ACETYLATION OF WOOD USING SUPERCRITICAL CARBON DIOXIDE

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Received August 2014

MATSUNAGA M, HEWAGE DC, KATAOKA Y, ISHIKAWA A, KOBAYASHI M & KIGUCHI M. 2016. **Acetylation of wood using supercritical carbon dioxide.** This study investigated the effects of acetylation using supercritical carbon dioxide (CO_2) on dimensional stability of four wood species grown in Sri Lanka. Heartwood specimens of *Paraserianthes falcata*, *Alstonia macrophylla*, *Pinus caribaea* and *Hevea brasiliensis* were acetylated with acetic anhydride using supercritical CO_2 (120 °C, 10–12 MPa), and their dimensional stability was evaluated. Results showed that anti-swelling efficiency values of the wood species increased to over 60% after 8 hours of acetylation. In particular, *A. macrophylla* exhibited a relatively high anti-swelling efficiency. High anti-swelling efficiency of *A. macrophylla* was caused by the large swelling of this high specific gravity wood.

Keywords: *Paraserianthes falcata*, *Alstonia macrophylla*, *Pinus caribaea*, *Hevea brasiliensis*, dimensional stability, weight per cent gain, bulking, anti-swelling efficiency

INTRODUCTION

It is well known that acetylation is one of the preferred methods of chemical modification for improving wood properties such as dimensional stability and resistance to biological degradation. Acetylation substitutes the hydroxyl groups of wood components with acetyl groups and decreases adsorption and desorption of water. The process consequently decreases the hygroscopicity of the treated wood and improves dimensional stability against the effects of water. Acetylated wood also has high weathering resistance and termite resistant properties (Rowell et al. 1983). Acetylation suppresses variations in the mechanical, rheological and acoustical properties of wood that occur because of humidity change (Norimoto et al. 1987, Sasaki et al. 1988). Acetylation has been re-evaluated in recent years because of its low negative environmental impact, and acetylated wood has found a multitude of applications such as exterior cladding, decking, louvers and kitchen tables.

Acetylation of *Cryptomeria japonica* heartwood showed that high dimensional stability could be obtained in short acetylation time (Matsunaga et al. 2010b, 2014). In this study, a new method of acetylation, which used supercritical carbon dioxide (CO_2, critical point: 31°C at 7.4 MPa), was used to improve selected wood properties. Supercritical CO_2 diffuses and penetrates like gas but has solvating properties similar to those of liquid. This solvent has already been used for extracting caffeine from coffee beans and for hop extraction for beer production. Studies regarding the application of wood using supercritical CO_2 have been reported, namely, improving water permeability (Matsunaga et al. 2005), penetration of wood preservatives (Matsunaga et al. 2007) and dewatering green wood (Matsunaga et al. 2010a, 2012a), From these studies, the ability of supercritical CO_2 to penetrate wood has been shown to be useful in extractives, preservative and dewatering treatments. Therefore, it is expected that an acetylation reagent can be made to penetrate wood using supercritical CO_2 as solvent and, thus, facilitate the acetylation process.

This new method of acetylation was used in the present study to improve dimensional stability of four wood species from Sri Lanka that have not been effectively utilised. The wood was acetylated using supercritical CO_2, and the weight per cent gain, per cent increase in oven-dry volume (bulking) and anti-swelling efficiency were measured. Performance of the acetylated wood was analysed and the effectiveness of the method, discussed.

MATERIALS AND METHODS

Materials

Heartwood specimens measuring 5 mm (longitudinal direction) × 20 mm (radial) × 20 mm (tangential) were prepared from four species of wood grown in Sri Lanka, namely, *Paraserianthes falcata*, *Alstonia macrophylla*, *Pinus caribaea* and *Hevea brasiliensis*. Similar size specimens were prepared from the heartwood of *C. japonica* to compare the results of acetylation using supercritical CO_2. The specimens were extracted with ethanol/benzene (v/v = 1:2) for 8 hours using Soxhlet extractor and then boiled in water under reflux for another 8 hours. Table 1 lists the specific gravity of the wood samples under oven-dry condition after extraction and the mean extractives content of each wood species.

