

Improvement of Hydrophobicity and Dimensional Stability of Thermally Modified Southern Pine Wood Pretreated with Oleic Acid

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The present work used a combined approach of oleic acid (OA) impregnation and thermal modification to improve the hydrophobicity and dimensional stability of southern pine (*Pinus* spp.). The wood samples were first treated with OA at a concentration of 5 or 10%, and then underwent thermal modification at 160, 180, or 200 °C. Thereafter, the water-related properties of modified wood including water absorption (WA), equilibrium moisture content (EMC), and volumetric swelling (VS) were investigated. Alterations in cell wall structure and chemical components were analyzed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR), based on the mechanisms discussed. While the results showed that both OA-treatment and thermal modification can each improve the water repellency and dimensional stability of wood, the combined system proved to be more effective. The synergistic increase of water-related properties was assumed to be caused by OA increasing the hydrophobicity of thermally modified wood as well as accelerating the decomposition of hydrophilic wood components during thermal modification. This assumption was supported by both SEM and FTIR results. Therefore, this research provides an approach for improving the accessibility to the energy-efficient thermal modification.

Keywords: Dimensional stability; Oleic acid; Thermal modification; Hydrophobicity; Southern pine

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INTRODUCTION

Southern pine, one of the main native softwood genus groups in the United States and Europe, is a dominant resource for the production of dimension lumber, railroad ties, poles, and other commodity forest products (Priadi and Hiziroglu 2013; Robinson *et al.* 2011). However, products made from southern pine in above-ground exposure are typically susceptible to undergo absorption/desorption cycles, thereby resulting in dimensional and conformational instability (Rowell 2006). The poor dimensional stability frequently leads to warping, splitting, and checking, which become the key issues for its further application (Schultz *et al.* 2007).

A variety of studies have been conducted to improve the dimensional stability of wood (Hill 2006). Thermal modification has been proven effective to enable wood to alleviate moisture adsorption and cell wall swelling (Esteves *et al.* 2007; Rowell 2012). The process is regularly performed by heating the wood to a temperature ranging from 160 to 260 °C with the protection of a shielding gas such as nitrogen or steam (Esteves and Pereira 2009; Militz 2002). Some processes, such as Thermowood (Finland), OHT-oil-heat treatment (Germany), Torrefaction (France), Bois Perdure (France), and PLATO-

wood (Netherlands) (Korkut *et al.* 2008) have been commercialized in European countries.

According to previous studies, the properties of thermally modified wood are highly dependent on mass loss of the modified wood due to elevated heating temperature (Esteves *et al.* 2007; Hakkou *et al.* 2005). It was also found that mass loss is mainly attributable to the degradation of hemicellulose (Borrega and Kärenlampi 2010; Esteves and Pereira 2009; Kocaefe *et al.* 2008), which is less thermally stable than cellulose and lignin.

As the heating temperature rises, the chemical components begin to degrade, reducing the number of hydrophilic groups (most frequently, -OH). With fewer sorption sites being accessible for water molecules, wood becomes more hydrophobic, resulting in lower hygroscopicity and equilibrium moisture content (EMC). Therefore, the dimensional changes of the wood are minimized (Esteves and Pereira 2009; Hill 2006). The other possible reasons for resulting stability, such as ether crosslinks, structural modifications and chemical changes of lignin, also have been well discussed (Kamdem *et al.* 2002; Repellin and Guyonnet 2005). For instance, lignin-condensation was found to play an important role in dimensional stabilization of thermally modified wood, firmly restricting the expansion of microfibrils by hardened polymeric networks (Funaoka *et al.* 1990; Tjeerdsma *et al.* 1998).

Though heat treatment can offer excellent performance in improving water-related properties, commercial application is still limited due to the dependency on high temperatures (Hill 2006). This may contradict the scenario for energy saving. However, for thermal treatment with low temperature, the improvement of water repellency and dimensional stability has been found to be insufficient for application (Hill 2006). Therefore, energy efficient thermal modification within a low temperature range needs more research for industrial application.

Apart from thermal modification, impregnating wood with hydrophobic materials such as waxes, organo-silicones, and vegetable oils seems to be another promising approach to reduce water sorption and the severity of swelling (Donath *et al.* 2006; Tomak 2010; Vetter *et al.* 2010; Zhang *et al.* 2007). Among these hydrophobic materials, vegetable oils have become more attractive for their environmental benefits. A few investigations have shown that the water repelling properties of wood can be improved by treatment with vegetable oils such as linseed oil, rape oil, palm oil, and soybean oil, suggesting the potential use of vegetable oils as water-repellents for wood (Tomak *et al.* 2010; Ulvcrone *et al.* 2006; Wang and Copper 2005). Usage of oils as a wood protection agent was also studied by Tomak *et al.* (2011b) and Lyon *et al.* (2007). Oleic acid (OA), a monounsaturated fatty acid, is an important component found in various vegetable oils (Menendez *et al.* 2005).

For fatty acids, hydrophobicity is predominantly dependent on their long chain unsaturated n-alkyl groups. Oleic acid is expected to be capable of excluding water molecules due its long hydroponic chain. Hitherto, no research has been conducted on OA treatment combined with thermal modification of wood for the purpose of improving its water-related properties.

A novel approach for wood modification was proposed in this study to impregnate wood with OA as a pretreatment prior to thermal modification within the low temperature range. The OA may function as the oil in the oil heat treatment (OHT) process, to accelerate the thermal degradation of cell wall components as well as promote heating and limiting oxygen. Therefore, the use of OA prior to thermal modification is expected

to synergistically improve the hydrophobicity of thermally modified wood. To confirm this hypothesis, water-related properties including water absorption (WA), EMC, and volumetric swelling (VS) were evaluated. Also, the alterations in cell wall structure and chemical components after treatment were specifically characterized and analyzed by SEM and FTIR for the mechanistic study.

