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Effect of *in-situ* formation of polymer from vinyl monomers on the morphology and durability of wood

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The current study demonstrates the effect of *in-situ* formation of polymer from vinyl monomers on the morphology and durability of wood. Mixed monomers of methyl methacrylate (MMA) and styrene (St) (1:1 molar ratio) were effectively vacuum/pressure impregnated into the cellular structure of a fast-growing poplar wood, *Populus ussuriensis* Kom, and then underwent a catalyst-thermal process to polymerize and form wood-polymer composite. Scanning electron microscopy (SEM) observation shows that polymer converted from monomers almost filled up wood cell cavities. Fourier transform infrared (FTIR) analysis indicates that the polymer mainly physical interacted with wood matrix. X-ray diffraction (XRD) analysis suggests that the *in-situ* generated polymer mainly remained as an amorphous form in cell lumen. The block of wood cavities by polymer coupled with the water resistance of polymer resulted in remarkable improvement of decay resistance and dimensional stability of wood.

Key words: Wood-polymer composite, characterization, morphology, durability, methyl methacrylate, styrene.

INTRODUCTION

With the development of society, the consumption of wood has been rapidly increasing year by year. In contrast, however, the production of high-quality wood has been fleetly decreasing. In addition, wood components are easy to be degraded by microorganisms, and susceptible to damage by fire as well as dimensional change by water or moisture (Hill, 2008; Li et al., 2011a, b, 2012). All these disadvantages limit the wider application of wood as high-quality materials. Such prominent contradictions, recently, have driven researchers to look for alternative low-quality resources for value-added applications. To achieve these goals, suitable technologies are needed to improve low-quality

resources (especially specific wood quality) attributes (for example, mechanical properties, dimensional stability, decay resistance and thermal stability) in order to meet end-use requirements (Wang, 2007; Zhang, 2006). As we known, wood possesses porous structures consisting of various sizes of cell walls, which are mainly composed of biopolymers, that is, carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin. The cellular structure of wood endows it with high strength-to-weight ratio, and thus makes it capable of being used as structural material. However, some fast-growing wood have lower mechanical properties or unsatisfactory durability, which limit their value-added applications. Thus, the modification of cellular structure is regarded as one of the main effective way for value-added treatment of low-quality wood (Stacy et al., 2010). As the aforementioned unfavorable behaviors of wood are fundamentally ascribed to the presence of numerous

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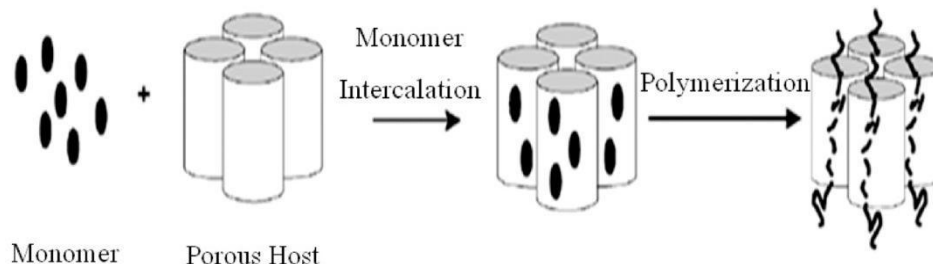


Figure 1. Scheme of preparation of wood-polymer composite by wood and monomer(s).

hydroxyl groups (reactive sites) in the wood major components and various cell cavities (major paths for moisture movement) within wood (Li, 2011a; Yang et al., 2012; Zhang, 2005), blocking these reactive sites or plugging the cavities could not only make the wood more resistant to moisture, but also improve its dimensional stability and mechanical as well as biodegradation properties. Consequently, treatment of wood to modify its structure and thus improve its comprehensive properties has been carried out via physical or chemical impregnation, compression treatment, thermal treatment at high temperature and so on (Habu et al., 2006; Li et al., 2012a; Manríquez and Moraes, 2010; Marcos et al., 2009).

