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Comparisons and Characteristics of Slicewood Acetylation with Acetic Anhydride by Liquid Phase, Microwave, and Vapor Phase Reactions

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This study compared and characterized slicewood acetylation with acetic anhydride using conventional liquid phase, microwave, and vapor phase reactions. The results revealed that there were no significant differences in the flexural properties between the unmodified and acetylated slicewood, regardless of the reaction method used. Furthermore, findings concluded that the slicewood acetylated with a vapor phase reaction required less modifying agent to achieve high levels of weight percent gain (WPG). The correlations between the anti-swelling efficiency (ASE) and the WPG of the slicewood acetylated with a vapor phase reaction were higher than the conventional liquid phase and microwave reactions. The reactivity of the cellulose hydroxyl groups was sensitive to the C2 and C6 reactive sites for all three acetylation methods. However, the reactivity was more pronounced at the C2 position with a vapor phase reaction compared to the other two reactions. Nevertheless, slicewood acetylation with acetic anhydride was found to not have a significant influence on viscoelastic properties for any of the different reaction methods.

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INTRODUCTION

Wood is a basic natural resource that plays an important role in everyday human lives and culture due to its aesthetic appearance and characteristic properties. As the supply of large trees diminishes and the cost of wood continues to increase, slicewood or veneer will become a more important part of the wood market (Hoadley 2000). However, slicewood or veneers have some undesirable properties such as dimensional instability, photodegradation, combustibility, and susceptibility to biological degradation. These serve to limit their exterior applications and long-term utilization (Saka and Ueno 1997; Li *et al.* 2011). Therefore, one unprecedented challenge stands on how to overcome these disadvantageous characteristics. Over the past six decades, several physical and chemical methods have been employed to improve the dimensional stability, thermostability, photostability, and the biological and weathering resistance of wood (Wu *et al.* 2004; Rowell 2006; Evans 2009). Among these various approaches, wood acetylation with acetic anhydride has received the most attention. Additionally, acetylated products have already been commercialized in the USA, Europe, and Japan (Rowell 2006; Minato *et al.* 2007; Jebrane *et al.* 2011a,b).

The conventional acetylation process includes impregnating dried wood with a liquid phase acetic anhydride before external heat is applied. The downside to this method is that the process is time-consuming and requires large quantities of modifying agent. The reaction rate increases with the temperature of the liquid phase reaction, but the use of elevated temperatures may induce changes in or even damage the wood tissue at the cell wall level (Hill 2006). To reduce the reaction duration and improve the distribution of modifying agent within the wood, a microwave reaction may be used to increase the efficiency of the acetylation process over that of the conventional method due to its rapid and uniform heating characteristics (Brelid and Simonson 1999; Brelid *et al.* 1999). Furthermore, it is well known that the reactivity of the chemical reagent in the vapor phase is higher than that used in the liquid phase. As a result, acetylation with acetic anhydride in the vapor phase reaction has some benefits, such as reducing the reagent consumption, decreasing the reaction time, and minimizing the environmental impact. Therefore, vapor-phase acetylation has been investigated by several researchers (Rowell 1983; Obataya and Minato 2009; Futemma and Obataya 2012). However, very few studies have addressed the influence of the modification process on the physico-mechanical and viscoelastic properties of the acetylated slicewood.

The objective of this study was to compare and characterize slicewood that was acetylated with acetic anhydride by the conventional liquid phase, microwave, and vapor phase reactions. To the best of our knowledge, this work is the first report to address the difference of acetylated slicewood by the three reaction methods at the same time.

EXPERIMENTAL

Materials

Sugi (*Cryptomeria japonica* D. Don) sapwood (20 to 30 years old) was supplied by the experimental forest of the National Taiwan University. The dimensions of the slicewood samples were 3 mm (R) x 12 mm (T) x 58 mm (L). The straight longitudinal grain, free of defects, and modulus of elasticity (MOE) ranged from 5.5 to 6.5 GPa for the oven-dried (OD) sugi specimens that were selected and used in this study. All the samples were used after the extraction in a Soxhlet apparatus for 24 h with a 1:2 (v/v) mixture of ethanol and toluene, followed by washing with distilled water before being dried at 105 °C for 12 h. Acetic anhydride (AA) was purchased from the Sigma-Aldrich Chemical Co. (St. Louis, MO, USA). The other chemicals and solvents used in this experiment were of the highest quality available.

