Acetylated Wood
The Science Behind the Material

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Background

Timber can be viewed as a classic renewable material. Trees absorb carbon dioxide and utilise water plus sunlight to produce a material that can be used in construction, to produce paper, or to provide chemical feedstocks; with the production of oxygen as a by-product. Furthermore, at the end of a product lifecycle, the material constituents can be combusted, or composted to return the chemical constituents to the 'grand cycles'. In essence, timber use represents a classic example of a cyclic materials flow, mimicking the flows of materials through natural cycles. Provided we manage our forests well and do not harvest beyond the capacity of the planet to provide timber, we have at our disposal an inexhaustible resource available in perpetuity.

The process of tree growth utilises atmospheric carbon in the production of wood biomass. Furthermore, this sequestered carbon can continue to be held in products that are manufactured from wood. Although much research has been done in investigating forests as actual or potential carbon sinks, there has been rather less work looking at the implications of the use of wood products as a medium-term carbon store.

It is important to emphasise that forestry is a long-term industry. Decisions taken now in the way that we manage our forests will have an effect way into the future, perhaps as much as a century later.

Increasing quantities of timber are being sourced from managed plantation forests, which are now being established at a rate of over 3 million ha per year. These plantation forests have usually been developed using fast growth species, where yield rather than timber quality is often the primary consideration for species choice, and management methods. Active management of plantation forests utilises thinning and pruning to maximise yield. Plantation forests in the temperate zones invariably utilise softwood species chosen for ease of conversion and management.

Fast grown softwood from plantation sources is generally characterised by a high proportion of juvenile wood and often poorly developed heartwood. A fast rate of growth results in wide growth rings, producing low-density timber exhibiting inferior mechanical properties, when compared with timber sourced from virgin forests. There is also evidence to show that the durability of plantation grown timber is often inferior to that sourced from natural growth forests. All of the above factors result in an inferior product compared with the material obtained from virgin forests, requiring some means of upgrading the timber to achieve comparable properties. The harvested timber from semi-natural forests may often be of higher quality, but reduced rates of production place more severe constraints upon the quantity of material that can be extracted in a given time period.

In the past, undesirable properties, such as susceptibility to biodegradation were overcome by the use of durable hardwood (in the main) species, particularly tropical hardwoods. This has contributed to tropical deforestation, although factors other than harvesting for industrial timber have had a greater effect. Nonetheless, extraction of target trees from virgin forest leads to substantial environmental impact and there is a strong tendency for settlement to follow logging roads, with practices such as slash and burn of the forest occurring. This has led to substantial public disquiet regarding tropical forest operations, and this poor public perception has gradually encompassed virtually all forestry operations. Furthermore, the quality and quantity of tropical wood has declined as the resource becomes scarcer and more expensive to extract.

As the availability of naturally durable species has declined, the industry has turned to softwoods and increasingly to softwoods from managed forests or plantations. In order to achieve acceptable longevity under service conditions, it has been necessary to use preservatives to prevent biological attack. Such preservatives have tended to rely upon broad-spectrum biocidal activity and have become very common, particularly for exterior applications.

Due to environmental concerns regarding the use of certain classes of preservatives (such as copper chromium arsenic), there has recently been a renewed interest in wood modification. Wood modification represents a process that is used to improve the material properties of wood, but produces a material that be disposed of at the end of a product lifecycle without presenting an environmental hazard any greater than that associated with the disposal of unmodified wood. Although wood modification has been the subject of a great deal of study at an academic level for over 50 years, it is only comparatively recently that there has been significant commercial development. Various types of wood modification are possible (e.g. thermal, resin impregnation), but this article is concerned with chemical modification of wood and specifically acetylation.

Wood modification can have other advantages besides improving the biological durability of the material. One of the most important allied benefits is a large improvement in dimensional stability (especially beneficial for uses in exterior situations). For some modifications, weathering performance is also markedly improved, particularly when the modified wood is coated with an opaque or clear coating. The whole area of wood modification has been covered in depth in a recent text book (Hill 2006).

