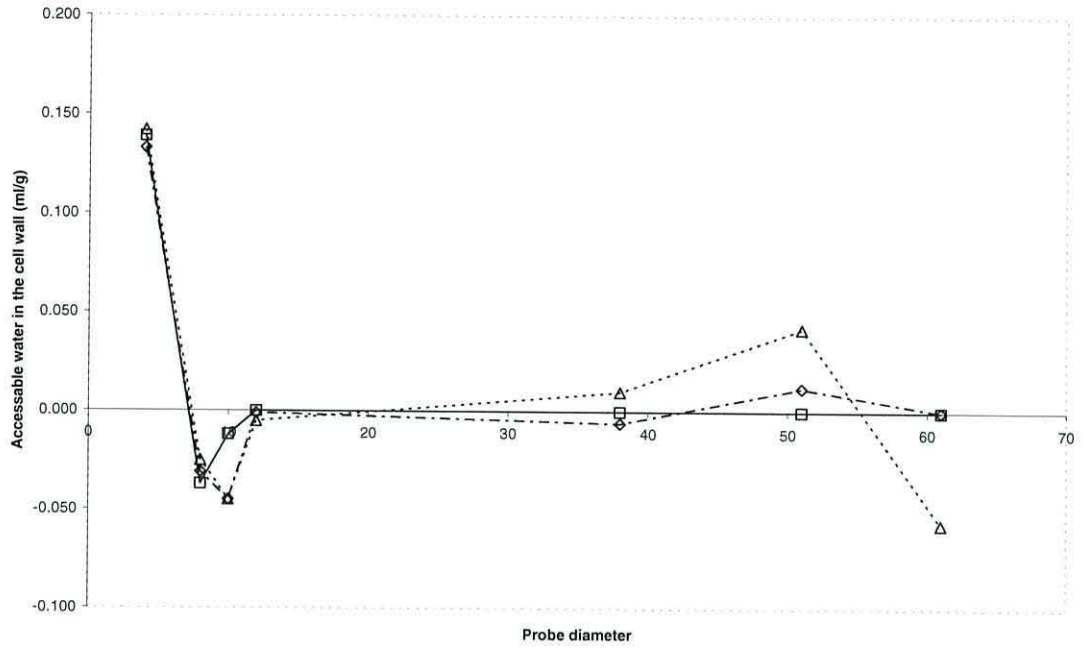


Figure 6.15: Graph to show the volume of accessible cell wall pores to different sized probes in Corsican pine modified to an average WPG of 19.08% melamine urea formaldehyde resin.

With all the studies shown here the cell wall accessibility was never reduced to zero, indicating that the cell wall was still accessible, but to a reduced degree. It can be seen however that the two resins reduced the accessibility of the cell wall considerably at high loadings. This is likely to be due to the resins procuring in the mouths of the cell wall micropores and whilst not blocking the pores entirely, reducing the accessibility to the larger probes considerably.

6.3.2 Fibre saturation point

The fibre saturation point (FSP) can be defined as the moisture content at which the cell walls are filled with bound water but there is no free water within the lumen (Pang & Herritsch, 2005).

Fibre saturation point is usually calculated by the measurement of volumetric change. Because FSP is the point at which all the adsorption sites of the sample are occupied but there is no free water within the cell lumen, FSP can be found

by monitoring the dimensional change in a sample when submerged in deionised water. At the point at which the volume increase ceases, the weight gain is measured and FSP can be calculated. Although this technique can be used to find an approximation of the FSP of a timber it can be troublesome to find the exact point at which all the adsorption sites are used and no free water is present in the samples.

This method can be modified to evaluate the effects of relative humidity upon wood. The swelling of wood is monitored as the relative humidity is increased. When the swelling of timber ceases at a particular relative humidity the mass can be measured and the FSP determined for that particular RH (%). However, when direct FSP measurements are taken at high RH, for example 98%, any slight change in environmental conditions will cause some of the moisture to become free water, therefore making the determination of FSP inaccurate. Therefore for investigations of this nature other methods are needed, such as the pressure plate method.

Solute exclusion can be used to calculate FSP. Solute exclusion allows the full volume of the wood cell to be measured (by the ingress of water, the smallest probe) and also the measurement of the lumen volume, by the use of the large dextrans that do not enter the cell wall micropores and therefore take the place of the free water. A simple subtraction of the cell volume accessible to the dextans from the cell volume accessible to the water will give a figure for the bound water, or the FSP.

Table 6.3 to Table 6.7 shows the FSP, as derived from the solute exclusion experiments.

Treatment	Replicate	WPG	FSP
Control	1	0	34.0%
	2	0	35.0%
	3	0	38.3%

Table 6.3: The FSP of the control Corsican pine

Table 6.3 shows the FSP as calculated by solute exclusion for the control samples of Corsican pine. The average FSP for control samples was calculated to be 36.1%. This measure for FSP is higher than would be expected using other techniques, but agrees with other FSP measures using the solute exclusion technique. Flournoy *et al.* (1991) calculated FSP of Sweetgum (*L. styraciflia*) to be 35% and Stone and Scallon (1967) calculated FSP of Black spruce (*P. mariana*) to be 40%.

Treatment	Replicate	WPG	FSP
Acetic anhydride	1	2.15	40.0%
	2	2.10	42.5%
	3	2.75	41.3%
	1	15.02	21.9%
	2	16.01	22.2%
	3	15.89	20.7%
	1	30.12	8.9%
	2	32.36	9.7%
	3	35.43	9.9%

Table 6.4: The FSP of the acetic anhydride modified Corsican pine

Treatment	Replicate	WPG	FSP
Hexanoic anhydride	1	5.04	43.4%
	2	4.87	43.2%
	3	5.02	41.2%
	1	16.05	27.5%
	2	15.87	27.9%
	3	15.97	28.0%
	1	51.98	19.8%
	2	52.02	17.9%
	3	47.98	18.4%

Table 6.5: The FSP of the hexanoic anhydride modified Corsican pine

Table 6.5 shows the fibre saturation points of hexanoic anhydride modified Corsican pine. It can be seen that the reduction in fibre saturation point is not as great as with acetic anhydride modification (Table 6.4). It can be hypothesised that this is due to cell wall damage occurring at the very high weight percent gains attained in the hexanoic anhydride modification.