Acetylation

The sugi slicewood was acetylated with AA using the conventional liquid phase, microwave, and vapor phase reactions. The microwave oven used in this work was a modified Panasonic NN-ST557 inverter system (2450 MHz, Shanghai, China) (Fig. 1). The AA amount for the conventional liquid phase and microwave reactions used 80 mmol *per* gram of OD wood (this ratio was the minimal reagent required to submerge the wood samples in the reactor). The vapor phase reaction used between 5 to 80 mmol of AA *per* gram of OD wood. All the reactions were conducted at 140 °C for 0 to 360 min to obtain acetylated sugi slicewood with different degrees of modification.

At the end of the reaction, the acetylated sugi samples were washed with distilled water and Soxhlet-extracted with acetone for 8 h. Finally, the acetylated sugi was dried at 105 °C for 12 h. The weight percent gain (WPG) for the wood materials was calculated based on the oven-dried method.
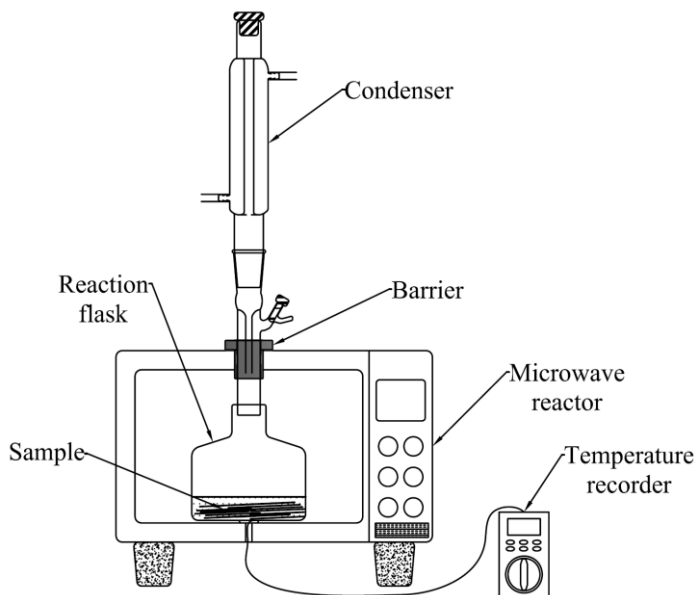

Fig. 1. Modified microwave reaction apparatus

Flexural Properties

The flexural properties (MOR and MOE) of the sugi samples were determined according to ASTM standard D790 (ASTM D790 2009). This included a three-point static bending test with a loading speed of 1.28 mm/min and a span of 48 mm (the specimen size was 3 mm x 12 mm x 58 mm). The samples were oven-dried at 105 °C for 12 h prior to testing. All tests were carried out in an air-conditioned room at 20 °C. Nine specimens were used for each determination.

Dimensional Stability

The dimensional stability of the acetylated slicewood was determined by assessing the volumetric swelling coefficient (S) and the anti-swelling efficiency (ASE) using the repeated water-soaking method described by Prakash and Mahadevan (2008). The samples were placed into a beaker and immersed in distilled water, then placed in a vacuum desiccator. Vacuum was applied for 30 min, released for 1 h, reapplied for 30 min, and released again for 24 h. Finally, the weight and volume of samples were measured. The soaking process was continued until the samples achieved a constant volume. Samples were then oven-dried at 105 °C and their weight and volume were re-measured. The soaking process was repeated five times. Nine specimens were used for each determination. Both the S (Eq. 1) and ASE (Eq. 2) values were determined from the following equations,

$$S\,(\%) = [(V_2 - V_1)\,/\,V_1]\;\mathrm{x}\;100 \tag{1}$$
$$\mathrm{ASE}\,(\%) = [(S_u - S_m)\,/\,S_u]\;\mathrm{x}\;100 \tag{2}$$

where V_1 is the volume of the OD sample, V_2 is the volume of the saturated sample, S_u is the swelling coefficient of the unmodified slicewood, and S_m is the swelling coefficient of the acetylated slicewood.

Dynamic Mechanical Analysis

The dynamic viscoelastic properties of the slicewood samples were measured using a single-cantilever bending test (DMA 8000, Perkin-Elmer, Buckinghamshire, UK) at a heating rate of 5 °C/min and a frequency of 1 Hz. The storage modulus (E') and loss modulus (E'') were recorded over a temperature range of -180 to 300 °C. The dimensions of the samples were 30 mm (L) x 12 mm (T) with a thickness of 3 mm. Duplicate specimens were used for each determination.

Solid-state CP/MAS ^{13}C-NMR Analysis

The slicewood samples were examined by solid state cross-polarization magic angle spin (CP/MAS) carbon 13 nuclear magnetic resonance (^{13}C-NMR). The spectra were recorded on a Bruker DSX-400WB FT-NMR spectrometer (Bremen, Germany) with a sampling frequency of 100 MHz. The chemical shifts were calculated relative to tetramethylsilane (TMS). Duplicate specimens were used for each determination.

