Polyurethane-Solid Wood Composites Prepared with Various Catalysts. I. Mechanical Properties and Dimensional Stabilities

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ABSTRACT: Polyurethane (PU)-solid wood composites were prepared by impregnating PU prepolymer into low-density fast-growing poplar solid wood and controlling the prepolymer cured or foamed within wood voids in the presence of the catalysts triethanolamine (TEA), diethylenetriamine (DETA), triethylenediamine (TEDA), and N-methyl morpholine (NMM), respectively. A scanning electron microscope (SEM) was used to observe the morphologies of the cured PU resin and the wood voids, and the effects of catalyst species on the mechanical properties and dimensional stabilities of PU-wood composites were evaluated. The results indicated that the PU prepolymer cured in the presence of various catalysts resulted in different morphologies and distributions within wood voids, and therefore led to various mechanical properties and dimen-sional stabilities of the PU-wood composites. Because of the fact that wood cell walls in the surface layer had apparently collapsed in the presence of catalyst DETA and therefore the wood was densified, the PU-wood composite prepared with DETA had the best mechanical properties and dimensional stabilities. The PU prepolymer was well impregnated and evenly foamed within the wood in the presence of catalyst NMM, giving the PU-wood composite prepared with NMM much better dimensional stability as the foamed PU blocked the water transfer between the cells. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1293–1299, 2009

Key words: polyurethane; composites; catalyst; morphology; mechanical properties

INTRODUCTION

Wood is a biodegradable and renewable native polymeric material that is widely used in various fields as it has many advantages over other materials such as metals, cement, and synthetic polymers. However, some disadvantages of wood, such as poor dimensional stability, relatively low strength, susceptibility to woodworm and decay, and poor fire resistance, prevent it from being utilized more widely.[1,2] Many studies have been devoted to tackling these disadvantages, so as to improve wood quality, increase its utilization, and add more value to the product. This is especially significant for fast-growing wood.

Preparing polymer-solid wood composites by impregnating resin into solid wood then controlling the resin cured within wood is one of the most effective methods of improving wood quality and increasing its utilization. Phenol–formaldehyde resin,[3,4] urea–formaldehyde resin,[5] melamine–form-aldehyde resin,[6] and polyethylene glycol[7] are com-monly applied. Recently, some isocyanate resins have been impregnated into wood, and these have improved the dimensional stability, decay preservation, and fire resistance of the wood.[8–11] However, some reports have indicated that isocyanate monomers could not improve the mechanical properties and dimensional stability simultaneously, and even decreased the mechanical properties.[12]

Isocyanate is a highly reactive compound that can react with most materials that have active hydrogen,[13] and which was used to prepare polyurethane (PU) adhesive. Wood is mainly composed of cellulose, lignin, and hemicellulose, all of which contain hydrophilic hydroxyl groups that lead to poor dimensional stability.[2] Isocyanate will react with these hydroxyl groups and form hydrophobic carbamate, which improves the dimensional stability of wood. It was used to prepare various PU foams industrially because it was converted into polyurea–urethane and released carbon dioxide after it had reacted with water.

In our previous study, the mechanical properties and dimensional stability of PU prepolymer-modified wood were simultaneously improved because we controlled part of the impregnated PU prepolymer foamed within the wood voids and the rest cured to form PU resin that was continuously deposited and thickened the wood cell walls.[12] It is well

known that the catalyst species has a great effect on the foaming or curing of PU resin, and may affect the final PU performance. Therefore, four amine catalysts for PU resin foaming were applied in this study, expecting to investigate their effects on the performance of PU-solid wood composite and to lay foundations for producing PU-solid wood composite with higher quality in further studies.

EXPERIMENTAL

Materials

Poplar (Populus ussuriensis) trees with averaged density of 339 kg/m^3 (oven-dried basis) were felled at a local wood farm. The fresh logs were cut into lumber with thickness of 25 mm, then enough air-dried, and finally cut into specimens with dimensions of 20 mm × 10 mm × 220 mm. The longest direction of the specimens was perpendicular to the annual growth rings. Regular specimens were selected without faults and with similar weight (to ensure equivalent density).