Acetylation of wood in supercritical CO_2

Figure 1 shows a schematic diagram of the supercritical CO_2 treatment apparatus and the interior of the reaction container. Two oven-dried specimens of each wood species (totalling 10 specimens) and 0.12 mL of acetic anhydride (> 97.0% purity) per litre of supercritical CO_2 were sealed in a batch container (inner diameter 80 mm and height 180 mm). The interior of the container was evacuated for 10 min using aspirator and filled with CO_2 (> 99.9% purity) that was directly transferred into the container from a gas cylinder under internal pressure of 6.0 MPa. Before attaining internal pressure of 6.0 MPa, cooled and liquefied CO_2 was injected into the container. A pump was used to raise the pressure up to 6.0 MPa. Temperature was raised and controlled at 120 °C using electric heater installed on the container exterior. During this time, internal pressure of the container reached 10.0–12.0 MPa within 35–40 min. Acetylation time was defined as zero when internal temperature of the container reached 120 °C. Acetylation process was then performed while stirring at 300 rpm using magnetic stirrer for 2, 4 or 8 hours. There were six treated specimens for each species of wood.

Measurement of weight per cent gain, bulking and anti-swelling efficiency

Weight per cent gain, bulking and anti-swelling efficiency were used as essential parameters for characterisation of acetylated wood. These values were calculated according to the following process. Acetylated specimens were leached in running water for 1 week. After air drying at room temperature, the specimens were oven dried at 60 °C under vacuum for 48 hours. Oven-dry weight and dimensions of the specimens were measured, and weight per cent gain and bulking were calculated using equations 1 and 2 respectively.

$$\text{Weight per cent gain} = (W_1 - W_0)/W_0 \times 100 \quad (1)$$

$$\text{Bulking (\%)} = (V_1 - V_0)/V_0 \times 100 \quad (2)$$

where W_0 and W_1 = oven-dry weights of specimens before and after acetylation respectively and V_0

Table 1 Mean values of specific gravity, extractives content and swelling coefficient of wood species after acetylation using supercritical CO_2

Species	Specific gravity (n = 6)	% Extractives content (n = 6)	% Swelling coefficient (n = 2)
Paraserianthes falcata	0.325	3.17	13.2
Alstonia macrophylla	0.605	2.72	17.3
Pinus caribaea	0.477	2.47	10.2
Hevea brasiliensis	0.543	1.47	15.7
Cryptomeria japonica	0.334	3.17	12.8

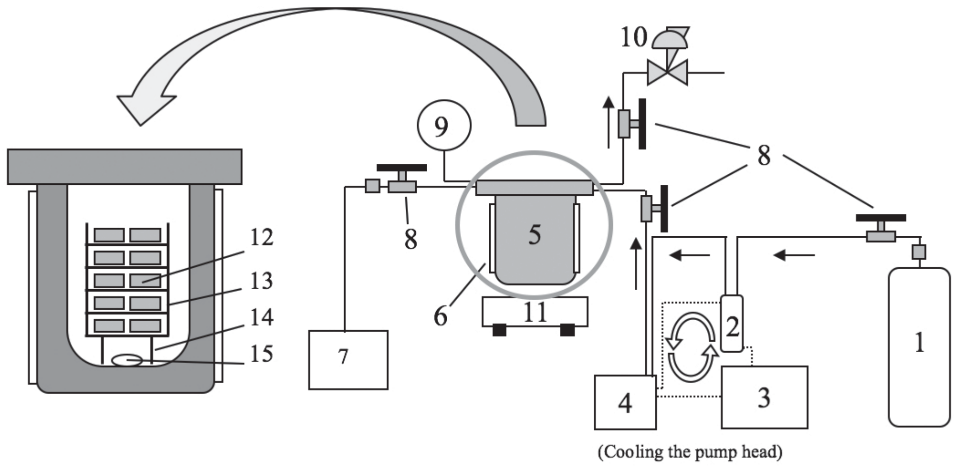

Figure 1 Schematic diagram of supercritical CO_2 treatment apparatus consisting of 1: CO_2 cylinder, 2: condenser, 3: cold water circulator, 4: pump, 5: batch container, 6: electric heater, 7: aspirator, 8: valve, 9: pressure gauge, 10: back pressure regulator, 11: magnetic stirrer, 12: wood specimens, 13: basket, 14: acetic anhydride and 15: stirrer bar

and V_1 = oven-dry volumes of specimens before and after acetylation respectively.

