CHEMICAL MODIFICATION OF SOLID WOOD AND WOOD RAW MATERIAL FOR COMPOSITES PRODUCTION WITH LINEAR CHAIN CARBOXYLIC ACID ANHYDRIDES: A BRIEF REVIEW

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This paper reviews recent results in the field of chemical modification of wood with linear chain anhydrides. Though the main focus is on work performed by the author, this is described in the context of related progress in the field. The combined research has demonstrated the effectiveness of chemical modification applied to solid wood and wood raw material for composites production in overcoming the main disadvantages of wood. Wood samples and wood chips/strands have been chemically modified with a series of anhydrides at equivalent levels of modification, under identical conditions, and the question was to determine which is the primary factor controlling the biological durability, the degree of cell wall bulking by the bonded adduct, or the extent of hydroxyl substitution. The results have clearly indicated that the degree of cell wall bulking caused by the adduct, rather than the extent of hydroxyl substitution, is the primary factor controlling the biological durability and water vapour sorption. Despite the large difference in OH substitution level, reaction with different anhydrides results in the same level of protection against decay, marine borers and termites, and in the same level of water vapour sorption. These observations suggest that the mechanism of protection is not chemical/biochemical in origin, but relates to the bulking of the cell wall by the reacted adduct.

Keywords: Wood; Chemical modification; Anhydrides; Dimensional stability; Decay; Composites

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INTRODUCTION

The fibrous nature of wood has made it one of the most appropriate and versatile raw materials for a variety of uses. However, two properties restrict its much wider use: dimensional changes when subjected to fluctuating humidity and susceptibility to biodegradation by microorganisms. The varying moisture content of wood and wood products results in dimensional and conformational instability, which can compromise the performance of other materials combined with wood, such as adhesives and surface coatings. This problem, until relatively recently, has been addressed mainly by impregnating wood with appropriate hydrophobes (Stamm 1964; Kumar 1994). Fungal activities in wood, on the other hand, limit its use by reducing its density, strength, and aesthetic properties. Preservation of wood by conventional methods has long been established to prevent, or eradicate wood-inhabiting fungi. Conventional wood

impregnation methods (water or oil type preservatives) are based primarily on the use of toxic chemicals. Environmental concerns, particularly with regard to disposal of treated wood at the end of product life, are now causing restrictions to be imposed upon the utilization of conventional chemical treatments.

It has been demonstrated and well documented that wood and wood composites may be modified chemically so that selected properties are enhanced in a more or less permanent fashion (Rowell 1983). The natural reactivity of lignocellulosics can be utilized to enhance their properties, with the resulting material being superior in terms of performance and versatility. The basic types of chemical modification use simple monofunctional modifying agents, while others use difunctional, or even polyfunctional modifying agents. The work described here reviews the most recent results in this field, focusing on the work performed in the author's laboratory. This work in general has demonstrated the effectiveness of esterification with a homologous series of linear chain carboxylic acid anhydrides, applied to solid wood and wood raw material for composites production in controlling and mitigating the main disadvantages of wood.

