Dimensional Stability and Mechanical Properties of Plantation Poplar Wood Esterified Using Acetic Anhydride

Yubo Chai,[a,]* Junliang Liu,[a] Zhe Wang,[a] and Yong Zhao [b]

Plantation poplar (*Populus ussuriensis*) wood was esterified using acetic anhydride without catalysts to improve its dimensional stability. The effects of acetylation temperature (100 °C, 120 °C, and 140 °C) on the dimensional stability, mechanical properties, microstructure, and functional groups of the resulting acetylated wood were systematically investigated. Results showed that the wood acetylated at 100 °C and 120 °C had an improved dimensional stability and comparable mechanical properties to those of the control wood. Wood acetylated at 140 °C had an improved dimensional stability and decreased mechanical properties as compared to those of the control wood. Scanning electron microscopic (SEM) analysis showed that the wood acetylated at 140 °C had obviously different microstructures than the control wood and the wood acetylated at 100 °C and 120 °C. The changes of functional groups in the acetylated wood were revealed by Fourier transform infrared spectroscopy (FTIR). The –OH groups of cellulose, hemicellulose, and lignin all were shown to participate in the acetylation reaction.

Keywords: Acetylation; Dimensional stability; Acetic anhydride; Plantation poplar wood

*Contact information: a: Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing 100091, P. R. China; b: Faculty of Forestry, University of Toronto, Toronto M5S 3B3, Canada; *Corresponding author: chaiyubo@caf.ac.cn*

INTRODUCTION

Wood is a renewable biomaterial and has been used for many applications from decoration to structural assembly due to its excellent strength-to-weight ratio, ease of processing, and aesthetic appearance. The main components of wood are cellulose, hemicellulose, and lignin. These polymers make up the cell wall and are responsible for the physical, mechanical, and chemical properties exhibited by wood. Cellulose and hemicellulose are hydrophilic in nature. The presence of hydroxyl groups and other oxygen-containing groups in these polymers attract moisture and participate in hydrogen bonding (Rowell 1983). As a result, the moisture content of wood changes with the surrounding temperature and humidity. Changes in wood moisture content result in dimensional instability and causes serious problems for wood utilization and limits its application.

Chemical modification of wood offers various protections and can enhance the properties of the wood (Rowell 1983). It involves chemical reaction between some reactive part of a wood component and single or multiple chemical reagents, with or without catalyst, to form a covalent bond between the chemical reagent and the wood substrate (Fuqua *et al.* 2012). Wood can be modified using esters, isocyanates, acetals, or epoxides depending on its end-use (Rowell 1983; Waldermar and André 2004).

Wood esterification has been found to be an effective chemical modification method to improve wood dimensional stability through converting hydrophilic hydroxyl groups into more hydrophobic groups. Acetic anhydride is one of the most frequently used chemical reagents for wood esterification with high cost efficiency (Rowell 1983; Waldermar and André 2004; Jebrane *et al.* 2011). The accessible hydroxyl groups in the wood cell wall are esterified with or without catalysts, and acetic acid is formed as a by-product (Rowell 2006; Cetin *et al.* 2011; Ozmen and Cetin 2012). At a weight gain greater than 17%, the acetylated wood has very good dimensional stability and resistance to fungal attack (Papadopoulos and Hill 2003; Papadopoulos 2006). Acetylation is a single addition reaction in which one acetyl group is added to one hydroxyl group without polymerization (Waldermar and Andre 2004; Sadeghifar *et al.* 2014).

In addition to acetic anhydride, fatty acids and their acid chlorides have been extensively investigated for wood esterification. It has been found that esterifying wood by a fatty acid chloride containing a long chain can provide a water repellent layer on the surface on the wood (Prakash and Mahadevan 2008). However, some concerns on increased thermoplasticity of wood modified using fatty acid chlorides in solvent systems have been reported. Thiebaud and Borrendon (1995) esterified wood sawdust by fatty acid chloride without using any solvents. They found that the thermal stability of the modified wood was improved. Prakash *et al.* (2006) reported that esterification of wood with octanoyl chloride improved the dimensional stability and photostability of the wood. Although other esterification reagents may in theory produce favorable products, their difficult processing requirements restrict their commercialization (Arni *et al.* 1961; Funakoshi *et al.* 1979; Shiraishi *et al.* 1979).