Among these techniques, one to improve wood properties, which has received considerable attention in the past few decades, is the fabrication of wood-polymer composites (WPC) through *in-situ* formation of polymer from unsaturated monomers within wood pores (vessels, tracheids, capillaries and ray cells) (Zhang et al., 2005). The scheme of process for wood-polymer composite is shown in Figure 1. The resultant polymer can both strengthen the mechanical properties of wood and defer or stop wood matrix from being attacked by water or microorganisms (Baysal, 2007; Yalinkilic, 1999). Such multifunctional treatment can help avoiding the potential damage of leached preservatives from chemically treated wood on environment (Obanda et al., 2008), deformation spring-back of compressed wood (Manríquez and Moraes, 2010) and color change of heat-treated wood (Marcos et al., 2009). Thus, such treatment became an environmentally friendly wood modification process.

In WPCs, vinyl type monomers are polymerized into the solid polymer by means of free radical mechanism, like the polymerization of pure monomers. This vinyl polymerization is an improvement over the condensation polymerization reaction because the free radical catalyst was neither acidic nor basic which degrades the cellulose chain and causes brittleness of the composite, nor does the reaction leave behind a reaction product that must be removed from the final composite, such as water. Vinyl polymers have large range of properties from soft rubber to hard, brittle solids depending upon the groups attached to the carbon-carbon backbone. Some examples of vinyl

monomers used in WPC are styrene (St), vinyl chloride (VC), vinyl acetate (VAc), many of the acrylates especially methyl methacrylate (MMA), glycidyl methacrylate (GMA) and acrylonitrile (Islam, 2011; Haque, 2009; Islam, 2009, 2010; Hamdan, 2010; Pandey, 2009; Devi, 2003; Hill, 2008; Devi and Maji, 2008, 2011).

In this study, two vinyl monomers, that is, methyl methacrylate and styrene, were explored to treat fast-growing poplar wood, *P. ussuriensis* Kom, because the two most commonly monomers are theoretically capable of copolymerizing through catalyst/thermal treatment within cell lumens. Although, previous papers have reported the combination use of MMA and St for wood-polymer composite, such treatment on poplar wood was rarely studied (Li et al., 2012b). Thus, this study mainly focused on the preparation of such wood-polymer composite, and further characterized its morphology and evaluated its durability.

EXPERIMENTAL DETAILS

Material

All chemicals were purchased in China. Applied chemicals after purification: Initiator, 2,2'-azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Factory, Shanghai); without purification: Pyrimidine as a catalyst (Hubei Xinjing New Material), and analytical grade methyl methacrylate (MMA) and styrene (St) (Tianjin Kermel Chemreagent, Tianjin). Poplar lumber (*P. ussuriensis* Kom) (poplar) was obtained from the original plantation areas in Maoershan located in the northeast of China. The wood samples were air-dried under room temperature for 3 months and then oven-dried at 105°C to constant weights for further use. All %-data are, if not otherwise indicated, based on weight. The impregnating equipment is self-made.

Preparation of wood-polymer composites (WPC)

2,2'-azobisisobutyronitrile (AIBN) as an initiator was dissolved in MMA and St (1:1 molar ratio) mixed solution to form 0.5% concentration. Poplar was vacuum/pressure impregnated with the solution (0.08 MPa for 20 min/0.8 MPa for 20 min). Then, the treated wood samples were wrapped in aluminum foils and oven-dried at 80°C for 8 h. The samples were labeled as Wood-P(MMA-co-St) Composite (WPC for short). The conversion rate was

calculated according to the following Equation 1:

$$\text{Conversion rate (\%)} = 100 \times (w_p - w_d) / (w_i - w_d) \quad (1)$$

where: w_p , w_d and w_i are the weights of polymer impregnated wood, virgin impregnated wood and monomer impregnated wood, respectively.