Statistical Analyses

All the results were expressed as the mean ± standard deviation (SD). The significance of the difference was calculated using Scheffe's test, with values of $P < 0.05$ considered to be significant.

RESULTS AND DISCUSSION

WPG, MOE, and MOR of Acetylated Wood

The WPG, MOE, and MOR of the acetylated slicewood from the three different reaction methods are shown in Table 1 as a function of the reaction time. As shown in Table 1, the WPG of the acetylated slicewood increased with the reaction time for all three reaction methods. At a reaction time of 0 min (*i.e.*, the time point at which the reaction temperature reached 140 °C, as shown in Fig. 2), the slicewood acetylated with the liquid phase reaction exhibited the highest WPG (13.6%), followed by the microwave reaction (9.7%), and the vapor phase reaction (9.4%). This tendency was likely influenced by the pre-heating duration. Figure 2 shows the temperature curves for the three modification methods with the heating rate of the microwave reaction being faster than the other two reactions. The time required to reach the reaction temperature (140 °C) was 2 min using the microwave reaction, whereas the liquid phase and vapor phase reactions required 6 and 13 min, respectively. These results indicated that the duration of the slicewood-AA interaction with the liquid phase reaction was longer than the other reactions. This is the probable reason why the WPG of the slicewood acetylated with the liquid phase reaction was higher at the initial acetylation stage. The pre-heating duration for the vapor phase reaction was the longest (13 min), but the WPG was significantly less than that of the liquid phase ($P < 0.01$), which had a reaction time of 0 min. This phenomenon is likely caused by insufficient available reagents (vapor phase) for acetylation before the temperature

reached the boiling point for AA (140 °C). Once the reaction time reached 30 min, there was no significant difference in WPG from the three reaction methods. In addition, the WPG of the slicewood acetylated by the vapor phase reaction with 40 mmol of AA *per* gram of OD wood was similar to that observed in the liquid phase or microwave reactions that used twice as much reagent (80 mmol AA/g of wood).

Table 1. Weight Percent Gain (WPG), Modulus of Elasticity (MOE), and Modulus of Rupture (MOR) of the Wood Acetylated with the Three Reaction Methods at Different Reaction Times

| Reaction time (min)	Liquid phase*			Microwave*			Vapor phase**		
	WPG (%)	MOE (GPa)	MOR (MPa)	WPG (%)	MOE (GPa)	MOR (MPa)	WPG (%)	MOE (GPa)	MOR (MPa)
Control	-	6.5 ± 0.4[a]	79 ± 14[a]	-	6.5 ± 0.4[a]	79 ± 14[a]	-	6.5 ± 0.4[a]	79 ± 14[a]
0	13.6 ± 1.2[c]	6.4 ± 0.2[a]	81 ± 17[a]	9.7 ± 0.6[e]	6.3 ± 0.3[a]	68 ± 5[a]	9.4 ± 2.5[f]	6.4 ± 0.9[a]	63 ± 8[b]
10	14.4 ± 0.7[c]	6.1 ± 0.1[a]	73 ± 13[a]	13.7 ± 0.5[e]	6.1 ± 0.1[a]	76 ± 22[a]	11.0 ± 2.0[e]	6.7 ± 0.4[a]	73 ± 15[a]
30	17.1 ± 0.4[b]	6.2 ± 0.1[a]	71 ± 15[a]	16.4 ± 0.6[d]	7.1 ± 1.4[a]	78 ± 2[a]	16.1 ± 0.8[d]	6.9 ± 0.8[a]	81 ± 5[a]
60	19.1 ± 0.4[b]	6.2 ± 0.1[a]	86 ± 8[a]	19.4 ± 1.7[c]	6.5 ± 0.1[a]	86 ± 23[a]	18.0 ± 0.8[c]	6.3 ± 0.3[a]	79 ± 11[a]
120	19.9 ± 0.9[b]	6.0 ± 0.2[a]	86 ± 13[a]	19.9 ± 0.7[bc]	6.1 ± 0.4[a]	79 ± 8[a]	20.7 ± 0.9[c]	6.2 ± 0.7[a]	79 ± 12[a]
180	21.0 ± 1.4[a]	5.8 ± 0.5[a]	74 ± 4[a]	21.6 ± 1.0[b]	6.0 ± 0.5[a]	74 ± 16[a]	22.3 ± 0.5[b]	6.5 ± 0.3[a]	78 ± 9[a]
360	22.9 ± 0.5[a]	6.4 ± 0.4[a]	84 ±16[a]	24.3 ± 0.8[a]	6.6 ± 0.5[a]	84 ± 7[a]	23.2 ± 1.3[a]	6.4 ± 0.2[a]	83 ± 10[a]