BIOLOGICAL PROPERTIES OF MODIFIED SOLID WOOD

Resistance Against Fungi

Many studies have been performed investigating the resistance of acetylated wood to biological degradation by fungi and other organisms. It is generally reported that a weight percent gain of *ca.* 20% is required before full protection is achieved. Goldstein *et al*. (1961) acetylated ponderosa pine using acetic anhydride in xylene. The modified wood was tested against six basidiomycete fungi, five brown rot and one white rot, with a weight percent gain (WPG) of 18% reported to be sufficient to provide decay resistance. Peterson and Thomas (1978), acetylated loblolly pine, green ash, and yellow poplar using acetic anhydride in xylene. The modified samples were tested against the brown rot fungus *G. trabeum* and the white rot fungus *Coriolus versicolor*. It was found that the white rot was generally easier to control than the brown rot, with levels of acetylation as low as 7% being able to provide protection. However, ash was still degraded by white rot, even at WPG levels of 20%. It was stated that '*blocking of action of fungal catalysts appears to be the primary protection mode of the acetylation technique*'. Levels of acetylation of 17-20% (WPG) were found to provide decay protection (with the exception of ash). The effect of the level of acetylation on the decay resistance of Japanese red pine, red beech, and albizzia was studied by Takahashi *et al*. (1989). Modified samples were exposed to the brown rot fungi *T. palustris*, *Serpula lachrymans*, the white rot fungus *C. versicolor*, and to soft rot in unsterile soil. Protection against *T. palustris* was observed in all wood species at a WPG of 20%. With *C. versicolor*, a WPG of 6% was sufficient to protect softwood, but hardwoods required a WPG of 16%. Beckers *et al*. (1994) determined the decay protection threshold levels for acetylated Scots pine to a variety of wood decay fungi. It was found that WPG levels of 18% were required against *C. puteana* and *G. trabeum*, over 20% against *P. placenta*, and 11% was required in an unsterile soft rot test. In ground contact stake tests of acetylated pine samples, it was found that an acetyl content of 20% prevented attack by brown, white, and soft rot fungi

(Larsson Brelid *et al*. 2000). Laboratory unsterile soil tests on acetylated mini-stakes showed that an acetyl content of 18.5% was able to provide significant protection against fungal attack. Vapour phase acetylated makamba (*Betula maximowiczii*) were exposed to a brown (*Tyromyces palustris*) and white-rot (*Coriolis versicolor*) fungus (Ohkoshi *et al*. 1999). Mass loss due to decay with the brown rot fungus was zero at 20% WPG, and with the white rot fungus at 12% WPG. Protection against soft rot has been reported for a WPG of 10.7% for pine, 14.4% for poplar, and 12.8% for beech (Beckers *et al*. 1995). Suttie *et al*. (1999) modified Scots pine with acetic, propionic, butyric, or hexanoic anhydrides and determined decay resistance against the brown rot fungi *Coniophora puteana, Gloeophyllum trabeum*, *Poria placenta,* and a white rot fungus (*Coriolus versicolor*) using European Standard method EN113 and a vermiculite overlay method. Resistance to soft rot attack was also determined using a modified ENV 807 stake test in unsterile soil. The effect of different levels of reaction upon decay resistance was only tested with the soft rot experiment. In this, it was found that a threshold of *ca*. 23% was required to ensure protection, regardless of the anhydride used.

It was not clear whether protection arises from a decrease in the moisture content of modified samples, because the cell wall polymer OH groups are masked, because the cell wall is bulked by adduct, or a combination of these phenomena. Brown rot fungi preferentially attack the cellulose and hemicellulose components of the cell wall, with depolymerisation of these polymers. The hemicellulose component is particularly susceptible to attack during the initial phase of degradation. Lignin attack is largely limited to demethoxylation of the aromatic residues, resulting in loss of the propyl side chain and incorporation of oxygen, with minor depolymerisation. It is known that the enzymes associated with the degradation of these components are too large to enter the cell wall of undegraded wood. For this reason, various low molecular weight diffusible agents have been proposed to initiate degradation thereby allowing enzymes to penetrate as decay proceeds (Eaton and Hale 1993; Green and Highley 1997). Any proposed mechanism by which chemical modification provides biological protection against fungal attack should therefore take account of the presence of these low molecular weight diffusible agents.

Results reported by Suttie *et al*. (1999) have shown that with soft rot attack, the WPG level, rather than the extent of hydroxyl substitution is the sole factor determining protection from decay. This indicates that a physical, rather than a chemical mechanism may be responsible for decay protection, at least as far as soft rot is concerned. Hill and Papadopoulos (2002) presented an assessment of the effectiveness of linear chain carboxylic acid anhydrides namely, acetic, propionic, butyric, valeric, and hexanoic anhydride, in improving the biological resistance of Corsican pine (*Pinus nigra* Schneid) sapwood. A brown rot fungus [*Coniophora puteana* (Schum.:Fr)] was selected in order to determine and compare the effectiveness (threshold value) of the linear chain anhydrides. The work has demonstrated that with all anhydrides studied, a weight gain of 18% following reaction ensured complete protection and indicated that degree of cell wall bulking by the bonded adduct, rather than extent of hydroxyl substitution is the primary factor controlling decay resistance.

