Mechanical properties, physical properties and fungal resistance of acetylated fast grown softwoods

I Small specimens

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Abstract

Small samples of Sitka spruce (*Picea sitchensis*), lodgepole pine (Pinus contorta) and Japanese larch (*Larix leptolepis*) selected from normal commercial stock have been acetylated using the facilities of Stichting Hout Research in the Netherlands. The weight percent gains (WPG) used were 14% and 17% with the spruce, 16% and 19% with the pine and 17% with the larch. The acetylated materials were subject to three point bending to evaluate mechanical property change, three cycle anti-shrink efficiency (ASE) testing, equilibrium moisture content measurement and fungal resistance assessment using *Coniophora puteana*. Mechanical properties showed no significant change following acetylation. Equilibrium moisture contents were much reduced, although there was little difference between the pine at 16WPG and 19WPG. The repeated wetting and drying cycles of the ASE tests indicated that the chemical modification was permanent and the fungal tests showed very significant improvement in durability. Taken overall the results are mostly consistent with those obtained using slower grown Northern European softwoods, and substantiate the property improvement claims made for the acetylation process.

Keywords

Acetylation, chemical modification, fast grown softwood, anti-shrink, efficiency, fungal durability.

Introduction

A previous publication (Birkinshaw 2000) has reviewed the processes for chemical modification of wood and the potential benefits available to Irish timber through modification. It is the intention here to give some preliminary results arising from an experimental project investigating the modification of Sitka spruce (*Picea sitchensis*), lodgepole pine (*Pinus contorta*) and Japanese larch (*Larix leptolepis*). The modification method used was acetylation, which was commissioned in the Netherlands, with the mechanical and physical testing carried out in the University of Limerick and the fungal decay work in the University of Wales, Bangor.

Chemical modification of wood is usually based on treating the wood with reagents which convert the moisture attracting hydroxyl groups on the hemicellulose, cellulose and lignin into more hydrophobic structures. It is well known that the mechanical and physical properties of wood are very dependent on the presence of these hydroxyl groups and their interaction with water, and therefore anything which blocks or removes them will change the properties of the wood. Acetylation, which has been used here, relies on reaction of

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the wood with acetic anhydride to convert the wood hydroxyls into acetate groups (Rowell et al. 1994). Acetylated wood has a much reduced equilibrium moisture content (Yasuda et al. 1995) and therefore better dimensional stability (Rowell et al. 1993), plus a greatly increased resistance to fungal attack (Suttie et al. 1997, Forster et al. 1997, Beckers et al. 1995). Decay resistance is improved through two factors. First, under ambient conditions and out of ground contact the moisture content of the wood is below that necessary for fungal growth, and second because of blockage of the action of fungally-released degradation catalysts (Forster et al. 1997, Peterson and Thomas 1979). Improvements in photostability (Dawson and Torr 1992) and weather resistance of modified wood and durability of modified wood painted surfaces are also reported (Beckers et al. 1998).

Currently there is much interest in chemical modification processes in Europe as they offer an environmentally acceptable way of achieving high levels of durability, with the added benefit of high dimensional stability under changing humidity conditions. Although modification reagents such as acetic anhydride are moderately hazardous and require careful handling, acetylated wood is non-toxic and can be used and disposed of without any special precautions. The regulatory environment in a number of EU countries is strongly against the continued use of heavy metal preservation systems and questions the continued use of creosote. Additionally there are restrictions on disposal of waste timber treated with CCA and similar materials. This regulatory background provides a strong incentive to develop more acceptable methods of preservation, and chemical modification through acetylation is seen as one of the most promising ways forward.

Stichting Hout Research (SHR), the timber research association, in the Netherlands have recently commissioned a pilot plant capable of treating 0.5 m^3 batches, which is sufficient to allow large scale trials of products made from acetylated wood to be initiated. Acetylation of Irish softwoods was carried out in conjunction with SHR who have considerable expertise in the area. This exercise was necessary because chemical modification efforts in Europe have concentrated on permeable and slower grown Scandinavian or Baltic softwoods and on poplar, and the published information deals with the response of these species. It was clearly important to evaluate the effects of modification processes with fast grown Irish timber and in some instances less permeable timbers and so, with the support of COFORD, a project was initiated to acetylate samples of Sitka spruce, lodgepole pine and Japanese larch. These materials were chosen on the basis of the future supply position and as representative of different permeability/penetration classes.