Values shown here are the means ± SD (*n* = 9). Different letters within a column indicate significant differences at $P < 0.05$
*: Wood : AA = 1 g : 80 mmol; ******: Wood : AA = 1 g : 40 mmol
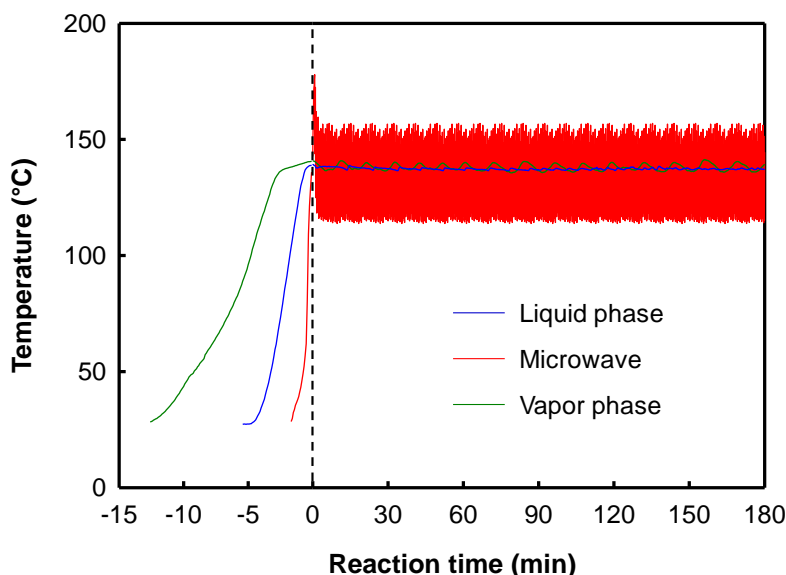
Fig. 2. The temperature curves of the three modification methods during the reactions

To further understand the effect of AA/wood ratio on the WPG of the slicewood acetylated with the vapor phase method, the reaction was studied as a function of reagent

ratio. Figure 3 shows the WPG of the slicewood acetylated by the vapor phase reaction for 120 min at different ratios of AA to wood. The results revealed that the WPG of the slicewood acetylated with 5 mmol of AA *per* gram of OD wood was 11%. However, a significant increase in the WPG was seen when the ratio increased to 10 mmol AA/g wood. No further increases were observed from the slicewood acetylated at higher ratios of AA to wood.
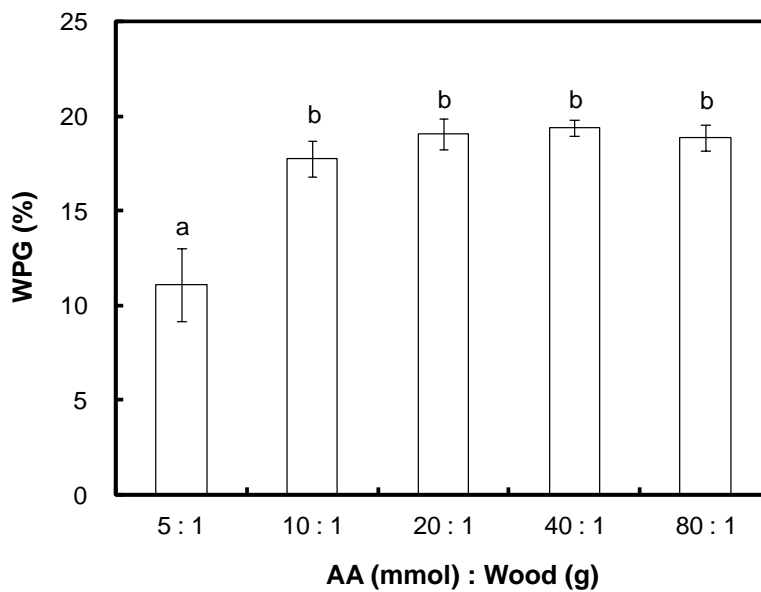

Fig. 3. The weight percent gain (WPG) of the wood acetylated with the vapor phase reaction for 120 min at different reagent concentrations. The values shown here are the means ± SD ($n = 9$). Bars with different lowercase letters indicate significant differences at $p < 0.05$

Table 1 also shows that there was no significant difference between the MOE and MOR for the acetylated and unmodified slicewood for all the acetylation methods, even at a WPG of 23%. This result reveals that the mechanical properties of the acetylated slicewood were not influenced by the degree of modification or the reaction method. Similarly, Rowell and Banks (1987) and Birkinshaw and Hale (2002) found that acetylation did not noticeably affect the mechanical properties of the softwoods studied (pine, lime, spruce and larch).