Chemical Modification of Wood

The chemical modification of wood is the reaction of a chemical reagent with the wood structural polymeric constituents resulting in the formation of a covalent bond between the reagent and the wood substrate. In the case of acetylation, the product obtained contains acetyl groups bonded to hydroxyl (OH) sites in the wood cell wall. Although reaction can take place using ketene, acetic acid, or acetyl chloride, the most useful process is acetylation of wood due to reaction with acetic anhydride (Figure 1).
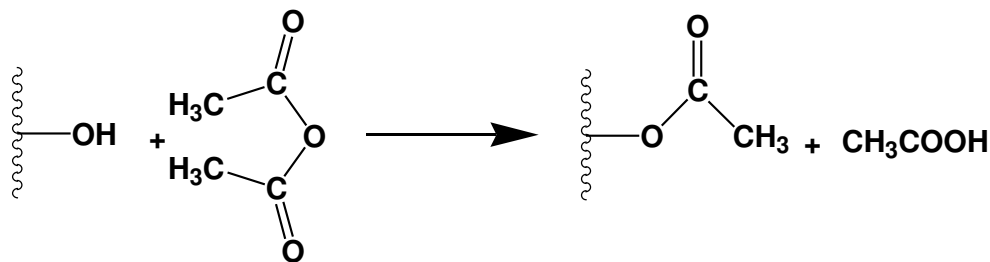
Figure 1: Reaction scheme for acetylation with acetic anhydride

In this reaction, acetic acid is produced as a by-product and it is important to remove this as well as unreacted acetic anhydride at the end of the reaction. Reaction with wood can take place with the anhydride in the vapour or liquid phase, the latter being used in the Accoya™ production plant at Arnhem in The Netherlands. With reactions of this type, it has been shown that the rate of reaction is diffusion dependent, with rapid reaction of the anhydride molecule with the cell wall polymer OH site once it has arrived there. Reaction rate can be increased by raising the temperature (Figure 2) and by using catalysts, although the presence of catalysts in the reaction medium is not used in commercial reactions. The extent of reaction of acetic anhydride with wood is invariably reported as acetyl weight percentage gain, abbreviated as WPG, calculated as shown in Equation 1, below.

$$WPG\ (\%) = [(W_{mod} - W_{unmod}) / W_{unmod}] \times 100 \qquad (1)$$

Where: W_{mod} is the oven dry weight of the modified wood and W_{unmod} is the oven dry weight of the wood prior to reaction.
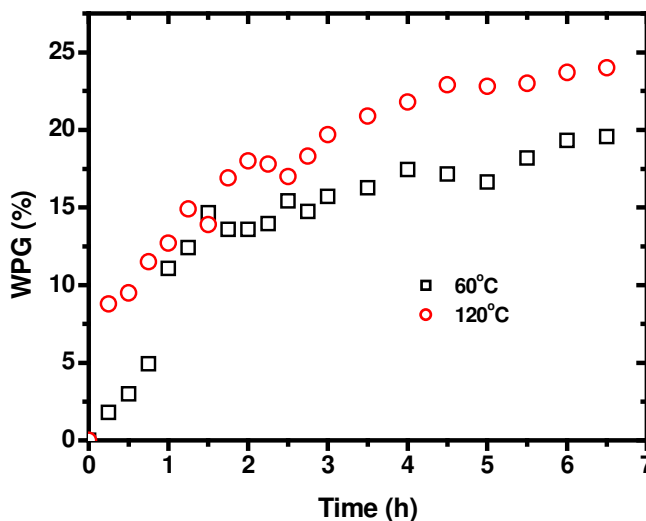
Figure 2: The effect of temperature upon the rate of reaction of acetic anhydride with Scots pine (reaction catalysed using pyridine)

In order to ensure rapid and even reaction throughout the wood it is necessary that the wood is in a partially swollen state, which can be achieved by using moist wood, or by having a percentage of acetic acid in the reaction medium (up to about 30 % by volume) (Rowell et al. 1990). The problem with using wood containing moisture, is that the water molecules will react with acetic anhydride to produce acetic acid,

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resulting in loss of reagent. However, drying wood to zero moisture content is not feasible in an industrial context and would almost certainly lead to irreversible damage to the wood in any case, so a compromise moisture content must be used (Beckers and Militz 1994). The reaction rate is also influenced by the wood itself, and in particular its permeability and density. Although there is often little difference in reactivity between heartwood and sapwood when small laboratory scale test pieces are modified (Figure 3), this is not the case for large sizes used for industrial production. For this reason, only sapwood is currently used for commercial production.
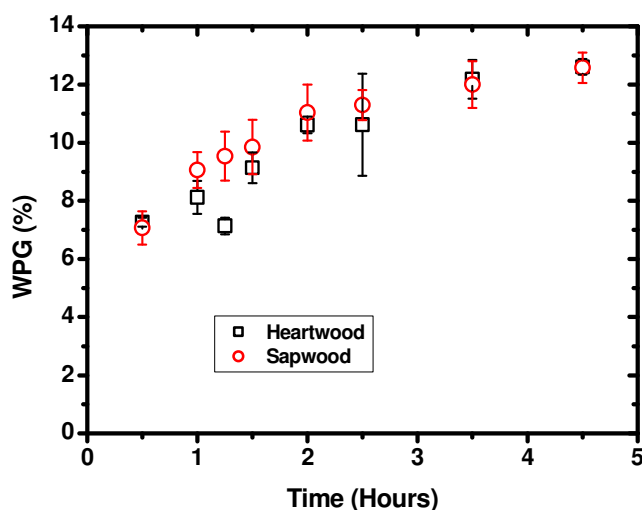
Figure 3: Reactivity of small Corsican pine sapwood and heartwood samples with acetic anhydride (100^oC with 20 % acetic acid by volume)

