Treatment of Fast-Growing Poplar with Monomers Using In Situ Polymerization. Part II: Static and Dynamic Mechanical Properties; Thermal Stability

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Abstract

Part I of this article described the treatment of specimens of fast-growing poplar (*Populus ×euramericana* NL-95) with styrene (ST) and glycidyl methacrylate (GMA) monomers. It detailed the results of tests for water absorption, dimensional stability, and termite and fungus resistance. This part continues the previous work. It examines the static and dynamic mechanical properties, as well as the thermal stability, of polymer-infused wood (PIW). Static mechanical properties of PIWs were assessed in terms of bending strength, compressive strength, and Brinell hardness. Our results showed that, as a result of the treatment, these properties were significantly increased. Moreover, the PIW treated with GMA-ST showed greater mechanical strength than PIW treated with ST alone. We believe that this is due to the formation of cross-linked bonds between the GMA-ST and the hydroxyl groups of the wood's cell walls. Dynamic mechanical analysis (DMA) demonstrated that, at normal temperatures, storage modulus E' and molecular structure stability of wood were significantly enhanced by the treatment. However the loss factor (tan δ) of PIWs was sharply elevated at a higher temperature range. Finally, thermogravimetric analysis (TGA) indicated that the thermal stability of wood was greatly improved by the treatment; the wood treated with GMA-ST showed slightly higher thermal stability than the wood treated with ST alone.

As noted in our first article, the global shrinkage of natural forest resources has been to some extent countered by widespread planting of various fast-growing trees. In China, the fast-growing poplar *Populus ×euramericana* has been planted on more than 14 million hectares (Hua and Jin 2008). However, fast-growing wood species are weaker (as measured by mechanical properties such as bending strength, resistance to compression, and hardness) than slow-growing, naturally occurring wood species; this is generally attributed to their rapid growth rate (Nemeth et al. 2006, Begum et al. 2008, Kojima et al. 2009). Such weakness means that it cannot be used in applications requiring high-strength timber. Fast-growing poplar is mainly used as raw material for charcoal or pulp (Kojima et al. 2009). If poplar wood could be made stronger, it could be used in more applications and would be more economically valuable.

Fortunately, such a technology exists. In recent decades, there has been much research into the in situ polymerization of wood treated with monomer infusions. The treated wood is much stronger than untreated wood. Polish researchers Lawniczak (1981) and Rozman et al. (1997, 1998) have studied aspen, birch, and other species infused with vinyl monomers. Their results indicate that polymer-infused woods (PIWs) treated with vinyl monomers show high

mechanical performance but do not show significantly superior durability and dimensional stability.

As detailed in Part I, this may be mainly attributed to the fact that wood substrates contain few functional groups that will react with vinyl groups. The monomers polymerize only in the lumen of the wood cells and not in the cell walls (Lawniczak 1981, Zhang et al. 2005).

However, it has been found that coupling agents will increase the affinity, compatibility, and adhesion between wood substrates and polymers (Lu et al. 2000). The most successful coupling agents are isocyanates, epoxides, anhydrides, silanes, and methacrylates. Glycidyl methacrylate (GMA) is one of the most popular coupling agents; it is widely used in the manufacture of wood–plastic composites. Research shows that it bonds wood and plastics because the glycidyl groups of GMA will bond with the hydroxyl groups of the wood's cell walls and its terminal double bonds will copolymerize with vinyl or acrylic monomers (Rozman et al. 1997, 1998; Devi et al. 2003).

In Part I of this study, we described the experimental preparation of specimens of fast-growing poplar: impregnation with styrene (ST) and a combination of GMA and ST (GMA-ST), followed by in situ polymerization using a thermal catalyst treatment. We then measured the dimensional stability and resistance to biodegradation of the treated wood. We also investigated and evaluated the microstructure of the treated wood specimens. The results showed that dimensional stability and resistance to biodegradation were significantly improved. Examination by Fourier transform infrared (FTIR) spectroscopy demonstrated the formation of cross-linked bonds between cell walls, ST, and GMA.

In the current phase of this study, we evaluate the static mechanical properties of the treated wood: bending strength, resistance to compression, and hardness. We also examine the dynamic mechanical properties, as well as the thermal stability of the treated specimens.

Experimental Procedures

Preparation of materials

Fast-growing poplar (*Populus ×euramericana* NL-95) lumber from a 15-year-old plantation in the county of Siyang, Jiangsu, People's Republic of China, was obtained. The lumber was stored for about half a year in a room kept at a constant 25°C and 65 percent relative humidity. After storage, it had a density of 0.38 ± 0.01 g/cm^3 and 12 percent moisture content (MC). Specimens were prepared from clear, defect-free wood. The dimensions of the specimens and sample sizes used in the various tests are shown in Table 1.

