

Polyurethane–Solid Wood Composites. II. Flammability Parameters

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ABSTRACT: Polyurethane (PU)–solid wood composites with good mechanical properties and dimensional stability have been prepared in the presence of four amine catalysts. Cone calorimetry and scanning electron microscopy (SEM) have been employed to characterize and evaluate the effects of the catalyst species on the flammability of the PU–wood composites. The results indicated that the PU–wood composites prepared in the presence of various catalysts had somewhat better flame resistance than the untreated wood control, as manifested in various flammability parameters (longer time to sustained ignition and time to peak heart rate release, larger mass and fire performance index (FPI), and lower mean HRR, mass loss rate, and peak HRR). The variations in the flame resistances of the PU–wood composites can be attributed to the various morphologies of the PU resin and the

wood that resulted from the use of the various catalysts, as indicated by SEM micrographs. The PU–wood composite prepared in the presence of *N*-methylmorpholine (NMM) as catalyst showed the best flame resistance, since the PU resin formed abundant PU foam that extended throughout the wood. This foam was effective in retarding the transfers of heat and combustible substances as well as the pyrogenation. In terms of FPI values, the flame resistances of these PU–wood composites decreased according to the catalyst used in the order NMM, triethanolamine, diethylenetriamine, and triethylenediamine. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3279–3285, 2009

Key words: polyurethanes; composites; flame retardance; morphology; biomaterials

INTRODUCTION

Wood has many inherently advantageous properties, such as good aesthetic quality, habitat–environment adjustability, and high strength-to-weight ratio, which make it a preferred building material for many applications.¹ However, some disadvantages of wood, such as poor dimensional stability, relatively low strength, susceptibility to woodworm attack and fungal decay, and poor fire resistance, prevent its wider utilization. Therefore, a vast amount of research has been carried out with a view to improving wood quality. For example, certain polymers, such as phenol–formaldehyde resin,^{2,3} urea–formaldehyde resin,⁴ and melamine–formaldehyde resin,⁵ have been impregnated into wood to impart strength and/or to improve dimensional stability. Industrially, fire retardants are introduced into wood or wood-based materials to improve flame resistance.

Isocyanate shows high reactivity toward hydroxyl groups and water within wood. If isocyanate-terminated polyurethane (PU) prepolymer with more than two functionalities is impregnated into wood, the active isocyanate groups will react with water present to form crosslinked polyurea with the elimination of carbon dioxide. During the crosslinking reaction, the active isocyanate groups will also react with the hydrophilic hydroxyl groups in the wood to form hydrophobic carbamate, thereby blocking the partial hydroxyl groups and leading to that the crosslinked PU resin is strongly adhered to the wood through chemical bonds. This results in better dimensional stability and higher mechanical strength.

In our previous studies, four amine catalysts⁶ and some PU prepolymers prepared with various NCO/OH molar ratios⁷ were applied to prepare PU–wood composites. It was found that both the mechanical properties and the dimensional stability of the PU–wood products were simultaneously improved compared with those of the untreated wood. SEM analyses indicated that some PU prepolymer foamed within the wood voids, whereas some was cured to form a continuous polymer layer that adhered to and therefore thickened the wood cell walls, thereby strengthening the wood. The improvement in the

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dimensional stability of the PU–wood products resulted from blocking of the partial hydrophilic hydroxyl groups by the substituent structure (carbamate) and hindrance of water transfer between the wood cells by the continuous PU layers on the wood cell walls. These two previous studies also indicated that both the PU prepolymer and catalyst species had obvious effects on the mechanical properties and dimensional stability of the PU–wood composites.

Wood and wood-based materials without fire-resistant treatment are materials that contribute to the growth of fires. The fire performances of wood and wood-based materials treated with fire retardants have been extensively studied and discussed.^{8,9} However, to the best of our knowledge, no study on the effect of isocyanate treatment on the flammability of wood has hitherto been reported. Therefore, the current research was extended to investigate the effect of catalyst species on the flammability of the PU–solid wood composites prepared by impregnating PU prepolymer into low-density, fast-grown, solid poplar wood and then controlling the curing or foaming of the prepolymer within the wood voids in the presence of various catalysts.