Poplar (*Populus ussuriensis*) is one of the main fast-growing Chinese plantation wood species. However, its low density and low dimensional stability have limited its applications. Resin impregnation has been used to improve the dimensional stability and mechanical properties of plantation poplar wood (Liu *et al.* 2002; Liu and Wang. 2004; Yue *et al.* 2010). There have been very few studies on the esterification of plantation poplar wood. Therefore, in this study, plantation poplar wood was esterified using acetic anhydride without catalysts under various conditions. The dimensional stability and mechanical properties of the acetylated wood were investigated. Meanwhile, the changes in the microstructure and functional groups of the wood acetylated at different conditions were investigated.

EXPERIMENTAL

Materials

Poplar plantation wood (*Populus ussuriensis*) was harvested from Baihe Forest Service Station, Jilin Province, P.R. China. The air-dried density of the wood was 0.39 g/cm^3. The sapwood was selected and cut into samples with dimensions of 400 mm × 25 mm × 25 mm (longitudinal × radial × tangential). The wood samples were acetylated using acetic anhydride (97% concentration, industrial grade, obtained from Shanghai Jiaohua Chemical. Co.) at various conditions.

Wood Acetylation

The wood samples were first oven-dried at 105 °C to constant weight and then subjected to acetylation at various conditions. The oven-dried wood samples were placed into a stainless reactor and vacuumed for 30 min. Then, the acetic anhydride was introduced to the stainless reactor and submersed the wood samples under a pressure of 1.0 MPa for 2 h at room temperature. After removing the acetic anhydride from the stainless reactor, nitrogen was pumped into the reactor and the reactor was heated to 100, 120, or 140 °C, and kept for 2 h under a pressure of 0.3 MPa. After acetylation, the reactor was cooled to 30 °C. The acetylated wood samples were kept in the reactor and washed with running fresh water for 24 h to remove the unreacted acetic anhydride and acetic acid. The acetylated wood was then vacuum dried at -0.09 MPa until constant weight. The drying schedule was 50 °C for 48 h, 80 °C for 72 h, and 105 °C for 48 h.

Characterization of the Acetylated Wood

Physical and mechanical properties of the acetylated wood

The weight percentage gain (WPG) of the acetylated wood under different reaction temperatures was determined on the basis of the oven-dried weight before and after acetylation. The weight percentage gain was calculated based on Eq. 1,

$$WPG = (W2\text{-}W1)/W1 \times 100\% \qquad (1)$$

where $W2$ is the oven-dried weight of the acetylated wood and $W1$ is the oven-dried weight of the wood before acetylation.

The moisture uptake and volumetric swelling coefficient of the acetylated wood were evaluated according to GB/T1934.2-2009. The mechanical properties of the acetylated wood, including modulus of elasticity (MOE) and modulus of rupture (MOR), were investigated according to GB/T 1936.1-2009 and GB/T 1936.2-2009, respectively.

SEM of the acetylated wood

Cubical blocks with the dimensions of 5 mm × 5 mm × 2 mm were cut from the acetylated and control wood samples. Transverse sections and radial sections were ion-sputter coated with gold and observed using scanning electron microscope (SEM, S4800, Hitachi, Japan).

FTIR of the acetylated wood

The acetylated and control wood samples were first grinded into powders and passed through a 100 to 120-mesh screen. The powder samples were then mixed with oven-dried potassium bromide (KBr) at approximately a 1:99 weight ratio to make pellets. Fourier transform infrared spectroscopy (FTIR, Magna-IR 750, Nicolet, USA) was used to scan the pellets at a wavelength range of 4000 to 650 cm^{-1} with 64 scans recorded per sample.

RESULTS AND DISCUSSION

Physical and Mechanical Properties of the Acetylated Wood

The weight percentage gain (WPG) of the wood samples was used as an indicator for the extent of wood acetylation. In general, a higher WPG indicated a higher degree of acetylation, *i.e.*, more hydroxyl groups were replaced and an improved dimensional stability of the resulting acetylated wood would be expected (Ramsden *et al.*1997; Li *et al.* 2000; Chang and Chang 2002).

The WPG of the wood acetylated at 100 °C, 120 °C, and 140 °C was 12.6%, 19.7%, and 21.3%, respectively. A higher acetylation temperature resulted in a higher extent of wood acetylation. However, with an acetylation temperature increase from 120 °C to 140 °C, the increase in WPG was not as high as that from 100 °C to 120 °C.

