Chemical Modification by Impregnation of Poplar Wood with Functional Composite Modifier

Xiaoshuai Han, Xinwei Miao, Xue Zheng, Liyan Xing, and Junwen Pu*

Poplar is a fast-growing tree with a short cultivation time; however, there are some disadvantages to poplar such as its low density and low dimensional stability. The aim of this work was to study the physical and chemical performance of poplar wood treated by its impregnation with functional composite modifiers followed by compression drying. The results showed that this approach not only significantly increased the dimensional stability of the wood but also enhanced its bending strength and compressive strength parallel to the wood grain. Fourier transform infrared analysis showed that the intensity of the hydroxyl (-OH) and carbonyl (C=O) absorption peaks decreased, which provided evidence that the $–NHCH_2OH$ of the modifier reacted with the wood's carboxyl and hydroxyl groups. The position of the XRD peaks did not change, which indicated that the crystallinity structure of cellulose was not noticeably affected by chemical modification. The TGA showed that the thermal stability of the modified wood was improved, while FESEM analysis showed that the wood cell lumens and vessels were filled with chemicals.

Keywords: Functional composite modifier; Compression drying; Poplar wood; Impregnation; Chemical modification

Contact information: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing, 100083, PR China; Key Laboratory of Wood Science and Technology of Zhejiang Province, Zhejiang Agriculture and Forestry University, Hangzhou Lin'an,311300, PR China;
** Corresponding author: jwpu@bjfu.edu.cn*

INTRODUCTION

Poplar (*Populus euramericana cv.* 'I-214*'*) is a fast-growing deciduous tree and is one of the most dominant species in broadleaf forests in China. Fast-growing woods possess a wealth of advantages, and as such they are expected to be used as an alternative raw material for construction production and nonstructural wood-based panels (Lang *et al.* 2012). Poplar has some undesirable inherent properties, however, including low bond strength, poor mechanical properties, and poor dimensional stability (swelling and shrinking), which limit its potential applications.

Chemical modification, in general, is an effective way to enhance the overall properties of fast-growing poplar. Chemical modification of wood can be defined as a chemical reaction between some reactive part of the wood and a simple chemical reagent, with or without a catalyst, to form a covalent bond between the two (Rowell 1980, 2006). Generally, wood is a naturally porous material consisting mainly of cellulose, hemicelluloses, and lignin (Devi *et al.* 2007). The presence of hydrophilic groups (hydroxyl) in the three major wood polymeric components (cellulose, hemicellulose, and lignin) is the main reason for the unfavorable attributes: swelling, dimensional instability, and poor mechanical properties. Chemical modification involves the treatment with various chemical polymers to reduce the content of hydroxyl groups. Recently, numerous projects have studied timber modification by impregnating wood with a variety of chemical reagents such as urea-formaldehyde prepolymer, 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) resign, phenol formaldehyde, and methyl methacrylate to optimize the characteristics of the wood.

Chemical modification of wood has been of great interest to many researchers (Rowell 1980; Rapp *et al.* 1999; Furuno *et al.* 2004; Gindl *et al.* 2007). For instance, fast-growing wood samples have been impregnated with chitosan acetate solutions. After polymerization, the physical properties of the embedded samples were significantly improved (Basturk and Guntenkin 2009). Urea-formaldehyde prepolymer treatment has been extensively used for better characteristics and quality in different woods (Yu *et al.* 2011; Wu *et al.* 2012; Lang *et al.* 2012; Miao *et al.* 2014). The physical and mechanical properties including density, bending strength, and compressive strength parallel to the grain showed obvious enhancement after modification compared to natural wood. Meanwhile, the moisture absorption and water uptake of modified wood decreased sharply due to the reduction of –OH groups *via* chemical reaction with the hydroxyl groups of wood. Urea-formaldehyde prepolymer treatment can improve the mechanical properties of wood, yet the dimensional stability of timber cannot be promoted efficiently.

The modification of wood using 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) has attracted attention over the past years (Hill 2006). DMDHEU-modified wood has a high number of pores smaller than 30 nm and a low fraction of bound water. This helps to explain why DMDHEU-treated materials exhibit limited water uptake and increased resistance to biological attack (Dieste and Kraus 2009). Additionally, it was found that wood treated with DMDHEU has good resistance to weathering (Pfeffer *et al.* 2012). DMDHEU treatment of wood partially reduces the degradation of lignin and cellulose and stabilizes the wood cell walls during artificial weathering (Xie and Krause 2005, 2008). Although there are many advantages to DMDHEU modification, some degree of strength loss of the treated wood is induced during modification (Yuan *et al.* 2013). All of these studies showed that the overall performance of softwood is improved by using these single modifiers.

