

Dimensional changes in Corsican and Scots pine sapwood due to reaction with crotonic anhydride

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Abstract The effects of the reaction temperature and varying level of weight gain on the dimensional stabilisation of crotonic anhydride modified Corsican and Scots pine sapwood were investigated. With Corsican pine at low levels of substitution, the reagent occupied larger molar volumes in the cell wall than at higher weight gains. With Scots pine the molar volume occupied by reagent was found to be temperature dependent at low levels of substitution. Dimensional stabilisation was determined by the water-soak/oven-dry method through a total of ten cycles in order to determine the stability of the ester bond to hydrolysis at neutral pH. It was found that the reaction temperature has no significant effect on dimensional stability provided the same weight gain level is obtained. At weight gain levels in excess of 30%, values of anti-shrink efficiency of 90% were obtained.

Introduction

One goal of the chemical modification of wood is to improve dimensional stability. Various chemical modification reactions have been studied for this purpose (Rowell 1983, Rowell and Banks 1985, Kumar 1994, Banks and Lawther 1994). Acetylation is the most studied area of wood modification. However, there have been few papers published concerning modification of wood with other linear chain anhydrides (Stamm and Tarkow 1947, Goldstein et al. 1961, Hill and Jones 1996).

The purpose of this paper is to show the effects of the reaction temperature and level of substitution on the dimensional stability of an unsaturated linear chain anhydride (crotonic anhydride) modified wood species namely Corsican (*Pinus*

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nigra) and Scots (*Pinus sylvestris*) pine sapwood. In order to determine the stability of the ester bond to hydrolysis, modified samples were subjected to a series of ten water-soak/oven-dry cycling tests.

Material and methods

Samples were prepared from kiln dried Corsican and Scots pine sapwood blocks of dimensions 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal). Samples for experimentation 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:methanol (4:1:1, by volume) for six hours; then oven-dried overnight at 105 °C. After that, oven-dried samples were allowed to cool in a desiccator containing silica gel.

The extracted oven-dried samples were numbered and weighed to an accuracy of ±0.0001 g. Dimensions were determined using a micrometer accurate to ±0.01 mm. Each reaction was carried out using five replicates and the results averaged. All chemical modification was performed under a standard set of conditions. Samples were modified using pyridine as a catalyst, with an equimolar solution of the anhydride based upon an estimate of the hydroxyl group concentration in the wood. Calculation of the OH group concentration was reported in a previous paper (Hill and Jones 1996). Wood samples were pre-impregnated with dry pyridine (stored over KOH) for one hour under six vacuum (98.4 KPa)/atmospheric pressure cycles. Each batch of samples was then added to a flask containing pyridine and heated in an oil bath at 60 °C, 80 °C, 100 °C and 120 °C (±0.5 °C) for one hour. Pre-heated reagent was then added to initiate the reaction. At the end of the reaction, the flask was removed from the oil bath and the still hot reagents decanted from the flask. Following that, the wood blocks were immersed in acetone 30 min, then transferred to a Soxhlet extractor and extracted using the standard 4:1:1 solvent system for six hours. This was found to be adequate to remove all traces of pyridine, reagent and by-product. After that, samples were oven-dried overnight at 105 °C. The products were stored in the desiccator until cool then weighed and new dimensions determined.

Following measurement, blocks were then vacuum impregnated (six vacuum (98.4 KPa)/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 hours, in order to ensure dryness to constant weight. Once fully dry, samples were again measured and re-weighed. This procedure was repeated for a total of ten oven-dry (OD) water-soak (WS) cycles.

The volumetric swelling coefficients were calculated according to the well known formula by Stamm (1964):

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

where

V_w = volume of water saturated wood.

V_d = volume of oven-dry wood.

The anti-shrink efficiency was calculated according to:

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

where

S_c = volumetric swelling coefficient of control (unmodified samples).

S_m = volumetric swelling coefficient of modified samples.

The S_c value was obtained from the average of four sample sets (i.e. 20 replicates).

