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Dimensional Stabilisation of Fast Growing Forest Species by Acetylation

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Abstract: The effect of acetic anhydride modification on dimensional stabilisation of three fast growing species namely poplar, willow and eucalyptus was studied. With acetylation, maximum ca. 15% WPG values were obtained for all samples. Dimensional stabilisation was determined by the water-soak/oven-dry method through a total of six cycles in order to determine the stability of ester bonds to hydrolysis at neutral pH. It was found that wood species has no significant effect on dimensional stabilisation as long as the same weight gain levels were obtained. With the studied wood species, at ca. 15% WPG values, around 60% ASE values were obtained.

Key words: Acetylation, acetic anhydride, poplar, willow, eucalyptus, dimensional stabilisation, chemical modification

INTRODUCTION

Wood has many technical advantages such as high specific strength and stiffness, good toughness, low processing energy, renewability and is aesthetically pleasing. However, it has some disadvantageous properties in comparison with other materials; such as water reactivity changing dimensions with varying moisture contents, biodegradability, photosensitivity (degradability by UV light), flammability etc. One of the main problem of solid wood in many applications, is its dimensional instability. Wood changes dimensions with changes moisture content of the surrounding atmosphere. Wood is mainly composed of three polymers namely cellulose, hemicelluloses and lignin. These cell wall polymers contain hydroxyl groups which attracts moisture through hydrogen bonding. Below the fibre saturation point, increase in moisture content cause fibre expansion. Beyond fibre saturation point, the fibre dimensions cannot be further changed by increasing moisture content, water exists in the form of free water in the void structure of wood. This process is reversible, when the moisture content starts to decrease below the fibre saturation point wood starts to shrink.

Chemical modification can be defined as a chemical reaction between reactive parts of wood cell wall polymers (hydroxyl groups generally) and a chemical reagent, with or without catalyst, to form a covalent bond between these two. The chemical modification of wood with various reagents including anhydrides (such as acetic, succinic, maleic, propionic, butyric, hexanoic, crotonic and methacrylic anhydrides), isocyanates, formaldehyde, acetaldehyde, epoxides (such as ethylene or propylene oxide, glycidyl methacrylate, allyl glycidyl ether etc.) has been the subject of research for many decades (Stamm and Tarkow, 1947; Rowell and Banks, 1985; Kumar, 1994; Hon, 1996; Rowell, 1983, 1991, 2006a, b; Hill, 2006).

While there has been a lot of research conducted with various chemical reaction systems; many of them focused on the acetylation of wood with acetic anydride. Most of the modifications have been performed to improve dimensional stability or decay resistance of the material. In spite of the vast amount of research on the acetylation of both bulk wood and wood particles (for composites), commercialisation has been limited. There are reports of a commercial acetylation plant for solid wood in Japan but few details are available (Rowell, 2004). Acetylation became commercial product recently. In Netherlands, Titan Wood is the first company to produce acetylated wood in commercial scale (its name is Accoya wood). Their production capacity is about 24.000 m^3 per annum. It was expected that in near future, acetylated wood will replace the more toxic preservative treatments in many application (Kattenbroek, 2005).

Everyday demand for wood or wood based product increases due to the increase of world population. In order to meet the demand, some alternative solutions have been proposed such as recycling wood or wood based products, utilising lignocellulosic residues from agricultural crops and planting fast growing forest species such as poplar, eucalyptus etc. (Rowell *et al*., 1991; Youngquist *et al*., 1993; Grigoriou *et al*., 2000). But one of the main problem with fast growing species is their dimensional instability. In the literature most of the acetylation studies of solid wood were performed on softwood species. In this study three fast growing hardwood species namely poplar, willow and eucalyptus sapwood samples were acetylated in order to obtain dimensionally stable material. Acetylation reaction was characterised by FTIR.