Swelling of Wood due to Acetylation

Wood is swollen by acetylation because the chemically bonded acetyl groups occupy space in the cell wall. Invariably, this swelling is determined by measuring the external dimensions of oven dry wood samples before and after modification. This is a perfectly acceptable procedure provided that this data is not used to determine changes in the cell wall volume. In some cases, actual change in cell wall volume and external volume will be the same, but this has to be established by independent measurements and cannot be assumed. A recent study by Hill and Ormondroyd (2004) compared volume changes by measuring external dimensions and by helium pycnometry, and it was found that the volume changes determined by the two methods were not comparable. This work has now been expanded (Rafidah Karim et al. 2006). An example is shown in Figure 4 for the same samples of Corsican pine (2 x 2 x 0.5 cm, radial x tangential x longitudinal) measured before and after acetylation to different weight gains using a micrometer and a helium pycnometer.
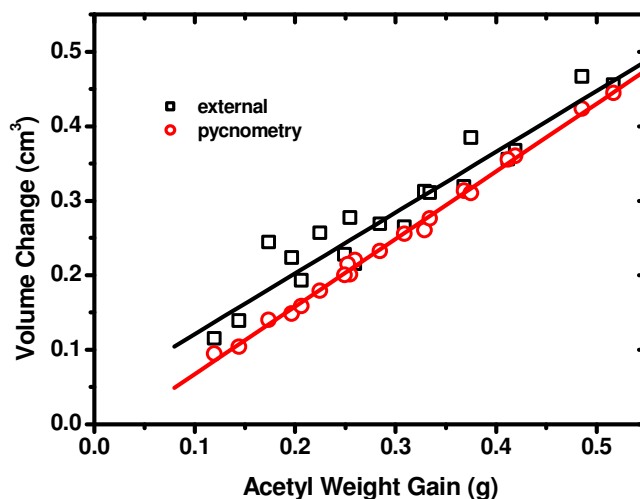
Figure 4: Volume change due to acetylation of samples of Corsican pine measured using external dimensions and helium pycnometry

By using helium pycnometry, a very accurate determination of the cell wall volume is possible, and from this data it is then possible to calculate the volume occupied in the cell wall by the bonded acetyl group. Usually, this is reported as a molar volume, which is the volume occupied by a mole of acetyl groups. This data for Corsican pine is shown in Figure 5.
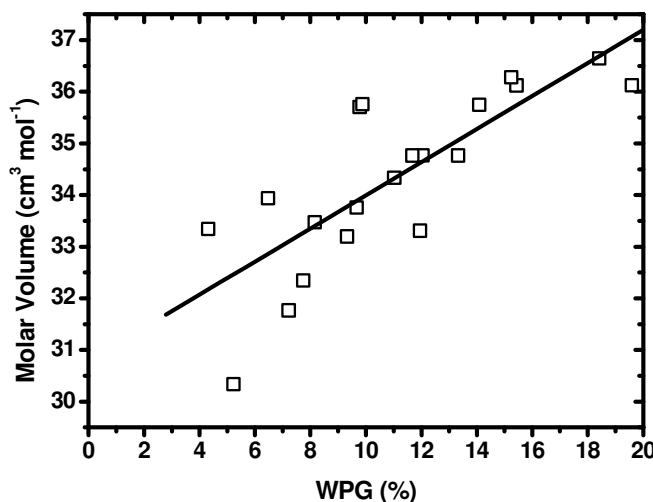
Figure 5: Relationship between molar volume and WPG using helium pycnometry data