Molar volumes (cm^3 per mole) were calculated according to:

$$M_v = \frac{(V_m - V_u)}{M}$$

where

V_m = volume of modified samples

V_u = volume of unmodified samples

M = number of moles of adduct (= [weight gain in gms]/molecular weight of adduct).

Results and discussion

Volume change due to modification

Figure 1 shows the reaction scheme for pyridine catalysed reaction of crotonic anhydride (CA) with wood. When the chemical reacts with wood, it causes an increase in volume proportional to the weight gain. For reaction periods up to 72 hours, CA modified Corsican and Scots pine samples gave maximum weight gains around 42.6% and 43.3% at 120 °C and 27.3% and 27.4% at 60 °C, respectively. In Fig. 2, the relationship between percentage volume change (VPC) due to modification and weight percent gain for Corsican pine modified at 120 °C (squares) and 60 °C (circles) is shown. At both reaction temperatures, the same relationship between volume change and weight percent gain is observed. The line represents the best fit through the data points. It can be seen that an approximately linear relationship exists between the two parameters apart from at low (below 10%) and high WPG's (above 35%). This relationship has been observed with other linear chain anhydrides (Hill and Jones 1999). At higher WPG's the possibility that degradation of the substrate is occurring at 120 °C allows for the possibility of new reactive sites becoming available for reaction resulting in the non-linear relationship between VPC and WPG. The non-linear relationship at low WPG's is not readily explained and will be dealt with later.

With Scots pine, different behaviour was observed (Fig. 3). A larger volume expansion occurs with samples modified at 120 °C compared with samples

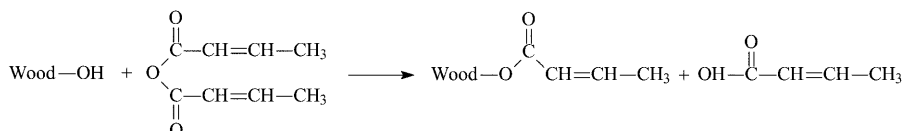


Fig. 1. Reaction scheme for modification of wood with crotonic anhydrides

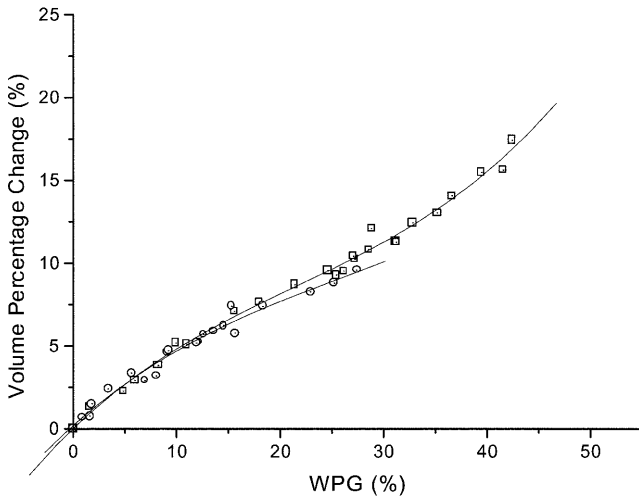


Fig. 2. The relationship between volume percentage change (%) and weight percentage gain (%) of crotonic anhydride modified Corsican pine at 60 °C (circles) and 120 °C (squares)