EXPERIMENTAL

Materials

Poplar (*P. ussuriensis*) logs of density 339 kg/m³ (oven-dry basis) were procured from a local wood farm. The fresh logs were cut into lumber of thickness 25 mm, air-dried, and finally cut into specimens of dimensions 20 mm × 10 mm × 220 mm. The longest dimension of each specimen was perpendicular to the annual rings. Regular specimens were selected, free from faults and of similar weight (to ensure equivalent densities).

The PU prepolymer was prepared in our laboratory as follows. A three-necked flask equipped with a condenser was charged with a stoichiometric ratio of polyaryl polymethylene isocyanate (P-MDI, Millionate MR-100, supplied by Nippon Polyurethane Industry, Tokyo, Japan) and polyethylene glycol (PEG, chemical reagent grade purity, supplied by Tiantai Chemicals, Tainjin, China), and then half weight of the total acetone was added. The reaction mixture was initially stirred and heated at 40°C for 30 min and then further heated to a gentle reflux, which was maintained for 3 h. It was then cooled to 50°C, whereupon the second half weight of the total acetone was added, and stirring was continued for 10 min. The resulting mixture was finally transferred to a container, which was sealed for storage. The solid content of the PU prepolymer was 70% and the content of isocyanate groups was 9.11 wt % (or

NCO/OH mole ratio 3.0). Before impregnating, the PU prepolymer was diluted with acetone to a concentration of 20% by weight.

The acetone used as solvent and the catalysts triethanolamine (TEA), diethylenetriamine (DETA), triethylenediamine (TEDA), and *N*-methylmorpholine (NMM) were obtained from the chemical market in Harbin.

Impregnation and foaming of PU resin

Wood pretreatment

All poplar specimens were free from faults and were moisture-conditioned at 20°C and 60% relative humidity for at least 30 days. Twenty specimens were selected at random, which were each weighed (W_1), dried at about 103°C for 5 h, and then weighed once more (W_2). The moisture content of each specimen could then be calculated as $MC\% = (W_1 - W_2)/W_2 \times 100\%$. The average MC% value of these 20 specimens represents the moisture content of the batch of poplar specimens after moisture conditioning.

Resin impregnation

Twenty moisture-conditioned specimens were selected at random, which were each labeled and weighed (W_3). These were then kept under vacuum (75 kPa) for 15 min to remove air from within the wood. They were then immersed in a 0.99 wt % solution of the respective catalyst in acetone for 20 min. After removal from the catalyst solution, the specimens were kept under vacuum (75 kPa) for a further 30 min. They were then immersed in a 15 wt % PU prepolymer solution in acetone for 20 min. After removal from the prepolymer solution, the specimens were washed with acetone to remove any resin on their surfaces.

Foaming (curing) and drying

Impregnated specimens were immersed in water for 5 min. Then, each specimen was wrapped in foil and dried at 120°C for 90 min. The foil and the foamed resin on the surfaces of the specimens were subsequently removed. Thereafter, the specimens were dried at 103°C and 85 kPa vacuum for 4 h, and each specimen was weighed (W_4).

Characterization of the PU–solid wood composites

Weight percentage gain

The weight percentage gain (WPG) was used to evaluate the amount of cured PU resin introduced into the wood and was determined from the difference in the oven-dried weight of each specimen

TABLE I
The Values of Flammability Parameters for PU–Wood Composites Compared with Those of Untreated Wood According to Cone Calorimeter Tests

Catalyst species	WPG (%)	Density (kg/m ³)	Flammability parameters							
			TTI (s)	THR (MJ/m ²)	PHRR (kW/m ²)	TPHRR (s)	MHRR (kW/m ²)	FPI (m ² s/kW)	MLR (g/s)	Mass (%)
None (the control)	N/A	339	16	25.2	346.0	77	155.3	0.0462	0.091	11.9
TEA	16.14	399	19	22.6	313.2	75	146.0	0.0607	0.089	16.4
TEDA	12.00	381	17	25.5	334.3	76	125.9	0.0509	0.078	14.0
DETA	14.64	384	17	26.0	296.2	84	134.1	0.0574	0.082	15.0
NMM	16.78	390	18	25.6	289.1	99	144.5	0.0623	0.083	19.1

before treatment [$W_3/(1 + MC\%)$] 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.