Dimensional Stabilisation

When wood is acetylated it is far less susceptible to shrinking and swelling in the presence of varying atmospheric conditions. The reason for this is simply explained: the cell wall is now filled with chemically bonded acetyl groups which take up space within the cell wall. As a consequence the wood is already in a swollen condition, the extent of which depends upon the level of modification, there is very little residual swelling when the wood is soaked in water. This can be proved by reacting with a range of anhydrides the structures of which are shown below in Figure 6.
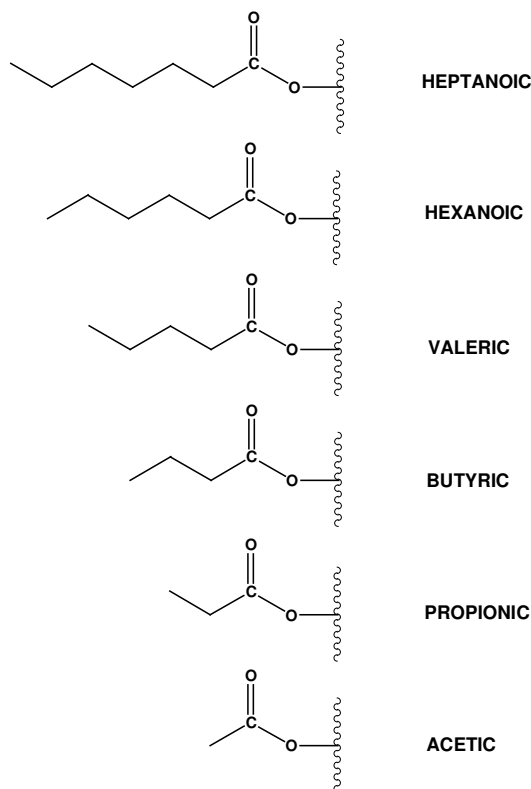
Figure 6: Acyl groups of different chain lengths obtained by reacting wood with a variety of anhydrides

It can be seen from the above, that heptanoic anhydride occupies much more space in the cell wall compared with acetic anhydride. For a given WPG, each anhydride will have reacted with a different number of OH groups which can be readily calculated as follows (Equation 2).

OH groups (mmoles g^{-1}) = [(W_{mod} – W_{unmod}) / W_{unmod}]/(MW-1)   (2)

Where MW is the molecular weight of the respective acyl group and 1 mass unit is subtracted to account for the hydrogen atom lost upon reaction.

The important point is that by performing reactions with different anhydrides, it is possible to determine which property is determined by substitution of OH groups and which property depends upon bulking of the cell wall.

In order to determine the dimensional stability of wood, a number of different experiments can be performed. A commonly used method is to soak the wood for five days in water and determine the volume by measuring the external dimensions of the sample. The wood sample is then placed in an oven at $105^{o}C$ for two days and the oven dry external dimensions determined (Rowell and Ellis 1978). This method is easily performed and can be used to determine the hydrolytic stability of the modification. However, it should be emphasised that it is an extremely harsh test which does not represent conditions likely to be encountered in service. From measurement of external dimensions, a swelling coefficient (S) can be calculated, as shown in Equation 3.

S (%) = (V_{wet} – V_{dry}) / V_{dry}] x 100   (3)

Where V_{wet} is the water saturated wood volume and V_{dry} is the volume of the same sample after oven drying. Although this is a useful determinant of the dimensional stability of wood, a much better indicator is the anti swelling efficiency (anti shrink efficiency), abbreviated as ASE, determined as shown in Equation 4.

$$ASE\ (\%) = [(S_{unmod} - S_{mod})\ /\ S_{unmod}]\ x\ 100 \qquad\qquad (4)$$

This measure is effectively normalised to account for differences between wood samples and species. When a plot is made of the anti shrink efficiency versus WPG the following relationship is obtained as shown in Figure 7 (Hill and Jones 1996).
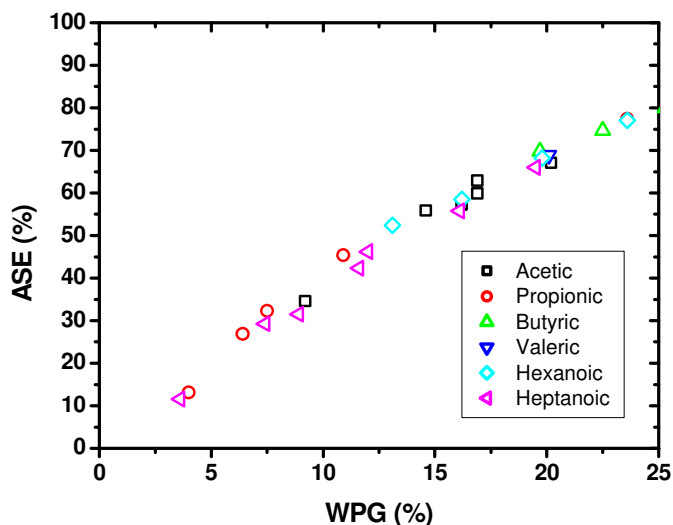
Figure 7: The dimensional stability of Corsican pine modified with different anhydrides

This shows conclusively that dimensional stability is produced as a result of bulking of the wood cell wall rather than the number of OH groups substituted.