From the statement above, one can appreciate that urea-formaldehyde prepolymer and DMDHEU can improve the properties of wood, respectively. However, the behavior of wood after the combined treatment with urea-formaldehyde and DMDHEU is unknown so far.

The purpose of the present research was to assess the influence of urea-formaldehyde and 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) modifier on fast-growing poplar. The physical and mechanical properties, thermal stability, group reactivity, and microstructure of the resulting modified wood were evaluated. The expectation is that the wood properties will be improved overall. Thus, the impregnation behavior of the functional composite modifier and the characteristics of modified wood will be in focus.

EXPERIMENTAL

Materials

Fresh poplar (*Populus euramericana cv.* 'I-214') wood was collected in the Beijing forestry university northern base, China. The tree-ages were about 4 to 5 years. Such wood has been used in research of key technologies for modification of fast-growing wood for furniture manufacturing. The initial moisture content of wood ranged from 60% to 75% before impregnation.

Methods

Preparation of functional composite modifier

A three-necked flask was charged with urea, formaldehyde, and ammonia at a certain molar ratio (Pu *et al.* 2009a). The reaction mixture was stirred and kept at 35 °C for 3 h. The pH was then adjusted with ammonium chloride to between 5 and 7. Finally, the reacted mixture was transferred to a container and sealed. The functional composite modifier consisted of methylolurea, DMDHEU, carbamide, and $MgCl_2$.

Pulse dipping and kiln drying

The logs were peeled and sawn into pieces sizing 1800 mm × 150 mm × 25 mm. A vacuum-impregnated tank was used to treat the wood veneer. The wood samples were impregnated with the methylolurea (20% w/w), DMDHEU (15% w/w), carbamide (15% w/w), $MgCl_2$ (1% w/w), and water (49% w/w) at 0.8 to 1.0 MPa for 3 h. After soaking, the samples were air-dried for about one day. Finally, it took approximately 120 h for kiln drying (approx. 120 °C), and the pressure on the timber was 0.5 MPa (Pu *et al.* 2009b).

Mechanical properties and dimensional stability

The samples were prepared for evaluating the mechanical properties and dimensional stability according to the following Chinese standards: method of testing in bending strength of wood (GB/T 1936.1-2009), method of testing in compression perpendicular to grain of wood (GB/T 1939-2009), method for determination of the swelling of wood (GB/T 1934.2-2009), method for determination of the shrinkage of wood (GB/T 1932-2009), and method for determination of the density of wood (GB/T 1933-2009). For bending strength testing, the specimens had dimensions of 300 mm × 20 mm × 20 mm, and for compression strength perpendicular to the grain the dimensions were 30 mm × 20 mm × 20 mm. The other tests were carried out with specimens of size 20 mm × 20 mm × 20 mm. Twelve specimens were tested for each measurement and the average was recorded.

Water uptake

The samples were prepared for evaluating the hydroscopicity according to the Chinese standard method for determination of the water absorption of wood (GB/T 1934.1-2009). Twelve specimens of natural and modified were analyzed respectively. The specimens were dried in an oven at 105 °C until the average weight change was less than 0.02 g over a 2 h period. The specimens were then soaked in water for 15 days. The water uptake by the specimen increased with immersion time. After immersion, the excess water on the surface was removed using a soft cloth, and the weights of the specimens were immediately taken. The increase in weight was calculated according to Eq. 1,

$$H\ (\%) = \frac{m_1 - m_0}{m_0} \times 100 \qquad (1)$$

where m_1 is the final mass and m_0 is the original mass.

X-ray diffraction (XRD) instrument

The natural and modified wood specimens were ground into wood powder (80 mesh), and the wood powder was used for X-ray diffraction tests. X-ray diffraction analysis was carried out using a Shimadzu model XRD 6000 (Kyoto, Japan) (CuKα radiation with graphite monochromator, 30 kV, and 40 mA). The patterns were obtained between 5° and 45° 2θ with 0.05° steps and scan speed of 2° min^{-1}. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions. The ratio of the crystallinity of specimens to the standard amorphous material was taken as the relative crystallinity. The degree of crystallinity was calculated according to Eq. 2,

$$Cr(\%) = \frac{Fc}{Fa + Fc} \times 100 \tag{2}$$

where Fc is the intensity for the crystalline region and Fa is the corresponding quantity for the amorphous region.