There were two parts to the evaluation programme. First, modification of small samples to allow mechanical and physical testing and fungal durability to be assessed in specimens which, because of the relatively small size, have received a uniform degree of treatment, and then, secondly to investigate penetration, dimensional stability under treatment and the effectiveness of treatment on samples of commercial cross-section and length. The first part of this work is reported here.

Materials and methods

The timbers evaluated were Sitka spruce (*Picea sitchensis*), lodgepole pine (*Pinus contorta*) and Japanese larch (*Larix leptolepis*), selected from normal commercial stock. Clear specimens were used for the testing in order to comply with the appropriate test standards, but other than this the timber used was not subject to special selection. Therefore it was not possible to reliably differentiate, by either inspection or staining, between heartwood and sapwood in the materials used. From an absolute scientific point of view it would be

Table 1. *Materials investigated (WPG = weight per cent gain caused by reaction).*

Sample code	*Degree of acetylation (WPG)*
Spruce 1	13.8
Spruce 2	16.9
Pine 174	16.4
Pine 177	19.5
Larch 1	17.1

appropriate to examine sapwood and heartwood separately, but this would require the selection of non-typical timber.

Modification of the prepared test specimens was carried out by SHR using their established procedure. This involved vacuum impregnation with acetic anhydride followed by heating to promote reaction. The acetylation reaction is exothermic and heat is only required for initiation of the process. Un-reacted anhydride and acetic acid by-product are removed by vacuum. The process was conducted to give a range of levels of modification (expressed in terms of weight per cent gain) (Table 1). As the pine and spruce were deemed the more important materials two levels of acetylation were used with them.

Acetylated samples were tested according to the following standards. Modulus of rupture and modulus of elasticity (MOR and MOE) were tested by three point bending to EN310 using specimens 350 x 20 x 20 mm. Prior to testing samples were conditioned at 20°C and 65% RH. Approximately 20 specimens of each type were tested with equal numbers being stressed in the radial and tangential directions. Fracture surfaces were examined by scanning electron microscopy.

Adsorption isotherms were measured according to the procedure of Martins and Banks (1991), by exposure of oven dried samples, 5 x 20 x 20 mm (longitudinal, radial, tangential), to seven different relative humidities over different types of saturated salt solutions at 20°C until constant weight was obtained. Five specimens of each type were used.

Anti-shrink efficiency (ASE) and treatment stability was obtained by comparing the swelling of the modified material with that of a control as the materials are cycled between oven dry and water saturated (Stamm 1964):

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

where S_C and S_m are the volumetric swelling, in percent, of the control and the modified materials respectively, and are given by:

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

where V_W and V_d are the wet and dry volumes.

Three cycles of water soaking for five days followed by oven drying at 105°C for two days were used. The specimens size was 5 x 20 x 20 mm (longitudinal, radial, tangential) and