EXPERIMENTAL

Materials

Samples of 20 × 20 × 20 mm (R, T, L) were machined from the sapwood of southern pine wood (*Pinus* spp.) with an air-dry density of 0.4 g cm⁻³ and an average growth ring width of 0.6 cm. All wood samples were dried to constant mass at 60 °C for impregnation. Oleic acid (XiLong Chemical Co., Ltd, China) with concentration levels of 5 and 10% (w/w) were prepared with anhydrous ethanol (BeiJing Chemical Works Co., Ltd, China) for impregnation.

Methods

Impregnation with oleic acid

Southern pine samples were impregnated with the prepared oleic acid solutions by using a full-cell process. The process began with wood samples exposed to an initial vacuum at -0.1 MPa for 30 min. Later, the treating cylinder was filled with different levels of oleic acid and the pressure for impregnation was increased to 0.5 MPa for 60 min. Once the impregnation was complete, the samples were removed and dried at 60 °C to constant mass, then weighed and recorded as W_b (g).

Weight percentage gains (WPG) of OA impregnated samples were calculated by Eq. 1,

$$\text{WPG} = \frac{W_b - W_a}{W_a} \times 100 \quad (1)$$

where W_a (g) is the initial dry mass before impregnation.

Thermal modification

After drying to the constant mass at 60 °C, selected oleic acid treated and untreated wood samples were thermally modified immediately at 160, 180, and 200 °C for 4 h in a modified drying oven connected with a water vapor supplying system (100% RH). The treatment groups are given in Table 1. After thermal modification, wood samples were taken out and dried at 60 °C to constant mass, then weighed and recorded as W_d (g). Mass losses of heat-treated samples were calculated according to Eq. 2,

$$\text{Mass loss} = \frac{W_c - W_d}{W_c} \times 100 \quad (2)$$

where W_c (g) is the dry mass prior to thermal modification.

Table 1. Labeling of Treatment Groups

Labels	Treatment	
	Oleic acid (%)	Temperature of thermal treatment (°C)
Control	0	60
160 °C	0	160
180 °C	0	180
200 °C	0	200
5% OA	5	60
5% OA+ 160 °C	5	160
5% OA+ 180 °C	5	180
5% OA+ 200 °C	5	200
10% OA	10	60
10% OA+ 160 °C	10	160
10% OA+180 °C	10	180
10% OA+200 °C	10	200

Water absorption (WA)

WA of the samples (6 replicates) completely submerged at room temperature (23 °C) for different durations of time (6, 24, 48, 96, and 192 h) were measured, which was mainly based on the method used by Temiz *et al.* (2006). In addition, the volumetric swelling of treated samples were measured after immersion for 192 h. Once the samples were removed from the vessels, the excess water was wiped off and the mass and dimensional changes of the samples determined. WA and volumetric swelling based on water absorption (VS_a) were calculated according to the Eq. (3) and Eq. (4), respectively.

$$WA = \frac{W_n - W_0}{W_0} \times 100 \quad (3)$$

$$VS_a = \frac{V_a - V_0}{V_0} \times 100 \quad (4)$$

where W_n (g) is the mass of the sample after n hours of immersion, W_0 (g) is the initial mass of the dried sample at 60 °C, V_a (cm³) is the volume of the sample after 192 h of immersion, and V_0 (cm³) is the initial volume of the dried sample at 60 °C.

Equilibrium moisture content (EMC)

The samples (6 replicates for each group) were conditioned in a climate chamber maintained at 23 °C and 96% RH (relative humidity) for 6 weeks to reach EMC, and the mass and dimensions were measured. EMC and volumetric swelling based on EMC (VS_b) of control and treated specimens were calculated by Eqs. 5 and 6,

$$EMC = \frac{W_{emc} - W_0}{W_0} \times 100 \quad (5)$$

$$VS_b = \frac{V_{emc} - V_0}{V_0} \times 100 \quad (6)$$

where W_{emc} (g) is the mass of the sample after conditioning and V_{emc} (cm³) is the volume of the sample after conditioning.

Scanning electron microscopy (SEM) analysis

The transverse and radial surface morphology of the control wood and the wood thermally modified under 200 °C, with and without 10% OA pretreatment, were observed by SEM. The samples were sputter-coated with a gold alloy and observed with a Hitachi S-3400 SEM instrument operating at an acceleration voltage of 15 kV.

Fourier transform infrared spectroscopy (FTIR) analysis

Wood flour (100 mesh) of thermally modified wood with and without 10% OA pretreatment were prepared for FTIR analysis. FTIR spectra were obtained by using a KBr pellet in an FTIR spectrophotometer (Bruker Vertex 70 v, German) in transmission mode within the range of 4000 to 400 cm^{-1} . All spectra were recorded at 2 cm^{-1} resolution, and 32 scans were accumulated.

Statistical analyses

Two-way analyses of variance for all statistics were performed using SPSS 11.0 software, with $P < 0.05$ considered statistically significant.

RESULTS AND DISCUSSION

WPG and Mass Loss

WPG of 5% OA and 10% OA impregnated wood were 7.38 and 14.09%, respectively, which were much lower than mass increase of about 50 to 70% in OHT-oil process (Esteves and Pereira 2009). Compared to the OHT-oil process, the present approach might reduce the excessive OA uptake and eliminate the unpleasant smell. Figure 1 presents the mass loss of thermally modified wood with and without OA pretreatment.

The mass losses of thermally modified wood without OA treatment were 0.43% for 160 °C, 2.14% for 180 °C, and 4.93% for 200 °C, respectively, which is thought to be associated with the decomposition of carbohydrates, especially hemicellulose (Kartal *et al.* 2007; Popescu *et al.* 2013). The OA-thermally modified wood showed a greater mass loss than thermally modified wood. For thermally modified wood with 10% OA pretreatment, the mass losses in 160 °C, 180 °C, and 200 °C were 3.96%, 8.39%, and 8.38%, respectively, which were higher than thermally modified wood with 5% OA pretreatment, corresponding to 3.21%, 4.31%, and 6.9%. It can be concluded that OA plays a crucial role in the heating process.