Characterization and analysis

Polymer distribution within wood and the morphology was demonstrated by environmental scanning electron microscopy (ESEM) Instrument (QUANTA 200, FEI Inc., Hillsboro, USA). The end grain of sample was cut with a surgical blade and the sample was mounted on sample holders with a double-sided adhesive tape, gold sputter-coated. FTIR spectra (KBr technique) were recorded with the instrument Magna-IR560 E.S.P (Thermo Nicolet Inc., Madison, USA). The resolution ratio was 4 cm^{-1} and 40 spectra were accumulated. Before the FTIR test, the WPC sample and untreated poplar sample for control were separately grounded into powder by a disintegrator and passed through a 100-mesh screen; this was followed by Soxhlet extraction with acetone for 24 h and then subsequent drying to a constant weight. X-ray diffraction (XRD) tests were made with D/max2200 (Rigaku Corporation, Japan). The test parameters selected for the XRD included Cu butt, 40 kV of voltage, 30 mA of current, $4^\circ/\text{min}$ rotating speed, and a 0.02° step distance. The water static contact angle was measured by contact angle instrument, JC2000A (Shanghai Zhongchen Corp., Shanghai, China). The water is deionized water, which was dropped on the wood samples and captured with camera at the same time. The contact angle was measured with specific software. The value of the static contact angle is the average data of five drops of water.

Evaluation of decay resistance and dimensional stability

The decay test was carried out according to the "Chinese forest industry standard - Laboratory methods for the toxicity test of wood preservatives on decay fungi (LY/T 1283-1998)", which is referred to the international fungal decay test, JIS K 1571-Qualitative standards and testing methods of wood preservatives (Furuno et al., 2003).

End-matched samples with dimensions of $20 \times 20 \times 10 \text{ mm}^3$ (radial (R) \times tangential (T) \times longitudinal (L)) were prepared from each pair of control and treated poplar. A minimum of five specimens were used for the test²⁸. An incubator was filled with water to a depth of 50 mm. Test samples after being autoclaved for 30 min were placed on wood feeder chips with dimensions of $22 \times 22 \times 2 \text{ mm}^3$ (R \times T \times L) in the incubator. Each incubator contains three wood samples, and each sample was placed on each wood feeder chip. The relative humidity value inside the incubator was 80%, and the temperature was 28°C . The sample weight loss was used to evaluate the decay resistance of each sample after exposing to decay fungi for 12 weeks. The fungi used in this study were brown decay fungus, *Gloeophyllum trabeum* (Pers. ex Fr.) Murr., and white decay fungus, *Phanerochaete chrysosporium* Burdsall.

The samples for dimensional stability tests were prepared according to the "China National Standard - Testing Methods for Wood Physical and Mechanical Properties (GB1928-1929-91)." End-matched samples with a dimension of $20 \times 20 \times 20 \text{ mm}^3$ (R \times T \times L) were prepared from each pair of control and WPC and were then immersed in distilled water for 720 h. The dimension of each sample was measured at different immersion times. The average data of five specimens for each kind of measurements were presented and drawn curves in terms of volume swelling efficiency vs. immersion times. The polymer loading was calculated according

to Equation 2:

$$R_m = (G_i - G_0) / G_0 \times 100\% \quad (2)$$

where: R_m represents polymer loading; G_i represents mass of Wood-P(MMA-co-St) Composite; G_0 represents mass of wood before any treatment.

The volume swelling efficiency was calculated by the following Equation 3:

$$V_m = (V_1 - V_0) / V_0 \times 100\% \quad (3)$$

where: V_m represents the volume swelling efficiency; V_1 represents the volume of samples after immersing in water for any hour; and V_0 represents the volume of samples before immersing.

RESULTS AND DISCUSSION

Polymer loading

All the WPC samples were prepared according to the afore-mentioned process with an average polymer loading of $(47.39 \pm 2.64) \%$ and average conversion rate of $(76.28 \pm 2.64) \%$, which indicated that the monomers successfully copolymerized within wood pores. And all the following experiments employed the samples with similar polymer loading, which guaranteed the effectiveness of property evaluation of the resulted wood-polymer composites.

Scanning electron microscopy (SEM) observations

Figure 2a clearly shows wood possessing porous structure with different pore sizes; while Figure 2b shows that the polymer was thermoformed in situ the pores and filled up most cell lumens in solid form, which indicates that the preparation craft was suitable for thermoforming of polymer. Figure 2b also shows that the resulting polymer contacted wood matrix without noticeable lacunae, indicating less shrinkage of the resulted polymers (Li et al., 2010).