At 20 % WPG (the level of acetylation reached with ACCOYA™) an impressive dimensional stability of 70 % is found. This means that wood modified to a WPG of 20 % will shrink and swell by about ¼ of the amount exhibited with unmodified wood; which is a significant improvement. However, it must be emphasised that under normal service conditions, the actual swelling and shrinkage would be far less, since wood in service is *never* oven dried for two days at 105ºC then immersed in water for five days continuously.

A more realistic measure of the dimensional stability of acetylated wood is obtained by determining the volume of wood samples at different relative humidity (RH) values. This is the principle behind the European Standard EN 1910 (2000). According to this standard, wood samples are pre-conditioned at a specified RH (50% or 65%) and temperature and then exposed to high atmospheric RH (75%, or 85%) and low RH (30%), for periods of four weeks. The difference in dimensions between the high and low RH regimes gives the dimensional stabilisation of the treatment or modification. It should be noted that there is not as yet any standard specified for determining the dimensional stability of acetylated wood and it is currently assessed as any other timber species would be (Van Acker 2003).

Stability of the ester bond

Potentially, the ester bond linking the acetyl group to the cell wall polymers can be hydrolysed and there have been studies to determine the stability of acetylated wood in service (Rowell et al. 1993). These have shown that under normal service conditions, acetylated wood exhibits good stability. Acetylated wood which has been exposed to cyclic humidity conditions over a 20 year period has shown little or no loss of acetyl (Rowell 2006).

Reducing the Moisture Content of the Cell Wall

When wood is placed in an environment at a specified RH and temperature it will after a period of time establish a constant moisture content, known as the equilibrium moisture content (EMC). This is reported on an oven dry basis as shown in Equation 5.

$$EMC\ (\%) = [(M_1 - M_2)\ /\ M_2]\ x\ 100 \qquad\qquad (5)$$

Where M_1 is the wood mass at a given RH and M_2 is the oven dry mass of the same wood specimen.

Acetylation reduces the EMC that wood reaches compared to unmodified wood at the same RH. But care must be taken when determining the EMC of acetylated wood, because the modified wood weighs more than the unmodified wood, so that even if the cell wall moisture content was the same, it would appear lower because of the acetyl weight gain. If all that is required is knowledge of the amount of water in the wood specimen then the above method is adequate, but if the data is being used to study the phenomenon in more depth then an alternative means of reporting the moisture content as reduced EMC (EMC_R) is preferred (Akitsu et al. 1993).

$$EMCR\ (\%) = [(M_1 - M_2)\ /\ M_0]\ x\ 100 \qquad\qquad (6)$$

Where M_0 is the oven dry mass of the same wood sample before modification.

This means that EMC is reported in terms of wood mass only rather than wood mass plus acetyl mass gain. Figure 8 shows the effect of modifying wood with acetic or hexanoic anhydride upon the EMC_R compared to unmodified wood. This shows very clearly the significant reduction in EMC_R, and also that such reduction is dependent upon WPG only and not cell wall OH substitution. Note that if EMC rather than EMC_R was used, then there would apparently be a slightly larger reduction in moisture content, but that this would still be equal for the two anhydrides.

Thus, once gain, the mechanism for reduction in EMC of the cell wall is due to bulking with the bonded acetyl group.
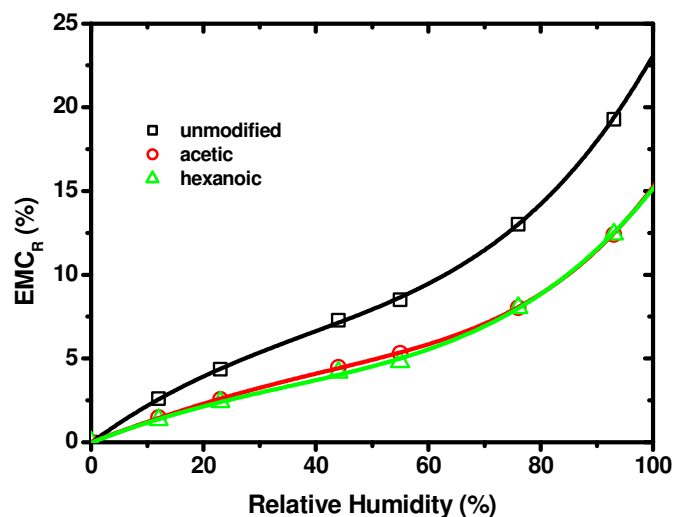
Figure 8: Sorption isotherms for unmodified acetylated (WPG 19.6%) and hexanoylated (WPG 19.5%) Corsican pine (reduced EMC calculated from data of Papadopoulos and Hill 2003)