The mechanism for the increased mass loss might include two aspects: (1) as a kind of fatty acid, OA could facilitate the degradation of wood components (Wang *et al.* 2012); and (2) the decomposition of OA due to the oxidation reaction was inevitable when the heating temperature was higher than 160 °C (Ataei *et al.* 2012). Interestingly, the mass loss of samples treated with 10% OA + 180 °C was almost equal to that of the 10% OA + 200 °C samples, which deviates somehow from expectation. This finding was thought to be caused by more severe decomposition of OA at 200 °C, and therefore less OA was able to catalyze the degradation of cell wall components during the thermal modification.

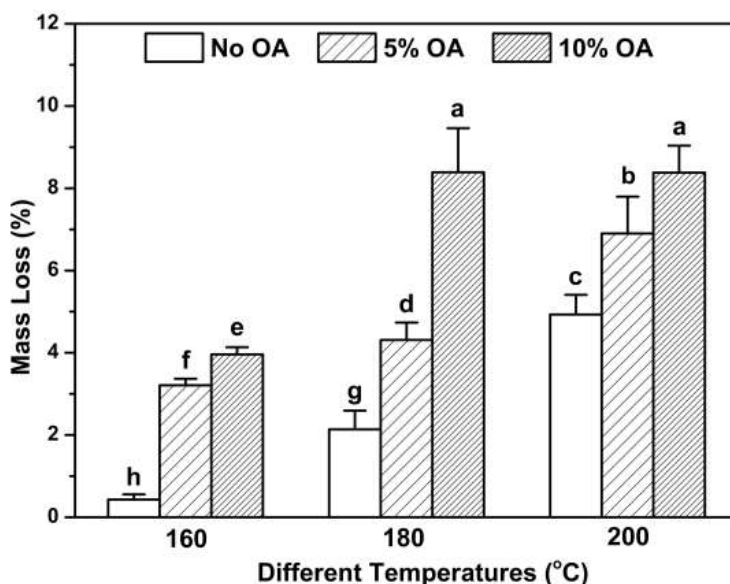


Fig. 1. Mass losses of thermally modified wood at 160 °C, 180 °C, and 200 °C with no OA (0% OA), 5% OA, and 10% OA pretreatment. Bars accompanied by a different letter (a, b, c, d, e, f, g, h) are significantly different at $p < 0.05$ (Tukey's HSD test).

Water absorption (WA)

The water absorption (WA) of the control and treated samples are illustrated in Fig. 2. It can be seen that WA of the OA-treated wood decreased compared to the untreated wood. This was thought to be related to the long-hydrophobic chain of OA (Menendez *et al.* 2005; Ulvcrona *et al.* 2006). However, the WA of 5% and 10% OA-treated groups after 6 h immersion were reduced by 22.46% and 34.44%, respectively, and the reduction gradually decreased to 6.87% and 13.16%, respectively, after soaking for 192 h (Fig. 2a). This suggests that the water repelling ability of OA is more significant for short-term soaking. It also leads to the assumption that the modifiers might attach to the cell walls as a cover layer to block the sorption sites in the cell wall; this cover layer, however, is quite thin and easily penetrated after being soaked. A similar phenomenon was found in silane-modified wood (Donath *et al.* 2006).

Figure 2b, 2c, and 2d show the effects of thermal modification and OA-thermal treatments on the WA rates. In most cases of thermally modified wood, the WA rates were smaller than the untreated wood due to the enormous losses of sorption sites accompanied by degradation of hemicellulose. Generally, the WA significantly decreased with the increased heating temperature. However, the samples modified at 160 °C without OA treatment failed in lowering the WA rates, especially at the end of water absorption test, water absorption of 160 °C thermally modified wood was greater than control. The possible explanation for increased WA was the escape of volatile organic extractives, which would release during a mild thermal modification at 160 °C (Tomak *et al.* 2011a; Kocafee *et al.* 2008).

The combined treated wood showed lower WA than either thermally modified wood or OA-treated wood (Fig. 2d). The results indicated that hydrophobicity enhancement was more apparent with either an increased concentration of OA or a higher temperature of thermal modification. This suggests that the introduction of OA can

synergistically improve the hydrophobicity of thermally modified wood. However, it should be noted that the samples that had undergone both 5% OA (10% OA) treatment and 160 °C thermal treatment showed similar water absorption values with OA-treated wood without thermal treatment. It was thought that OA impregnation had achieved a dominant position in the combined treatment at low temperature. This implies that in combined treatment, 180 °C is the minimum requirement for achieving improvements on water absorption. Another finding was that there was no statistically significant ($p < 0.05$) difference between 10% OA + 180 °C and 10% OA + 200 °C treated samples, which was consistent with the results of mass loss. Again, this demonstrates that mass loss of thermally modified wood is well connected with its performance. Further investigations with respect to the analysis of microstructure and chemical composition of treated wood are necessary for validating these results.