It should be noted from Table 6.4 and Table 6.5 that the FSP for both the acetic anhydride modification and the hexanoic anhydride modification increases at low WPGs. This could have been expected for the hexanoic anhydride modified timber as pyridine was used to swell the timber prior to the modification of the wood. However, this was not the case for the acetic anhydride modified wood. It is likely that, within this experiment, cell wall damage has occurred at the low levels of modification.

Figure 6.16 shows the relationship between WPG of modified wood and FSP. It can be seen that the acetic anhydride data falls on a linear fit with an r^2 value of 0.9414, this indicates that the FSP has a direct relationship to WPG. It can be seen that the fit is not as good as for the hexanoic anhydride modified wood (r^2=0.8193). It can been suggested that the change in FSP occurs due to the WPG

and not due to the amount of adduct that enters the cell wall. Figure 6.17 shows both acetic and hexanoic anhydride modifications being graphed together and a linear trend line being added. The erroneous data for the high hexanoic WPG has been removed for the purpose of this graph. The trend line has an r^2 of 0.9267 which is acceptable. This graph confirms that it is likely to be the WPG and not the amount of hydroxyl substitution that governs the change in FSP.

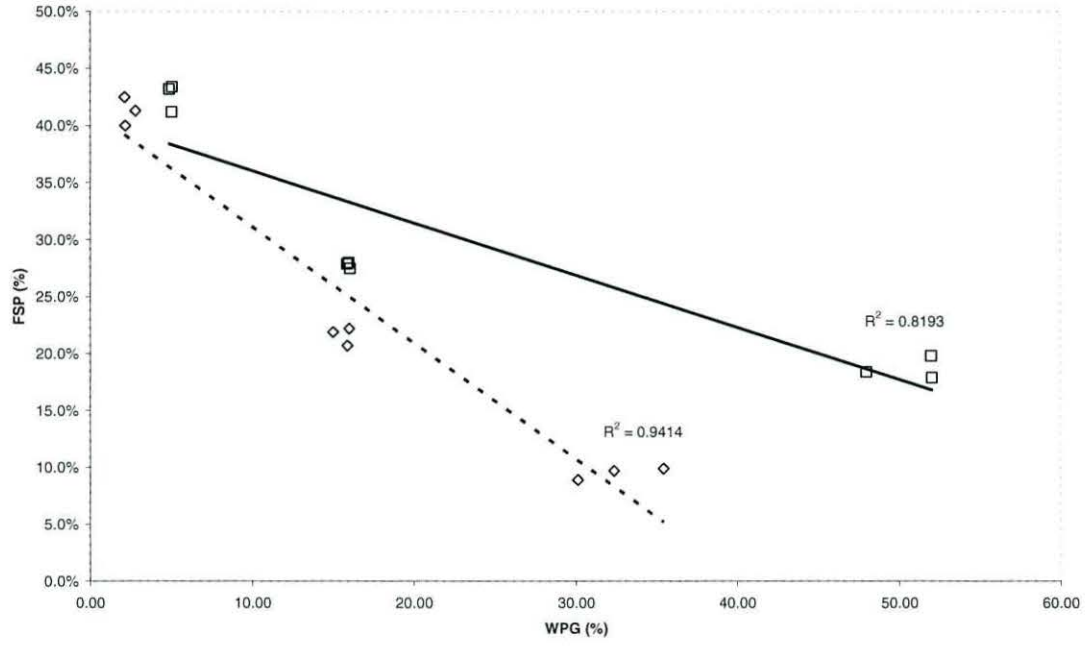


Figure 6.16: Fibre saturation point calculated by solute exclusion for acetic anhydride modified timber (dashed line) and hexanoic anhydride modified timber (solid line)

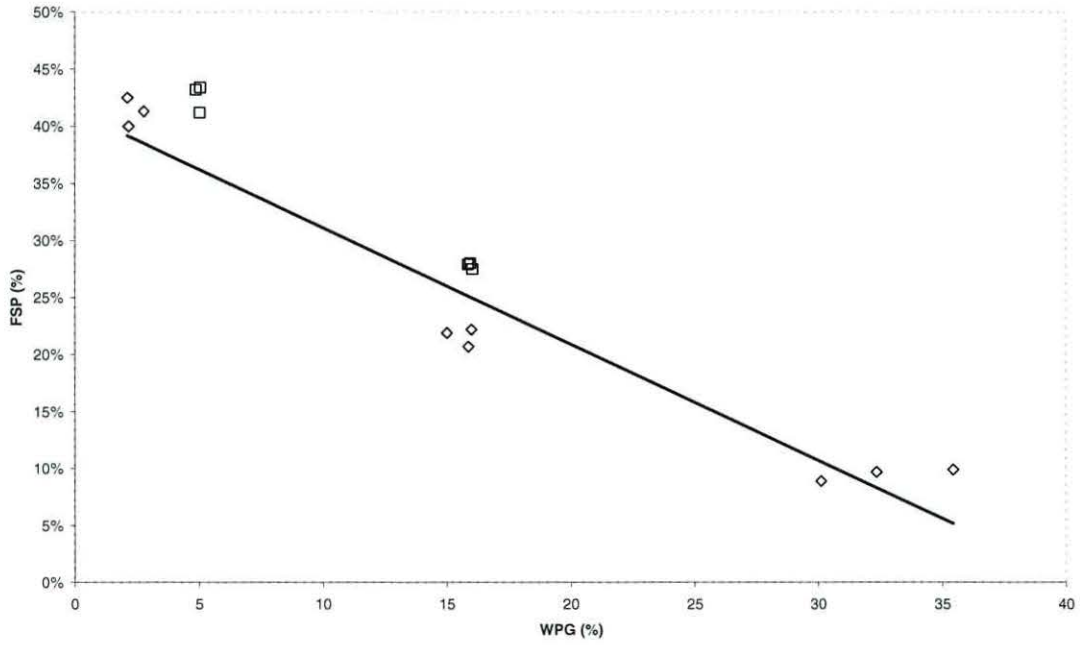


Figure 6.17: FSP vs. WPG for acetic (diamonds) and hexanoic (squares) anhydride modifications

Treatment	Replicate	WPG	FSP
MF	1	9.87	34.5%
	2	10.02	34.7%
	3	11.29	34.6%
	1	16.57	16.9%
	2	17.68	19.1%
	3	16.57	16.2%
	1	23.22	9.3%
	2	22.22	9.3%
	3	24.32	8.4%

Table 6.6: The FSP of melamine formaldehyde modified Corsican pine

Treatment	Replicate	WPG	FSP
MUF	1	7.54	34.7%
	2	7.65	36.9%
	3	7.81	34.0%
	1	12.58	21.9%
	2	12.43	20.1%
	3	12.54	18.9%
	1	19.02	13.3%
	2	19.00	13.9%
	3	19.21	14.2%

Table 6.7: The FSP of melamine urea formaldehyde modified Corsican pine

The reduction in FSP is important in the use of benign methods of wood preservation. It has already been mentioned in Chapter 1 that fungi do not attack wood when the moisture content is below 20%.