Analytical grade GMA, purchased from Sansyo Co., Ltd. (Japan), was distilled for further purification before use. Analytical grade ST was also obtained from Sansyo Co. The ST was cleaned using sodium hydroxide, dried with anhydrous CaCl$_2$, and distilled under vacuum pressure for further purification. This process removed the polymerization inhibitor 2.6-dinitro-*P*-cresol. An initiator, 2,2′-azobis-2-(methylbutyronitrile) (AIBN), was also supplied by Sansyo.

Composition of the impregnation solutions

Two solutions were prepared: ST monomer and a combined solution of ST and GMA monomers (at a 4:1

Table 1.—Specimen dimensions and sample size.

Property tested[a]	Dimensions of specimens used (mm)[b]			Sample size
	R	T	L	
Bending (//)	15	15	200	30
Bending (⊥)	200	15	15	30
Compressive (//)	20	20	30	30
Compressive (⊥)	30	20	20	30
Brinell hardness	70	4.5	55	30
DMA	3	8	60	9

[a] // = parallel to wood grain; ⊥ = perpendicular to wood grain; DMA = dynamic mechanical analysis.
[b] R, T, and L = the radial, tangential, and longitudinal directions, respectively.

molar ratio). AIBN was respectively added into both solutions as an initiator at a percentage of 1.0 by weight.

Impregnation procedure and polymerization method

The precise details of the impregnation and polymerization process are given in Part I.

The polymer loading of ST- and GMA-ST–treated wood specimens was approximately 118 percent. At this value, the cell lumens were fully saturated. We conducted preliminary research on specimen preparation procedures and found that this particular protocol gave the best polymer loading.

The average densities of the wood specimens treated with ST and GMA-ST were approximately 0.84 g/cm^3.

In addition, polystyrene and GMA-ST copolymer were prepared according to the same polymerization method described in Part I. The average densities of polystyrene and GMA-ST copolymer were 1.04 and 1.12 g/cm^3, respectively. We measured the hardness and dynamic mechanical properties, as well as the thermal stability, of polystyrene and GMA-ST copolymer, to be used as references.

Measurements

Bending tests.—Three-point bending tests were performed to measure the modulus of elasticity (MOE) and modulus of rupture (MOR) of the untreated and treated wood specimens. A universal test machine (Model AG-100kNG; Shimadzu Corporation, Japan) was used. Tests were performed with a load cell with a capacity of 10 kN and at a crosshead speed of 2.0 mm/min; this procedure followed the method prescribed by the American Society for Testing and Materials (ASTM) D143 (ASTM 1996). Span length was 90 mm; bending load–applied planes were the longitudinal–radial and radial–tangential surfaces of the wood specimens. Ten samples were measured for each wood composite. The MOR of the specimens was calculated as follows:

$$MOR = \frac{3P_{max}L_s}{2bh^2} \qquad (1)$$

where P_{max} is the maximum failure load, L_s is the span, b is the width of the cross section, and h is the depth of the cross section. The MOE was calculated from the load and deflection curve under proportional limits using the following formula:

$$MOE = \frac{(P_2 - P_1)L_s^3}{4bh^3(d_2 - d_1)} \qquad (2)$$

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where L_s is the span, $P_2 - P_1$ is the increment of load on the straight line portion of the load-deformation curve, b is the width of the cross section, h is the depth of the cross section, and $d_2 - d_1$ is the increment of deformation corresponding to $P_2 - P_1$.

Compression tests.—Compression tests were carried out in a load frame attached to a universal test machine (Model AG-100kNG). Tests were carried out at a crosshead speed of 1.0 mm/min, in accordance with the specifications of the Chinese National Standard GB1928-1929-91 (1999). Treated and untreated specimens were tested for compression strength (f_c) and Young's modulus (E). At least 10 samples of each wood composite were tested. Results were calculated using Equation 3, which gives compression strength, and Equation 4, which yields Young's modulus.

$$f_c = F_{max}/A_t \qquad (3)$$

$$E = \Delta\sigma/\Delta\varepsilon \qquad (4)$$

Here, F_{max} is the maximum compression force, A_t is the cross-section area of the specimen, $\Delta\sigma$ is the stress produced by wood specimens under loading, and $\Delta\varepsilon$ is the strain of wood specimens corresponding to the stress.

Brinell hardness.—Hardness tests were conducted on specimens using a universal test machine (Model A6-5000A; Shimadzu Corporation). Tests followed the standard outlined in the Chinese National Standard GB1928-1929-91 (1999). The test consisted of lowering an indenter (a steel ball with a diameter of 11.3 mm, attached to the loading platen of the test machine) onto the surface of the test specimen. A preload of 1 to 2 N was applied to stabilize the test specimen. The applied load was then increased to reach a target load of 1,000 N in 15 seconds; it was maintained at this pressure for 25 seconds. The area in actual contact with the indenter was used to calculate the hardness of the specimen. The load-deformation data were collected at a sampling rate of 10 data points per second. Ten samples were used for each test.