The moisture uptake and volumetric swelling coefficient were used as the parameters for the evaluation of dimensional stability of the acetylated wood.

Figure 1 shows the moisture uptake of the wood acetylated under different temperatures. The acetylated wood had a significantly lower moisture uptake as that of the control wood under all tested relative humidities. The acetylated wood with a higher WPG had a lower moisture uptake than that of wood with a lower WPG. However, there was no drastic difference between the moisture uptakes of acetylated wood with WPGs of 19.7% and 21.3%.

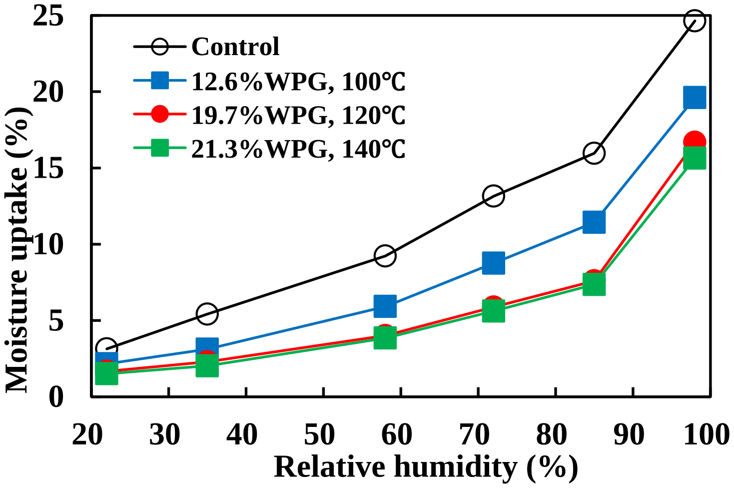

Fig. 1. The moisture uptake of the untreated and acetylated wood under different relative humidity conditions

The volumetric swelling coefficients of the wood acetylated under different temperatures is shown in Fig. 2. The volumetric swelling coefficient of the acetylated wood was significantly lower than that of the control wood under all relative humidity conditions. A higher WPG of acetylated wood resulted in a lower volumetric swelling coefficient. When the WPG of acetylated wood increased from 19.7% to 21.3%, the volumetric swelling coefficient of the acetylated wood did not change noticeably.

The anti-swelling efficiency (ASE) of the acetylated wood with different WPG is shown in Fig. 3. It can be seen that the acetylated wood with a higher WPG had a higher ASE under the same relative humidity. The acetylated wood with the WPG of 19.7% and 21.3% had the ASE of 60%-70% under all the selected relative humidity conditions, which was compared to the ASE of the acetylated wood of *Pinus sylvestris* and *P. hinoki* with the WPG of 20% reported in previous studies (Li *et al.* 2000; Epmeier *et al.* 2004). In addition, the ASE of the acetylated wood were found to increase linearly with the initial increment of WPGs, but the increasing tendency started to decline when the WPGs exceeded 20% (Li *et al.* 2000; Masahiro *et al.* 2010).