Fourier transform infrared (FTIR) spectra

FTIR analysis was carried out using a Tensor 27 (Bruker, Germany). The spectra consisted of an average of 32 scans recorded in the wave number range of 4000 to 400 cm^{-1} with a spectral resolution of 2 cm^{-1}. The natural and modified wood specimens of 120 mesh size were directly used in the FTIR spectroscopy measurement and the samples were mixed with dried KBr (80:1 by weight) and pressed into discs.

Thermogravimetric analysis (TGA)

The thermal properties of the natural and modified samples were measured using a thermogravimetric analyzer (DTG-60, Shimadzu, Japan). The sample pan was placed on a Pt basket in the furnace and heated from 10 to 600 °C at a rate of 10 °C min^{-1}. α-Al_2O_3 was used as the reference material. During testing, the heating unit was flushed with a continuous nitrogen flow at a pressure of 8 kPa. The powder (100 mesh) of the wood samples (5 to 10 mg) was placed in the platinum crucible with a diameter of 8 mm.

Field emission scanning electron microscope (FESEM) analysis

The natural and modified wood samples were cut into small wooden bars having the dimensions 10 mm × 1.5 mm × 1.5 mm. Then these wooden bars were sprayed with metal and used for FESEM analysis. A US 8020 model scanning electron microscope (SEM) was used to observe the natural and modified wood. The samples containing the prepared transverse and radial faces to be observed under the FESEM were mounted on aluminum stubs with conductive adhesive tape. The working conditions were as follows: working distance of 20 mm, accelerating voltage of 1 kV, and illuminating current of 0.7 Na.

RESULTS AND DISCUSSION

Mechanical Properties

The physical and mechanical properties of specimens are shown in Table 1. The treated wood exhibited higher density in comparison with the natural wood. According to Fig. 1, the effect of modification on water uptake was significant. The basic density of the modified wood was 20.5% greater than the natural wood and the oven-dried density of the treated wood was 40.5% greater. The increase in density may have been caused by the formation of bonding between the wood fiber and the functional composite modifier. The impregnation and compression could have also increased the density of wood. The improved physical and mechanical properties can be explained by impregnation of the functional composite modifier and compression drying.

The mechanical properties of bending strength and compressive strength parallel to the grain are also shown in Table 1. The modified wood exhibited significantly higher bending strength and compressive strength parallel to the grain in comparison to the natural wood samples. The bending strength and compressive strength parallel to the grain were, respectively, 67.53 % and 114.10 % greater than the natural wood samples.

The results indicate that the cross-linking reaction played an important role in the mechanical properties. Usually in the course of high temperature thermal treatment the hemicelluloses are degraded to a greater extent than the other macromolecular components (Shafizadeh and Chin 1977). This results in the production of acetic acid derived from the hemicelluloses; formic acid and methanol are also formed, as well the production of noncondensable gases (mainly CO_2), as the temperature is raised further. The heating of wood in the presence of water or steam results in the accelerated formation of organic acids (primarily acetic acid), which catalyse the hydrolysis of hemicelluloses, and to a lesser extent the amorphous cellulose (Mitchell 1988). Compared with a single modifier, the functional composite modifier had a better modification effect on density, bending strength, and compressive strength parallel to grain. There are some reasons for these fruitful results. Firstly, the functional composite modifier impregnation helped prevent the polysaccharide components from severe degradation through various reactions. The heat treatment of wood also causes degradation, but to a lesser extent. More importantly, the functional composite modifier can react more deeply with wood components, allowing the mechanical properties of the modified wood to be enhanced.

Table 1. Physical and Mechanical Properties of Natural and Modified Wood

Properties	Natural	Modified	Improvement
Basic density ($g \cdot cm^{-1}$) (SD)	0.39 (0.06)	0.47 (0.05)	20.51%
Oven-dried density ($g \cdot cm^{-1}$) (SD)	0.42 (0.08)	0.59 (0.04)	40.48%
Bending strength (MPa) (SD)	62.80 (9.26)	105.21 (11.57)	67.53%
Compressive strength parallel to grain (MPa) (SD)	39.50 (1.78)	84.57 (1.23)	114.10%

Water Uptake

Figure 1 represents the hygroscopicity of the natural and modified wood samples. The figure shows the results of cold water immersion for 15 days. As shown, the water uptake of the treated wood was significantly decreased compared with the untreated samples. Both the treated and natural wood absorbed water quickly until 24 h, and afterwards the curve of the natural wood continued to increase rapidly.

The modified wood had a lower water content compared to the natural samples. In a wood cell, the hydroxyl groups in the wood promote increased water absorption;

however, the chemical modification reduces the hydroxyl groups and reduces the water absorption due to the crosslinking reaction between the functional composite modifier and the wood (Rahman *et al.* 2010).