The PU prepolymer was prepared in the authors' laboratory as follows. In a three-necked flask equipped with a condenser, polyethylene glycol (PEG, supplied by Tiantai Chemicals, Tainjin, China) and the first portion of acetone solvent were charged into stoichiometric polyaryl polymethylene isocyanate (P-MDI, Millionate MR-100, supplied by Nippon Polyurethane Industry, Japan). The reaction mixture was stirred and heated to 40°C and then kept for 30 min, after that heated until the condenser was just refluxing and held for 3 h. Then after cooling to 50°C, the second portion of acetone was added with further stirring for 10 min. Finally, the reaction mixture was transferred to a container and sealed for storage. The solid content of PU prepolymer was 70% and the content of isocyano groups was 9.1 wt %. Before impregnation, the PU prepolymer was diluted with acetone to a concentration of 15% by weight.

The solvent acetone, and catalysts triethanolamine (TEA), diethylenetriamine (DETA), triethylenediamine (TEDA), and N-methyl morpholine (NMM) were obtained from a chemical market in Harbin.

Impregnation and foaming of PU resin

Wood pretreatment

All poplar specimens without any faults were moisture-conditioned at 20°C and 60% relative humidity for more than 30 days. Then, 20 specimens were taken at random and weighed (W_1) with an analytical balance (accurate to ±0.01 g), then dried at about 103°C for 5 h, and each specimen weighed (W_2)

again. The moisture content of the specimens can be calculated as MC% = $(W_1 - W_2)/W_2 \times 100\%$.

Resin impregnation

Twenty moisture-conditioned specimens were selected at random, labeled, and weighed (W_3). They were then held under vacuum (75 kPa) for 15 min to remove the air within the wood. After that 0.9 wt % catalyst-acetone solution was infused under vacuum without leaking and held for 20 min (the specimens were immersed in the solution). Then, the specimens were removed from the catalyst solution and held under vacuum (75 kPa) for another 30 min. Then, 15 wt % PU prepolymer acetone solution was infused under vacuum without leaking and held for 20 min (the specimens were immersed in the solution). Finally, the wood specimens were taken out of the solution and washed with acetone to remove the resin on the surface.

Foaming (curing) and drying

The impregnated specimens were immersed within water for 5 min. Then, each specimen was wrapped in foil film and dried at 120°C for 90 min, after that the foil film was removed and the foamed resin on the surface was also removed. Finally, each specimen was dried at 103°C for 4 h and weighed immediately (W_4).

Characterization of PU-solid wood composite

Weight percentage gain

The weight percentage gain (WPG) was used to evaluate the amount of cured PU resin introduced into the wood, and it was determined from the difference in the oven-dried weight of each specimen before treatment (W_3) and after treatment (W_4) according to the equation [WPG = $(W_4 - W_3 + W_4 \times$ MC%$)/W_3 \times 100$], where MC% refers to the averaged moisture content of the specimens. The average WPG value of the 20 specimens is reported here.

Dimensional stability

The dimensional stability was evaluated in terms of the 24-h volumetric swelling coefficient (VSC$_{24h}$) and the 24-h water absorption coefficient (WAC$_{24h}$). The dimensions (length, width, and thickness) and weight of each specimen before soaking (l_1, w_1, t_1, and W_1) and after soaking (l_2, w_2, t_2, and W_3) in 20°C ± 0.5°C water for 24 h were determined by micrometer and analytical balance (accurate to ±0.01 g), respectively. VSC$_{24h}$ was calculated according to the equation [VSC$_{24h}$ = $(l_2w_2t_2 - l_1w_1t_1)/l_1w_1t_1 \times 100$]. WAC$_{24h}$ was calculated according to the

equation [$WAC_{24h} = (W_3 - W_1)/W_1 \times 100$]. The averaged VSC_{24h} and WAC_{24h} values of 10 specimens are reported here.

Mechanical properties

The mechanical properties were evaluated in terms of the modulus of rupture (MOR) and the modulus of elasticity (MOE). MOR and MOE measurements were referred to ISO Standard 3133/1975 and 3349/1975, respectively, using a three-point bending test. The results were calculated according to the equations:

$$MOR = \frac{3PL}{2bd^2}$$

$$MOE = \frac{PL^3}{3.6bd^3\Delta}$$

where P is the load at some point below the proportional limit (in the case of MOE) and the maximum load (in the case of MOR) (N), L is the distance between supports for the specimen (200 mm), b is the specimen width (accurate to ±0.01 mm), d is the specimen thickness (accurate to ±0.001 mm), and Δ is the deflection corresponding to the load P.