Biological degradation

For more than fifty years there has been discussion as to why it is that acetylated wood is protected against attack by microorganisms. There have been many statements made to the effect that 'the enzymes responsible for degrading the wood polymers are no longer able to recognise the material'. But it must be appreciated that enzymes commonly produced by fungi are not capable of penetrating the cell wall and so the blocking of enzyme activity is unlikely to be a significant mechanism. So what is the mechanism?

Once again, by modifying wood with a variety of anhydrides it is possible to determine the relative importance of OH substitution against cell wall bulking as a protection mechanism. The first such study was of Corsican pine reacted with a variety of anhydrides and exposed to the brown rot fungus *Coniophora puteana* was reported by Papadopoulos and Hill (2002), the data from which is reproduced in Figure 9. Following on from this work, a study was made to attempt to better understand the mechanism by which fungal attack was prevented (Hill et al. 2005). The conclusions from this study were that the reduction in cell wall moisture content due to the space occupied by the acetyl groups was responsible for the decay resistance. In this paper, the relationship between the fibre saturation point (FSP) of the cell wall (which is the maximum amount of water that the cell wall can contain) and WPG was presented. The FSP was determined using the technique of solute exclusion and a theoretical fit to the data was calculated from helium pycnometry data. The assumption being that any volume occupied in the cell wall by acetyl or hexanoyl groups was thereby denied to water molecules. The fit that was obtained is shown in Figure 10. From these two sets of results it is now possible to produce a plot of mass loss due to decay against FSP and this is shown in Figure 11. From this it can be seen that the mass loss due to decay by *Coniophora puteana* is effectively zero at a FSP of 22%, which is very close to the moisture content threshold below which fungal attack of wood does not occur (Eaton and Hale 1993, Viitanen and Paajanen 1988). In the absence of an alternative hypothesis, the reduction in cell

wall moisture content would appear to be the explanation for the decay resistance of acetylated wood. The wood cell wall is not degraded because it is too dry.
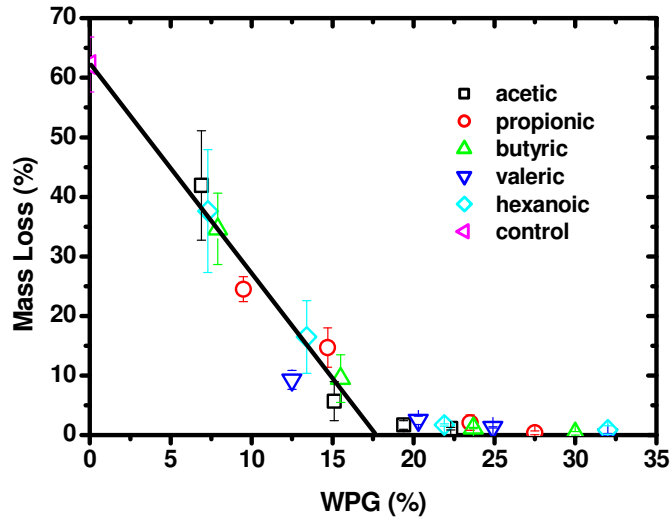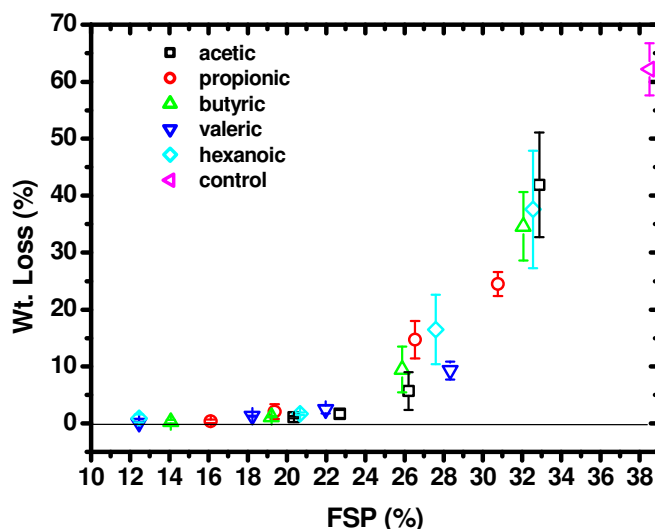