Dimensional Stability of Acetylated Wood

In this study, the ASE was used to evaluate the dimensional stability of the acetylated slicewood produced with the three reaction methods. Figure 4 shows that the ASE increased with the reaction time over the first 120 min for a conventional liquid phase reaction before gradually declining. The ASE decreased from 64 to 41% as the reaction time increased from 120 min (WPG of 19.9%) to 360 min (WPG of 22.9%). A significant decrease in the dimensional stability of the slicewood acetylated with the liquid phase reaction was observed over the period from 120 to 360 min. One possible explanation for this observation is that the volume of added chemicals (bonded acetyl groups) was enough to rupture the cell wall for the acetylated slicewood with a high WPG, which led to an

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increase in the swelling coefficient and a decrease in the ASE. A similar trend was observed by Rowell and Youngs (1981) and Li *et al*. (2000). Additionally, the ASE of the slicewood acetylated with the microwave reaction was generally consistent with the trends observed for the liquid phase reaction, even though the values were smaller. In contrast, the ASE of the slicewood acetylated with the vapor phase reaction increased as the reaction time increased to 60 min before leveling off and remaining constant up to 360 min. This result was similar to that obtained by Obataya and Minato (2009), who reported that the ASE of the wood acetylated with the vapor phase reaction increased with increasing WPG.
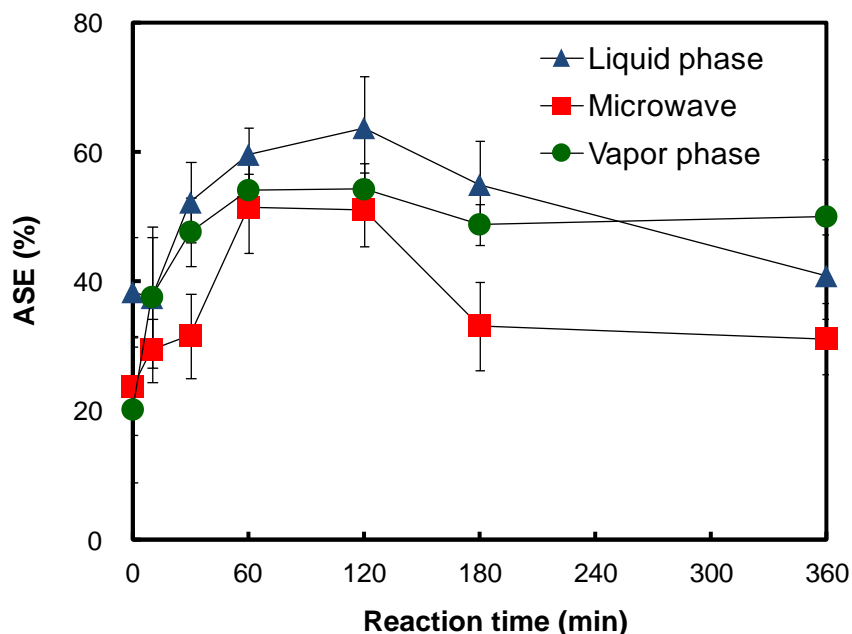

Fig. 4. The anti-swelling efficiency (ASE) of the acetylated wood for the three reaction methods at different reaction times. The values shown here are the means ± SD (*n* = 9)

Figure 5 presents the relationship between the ASE and the WPG of the slicewood acetylated with the three different reaction methods. Of these, the slicewood acetylated with the vapor phase reaction exhibited the highest correlation coefficient (*r* = 0.80), followed by the microwave reaction (0.59) and the liquid phase reaction (0.50). This result implies that the cell wall rupture of the slicewood acetylated with the vapor phase reaction were smaller than those formed by the liquid phase or microwave reactions. Other possible explanation is that the exothermic nature of the liquid reaction, which led to delignification and cell wall degradation (Fadl and Basta 2005). Accordingly, the ASE of the slicewood acetylated with the vapor phase reaction had a high positive correlation with the WPG.