MATERIALS AND METHODS

Preparation of wood blocks: For wood modification, samples were prepared from kiln dried the clone 'I-214' poplar (*Populus* x *Euramenica* (Dode) Guiniver cv cultivar 'I-214'), Willow (*Salix alba* L.) and Eucalyptus (*Eucalyptus camaldulensis* Dehin.) sapwood blocks of dimensions 20×20×5 mm (radial x tangential x longitudinal). The thickness was chosen to ensure reasonable access to the treatment liquid. Samples were screened for defects, such as small knots, sloping or curvy grain and splits or cracks. They were carefully selected so the growth rings were parallel to the tangential direction. Before reaction, the samples were subjected to Soxhlet extraction with a mixture of toluene:acetone:ethanol (4/1/1, vol./vol.) for 6 h; then oven-dried overnight at 105°C. After that, oven-dried samples were allowed to cool in a desiccator containing phosphorous pentoxide, to cool to ambient temperature, before weighing and determination of dimensions.

Acetylation of wood samples: Extractive free wood samples were used for acetylation reaction. In a round bottom flask equipped with a condenser and a magnetic stirrer, 5 wood blocks, 0.7 mmol Py/g of dry wood, 1.4 mmol acetic anhydride (AA)/g of dry wood and 40 mL of DMF were introduced. The reaction mixture was heated at 100°C for various reaction times to obtain desired WPG values. At the end of the reaction, the modified samples were placed in a Soxhlet apparatus for solvent extraction, with the standard 4/1/1 mixture (toluene:acetone:ethanol) for 6 h and subsequently oven dried overnight at 105°C. The samples were transferred to a desiccator containing phosphorus pentoxide until cool and weight gain levels were calculated.

The Weight Percentage Gain (WPG) and Volume Change (VC) were calculated according to following equations, respectively;

$$WPG\ (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

W_1 = Before treatment sample weight
W_2 = After treatment sample weight

$$VC\ (\%) = \frac{V_2 - V_1}{V_1} \times 100$$

V_1 = Original volume of the sample
V_2 = After treatment volume of the sample

Dimensional stability test: The dimensions of the oven-dried modified samples were measured by using a micrometer accurate to ±0.01 mm. Following measurement, blocks were then vacuum impregnated/atmospheric pressure cycles with deionised water for the water-soak test. Samples were soaked for a total of five days before determination of the water-saturated volume. Following measurement, blocks were transferred to an oven set at 105°C for a total of 72 h, in order to ensure dryness to constant weight. Once fully dry, samples were again measured. This procedure was repeated for a total of six oven-dry (OD) water-soak (WS) cycles.

The volumetric swelling coefficients (S(%)) were calculated according to the well known equation (Stamm, 1964):

$$S(\%) = \left(\frac{V_w - V_d}{V_d}\right) \times 100$$

V_w = Volume of water saturated wood
V_d = Volume of oven dry wood

The anti-shrink efficiency (ASE (%)) was calculated according to following equation:

$$ASE(\%) = \left(\frac{S_c - S_m}{S_c}\right) \times 100$$

S_c = Volumetric swelling coefficient of control (unmodified samples)
S_m = Volumetric swelling coefficient of modified samples

Infrared spectroscopy: Infrared absorption spectra of acetylated and unmodified wood flour were obtained with the KBr (potassium bromide) technique, using a Perkin-Elmer Paragon 1000 PC FT-IR spectrometer (Perkin Elmer) with a HLLT detector, at a resolution of 4 cm^{-1} (100 scans). In each case, 1% w/w of oven dry wood flour was dispersed in a matrix of KBr and pressed to form pellets.

