

# Treatment of Fast-Growing Poplar with Monomers Using In Situ Polymerization. Part I: Dimensional Stability and Resistance to Biodegradation

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## Abstract

Fast-growing poplar (*Populus ×euramericana* NL-95) has been extensively cultivated in China. However, because of its poor quality, poplar wood is commonly used only in the manufacture of low-grade wood products. If the wood could be improved by postharvest treatment, it would be more useful and more saleable. Such modification is possible. Our team has developed a protocol to modify fast-growing poplar by impregnating poplar wood with styrene (ST) and glycidyl methacrylate (GMA); this treatment is followed by in situ polymerization by means of thermal treatment. Experimental results show that the treated wood absorbed only one-fifth of the water absorbed by untreated wood when both were submerged in water for 1 week. The treated wood was also two times as dimensionally stable. When treated and untreated wood specimens were exposed to termites and to the fungi that cause dry rot, the treated wood was 9.3 times as resistant to termites and 3.8 times as resistant to fungi. Specimens of treated wood were examined using Fourier transform infrared spectroscopy, which showed that a grafting reaction and copolymerization had occurred, bonding the hydroxyl groups of the wood cell walls to the GMA and ST. Scanning electron microscope observation of the treated wood showed that the cell lumens had been filled with polymers and that the interfaces between wood cell walls and polymer were hard to distinguish.

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Human population growth and increasing industrialization have led to the destruction of much of the world's natural forest resources. The former forest lands are sometimes replanted with fast-growing trees. Wood from these fast-growing trees is inferior in many respects to slow-growth wood species, i.e., xylem is less dense and wood fibers are shorter, there are more juvenile and gelatinous fibers, and there is more growth stress (Nemeth et al. 2006, Begum et al. 2008). Such weaknesses have limited the use of wood from fast-growing species to applications that do not require strong timber.

One such species, fast-growing poplar (*Populus ×euramericana* NL-95), has been extensively cultivated in China. Poplar plantations now cover more than 14 million hectares (Hua and Jin 2008). This poplar wood is mainly used as raw material for the charcoal or pulp industries. Its economic value is low, compared with that of wood from slow-growing trees.

Any process that could improve wood quality would increase the economic yield of the poplar plantations and also reduce the pressure on natural forest resources.

In the past few decades, techniques that turn low-quality solid wood into stronger, more durable polymer-infused wood (PIW) have been increasingly used. One widespread commercial process consists of impregnating wood with vinyl monomers or polymeric resins and applying radiation

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or thermal treatment to catalyze in situ polymerization (Chao and Lee 2003, Asghar and John 2004, Gao and Dong 2007).

We have explored various treatment methods to determine which processes and materials produce the best PIWs.

Meyer (1981) and Rowell (1991) tested wood treated with styrene (ST), a vinyl monomer, and report that the ST significantly improves the hardness and bending strength of aspen (*Populus*) and birch (*Betula*). Fruno and Gato (1978) and Rozman et al. (1998) note that ST-treated, polymer-infused rubberwood (*Hevea brasiliensis*) shows greater mechanical strength and increased resistance to fungal biodegradation. However, they add that these wood products do not show significant improvement in dimensional stability. They surmise that this could be due to the fact that wood substrates contain few functional groups that will readily react with vinyl groups. This restricts polymerization with ST mainly to the lumens of the wood cells, leaving most of the cell walls untouched (Zhang et al. 2006).

The process can be improved if coupling agents are used. These agents are substances used in small quantities to obtain an interfacial bond between wood and polymers. The coupling agent glycidyl methacrylate (GMA) is widely used in traditional wood-plastic composites because its glycidyl group reacts with the wood's hydroxyl groups, while its terminal double bond copolymerizes with vinyl monomers (Devi et al. 2003). Rozman et al. (1997) used GMA and diallyl phthalate on rubberwood and noted increased dimensional stability, which they attributed to improved cross-linking between the wood and the vinyl. Recent studies show that the use of GMA when treating Scots pine (*Pinus sylvestris*) and sugar maple (*Acer saccharum*) promotes resistance to mold, fungi, marine wood borers, and insects (Takahashi 1996, Forster et al. 1997, Militz et al. 1997).

However, there has been a small amount of published research on the in situ polymerization, using GMA and ST, of fast-growing poplar. Such research would be of extreme economic benefit to the wood industry, while also advancing our knowledge of wood polymerization processes. The present study presents the results of one such research program, in which some poplar specimens were impregnated with ST and some with a combination of GMA and ST (GMA-ST); they were then subjected to in situ polymerization by means of thermal treatment. The treatment resulted in a PIW with increased resistance to water absorption, greater dimensional stability, and improved resistance to termites and the fungi that cause dry rot. Treated and untreated wood specimens were tested to measure the extent of the improvements. The microstructures of the fast-growing poplar PIW were also investigated.

## Experimental Procedures

### Preparation of experimental materials

Our study used fast-growing poplar (*Populus × euramericana* NL-95) wood from a 15-year-old plantation located in the county of Siyang, Jiangsu, People's Republic of China. Before the tests, the lumber was stored for 6 months in a room kept at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and  $65 \pm 3$  percent relative humidity (RH). After storage the wood had a density of  $0.38 \pm 0.05$  g/cm<sup>3</sup> and 12 percent moisture content. Cylindrical wood specimens were prepared from clear, defect-free wood.

- Specimens to be tested for water absorption and dimensional stability were cut to the following dimensions: 25 (L) by 10 (T) by 25 (R) mm, where R, T, L represent the radial, tangential, and longitudinal measurements of the specimens.
- Specimens to be tested for resistance to decay were cut to the following dimensions: 10 (L) by 20 (T) by 20 (R) mm.
- Specimens to be tested for termite resistance were cut to the following dimensions: 6.4 (L) by 25 (T) by 25 (R) mm.
- Specimens to be investigated by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were cut to the following dimensions: 15 (L) by 20 (T) by 20 (R) mm.