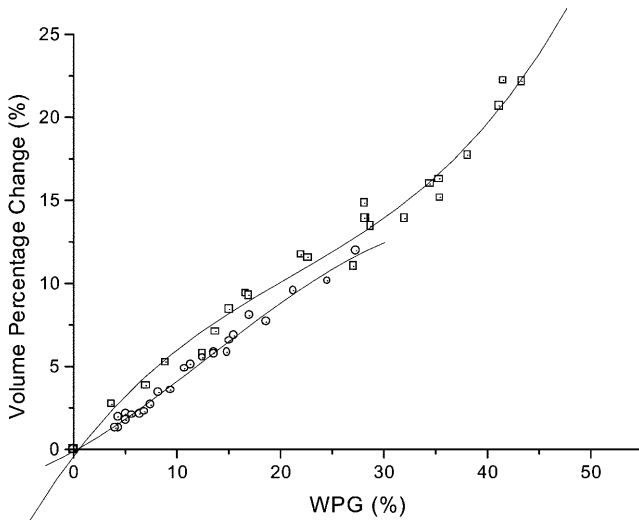


Fig. 3. The relationship between volume percentage change (%) and weight percentage gain (%) of crotonic anhydride modified Scots pine at 60 °C (circles) and 120 °C (squares)

modified to comparable WPG's at 60 °C. As with Corsican pine, a deviation from linear behaviour is noted at WPG's in excess of 30% and a VPC of 15% (which corresponds to the green volume of the samples). Again, this is due to substrate degradation occurring at these high levels of substitution. At lower weight gains a non-linear relationship is also observed, but the behaviour is different with modifications at the two temperatures.

In order to determine the volume occupied by the reagent in the wood cell wall, the data were plotted in terms of molar volume versus WPG. The molar volumes (cm^3 per mole) were calculated by the volume increase due to modification by

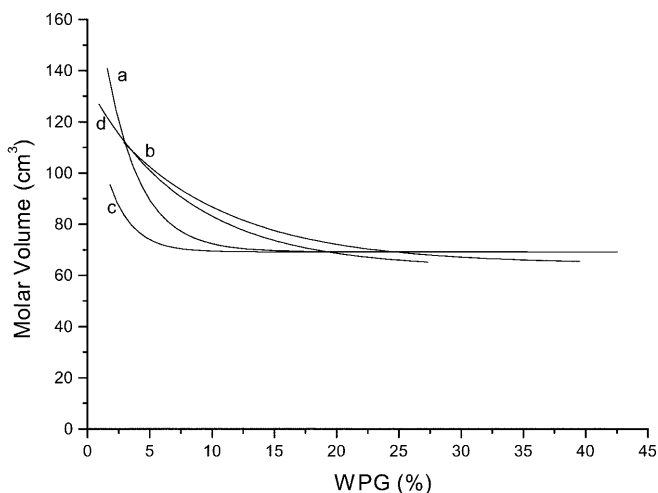


Fig. 4. Variation in molar volume with weight percent gain for Corsican pine modified with crotonic anhydride at 120 °C (a), 100 °C (b), 80 °C (c), 60 °C (d)

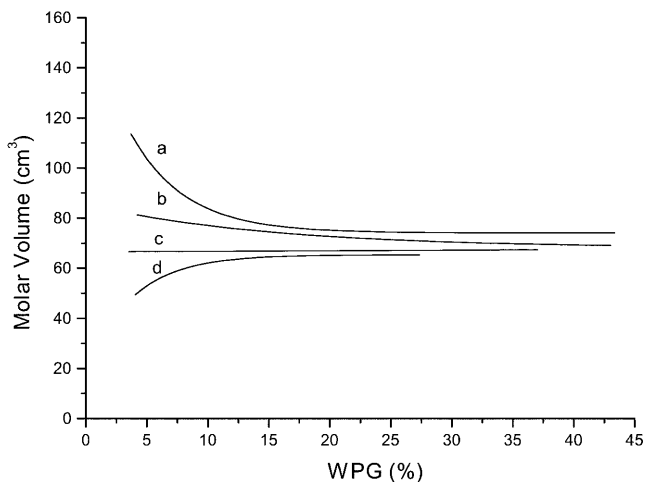


Fig. 5. Variation in molar volume with weight percent gain for Scots pine modified with crotonic anhydride at 120 °C (a), 100 °C (b), 80 °C (c), 60 °C (d)