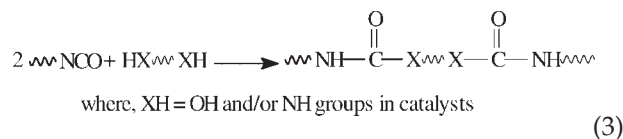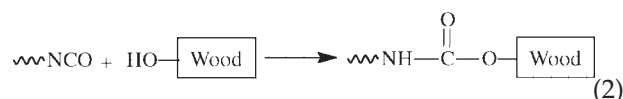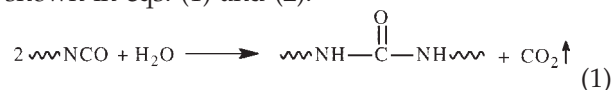The averaged MOR and MOE values of 10 specimens are reported.

Scanning electron microscope analysis

Samples cut from dry untreated and treated specimens were hand-split along the cross-sectional and tangential surfaces. The scanning electron microscope (SEM) samples were coated with $\sim$ 10–20 nm of gold before examination with a QUANTA-200 SEM with a working distance of 10 mm at 15 or 20 kV.

RESULTS AND DISCUSSION

When the PU prepolymer containing isocyano groups was cured within wood in the presence of water, part of the PU prepolymer crosslinked to form polyurea by the reaction of the isocyano groups with water, during which carbon dioxide was produced, as shown in eq. (1). This is called a crosslinking reaction. During the crosslinking, some of the isocyano groups in the PU prepolymer could also react with the hydroxyl groups in the wood and formed carbamate, as shown in eq. (2). This reaction is often called a chemical bonding reaction. In the presence of amine catalyst, both crosslinking and bonding reactions will be accelerated; however, the amine catalyzes the crosslinking reaction faster than the bonding reaction.[14] If the catalyst contains active

hydrogen such as hydroxyl groups and amino groups, these will crosslink PU prepolymer as well, as shown in eq. (3). Because of the fact that just a small amount (0.9%) of catalyst is used, the main reactions of PU prepolymer within wood were those as shown in eqs. (1) and (2).

$$2\,\text{NCO} + H_2O \longrightarrow \text{NH}-\overset{\overset{\textstyle O}{\|}}{C}-\text{NH} + CO_2\uparrow \tag{1}$$

$$\text{NCO} + HO-\boxed{\text{Wood}} \longrightarrow \text{NH}-\overset{\overset{\textstyle O}{\|}}{C}-O-\boxed{\text{Wood}} \tag{2}$$

$$2\,\text{NCO} + HX\,XH \longrightarrow \text{NH}-\overset{\overset{\textstyle O}{\|}}{C}-X\,X-\overset{\overset{\textstyle O}{\|}}{C}-\text{NH} \tag{3}$$

where, XH = OH and/or NH groups in catalysts

After crosslinking, the PU prepolymer is converted into a solid and continuous polymer layer that is generally deposited on the surface of the wood cell walls. The chemical bonding reaction as shown as eq. (2) resulted in the continuous polymer layer strongly adhering to the wood cell walls, and therefore thickening the wood cell walls. The hydrophobic polymer layer would not only reinforce the wood by thickening the wood cell walls but also improve the dimensional stability of wood by blocking the transfer passageways for water within the wood. In addition, the chemical bonding reaction converted the hydrophilic hydroxyl groups of wood into hydrophobic carbamate, which further improved the dimensional stability of the wood.

The crosslinking reactions of PU prepolymer in the presence of water might form PU foam if the increase in PU molecular weight was rapid enough to obtain a viscosity, or gel strength to be exact, to prevent carbon dioxide escaping from the reactants. Therefore, four amine catalysts, TEA, DETA, TEDA, and NMM, were introduced, respectively. The addition of catalyst was expected to accelerate the increase in PU molecular weight during crosslinking to retain carbon dioxide, and therefore resulted in foamed PU that filled up and then further supported the wood voids. The order of the catalytic activity of the four catalysts is as follows: TEDA > TEA > NMM > DETA. In addition to good catalysis, the catalyst TEA contains three hydroxyl groups that can crosslink the PU prepolymer by reacting with isocyano groups to form carbamate. DETA is not a good catalyst as it has no tertiary amino structure; however, it contains two primary and one secondary amino group that can more rapidly crosslink the PU prepolymer by reacting with isocyano groups to form polyurea. It has been reported that the resultant polyurea may have a weak catalytic effect on the reaction of isocyanate.[15]