Analytical grade GMA, purchased from Sansyo Co., Ltd. (Japan), was purified by a course of reduced pressure distillation at  $100^{\circ}\text{C}$  to  $105^{\circ}\text{C}$  and 1.1 to 1.6 KPa. Analytical grade ST, purchased from Sansyo Co., Ltd., was cleaned using sodium hydroxide and distilled water dried with anhydrous CaCl<sub>2</sub> for 12 hours and was subjected to reduced pressure distillation at  $50^{\circ}\text{C}$  to  $60^{\circ}\text{C}$  and 1.1 to 1.6 KPa. An initiator, 2,2'-azobis-2-(methylbutyronitrile) (AIBN), was also supplied by Sansyo.

### Preparation of the impregnation solutions

Two solutions were prepared: ST monomer and a combined solution of GMA-ST at a 1:4 molar ratio; AIBN was added into both solutions as an initiator at a percentage of 1.0 by weight.

### Impregnation procedure and polymerization method

The specimens were oven dried at  $103^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 24 hours. We measured and recorded specimen dimensions and weights after drying and before impregnation. Specimens to be treated were then placed in an airtight impregnation case in such a manner that they were not in contact with each other and solution could flow freely around the exposed surfaces. They were covered with a weight so that they would not float. A vacuum of 0.05 MPa was applied for 15 minutes, removing air from the pores of the specimens. The selected chemical agent was introduced into the case, immersing the specimens. Compressed air was pumped into the system at a pressure of 0.1 MPa for 30 minutes. The pressure was then released, and the specimens were immersed under ambient pressure.

The impregnation time was 4 hours for the ST solution. Preliminary experiments had established that this time period gave the largest impregnation loading. In order to obtain the same polymer loading in the GMA-ST-treated specimens, the impregnation time was decreased to 3 hours. The time chosen was based on the different densities of the two monomers (ST at 0.9059 g/mL and GMA at 1.073 g/mL) as well as the different conversion rates of ST and GMA (ST, 47%; GMA, 85%).

After impregnation, the specimens were taken out of the case and excess chemicals were wiped from their surfaces. Treated specimens were wrapped in aluminum foil and cured at  $103^{\circ}\text{C} \pm 2^{\circ}\text{C}$  for 24 hours in an oven. The foil was removed, and sandpaper was used to remove excess polymer from the surface of the wood. The new weights and dimensions of the PIWs were recorded.

The polymer loading ( $W_p$ ) was calculated according to the following equation:

$$W_p = (W_f - W_d)/W_d \quad (1)$$

where  $W_f$  is the weight of the wood specimen after the final treatment and  $W_d$  is the weight of the dry wood specimen before any treatment. The polymer loadings of PIW specimens treated with ST and GMA-ST were  $116.5 \pm 10.6$  percent and  $118.4 \pm 8.4$  percent, respectively, and their average densities were  $0.83 \pm 0.41$  and  $0.84 \pm 0.35$  g/cm<sup>3</sup>, respectively.

### Water absorption and dimensional stability measurements

The untreated and treated specimens were marked on the length, width, and thickness directions. Specimens were secured in a plastic frame, to prevent them from floating, and immersed in a water-filled tray at  $25^\circ\text{C} \pm 2^\circ\text{C}$  for up to 168 hours. Measurements were taken at 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 hours. Weights of the specimens were recorded, and dimensions of the specimens were measured at marked positions, after excess water had been wiped off. These records were used to calculate water absorption (using changes in weight) and dimensional stability (using changes in volume).

Water-repelling efficiency (WRE), or resistance to water absorption, was defined as

$$\text{WRE} (\%) = (A_c - A_{\text{PIW}})/A_c \times 100 \quad (2)$$

where  $A$  is the water absorption of a specimen, and subscripts  $c$  and PIW are the untreated and treated wood specimens, respectively.  $A$  was expressed as

$$A (\text{wt}\%) = (w_{\text{soak}} - w_0)/w_0 \times 100 \quad (3)$$

where  $w_0$  is the initial weight of the oven-dried specimen and  $w_{\text{soak}}$  is the weight after immersion in water for 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 hours.

The swelling coefficient ( $S$ ), or measure of dimensional stability, was calculated as

$$S (\%) = (\alpha_{\text{soak}} - \alpha_0)/\alpha_0 \times 100 \quad (4)$$

where  $\alpha$  is the specimen volume,  $\alpha_{\text{soak}}$  is the specimen volume after soaking for 0.5, 2, 6, 24, 48, 96, 120, 144, and 168 hours, and  $\alpha_0$  is the volume of the oven-dried specimen.

Antiswelling efficiency (ASE) was calculated as

$$\text{ASE} (\%) = (S_{\alpha-c} - S_{\alpha-\text{PIW}})/S_{\alpha-c} \times 100 \quad (5)$$

where  $S_{\alpha-c}$  is the swelling coefficient for the untreated specimen and  $S_{\alpha-\text{PIW}}$  is the swelling coefficient for the PIW specimen.

### Testing for resistance to termites

The untreated and treated wood specimens were exposed to subterranean termites (*Coptotermes formosanus*) using a test protocol approved by the Japan Wood Preserving Association (Tsunoda and Nishimoto 1986, Tsunoda 1991). Each specimen was placed at the center of the plaster bottom of a cylindrical test container (80-mm diameter). The assembled containers were set on damp cotton pads; moisture could filter through the plaster, keeping the specimens at an RH equal to  $80 \pm 3$  percent. Containers were stored at normal environmental temperature ( $25^\circ\text{C} \pm$

$2^\circ\text{C}$ ). The termite test containers were examined at the same time daily, and the dead termites were removed and tallied. The numbers of living termites in each container were counted after 3 weeks of exposure. At the end of the test period the wood specimens were washed, dried at  $60^\circ\text{C} \pm 2^\circ\text{C}$  for 48 hours, and weighed. The loss of mass from the specimens was then calculated.