Specimens of polystyrene and GMA-ST copolymer were prepared, which were cut to the same dimensions as the wood specimens. Six samples of each polymer were subjected to the hardness measurement procedures described above.

Brinell hardness was calculated from following equation:

$$H_B = \frac{F}{(\pi D/2)(D - (D^2 - d^2)^{1/2})} \qquad (5)$$

where H_B is the Brinell hardness, F is the maximum applied force, D is the diameter of the steel ball, and d is the diameter of the indentation under load.

Dynamic mechanical analysis (DMA).—DMA was performed using a DMA 242 C dynamic mechanical analyzer manufactured by Netzsch-Gerätebau GmbH, Germany. Dual cantilever bending mode was used. The specimens were ramped at 5°C/min from −150°C to 150°C under a flow of nitrogen. Oscillation frequency was fixed at 1 Hz. All experiments were performed three times to confirm results.

Specimens of polystyrene and GMA-ST copolymer, of the same dimensions as the wood specimens described above, were prepared and subjected to DMA. Each type of polymer was tested at least twice.

Thermogravimetric analysis (TGA).—Treated and untreated wood specimens, as well as polystyrene and GMA-ST copolymer, were tested using a DTG-60AH thermogravimetric analyzer manufactured by the Shimadzu Corporation. These samples were cut into small pieces with a razor blade and ground in a ball mill to a fine power (modal particle size of 180 μm). Specimens were then ramped at a heating rate of 10°C/min up to 600°C under a flow of nitrogen. This method measures the change in weight as a function of temperature with a resolution of 0.1 and 7.1 mg. To verify the reproducibility of the obtained mass loss curves, two sample runs were performed under the same experimental conditions.

Statistical analysis.—Analysis of variance and Duncan tests were used to evaluate the results of the static mechanical tests; statistical evaluations were made on homogeneity groups (HG), of which different letters reflected statistical significance. The storage modulus E' and loss factor (tan δ) curves were plotted with Origin 6.1 commercial software from Laboratory Network. The thermogravimetric mass loss (TG) and derivative thermogravimetric mass loss (DTG) curves obtained from TGA runs were smoothed using the least squares method, at a smoothing region width of 0.2°C, with Universal Analysis 2000 software from Thermal Advantage.

Results and Discussion

Static mechanical properties

Tables 2 and 3 show the results of tests of bending strength and compression resistance on untreated and treated wood specimens. Tests were conducted both parallel and perpendicular to the wood grain. Researchers found that the PIW samples were more than twice as dense as the untreated wood specimens. This significant improvement in density may be attributed to the lower xylem density and larger pore

Table 2.—Modulus of elasticity (MOE) and modulus of rupture (MOR) of untreated and treated wood specimens, tested both parallel and perpendicular to wood grain.[a]

Wood specimen[b]	Polymer loading (%)	Density (g/cm³)	MOE (GPa)[c]	MOR (MPa)[c]
Untreated (//)		0.38 ± 0.05	5.63 ± 0.34 C	42 ± 8 C
ST treated (//)	117.6 ± 9.4	0.83 ± 0.07	6.98 ± 0.49 B	59 ± 11 B
GMA-ST treated (//)	118.3 ± 6.8	0.84 ± 0.08	8.63 ± 0.57 A	70 ± 12 A
Untreated (⊥)		0.35 ± 0.07	0.95 ± 0.06 E	8 ± 2 EF
ST treated (⊥)	116.5 ± 8.5	0.85 ± 0.10	1.32 ± 0.09 DE	12 ± 3 E
GMA-ST treated (⊥)	118.4 ± 7.1	0.86 ± 0.12	1.46 ± 0.11 D	13 ± 3 E

[a] Values are means ± standard deviations.

[b] // = parallel to wood grain; ⊥ = perpendicular to wood grain; ST = styrene; GMA = glycidyl methacrylate.

[c] Letters represent homogeneity groups obtained by statistical analysis with different letters in each column reflecting statistical significance at the 95 percent confidence level.

Table 3.—*Young's modulus and compressive strength of untreated and treated wood specimens, tested both parallel and perpendicular to wood grain.*[a]

Wood specimen[b]	Polymer loading (%)	Density (g/cm^3)	Young's modulus (Pa)[c]	Compressive strength (MPa)[c]
Untreated (//)		0.37 ± 0.07	4.93 ± 0.55 C	36 ± 8 C
ST treated (//)	116.8 ± 10.2	0.85 ± 0.11	7.72 ± 0.84 B	65 ± 17 B
GMA-ST treated (//)	118.7 ± 8.5	0.85 ± 0.09	10.77 ± 1.06 A	81 ± 21 A
Untreated (⊥)		0.36 ± 0.05	0.89 ± 0.10 E	10 ± 3 E
ST treated (⊥)	115.2 ± 7.4	0.85 ± 0.12	1.38 ± 0.15 D	16 ± 5 DE
GMA-ST treated (⊥)	118.6 ± 6.7	0.85 ± 0.9	1.71 ± 0.22 D	21 ± 6 D