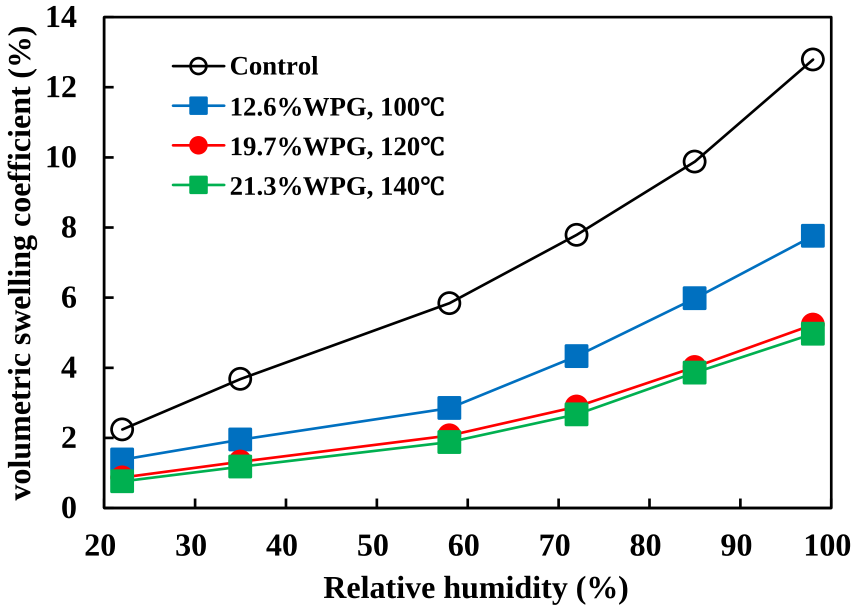

Fig. 2. The volumetric swelling coefficients of the untreated and acetylated wood under different relative humidity conditions

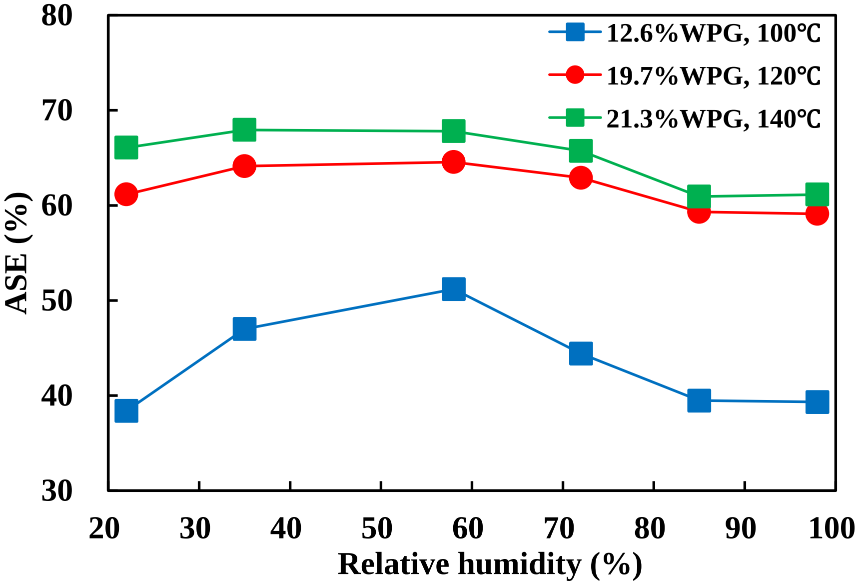

Fig. 3. The anti-swelling efficiency (ASE) of the untreated and acetylated wood under different relative humidity conditions

Previous studies have indicated that acetylation generally has no obvious effect on the mechanical properties of the resulting acetylated wood (Larsson and Simonson 1994; Papadopoulos 2008). However, a slightly decreased modulus of elasticity (MOE) and modulus of rupture (MOR) of acetylated wood have been reported (Dreher *et al.* 1964).

The mechanical properties of the acetylated wood are shown in Fig. 4. The acetylated wood samples with WPGs of 12.6% and 19.7% obtained under the acetylation temperature of 100 °C and 120 °C had comparable MOEs and MORs to that of the control wood. However, the wood with a WPG of 21.3% acetylated under 140 °C had a markedly lower MOE and MOR than that of the control wood and the wood acetylated under 100 °C and 120 °C. The possible reason could be the acetic acid formed during the acetylation process, which would promote the hydrolysis and degradation of the structural carbohydrate polymers such as cellulose and hemicelluloses at 140 °C.