### Testing for resistance to decay

A monoculture decay-resistance test was conducted according to Japanese Industrial Standard A-9201 (JIS 1991), using the dry rot fungus *Fomitopsis palustris*. Ten specimens were weighed and sterilized with gaseous ethylene. Specimens were placed in a glass jar that contained a medium of 250 g of quartz sand and 80 mL of nutrient solution and inoculated with liquid fungal cultures. The jars were then incubated at  $25^\circ\text{C} \pm 2^\circ\text{C}$  and  $70 \pm 4$  percent RH for 12 weeks. Wood specimens were then taken out and weighed. Any weight loss in the specimens was construed as evidence of the extent to which the wood had been degraded by fungal attack.

### Analysis using FTIR

FTIR spectroscopy was used to analyze the characteristic groups of PIWs. Untreated and treated specimens were prepared for spectroscopy by cutting them into small pieces with a razor blade and grinding them in a ball mill to a fine powder (median particle size, 100  $\mu\text{m}$ ; particles were filtered through a 400-mesh filter). The wood and PIW powders were pelletized with KBr powder in 1:300 ratios (milligrams per milligram). Pellets were scanned at a range of 500/cm to 4,000/cm; synthesized manganese oxide specimens were recorded using a Nicolet Impact 410 spectrophotometer.

### Analysis using an SEM

An SEM (an FEI Quanta 200 SEM manufactured in Holland) was used to examine the microstructure of the untreated and treated wood specimens. Thin cross sections (about 75- $\mu\text{m}$  thick) were cut from the specimens with a microtome. Edges were trimmed so that the final dimension was approximately 1 by 1 mm. The sections were coated with a carbon and gold sputter and examined at  $\times 400$  and  $\times 2,000$  magnifications.

## Results and Discussion

### Water absorption and dimensional stability

The water absorption ( $A$ ) of untreated and treated wood specimens, as measured after various immersion times, is shown in Figure 1. Note that the untreated wood absorbed water very rapidly during the first 48 hours of immersion. Water absorption leveled off after the rapid initial gain.

ST-treated PIW showed an  $A$  of 40 percent after a week (168 h) of immersion. The untreated wood, in contrast, had an  $A$  of 150 percent. The  $A$  of the ST-treated PIW was close to one-fourth of that of untreated wood. It seems likely that is because the polymer had filled many of the wood cell lumens and wood pores, which prevented water entry (Rowell 1991, Fuller et al. 1997).

The GMA-ST-treated PIW exhibited even lower water absorption (an  $A$  of 30%) than the ST-treated PIW. Its  $A$  was only one-fifth of that of untreated wood. Its superior performance can perhaps be attributed to a grafting reaction

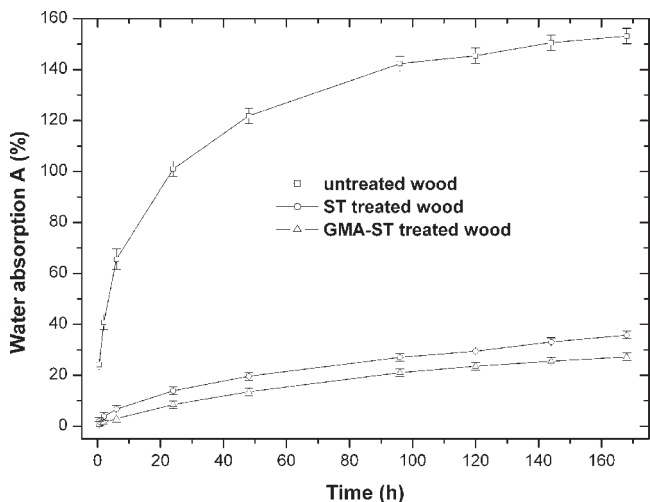
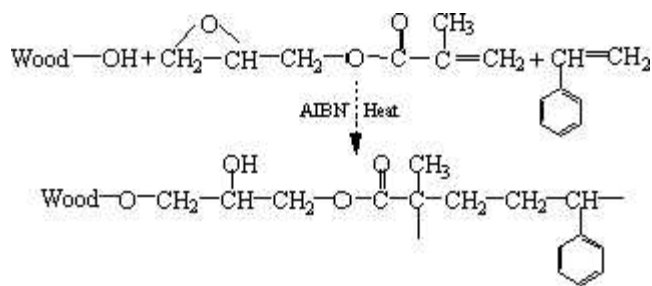


Figure 1.—Water absorption A (percent) of untreated and treated specimens over time. ST = styrene; GMA = glycidyl methacrylate.

between the GMA and the wood's cell walls. The polymer may have strengthened the cell walls and further restrained water penetration (Devi et al. 2003, Devi and Maji 2006). The probable reaction between wood cell walls, ST, and GMA is shown in Scheme 1.

Table 1 shows the WRE of PIW specimens immersed in water for various lengths of time. It was noted that the observed values were higher than those reported in prior research (Mathias et al. 1991, Devi and Maji 2006, Zhang et al. 2006). Those studies (of sugar maple and pine infused with monomers alone, or monomers and coupling agents) found WRE values that varied from 40 to 60 percent. In the present study, values varied from approximately 76 to 97 percent. Perhaps the higher WRE values for fast-growing hybrid poplar might be attributed to its lower xylem density, which allowed the monomers to more easily fill voids and penetrate cell walls. Hybrid poplar wood also has large pores, which may have filled with polymer and retarded water absorption.

The swelling coefficients,  $S$ , of untreated and treated wood specimens immersed in water for different impregnating periods are shown in Figure 2. Both kinds of PIWs show a lower  $S$  than that of untreated wood. The final  $S$  for untreated wood was approximately 15 percent, ST-treated PIW had a final  $S$  of approximately 11.5 percent, and GMA-ST-treated PIW was lowest at approximately 7 percent. GMA-ST-treated PIW was twice as resistant to swelling as untreated wood.



Scheme 1.—Grafting reaction and copolymerization between wood hydroxyl groups, glycidyl methacrylate, and styrene.

Table 1.—Water-repelling efficiency (WRE) of polymer-infused woods (PIWs) over time.