[a] Values are means ± standard deviations.
[b] // = parallel to wood grain; ⊥ = perpendicular to wood grain; ST = styrene; GMA = glycidyl methacrylate.
[c] Letters represent homogeneity groups obtained by statistical analysis with different letters in each column reflecting statistical significance at the 95 percent confidence level.

spaces of the fast-growing poplar; this allows the monomers to easily enter voids and penetrate cell walls. It is clear that bending strength and compression strength were greatly enhanced by treatment. It is also clear that wood treated with GMA-ST was stronger than wood treated with ST alone.

When ST-treated specimens were loaded parallel to the wood grain, the MOE increased 23 percent and the MOR increased 40 percent, compared with untreated wood. The Young's modulus increased 56 percent, and the compressive strength increased 80 percent.

When GMA-ST–treated specimens were loaded parallel to the wood grain, the MOE increased 53 percent and the MOR increased 67 percent, compared with untreated wood. The Young's modulus increased 118 percent, and the compressive strength increased 125 percent.

When specimens were loaded perpendicular to the wood grain, similar increases were seen.

It is generally believed that such significant improvements in bending strength and compression strength can be attributed to the filling of the voids and pores in the wood with polymer. This polymer absorbs energy through deformation (Schneider et al. 1990). Furthermore, the treatments created cross-linked bonds between GMA, ST, and hydroxyl groups in the wood's cell walls; these links allow load transfer from the wood to the polymer (Rozman et al. 1998).

Table 4 shows the Brinell hardness values for untreated and treated wood specimens, polystyrene, and GMA-ST copolymer. After treatment, hardness increased by 127 percent in the ST-treated PIW and by 183 percent in the GMA-ST–treated PIW. Nevertheless, the hardness values of PIWs were slightly lower than those of the polystyrene and GMA-ST copolymer specimens. This could be explained by the fact that PIWs are less dense than polystyrene and GMA-ST copolymer.

The PIW treated with GMA-ST exhibited an even greater increase in hardness than the PIW treated with ST alone. This is probably due to the formation of cross-linked bonds between the GMA, ST, and the hydroxyl groups of the cell walls.

Note that there was, for the results of mechanical properties of PIWs, a larger percentage of increase in hardness than in bending and compressive strength. This might reasonably be attributed to the greater hardness of polystyrene. This result is consistent with previous published research (Rozman et al. 1998, Devi et al. 2003).

Dynamic mechanical analysis

The storage modulus E' of untreated and treated wood specimens is presented in Figure 1A. We note that as temperature rises, storage modulus decreases in all specimens. This is best explained by the fact that dynamic storage modulus E' is a structure-dependent property. During the DMA tests, as the materials are heated, they expand,and the free volume of the chain segment of the polymer increases, and its ability to move in various directions also increases. As the temperature continues to increase, there is increasing movement in the localized bonds and side chains, leading to a further decrease in storage modulus E' (Becker and Noack 1968, Norimoto and Yamada 1996, Sun et al. 2007).

However, the storage modulus E' of treated wood was significantly higher than the E' values of both the untreated wood and polymer samples, over the whole range of testing temperatures. This should be attributed in large part to the expansion of the infused polystyrene, which compensates for the shrinkage of the wood components. This maintains the integrity of the microstructure in the composites.

Note that the GMA-ST–treated wood showed the highest E' at a temperature range of −150°C to 50°C, which

Table 4.—*Brinell hardness of untreated and treated wood specimens, polystyrene, and glycidyl methacrylate–styrene (GMA-ST) copolymer.*[a]

Specimen	Polymer loading (%)	Density (g/cm^3)	Brinell hardness (MPa)[b]
Untreated wood		0.37 ± 0.05	37 ± 8 C
Polystyrene		1.04 ± 0.02	98 ± 3 AB
GMA-ST copolymer		1.10 ± 0.02	103 ± 2 A
Wood treated with ST	116.7 ± 8.4	0.84 ± 0.04	93 ± 4 AB
Wood treated with GMA-ST	117.6 ± 8.3	0.85 ± 0.07	96 ± 3 AB