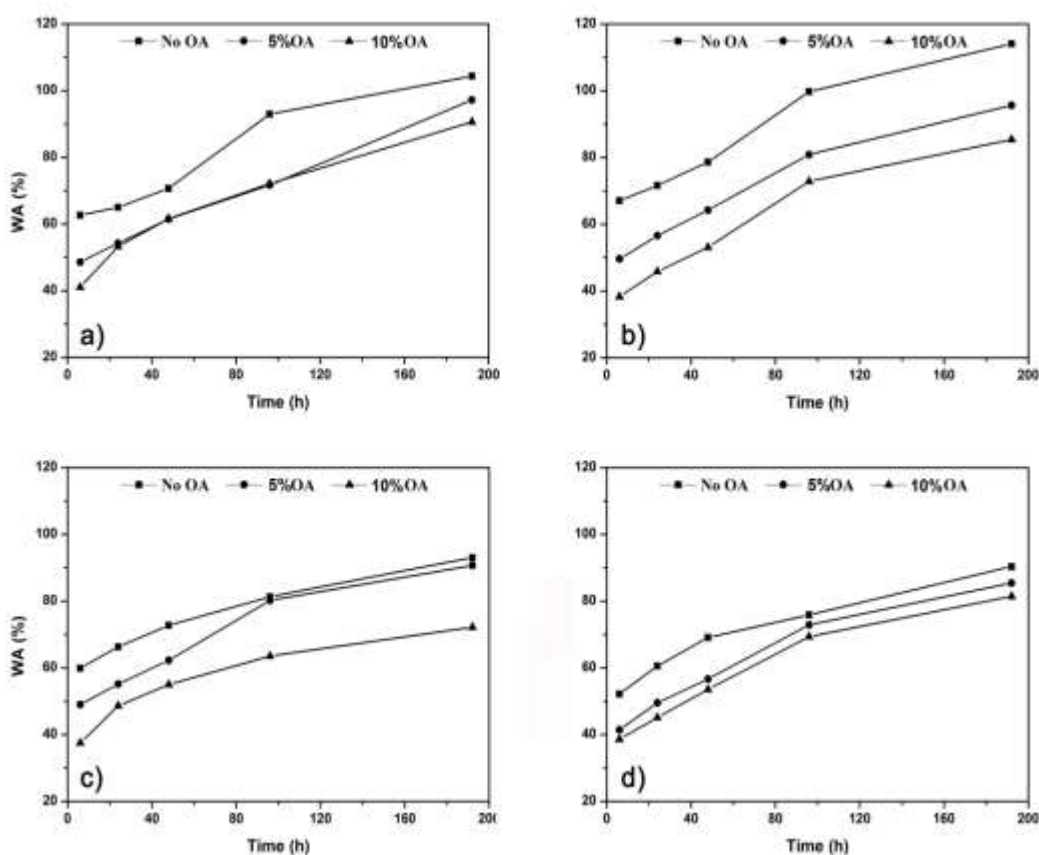


Fig. 2. WA of 0% OA, 5% OA, or 10% OA-treated wood with thermal modification of 60 °C (a), 160 °C (b), 180 °C (c) or 200 °C (d)

The volumetric swelling by the water-soaking test was also studied (Fig. 3). This shows that the OA-treated wood yielded lower VS_a than the control. The hypothesis of a decrease in swelling was based on the improved hydrophobicity and cell wall bulking. For thermally modified wood without OA pretreatment, the enhanced dimensional stability was not distinctive until the heating temperature had been increased to 200 °C. Although thermally modified wood up to 180 °C could improve the water repellency by decreasing the amount of hydroxyl groups, VS_a barely decreased. An explanation for this phenomenon is that the swelling of wood is not only attributable to the loss of sorption

sites but also to other phenomena such as structural modification and chemical changes of lignin. For example, inefficient cross-linking of lignin was reported to form a firm and inflexible network to diminish the expansion of cellulose microfibrils (Funaoka *et al.* 1990; Repellin and Guyonnet 2005; Tjeerdsma *et al.* 1998). As expected, the VS_a of thermally modified wood with OA pretreatment were much lower than the other groups. The biggest reduction of VS_a was the 33.24% achieved in 10% OA + 200 °C modified wood, suggesting the synergistic effect of combined treatments on dimensional stability. The following mechanisms may be responsible for this improvement: (1) bulking effect due to the penetration of OA into the wood restrained the swelling of the cell wall; (2) deposition of OA on the cell wall hindered movement of water molecules; and (3) OA accelerated the degradation and cross-linking of cell wall components, which further improved the dimensional stability of wood.

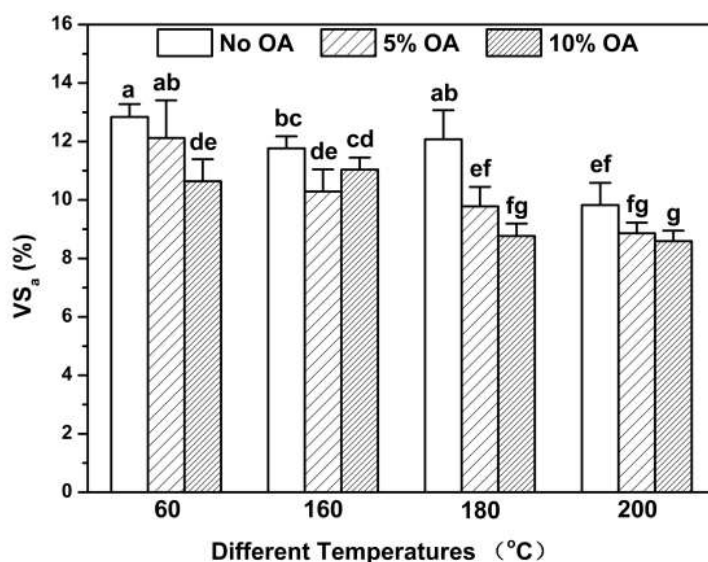


Fig. 3. Volumetric swelling based on water absorption of control and treated samples. Bars accompanied by a different letter (a, b, c, d, e, f, g) are significantly different at $p < 0.05$ (Tukey's HSD test).

Equilibrium moisture content (EMC)

The EMC values of the treated and untreated wood at equilibrium (23 °C, 96% RH) are presented in Fig. 4. After a long conditioning period, subtle differences in EMC values were observed between OA-treated wood and control. This indicated an unfavorable efficacy of OA in long-term water resistance, which was similar to the WA results. However, thermal modification can effectively reduce the EMC of wood, as consistent with the previous studies (Borrega and Kärenlampi 2010; Metsä-Kortelainen *et al.* 2006). Additionally, when wood was heated to a higher temperature, the moisture-sorption capacity of thermally modified wood decreased more, apparently due to enormous losses of primary sorption sites (-OH).