Acetylated and non-acetylated specimens were immersed in water under vacuum for 1 week, and the swelling coefficient was measured. Anti-swelling efficiency was calculated from the swelling coefficient of non-acetylated (D_n) and acetylated (D_a) specimens using equations 3 and 4 respectively.

$$\text{Anti-swelling efficiency (\%)} = (D_n - D_a)/D_n \times 100 \quad (3)$$

$$D\ (\%) = (V_1 - V_0)/\ V_0 \times 100 \quad (4)$$

where V_0 and V_1 = oven-dry volumes of specimens before and after immersion in water respectively. Table 1 lists the mean swelling coefficient of non-acetylated specimens of each wood species.

RESULTS AND DISCUSSION

Variation of weight per cent gain, bulking and anti-swelling efficiency in the acetylation process

Weight per cent gain increased with increasing acetylation time from 12 to 20% after 8 hours of treatment (Figure 2). Generally, the four species of wood from Sri Lanka demonstrated lower weight per cent gain compared with *C. japonica*. In contrast to weight per cent gain, the four species of wood, especially *A. macrophylla*, had higher bulking values than *C. japonica* (Figure 3). In our previous study, Japanese wood species with higher specific gravity had higher bulking value when acetylated using supercritical CO_2, except for *C. japonica*, which had lower specific gravity and intermediate bulking value (Matsunaga et al. 2012b). In general, wood species with higher specific gravity have relatively smaller cell lumen, leading to larger extent of swelling when bulky acetyl groups are introduced into the cell walls (Matsunaga et al. 2014). Similar trend was observed in the present study.

The relationship between anti-swelling efficiency and acetylation time is shown in Figure 4. The anti-swelling efficiency values of the four wood species were widely scattered at the shorter acetylation times. However, after 8 hours of acetylation, all specimens attained mean values of anti-swelling efficiency values greater than 60%. It has been reported that the effect of bulking, rather than decreased hygroscopicity, is the key factor that determines dimensional stability provided by acetylation (Stamm 1964, Minato et al. 2003). Anti-swelling efficiency of acetylated wood improves as the effect of bulking is enhanced (Obataya et al. 2002). Thus, wood from the four species showed