It is well known that wood modification improves the dimensional stabilization by two mechanisms: cell wall bulking and cross-linking between the cell wall polymeric components (Hill 2006). When determining the dimensional stability of modified wood, it is essential to determine the change in the volumetric swelling behavior over a number of water-soaking/oven-drying cycles.
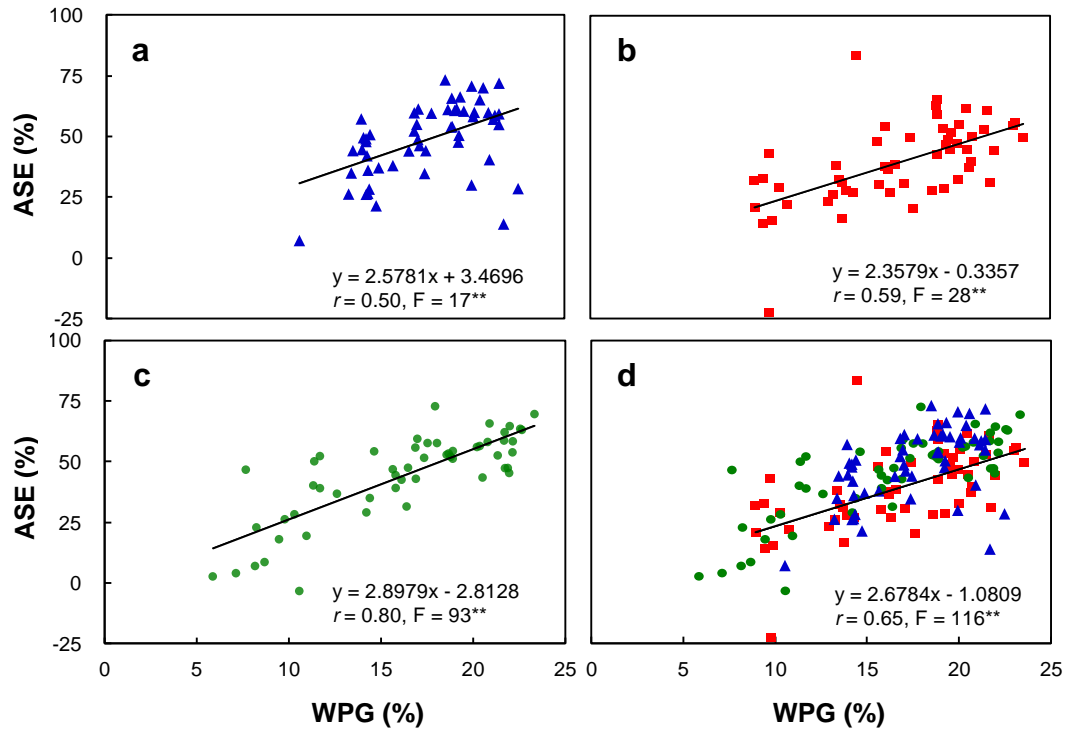
Fig. 5. The relationship between the anti-swelling efficiency (ASE) and the weight percent gain (WPG) of the wood acetylated with the three reaction methods: (a) the liquid phase method, (b) the microwave method, (c) the vapor phase method, (d) all acetylated wood
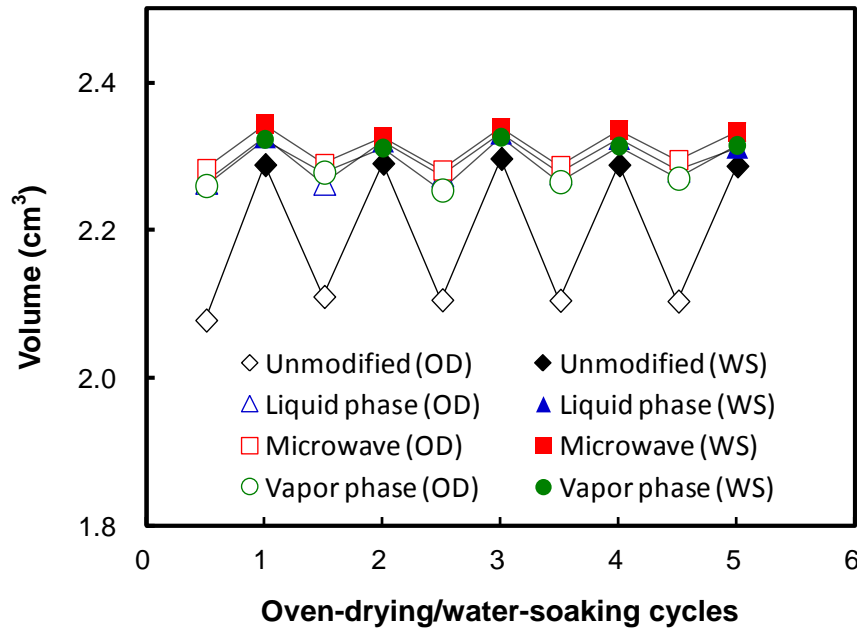

Fig. 6. The volume changes of wood acetylated with the three reaction methods for 360 min (WPG ~21%) over five oven-drying (OD)/water-soaking (WS) cycles. Values given here are means ($n = 9$)

Figure 6 shows the volume changes for the slicewood acetylated with the three reaction methods over five cycles. The results revealed that the dimensional stability of the slicewood can be remarkably improved by acetylation. The reduction in the volume swelling of the acetylated slicewood is attributed to the volume occupied by the modifying agent, which led to a decrease in additional swelling of the modified wood when exposed to water soaking (Ohmae *et al.* 2002). Moreover, there was not a significant difference in the water-saturated volume and in the OD volume during the five oven-drying/water-soaking cycles for all the acetylated slicewood. In other words, regardless of the reaction method used, the mechanism responsible for the dimensional stabilization of the modified slicewood is cell wall bulking.