It is possible that the reduction of the FSP of the wood affords protection in another way. It is known that fungi decay timber via an enzyme mechanism. However it has been found that at low levels of decay these enzymes do not penetrate the cell wall (Daniel *et al.* 1989) and for this reason low molecular weight diffusible agents (LMWDA) have been suggested as being responsible for initiating decay. It has been shown here that the accessible pore geometry changes with modification and therefore the ability for the probes, or in the case of decay, the low molecular weight diffusible agents to enter the cell wall is impeded.

The FSPs reported here are rather higher than those reported by differing techniques (which range from 24% to 31% for unmodified wood (Siau, 1984)). However it has been well established that solute exclusion gives higher values for FSP. Siau (1984) considered that the reason for the higher values is that

solute exclusion investigations are usually undertaken on pulps or microtomed wood and therefore the cell wall is under less restraint than in solid wood. however, this investigation has been undertaken on wood blocks in which the restraint on the cells would be the same as in full size samples of wood and therefore Siau's theory does not hold true. At the present time it is still unclear why a higher value for FSP is seen with the solute exclusion technique.

6.4 Conclusions of Chapter 6

Solute exclusion has been used here to assess the reduction in cell wall micropore accessibility when timber is modified by two differing types of modification, namely resin modification and anhydride modification. The fibre saturation point was also calculated for both types of modification.

It has been shown that with wood modification, whether anhydride or resin, the cell wall accessibility decreases. However it has been shown that even after WPG levels of over 20% the cell walls are still accessible to some probes. It has also been shown that the modification of resins at relatively low weight percent gains give a higher than expected reduction in cell wall accessibility. This has been attributed to the micropore openings in the cell wall being blocked and not the whole micropore.

The fibre saturation points calculated here using the solute exclusion technique are in agreement with work done by other investigators (Farahini (2003)). It was also shown here that with low amounts of anhydride reactions the amount of accessible water in the cell wall increases. This is due either to the cell wall pores being enlarged by the presence of the anhydride molecules or to an amount of cell wall damage taking place at the beginning of the reaction. It is likely that the increase in FSP is due to damage taking place because of the high amount of heat used in this reaction. It is also possible that cell wall damage will take place when pyridine is used as a swelling agent, the pyridine will solubilise cell wall components especially the lignin.

It can be noted that as the WPG of both the MF modified wood and the acetic anhydride modified wood reaches 30% the FSP drops below 10%, which will be significant in preventing decay of wood by micro organisms. The MUF treated wood is below 15% which also may be low enough to prevent decay.

7 Summary, further work and conclusions

7.1 Summary of work

This thesis has explored the effects of two differing types of novel wood protecting agents, namely resin modification (both with and without a biocide) and anhydride modification.

The resin modification used a novel biocide supplied by Arch timber protection which is deemed to have a low environmental impact, in that after exposure to light and excess water it breaks down into non-harmful components. This however caused issues when in use as a wood preservative. It was undesirable for the preservative to break down prior to the end of service life and therefore the biocide needed to be 'locked' into the cell wall until such a time that it was needed to aid decay resistance. Three commercially available resins were used in the thesis, urea formaldehyde, melamine formaldehyde and melamine urea formaldehyde. It is already widely known that urea formaldehyde is readily hydrolysed; however the hydrolysis acted as a form of accelerated aging and therefore is interesting in this study to give an indication to the effects of longer term exposure on the other two resins.

It has been found that when Corsican pine is modified with only the resins that, with exception to the MUF modified samples decayed with *C. puteana*, all the timbers modified with melamine containing resins show a linear regression that is significantly different to that of the UF containing resins. It has been found that the all the linear regressions for the woods decayed with *C. versicolor* are all significantly different to one another. It can be seen that there are no significant differences between the mass losses of the resin modified beech samples.

It was found that the threshold values for the Corsican pine modified with the three different resins did not exhibit any significant differences (~28%). It was

also found that the three fungi exhibited similar threshold values when used to modify beech (~22%). This was found to be important to understanding the decay prevention mechanisms associated with resin modified woods. The fungi used to decay the timber had varying virulences and therefore if the wood was modified with a chemically active agent it would have been expected that the threshold values for the more virulent fungi would be higher than those for the less virulent. However it can be hypothesised that because all three fungi exhibit significantly similar threshold values that the decay resistance mechanism has to be benign and a mechanical instead of a chemical mechanism.

Modification with the resin coupled with the biocide was undertaken using two systems, a co-delivery system and a sequential delivery system. It was found that at high resin loadings the biocide had no effect on the decay resistance of the wood in an EN113 experiment. This is due to the decay resistance of the resin only treated wood being enough to prevent decay. At lower resin WPGs the biocide had an effect on the decay resistance of the timber. It can be hypothesised that the resin did not sufficiently block the cell wall micropores and therefore the wood was decayed thus releasing the biocide, which consequently prevented further decay.

The decay results for the UF treated Corsican pine were of great interest. It has be seen that there are significant differences between the resin only treated and the resin and biocide treated samples when being decayed with *C. puteana* and *P. chrysosporium* (however not with sequential delivery but this was deemed due to the spread of the data). These significant differences showed the resin and biocide providing greater decay resistance than the resin alone. This was deemed due to the biocide being released by the resin when it was broken down by hydrolysis. It is has also been found that, in the case of the UF and biocide treated Corsican pine decayed with *P. chrysosporium*, the sequential delivery exhibits better decay resistance than the co-delivery. This was attributed to the sequential delivery causing the release of a greater amount of biocide on hydrolysis than the co-delivered system in which the biocide is locked in the resin.

The differences between the decay resistances imparted to beech by the different modifications were not significant for any of the fungi or resin types.