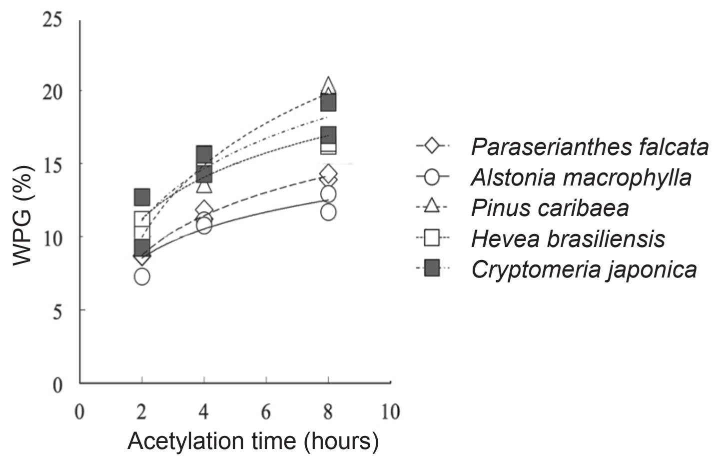

Figure 2 Relationship between weight per cent gain (WPG) and acetylation time

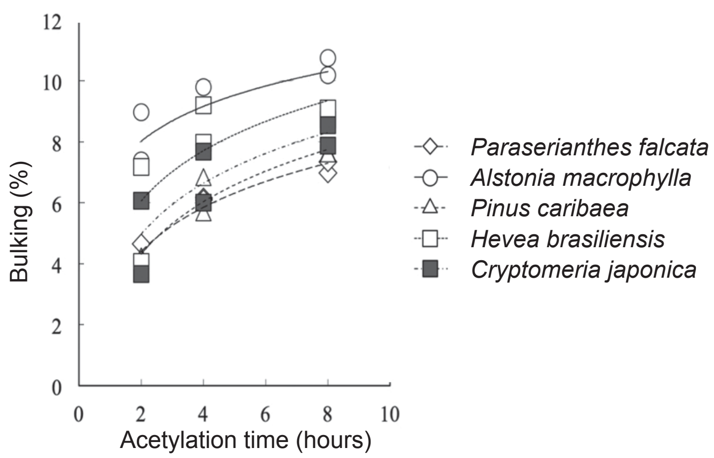

Figure 3 Relationship between bulking and acetylation time

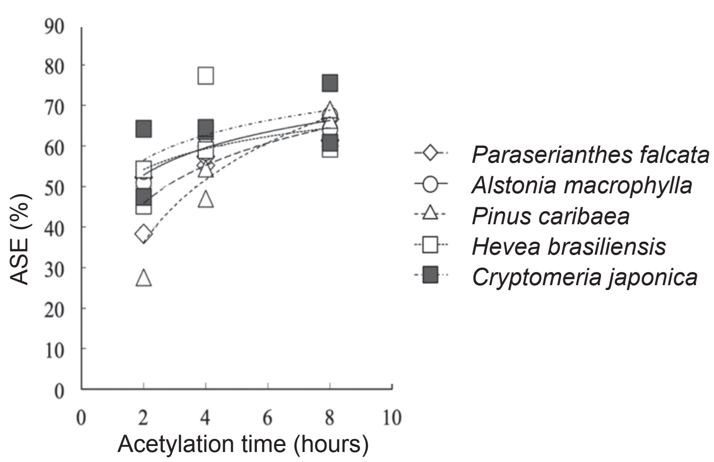

Figure 4 Relationship between anti-swelling efficiency (ASE) and acetylation time

relatively high anti-swelling efficiency because of high bulking that was provided by acetylation using supercritical CO_2.

Effectiveness of acetylation using supercritical CO_2 from Sri Lanka wood

Wood of *A. macrophylla* demonstrated extremely high bulking values compared with the rest of the species (Figure 5). *Paraserianthes falcata* and *H. brasiliensis* had slightly higher bulking values than *C. japonica*. Between the four wood species, *A. macrophylla* had slightly higher weight per cent gain values than *C. japonica* while *P. falcata* had almost similar values (Figure 6). Meanwhile, *H. brasiliensis* had scattered values while *P. caribaea*, generally lower.

Specific gravity of *A. macrophylla* was the highest in this study with a mean value of 0.605 (Table 1). Wood species having higher specific gravity tend to obtain relatively higher bulking effect from acetylation process. Therefore, the high anti-swelling efficiency of *A. macrophylla* may be due to its high specific gravity. However, since bulking of *A. macrophylla* is extremely high. it is assumed that some additional factors may enhance the bulking effect of *A. macrophylla*.

The effectiveness of acetylation using supercritical CO_2 may also be affected by the morphological characteristics of wood. Effective penetration of wood using supercritical CO_2 depends not only on specific gravity but also the structure of the wood tissue (Matsunaga et al. 2005). Despite having low specific gravity, *C. japonica* exhibited intermediate bulking when acetylated using supercritical CO_2 (Matsunaga et al. 2012b). Only 65 to 80% of the bordered pits in tracheid cell walls of *C. japonica* heartwood are completely aspirated (Matsumura et al. 1994). According to another study, this value varies between 20 and 80% (Fujii et al. 1997). The *C. japonica* specimens may have been effectively acetylated because incompletely aspirated pits facilitated rapid penetration of supercritical CO_2 and acetic anhydride into the reaction sites of the wood (Matsunaga et al. 2005).