Viscoelastic Properties of Acetylated Wood

The viscoelastic properties of the oven-dried unmodified and acetylated slicewood were investigated by dynamic mechanical analysis (DMA). As shown in Fig. 7A, there was a clear difference in the retention ratio of the storage modulus (E') (*i.e.*, the ratio of E' to the initial E') of the unmodified slicewood and the acetylated slicewood. The E' retention ratio for all the acetylated slicewood was higher than that of the unmodified slicewood (control) at temperatures below 150 °C. However, the acetylated slicewood exhibited a dramatic decrease in the E' retention ratio as the temperature increased beyond 150 °C. This change is attributed to the acetyl groups functioning as an internal plasticizer at high temperatures (Obataya *et al.* 2003). Some of the hydrogen bonds between the amorphous molecules were severed as the acetyl groups were introduced into the system, resulting in an increased mobility in the amorphous molecules. Figure 7B reveals that the loss modulus (log E'') of the unmodified slicewood displayed three distinct relaxation processes labeled α, β, and γ in order of decreasing temperature. The α, β, and γ transitions are attributed to the micro-Brownian motions of lignocellulose polymers in the non-crystalline regions, the motions of lignin and/or lignin-hemicellulose complexes plasticized with residual moisture, and the motions of the methylol groups of the lignocellulose polymers in the amorphous zones, respectively (Obataya *et al.* 2001; Jiang and Lu 2009; Jebrane *et al.* 2011a).
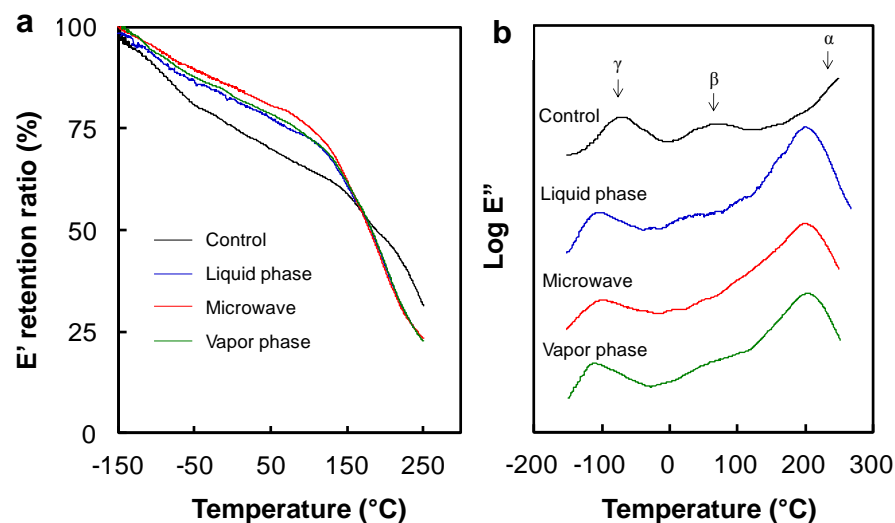

Fig. 7. *E'* retention ratio (a) and log *E''* (b) of the wood acetylated (WPG ~21%) with the three reaction methods

Regardless of the reaction method used, the α transition of the acetylated slicewood not only increased in intensity but also shifted to lower temperatures compared to the unmodified slicewood. This result indicated that the lignocellulose polymers mobility was improved in the non-crystalline regions because some of the hydrogen bonds between the amorphous molecules were severed with the introduction of the acetyl groups. A similar tendency was also observed with the β transition in the acetylated slicewood. This is believed to be caused by a reduction in the hygroscopicity of the slicewood after acetylation, which decreased the intensity of β transition related to the residual moisture. Additionally, the γ transition temperature shifted from -75 °C to about -100 °C after acetylation. This result was similar to that reported by Jebrane *et al.* (2011a), who demonstrated that the downshift of the γ transition temperature may be attributed to the substitution of the methylol groups by acetyl moieties after acetylation and overlapping relaxation processes for these two side-chains at the lower temperature level. These results showed that the slicewood acetylation with acetic anhydride did not have a strong influence on the viscoelastic properties of the modified slicewood.