[a] Values are means ± standard deviations.
[b] Letters represent homogeneity groups obtained by statistical analysis with different letters reflecting statistical significance at the 95 percent confidence level.
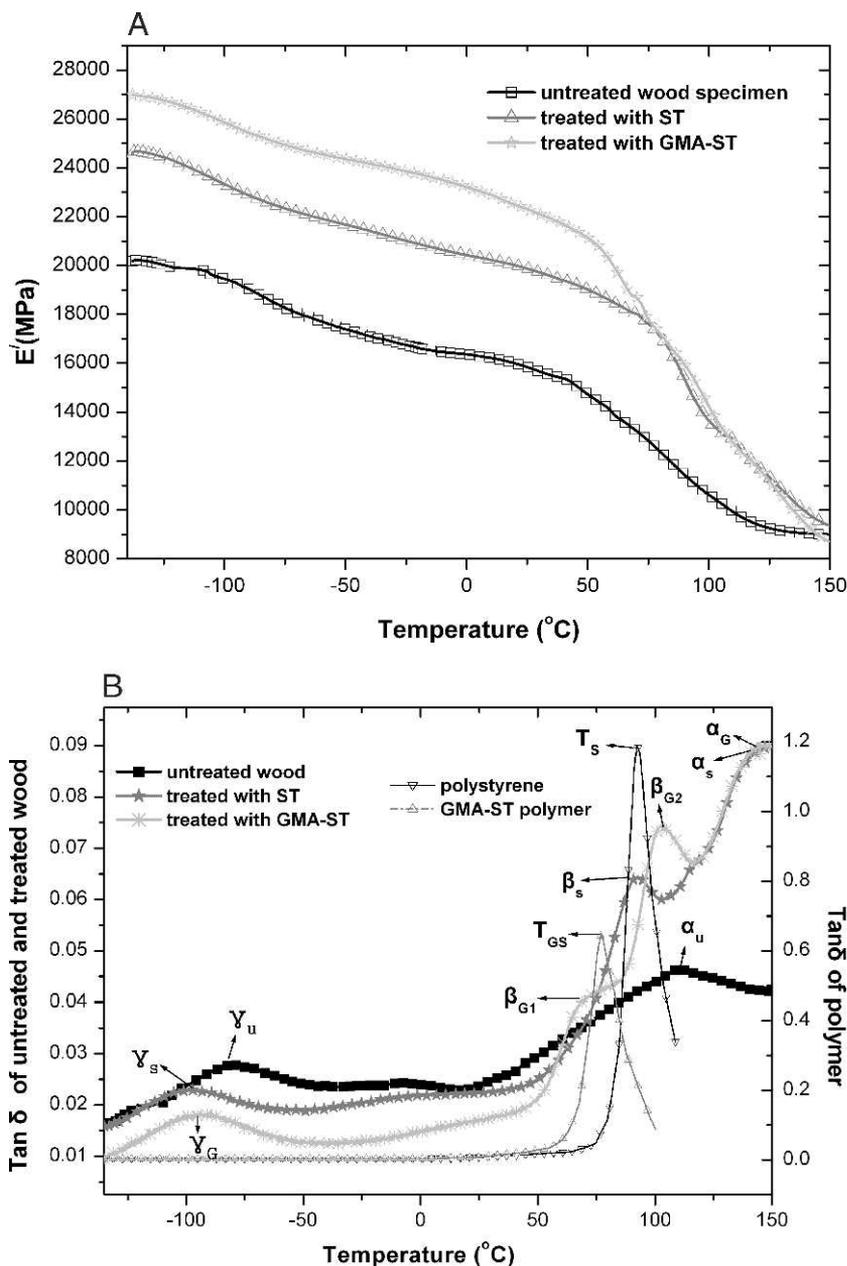
Figure 1.—(A) Storage modulus E' of untreated and treated wood specimens. (B) Damping factor (tan δ) of untreated and treated wood specimens, and glycidyl methacrylate–styrene (GMA-ST) copolymer.

demonstrates that the addition of GMA further enhances the interaction between wood cell and polymers.

Figure 1B shows the relaxation process of treated and untreated wood materials, as measured by the mechanical loss factor (tan δ), across the range of temperatures tested. The tan δ curves of polystyrene and GMA-ST copolymer are displayed as auxiliary references. T_s and T_{GS} mark the glass-transition (T_g) temperatures of the polystyrene and GMA-ST copolymers, respectively.

Note that two relaxation processes can be detected in the tan δ curve of the untreated wood.

- The relaxation process, spiking at around 110°C, labeled α_u, might be attributed to the T_g of wood lignin (Becker and Noack 1968, Norimoto and Yamada 1996). The T_g temperatures of absolutely dry wood, as measured for

cellulose, hemicelluloses, and lignin, occur at 200°C to 250°C, 150°C to 220°C, and 130°C to 205°C, respectively. However, adsorbed water acts as a plasticizer to decrease the T_g value of wood constituents (Back and Salmen 1982).