Impregnation time (h)	%WRE $\pm$ SD <sup>a</sup>	
	ST-treated PIW <sup>b</sup>	GMA-ST-treated PIW <sup>c</sup>
0.5	91.9 $\pm$ 2.1	97.2 $\pm$ 1.8
2	90.82 $\pm$ 1.5	96.4 $\pm$ 1.1
6	89.8 $\pm$ 2.1	95.4 $\pm$ 1.5
24	86.2 $\pm$ 1.1	91.6 $\pm$ 1.7
48	83.9 $\pm$ 1.1	88.9 $\pm$ 1.6
96	81.0 $\pm$ 1.2	85.2 $\pm$ 1.2
120	79.7 $\pm$ 1.1	83.8 $\pm$ 1.1
144	78.0 $\pm$ 1.3	83.1 $\pm$ 0.9
168	76.6 $\pm$ 1.5	82.2 $\pm$ 0.8

<sup>a</sup> SD = standard deviation; ST = styrene; GMA = glycidyl methacrylate.

<sup>b</sup> Polymer loading, 116.5  $\pm$  10.3.

<sup>c</sup> Polymer loading, 118.4  $\pm$  8.4.

The dimensional instability of the untreated wood is best ascribed to the presence of numerous hydroxyl groups in wood cells as well as to cell cavities (lumens). The hydroxyl groups are believed to be reactive sites; the cell cavities are major paths for moisture movement in wood (Zhang et al. 2005, 2006). It seems reasonable to attribute the low  $S$  of GMA-ST-treated PIW to the grafting reaction between the GMA and the hydroxyl groups (which reduced reactive sites) and the filling of cell cavities with polymer (which blocked moisture movement).

The ASE values of PIWs are shown in Table 2. Higher ASE values for PIWs are further evidence of significant improvement in dimensional stability.

### Termite resistance

Mass loss from termite feeding on untreated and treated wood specimens is shown in Figure 3. Visual proof of the differences in susceptibility to termites is shown in Figure 4.

The untreated wood was severely attacked by termites; it showed the largest mass loss, at approximately 25 percent. The mass losses of ST-treated and GMA-ST-treated PIWs were 4.6 and 2.7 percent, respectively. The PIWs exhibited strong resistance to termite feeding.

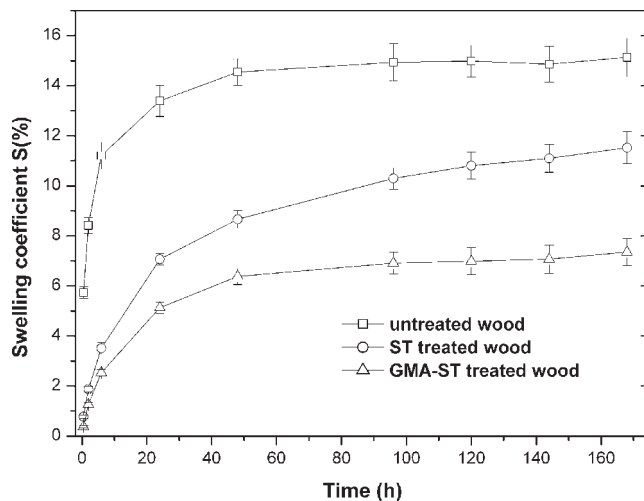


Figure 2.—Swelling coefficient  $S$  (percent) of untreated and treated specimens immersed in water over time. ST = styrene; GMA = glycidyl methacrylate.

Table 2.—Anti-swelling efficiency (ASE) of polymer-infused woods (PIWs) over time.

Impregnation time (h)	%ASE $\pm$ SD <sup>a</sup>	
	ST-treated PIW <sup>b</sup>	GMA-ST-treated PIW <sup>c</sup>
0.5	88.4 $\pm$ 1.8	93.4 $\pm$ 4.5
2	88.4 $\pm$ 1.8	84.5 $\pm$ 2.9
6	68.6 $\pm$ 2.8	77.4 $\pm$ 2.1
24	47.2 $\pm$ 3.1	61.2 $\pm$ 2.8
48	40.4 $\pm$ 3.1	56.2 $\pm$ 4.8
96	31.0 $\pm$ 4.6	53.1 $\pm$ 3.2
120	27.8 $\pm$ 3.7	53.7 $\pm$ 2.4
144	25.3 $\pm$ 2.4	52.7 $\pm$ 3.1
168	23.9 $\pm$ 3.1	51.2 $\pm$ 2.6

<sup>a</sup> SD = standard deviation; ST = styrene; GMA = glycidyl methacrylate.

<sup>b</sup> Polymer loading, 116.5  $\pm$  10.3.

<sup>c</sup> Polymer loading, 118.4  $\pm$  8.4.

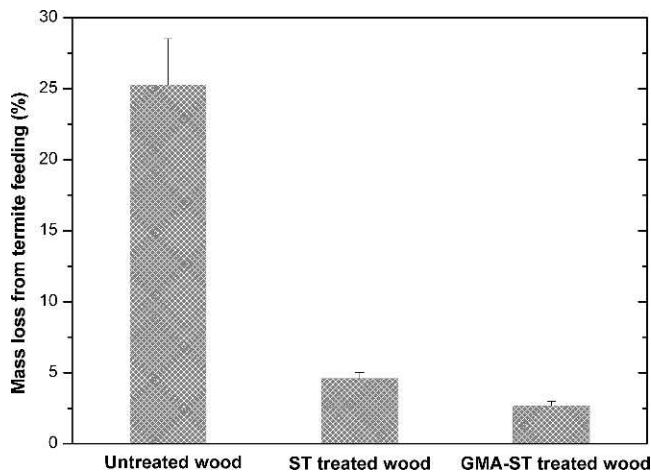


Figure 3.—Mass loss (percent) from termite feeding on untreated and treated specimens. ST = styrene; GMA = glycidyl methacrylate.

Figures 4A through 4C show untreated wood and treated wood specimens after being subjected to termite feeding. Note the large, deep grooves on the surface of the untreated specimen, evidence of termite attack. There are a few small, shallow grooves on the surface of the ST-treated PIW. There are even fewer grooves on the surface of the GMA-ST-treated PIW. This is persuasive visual confirmation of the efficacy of polymer infusion in promoting termite resistance.