Fourier transform infrared (FTIR) analysis

From Figure 3, it can be known that comparing the characteristic peaks of both untreated wood and Wood-P(MMA-co-St) composite, there is no obvious difference. It indicates that MMA monomer and St monomer copolymerized and physically filled up wood cell lumens (SEM observation) without chemical bond. In other words, the monomers could not chemically react with wood components during the polymerization within wood cell lumens. However, as seen from SEM observation, the physical interaction between wood and polymer may be strong, for less shrinkage happened on the resulted polymers.

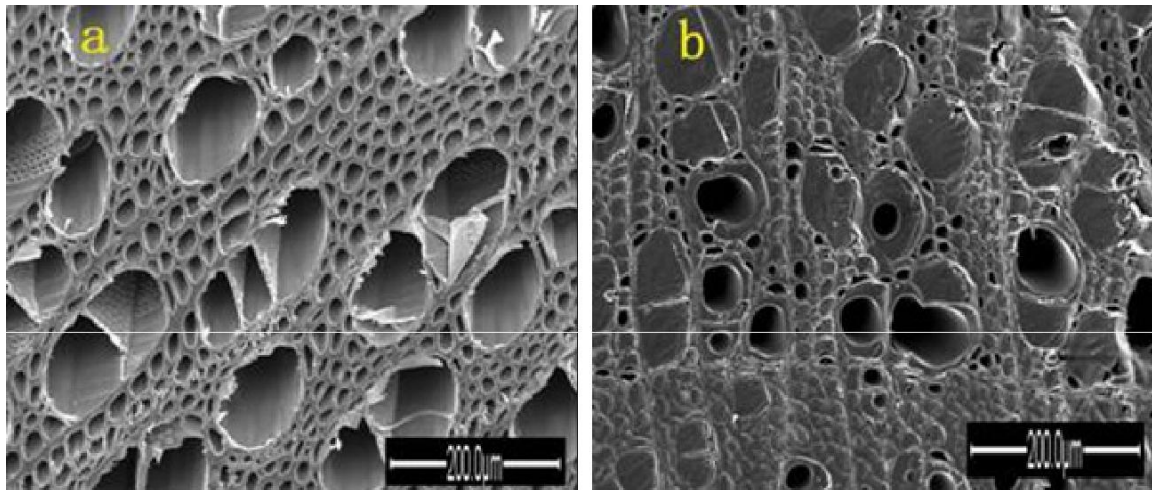


Figure 2. SEM morphologies of wood (a) and wood-P(MMA-co-St) composite (b).

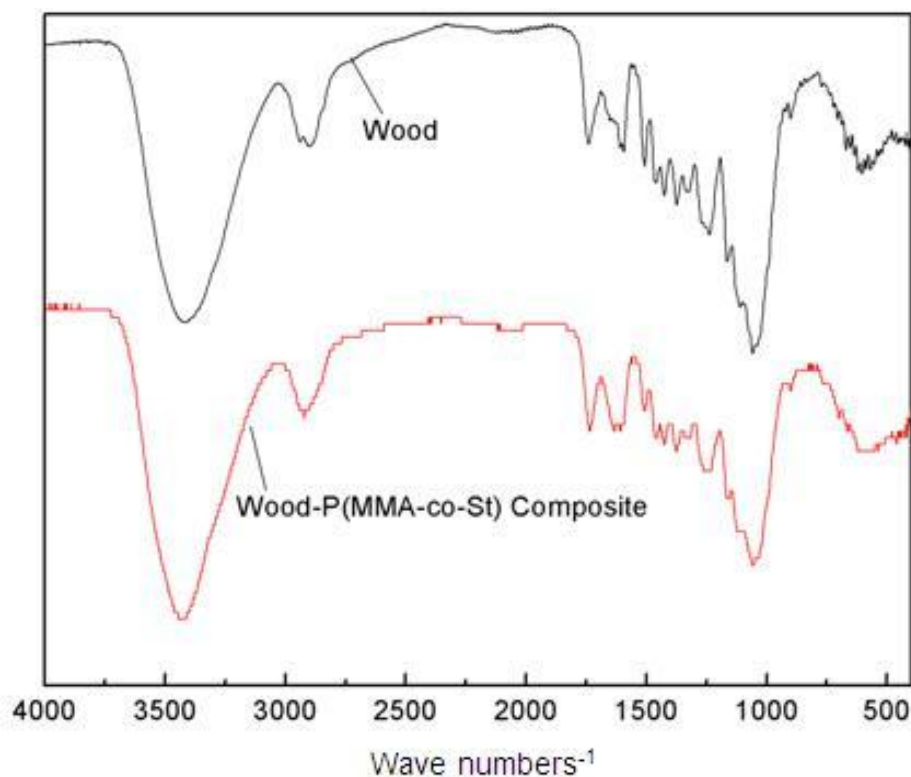


Figure 3. FTIR spectra of wood and wood-P(MMA-co-St) composite.