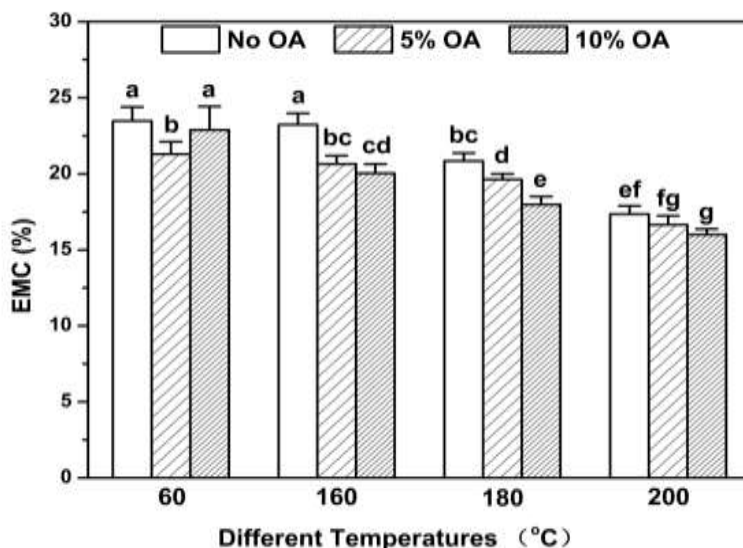


Fig. 4. EMC of control and treated samples. Bars accompanied by a different letter (a, b, c, d, e, f, g) are significantly different at $p < 0.05$ (Tukey's HSD test)

The use of OA combined with thermal modification can lower the EMC of thermally modified wood. Moreover, when thermal modification was processed at the same temperature, the groups with 10% OA pretreatment showed lower EMC than the groups pretreated with 5% OA. This indicates that although OA is not capable of decreasing the EMC of wood, it can improve the efficiency of thermal modification probably by accelerating the thermal degradation processes. Furthermore, the higher the concentration of OA, the greater the degradation of the wood components occur. The result suggests that combined treatments show great advantages in reducing hygroscopicity compared with any single treatment.

Figure 5 provides the VS_b values to evaluate the dimensional stability of each treatment under adsorption conditions. As illustrated, the OA-treated wood showed lower VS_b than the control (11.59%). The VS_b values were 9.43% and 9.48%, corresponding to 5% and 10% OA-treated wood, respectively. The decreased swelling should be mainly attributed to the bulking effects of OA-treated wood rather than the hydrophobicity. The results indicate that the concentration levels of OA seemed to make no difference in improving dimensional stability based on EMC. The 5% OA treatment was probably enough to achieve the maximum bulking of the cell wall. It should be noted that the VS_b values of thermally modified wood were positively correlated with hygroscopicity EMC, which was well documented in previous research (Ates *et al.* 2009; Hill 2006). Obviously, the combined treatments exhibited the lowest VS_b . The reduction of volumetric swelling for OA-thermally modified wood may be as high as 44.99%, which was explained by the decreased hygroscopicity and bulking effects of modified wood.

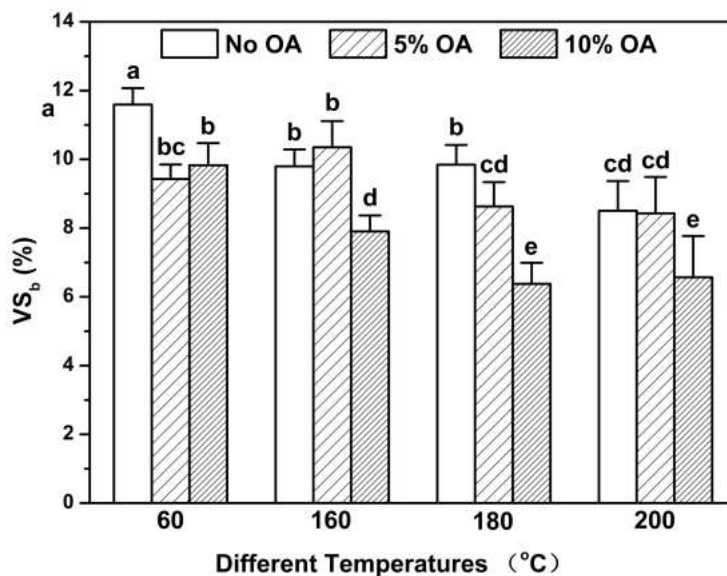


Fig. 5. Volumetric swelling based on EMC of control and treated samples. Bars accompanied by a different letter (a, b, c, d, e) are significantly different at $p < 0.05$ (Tukey's HSD test)

Changes of cell wall structure and chemical components

Micrographs in Fig. 6 showed a distinct difference in morphology between treated and untreated samples. In comparison with the control in the transverse and radial sections (Fig. 6a), an oily surface was clearly identified for 10% OA-treated wood (Fig. 6c), especially in radial section. In addition, OA seemed to be uniformly distributed on the cell wall, probably explaining the formation of the hydrophobic layer on the cell wall. Thickening of the cell wall was also observed in the transverse section of 10% OA-treated wood, which was a strong indication of cell wall bulking. As Fig. 6b illustrates, thermally modified wood at 200 °C showed partial destruction of the tracheids, and some small cracks appeared on the cross section of the cell wall. It indicates that thermal modification at 200 °C could cause a certain extent of cell wall degradation, which has been reported previously (Awoyemi and Jones 2011). Compared to the micrographs of the 200 °C thermally modified wood (Fig. 6c), the 10% OA + 200 °C modified wood showed more seriously destroyed surfaces, such that more and larger cracks appeared in the transverse section (Fig. 6b and d). Thus, it was confirmed that the process of thermal degradation was accelerated by OA. However, the SEM micrographs of 10% OA + 200 °C modified wood showed a lower amount of attachment than 10% OA-treated wood (Fig. 6c and d). This result is in agreement with mass loss values, showing that the decomposition of OA did occur during the thermal treatment when heating temperature exceeded 160 °C (Ataei *et al.* 2012).