Density

The densities of PU–solid wood composites were measured as follows. After the composites were oven-dried at 103°C and 85 kPa vacuum for 4 h and then cooled down in the desiccator, the length (l) of each specimen was measured with a ruler (accurate to ± 0.1 mm), and the areas (width \times thickness, $a = w \times t$) of three sections in the two sides and the middle of each specimen were measured with a micrometer, respectively. The averaged section area (a_{av}) was used to calculate the density as follows: Density = $W_4/(l \times a_{av})$. The average density of total 20 specimens was reported.

Flammability test by cone calorimetry

A sample block of dimensions 100 mm \times 20 mm \times 10 mm (length \times width \times thickness) was cut off from one side of a specimen of the PU–wood composite or the control, and then a 3-mm surface layer was cut off in the direction of the sample thickness to ultimately obtain a sample with dimensions 100 mm \times 10 mm \times 3 mm (length \times width \times thickness). From one batch of PU–wood composites, a total of five 3-mm layers were obtained from five respective specimens. These five 3-mm layers were arranged together and fixed into the specimen holder of the FTT cone calorimeter to make a single specimen for a flammability test of dimensions 100 mm \times 100 mm \times 3 mm (length \times width \times thickness).

The reaction-to-fire tests were conducted in accordance with ISO 5660¹⁰ (cone calorimeter, England FTT Company) at a heat flux of 50 kW/m². During the tests, the following parameters were determined: time to sustained ignition (TTI), heat release rate (HRR), peak HRR (PHRR), time to peak HRR (TPHRR), total heat released (THR), mean heat

release rate (MHRR), fire performance index (FPI), mass loss rate (MLR), and mass residue (Mass).

Scanning electron microscopy analysis

Samples cut from dry untreated and treated specimens were manually split to obtain cross-sectional and tangential surfaces. Scanning electron microscopy (SEM) samples were coated with approximately 10–20 nm of gold prior to examination with a QUANTA-200 SEM (FEI Company, USA) at 15 or 20 kV.

RESULTS AND DISCUSSION

The results of flammability tests on the PU–wood composites prepared in the presence of various catalysts and the control (the wood without treatment) are presented in Table I. In general, the PU–wood composites showed longer TTI and TPHRR, larger Mass and FPI, and lower MHRR, MLR, and PHRR than the control, thus indicating that all of the PU–wood composites had somewhat better flame resistance than the untreated wood (the control).

The TTI of the PU–wood composites ranged from 17 to 19 s and so were slightly longer than that of the untreated wood control (16 s). The PU–wood composite prepared with TEA as catalyst, which had the highest density but only the second highest WPG, displayed the longest TTI, suggesting that the TTI values correlated with the densities rather than the WPG of the PU–wood composites prepared with the various catalysts. Thus, the PU–wood composite prepared with NMM as the catalyst displayed the second highest TTI and the second highest density, though it had largest WPG, whereas the composites prepared with TEDA or DETA showed the shortest TTI values. It has been reported¹¹ that the TTI values of some wood-based composites, such as plywood, PB, and MDF, are affected by their densities. The THR of the PU–wood composites, which ranged from 22.6 to 26.0 MJ/m², were quite similar to that of the untreated wood control (25.2 MJ/m²), with differences of less than 10.3%.