X-ray diffraction (XRD) analysis

The XRD curves of the unmodified poplar and WPC were shown in Figure 4. As shown in the XRD pattern, the maximum peak values of the poplar wood and WPC for the 002 side at $2\theta = 22.5^\circ$ were degressive, whereas their minimum wave trough values for the 101 side at $2\theta =$

18.5° were increasing. According to the Segal method (Equation 4), (Li et al., 2010) the relative crystallinity value of untreated wood and WPC was calculated to be 43.8 and 35.6%, respectively. In general, the 2θ diffraction patterns for the two samples were similar, although there was little difference in the intensity, which represents the difference in the relative crystallinity value.

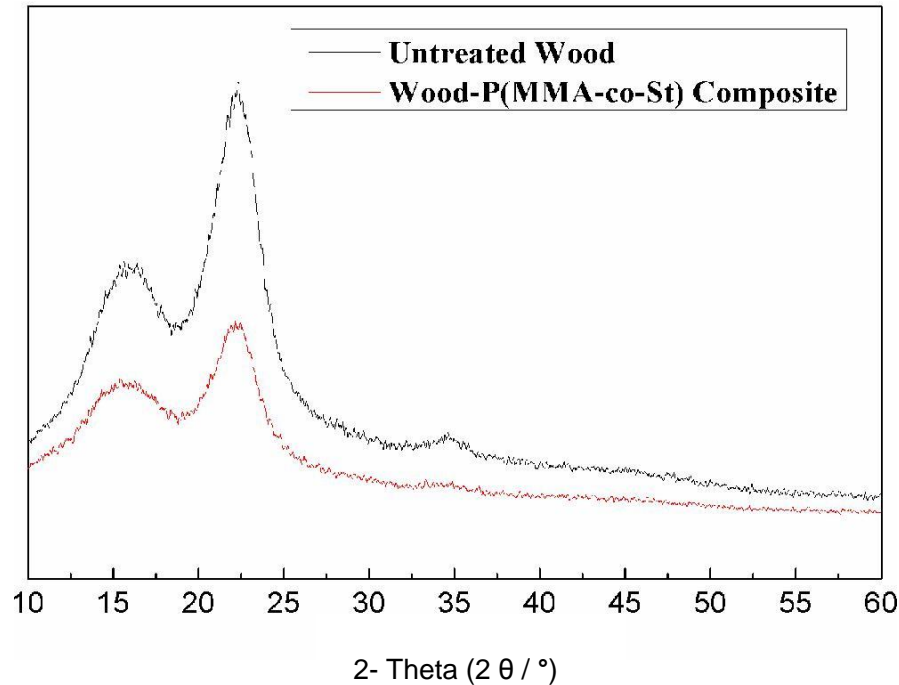


Figure 4. XRD patterns of untreated and wood-P(MMA-co-St) composite.

Table 1. Decay resistance of untreated poplar wood and Wood-P(MMA-co-St) composite against the brown decay fungus (*Gloeophyllum trabeum* (Pers. ex Fr.) Murr.) and white decay fungus (*Phanerochaete chrysosporium* Burdsall)

Sample ID	<i>Gloeophyllum trabeum</i> (Pers. ex Fr.) Murr.		<i>Phanerochaete chrysosporium</i> Burdsall	
	Weight loss/%	Change*/%	Weight loss/%	Change*/%
Untreated Wood	79.28(3.91)	-	27.61(1.34)	-
Wood-P(MMA-co-St) composite	26.26 (1.21)	66.88%	5.99(0.50)	78.30

*Change is comparison of the modified poplar wood to untreated poplar wood. The data in parentheses are standard deviations.