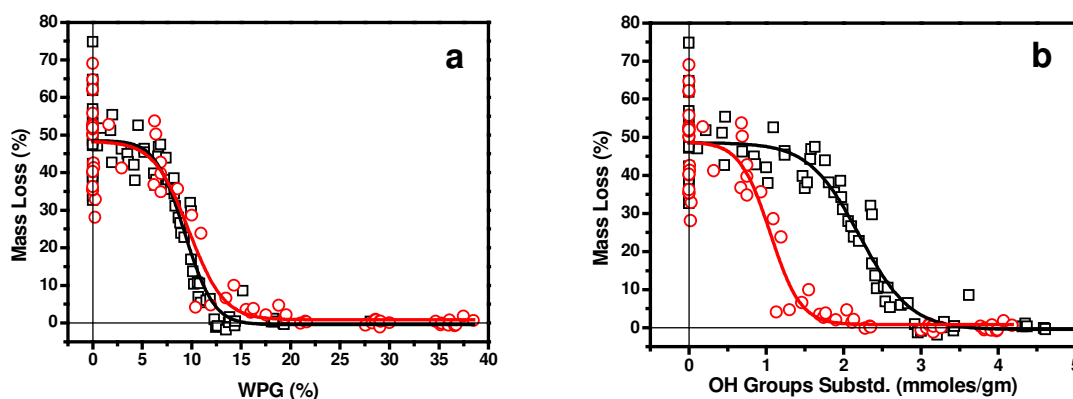*Figure 9: Mass loss of anhydride modified Corsican pine exposed to Coniophora puteana*
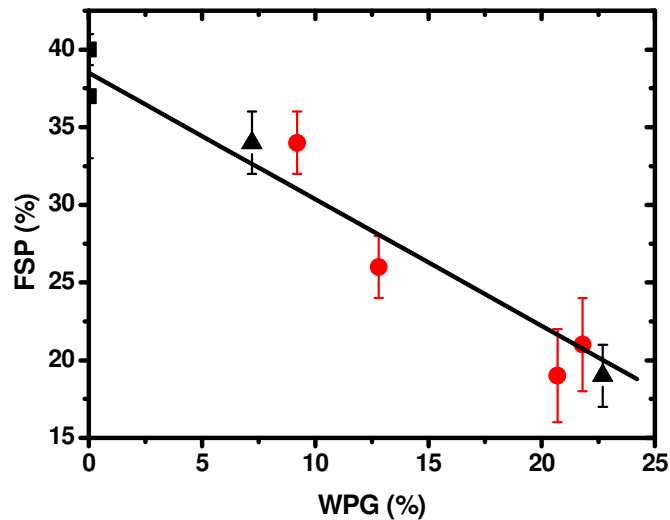
Figure 10: The relationship between fibre saturation point and weight percentage gain for unmodified (black squares) acetylated (red circles) and hexanoylated (black triangles) Corsican pine. The linear fit was derived independently from helium pycnometry data.

A more recent study (Hill et al. 2006) has investigated the decay of Corsican pine modified with acetic or hexanoic anhydride, showing conclusively that it is WPG rather than OH substitution that determines the degree of decay resistance (Figure 12). Further research into this phenomenon is continuing. According to the criteria for determination of natural durability as described in EN350 (1994), Corsican pine sapwood moves from class 5 (not durable) into class 1 (very durable) at 20% WPG.

Figure 11: The relationship between FSP and decay mass loss produced by combining data from Figure 9 and Figure 10.

Figure 12: Results from C. puteana exposure of Corsican pine modified with acetic (black) or hexanoic anhydride (red) plotted in terms of decay mass loss against WPG (a) and against OH substitution (b).

Weathering of Acetylated Wood

Acetylation has been investigated as a potential method for altering the chemical nature of the substrate, so that it is more effectively protected against exposure to solar radiation. In outdoor weathering tests, discolouration of uncoated acetylated wood occurs in a similar fashion to unmodified wood. However, experiments where clear coatings have been applied to acetylated wood have shown that acetylation does provide additional stability when these samples are exposed to UV light (Plackett *et al.* 1992, Beckers *et al.* 1998). In some part, this stability arises due to the higher checking resistance of acetylated wood when exposed outdoors (Dunningham *et al.* 1992). This is a direct result of the bulking of the cell wall of the modified wood by the acetyl substituents. Acetylation results in a substantial reduction in the polarity of the wood surface, which may affect the adhesion characteristics of surface coatings.