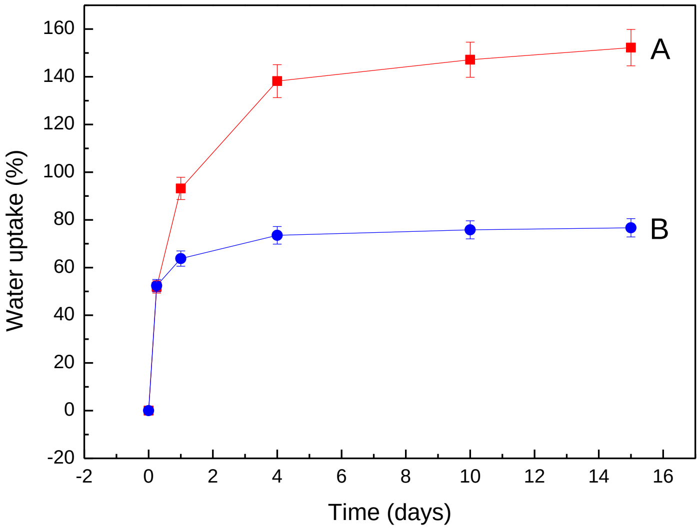

Fig. 1. Water uptake curves of wood: (A) natural wood and (B) modified wood

FTIR Analysis

FTIR spectroscopy was used to characterize the chemical changes of the natural and modified wood, and the spectra are shown in Fig. 2. Significant changes in the FTIR spectra were observed after the modification. The –OH absorbance was at 3400 cm^{-1} for the natural wood, and the corresponding band for the modified wood shifted to 3350 cm^{-1}. The intensity also increased, which was attributed to DMDHEU; there is an abundance of –OH groups in the DMDHEU molecule, and they were inserted into the cellulose, hemicelluloses, and lignin. The chemical bonding was confirmed by the clear decrease at 2910 cm^{-1} for –C-H stretching and at 1028 cm^{-1} for aromatic C-H in the plane deformation after the chemical treatment, which could be a result of the reaction between the group $–NHCH_2OH$ in the methylolurea and the lignin in wood. The decrease in the intensity at 1735 cm^{-1} is attributed to a reduction of absorption associated with carbonyl (C=O) stretching vibrations, indicating that xylan in the hemicelluloses degradation occurred and carbonyl or reaction involving the polymer occurred. The modifier impregnation was evidenced by strong absorption at 1650 cm^{-1}, corresponding to amide (N-C=O), which was from the methylolurea and urea. The increased band at 1157 cm^{-1} (C-O-C asymmetric stretching of cellulose and hemicelluloses) could be a result of the reaction between $–NHCH_2OH$ in the methylolurea and the –OH groups in the timber.

The wood modifier dispersed and adhered in the fiber lumens, pit holes, and other void spaces in the matrix. The structure of wood lignin, cellulose, and hemicelluloses had also been changed by the chemical modification. Chemical reactions occurred between the wood components and modifier and created crosslinking during the treatment. The reaction played a key role in enhancing the mechanical properties and improving the density of the wood.

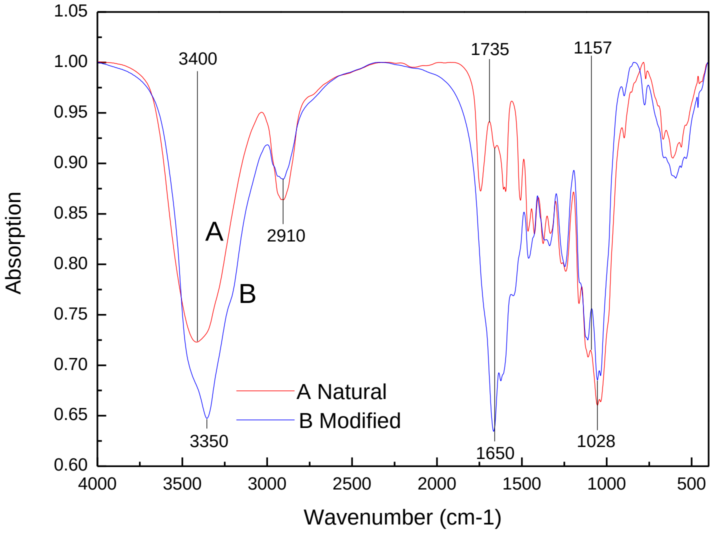

Fig. 2. FTIR spectrum of natural and modified wood

XRD Analysis

XRD was used to identify the intercalated structure of wood. Figure 3 presents the curves of the natural and modified wood samples. The natural wood shows a maximum at 16.1° 2θ (cellulose crystal diffraction, 101), and the pattern extended to a minimum at 18.8° 2θ, a region that is characteristic of the amorphous cellulose.