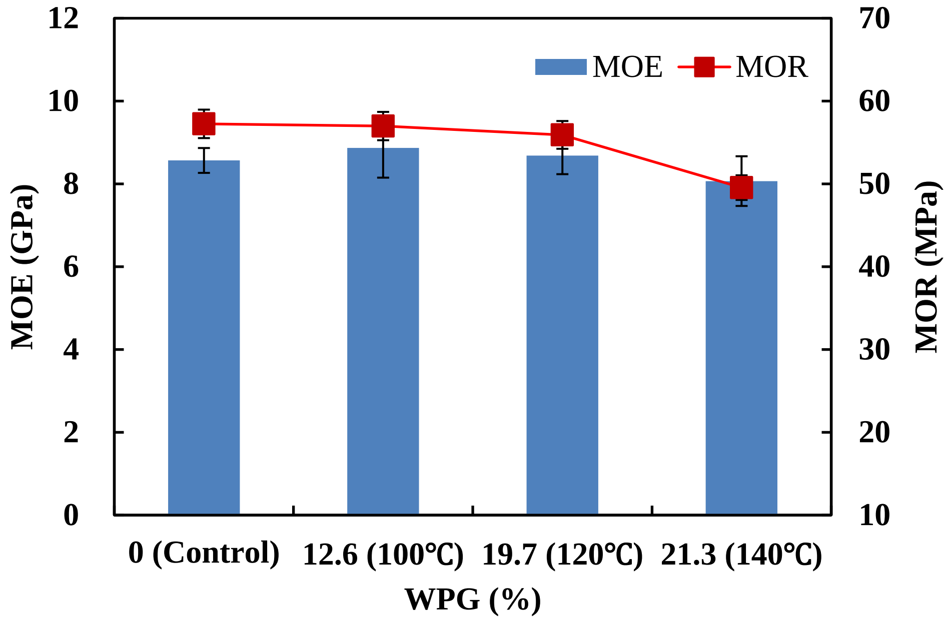

Fig. 4. The mechanical properties of the untreated and acetylated wood

SEM of the acetylated wood

The SEM images of transverse and radial sections of the acetylated wood are shown in Fig. 5. It can be found that the vessels and the cell wall of the wood fibers did not change after acetylation under 100 °C and 120 °C in the transverse section (Figs. 5c and 5e). As is shown in the SEM images of the radial section, the wall of the vessels and cell wall of the wood fibers as well as the pits did not experience any obvious changes or damages in the acetylated wood (Figs. 5d and 5f). For the wood acetylated under 140 °C, the deformation of vessels and broken wood fibers were found in the SEM images of both the transverse section and radial section (Figs. 5g and 5h). This observation explains the decreased MOE and MOR of the wood acetylated under 140 °C. Wood acetylation under 120 °C was more favorable than those under the other conditions, due to the better dimensional stability and less visible damage to the wood cell structure. Similar results were also reported in earlier studies (Liu and Xing 1999; Sander *et al.* 2003).

During acetylation, the –OH groups of the wood reacted with the acetic anhydride and acetic acid was formed as a by-product. Since the boiling point of acetic anhydride is 139 °C and the boiling point of acetic acid is 118 °C, when the wood acetylated under 140 °C the evaporation of acetic anhydride and acetic acid caused shrinkage, deformation, and destruction of the wood cell. Meanwhile, the high temperature and acidic environment of acetylation could synergistically promote chemical degradation of the wood cells and caused a subsequent decrease in mechanical properties of the resulting acetylated wood (Hill *et al.* 1998).