TABLE I
Properties of PU-Wood Composites Prepared with Various Catalysts

Properties	Control (wood only)	Catalyst species			
		TEA	TEDA	DETA	NMM
WPG (%)	–	16.14	12.00	14.64	16.78
Density (kg/m^3)	339	399	381	384	390
VSE$_{24h}$ (%)	12.15	8.01	8.36	1.42	2.23
ASE$_{24h}$ (%)	71.80	28.90	53.20	38.90	57.40
MOR (MPa)	82.85	118.32	127.72	154.48	118.87
MOE (GPa)	5.54	10.77	11.40	12.68	13.33

Because of the fact that the PU resin introduced into the PU-wood composites could fill in the voids within solid wood to some extent (in terms of the WPG), the densities of the composites, ranging from 381 to 399 kg/m^3, were greater than the control wood (339 kg/m^3), as shown in Table I. This table also indicates that the PU-wood composite prepared with PU prepolymer in the presence of various catalysts had better mechanical properties and dimensional stabilities than the control wood, resulting in a maximal MOR increase with the catalyst DETA (86.46%), maximal MOE increase for the catalyst NMM (140.69%), maximal VSC$_{24h}$ decrease for the catalyst DETA (88.31%), and maximal WAC$_{24h}$ decrease for the catalyst TEA (59.75%). In this study, all conditions and procedures were the same except for the catalyst used, indicating that the obvious variations in the properties of PU-wood composites must be attributed to the catalysts. SEM was therefore used to observe the morphologies and distributions of the cured/foamed PU resin within wood, by which the effects of the catalyst species on the properties of PU-wood composite were evaluated.

Figure 1 shows SEM images of the control wood without PU prepolymer impregnation. In both the cross-sectional [Fig. 1(A)] and tangential surfaces [Fig. 1(B)], the wood voids are clear and contain no foreign matter, and the cell walls are relatively even and smooth. Because of the low strength of the fast-growing poplar wood, the cleaved cell walls in the tangential surface seem to be very smooth.

The SEM images of PU-wood composites prepared with various catalysts are shown in Figures 2–5. The processes of resin impregnation in the experimental portion of this study indicated that the first impregnated PU prepolymer would quickly react, in the presence of catalyst, with water (in the wood) and/or some catalysts (namely TEA and DETA with active hydrogen) to form larger-molecular weight crosslinking structures that blocked the following PU prepolymer from further impregnating into the center layer of the wood. Therefore, the PU resin within all PU-wood composites, except those prepared with NMM catalyst, was distributed unevenly, with generally more PU resin in the surface layer than at the center, as shown in Figures 2–4.

The SEM images of PU-wood composite also indicate that the cured PU prepolymer formed continuous resin layers on the surfaces of the wood cell walls, especially on the surface layer of composites, in addition to some PU prepolymer foamed or microfoamed within wood voids, as shown in Figures 2(C), 3(A), and 4(A). The continuous resin layer thickened the wood cell walls and the PU foam
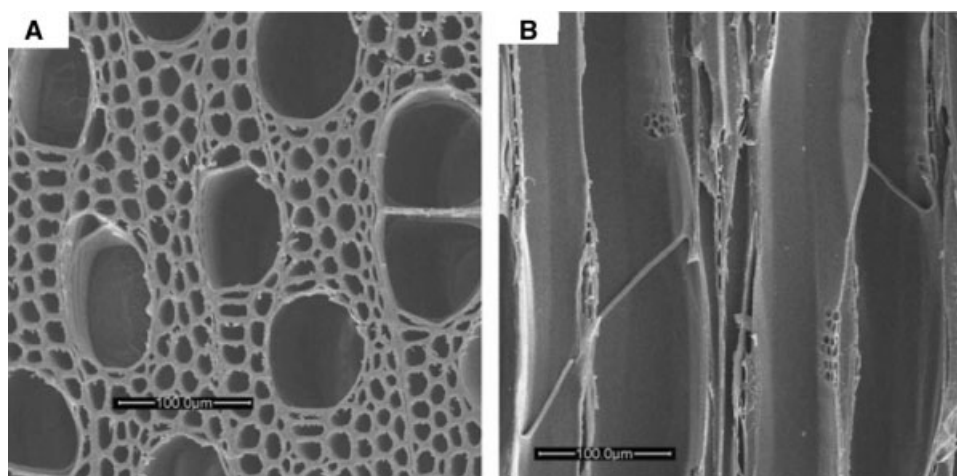