The most significant diffraction peak (002) of the cellulose crystal is near 22.5° 2θ, whereas a small diffraction peak (040) occurs near 35° 2θ (Cave 1997; Mulinari *et al.* 2010). The diffraction profile, however, changed a little for the treated wood. The difference between the maximum at 16.1° 2θ and the minimum at 18.8° 2θ became less pronounced, whereas the maximum diffraction peak (002) near 22.5° 2θ was enhanced, and the diffraction peak (040) near 35° 2θ was slightly higher. Meanwhile, the maximum diffraction peak (002) of modified wood shifted from 22.5° 2θ to 22° 2θ. The reason may be that functional composite modifier reacted with cellulose, which made the cellulose crystal change.

Cellulose Ⅰ was transformed to cellulose Ⅱ partly, so the maximum diffraction peak (002) shifted to minor diffraction angle (French 2014). According to the results of the experiment, the untreated and treated wood showed 35.66% and 37.13% crystallinity, respectively.

The higher crystallinity of the treated wood may have been caused by the kiln drying process, because usually a high temperature degrades the hemicelluloses to a greater extent than the other macromolecular components (Bourgios *et al.* 1989). The most important explanation is that the quasi-crystalline form occurred between groups of the functional complicate modifier and the hydroxyl groups of the wood. Furthermore, carbamide is a polar molecule, which can penetrate into the amorphous region of the wood cellulose cell wall; hence, after impregnation with carbamide, a crystalline region can be formed by rearranging the cellulose molecule chains.

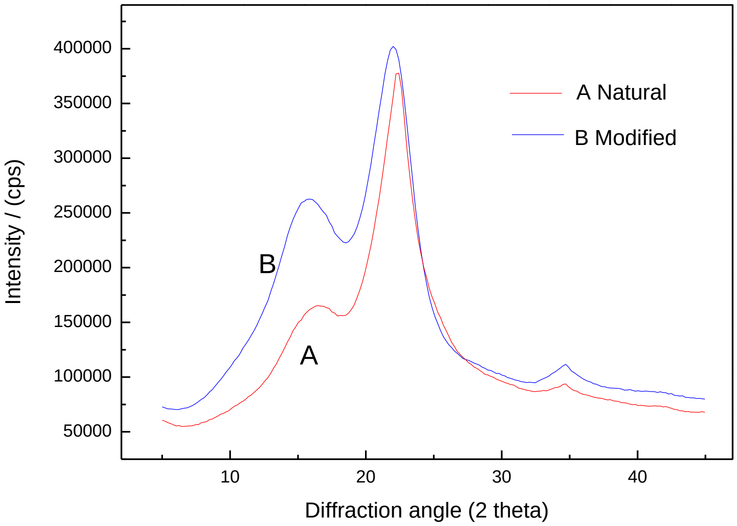

Fig. 3. XRD patterns of natural and modified wood

Thermogravimetric Analysis (TGA)

The thermogravimetric curves of the natural and modified wood are shown in Fig. 4. The curve of the natural samples shows four stages of thermal degradation. The first stage corresponds to the loss of free water and bound water (up to 175 °C) with a 3% mass loss. The second stage refers to the decomposition of the hemicelluloses and unstable cellulose (175 to 265 °C) with a 14% mass loss. The third stage is associated with the combustion and degradation of cellulose (265 to 360 °C) with a 55% mass loss. The last stage is relevant to the degradation of lignin.

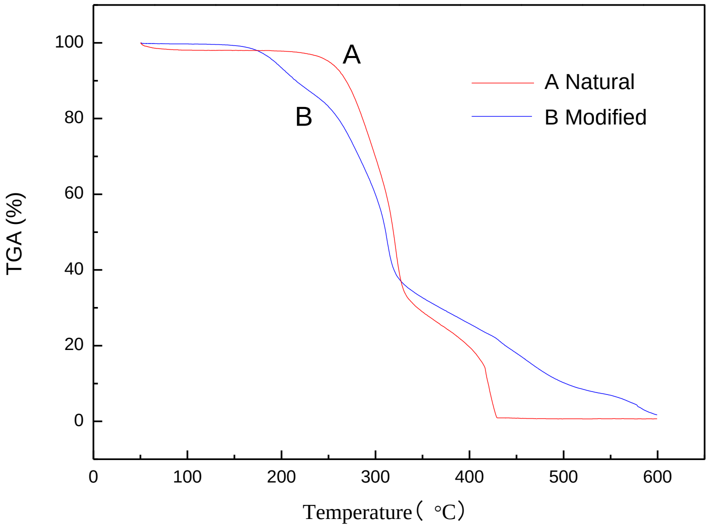

Fig. 4. Thermogravimetric analysis curves of wood: (A) natural wood and (B) modified wood