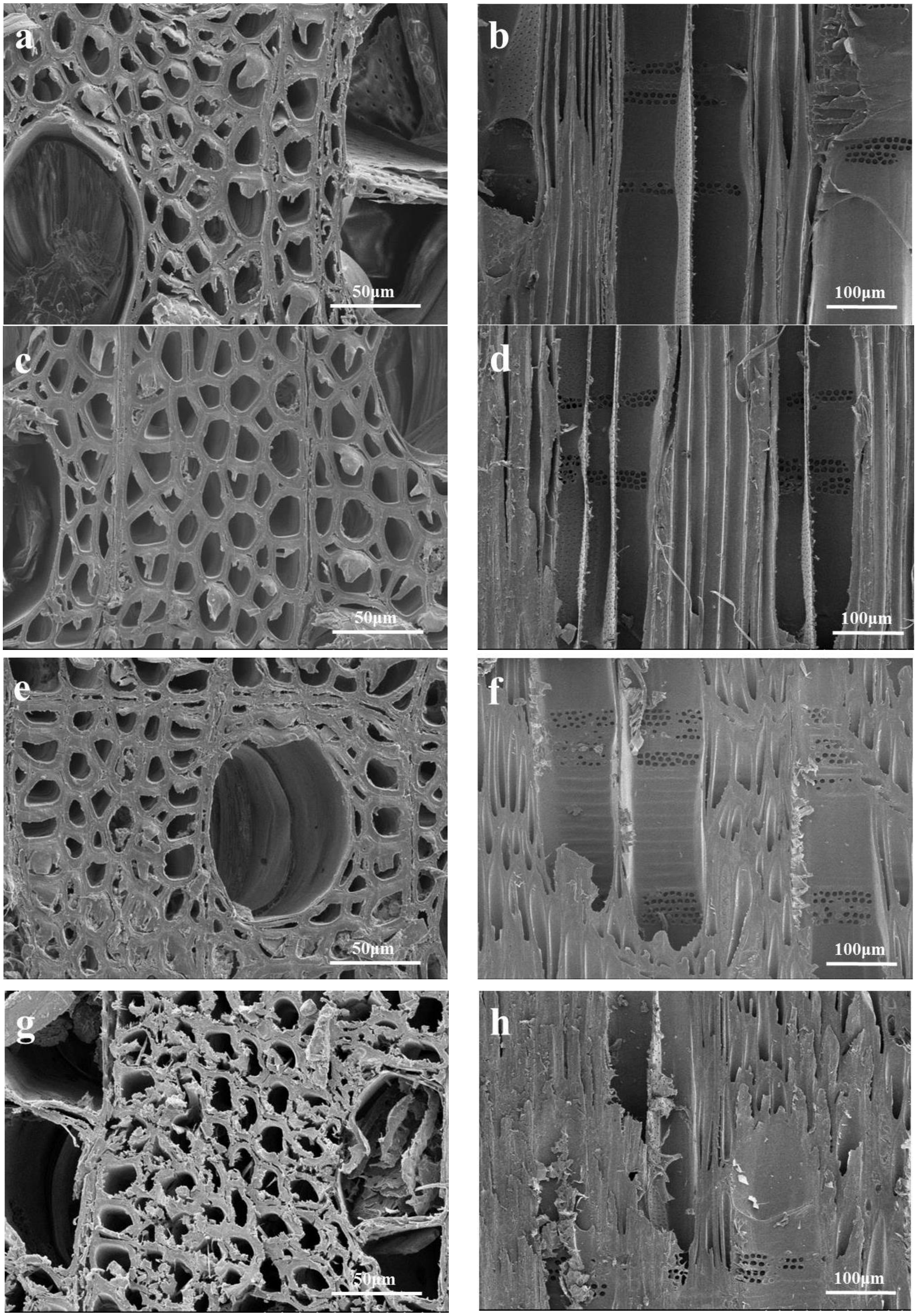

Fig. 5. The SEM images of the untreated wood and acetylated wood (a, b: cross and radial sections of the untreated wood; c, e, and g: cross sections of the acetylated wood under 100 °C, 120 °C, and 140 °C, respectively; and d, f, and h: radial sections of the acetylated wood under 100 °C, 120 °C, and 140 °C, respectively)

FTIR spectra of the acetylated wood

The FTIR spectra of the acetylated wood with different WPGs and the control wood are shown in Fig. 6.