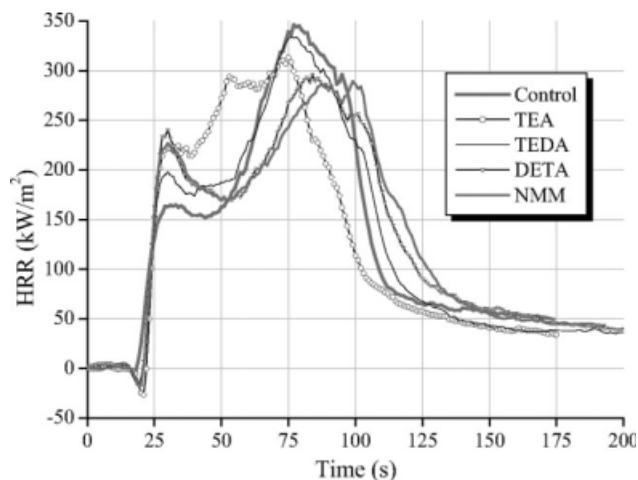


Figure 1 Heat release rate (HRR) curves of the PU-wood composites and the control.

The MLR reflects the averaged pyrogenating rate of the material during combustion. The MLR values of the composites, which ranged from 0.078 to 0.089 g/s, were smaller than that of the untreated wood control (0.091 g/s), implying that the cured PU polymer could to some extent inhibit the pyrogenation of wood during combustion. The catalyst TEDA resulted in better inhibition compared to the others.

The Mass is the weight of the material that remains after combustion. In the current study, the Mass represented the charring yield, since all of the constituent substances of the composite (wood, cured PU resin, and a small quantity of amine catalyst) were organic. The Mass from each PU-wood composite ranged from 14.0% to 19.1%, all of which were higher than that from the untreated wood (11.9%). The composites prepared in the presence of NMM as the catalyst showed the highest Mass, which was 60.5% greater than that from the wood. The detailed mass losses of each composite and the untreated wood are presented in Figure 1. During the whole combustion, the untreated wood had less mass residue (or more mass loss) than the composites prepared in the presence of DETA, TEDA, and NMM, whereas the PU-wood composite prepared in the presence of TEA showed less mass residue than the untreated wood during middle-stage combustion which was corresponded with the second peak in the HRR curves in Figure 1. More Mass loss during combustion indicates more substance pyrogenated into volatile combustible substances and therefore faster spread of the flame. Thus, the Mass curves in Figure 1 further confirm that the cured PU polymer could to some extent inhibit the pyrogenation of wood during combustion.

The main property determined in the flammability tests was the HRR, which is a basic and important parameter for fire modeling.^{12–14} Larger HRR (or

PHRR or MHRR) and smaller TPHRR equate to more heat being released from a certain surface area of the material when combusted for a certain period of time, resulting in a faster pyrogenating rate and more volatile combustible substances being formed and therefore accelerating the spread of flames.

The data in Table I indicate that the PU-wood composite prepared in the presence of NMM had the smallest PHRR, which was 16.4% less than that of the control wood, whereas its TPHRR was the longest (99 s), 28.6% longer than that of the control. However, the PU-wood composite prepared in the presence of TEDA had the smallest MHRR, 18.9% less than that of the control wood. The heat release rates of the wood and the PU-wood composites prepared in the presence of various catalysts are presented graphically in Figure 2. The HRR curve of the untreated wood (control) in the current study shows the typical characteristics of the HRR curves of wood products, i.e., a double-peak feature.^{8,15} This double-peak shape was also observed in the HRR curves of the PU-wood composites prepared with the catalysts TEDA, DETA, and NMM, whereas the curve of the composite prepared in the presence of TEA as the catalyst displayed a new feature, a triple peak, as shown in Figure 2.

Comparing the HRR curves of the composites prepared with TEDA, DETA, and NMM with that of the control, the maximum values of the first peak are seen to decrease in the order DETA, NMM, TEDA, control, whereas the second peaks decrease in the order control, TEDA, DETA, and NMM. The second HRR peak of the untreated wood was narrow in shape and reached the highest value, indicating that the untreated wood was the most flammable, since more heat was released in a shorter time. Conversely, the second peak of the PU-wood composite prepared with NMM was the widest and