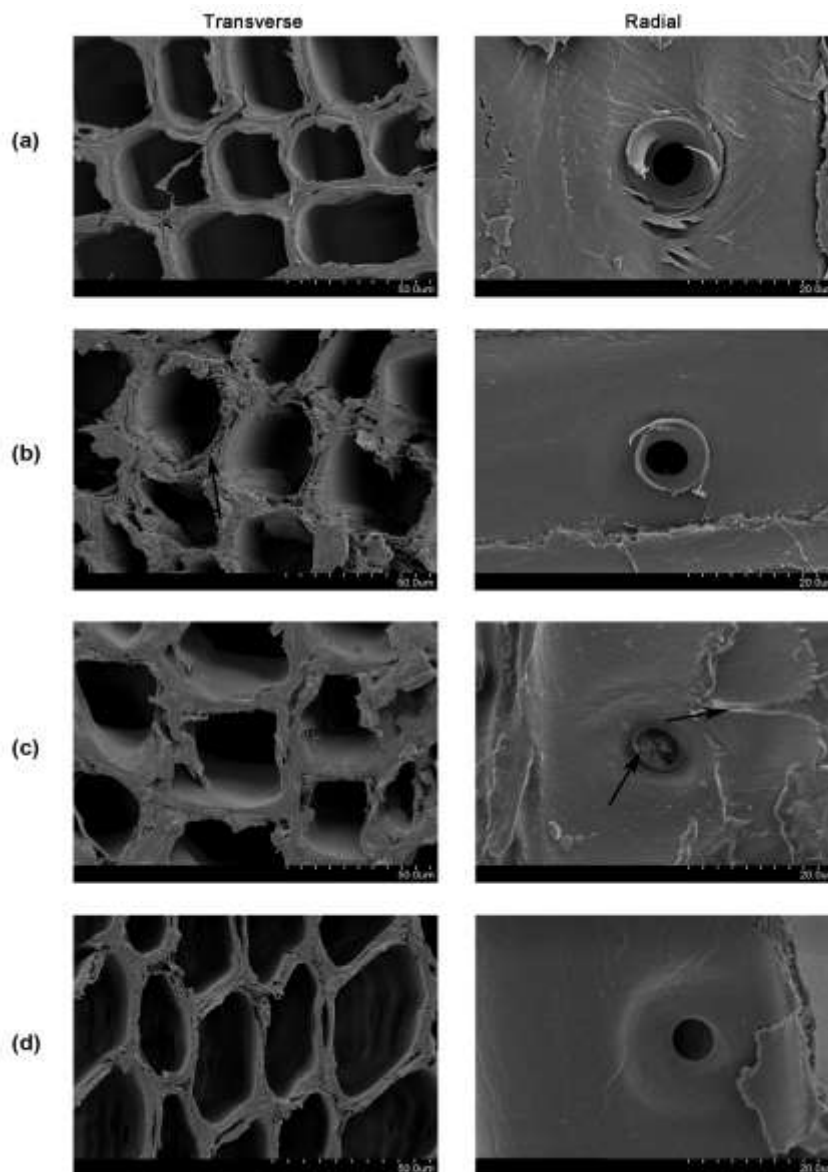


Fig. 6. SEM micrographs in transverse and radial section of control (a), 200 °C (b), 10% OA, (c) and 10% OA + 200 °C, (d) treated wood

Table 2. Assignments for FTIR Absorption Peaks

Wavenumber (cm ⁻¹)	Assignments and Remarks
2924	-CH ₂ , asymmetric deformation in OA
2854	-CH ₂ , symmetric deformation in OA
1738	C=O, stretching (unconjugated) in hemicellulose
1650	C=O, stretching (conjugated) in lignin
1639	COO ⁻ , symmetric stretch in OA
1596	C=C, Aromatic skeletal vibration in lignin
1505	C=C, Aromatic skeletal vibration in lignin

FTIR spectra of selected samples are shown in Fig. 7, and the assignments for FTIR absorption peaks are listed in Table 2. By comparing the spectra of control and thermally modified wood (Fig. 7a), slight reduction of intensities of the peaks located at

1738 cm^{-1} (C=O) appeared until the heat temperature increased to 200 °C, corresponding to deacetylation of the hemicellulose (Tjeerdsma *et al.* 1998; Wang *et al.* 2013). The slight increase in intensity of the absorption bands at 1596 cm^{-1} (C=C) and 1505 cm^{-1} (C=C) observed for the 200 °C thermally modified wood attributed to cross-linking of lignin (Ataei *et al.* 2012; Lima *et al.* 2013). This suggests that the degradation of hemicellulose and the cross-linking of lignin are the main chemical transformations during the thermal modification, which are responsible for enhanced hydrophobicity and dimensional stability (Boonstra and Tjeerdsma 2006; Tjeerdsma and Militz 2005).