Anhydride modification was also trialed as a novel commercial form of wood preservation. It is known that anhydride modification imparts dimensional stability to timber. It is also known that the anhydride adduct will bond in the cell wall micropores thus blocking them, it was not known where the resin is found whe this work began. Two anhydrides were trialed, acetic anhydride and hexanoic anhydride, these were chosen for their differing molecular weights. Again EN113 type tests were undertaken.

It was found that high amounts of decay resistance were imparted to the wood by very low levels of anhydride modification. A WPG of 5% reduced mass loss due to decay from 75% (highest virulence mass loss) to 47% when Corsican pine is modified with acetic anhydride and then decayed with *C. puteana*. The assessment of the cell wall accessibility shows a possible mechanism for the high amount of decay resistance at low WPG. It was found that although FSP was not effected at low weight percent gains when wood was modified with anhydrides, it showed that the accessibility to 10Å and greater molecules was greatly reduced.

The threshold values were calculated for each of the modified wood for decay with the three fungi. It had been found that the threshold values are independent of both fungi and timber species. The anhydride modified timber was found to have a 15% threshold value while the hexanoic modified timber has a 22% threshold value. The difficultly to compare threshold values was discussed, however it should be noted that the acetic anhydride decay tests were all completed in the same trial as were all of the hexanoic anhydride decay tests, therefore it can be assumed that these tests are comparable. As with the resin modification it was found that the threshold values remained the same regardless of the fungi used to decay the samples. This again suggests that the decay resistance mechanism is a benign physical one.

Anhydride modification offers two possible routes for decay resistance; the first is cell wall bulking and micropore blocking. Cell wall bulking will prevent decay by blocking the micropores to the ingress of water and decay metabolites into the cell wall. The second route for decay resistance is the substitution of the hydroxyl groups with the acyl groups which will prevent the enzymatic attack of the cell wall. It has been suggested that this prevention is due to the enzymes not being able to recognise the substrate. It was found that the decay resistance afforded to timber by the modification by anhydride is due to the cell wall bulking and not by hydroxyl substitution. In every case shown in this experiment there is no significant difference between the mass losses of acetic and hexanoic anhydride treated timbers when graphed against WPG whilst there is when graphed against hydroxyl substitution. If hydroxyl substitution played a role in the decay prevention the WPG of the hexanoic anhydride treated samples would have to be greater than that of acetylated wood, as hexanoic anhydride has a higher molecular weight than acetic anhydride.

It was found that the difference in the two threshold values for acetic and hexanoic anhydride modified timbers do not correspond with an agreement in the amount of hydroxyl substitution that takes place.

Helium pycnometry and external dimension measurements were used to measure dimensional changes when modified with three resins and two anhydrides. The cell wall density of the unmodified wood was found to be 1.4200 (+/-0.0060) g cm^{-3} when measured by helium pycnometry.

It has been found that the measurement of the external dimensions of wood specimens does not give true information regarding changes in cell wall volume.

It can be seen that the relationship between the WPG and the volume change (calculated from external dimensions) is curvilinear with Corsican pine modified with acetic anhydride, which is in agreement with the work of Hill and Jones

(1998). The volume changes determined via helium pycnometry can be best described by a linear fit. It should also be noted that the lines of best fit cross, indicating that the external measurement over-estimates the volume changes at low WPG's and under-estimates them at high WPG's. The under and over estimations can be attributed to the expansion of the cell wall, at high WPG's, in to the lumen.

When wood is modified with resin the volume change profile is very different to that of the anhydride modified wood. With all the resins that the percentage volume change as measured by helium pycnometry are very high. Percentage volume changes of 300 - 400% have been calculated. It can be seen that the increase in volume of the resin modified wood approaches the theoretical volume of a solid cylinder of the same dimensions as the sample. Cell wall bulking does take place and this can be deduced from the swelling that has been calculated from the external measurements, however the volume change measured by helium pycnometry is significantly larger and therefore it can be deduced that there may be polymerisation of the resin occurring as the resin enters the cell wall resulting in the blocking of the micropores preventing further ingress of resin.

The mechanism for decay resistance via resin impregnation is not that of chemically altering the wood but of reducing the moisture content of the wood to a level below that required by the fungi. It has also been seen that fungi do not attack wood below 20% moisture content. As the resin penetrates the wood and blocks the cell wall micro pore openings and reduces the lumen area, it also reduces the woods ability to uptake water, thus when sufficient modification has taken place the moisture content of the wood can not reach 20% and thus fungal decay will not take place.

Solute exclusion techniques were used to assess the effect that the two forms of modification had on the accessibility of water into the modified wood.

It was found that with wood modification, whether anhydride or resin, the cell wall accessibility decreases. However it has been shown that even after WPG levels of over 20% the cell walls are still accessible to some probes. It has also been found that the modification of resins at relatively low weight percent gains give a higher than expected reduction in cell wall accessibility. This has been attributed to the micro pore openings in the cell wall being blocked and not the whole micro pore.

It can be noted that as the WPG of both the MF modified wood and the acetic anhydride modified wood reaches 30% the FSP drops below 10%, which will be significant in preventing decay of wood by micro organisms.

7.2 Further work

This thesis has investigated the use of novel forms of wood treatment as aids to the prevention of wood degradation due to biological activity. However there is further work that needs to be undertaken to improve on the conclusions drawn in this study.

7.2.1 Resin modified timber.

Further studies should be undertaken to assess accurately if the resin is penetrating the cell walls at all or whether the resin is in fact blocking the entrances to the cell wall micropores. This should be undertaken by a series of environmental scanning electron microscope (ESEM) pictures. ESEM unlike conventional scanning electron microscopy does not need the sample to be impregnated with resin and coated with gold or carbon. This will then allow sections to be taken of the treated samples and an assessment of the resin penetration into the cell walls to be undertaken.

The decay resistance of the modified timbers throughout this thesis was tested using the EN113 pure culture tests. These however last for only 16 weeks and

although they are accelerated tests they are not long term and thus was found that at high resin loadings the presence of the biocide had no effect on the decay resistance of the wood. However it can be hypothesised that the biocide will still have an effect on the decay resistance of the modified wood beyond the timescale of the EN113 tests. Therefore longer term decay test should be performed.