dividing the number of moles of adduct. This value represents the volume occupied by one mole of reagent in the samples. Figures 4 and 5 show molar volumes for different WPG levels of crotonic anhydride modified Scots and Corsican pine samples at 60 °C, 80 °C, 100 °C and 120 °C, respectively. The lines represent the best fit through the data points. Two different types of behaviour were observed for the two species in this investigation. With Corsican pine (Fig. 4), modification yielded larger volume increases (molar volumes) at lower levels of substitution. This has previously been noted for modification of Corsican pine with other linear chain anhydrides (Hill and Jones 1996). In this work, it was additionally noted that reaction temperature also affected the volume increase of

samples due to modification. Reaction at 120 °C, 100 °C and 60 °C yielded curves which exhibited similar behaviour, but reaction at 80 °C resulted in lower volume increases (molar volumes) than observed at the other temperatures. Above WPG of ca. 15% all of the curves begin to fall much closer to one another. An ultimate molar volume of 68.4 cm³ per mole of adduct is finally realised. The corresponding value for butyric anhydride, which has the same number of attached carbon atoms, and differs only in the respect that it has no double bond is 81.2 cm³.

With Scots pine, significantly different behaviour is observed (Fig. 5). Modification at 120 °C leads to larger molar volumes being obtained at low WPG's as observed with Corsican pine. However, at lower reaction temperatures of 100 °C and 80 °C the molar volumes obtained at low WPG's are very close to those obtained at higher WPG's. At 60 °C lower molar volumes are obtained at low WPG's. Thus the volume occupied by reagent in the Scots pine samples is temperature dependent at low WPG. Two reasons may be postulated for this behaviour. Firstly there may be ultra-structural differences between the two woods which lead to differences in the accessibility of reactive sites to reagent, or to differences in the way that the wood responds to the modification. Secondly the difference in density of the wood between the two sample sets (0.407 g/cm³ Corsican pine, 0.465 g/cm³ Scots pine) may be affecting behaviour.

The location of reagent within the wood depends upon the rate of reaction of the chemicals with the active sites and upon the rate of diffusion of the reagent to the sites. This has been shown to affect the reaction kinetics (Hill et al. 1998). It has further been shown that at low levels of substitution, the S₂ layer of the wood cell wall shows higher levels of adduct than the middle lamella (Rowell et al. 1994). If the reaction is under diffusion control, then the density of the substrate would affect the distribution of substitution, with regions of higher density exhibiting lower levels of substitution during the initial stages of the reaction. With acetic anhydride, the reaction kinetics have been shown to be diffusion controlled (Hill et al. 1998), hence regions of lower density would exhibit higher levels of substitution initially. With longer chain anhydrides the reaction kinetics are more complex, exhibiting a mixture of diffusion and chemical kinetic processes. The temperature dependence of the relative rates of diffusion and chemical reaction will be related to the activation energies of the two processes. If initially the reaction occurs with surface groups only, then lower volume changes of the substrate would be expected than later in the reaction, since the reagent will not be located within the cell wall. This may explain why lower volume changes occur when Scots pine is modified at 60 °C. As the temperature of the reaction increases the diffusion of reagent into the substrate assumes greater importance, with regions of low density reacting to a greater extent. Although the above remains speculative at present, it is clear that the volume behaviour of samples when modified at different temperatures is a complex process and worthy of further investigation. It should be further noted that with both Scots and Corsican pine samples, the same molar volume is occupied by reagent at higher WPG's (70.6 cm³ for Scots pine).

Dimensional stabilisation due to modification

In order to determine the effect of modification with crotonic anhydride upon dimensional stability, samples were subjected to water-soak (5 days) and oven-dry (3 days) tests. For the water-soak/oven-dry (ws/od) cycle test, modified samples were chosen with weight gains of approximately 5 to 30% and 5 to 40%,