Two explanations have been advanced for this resistance. Stamm (1964) and Akio et al. (1990) have suggested that polymer impregnation filled voids and prevented water absorption; termites do not thrive in the absence of moisture. Kartal et al. (2004) suggested that the polymers are slow-acting toxicants that can kill termites after being ingested as food.

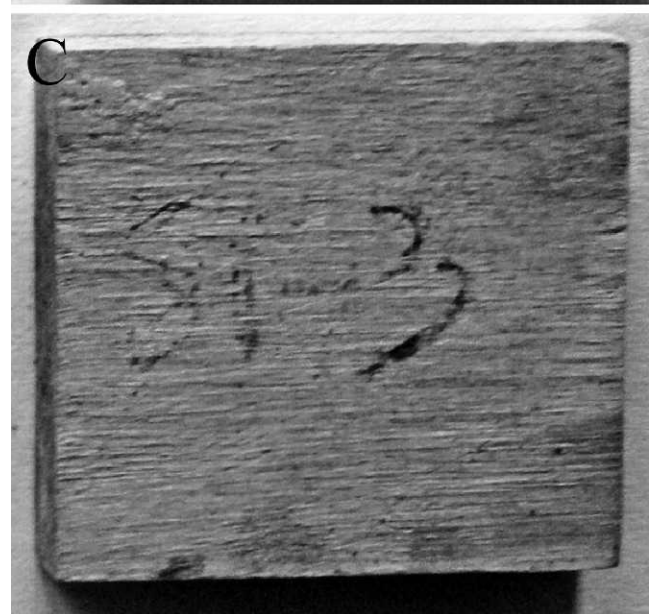
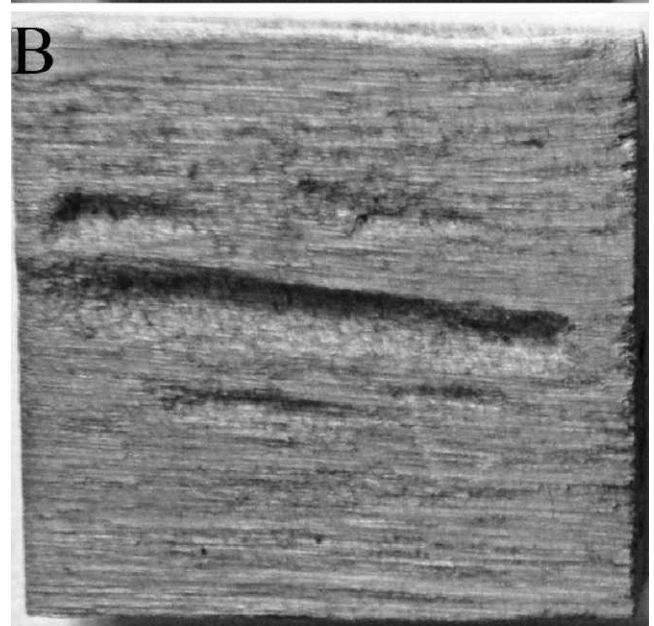
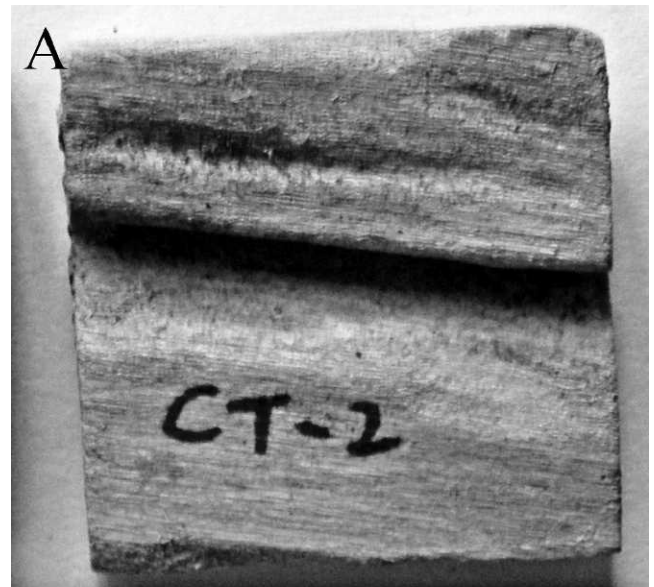


Figure 4.—Untreated and treated specimens after termite feeding: (A) untreated specimen; (B) ST-treated PIW; (C) GMA-ST-treated PIW. ST = styrene; PIW = polymer-infused wood; GMA = glycidyl methacrylate.

## Resistance to fungus

PIWs were also tested for resistance to dry rot (also known as brown rot) caused by the fungus *Fomitopsis palustris*. The results are shown in Figure 5.

Of the three kinds of specimens exposed to the fungus, the two kinds of PIW were clearly the most resistant to decay. The untreated wood showed a mass loss of approximately 29.8 percent, ST-treated wood showed a loss of approximately 14.2 percent, and the GMA-ST-treated wood lost only about 7.9 percent.

The enhanced decay resistance of PIWs might be attributed to the efficiency of polymerization in excluding moisture and inhibiting mycelia spread (Yalinkilic et al. 1998, 1999). The GMA-ST-treated PIW may have shown greater decay resistance than ST-treated PIW because the grafting reaction between the hydroxyl groups of the wood's cell walls and the glycidyl groups of GMA made the cell walls even stronger, further discouraging moisture and mycelia spread.

## FTIR study

The FTIR spectra of untreated and treated wood specimens are presented in Figure 6. Characteristic groups of ST and GMA-ST PIWs and their corresponding absorption frequencies are shown in Table 3.

Martínez-Pardo et al. (1998) and Bodírlău et al. (2009) characterized the peak at 3,404/cm, located on the curve of the GMA-ST-treated PIW, as a result of the stretching vibration of hydroxyl groups. This peak is weaker than those of the ST-treated and untreated wood specimens; it also shifted toward lower wave numbers as the intensity decreased.