RESULTS AND DISCUSSION

Acetylation of wood blocks: In order to determine the reactivity of wood species, poplar, willow and eucalyptus wood blocks were modified with acetic anhydride (AA) and the results are shown in Fig. 1. As can be seen in the figure, poplar and willow blocks showed similar reaction profiles and gave maximum WPG's of about 15% (after 6 h reaction). Eucalyptus wood blocks showed a slightly lower reactivity, a maximum WPG of 13% being obtained in that case (in the same conditions). For the three wood species, it is apparent that all accessible reactive sites were reacted within the first hour of acetylation. Further increment in the reaction time did not

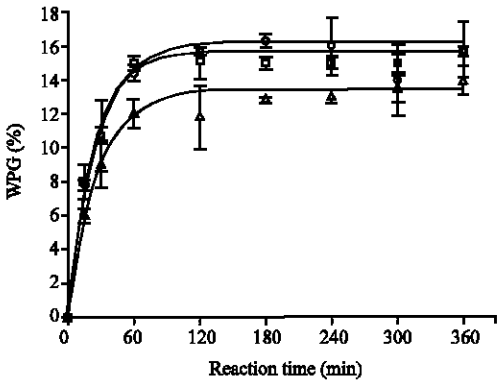

Fig. 1: Effect of reaction time on WPG (%) values of acetylation of poplar (square), willow (circle) and eucalyptus (triangle) wood species at 100°C

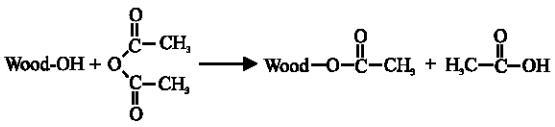

Fig. 2: Acetylation of wood with acetic anhydride (AcWF)

induce any significant increase in the weight gain values. In previous studies (Cetin, 2000; Cetin and Ozmen, 2001, 2005), acetylation of Scots, Corsican and Turkish pine gave maximum WPG values of about 25%. This difference can be attributed to the different chemical composition of softwood compared with hardwood species (Fengel and Wegener, 1989) but also to their different microstructure.

The reaction mechanism between wood hydroxyl groups and AA is shown in Fig. 2. The proof of the reaction between acetic anhydride and poplar, willow or eucalyptus was obtained by analysing the samples with FTIR spectroscopy. The emergence of a carbonyl stretching vibration at 1750 cm^{-1} ($\nu_{C=O}$) in the spectra of acetylated wood confirmed the formation of ester bonds after reaction with AA. Figure 3 shows the FTIR spectra of AA-modified and unmodified poplar (a, b), willow (c, d) and eucalyptus (e, f), respectively. In addition to the $\nu_{C=O}$ at 1750 cm^{-1}, the intensity of the band at 1241 cm^{-1} also increased and was associated to the C-O stretching vibration (ν_{C-O}) of the acetyl moieties. The intensity of the bands located at 1376 cm^{-1} was also enhanced after acetylation. This band was attributed to the C-H bending ($\delta_{s\ C-H}$) vibrations of the methyl groups introduced (Silverstein *et al.*, 1991). The intensity of the band at 604 cm^{-1} also increased and was associated to some vibrations of the grafted methyl groups (not precisely identified).

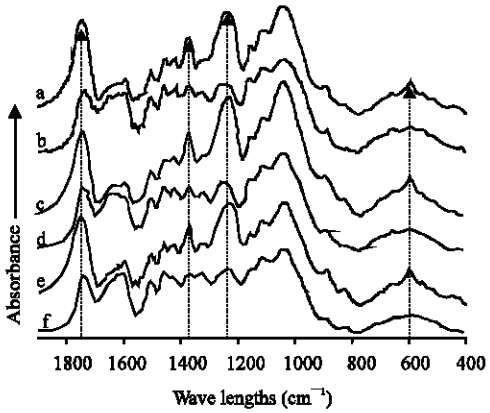

Fig. 3: FTIR spectra of acetylated (a, 15.9% WPG) and unmodified poplar (b), acetylated (c, 15.7% WPG) and unmodified willow (d), acetylated (e, 13.3% WPG) and unmodified eucalyptus (f) wood blocks