Further experimentation should take place on larger sized samples of timber. It is known that the resin treatment creates an envelope of treatment. the modification of the wood with resin should take place on larger samples and thus the problems of penetration and 100 % coverage of the big samples can be assessed. The modification of larger samples should also be coupled with outdoor exposure tests. These will subject the samples to both adverse environmental conditions and to fungal and bacteria attack at the same time, thus taking into account any interactions between different fungi and bacteria and the adverse effects this will have on the modified wood.

Studies should be undertaken to trial isocyanate based resins. These were initially dismissed from this study due to their poor handling qualities and the health and safety issues. It has been found in this study that the decay resistance of the modified wood is due to the reduction in the FSP and reduction of the micropore porosity. Isocyanates form polyurethanes when they cure and therefore form a very moisture resistant coating, which would be highly suited for this application. However, the curing of isocyanates does require a higher moisture content to the wood than with conventional resins and therefore this may be detrimental to the stability of the biocide.

7.2.2 Anhydride modification.

The modification of wood with acetic and hexanoic anhydride has been extensively studied both here and elsewhere. However all the studies undertaken so far have had a minimum modification time of 15 minutes, giving a weight percent gain of around 5%. It has been noted here that a weigh percent gain of

5% increases decay resistance by approximately 20%. It has been noted earlier that this is a significant drop in mass loss and that it is unclear to why this is. Wood should be modified with low amounts of anhydrides (below 5%) these should be then subjected to the pure culture decay tests to establish what is happening in the early stages of modification.

It was found that at low weight percent gains anhydride modification gave surprisingly high amounts of decay protection. It has been hypothesised that this could be due to the modification of certain components of the cell wall in preference to others, for example the lignin could be modified prior to the cellulose. An experiment should be undertaken to quantify whether preferential modification does take place.

7.3 Conclusions

The aim of the work in this thesis was to investigate a novel wood preservative with a low environmental impact and the following conclusions can be drawn:

The durability of wood can be increased by the use of benign wood modifications, whether they are resin modification or anhydride modification.

The two modifications have similar mechanisms, however these are not identical.

The mechanism for decay prevention found for the anhydrides is as follows; the anhydrides enter the cell wall micropores and react with the cell wall. This blocks the micropores reducing the wood FSP. The reduction in FSP and the reduction in the size of molecule able to enter the micropores prevent the decay of the wood.

The mechanism for decay prevention by resin modification is similar, however it is a gross protection filling the lumen with resin this again stops the ingress of moisture and lowers the FSP of the wood, therefore the decay via fungi is prevented.

The type of resin used has an effect on the decay resistance of the wood. UF resin suffers from hydrolysis in the presence of moisture and therefore is not suitable for an end product. Melamine urea does not suffer from the hydrolysis and therefore is suitable.

The addition of the biocide to the resin prevents decay at lower WPG than just the resin alone. This is due to the biocide being 'released' from resin when needed and not before.

The addition of the resin seems to prevent the break down of the biocide. This is achieved by the reduction of the ingress of moisture into the wood.

Appendices

Appendix A – Calibration Curves for the Refractometry Study.

Figure 8.1 to Figure 8.6 shows the calibration curves used in this work for each of the sugars.