Figure 1 SEM images of the control (wood only). (A) Cross-sectional surface and (B) tangential surface.
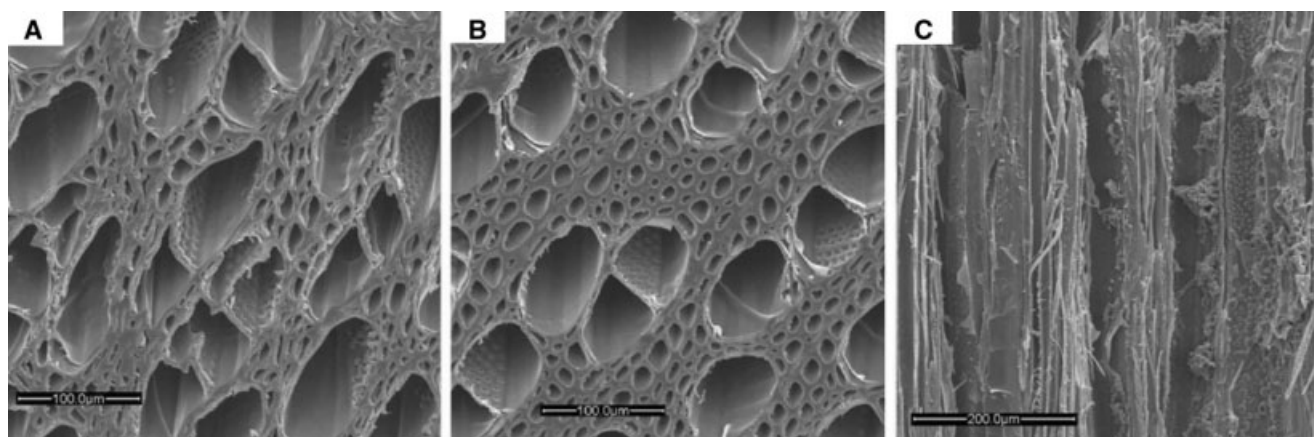
Figure 2 SEM images of PU-wood composite with TEA. (A) Cross section at surface layer, (B) cross section at center layer, and (C) tangential surface.

filled up the wood voids, which therefore reinforced the wood cells and improved the mechanical properties of the PU-wood composites, as shown in Table I. The continuous resin layer strongly adhered to the cell walls by the reaction as shown in eq. (2), which would block the passageways for water transfer within the wood. In addition, the reaction as shown in eq. (2) could convert some hydrophilic hydroxyl groups into hydrophobic carbamate. All of these resulted in good dimensional stabilities of PU-wood composites (in terms of VSC_{24h} and WAC_{24h} as shown in Table I).