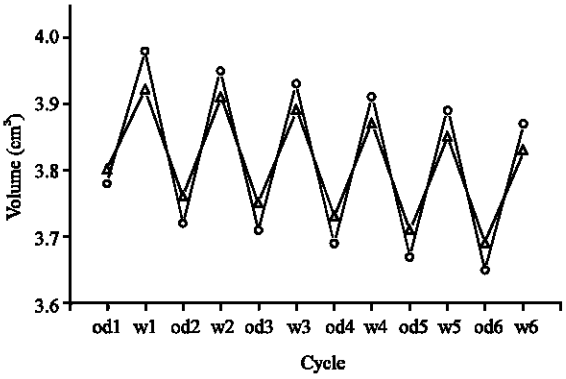

Fig. 4: Change in water saturated and oven dry volumes for acetic anhydride modified poplar wood blocks (circle, 10.7% WPG and triangle, 15.9% WPG) at 100°C

Dimensional stabilisation test: The effects of WPG on the dimensional stabilisation of acetic anhydride modified poplar, willow and eucalyptus sapwood was investigated. Water-soak (5 days)/oven-dry (3 days) cycle tests were performed (a total of six cycles) with modified samples having two different WPG's i.e., 10 and 15%.

Unmodified willow and eucalyptus samples exhibited similar swelling coefficients (≅ 10%) but not unmodified poplar (swelling coefficient ≅ 14%).

The changes in water-saturated and oven-dry volumes for the AA-modified poplar blocks are shown in Fig. 4. The AA modified samples showed no decrease in dimensional stability as the cyclic test proceeded. This indicates that hydrolysis of the ester bond is not occurring during the water soak phase of the tests.

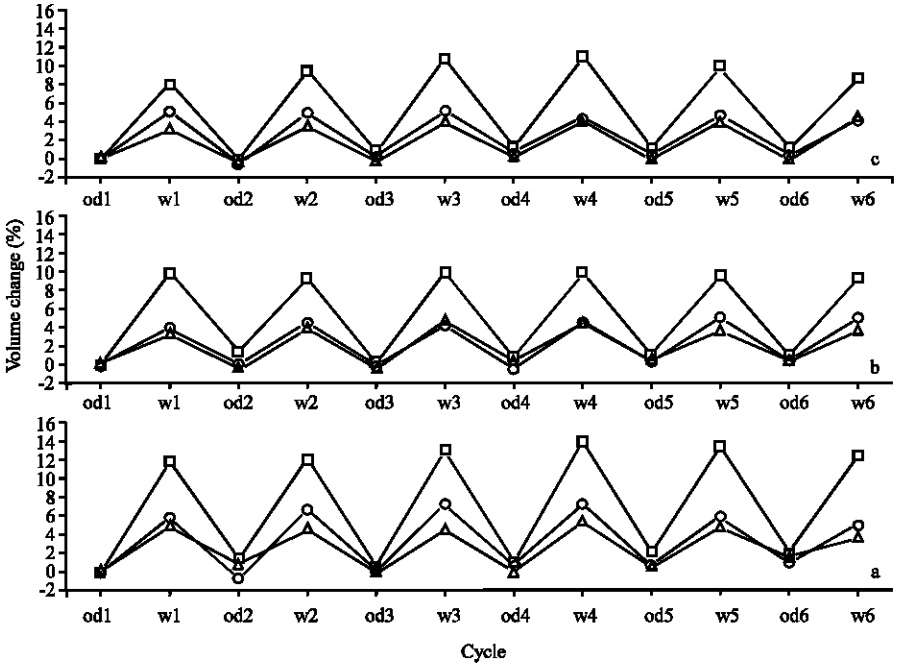

Fig. 5: The percentage volume change of acetic anhydride modified poplar (a, squares, untreated; circles, 10.7% WPG; triangles, 15.9% WPG); willow (b, squares, untreated; circles, 10.8% WPG; triangles, 15.7% WPG) and eucalyptus (c, squares, untreated; circles, 8.9% WPG; triangles, 13.3% WPG) at 100°C during water-soak and oven-dry test