According to the reaction principle shown in Scheme 1, we could reasonably assume that the decrease in hydroxyl groups was due to the nucleophilic substitution reaction of some cell-wall hydroxyl groups with GMA. The grafting of the polymers on the wood cell walls resulted in a decrease in the hydroxyl numbers in the GMA-ST-treated PIW. The corresponding shift to lower wave numbers was probably due to the transfer of some of the hydroxyl groups from cell walls to polymer chains.

At the same time, the curve of GMA-ST-treated PIW in Figure 6 shows a slightly enhanced peak for the aromatic

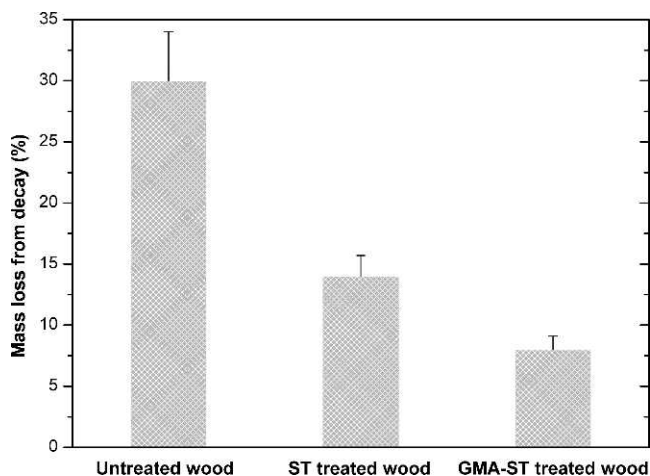


Figure 5.—Mass loss (percent) from decay of untreated and treated specimens. ST = styrene; GMA = glycidyl methacrylate.

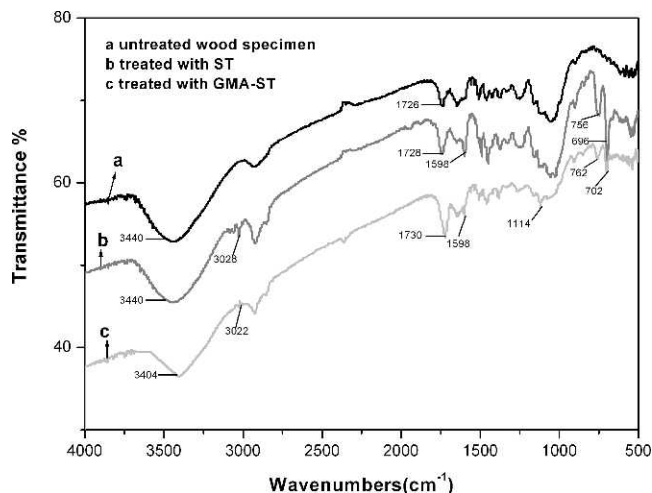


Figure 6.—Fourier transform infrared spectroscopy of untreated and treated specimens. ST = styrene; GMA = glycidyl methacrylate.

skeletal vibrations observed at 1,598/cm, a small peak for Ar-H stretching vibrations ( $\nu_{\text{Ar-H}}$ ) at 3,022/cm, and two increased peaks for single and substituted Ar-H out-of-plane bending-wagging ( $\delta_{\text{Ar-H}}$ ) at 762/cm and 702/cm (Martínez-Pardo et al. 1998, Rutkowski 2009).

All of these observations of the FTIR spectra for GMA-ST-treated PIW suggest that the polymers grafted to the wood cell walls contained some phenyl groups, which resulted from the copolymerization of ST with GMA by means of their double bonds. However, the content of phenyl groups in the polymer seems to be quite low compared with that of the ST-treated PIW.

In addition, a slightly enhanced peak at 1,114/cm for C-O-C asymmetrical stretching vibrations may be evidence for a reaction of wood hydroxyl groups with GMA, resulting in polyether (Zhou et al. 2008, Sailaja and Seetharamu 2009).

## Microstructure of untreated and treated wood characterized with SEM

SEM micrographs of untreated and treated wood specimens are shown in Figure 7. Figure 7A shows a cross section of the vessels and lumens of untreated wood at  $\times 400$  magnification. Figure 7B is of ST-treated PIW at  $\times 2,000$

Table 3.—Characteristic groups of polymer-infused woods (PIWs) and their corresponding absorption frequencies.

Main characteristic group	Wave no. (cm <sup>-1</sup> ) <sup>a</sup>	
	ST-treated PIW	GMA-ST-treated PIW
O-H stretching vibration ( $\nu_{\text{O-H}}$ )	3,440	3,404
Ar-H stretching vibration ( $\nu_{\text{Ar-H}}$ )	3,028	3,022
CH <sub>2</sub> asymmetrical stretching vibration ( $\nu_{\text{asC-H}}$ )	2,919	2,931
C=O stretching vibration		1,732
Phenyl skeletal vibration	1,598	1,598
C-O-C asymmetrical stretching vibration		1,132
Single and substitution Ar-H out-of-plane bending-wagging ( $\delta_{\text{Ar-H}}$ )	696	762, 702

<sup>a</sup> ST = styrene; GMA = glycidyl methacrylate.