- The other relaxation peak, spiking at around −79°C (labeled γ_u), is likely due to the motion of the methylol groups with adsorbed water. Obataya et al. (1996, 2001) and Sugiyama et al. (1995, 1998) studied absolutely dry wood and found a peak spiking at around −105°C, which they explain as a result of the movement of methylol side groups. With even a slight bit of moisture (0.7%), another peak appears, at around −40°C. They attribute this to the rotational motion of the adsorbed water. With increasing moisture content, the −40°C peak moves toward lower temperatures, while the peak at −105°C decreases in

height and eventually disappears at about 2 percent moisture content. In the present experiment, although the untreated wood was dried at 105°C for 24 hours, it would absorb a small quantity of moisture when exposed to atmospheric conditions; thus, the peak at −105°C could have shifted to the location at −79°C.

For ST-treated wood, three relaxation processes were observed in the tan δ figures. These peaks are labeled α_s (146°C), β_s (92°C), and γ_s (−100°C), in order of decreasing temperature.

- Because there was no other peak appearance around −40°C, we could speculate that the ST-treated wood was close to absolutely dry, and therefore the peak γ_s might be due to the movement of methylol side groups of wood.
- The β_s peak is likely due to the T_g of the polystyrene that has filled the lumens of the wood cells. The location of β_s matches the T_s peak of pure polystyrene.
- The peak α_s might be caused by the T_g of wood lignin (Back and Salmen 1982). The T_g of lignin could have shifted to a higher temperature, which would mean that the stability of the molecular structure of the wood had been enhanced. This could be attributed to the expansion of polystyrene, which might compensate for the shrinkage of the wood components and maintain the stability of the PIW.

Three peaks and one shoulder were observed for the GMA-ST–treated wood. The peaks are labeled α_G (146°C), β_{G2} (112°C), and γ_G (−100°C); the shoulder is β_{G1} (76°C).

- The γ_G peak might be attributed to the movement of methylol side groups of wood components; nevertheless, it showed lower tan δ value than the γ_s peak. This could be attributed to a reduction in the number of methylol groups caused by the substitution of some of the hydroxyl groups with the glycidyl groups of the GMA (Sugiyama et al. 1998).
- The location of shoulder β_{G1} matches the peak at T_{GS}, for GMA-ST copolymer. This could be due to the T_g of uncombined GMA-ST copolymer, a portion of which did not react with the wood's hydroxyl groups.
- The peak β_{G2}, found at a temperature slightly higher than that of the T_s peak of polystyrene, could perhaps be attributed to the T_g peak of the GMA-ST copolymer; its side chains would have grafted to the wood's hydroxyl groups.
- The α_G peak was seen at the same temperature as the α_s peak. We believe that it can be ascribed to the T_g of wood lignin.

These results indicate that the GMA-ST–treated wood did not exhibit significant improvement in molecular structure stability when compared with the ST-treated wood. Thus, it is not difficult to explain why the tan δ values of the PIWs showed a marked increase at higher temperature ranges. When the temperature is above 50°C, the polymers in the cell lumens and in the cell walls begin to soften and then melt. This phenomenon can explain the sharp decrease in the E' of PIWs at higher temperatures.

Thermal stability analysis

Untreated and treated wood specimens lost mass as temperature increased, as did polystyrene and GMA-ST copolymer. The mass loss curves are shown in Figure 2A.

The major chemical components of wood are cellulose, hemicellulose, lignin, and extractives; these materials degrade at different temperatures.

Cellulose is highly crystalline, which makes it thermally stable. At higher temperature, the decomposition takes place in two competing pathways. The first pathway dominates at temperatures below 300°C. The cellulose undergoes dehydration, rearrangement, formation of carbonyl and carboxyl groups, and formation of char residue. The second pathway involves the end-group depolymerization of cellulose; the primary yield of this process is volatile tarry products (Liu et al. 2004).

Hemicelluloses and lignin, on the other hand, are amorphous rather than crystalline; they start to degrade at lower temperatures. Hemicelluloses, composed primarily of xylans and mannans, are the least thermally stable wood component; this is due to the presence of acetyl groups. The typical products from hemicellulose pyrolysis include methanol, acetic acid, carbon dioxide, carbon monoxide, etc. (Hosoya et al. 2007).

Lignin has a complex three-dimensional polymer structure. Various functions are attached to the aromatic rings, so that the material degrades continuously over a wide temperature range, starting at relatively low temperatures (Shen et al. 2010).

As we see from Figure 2A, the untreated and treated wood specimens showed a small weight loss before 100°C, which can be attributed to the evaporation of water. The weight loss of untreated wood gradually increased above 200°C, and a sharp weight loss appeared between 250°C and 380°C. The PIW displayed a distinct weight loss between 280°C and 440°C. We also see a difference between the results for the ST-treated PIW and the GMA-ST–treated PIW. The latter showed a higher initial degradation temperature, in the region of 300°C.

In sum, the treated wood specimens began to degrade at a higher temperature than did the untreated wood specimens. The polystyrene and GMA-ST copolymer exhibited an acute mass loss at about 400°C, and the degradation temperature of the former was slightly lower than that of the latter.