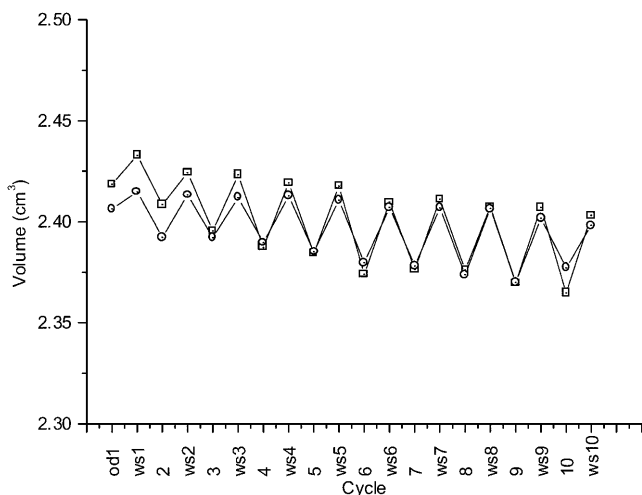


Fig. 6. Change in water-saturated and oven-dry volumes for crotonic modified samples at 120 °C, Corsican pine at WPG 41.6% (circles), Scots pine at WPG 41.5% (squares)

with ca. 5% weight gain intervals for blocks modified at 60 °C and 120 °C, respectively. As stated earlier (Hill and Jones 1996), there is a close positive correlation between water saturated volumes and the ambient temperature of the laboratory. To prevent such temperature fluctuations, the temperature of the laboratory was kept constant at around 18 ± 2 °C by using a thermostat heater. Nearly half of the control Scots pine samples (7 out of 20 samples) did not complete the full ten cycles, serious checking and splitting occurring after as few as 3 cycles. Two of the control Corsican pine samples did not complete the ten cycles.

As can be seen from Fig. 6, chemical treatment is very effective at providing dimensional stability. Control Corsican and Scots pine samples exhibited different swelling coefficients (10% and 14%, respectively). The reason for this difference may be attributed to difference in density of Corsican and Scots pine samples, since Scots pine samples had slightly higher density than Corsican pine samples. As reported earlier (Stamm 1964) denser wood shows a higher swelling ratio than less dense wood. Both oven-dry and water-soak volumes of modified samples exhibit a decrease as the test proceeds. However, there was not a decrease in dimensional stability associated with this change. The only exception to this was a significant difference in dimensional stability between cycle 1 and all subsequent cycles. Such observations have been noted previously with linear chain anhydrides (Hill and Jones 1996). The difference between cycle 1 and subsequent cycles has been attributed to loss of non-bonded reagent (Rowell and Ellis 1978) or to an annealing process due to rearrangement of the molecular chains of the adduct during the water-soaking cycle (Hill and Jones 1996). The decrease in volumes during cycling is related to loss of material from the wood, presumably due to the high temperature of the oven-drying phase leading to degradation of the hemicellulosic content, resulting in water leachable fragments. It is interesting to note that an inverse relationship occurs between cumulative weight loss during the 10 cycles and level of substitution (Table 1). Thus modification appears to offer protection against thermal degradation, or the thermo-

Table 1. Total weight loss (g) for CA treated Corsican and Scots pine at 60 °C and 120 °C with successive water-soak/oven-dry cycles, compared with unmodified wood (control)

Corsican 60 °C									
WPG	Control	5.63	9.2	15.3	18.34	25.25	27.39		
WL (g)	0.0441	0.0237	0.0189	0.0172	0.0136	0.0079	0.0065		
Corsican 120 °C									
WPG		4.85	9.95	15.59	21.44	25.47	31.23	35.8	41.56
WL (g)		0.0301	0.0189	0.0121	0.0180	0.0180	0.0067	0.0084	0.0065
Scots 60 °C									
WPG	Control	5.02	10.73	15.52	21.24	24.54	27.34		
WL (g)	0.0695	0.0313	0.0223	0.0182	0.0108	0.0122	0.0139		
Scots 120 °C									
WPG		3.7	8.91	15.06	22.01	27.06	28.75	35.25	41.55
WL (g)		0.0715	0.0221	0.0199	0.0146	0.0114	0.0094	0.0095	0.0090

WPG = Weight percent gain (%); WL = Weight loss (gram)

formed fragments may not be so readily water soluble due to increased hydrophobicity from such modification.