The SEM images show that the degree of foaming of PU prepolymer and the morphologies of PU foams in various PU-wood composites are quite different. The PU prepolymer in the presence of catalyst NMM is well distributed throughout the wood and forms abundant large hollow thin-walled PU foams within wood, as shown in Figure 5(B,C); the diameters of the PU foams range from 10 to 50 μm. In addition, the morphologies of the PU foams and the wood cells in the surface layer, as shown in Figure 5(A), are almost the same as that in the center layer. In the surface layer of the composite prepared in the presence of catalyst TEA, some PU prepolymer forms obvious microfoams that assume the form of piled microspheres, as shown in Figure 2(C; right area); whereas in the center area, very few microfoams are observed. In the presence of catalyst TEDA or DETA, only a few microfoams are observed in the surface layer of the composite, as shown in Figures 3 and 4, respectively. All of these indicate that the foaming degree of PU prepolymer is opposite to the catalytic activities of the catalyst presented. To obtain a good PU foam, the foaming reaction of the reacting isocyano groups with water is indispensable. However, it is also indispensable to accelerate the increase in PU molecular weight by crosslinking during the foaming reaction to retain carbon dioxide within the PU resin, otherwise the carbon dioxide formed during the PU foaming reaction might escape because of the poor retention of the PU resin with lower molecular weight (lower gel strength to be exact). Therefore, in addition to the
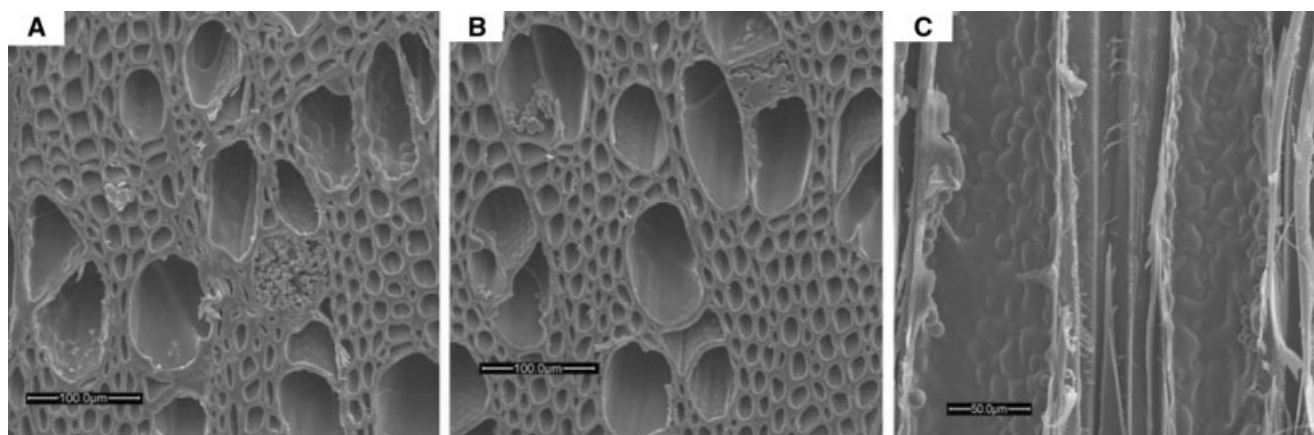

Figure 3 SEM images of PU-wood composite with TEDA. (A) Cross section at surface layer, (B) cross section at center layer, and (C) tangential surface.
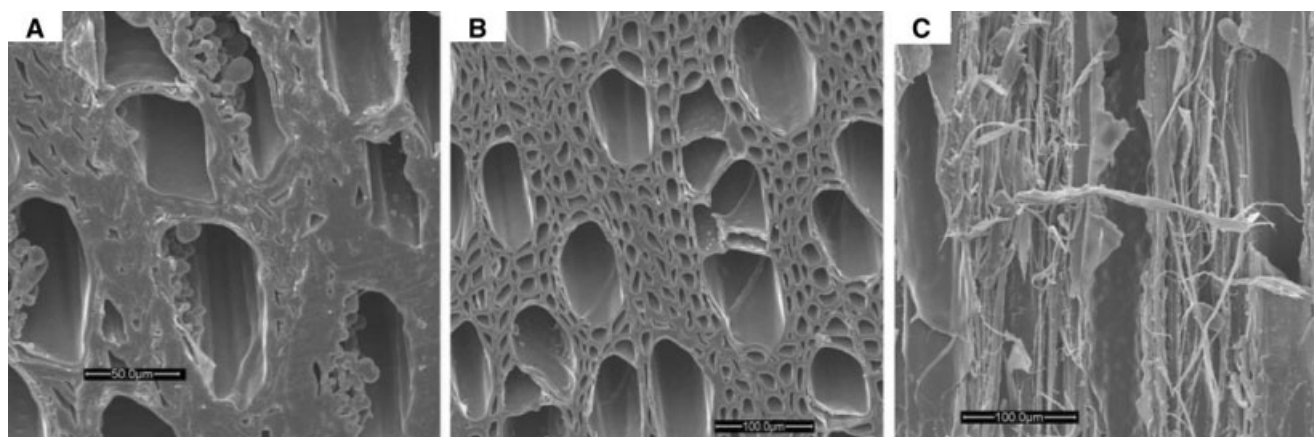
Figure 4 SEM images of PU-wood composite with DETA. (A) Cross section at surface layer, (B) cross section at center layer, and (C) tangential surface.

amine catalyst, some additives such as foam stabilizer and tin catalyst are necessary for manufacturing PU foams industrially.[16]