After chemical modification, the TGA curve of the modified sample showed a sharp change. The first stage was similar to the natural sample. For the second stage, the modified wood had a 14% rapid mass loss, which was associated with the combustion and degradation of unstable modifiers. In the third stage, there was a more gentle degradation than in the natural sample. The reason for this can be summarized by the fact that the reaction between the wood modifier and the wood enhanced the stability of the hemicelluloses and cellulose. Meanwhile, in the third stage, the mass loss involved the decomposition of some inactive fragmentation from the wood modifier. From the curve it is seen that in the fourth stage there was a strong bond reaction between the modifier and lignin.

Scanning Electron Microscopy (SEM) Analysis

Figure 5 shows the SEM micrographs of the natural wood and modified wood. Figure 5A shows that the natural wood samples exhibited a highly void structure. After impregnation, the cell wall and vessels were filled with chemicals. It can be seen that the functional composite modifier was homogeneously dispersed in the cell wall. The radial sections of the natural and modified wood are shown in Fig. 5C and Fig. 5D. It is clear that the natural woods were covered with an uneven layer and had a number of void spaces. The empty cell wall, the pit, and parenchyma are observed in the micrographs. The surface of the modified wood was smooth and substantially more uniform than that of the natural wood.

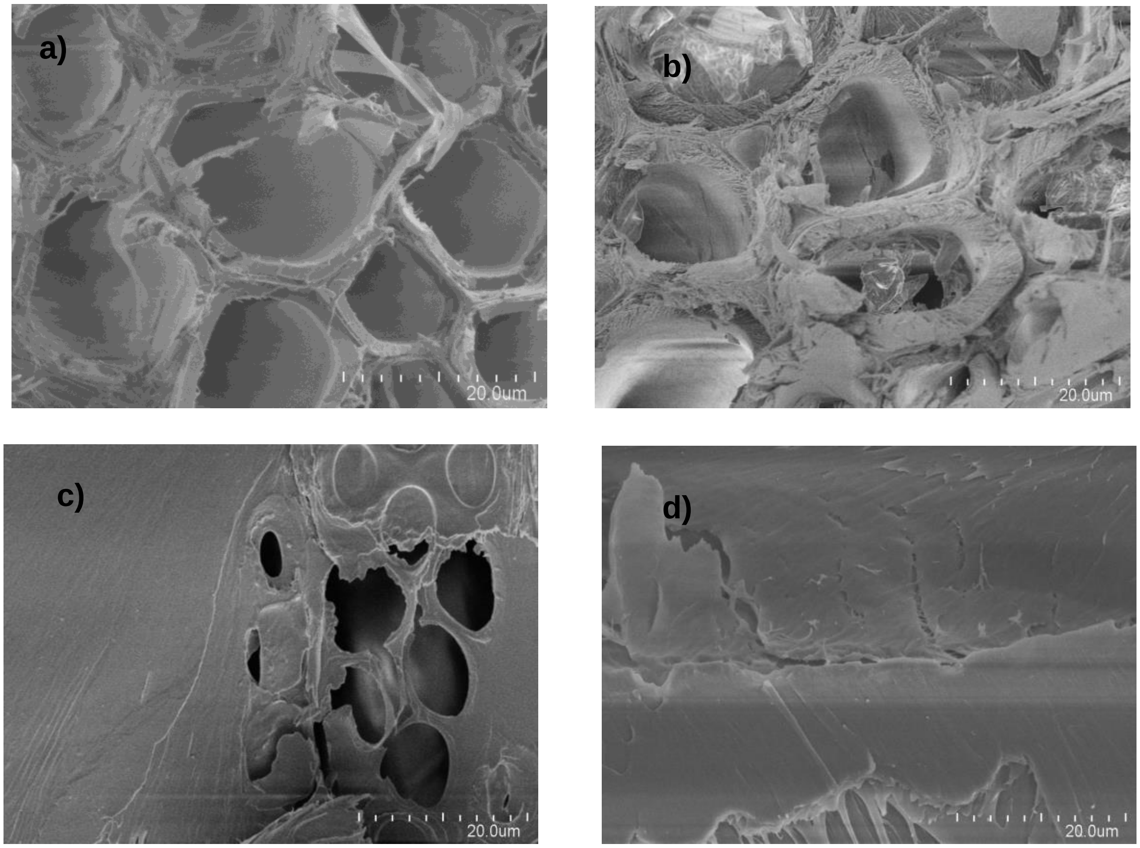

Fig. 5. FESEM micrographs of modified and natural wood: (a) transverse section of natural wood, (b) transverse section of modified wood, (c) radial section of natural wood, and (d) radial section of modified wood