Resistance against Marine Wood Borers

Limited studies have investigated the influence of chemical modification in protecting wood from attack by invertebrates (Kartal *et al*. 2004; Manabendra *et al*. 2002; Suttie *et al*. 1999) including marine wood borers (Johnson and Rowell 1988). In the latter study, southern yellow pine modified with use of propylene oxide, butylene oxide, or butyl isocyanate was exposed to marine borers in the field. Treated panels were found to resist attack by *L. tripunctata* and out-performed creosote-treated samples at the same site. The resistance of pine wood modified with linear chain carboxylic acid anhydrides to the crustacean wood borer *Limnoria quadripunctata* was assessed by measuring faecal pellet production and mortality following feeding over 3 weeks in the laboratory (Papadopoulos *et al*. 2008a). The study assessed whether modification of Corsican pine sapwood confers resistance to the crustacean wood borer *Limnoria* using a rapid laboratory test developed by Borges *et al.* (2003). The technique used to assess resistance to *Limnoria* attack exposes wood in such a way that animals have ready access to wood under conditions optimal for tunnelling. The level of attack is assessed by using faecal pellet production to measure feeding and measuring mortality. Low faecal pellet production and high mortality are taken as measures of resistance to attack. The results showed that all wood modification measures resulted in a reduction in the number of faecal pellets produced, with pine treated to WPG's of 24.1% and 31% having the greatest reduction. This indicated that feeding is slowed by modification at these levels. No significant reduction was found when feeding above 24.1%, as statistical analysis revealed, suggesting that modification to WPG's greater than this did not confer additional protection. The type of anhydride employed had little influence on feeding, since similar numbers of faecal pellets were produced by *Limnoria* feeding off wood treated to similar WPG's with different carboxylic anhydrides.

Resistance Against Termites

The protection afforded to Corsican pine sapwood modified to a range of WPG's with various linear chain anhydrides, against attack by the subterranean termites *Reticulitermes flavipes* was studied by Papadopoulos *et al*. (2008b). The work has demonstrated that chemically modified Corsican pine sapwood afforded bioprotection against the subterranean termites *Reticulitermes flavipes.* There was found to be no significant reduction in feeding above 16% WPG, suggesting that modification to WPG's greater than this did not confer additional protection. Again, the type of anhydride employed had little influence on resistance against termites.

WATER VAPOUR SORPTION OF MODIFIED SOLID WOOD

A number of authors have investigated the sorption isotherms of acetylated wood specimens at only one level of substitution (Risi and Arseneau 1957; Spalt 1958; Popper and Bariska 1972; Yasuda *et al*. 1995). Although the effect on overall stabilisation in response to liquid water soaking was well documented (Stamm 1964; Rowell 1983; Hill and Jones 1996), there was little evidence of how sorption is influenced by esterification with anhydrides. The effect of molecular size of substituent group on sorption of water

vapour had not been addressed so far. A comprehensive investigation into the effect of molecular size of the substituent group of softwood modified with linear chain carboxylic acid anhydrides upon the sorption of water vapour was performed by Papadopoulos and Hill (2003). They modified wood with a variety of anhydride molecules of different size and produced similar levels of cell wall bulking at different levels of hydroxyl substitution. The sorption isotherms for untreated and chemically modified wood were analysed using the Hailwood-Horrobin model, which allows the separation of the total sorption into monomolecular and polymolecular sorption. The experimental analysis of the sorption isotherms showed that esterification affected the total, polymolecular, and monomolecular sorption. The effect of molecular size of the substituent group on site accessibility was addressed by comparing the effect on water vapour sorption produced by adducts with differences in molecular size. Similar levels of cell wall bulking were produced at different levels of hydroxyl substitution. Analysis of the sorption isotherms at comparable weight percentage gain revealed that the five anhydrides used show similar effectiveness in total, polymolecular, and monomolecular sorption, despite the substantial difference in the proportion of hydroxyl groups reacted. It was concluded that the reduction in total, polymolecular, and monomolecular sorption produced by the linear chain anhydrides is primarily determined by the volume of adduct deposited in the cell wall (bulking) rather than by the number of hydroxyl groups which have been substituted.