The NMM has the weakest catalysis to PU foaming among the three tertiary amine catalysts; in addition, it contains no active hydrogen for the crosslinking reaction. Therefore, the PU prepolymer had little molecular weight increase during resin impregnation in the presence of catalyst NMM, resulting in the most PU prepolymer impregnated into wood as indicated by the largest WPG (16.78%) in Table I. During curing at 120°C, the PU prepolymer formed large hollow PU foams with very thin walls as shown in Figure 5(C). These large hollow thin-walled foams could efficiently block the water transfer between two wood cells and reserve the water within the cavity of PU foam, resulting in almost the lowest VSE_{24h} but the highest WAE_{24h} value of the PU-wood composite, as shown in Table I. However, these large hollow thin-walled foams had the lowest thickening to wood cell walls, resulting in almost the lowest MOR among the four PU-wood composites.

The wood morphologies of the PU-wood composite prepared with catalyst DETA were quite different from the others. In the surface layer of the composite, the cell cavities of the wood fibers had all collapsed and the cell walls adhered to each other with PU resin to form a compact PU-wood entity as shown in Figure 4(A), while the cavities of vessels were just distorted and the continuous resin layers on the surface of the cavities were obvious. At the center of the composite, the cavities of the wood fibers and vessels were just distorted and less PU resin layer was observed, as shown in Figure 4(B). In the tangential surface of cleaved composite, the broken cell walls seemed thread-like, indicating that the strength of the PU-wood composite was clearly improved. This corresponded to the highest MOR (154.48 MPa, almost twofold as much as the control) as shown in Table I. The SEM image in Figure 4(A) indicates that catalyst DETA had a good softening interaction with wood. The collapse of the wood fibers might be produced when the wood was subjected to a large shrinking stress during heating to
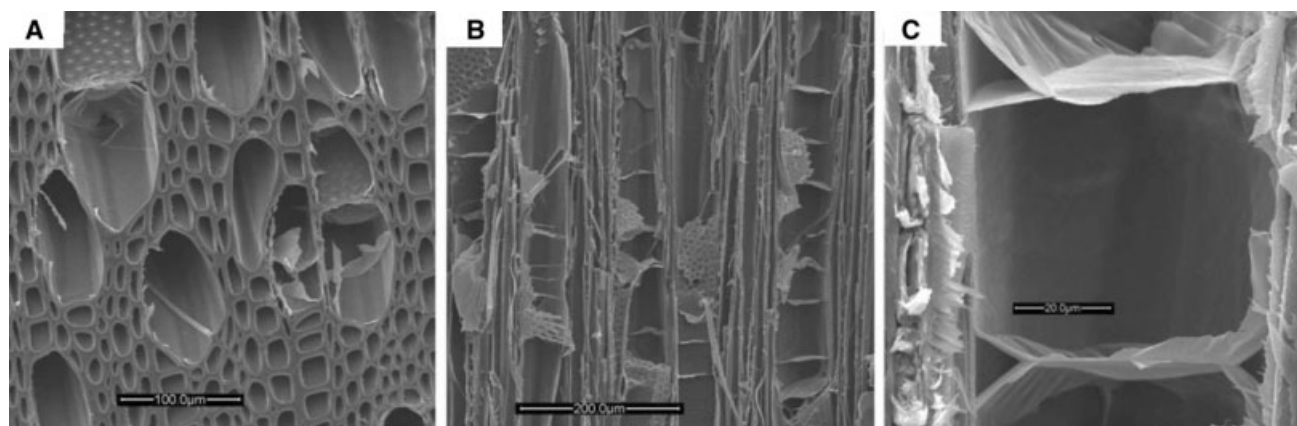

Figure 5 SEM images of PU-wood composite with NMM. (A) Cross section surface, (B) tangential surface, and (C) magnified area.

120°C for PU curing; when PU prepolymer cured, the collapse structures were bonded and therefore fixed by the cured PU that impregnated into the cell cavities. The collapse of the cell walls in the surface layer of the composite led to densification of the wood, resulting in the lowest VSE_{24h} and much lower WAE_{24h} because the water could not penetrate or transfer into the interior of the wood.

To sum up, the best mechanical properties and dimensional stabilities of PU-wood composite prepared with catalyst DETA were mainly attributed to wood densification in the surface layer. Although the catalyst DETA had very weak catalytic activity to PU resin, DETA would quickly crosslink the PU prepolymer as it contains two primary and one secondary amino group, resulting in the rapid increase in molecular weight of the prepolymer that retarded further impregnation of the following PU prepolymer. Therefore, the amount of PU resin in the surface layer of the composite was more than that at the center, as shown in Figure 4(A,B).