Besides the untreated and treated wood, the DTG curves of polystyrene and GMA-ST copolymer are also displayed in Figure 2B. The P_s and P_{GS} represented the degradation peaks of polystyrene and GMA-ST copolymer, respectively. Similarly, the DTG peaks in the curves of untreated and treated wood, at temperatures approaching 100°C, were ascribed to the evaporation of water.

In the degradation profile of untreated wood, two shoulders and one peak were observed at around 285°C, 320°C, and 340°C, which were labeled P_h, P_c, and P_l, respectively.

- The relatively broader shoulder P_h may be due mainly to the decomposition of hemicelluloses. Most previous research on hemicellulose pyrolysis (Shebani et al. 2008, Yao et al. 2008, Shen and Gu 2009) has noted a sharp mass loss stage within a narrow range of temperature (from 200°C to 300°C). This mass loss indicates hemicellulose decomposition.
- The P_c peak should perhaps be attributed to the degradation of cellulose. The high DTG value could be explained by the high percentage (40% to 60%) of cellulose in wood components. Other researchers have noted that wood-derived cellulose fiber rapidly decom-
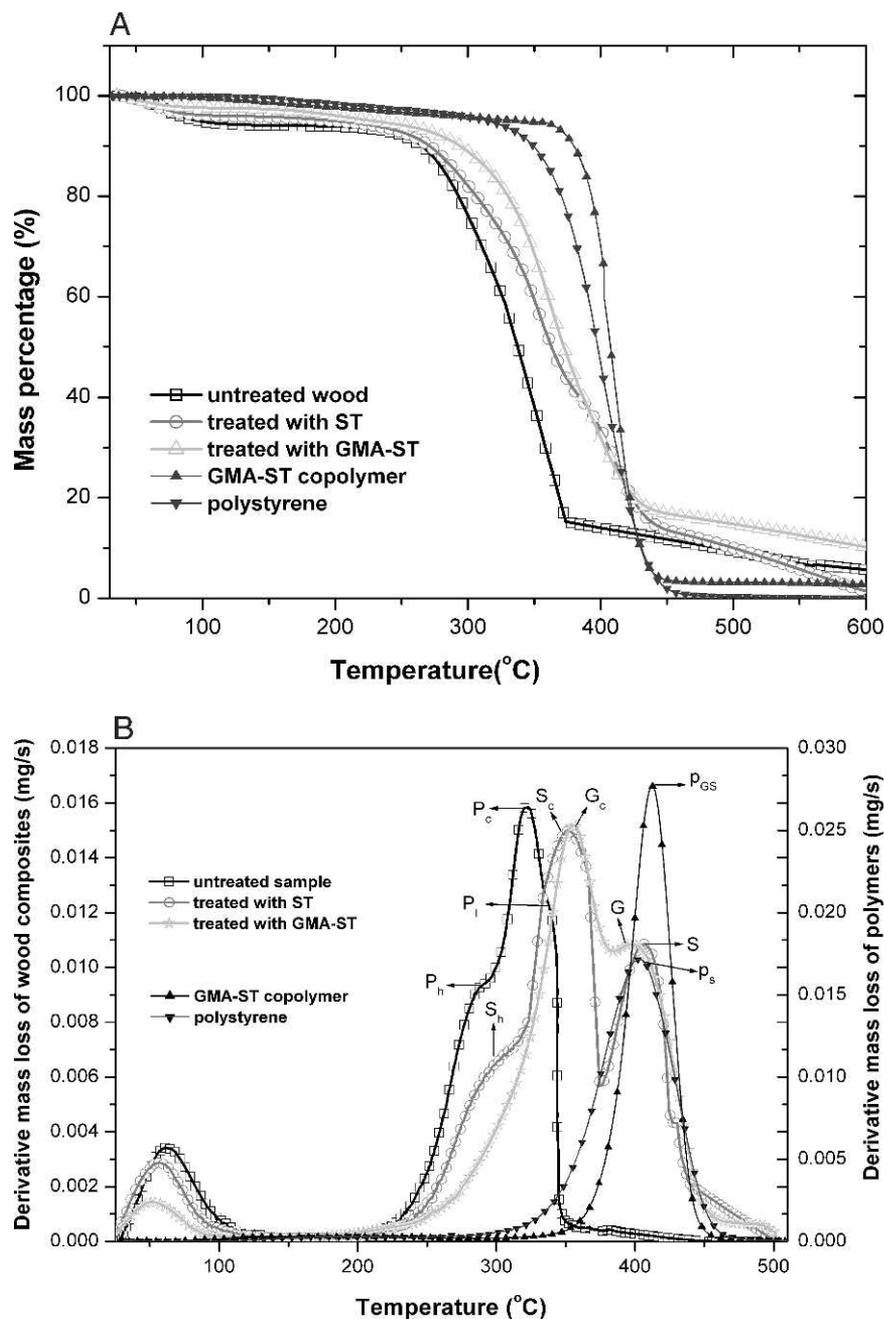
Figure 2.—(A) Thermogravimetric analysis (TGA) curves of untreated and treated wood specimens, polystyrene, and glycidyl methacrylate–styrene (GMA-ST) copolymer. (B) Derivative mass loss (DTG) curves of untreated and treated wood specimens, polystyrene, and GMA-ST copolymer.

poses between 300°C and 350°C (Statheropoulos and Kyriakou 2000, Statheropoulos et al. 2002, Yao et al. 2008).