Volumetric swelling coefficient values (S %) and anti-shrink efficiency (ASE %) results

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 also been noted. However, in these experiments, only slight fluctuations between cycles were noted (although cycle 1 was an exception). The S % values were averaged over the last nine cycles and Fig. 7 shows the relationship between averaged S % values and WPG of CA modified Corsican and Scots pine blocks. It can be seen from Fig. 7 that CA modified Corsican pine samples at 60 °C and 120 °C gave similar S % values at comparable WPG's. However, with Scots pine different behaviour is again noted with the two different reaction temperatures. Again, whether such variations are the result of ultra-structural or density differences between the two woods is not known.

In order to take some account of the differences between the swelling coefficients of the control samples of the two wood species, the data has also been plotted in terms of anti-shrink efficiency (ASE) versus WPG. Figure 8 illustrates the relationship between the anti-shrink efficiency and WPG for the samples investigated. The curves show asymptotic behaviour. In our results, about 41% weight gain were obtained with extended reaction time (72 hours) for CA modified Corsican and Scots pine samples. The curve has essentially become a plateau at an ASE value of ca. 90%, in agreement with similar results reported in the previous publication concerning modification with other anhydrides (Hill and Jones 1996).

It was stated (Rowell et al. 1976) that with epoxide modified southern pine samples the maximum (60–70%) ASE was obtained with weight gains of 20–33%. But when weight gain was above 33%, ASE started to decrease. It was suggested that the drop in ASE might be due to the volume of added chemical becoming

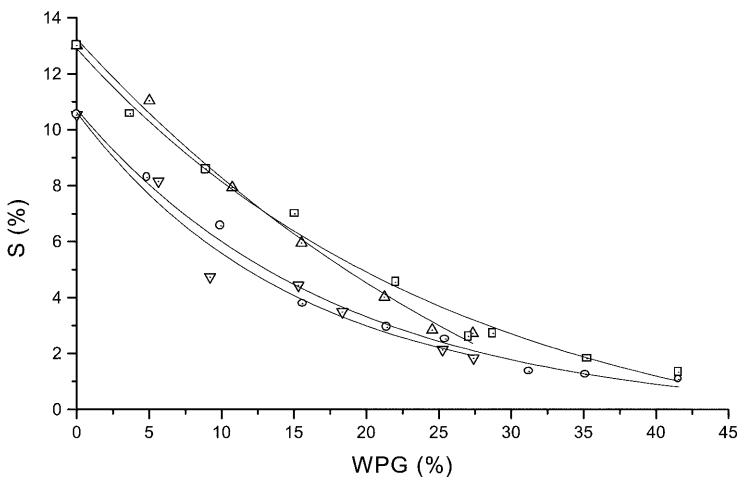


Fig. 7. Comparison of average swelling coefficient (S%) of crotonic modified Corsican and Scots pine samples at 60 °C and 120 °C, Corsican modified at 60 °C (down triangles) and at 120 °C (circles), Scots modified at 60 °C (up triangles) and at 120 °C (squares)

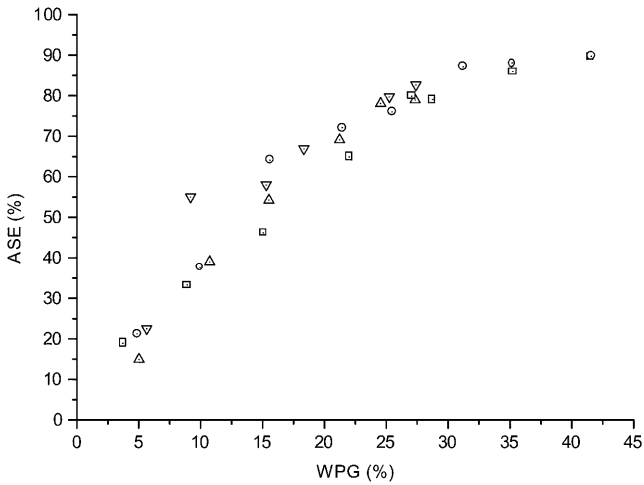


Fig. 8. ASE (%) of crotonic modified Corsican and Scots pine at 60 °C and 120 °C, Corsican modified at 60 °C (down triangles) and at 120 °C (circles), Scots modified at 60 °C (up triangles) and at 120 °C (squares)