Reactive Characteristics

In this study, solid state CP/MAS ^{13}C-NMR was used to elucidate the characteristics of the sugi specimens before and after acetylation. Figure 8 displays various characteristic carbohydrate patterns such as C1 (105.0 ppm), C4 (88.7 ppm and 83.1 ppm), C2 (74.9 ppm), C3, C5 (72.4 ppm), and C6 (65.0 ppm and 62.5 ppm) for the unmodified slicewood (Boonstra *et al.* 1996; Hung and Wu 2010; Jebrane *et al.* 2011b).
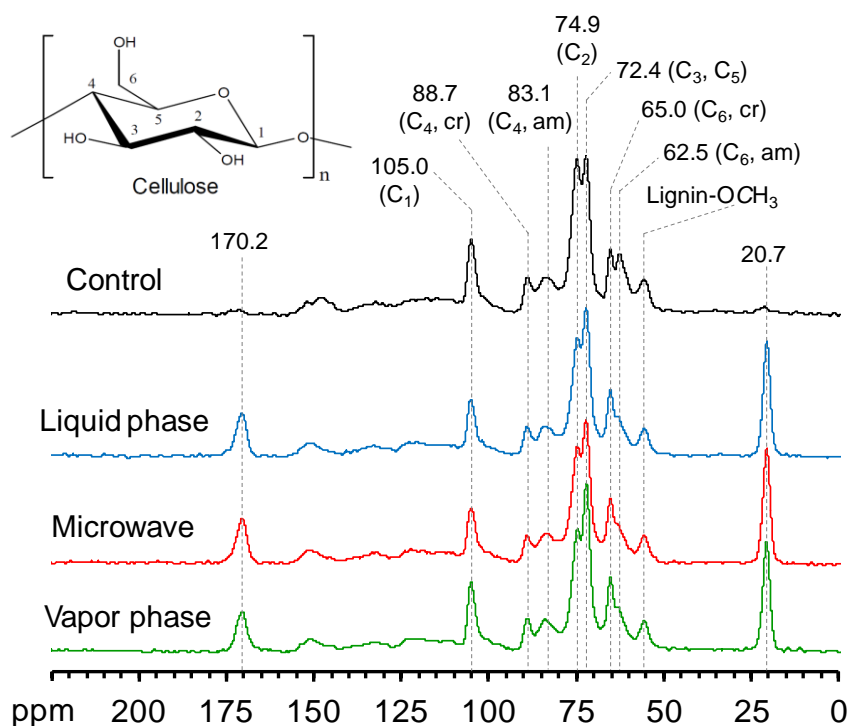
Fig. 8. Solid state ^{13}C NMR spectra of the wood acetylated (WPG ~21%) with the three reaction methods. Cr: crystalline; am: amorphous

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Hemicellulose carbons displayed similar resonance in the same field as the cellulose carbon. Because of this overlap, it was not possible to draw conclusions as to the identity of contributions to the signal. The chemical shift at 56.1 ppm and the broad signal between 125 and 160 ppm corresponded to the methoxy groups and aromatic rings of lignin, respectively. However, the intensity of the peaks at 74.9 (C2) and 62.5 (amorphous C6) ppm decreased and shifted downfield after acetylation, whereas there was no significant change observed at 72.4 ppm (C3). In addition, the peaks at 170.2 and 20.7 ppm, which were assigned to the acetyl group, were also found in all the spectra from the acetylated slicewood. These results indicated that the order of the reactivity of the cellulose hydroxyl groups was C2,6–OH > C3–OH when the sugi slicewood was modified with acetic anhydride. Furthermore, the decrease in the signal intensity was more pronounced at the C2 position (74.9 ppm) for the vapor phase reaction compared to the liquid phase and microwave reactions. This result implied that the accessibility of the modifying agent for the vapor phase reaction was different than the other two reactions.

CONCLUSIONS

1. The dimensional stability was found to be improved after acetylation for all three different reaction methods. In addition, the E' retention ratio for all the acetylated slicewood was higher than that of the unmodified slicewood at temperatures below 150 °C.

2. The ASE of all acetylated slicewood increased with the initial increment of reaction time, but the increasing trend was found to decline when the reaction time exceeded 120 min (WPG ~20%), except for the vapor phase reaction.

3. The accessibility of the modifying agent with the vapor phase reaction was different than in the other two reactions. However, regardless of the reaction method used, the mechanism responsible for the dimensional stabilization of the modified slicewood is cell wall bulking.

4. The acetylation using the vapor phase reaction could be considered as a serious alternative process, but this reaction method with acetic anhydride has a well-known drawback of the generation of acetic acid by-product. Therefore, any future studies should focus on not only determining a new approach for wood acetylation that does away with the unfavorable by-products generated from the vapor phase reaction, but also the penetration of the vapor into the wood.

ACKNOWLEDGMENTS

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