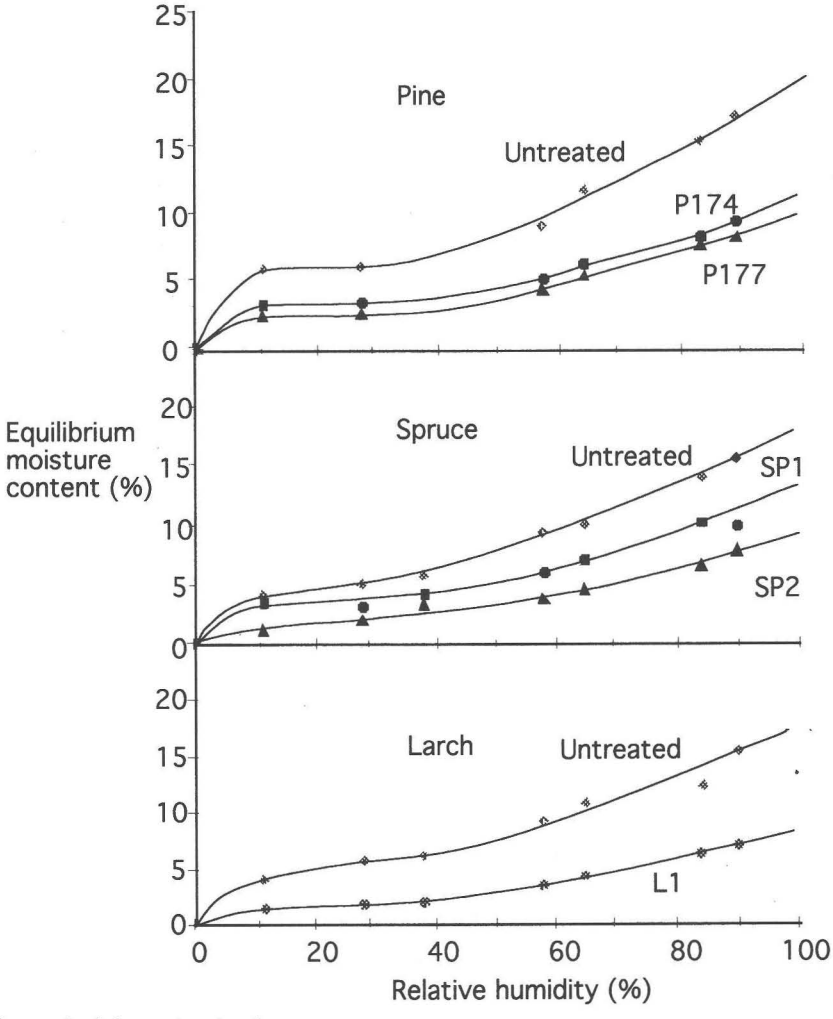

Figure 1. *Adsorption isotherms.*

again five specimens of each type were used.

Decay resistance was assessed by exposure to the brown rot fungus, *Coniophora puteana* (strain, BAM EB15) over 4% malt agar in 150 mm pre-sterilised round plastic Petri-dishes (Corning). Plates were inoculated with the fungus and incubated for 2 weeks at 22°C and then irradiation sterilised (2.5 Mrad) modified and unmodified wood blocks (each nominally 5 x 10 x 100 mm, tangential, radial, longitudinal) were planted, five per Petri-dish, onto the growing cultures. The blocks were separated from the agar by supporting them on an autoclave sterilised high density polyethylene mesh (7 mm mesh spacing). A control set of Petri-dishes, without fungus, was also included for comparison.

Table 2. *Modulus of rupture (MOR) and modulus of elasticity (MOE) results.*

Material	*MOR*	*MOE*
	MPa (standard deviation)	
Spruce		
unmodified	2.81 (0.15)	5.40 (1.28)
13.8 WPG	2.92 (0.55)	5.06 (1.31)
16.9WPG	3.14 (0.60)	6.20 (1.16)
Pine		
unmodified	3.36 (0.40)	5.87 (0.66)
16.4 WPG	4.01 (0.39)	6.71 (0.77)
19.5 WPG	3.81 (0.60)	6.00 (0.64)
Larch		
unmodified	3.78 (0.62)	8.21 (1.98)
17.1 WPG	3.06 (0.92)	6.37 (2.20)

The blocks were incubated for a further 12 weeks at 22°C, 70% RH. For the spruce and larch tests 10 blocks per acetylation level were tested but for the pine 20 were tested. The decay was primarily assessed by weight loss; this was achieved by comparison of the initial oven dry weights and oven dry weights after exposure and expressed as percentage weight loss. The moisture content at the end of the test was also assessed and results were calculated to give moisture contents on a percentage dry weight basis. Blocks which were waterlogged through making contact with the agar were excluded for the purposes of data comparison.

Results and discussion

The adsorption isotherms (Figure 1) show reductions in equilibrium moisture content for all three modified timbers at all relative humidities. The form of the isotherms is generally similar to that reported by others (Yasuda et al. 1995). Under ambient conditions the treated materials contain about half the moisture content of the untreated controls, and with the pine and the spruce, where two degrees of acetylation were used, increasing the degree of acetylation slightly reduces the equilibrium moisture content. However the effect of increasing the degree of acetylation is relatively small, particularly with the pine. This is somewhat different to the European experience.

From the mechanical property results (Table 2) it is apparent that both the pine and the spruce show some increase in stiffness and strength following acetylation, while the larch shows a drop in both of these properties. Comparison of scanning electron micrographs of fracture surfaces of the acetylated materials and the controls showed no differences in the mechanisms of fracture. In interpreting these results two considerations have to be borne in mind. First, in all cases the standard deviations are large, presumably because of the relatively coarse character of the materials relative to the sample cross-sections,

Table 3. *Anti shrink efficiency as a function of wetting and drying cycles.*

Material	*1st cycle*	*2nd cycle*	*3rd cycle*
		%	
Spruce 13.8 WPG	54.17	48.85	60.34
Spruce 16.9 WPG	62.06	52.42	72.97
Pine 16.4 WPG	55.63	51.58	73.17
Pine 19.5 WPG	60.09	49.61	70.55
Larch 17.1 WPG	62.08	61.63	72.12