BIOLOGICAL PROPERTIES OF WOOD COMPOSITES MADE FROM MODIFIED RAW MATERIAL

Chemical modification has also been employed to improve the biological properties of wood composites manufactured from modified raw material, mainly with acetic anhydride (Rowell *et al.* 1997; Papadopoulos 2006, 2009). The results showed that both acetylated particleboards and oriented strand boards (OSB), above 20% WPG, imparts excellent protection against decay, even after six years of testing, in ground contact. Limited studies, however, had been published concerned the production of wood composites with modified raw material from with other linear chain anhydrides. Particleboards have been manufactured from chemically modified wood chips with propionic anhydride (Papadopoulos 2007). After three years of testing, results showed that propionylation provides excellent protection against fungal attack. An interesting point is that both propionylated particleboards and acetylated OSB at equivalent levels of modification showed the same behaviour against decay, when both were exposed in the same place. This indicated that the type of anhydride employed has little influence on resistance against decay.

PHYSICAL PROPERTIES OF WOOD COMPOSITES MADE FROM MODIFIED RAW MATERIAL

The dimensional stability of OSB produced from acetylated strands (11.2% and 20.4% WPG) was investigated (Papadopoulos and Traboulay 2002). Boards exhibited

superior dimensional stability when produced by this method, since an approximately 147% improvement in thickness swelling value after 24 hours immersion in water was reported. Propionylated boards have also been appeared in the literature (Papadopoulos and Gkaraveli 2003). Propionylation resulted in improved dimensional stability, since thickness swelling values for propionylated boards were about 104% lower than controls.

Propionylation of chips, however, resulted in significant decrease in internal bond strength, since the values were about 48% lower than controls. This reduction appeared to be higher that the corresponding reduction due to acetylation. For example, Papadopoulos and Traboulay (2002) have reported that acetylation of strands to about 11.2 and 20.4% WPG resulted in 17.5% and 30% decrease in IBS, respectively. Similar reductions in IBS values were reported for acetylated flakeboards (36%) and particleboards (25%) (Youngquist *et al.* 1986; Fuwape and Oyagade 2000). It was suggested that the hydrophobic nature of propionylated wood caused reduced wetting compared to the acetylated wood.

An interesting study appeared in the literature (Papadopoulos *et al.* 2006), which evaluated the bonding behaviour of chemically modified wood particles towards formaldehyde-based and isocyanate-based resin system, as this was determined from the internal bond strength of the boards. The results indicated that modification of wood chips and strands did not significantly affect the bonding efficiency of isocyanate resin, but the bonding efficiency of formaldehyde resins were strongly influenced, and consequently the results suggested that the isocyanate resin system is more suitable for use in boards made from modified raw material than the formaldehyde resin system.

CONCLUSIONS

1. A review of recent published results, with an emphasis on work in the author's labs, has demonstrated the effectiveness of chemical modification applied to solid wood and wood raw material for composites production in controlling the main disadvantages of wood, namely inadequacies in dimensional stability and biological resistance.
2. The review clearly indicated that the degree of cell wall bulking caused by the adduct, rather than the extent of hydroxyl substitution, is the primary factor controlling the biological durability and water vapour sorption. Despite the large difference in OH substitution level, reaction with different anhydrides results in the same level of protection against decay, marine borers and termites, and in the same level of water vapour sorption.
3. It is suggested that the mechanism of protection is not chemical/biochemical in origin, but relates to the bulking of the cell wall by the reacted adduct.

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