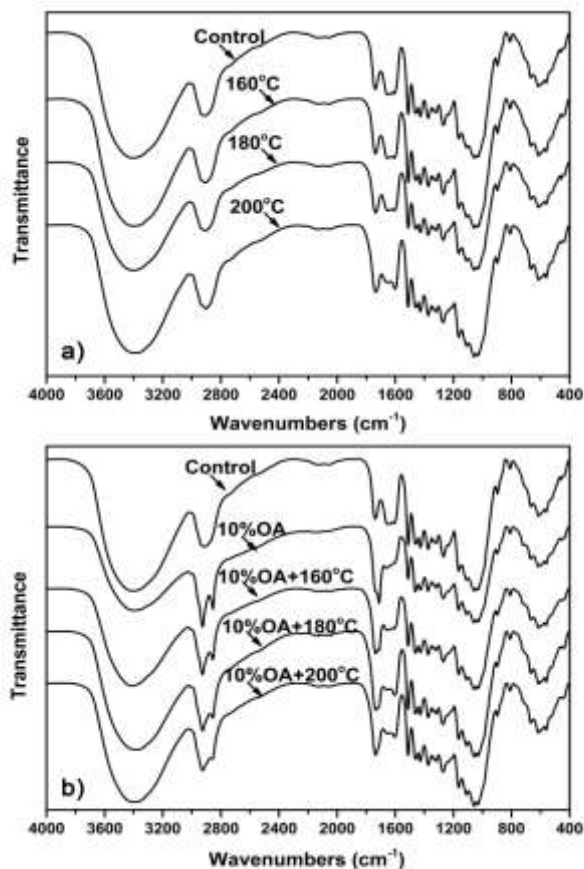


Fig. 7. FTIR spectra of control (a) 0% OA-thermally modified wood, and (b) 10% OA-thermally modified wood

Two new absorption bands at 2924 cm^{-1} and 2854 cm^{-1} appeared in the FTIR spectrum of all the samples with OA treatment corresponding to the asymmetric and symmetrical stretching of methylene (Fig. 7b) (Zhang *et al.* 2006). In addition, the increment in the intensities of the absorption bands at 1738 cm^{-1} (C=O) and 1639 cm^{-1} (COO-) were observed after OA treatment (Zhang *et al.* 2006). Both of them verify the existence of OA in the OA-treated wood.

However, once the OA-treated wood was coupled with thermal modification, the intensity of absorption bands at 2924 cm^{-1} (-CH₂, asymmetric) and 2854 cm^{-1} (-CH₂, symmetric) became more significant at the elevated temperature. This result suggests the decomposition of OA. However, the intensity of the absorption bands at 1738 cm^{-1} (C=O) went up instead of decreasing, probably due to the esterification between OA and cell

wall (Tjeerdsma and Militz 2005). An important finding of this work was that the increased intensity of the peak at 1596 cm^{-1} (C=C) and 1505 cm^{-1} (C=C), in the presence of 10% OA, emerged in advance from $200\text{ }^{\circ}\text{C}$ to $180\text{ }^{\circ}\text{C}$. This finding indicates that the condensation of lignin can be promoted by OA pretreatment (Ataei *et al.* 2012; Lima *et al.* 2013). However, the increase of peak values at 1596 cm^{-1} (C=C) was more obvious in the 10% OA-treated wood at $180\text{ }^{\circ}\text{C}$ rather than at $200\text{ }^{\circ}\text{C}$. This characterization was further evidence of more decomposition of OA, and therefore less OA was left to accelerate the process of thermal modification at $200\text{ }^{\circ}\text{C}$. Presently, no obvious negative effect on the chemical degradation was found in OA-thermally modified wood.

CONCLUSIONS

1. Both OA treatment and thermal modification can improve the hydrophobicity and dimensional stability of wood individually, while the combined treatment presented in this study was shown to be the most efficient method.
2. As investigated by SEM and FTIR analysis, OA pretreatment was able to accelerate the degradation process of thermal modification. Furthermore, the decomposition of OA was also confirmed.

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REFERENCES CITED

- Ataei, S., Yahya, R., Gan, S., and Hassan, A. (2012). "Study of thermal decomposition kinetics of palm oleic acid-based alkyds and effect of oil length on thermal stability," *J. Polym. Environ.* 20(2), 507-513.
- Ates, S., Akyildiz, M., and Ozdemir, H. (2009). "Effects of heat treatment on Calabrian pine (*Pinus brutia* Ten.) wood," *BioResources* 4(3), 1032-1043.
- Awoyemi, L., and Jones, I. (2011). "Anatomical explanations for the changes in properties of western red cedar (*Thuja plicata*) wood during heat treatment," *Wood. Sci. Technol.* 45(2), 261-267.
- Boonstra, M., and Tjeerdsma, B. (2006). "Chemical analysis of heat treated softwoods," *Holz. Roh. Werkst.* 64(3), 204-211.
- Borrega, M., and Kärenlampi, P. (2010). "Hygroscopicity of heat-treated Norway spruce (*Picea abies*) wood," *Eur. J. Wood. Prod.* 68(2), 233-235.
- Donath, S., Militz, H., and Mai, C. (2006). "Creating water-repellent effects on wood by treatment with silanes," *Holzforschung* 60(1), 40-46.
- Esteves, B., Marques, A., Domingos, I., and Pereira, H. (2007). "Influence of steam heating on the properties of pine (*Pinus pinaster*) and eucalypt (*Eucalyptus globulus*) wood," *Wood. Sci. Technol.* 41(3), 193-207.