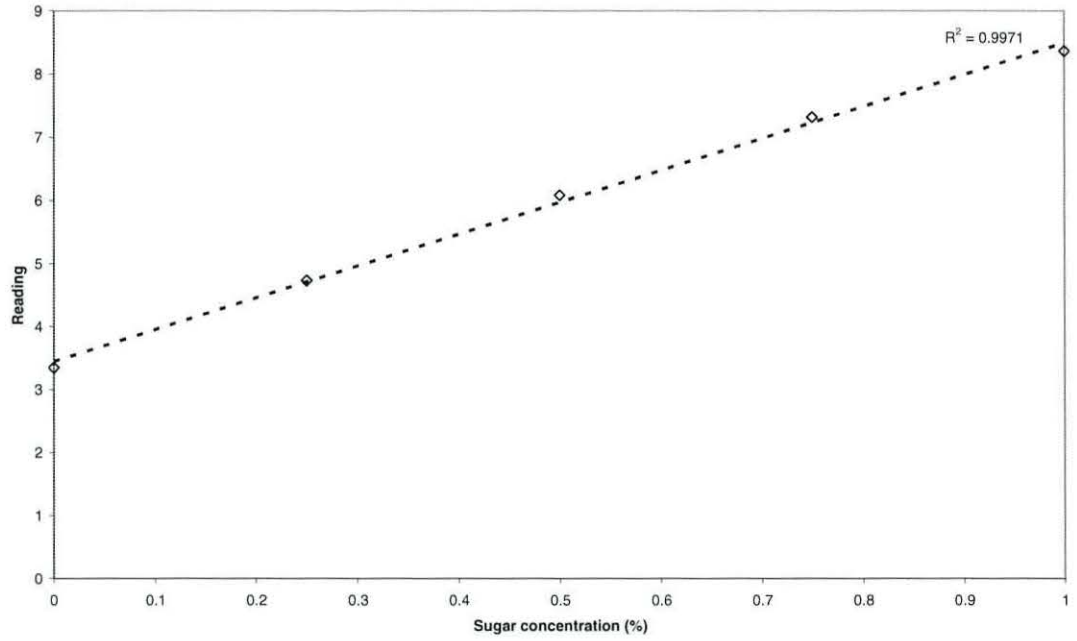


Figure 8.1: Calibration graph for the refractometry of Glucose

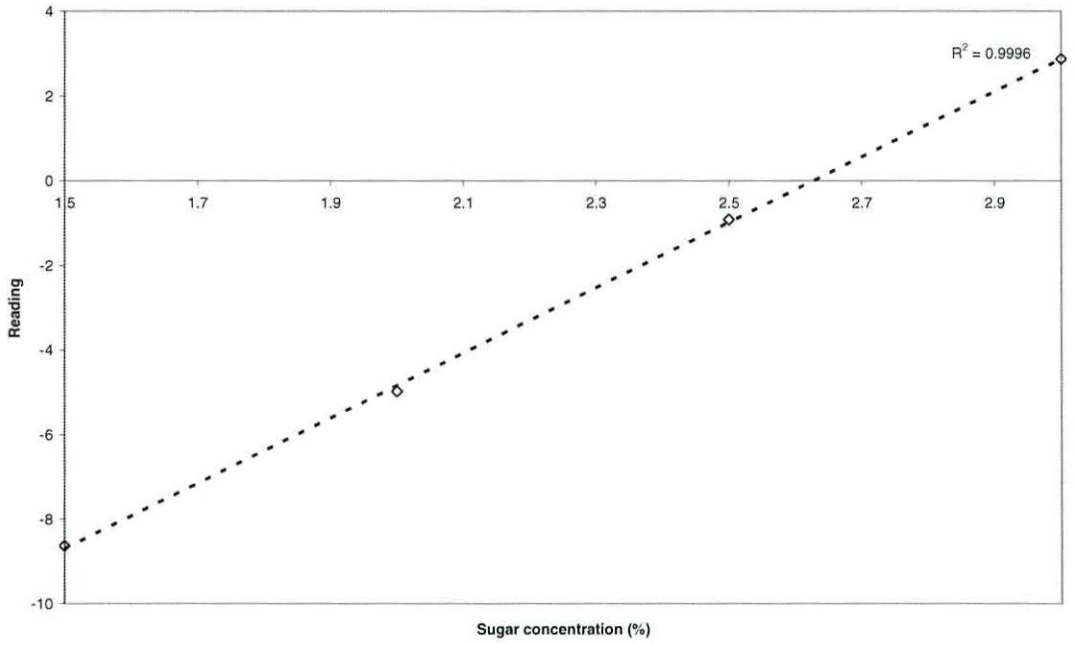


Figure 8.2: Calibration graph for the refractometry of Maltose

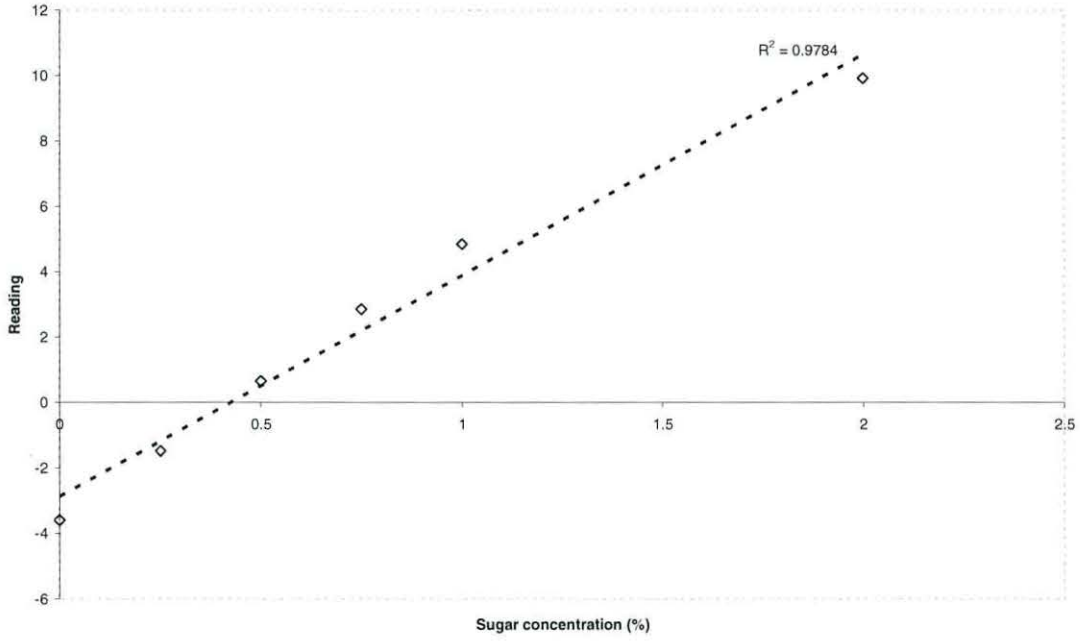


Figure 8.3: Calibration graph for the refractometry of raffinose

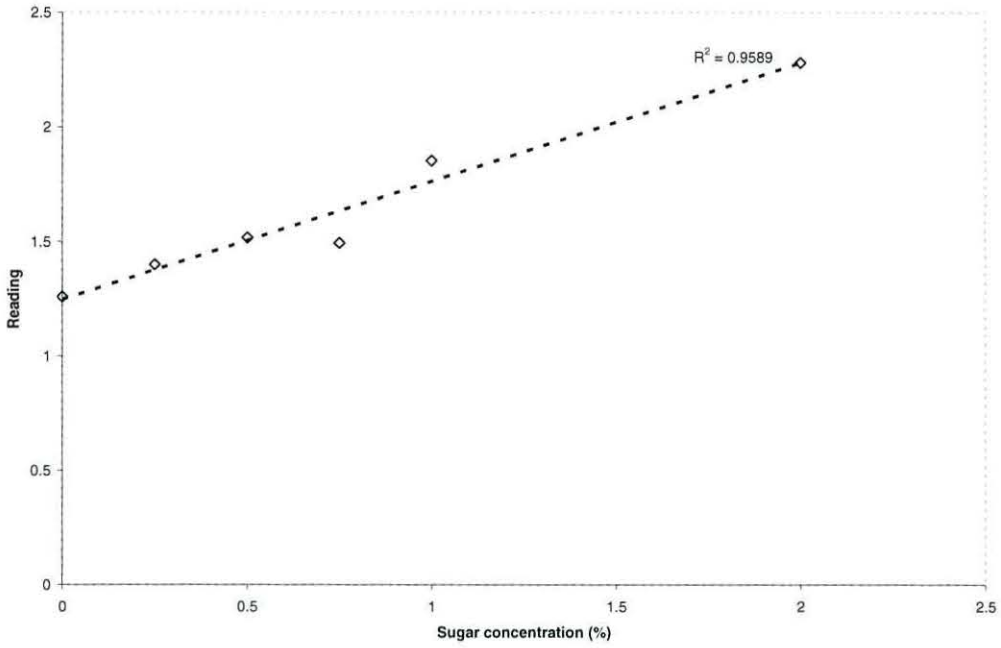


Figure 8.4: Calibration graph for the refractometry of the Fluka AG

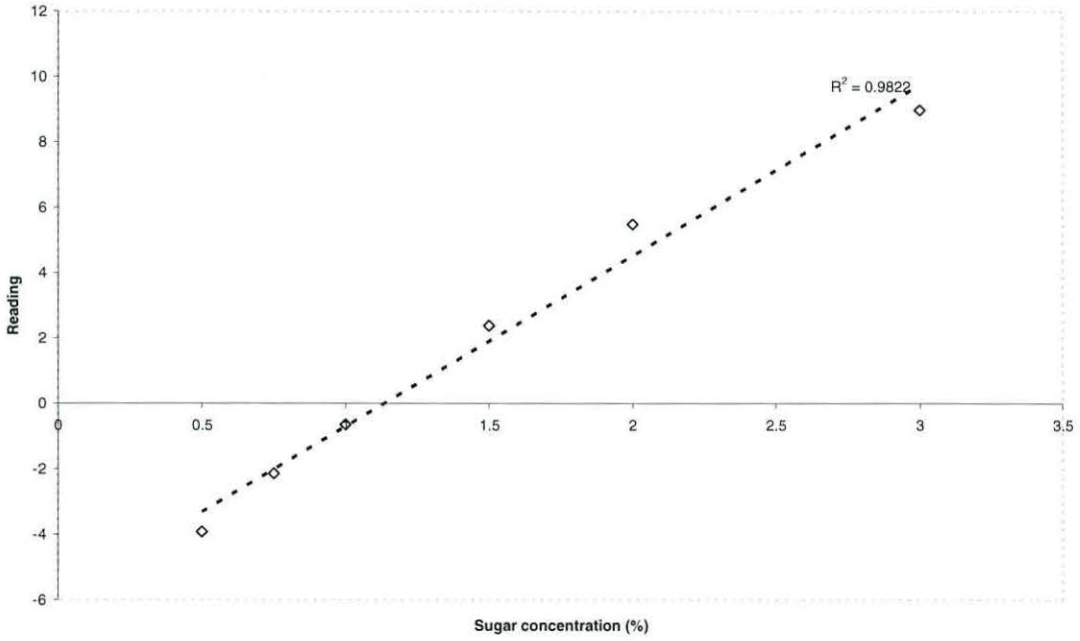


Figure 8.5: Calibration graph for the refractometry of the Pharmacia T10

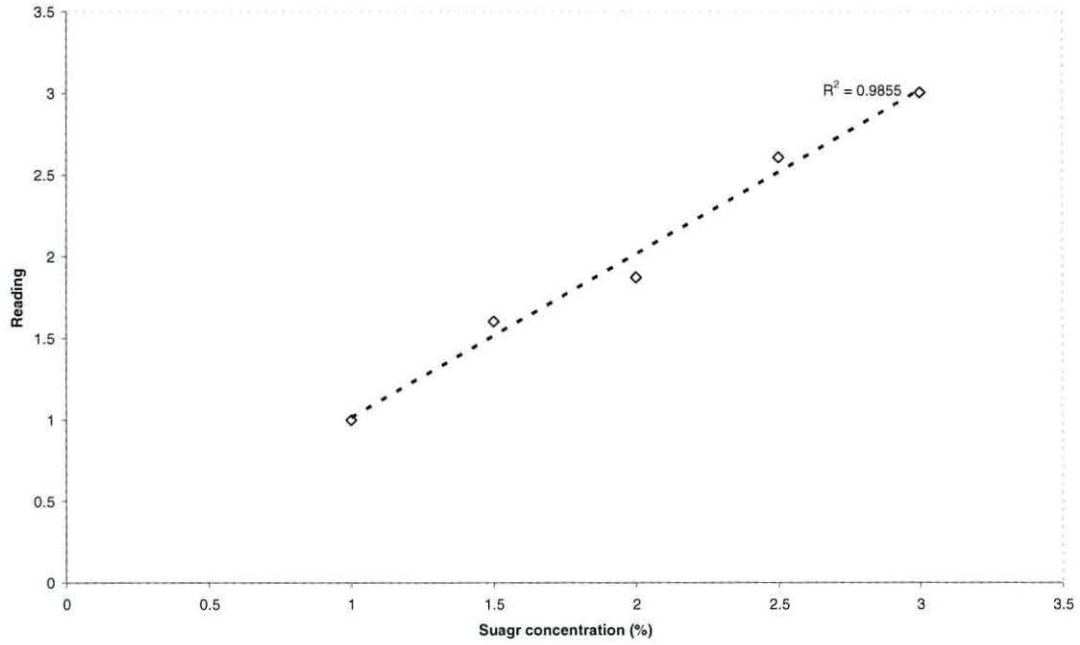


Figure 8.6: Calibration graph for the refractometry of the Polysciences 15-20K

Table 8.1 shows the equations for the linear fits for each of the sugars. These equations were used to calculate the dilution of the sugar solution.

Solute	Equation	R^2 value
Glucose	Y=5.0488x+3.4458	0.9971
Maltose	Y=7.7134x-20.263	0.9996
Raffinose	Y=6.7534x-2.8652	0.9784
Fluka AG	Y=0.5161x+1.2477	0.9589
Pharmacia A10	Y=5.2236x+5.9259	0.9822
Polysciences 15-20K	Y=1.0014x+0.0148	0.9855

Table 8.1: Equations for linear fits of the refractometry calibration curves

It should be noted that the actual reading has no meaning beyond the particular trial. The refractometer is very sensitive to temperature, air pressure, user quirks and other external factors and therefore the calibration curves have to be repeated every time the experiment is repeated.