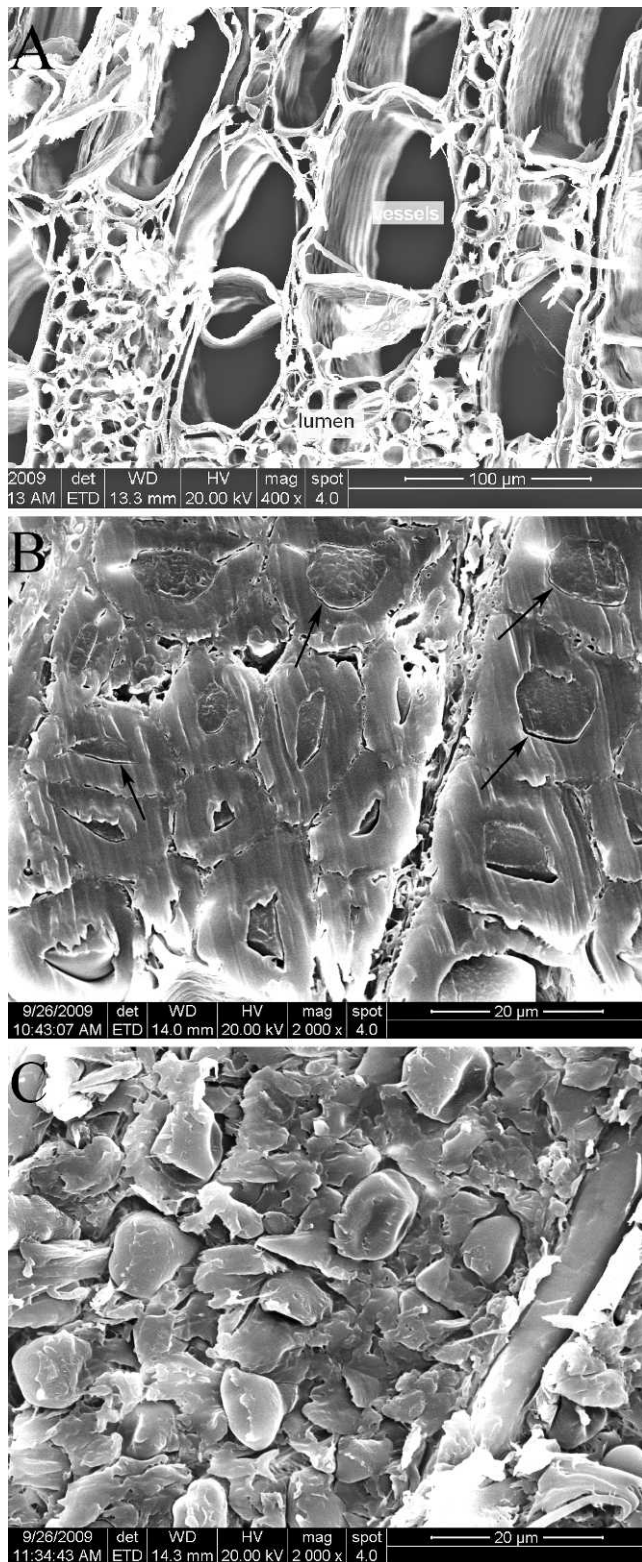


Figure 7.—Scanning electron micrographs of cross sections of untreated and treated wood: (A) untreated; (B) ST-treated PIW; (C) GMA-ST-treated PIW. ST = styrene; PIW = polymer-infused wood; GMA = glycidyl methacrylate.

magnification; Figure 7C is of GMA-ST-treated PIW at  $\times 2,000$  magnification. It is easy to see that in Figures 7B and 7C, the wood cell lumens have been filled with polymer by the impregnation treatments.

Note that in the ST-treated PIW, the polymer did not seem to form an intimate contact with the cell walls. There are obvious gaps between the solid polymer and the cell walls. Clearly, the ST did not form a strong bond with the cell walls during polymerization. Just as clearly, the GMA-ST did. Figure 7C displays no obvious gaps between the polymer and the cell walls. This suggests that there were strong interactions between the polymers and wood cell walls during impregnation, interactions that could have been physical, or chemical, or a combination of both.

## Conclusions

The results from this study suggest that fast-growing poplar PIWs show great improvements over untreated wood. They exhibit

1. greater resistance to water absorption (3.7 times greater than untreated wood for ST-treated PIW, 5 times for GMA-ST-treated PIW),
2. greater dimensional stability (1.3 times greater than untreated wood for ST-treated PIW, 2.1 times for GMA-ST-treated PIW),
3. greater resistance to termites (5.4 times greater than untreated wood for ST-treated PIW, 9.3 times for GMA-ST-treated PIW), and
4. greater resistance to dry rot caused by fungus (2.1 times greater than untreated wood for ST-treated PIW, 3.8 times for GMA-ST-treated PIW).

Our analysis of the FTIR spectroscopy results suggests that these improvements were in large part due to the filling of cell lumens with polymer, as well as to grafting reactions and copolymerization between cell-wall hydroxyl groups and GMA-ST. SEM observations also showed that the in situ treatment had filled the cell lumens with polystyrene or GMA-ST copolymer; in addition, in view of the GMA-ST-treated PIW, the interfaces between wood cell walls and polymers were difficult to distinguish, again suggesting grafting reactions and copolymerization between cell-wall hydroxyl groups and GMA-ST.

In the second part of this article, we will present the results of studies on the static and dynamic mechanical properties, as well as the thermal stability, of hybrid poplar PIWs. Those results merely add to the list of performance improvements due to in situ polymerization.

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## Literature Cited

- Akio, E., T. Hiromi, Y. Sachiko, and F. Goro. 1990. Fungal and termite resistance of etherified wood and its dimensional stability. *Mem. Fac. Agric. Kinki Univ. (Kinki Daigaku Nogakubu Kiyo)* 23(1):25–32.
- Asghar, O. and R. John. 2004. The influence of low styrene content on the decay resistance of an aspen. *Forest Prod. J.* 10(1):54–57.
- Begum, S., S. Nakaba, V. Bayramzadeh, Y. Oribe, T. Kubo, and R. Funada. 2008. Temperature responses of cambial reactivation and xylem differentiation in hybrid poplar under natural conditions. *Tree Physiol.* 28(12):1813–1819.
- Bodîrlău, R., C. A. Teaca, and I. Spiridon. 2009. Preparation and characterization of composites comprising modified hardwood and wood polymers/poly(vinylchloride). *BioResources* 4(4):1285–1304.