The SEM studies provide evidence that the wood modification resulted in better dispersion of the functional composite modifier in the wood fiber and other vertical cells; moreover, the chemical particles of the wood modifier had better interfacial adhesion between the wood and the polymer. The good dispersion of the modifier led to a significant improvement in mechanical properties of the modified wood.

CONCLUSIONS

1. The properties of poplar wood modified by a functional composite modifier and compression-drying can be improved in a comprehensive manner. The basic density, oven-dried density, bending strength, and compressive strength parallel to grain of modified wood showed an obvious enhancement compared to the natural wood. At the same time, the water uptake of modified wood was decreased sharply.
2. The FTIR test showed that the intensity of hydroxyl and carbonyl absorption peaks was reduced obviously, which indicated that the functional composite modifier partly bonded to the wood carboxyl (C=O) and hydroxyl (-OH) groups via a cross-linked reaction.
3. On the XRD spectrum, the structure of cellulose did not completely change compared with the nature wood. However, there was a minor shift in the maximum diffraction peak. These findings indicated that cellulose Ⅰ was transformed to cellulose Ⅱ partly after modification.
4. The TGA indicated that the thermal stability of the modified wood was enhanced. The results from SEM micrographs showed the wood modifier was evenly distributed in the wood cell lumens and vessels.

ACKNOWLEDGMENTS

The authors are grateful for the support of Special Fund for Forestry Research in the Public Interest (Project 201204702): Research and demonstration of key technologies of modification fast-growing wood for furniture manufacturing and Research of synthesis and application of SOW wood modifier (2014ygcz008).

REFERENCES CITED

Basturk, M. A., and Guntekin, E. (2009). "Effects of chitosan treatment on some particleboard properties," *Wood Research* 54(4), 91-98.

Bourgois, J., Bartholin, M. C., and Guyonnet, R. (1989). "Thermal treatment of wood: Analysis of the obtained product," *Wood Sci. Technol*. 23(4), 303-310. DOI: 10.1007/BF00353246

Cave, I. D. (1997). "Theory of X-ray measurement of microfibril angle in wood," *Wood. Sci. Technol*. 31, 143-152. DOI: 10.1007/BF00705881

Devi, R. R., Saikia, C. N., Thakur, A. J., and Maji, T. K. (2007). “Modification of rubber wood with styrene in combination with diethylallyl phosphate as the flame-retardant agent,” *J. Appl. Polym. Sci.* 105(5), 2461-2467. DOI: 10.1002/app.26342

Dieste, A., and Kraus, A. (2009). “Modification of *Fagus sylvatica* L. with DMDHEU. Part 2: Pore size distribution determined by DSC,” *Holzforschung* 63(1), 89-93. DOI: 10.1515/HF.2009.023

French, A. D. (2014) “Idealized powder diffraction patterns for cellulose polymorphs” *Cellulose* 21(2), 885-896. DOI:10.1007/s10570-013-0030-4

Furuno, T., Imamura, Y., Kajita, H. (2004). “The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: A properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls,” *Wood Sci. Technol.* 37(5), 349-361. DOI: 10.1007/s00226-003-0176-6

GB/T 1932. (2009). “Method for determination of the shrinkage of wood,” Chinese National Standardization Management Committee, Beijing, China.

GB/T 1933. (2009). “Method for determination of the density of wood,” Chinese National Standardization Management Committee, Beijing, China.

GB/T 1934.1. (2009). “Method for determination of the water absorption of wood,” Chinese National Standardization Management Committee, Beijing, China.

GB/T 1934.2. (2009). “Method for determination of the swelling of wood,” Chinese National Standardization Management Committee, Beijing, China.

GB/T 1935. (2009). “Method of testing in compressive strength parallel to grain of wood,” Chinese National Standardization Management Committee, Beijing, China.

GB/T 1936.1. (2009). “Method of testing in bending strength of wood,” Chinese National Standardization Management Committee, Beijing, China.

Gindl, W., Müller, U., and Teischinger, A. (2007). “Transverse compression strength and fracture of spruce wood modified by melamine-formaldehyde impregnation of cell walls,” *Wood Fiber Sci*. 35(2), 239-246.