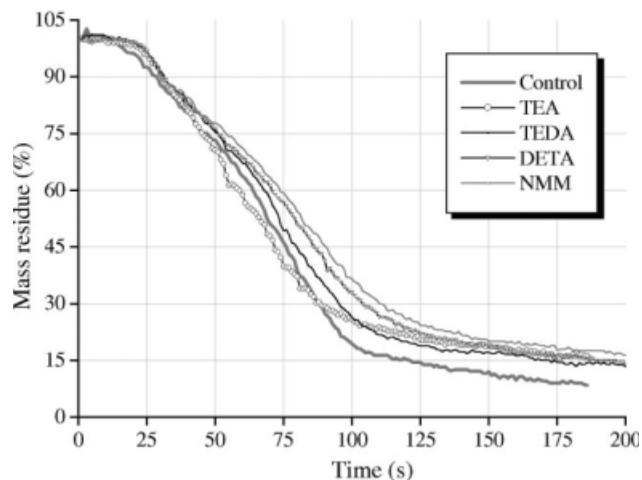


Figure 2 Mass residue (Mass)-time curves of the PU-wood composites and the control.

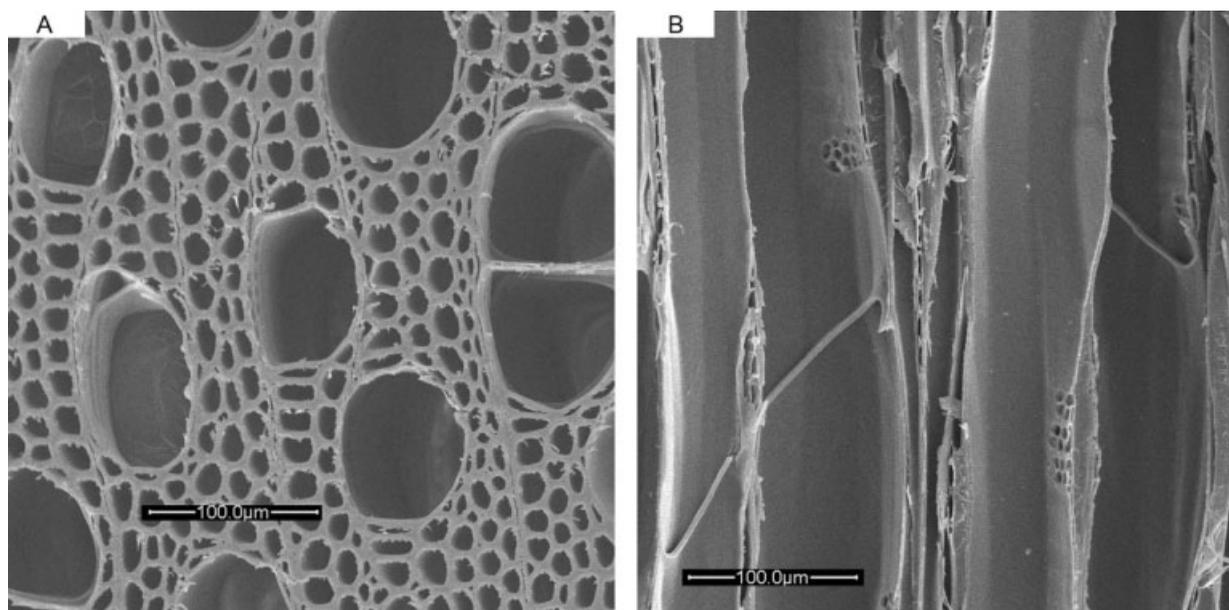


Figure 3 SEM micrographs of the control (untreated wood): (A) cross-section; (B) tangential surface.

the lowest, implying that this composite had the best flame resistance, since a similar amount of heat (as indicated by the THR: 25.2 MJ/m² for the control vs. 25.6 MJ/m² for this composite) was released over a longer time. The second peak of the composite prepared with TEDA as the catalyst was quite similar to that of the control, but a little lower and wider, indicating slightly better flame resistance than that of the control. The flammability of the composite prepared with DETA was intermediate between those of the products prepared with NMM and TEDA, as indicated by moderate height and width of the second HRR peak. The triple-peak HRR curve of the composite prepared with TEA shown in Figure 2 was indicative of the shortest combustion time, and this composite gave the lowest THR (as shown in Table I). The heat was released more smoothly during combustion of this composite as compared with the others.