Table 4. *Weight loss (%) and final moisture content (% dry weight basis) of modified and unmodified blocks exposed to Coniophora puteana and their sterile controls. (Standard deviations given in brackets).*

Material	*Coniophora puteana*			Sterile Controls		
	Repli-cates	*Moisture content* %	*Weight loss*	*Repli-cates*	*Moisture content* %	*Weight loss*
Spruce						
Unmodified	8	82 (10.63)	39.8 (2.34)	10	33 (1.64)	-0.1 (0.15)
13.8 WPG	6	86 (11.50)	1.19 (1.42)	7	31 (4.53)	0.41 (0.11)
16.9 WPG	7	46 (10.13)	-0.86 (0.04)	10	18 (2.62)	0 (0.16)
Pine						
Unmodified	5	75 (4.25)	36.5 (2.71)	9	45 (3.93)	-0.18 (0.29)
16.4 WPG	20	61 (10.63)	6 (7.29)	12	25 (1.88)	0.21 (0.13)
	6	62 (5.65)	15.07 (6.78)			
19.5 WPG	20	53 (17.60)	-0.07 (1.00)	16	22 (4.98)	0.12 (0.16)
	16	50 (14.88)	1.05 (0.08)	16	20 (2.46)	0.15 (0.12)
Larch						
Unmodified	10	60 (11.20)	17 (11.19)	10	37 (4.16)	0.2 (0.05)
	7	61 (10.84)	23.24 (6.62)	10	37 (4.16)	0.2 (0.05)
17.1 WPG	10	45 (20.13)	-0.3 (1.16)	10	18 (2.72)	0.4 (0.25)
	8	37 (9.75)	0.12 (0.38)	10	18 (2.72)	0.4 (0.25)

and therefore small changes in properties following modification should not be treated as significant. Second, all materials were subject to the same pre-testing conditioning routine and, as the adsorption isotherms indicate, this means that the moisture content at the time of testing was much lower in the acetylated materials. Absorbed water has a plasticising effect, reducing stiffness, and so the predominant trend towards greater stiffness after acetylation can, almost certainly, be ascribed to the lower equilibrium moisture content. However some reduction in mechanical properties may have occurred because of acetic acid hydrolysis of the cellulose, but this effect is likely to be small relative to the influence of moisture content. Overall the results indicate that acetylation has no significant adverse effect on mechanical properties.

Significant improvements in the anti-shrink efficiency are apparent (Table 3) with the acetylated materials; in all cases the swelling of saturated acetylated samples is less than half that of the controls. Again though, in comparing pine at 16.4 WPG with pine at 19.5 WPG, there seems to be little additional advantage from the higher degree of acetylation. With the spruce, differences in the degree of acetylation have a more pronounced effect.

The anti-shrink efficiency remains relatively constant through the repeat wetting and drying experiments (Figure 2), suggesting that the acetylation is stable within the limits of the experiment and again this is consistent with the experience obtained with more permeable timbers and with wood composites (Larsson and Tillman 1989, Hill and Jones 1996). This result confirms that the modifying reagent is chemically bound to the lignocellulosic materials of the wood. This effect is an important improvement in wood properties.

The untreated spruce and pine test pieces showed high decay giving average weight losses of 40 and 37% respectively (Table 4). The weight losses with the larch were somewhat less (average 17%) but showed greater variation (SD = 11.2) and three of the blocks showed very little decay, presumably an effect of heartwood durability.

Acetylation reduced decay at the lower level of modification in both spruce and pine but unexpectedly it was much more effective in the spruce (only 1.2% weight loss at 13.8 WPG in spruce compared to 6% at 16.4 WPG in pine). At the 13.8 WPG level only one of the ten spruce blocks showed any signs of decay whereas at 16.4 WPG seven of the twenty pine blocks showed appreciable decay and an average of the six most decayed pine blocks was 15% (SD = 6.8). At the higher levels of modification all blocks showed good protection and no decay was noted, although it is interesting to note that the spruce was protected at a modification which was close to that which failed in pine (spruce 16.9 WPG, pine 16.4 WPG). This difference is attributed to different distribution patterns of the modification such that spruce would be expected to show higher modification at the wood surfaces due to its lower overall permeability; alternatively the lower density of the spruce, i.e. thinner cell walls may have had an influence on this.