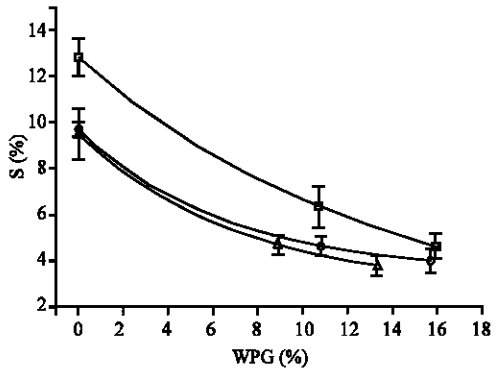

Fig. 6: Comparison of average swelling coefficient (S %) of acetic anhydride modified poplar (square), willow (circle) and eucalyptus (triangle) wood blocks at 100°C

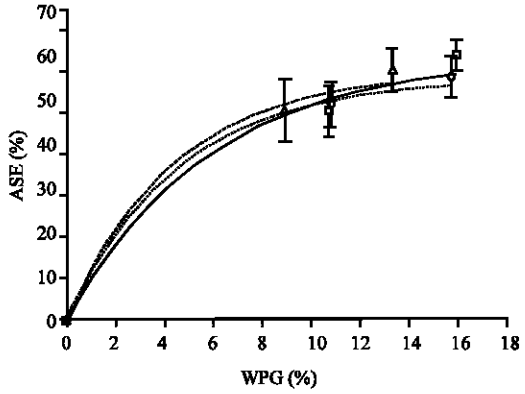

Fig. 7: ASE (%) of acetic anhydride modified poplar (square), willow (circle) and eucalyptus (triangle) wood blocks at 100°C

Since all wood blocks have different volumes, it is difficult to compare the results. For this reason, volume change of the samples due to oven-drying and water-soaking are calculated as a percentage volume change and shown in Fig. 5. It is clear from Fig. 5 that the effect of modification on dimensional stability was significant.

It has been reported (Rowell *et al*., 1976) that S% values obtained for the first cycle are unrepresentative. Cycle to cycle fluctuations in S% have been also noted. However, in these experiments, only slight fluctuations between cycles were observed. The S% values were averaged over the last five cycles and Fig. 6 shows the relationship between averaged S% values and WPG of AA-modified poplar, willow and eucalyptus blocks. It can be seen from Fig. 6 that AA-modified willow and eucalyptus samples gave similar S% values at comparable WPG's. On the other hand, AA-modified poplar samples gave slightly higher S% values at similar WPG (%) values.

Figure 7 illustrates the relationship between the anti-shrink efficiency and WPG for AA-modified poplar,

willow and eucalyptus samples. It was noted that the wood species do not affect the ASE (%) as long as the same level of modification is achieved. The curves show asymptotic behaviour.

Maximum ASE value of ca. 60% was obtained with a 15% modification level. It is in agreement with results that have been reported with other anhydrides (Hill and Jones, 1996; Cetin and Ozmen, 2001). Acetylated Scots and Corsican pine wood exhibited similar anti-shrink efficiencies at similar WPG levels. For example, acetylated Scots and Corsican pine wood blocks showed ca. 40% ASE at 10% WPG and 63% ASE at 15% WPG (Cetin, 2000).

CONCLUSIONS

Acetylation of three hardwood species namely poplar, willow and eucalyptus with acetic anhydride, maximum ca. 15% WPG values were obtained with after 6 h reaction time. These WPG values obtained in the first hour of the reaction and increment in reaction time did not increase further the WPG values. In previous studies with softwood species (Scots, Corsican and Turkish pine) a maximum WPG of 25% was obtained after acetylation (Cetin, 2000; Cetin and Ozmen, 2005). Effective dimensional stabilisation of fast growing hardwood species can be obtained by anhydride modification (*ca.* 60% ASE). The effect of wood species on dimensional stability did not appear to be significant, as long as the same weight gain levels were obtained.

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