Hill, C. A. S. (2006). *Wood Modification. Chemical, Thermal and Other Process*, John Wiley & Sons Ltd., Chichester, England. DOI: 10.1002/0470021748

Lang, Q., Bi, Z., Miao, X. W., Zheng, X., and Pu, J. W. (2012). “Effect of urea-formaldehyde prepolymer on fast-growing wood,” *Wood Research* 58(3), 351-360.

Miao, X. W., Chen, H. Y., Lang, Q., Bi, Z., Zheng, X., and Pu, J. W. (2014). “Characterization of *Ailanthus altissima* veneer modified by urea-formaldehyde pre-polymer with compression drying,” *BioResources* 9(4), 5928-5939. DOI: 10.15376/biores.9.4.5928-5939

Mitchell, P. H. (1988). “Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen,” *Wood Fiber Sci.* 20(3), 320-355.

Mulinari, D. R., Voorwald, H. C., Cioffi, M. O. H., and Rocha, G. J. (2010). “Surface modification of sugarcane bagasse cellulose and its effect on mechanical and water absorption properties of sugarcane bagasse cellulose / HDPE composites,” *BioResources* 5, 661-671.

Pfeffer, A., Mai, C., and Militz, H. (2012). “Weathering characteristics of wood treated with water glass, siloxane and DMDHEU,” *Eur. J. Wood Prod.* 70 (1-3), 165-176. DOI: 10.1007/s00107-011-0520-8

Pu, J. W., Ma, F. M., Wu, G. F., and Jiang, Y. F. (2009a). “A new mechanism for dipping on wood modification,” Chinese Patent CN101618559.

Pu, J.W., Ma, F. M., Wu, G. F., and Jiang, Y. F. (2009b). “A new mechanism for hot-press drying on wood modification,” Chinese Patent CN101531018.

Pu, J. W., Wu, G. F., and Jiang, Y. F. (2009c). "A new method for wood modification," Chinese Patent CN101549508.

Rahman, M. R., Hamdan, A. S., and Islam, M. S. (2010). "Mechanical and biological performance of sodium metaperiodate-impregnated plasticized wood (PW)," *BioResources* 5(2), 1022-1035.

Rapp, A. O., Bestgen, H., Adam, W., and Peek, R. D. (1999). "Electron energy loss spectroscopy (EELS) for quantification of cell-wall penetration of a melamine resin," *Holzforschung* 53, 111-117. DOI: 10.1515/HF.1999.018

Rowell, R. M. (1980). "Distribution of reacted chemicals in southern pine modified with methylisocyanate," *Wood Sci.* 13(2), 102-110.

Rowell, R. M. (2006). "Acetylation of wood," *Forest Prod J.* 56(9), 4-12.

Shafizadeh, F., and Chin, P. P. S. (1977). "Thermal deterioration of wood," *Wood Technology: Chemical Aspects,* Goldstein, I. S. (ed.), ACS Symposium Series, 43, pp. 57-81. DOI: 10.1021/bk-1977-0043.ch005

Wu, G. F., Jiang, Y. F., Qu, P., Song S. P., and Pu, J. W. (2012). "Study on urea-formaldehyde prepolymer and hot-press treatment of Italian poplar wood," *Forest Prod. J.* 62(5), 406-411. DOI: 10.13073/0015-7473-62.5.406

Xie, Y., and Krause, A. (2005). "Weathering of wood modified with the N-methylol compound 1,3-dimethylol-4,5-dihydroxyethyleneurea," *Polymer Degradation and Stability* 89(2), 189-199. DOI: 10.1016/j.polymdegradstab.2004.08.017

Xie, Y., and Krause, A. (2008). "Weathering of uncoated and coated wood treated with methylated 1,3-dimethylol-4,5-dihydroxyethylenurea (mDMDHEU)," *Holz Roh Werkst.* 66(6), 455-464. DOI: 10.1007/s00107-008-0270-4

Yu, X. C., Sun, D. L., and Li, X. S. (2011). "Preparation and characterization of urea-formaldehyde resin-sodium montmorillonite intercalation-modified poplar," *J. Wood Sci.* 57, 501-506. DOI: 10.1007/s10086-011-1203-0

Yuan, J., Hu, Y. C., Li, L. F., and Cheng, F. C. (2013). "The mechanical strength change of wood modified with DMDHEU," *BioResources* 8(1), 1076-1088. DOI: 10.15376/biores.8.1.1076-1088

Article submitted: March 27, 2015; Peer review completed: June 10, 2015; Revised version received and accepted: June 28, 2015; Published: July 2, 2015.
DOI: 10.15376/biores.10.3.5203-5214