These considerable differences in the reaction-to-fire parameters observed for the various PU–wood composites indicated that the catalyst species had significant effects on the flammabilities of the PU–wood composites. In view of the fact that the amounts of catalysts introduced into the wood were less than 0.33 wt % of the dry wood, their direct effects on the flammability of each PU–wood composite should be negligible at these low levels. Because these PU–wood composites were prepared with the same processing and using the same raw materials apart from the catalyst species, the observed differences in the flammability parameters must be attributed either to different PU morphologies resulting from the presence of the various catalysts in the wood, or to the influence of the catalysts

on the wood. Therefore, SEM analysis was employed to investigate the morphologies of the PU resin and the wood cells in the PU–wood composites.

Figure 3 shows SEM photos of the control wood without impregnation by PU prepolymer. In both the cross section [Fig. 2(A)] and tangential surface [Fig. 2(B)], the wood voids are clear and contain no foreign matter, and the cell walls are relatively even and smooth.

The PU–wood composites prepared with TEA and TEDA as catalysts display similar morphologies, i.e., most of the cured PU resin forms a continuous polymer coating that adheres to the surfaces of the wood void walls, whereas only a small quantity of the PU resin forms microfoams. Besides, the catalyst TEA had a slight softening effect on the wood, as indicated by obvious distortions of the void walls within the composite, as shown in Figure 3(A), whereas the catalyst TEDA had no softening effect on the wood, since the void walls of the PU–wood composites remained essentially undistorted and were similar to those of the control, as shown in Figure 4(A,B), respectively. In our previous study,⁶ we confirmed that this continuous PU layer was effective in blocking or retarding the transfer of water within the wood cells, as expressed by the 24-h volumetric swelling coefficient (VSC_{24 h}) and the 24-h water absorption coefficient (WAC_{24 h}), as shown in Figure 5. The VSC_{24 h} was calculated according to the equation $[VSC_{24 h} = (l_2 w_2 t_2 - l_1 w_1 t_1) / l_1 w_1 t_1 \times 100]$ and the WAC_{24 h} was calculated according to the equation $[WAC_{24 h} = (W_3 - W_1) / W_1 \times 100]$, where l_1 , w_1 , t_1 , and W_1 refer to the dimensions (length, width and thickness) and weight of each specimen before soaking and l_2 , w_2 , t_2 , and W_3 after soaking in

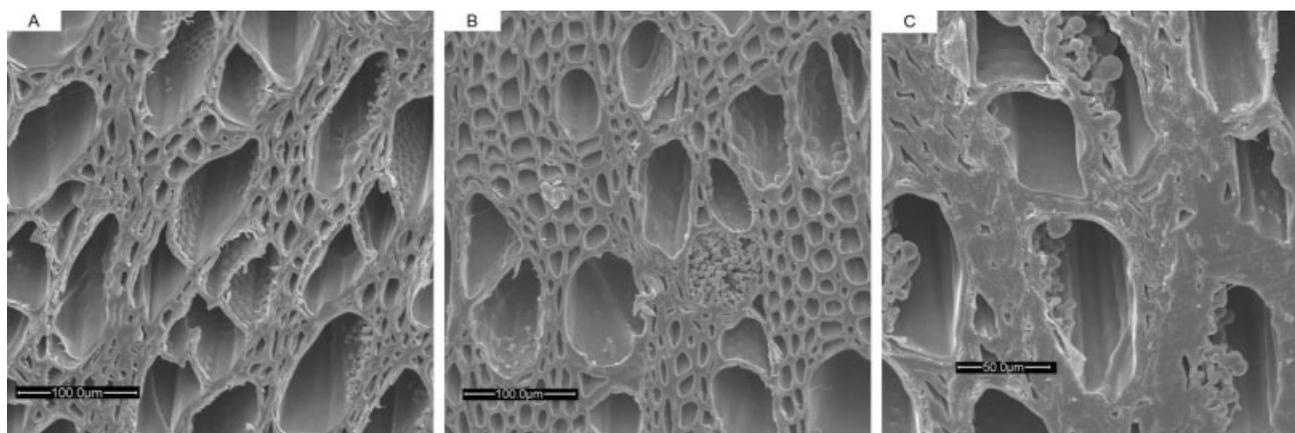


Figure 4 SEM micrographs of PU–wood composites prepared with three different catalysts. (A) TEA as catalyst; (B) TEDA as catalyst; (C) DETA as catalyst.