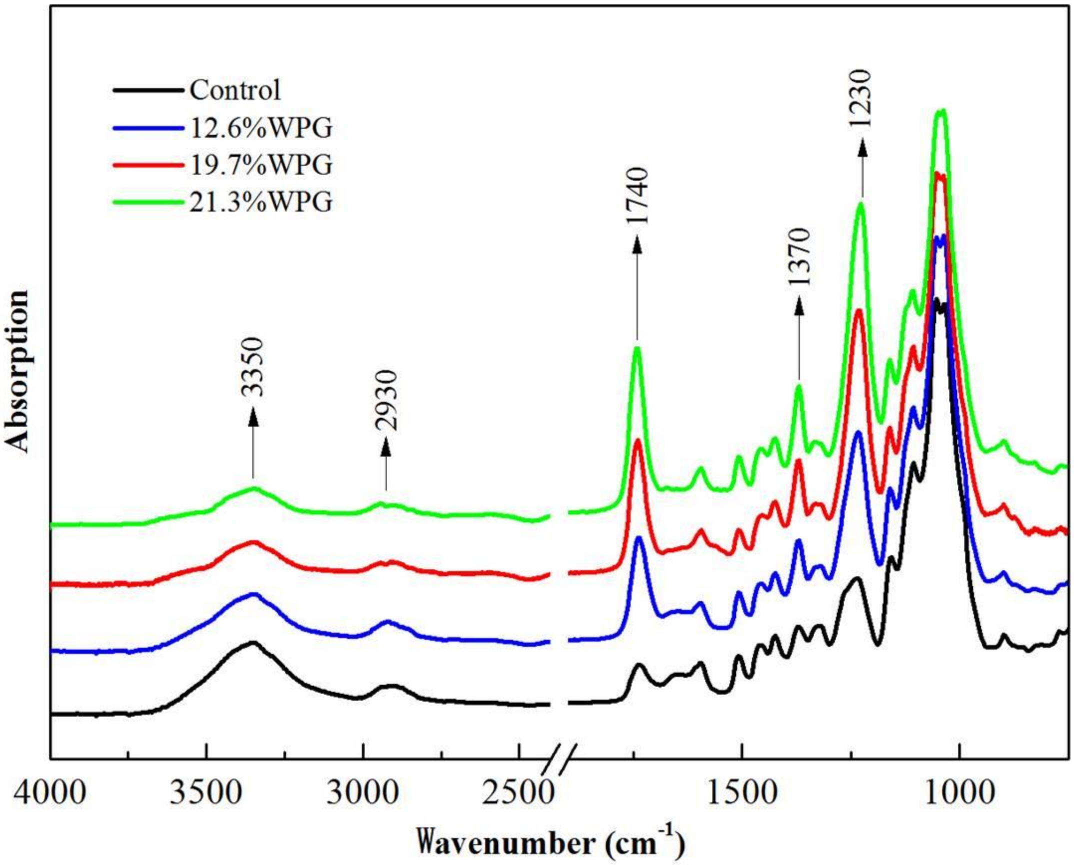

Fig. 6. The FTIR spectra of the acetylated wood with different WPGs and the control wood

The peaks at 3350 and 2930 cm^{-1} can be attributed to the –OH groups and CH_2 groups of cellulose, hemicellulose, and lignin in control wood and acetylated wood. It was found that the peak intensity of –OH groups in the acetylated wood was much weaker than those in the control wood, indicating that the –OH groups were replaced during the wood acetylation process. Meanwhile, the peak intensity of –OH groups decreased with an increase in WPG of acetylated wood, indicating that more –OH groups were replaced with an increased extent of wood acetylation. Since the –OH groups mainly contribute to the hydrophilicity of wood, the decrease in –OH group content would improve the dimensional stability of the resulting acetylated wood (Rowell 1983; Ohkoshi *et al.* 1997; Ohkoshi and Kato 1997). The –OH groups from cellulose, hemicellulose, and lignin could all participate in the acetylation reaction.

The peak at 1370 cm^{-1} was assigned to the CH vibration of cellulose and hemicellulose. The peak at 1230 cm^{-1} was from the syringyl (S) unit of lignin and C-O vibration of xylan of hemicellulose. The peak at 1740 cm^{-1} was associated with the acetyl group C=O of xylan of hemicellulose (Mohebby 2008). These peak intensities increased with increasing WPG of the acetylated wood, suggesting that cellulose, hemicellulose, and lignin all participated in the acetylation reaction.

CONCLUSIONS

1. The acetylated plantation poplar wood had a drastic improvement in dimensional stability, *i.e.*, an obviously lower moisture uptake and volumetric swelling coefficient than those of the control wood under all relative humidity tested. The moisture uptake and volumetric swelling coefficient of the acetylated wood were dependent on the WPG. The WPG of the acetylated wood increased with increasing acetylation temperature. However, when the acetylation temperature increased from 120 to 140 °C, the increase in WPG was not as much as that from 100 to 120 °C.
2. The wood that was acetylated under temperatures of 100 and 120 °C had comparable MOEs and MORs to those of the control wood. However, the wood that was acetylated under the temperature of 140 °C had a markedly lower MOE and MOR than those of the control wood and wood acetylated under 100 and 120 °C.
3. Acetylation at 100 and 120 °C did not change the microstructure of the resulting acetylated wood. However, when the acetylation temperature was 140 °C, the deformation of vessels and broken wood fibers were found in the resulting acetylated wood.
4. Changes in functional groups of the acetylated wood were affected by the acetylation conditions. –OH groups from cellulose, hemicellulose, and lignin showed to all participate in the acetylation reaction.
5. The degradation of the cell walls and the decrease in MOE and MOR of the acetylated wood at 140 °C could be attributed to the acetic acid, which would promote the hydrolysis and degradation of the structural carbohydrate polymers including cellulose and hemicelluloses.

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