The catalyst TEA had a weak softening interaction with the wood, indicated only by distortions of the cell cavities in the surface layer of the PU-wood composite prepared with TEA, as shown in Figure 2(A). On the other hand, the other two catalysts, namely TEDA and NMM, had no softening interaction with wood as the cell cavities of the PU-wood composites had no distortion or collapse, as shown in Figures 3 and 5.

The catalyst TEDA had the highest catalytic activity to the PU forming reaction; therefore, the first impregnated PU prepolymer would quickly react with water to increase the molecular weight that retarded the further impregnation of following PU prepolymer into the center of the wood, as indicated by the lowest WPG (12.00%) among the four PU-wood composites. Because of the highest catalytic activity of the TEDA, the increasing rate of gel strength of the PU resin was much less than the foaming rate, and therefore, the carbon dioxide could not be retained within the PU resin to form PU foams and finally formed a continuous PU layer with few microfoams, as shown in Figure 3(A,B). The many bulges in the continuous PU layer on the walls of the vessels, as shown in Figure 3(C), indicated that the PU prepolymer was once rapidly foamed at the early stage of the curing reaction.

CONCLUSIONS

PU-solid wood composites were prepared by impregnating PU prepolymer into low-density fast-growing poplar solid wood and controlling the PU prepolymer cured or foamed within wood voids with various catalysts. Both the mechanical properties and dimensional stabilities of the PU-wood composites were much better than for the control wood.

The variations of the mechanical properties and dimensional stabilities of the PU-wood composites resulted from the catalyst species that had obvious effects on the distribution and morphologies of the PU resin within wood voids. The improvement in mechanical properties was attributed to the thickened wood cell walls as a result of the continuous PU resin layer, the sustentation of the PU foam that filled in the wood voids, and/or the densification of wood resulting from the collapse of the wood cell walls. All the elements that improved the mechanical properties could block or retard the water transfer within the wood, and therefore improve the dimensional stability.

The PU-wood composite prepared with the catalyst DETA had the best mechanical properties, and the dimensional stabilities for DETA could soften the wood and therefore resulted in wood densification in the surface layer of the composite. The PU prepolymer was well impregnated and evenly foamed within the wood in the presence of catalyst NMM. The large hollow thin-walled PU foam could efficiently block the water transfer between wood cells, and therefore greatly improve the dimensional stabilities of PU-wood composite prepared with catalyst NMM.

References

1. Galperin, A. S. Holzforschung 1995, 49, 45.
2. Haygreen, J. G.; Bowyer, J. L. Forest Products and Wood Science—An Introduction, 3rd ed.; Iowa State University Press: Ames, 1996.
3. Keiko, S.; Masahiro, M.; Kazuya, M. J Wood Sci 1999, 45, 227.
4. Wu, Y.; Hiroaki, M.; Yutaka, K. Scientia Silvae Sinicae 2003, 39, 136.
5. Deka, M.; Saikia, C. N. Bioresour Technol 2003, 73, 179.
6. Chen, D. China Wood Ind 1997, 10, 9.
7. Makoto, O. J Wood Sci 2002, 48, 394.
8. Williams, F. C.; Hale, M. D. Holzforschung 1999, 53, 230.
9. Engonga, P. E.; Schneider, R.; Gerardin, P.; Loubinoux, B. Holzforschung 1999, 53, 272.
10. Chen, G. C. Holzforschung 1994, 48, 181.
11. Ellis, W. D. Wood Fiber Sci 1998, 25, 236.
12. Gao, Z. H.; Li, D. J Appl Polym Sci 2007, 104, 2980.
13. Gao, Z. H.; Gu, J. Y.; Wang, X.-M.; Li, Z. G.; Bai, X. D. Pigment Resin Technol 2005, 34, 282.
14. Seneker, S. D.; Potter, T. A. J Coat Technol 1991, 63, 19.
15. Luo, N.; Wang, D. N.; Ying, S. K. J Appl Polym Sci 1996, 61, 367.
16. Xie, H.; Chen, H.; Wang, Z.; Wang, W. Plast Sci Technol 2007, 35, 62.