20°C ± 0.5°C water for 24 h by determining by micrometer and analytical balance (accurate to ±0.01 g), respectively. The averaged $VSC_{24\text{ h}}$ and $WAC_{24\text{ h}}$ values of 10 specimens are reported here. Hence, the continuous PU layer on the wood void wall resembles a partition wall that will also inhibit to some extent the further transfer of heat into the internal layer closed to the flame during combustion, thereby resulting in decreased pyrogeneration of the internal layer and less combustible substances to contribute to sustained combustion of the composites. Therefore, these two composites had longer TTI, less MLR, and more Mass compared with the control.

In the presence of the catalyst DETA, the PU–wood composite not only formed a continuous PU layer on the wood void walls, but most of the void walls of the wood fibers at the surface layer of the composite also collapsed and became adhered to one another by PU resin to form a compact PU–wood entity, as shown in Figure 4(C). This densification of the surface layer of the composite increased the overall density, which in turn led to faster con-

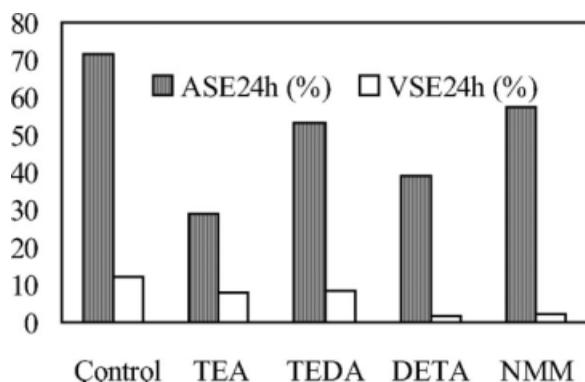


Figure 5 The 24-h volumetric swelling coefficient ($VSC_{24\text{ h}}$) and 24-h water absorption coefficient ($WAC_{24\text{ h}}$) of the PU–wood composites and the wood control.

duction of heat to the center layer closed to the flame and therefore decreased the flammability through reducing the temperature. Therefore, the TPHRR (84 s) of this PU–wood composite was much longer than that of the control (77 s); meanwhile, the PHRR (296.2 kW/m²) and MLR (0.082 g/s) were much smaller than those of the control, 346.0 kW/m² and 0.091 g/s, respectively.

Within the PU–wood composite prepared in the presence of the catalyst NMM, the PU resin was not only evenly distributed throughout the wood but also formed abundant thin-wall PU foam with large hollows, as shown in Figure 6(A,B); the diameters of these hollows in the PU foam were in the range 10–50 μm. These large-hollow, thin-wall foams were effective in blocking the transfer pathways of water and nutrients between the wood cells, thereby inhibiting the pyrogeneration of some combustible substances from the wood cells and/or the PU resin during combustion. In addition, these evenly distributed foams acted as good partition walls, retarding the inward conduction of heat to the area closed to the flame, resulting in less combustible substances being from the wood cells and/or the PU resin. In summary, the evenly distributed foams retarded the transfers of heat and combustible substances, and hence the pyrogeneration, and were therefore effective in inhibiting the combustion of this composite, as indicated by the lowest PHRR, the longest TPHRR, and the highest Mass among the composites (as shown in Table I and Fig. 2).