- Chao, W. Y. and A. W. C. Lee. 2003. Properties of southern pine wood impregnated with styrene. *Holzforschung* 57(3):333–336.
- Devi, R. R., I. Ali, and T. K. Maji. 2003. Chemical modification of rubber wood with styrene in combination with a crosslinker: Effect on dimensional stability and strength property. *Bioresour. Technol.* 88(3): 185–188.
- Devi, R. R. and T. K. Maji. 2006. Effect of chemical modification with styrene and glycidyl methacrylate on the properties of pinewood. *Indian J. Eng. Mater. Sci.* 13(2):149–154.
- Forster, S. C., M. D. Hale, and W. G. Williams. 1997. Efficacy of anhydrides as wood protecting chemicals. Document No. IRG/WP97-30162. International Research Group on Wood Preservation, Stockholm.
- Fruno, T. and T. Gato. 1978. Structure of interface between wood and synthetic polymer (XI). The role of polymer in the cell wall on the dimensional stability of wood polymer composite. *J. Jpn. Wood Res. Soc. (Mokuzai Gakkaishi)* 24(5):287–293.
- Fuller, B. S., W. D. Ellis, and R. M. Rowell. 1997. Hardened and fire retardant wood products. US patent 5605767; filed February 2, 1996, issued February 25, 1997.
- Gao, Z. H. and L. Dong. 2007. Chemical modification of poplar wood with foaming polyurethane resins. *J. Appl. Polym. Sci.* 104(5): 2980–2985.
- Hua, Y. K. and J. W. Jin. 2008. Products and manufacturing processes of poplar plywood. Presented at the 23rd Session of the International Poplar Commission and 44th Session of its Executive Committee, October 26–30, 2008, Beijing.
- Japanese Industrial Standards (JIS). 1991. Qualitative standards and testing methods of wood preservatives. JIS A 9201. Japanese Standards Association, Tokyo.
- Kartal, S. N., T. Yoshimura, and Y. Imamura. 2004. Decay and termite resistance of boron-treated and chemically modified wood by *in situ* co-polymerization of allyl glycidyl ether (AGE) with methyl methacrylate (MMA). *Int. Biodeterior. Biodegrad.* 53(2):111–117.
- Martinez-Pardo, M. E., J. Cardoso, and H. Vazquez. 1998. Characterization of MeV proton irradiated PS and LDPE thin films. *Nucl. Instrum. Methods B* 140:325–340.
- Mathias, L. J., S. Lee, J. R. Wright, and S. C. Warren. 1991. Improvement of wood properties by impregnation with multifunctional monomers. *J. Appl. Polym. Sci.* 42:55–67.
- Meyer, J. A. 1981. Wood polymer materials: State of the art forest products. *Wood Sci.* 14(2):49–54.
- Militz, H., E. P. J. Beekers, and W. J. Homan. 1997. Modification of solid wood: Research and practical potential. Document No. IRG/WP 97-40098. International Research Group on Wood Preservation, Stockholm.
- Nemeth, R., S. Molnar, J. Abraham, S. Koman, and L. Denes. 2006. Wood anatomy and mechanical characteristics of several fast growing robinia variety candidates grown on different sites. *Wood Struct. Properties* 6:518–528.
- Rowell, R. M. 1991. Chemical modification of wood. In: *Wood and Cellulosic Chemistry*. D. N. S. Hon and N. Shiraiishi (Eds.). Marcel Dekker, Inc., New York. pp. 703–756.
- Rozman, H. D., R. N. Kumar, A. Abusamah, and M. J. Saad. 1998. Rubberwood-polymer composites based on glycidyl methacrylate and diallyl phthalate. *J. Appl. Polym. Sci.* 67(7):1221–1226.
- Rozman, H. D., R. N. Kumar, H. P. S. Khalil, A. Abusamah, R. Abu, and H. Ismail. 1997. Fibre activation with glycidyl methacrylate and subsequent copolymerization with diallyl phthalate. *Eur. Polym. J.* 33(8):1213–1218.
- Rutkowski, P. 2009. Influence of zinc chloride addition on the chemical structure of bio-oil obtained during co-pyrolysis of wood/synthetic polymer blends. *Waste Manag.* 29(12):2983–2993.
- Sailaja, R. R. N. and S. Seetharamu. 2009. Mechanical and thermal properties of LDPE-cellulose acetate phthalate blends—Effect of maleic anhydride grafted LDPE compatibilizer. *J. Appl. Polym. Sci.* 112(2):649–659.
- Stamm, A. J. 1964. *Wood and Cellulose Science*. Ronald Press, New York. pp. 312–342.
- Takahashi, M. 1996. Biological properties of chemically modified wood. In: *Chemical Modification of Lignocellulosic Materials*. D. N. S. Hon (Ed.). Marcel Dekker, Inc., New York. pp. 331–336.
- Tsunoda, K. 1991. Termite bioassays for evaluation of wood preservatives. *Soc. Biol.* 19(1):245–255.
- Tsunoda, K. and K. Nishimoto. 1986. Japanese standardized methods for testing effectiveness of chemicals against termite attack. Document No. IRG/WP/1290. International Research Group on Wood Preservation, Stockholm.
- Yalinkilic, M. K., Y. Imamura, and M. Takahashi. 1999. Biological, mechanical, and thermal properties of compressed-wood polymer-composite (CWPC) pretreated with boric acid. *Wood Fiber Sci.* 31(2): 151–163.
- Yalinkilic, M. K., K. Tsunoda, and M. Takahashi. 1998. Enhancement of biological and physical properties of wood by boric acid-vinyl monomer combination treatment. *Holzforschung* 52(6):667–672.
- Zhang, Y., H. Wan, and S. Y. Zhang. 2005. Characterization of sugar maple wood-polymer composites: Monomer retention and polymer retention. *Holzforschung* 59(10):322–329.
- Zhang, Y., S. Y. Zhang, D. Yang, and W. Hui. 2006. Dimensional stability of wood-polymer composites. *J. Appl. Polym. Sci.* 102: 5085–5094.
- Zhou, P., H. G. Xiong, and S. W. Tang. 2008. Natural weathering of rape straw flour (RSF)/HDPE and nano-SiO<sub>2</sub>/RSF/HDPE composites. *Carbohydr. Polym.* 73(3):378–383.