- Esteves, B., and Pereira, H. (2009). "Wood modification by heat treatment: A review," *BioResources* 4(1), 370-404.
- Funaoka, M., Kako, T., and Abe, I. (1990). "Condensation of lignin during heating of wood," *Wood. Sci. Technol.* 24(3), 277-288.
- Hakkou, M., Pétrissans, M., ElBakali, I., Gérardin, P., and Zoulalian, A. (2005). "Wettability changes and mass loss during heat treatment of wood," *Holzforschung* 59(1), 35-37.
- Hill, C. (2006). *Wood Modification-Chemical, Thermal, and Other Processes*, Wiley, Sussex.
- Kamdern, D., Pizzi, A., and Jermannaud, A. (2002). "Durability of heat-treated wood," *Holz. Roh. Werkst.* 60(1), 1-6
- Kartal, N., Hwang, W., and Imamura, Y. (2007). "Water absorption of boron-treated and heat-modified wood," *J. Wood. Sci.* 53(5), 454-457.
- Kocafe, D., Poncsak, S., and Boluk, Y. (2008). "Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen," *BioResources* 3(2), 517-537.
- Korkut, S., Akgül, M., and DüNDAR, T. (2008). "The effects of heat treatment on some technological properties of Scots pine (*Pinus sylvestris* L.) wood," *Bioresour. Technol.* 99(6), 1861-1868.
- Lima, R., Raza, R., Qin, H., Li, J., Lindström, M., and Zhu, B. (2013). "Direct lignin fuel cell for power generation," *RSC. Adv.* 3(15), 5083-5089.
- Lyon, F., Thevenon, M., Hwang, W., Imamura, Y., Gril, J., and Pizzi, A. (2007). "Effect of an oil heat treatment on the leachability and biological resistance of boric acid impregnated wood," *Ann. For. Sci.* 64(6), 673-678
- Menendez, J., Vellon, L., Colomer, R., and Lupu, R. (2005). "Oleic acid, the main monounsaturated fatty acid of olive oil, suppresses Her-2/neu (erbB-2) expression and synergistically enhances the growth inhibitory effects of trastuzumab (Herceptin™) in breast cancer cells with Her-2/neu oncogene amplification," *Ann. Oncol.* 16(3), 359-371.
- Metsä-Kortelainen, S., Antikainen, T., and Viitaniemi, P. (2006). "The water absorption of sapwood and heartwood of Scots pine and Norway spruce heat-treated at 170 °C, 190 °C, 210 °C, and 230 °C," *Holz Roh Werkst.* 64(3), 192-197.
- Militz, H. (2002). "Thermal treatment of wood: European processes and their background," in: 33rd Annual Meeting, 12-17 May, Cardiff, Wales, IRG/WP 02-40241.
- Popescu, M. C., Froidevaux, J., Navi, P., and Popescu, C. M. (2013). "Structural modifications of *Tilia cordata* wood during heat treatment investigated by FT-IR and 2D IR correlation spectroscopy," *J. Mol. Struct.* 1033(6), 176-186.
- Priadi, T., and Hiziroglu, S. (2013). "Characterization of heat treated wood species," *Mater. Des.* 49, 575-582.
- Repellin, V., and Guyonnet, R. (2005). "Evaluation of heat-treated wood swelling by differential scanning calorimetry in relation to chemical composition," *Holzforschung* 59(1), 28-34.
- Robinson, T. J., Via, B. K., Fasina, O., Adhikari, S., and Carter, E. (2011). "Impregnation of bio-oil from small diameter pine into wood from moisture resistance," *BioResources* 6(4), 4747-4761.
- Rowell, R. (2006). "Chemical modification of wood: A short review," *Wood. Mater. Sci. Eng.* 1(1), 29-33.

- Rowell, R. (2012). *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton.
- Schultz, T. P., Nicholas, D. D., and Ingram Jr., L. L. (2007). "Laboratory and outdoor water repellency and dimensional stability of southern pine sapwood treated with a waterborne water repellent made from resin acids," *Holzforschung* 61(3), 317-322.
- Temiz, A., Terziev, N., Jacobsen, B., Eikenes, M. (2006). "Weathering, water absorption, and durability of silicon, acetylated, and heat-treated wood," *J. Appl. Polym. Sci.* 102(5), 4506-4513
- Tjeerdsma, B., Boonstra, M., Pizzi, A., Tekely, P., and Militz, H. (1998). "Characterisation of thermally modified wood: Molecular reasons for wood performance improvement," *Holz. Roh. Werkst.* 56(3), 149-153.
- Tjeerdsma, B., and Militz, H. (2005). "Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood," *Holz. Roh. Werkst.* 63(2), 102-111.
- Tomak, E., Hughes, M., Yildiz, U., and Viitanen, H. (2011a). "The combined effects of boron and oil heat treatment on beech and Scots pine wood properties. Part I: Boron leaching, thermogravimetric analysis, and chemical composition," *J. Mater. Sci.* 46(3), 598-607.
- Tomak, E., Hughes, M., Yildiz, U., and Viitanen, H. (2011b). "The combined effects of boron and oil heat treatment on beech and Scots pine wood properties. Part II: Water absorption, compression strength, color changes, and decay resistance," *J. Mater. Sci.* 46(3), 608-615.
- Tomak, E., Yildiz, U., and Can, A. (2010). "Treatment of Scots pine wood with oil in water and water in oil emulsion systems effects on boron leaching and water absorption," in: *41st Annual Meeting*, 9-13 May, Biarritz, France, IRG/WP 10-30535.
- Ulvcrona, T., Lindberg, H., and Bergsten, U. (2006). "Impregnation of Norway spruce (*Picea abies* L. Karst.) wood by hydrophobic oil and dispersion patterns in different tissues," *Forestry* 79(1), 123-134.
- Vetter, L., Bulcke, J., and Acker, J. (2010). "Impact of organosilicon treatments on the wood-water relationship of solid wood," *Holzforschung* 64(4), 463-468.
- Wang, J., and Cooper, P. (2005). "Properties of hot oil treated wood and the possible chemical reactions between wood and soybean oil during heat treatment," in: *36th Annual Meeting*, 24-28 April, Bangalore, India, IRG/WP 05-40304.
- Wang, W., Cao, J., Cui, F., and Wang, X. (2012). "Effect of pH on chemical components and mechanical properties of thermally modified wood," *Wood. Fiber. Sci.* 44(1), 46-53.
- Wang, W., Zhu, Y., and Cao, J. (2013). "Evaluation of copper leaching in thermally modified southern yellow pine wood impregnated with ACQ-D," *BioResources* 8(3), 4687-4701.
- Zhang, L., He, R., and Gu, H. (2006). "Oleic acid coating on the monodisperse magnetite nanoparticles," *Appl. Surf. Sci.* 253(5), 2611-2617.
- Zhang, Y., Jin, J., and Wang, S. (2007). "Effects of resin and wax on the water uptake behavior of wood strands," *Wood. Fiber. Sci.* 39(2), 271-278.

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