In the sterile controls of the decay test the final moisture contents of the blocks, which represents the equilibrium moisture content of the wood blocks over agar, reduced dramatically with increasing level of acetylation. This effect was apparent with the decayed blocks but at the lower level of modification in spruce there was no difference in moisture content to the untreated control blocks.

Comparison of the anti-shrink efficiency (Table 3) with the decay results (Table 4) shows that decay can be controlled at levels of modification which do not entirely reduce swelling.

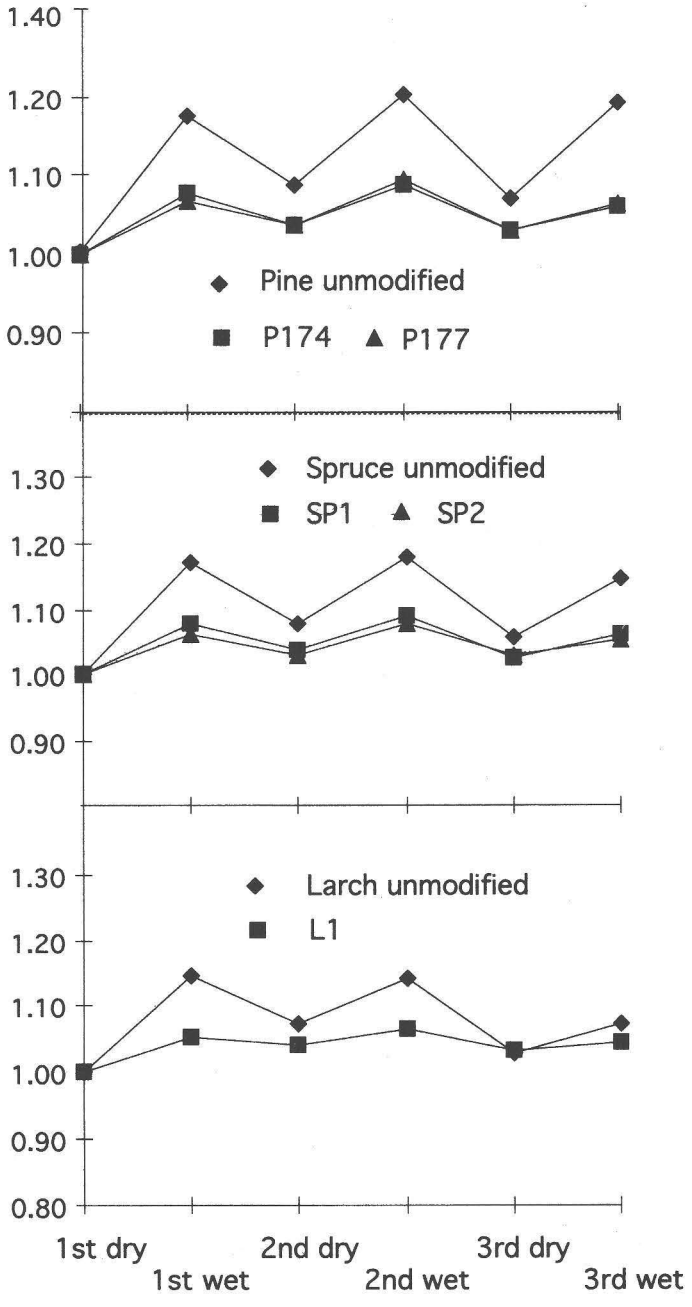

Figure 2. *Swelling stability results. The vertical ordinate shows the relative volume change.*

Conclusions

Mechanical and physical test results obtained with the acetylated materials are broadly in line with what was expected from the European experience.

The most surprising result is that increasing the degree of acetylation of the pine from 16 WPG to 19 WPG has relatively little effect on the moisture absorption behaviour. In all cases the scatter in the results was large. The scatter is thought to arise from two factors. First, the relatively coarse nature of the timber arising from the fast growth and wide ring spacing, and secondly there is the probability that the samples tested contained both heartwood and sapwood. This would affect both the response to acetylation and the subsequent response to moisture change in the acetylated materials. Despite these factors it is considered that the overall pattern of results obtained is reliable.

The results from the fungal decay experiments have demonstrated the increased durability expected but the better performance of the spruce than the pine was surprising given that in the untreated condition it was less durable, and that it is regarded as less permeable to reagents.

Overall the results confirm that the acetylation process offers benefit with the materials examined. It is now necessary to proceed with acetylation experiments using specimens of commercial cross-section.

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