Gluing

Adhesion to the surface of wood depends upon the surface energy of the modified wood and it is only with this physical effect that there is no longer a relationship between WPG and wettability of the surface. This is shown in Table 1, where the contact angle between water and the surface of wood modified with different anhydrides is shown. Because of the loss of OH groups the surface is more hydrophobic and adhesives which are normally used for bonding wood may no longer be appropriate. A comprehensive study of adhesives with acetylated wood was reported by Vick and Rowell (1990) who studied the adhesive bonding of acetylated yellow poplar, with eighteen different thermoplastic and thermosetting adhesives. Effectiveness of the adhesives was examined by determination of bond shear strength (and wood failure) of 6 mm thick, bonded wood strips after conditioning at $27^{o}C$ and 65 % RH and after water soaking. Various classes of adhesives were investigated (polyurethanes, polyvinyl acetate, rubber-based contact, casein, epoxy-polyamide, amino resin, resorcinol and phenol-resorcinol, phenolic). In general, adhesives relying on H-bonding with the wood surface such as UF generally perform less well with acetylated wood, whereas polyurethanes (for example) show very good performance.

Table 1: Contact angles for water on unmodified and anhydride modified wood

Sample	WPG (%)	Contact angle (degrees)
Unmodified	0	45
Acetylated	24	98
Propionylated	4	108
Propionylated	8	117
Propionylated	11	123

Mechanical Properties

There are two competing effects influencing the mechanical properties of wood when it is acetylated. Acetylation of wood results in a decrease in equilibrium moisture content at a given relative humidity, which in turn yields a concomitant increase in tensile strength, MOR and MOE (Dinwoodie 2000). However, some degradation of the cell wall may also occur, due to the application of heat over extended periods and also due to the generation of acetic acid by-product in the cell wall. The extent of degradation will be strongly dependent upon the temperature and time of the modification reaction. It should also be noted that because the wood swells as a result of the presence of bonded acetyl groups in the cell wall, a given cross-sectional area of modified wood would therefore contain fewer fibres. If account is taken of the increase in the cross-sectional area of a sample as a result of modification, then a sample exhibiting the same strength/stiffness before and after modification would appear to exhibit a reduction in these properties, which could then be falsely interpreted as degradation due to modification.

A study of the scientific literature gives a complicated picture with some workers reporting a slight increase in mechanical properties and some a slight decrease. Because of the many different ways in which the results can be presented, this accounts for at least some of the confusion (Rowell 1996). Until recently most of the research has concentrated upon laboratory samples that are free of defects such as knots (known as clears).

Larsson and Simonson (1994) studied the mechanical properties of acetylated pine (*Pinus sylvestris*) and spruce (*Picea abies*). The MOR and MOE decreased by about 6 % for pine, but increased by about 7 % with spruce samples after acetylation. Samples for this study were vacuum/pressure impregnated with acetic anhydride, excess anhydride was then drained off and samples heated at $120^{\circ}C$ for six hours. Hardness of the acetylated wood samples was also found to increase, which was considered to be as a result of the lower MC of the modified wood. Acetylated samples were also found to be less susceptible to deformation when subjected to varying RH. Birkinshaw and Hale (2002) found that acetylation did not significantly affect the mechanical properties of the softwoods studied (pine, spruce, larch). Militz (1991) reported a slight increase in MOR and a small decrease in MOE when beechwood was acetylated. Bongers and Beckers (2003) performed a comprehensive analysis of the mechanical properties of wood, obtained from samples up to 4 m in length that had been acetylated in a pilot scale reactor. Samples for the determination of mechanical properties were then machined from these larger pieces. Variable results were obtained, with some species showing increases in some properties and other decreases, but results were consistent within a species.

In a recent study of the mechanical properties of *structural size* pieces of acetylated wood, it was reported that acetylation made little difference to the mean strength properties. (Jorissen et al. 2005). However, due to a greater variability in strength properties, the characteristic value was found to drop by about 35%. It was recommended that a grading system be employed after acetylation to overcome this disadvantage.

The future

We are now in a position where acetylated wood will be appearing in the market in significant quantities. Although there is much known about the material, we still have a lot to understand at an academic level. As acetylated wood becomes established as a mainstream product it will become necessary to address the issue of disposal of this material. Due to its nature, it could be ground down to a form suitable for composting, or incinerated without release of toxic materials into the environment. A more appropriate strategy would be to develop a materials cascade approach. Acetylated wood would be used as a feedstock for particleboard, MDF or other reconstituted wood products to make more dimensionally stable products. At the end of life of these products pyrolysis would be used to release bonded acetyl as acetic acid which would then be used as a feedstock for new acetic anhydride. The residue from this process would then be burnt to provide process energy for the acetylation plant. This would then be a truly cyclic materials flow process.

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