The FPI, defined as the ratio of TTI to PHRR, is a parameter that relates to the time available to escape in a real fire situation.¹⁶ A larger FPI indicates better flame resistance. The FPI values of the PU–wood composites prepared in the presence of the various catalysts, as shown in Table I, ranged from 0.0509 to 0.0623 m²s/kW, and were thus 24.2–34.8% higher than that of the untreated wood (0.0462 m²s/kW). In

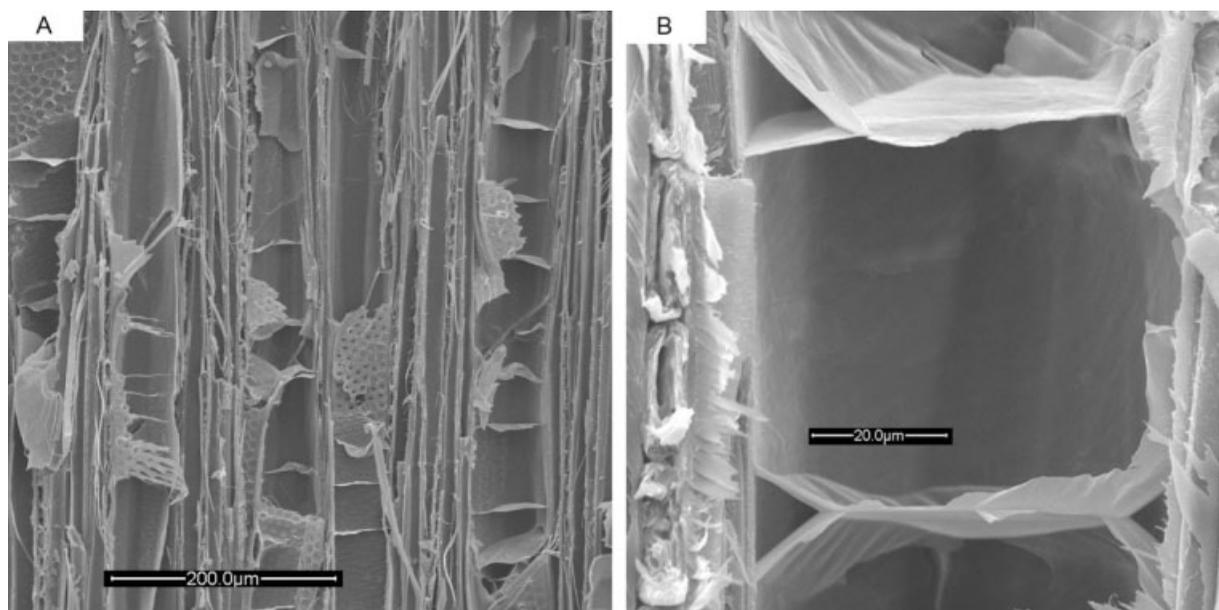


Figure 6 SEM micrographs of the PU–wood composite prepared with *N*-methylmorpholine. (A) tangential surface; (B) magnification of a local area.

terms of the FPI values, the flame resistances of these PU–wood composites decreased in the order NMM (0.0623), TEA (0.0607), DETA (0.0574), and TEDA (0.0509).

CONCLUSION

PU–solid wood composites were prepared by impregnating PU prepolymer into low-density, fast-grown, solid poplar wood and controlling the curing or foaming of the PU prepolymer within the voids in the wood in the presence of the catalysts TEA, TEDA, DETA, or NMM. The flame resistances of the resulting composites were somewhat improved and decreased in the order NMM, TEA, DETA, and TEDA.

The variations in the flammability of these composites may be attributed to different morphologies of the PU resin and the wood that resulted from the presence of the respective catalysts. A continuous PU layer adhered to the wood cell walls or a PU foam within the composite is effective in blocking the transfers of heat and combustible substances and therefore inhibits the flammability. Densification of the surface layer of the composite, through collapse and adhesion of the wood cell walls, may also decrease the flammability by reducing the temperature of the flame.

The PU–wood composite prepared in the presence of NMM as the catalyst showed the best flame resist-

ance, since the PU resin formed abundant PU foam that extended throughout the wood, and this retarded the transfers of heat and combustible substances and hence the pyrogenation.

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