Appendix B – Raw Data for the Chapter 6

Treatment	Replicate	WPG	Accessible water in the wood cell wall (ml/g)						
			4 Å	8 Å	10 Å	12 Å	38 Å	51 Å	61 Å
Control	1	0	1.565	1.508	1.509	1.343	1.319	1.565	1.508
	2	0	1.537	1.473	1.445	1.281	1.263	1.537	1.473
	3	0	1.457	1.431	1.416	1.261	1.218	1.457	1.431
Acetic anhydride	1	2.15	1.436	1.371	1.379	1.292	1.217	1.436	1.371
	2	2.10	1.436	1.392	1.324	1.269	1.234	1.436	1.392
	3	2.75	1.414	1.397	1.370	1.254	1.250	1.414	1.397
	1	15.02	1.331	1.277	1.230	1.219	1.209	1.331	1.277
	2	16.01	1.412	1.322	1.307	1.284	1.290	1.412	1.322
	3	15.89	1.340	1.259	1.258	1.214	1.248	1.340	1.259
	1	30.12	1.242	1.232	1.242	1.233	1.241	1.242	1.232
	2	32.36	1.260	1.253	1.256	1.247	1.229	1.260	1.253
	3	35.43	1.230	1.239	1.225	1.220	1.254	1.230	1.239
Hexanoic anhydirde	1	5.04	1.553	1.475	1.438	1.337	1.319	1.553	1.475
	2	4.87	1.474	1.424	1.367	1.305	1.263	1.474	1.424
	3	5.02	1.436	1.333	1.385	1.212	1.218	1.436	1.333
	1	16.05	1.340	1.329	1.317	1.277	1.229	1.340	1.329
	2	15.87	1.521	1.396	1.326	1.236	1.243	1.521	1.396
	3	15.97	1.301	1.336	1.328	1.185	1.232	1.301	1.336
	1	51.98	1.295	1.264	1.246	1.209	1.213	1.295	1.264
	2	52.02	1.431	1.312	1.302	1.288	1.279	1.431	1.312
	3	47.98	1.335	1.333	1.232	1.214	1.240	1.335	1.333
MF	1	9.87	1.359	1.413	1.351	1.231	1.230	1.359	1.413
	2	10.02	1.436	1.339	1.313	1.257	1.213	1.436	1.339
	3	11.29	1.349	1.374	1.423	1.245	1.270	1.349	1.374
	1	16.57	1.422	1.398	1.364	1.319	1.319	1.422	1.398
	2	17.68	1.330	1.317	1.284	1.275	1.274	1.330	1.317
	3	16.57	1.330	1.292	1.278	1.218	1.249	1.330	1.292
	1	23.22	1.204	1.197	1.196	1.133	1.216	1.204	1.197
	2	22.22	1.212	1.200	1.149	1.177	1.196	1.212	1.200
	3	24.32	1.207	1.277	1.255	1.280	1.272	1.207	1.277
MUF	1	7.54	1.348	1.343	1.351	1.209	1.231	1.348	1.343
	2	7.65	1.430	1.381	1.410	1.279	1.310	1.430	1.381
	3	7.81	1.398	1.396	1.358	1.208	1.293	1.398	1.396
	1	12.58	1.289	1.244	1.230	1.240	1.223	1.289	1.244
	2	12.43	1.275	1.256	1.244	1.252	1.236	1.275	1.256
	3	12.54	1.307	1.240	1.235	1.247	1.210	1.307	1.240
	1	19.02	1.288	1.274	1.318	1.313	1.331	1.288	1.274
	2	19.00	1.226	1.251	1.263	1.263	1.263	1.226	1.251
	3	19.21	1.193	1.173	1.213	1.228	1.260	1.193	1.173

Table 9.1: Average pore volumes (over 7 samples) (including lumen) of chemically modified and resin modified wood accessible to probes of various sizes

Treatment	Replicate	WPG	Accessible water in the wood cell wall (ml/g)						
			4 Å	8 Å	10 Å	12 Å	38 Å	51 Å	61 Å
Control	1	0	0.345	0.246	0.189	0.190	0.024	0.000	-0.025
	2	0	0.355	0.274	0.210	0.182	0.018	0.000	0.000
	3	0	0.383	0.239	0.213	0.198	0.043	0.000	0.024
Acetic anhydride	1	2.15	0.423	0.219	0.154	0.162	0.075	0.000	-0.057
	2	2.10	0.425	0.212	0.168	0.100	0.045	0.010	-0.022
	3	2.75	0.424	0.187	0.170	0.143	0.027	0.023	-0.098
	1	15.02	0.219	0.122	0.068	0.021	0.010	0.000	-0.017
	2	16.01	0.222	0.134	0.044	0.029	0.006	0.012	-0.013
	3	15.89	0.207	0.122	0.041	0.040	-0.004	0.030	-0.020
	1	30.12	0.089	0.012	0.002	0.012	0.003	0.011	-0.017
	2	32.36	0.097	0.019	0.012	0.015	0.006	-0.012	-0.017
	3	35.43	0.099	0.010	0.019	0.005	0.000	0.034	-0.017
Hexanoic anhydirde	1	5.04	0.434	0.234	0.156	0.119	0.018	0.000	0.000
	2	4.87	0.432	0.211	0.161	0.104	0.042	0.000	-0.012
	3	5.02	0.412	0.218	0.115	0.167	-0.006	0.000	-0.039
	1	16.05	0.275	0.123	0.112	0.100	0.060	0.012	-0.054
	2	15.87	0.279	0.297	0.172	0.102	0.012	0.019	-0.012
	3	15.97	0.280	0.074	0.109	0.101	-0.042	0.005	0.000
	1	51.98	0.198	0.086	0.055	0.037	0.000	0.004	-0.020
	2	52.02	0.179	0.153	0.034	0.024	0.010	0.001	-0.001
	3	47.98	0.184	0.117	0.115	0.014	-0.004	0.022	-0.012
MF	1	9.87	0.345	0.129	0.183	0.121	0.001	0.000	0.000
	2	10.02	0.347	0.195	0.098	0.072	0.016	-0.028	0.011
	3	11.29	0.346	0.129	0.154	0.203	0.025	0.050	0.040
	1	16.57	0.169	0.103	0.079	0.045	0.000	0.000	0.000
	2	17.68	0.191	0.067	0.054	0.021	0.012	0.011	-0.017
	3	16.57	0.162	0.112	0.074	0.060	0.000	0.031	-0.034
	1	23.22	0.093	-0.013	-0.020	-0.021	-0.084	-0.001	-0.001
	2	22.22	0.093	-0.012	-0.024	-0.075	-0.047	-0.028	-0.082
	3	24.32	0.084	-0.020	0.050	0.028	0.053	0.045	0.027
MUF	1	7.54	0.347	0.139	0.134	0.142	0.000	0.022	0.000
	2	7.65	0.369	0.152	0.103	0.132	0.001	0.032	-0.020
	3	7.81	0.340	0.180	0.177	0.140	-0.010	0.075	-0.100
	1	12.58	0.219	0.059	0.014	0.000	0.010	-0.007	-0.008
	2	12.43	0.201	0.034	0.015	0.003	0.011	-0.005	-0.008
	3	12.54	0.189	0.087	0.020	0.015	0.027	-0.010	-0.010
	1	19.02	0.133	-0.031	-0.045	-0.001	-0.006	0.012	0.000
	2	19.00	0.139	-0.037	-0.012	0.000	0.000	0.000	0.000
	3	19.21	0.142	-0.025	-0.045	-0.005	0.010	0.042	-0.057

Table 9.2: Average cell wall pore volumes of chemically modified and resin modified wood accessible to probes of various sizes

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