great enough to rupture the cell wall. This is because the wood is swollen above the green volume and this expansion causes a break-up of the wood structure which leads to the creation of new hydrophilic sites.

It is possible to assume that even high chemical add-on causes swelling to beyond the green volume of wood, breaking up of the wood structure, and creation of new hydrophilic sites. These new sites react with unreacted excess reagent present in the reaction environment and create hydrophobic sites. This damage to the wood structure does not effect S % or ASE values, although it may deteriorate the strength and tensile properties, a question which is under investigation at present.

Conclusion

Corsican pine samples modified with crotonic anhydride exhibited larger volume changes (molar volumes) at low WPG's. With Scots pine the observed volume changes at low WPG's were related to the temperature of the reaction. This difference in behaviour may be ultra-structural in origin or due to the difference between the densities of the samples. Effective dimensional stabilisation of wood can be obtained by CA modification (ca. 90% ASE). The effect of modification temperature on dimensional stability does not appear to be significant, as long as same weight gain levels are obtained. Reaction with Scots pine at 120 °C did, however, provide a lower level of dimensional stabilisation than with the other samples tested. It is apparent that high weight level samples still gave high ASE's contradicting earlier work (Rowell et al. 1976).

References

- Banks WB, Lawther JM** (1994) Derivatization of wood in composites. In: Gilbert RD (ed) Cellulosic Polymers Blends and Composites. pp. 131–155. Cincinnati, Munich, Vienna, New York: Hanser/Gardner publications, Inc.
- Hill CAS, Jones D** (1996) The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length. *Holzforschung* 50: 457–462

- Hill CAS, Jones D** (1999) Dimensional changes in Corsican pine sapwood due to chemical modification with linear chain anhydrides. *Holzforschung* 53: 267-271
- Hill CAS, Jones D, Strickland G, Cetin NS** (1998) Kinetic and mechanistic aspects of the acetylation of wood with acetic anhydride. *Holzforschung* 52: 563-676
- Goldstein IS, Jeroski EB, Lund AE, Nielsen JF, Weaver JW** (1961) Acetylation of wood in lumber thickness. *Forest Prod J* 11: 363-370
- Kumar S** (1994) Chemical modification of wood. *Wood Fiber Sci* 26(2): 270-280
- Rowell RM** (1983) Chemical modification of wood. *For Prod Abstr* 6: 363-382
- Rowell RM, Gutzmer DI, Sachs IB, Kinney, RE** (1976) Effect of alkylene oxide treatments on dimensional stability of wood. *Wood Sci* 9: 51-54
- Rowell RM, Ellis WD** (1978) Determination of dimensional stabilization of wood using the water soak method. *Wood and Fibre* 10: 104-111
- Rowell RM, Banks WB** (1985) Water repellency and dimensional stability of wood. US Dep. of Agr. Forest. Sci. Forest. Prod. Lab. General Tech. Report FPL-50: 1-21
- Rowell RM, Simonsen R, Hess S, Plackett DV, Cronshaw D, Dunningham E** (1994) Acetyl distribution in acetylated whole wood and reactivity of isolated cell wall components to acetic anhydride. *Wood and Fiber Sci* 26: 11-18
- Stamm AJ** (1964) *Wood and Cellulose Science*. Ronald Press Co., New York
- Stamm AJ, Tarkow H** (1947) Dimensional stabilisation of wood. *J Phys Colloid Sci* 51: 493-505