Alstonia spp. have simple perforation plates, and the tyloses are not frequent in the vessels (Sidiyasa & Baas 1998, Ogata et al. 2008). This penetrable structure of *A. macrophylla* wood due to the less dense tylosis in vessels is assumed to be desirable for supercritical CO_2 treatment because of enhanced penetration of acetic anhydride into the core of the wood. Thus, acetylation of *A. macrophylla* using supercritical CO_2 provided high bulking effect and anti-swelling efficiency.

Results obtained in this study indicated that acetylation in supercritical CO_2 was sufficiently effective for the heartwood of *A. macrophylla*. *Alstonia macrophylla* in particular obtained relatively high dimensional stability. It is expected that the utilisation of lumber derived from this species will be expanded in the future because of wood improvement by acetylation using supercritical CO_2.

CONCLUSIONS

The heartwood of four species from Sri Lanka was acetylated with acetic anhydride using supercritical CO_2 (120 °C, 10–12 MPa). The anti-swelling efficiency values of the species were widely scattered at short acetylation times. However, anti-swelling efficiency of wood of all species demonstrated values above 60% after 8 hours of acetylation. Between the four species evaluated, wood of *A. macrophylla* exhibited a relatively high anti-swelling efficiency.

ACKNOWLEDGMENT

This study was partially supported by the Japan Society for the Promotion of Science Grants-in-Aid for Scientific Research (KAKENHI) No. 23580239.

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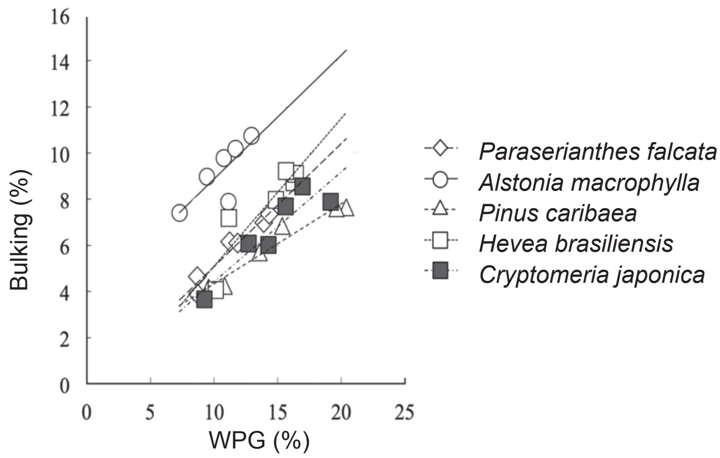

Figure 5 Relationship between bulking and weight per cent gain (WPG)

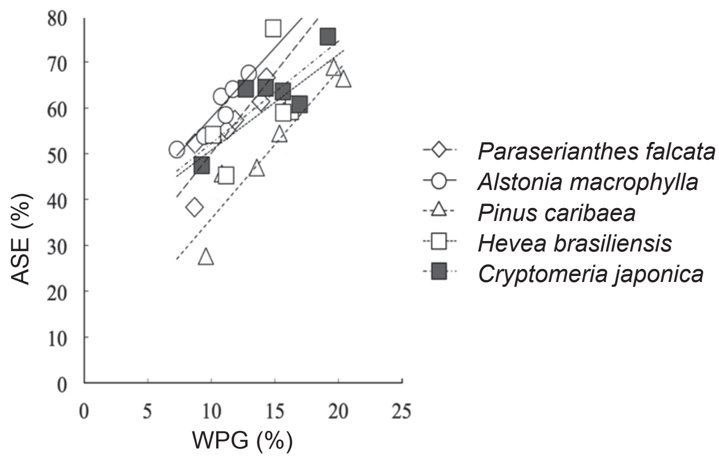

Figure 6 Relationship between anti-swelling efficiency (ASE) and weight per cent gain (WPG)

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