- The narrower shoulder P_l might be attributed to the decomposition of lignin (Shen and Gu 2009). Thermogravimetric studies show that lignin is the most heat-resistant component of wood (Gardner et al. 1985, Koufopanos et al. 1989).

The ST-treated wood showed one shoulder (close to 310°C) and two peaks (at 350°C and 400°C), labeled S_h, S_c, and S (in order of increasing temperature).

- The shoulder S_h and peak S_c probably represent the decomposition of hemicelluloses (S_h) and celluloses (S_c).
- Peak S occurs at the same temperature as peak T_s in the DTG curve of polystyrene; it is reasonable to conclude that the peak S is due to the decomposition of the polystyrene infusing the wood cells.

The slight shoulder in the curve for untreated wood, close to 300°C (P_l), did not seem to be echoed by the DTG curve of ST-treated wood. This can be explained by the fact that the shoulder was masked by the cellulose main peak due to the relative reduction of wood.

The GMA-ST–treated wood only showed one peak (G_c) and one shoulder (G). Compared with the DTG curve of the ST-treated wood, that for the GMA-ST–treated wood was slightly shifted to a higher temperature range. In addition, the shoulder S_h disappeared and the peak S devolved into a shoulder, G.

The peak G_c might be due to the decomposition of cellulose, in which the shoulder S_h was also masked.

The location of shoulder G matched that of the T_{GS} peak. We might ascribe this finding to the degradation of side chains of GMA-ST copolymer linked to the cell wall's hydroxyl groups. This is another indication of cross-linked bonds.

Table 5 summarizes the degradation temperatures for treated and untreated wood specimens, as well as for polystyrene and GMA-ST copolymer. T_0 is the onset temperature. T_1, T_2, T_3, and T_p were determined by the DTG shoulder or peak where the maximum decomposition rate was observed. T_f is the final decomposition temperature above which the sample does not degrade any further and a mass residue remains.

In sum, compared with the untreated wood, the treated wood showed higher decomposition temperatures during the whole temperature range. The wood treated with GMA-ST displayed slightly higher thermal stability than ST-treated wood, which might be attributed to the greater heat resistance of GMA-ST copolymer and to the formation of cross-linked bonds between the copolymer and the wood's cell walls, which further delayed wood decomposition.

Conclusions

Although fast-growing poplar has a lower density than slow-growing, naturally occurring wood species and is weaker when untreated, this wood exhibits superior performance after treatment.

1. Static mechanical properties in terms of bending strength, compressive strength, and Brinell hardness of PIWs were greatly increased. Moreover, the PIWs treated with GMA-ST were stronger than PIWs merely treated with ST. However, it should be noted that the PIWs were not as hard as the polystyrene and GMA-ST copolymer samples.
2. DMA displayed that storage modulus E' of PIWs was higher than the E' values found in both untreated wood and in the polymer samples; the T_g of wood lignin was also elevated. However, the tan δ of PIWs was higher

than that of untreated wood during higher temperature range, and the PIW treated with GMA-ST did not exhibit higher structure stability than the PIW treated with ST in this higher temperature region.
3. TGA tests demonstrated that thermal stability of PIWs was significantly improved as shown by TG curves and DTG curves, as well as specific degradation temperatures. Compared with the PIW treated with ST, the PIW treated with GMA-ST showed slightly higher thermal stability.

Researchers expect that PIWs prepared from fast-growing poplar materials will cost no more to prepare than other woods; owing to the low cost of the poplar, the resulting PIW should be significantly cheaper. This suggests that the product will easily achieve consumer acceptance.

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Table 5.—Decomposition temperature of the untreated and treated wood specimens, polystyrene, and glycidyl methacrylate–styrene (GMA-ST) copolymer.

Specimen	Temperature (°C)[a]				
	T_0	T_1/T_p	T_2	T_3	T_f
Untreated	235	285	320	334	345
ST treated	245	310	350		475
GMA-ST treated	258		355		484
ST	330	402			457
GMA-ST copolymer	354	413			448

[a] T_0 = initial degradation temperature; T_1, T_2, and T_3 = degradation temperature of hemicelluloses, cellulose, and lignin, respectively; T_p = the decomposition temperature of polymers; T_f = the final degradation temperature.

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