Compared to poplar, the relative crystallinity of the WPC decreased, indicating that the resulting polymers in cell lumen mainly remaining as an amorphous form, which enhanced the proportion of amorphous components in the whole wood composites.

$$C_{rl} = (I_{002} - I_{am}) / I_{002} \times 100\% \quad (4)$$

where: C_{rl} is the percentage of the relative crystallinity degree, I_{002} is the maximum intensity of the diffraction angle for the 002 side at approximately $2\theta = 22.5^\circ$, and I_{am} is the dispersion intensity of the noncrystalline background for the 101 side at approximately $2\theta = 18.5^\circ$.

Durability

Decay resistance

Table 1 shows that the decay resistance of WPC in terms of weight loss against the brown and white decay fungus

was improved 66.9 and 78.3%, respectively, over those of untreated wood, which indicated that the wood after treatment by *in-situ* formation of polymer obtained improved decay resistance. The *in-situ* formed polymer excluded water and moisture to access to wood cell wall, which resulted in insufficient moisture content within wood cell wall for most of decay survival (Hill et al., 2006). Moreover, the polymer physically blocked the microorganisms to access the wood components, which also contributed to the improvement of decay resistance of WPC (Li et al., 2011b). However, as the content of holocellulose was larger than that of lignin, the value of decay resistance of both treated and untreated wood against the white fungus was corresponding higher than those against the brown fungus.

Volumetric swelling efficiency (VSE)

Figure 5a shows the variation of volume swelling efficiency of wood and WPC with time. For wood, the

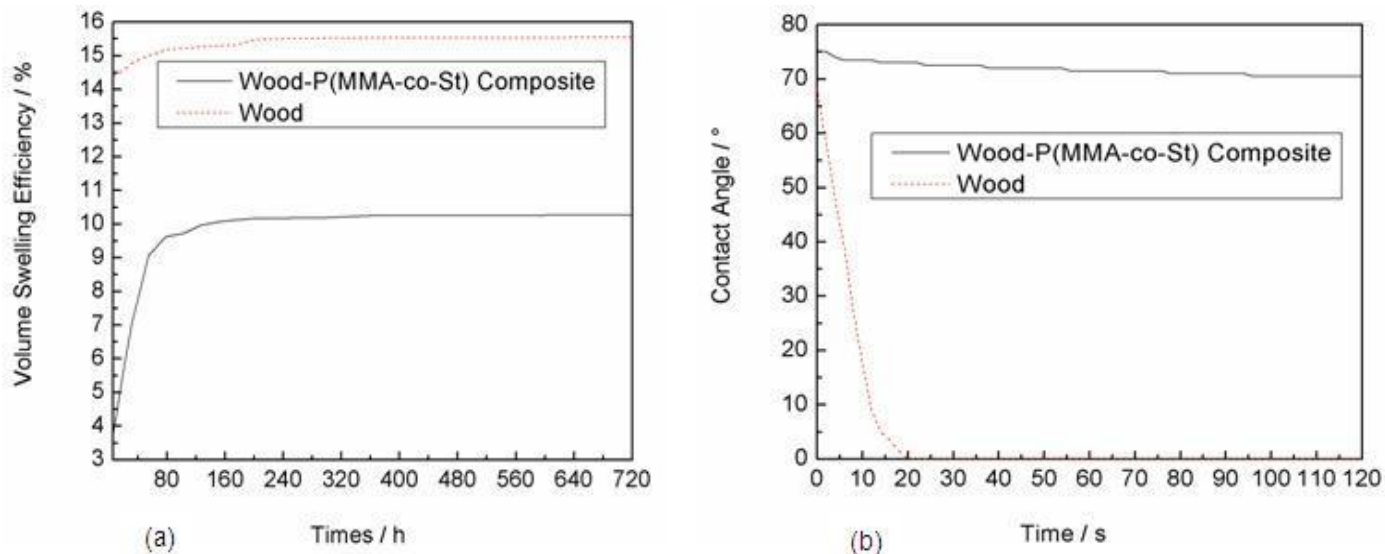


Figure 5. The curves of VSE vs. times (a) and contact angle vs. times (b) for wood and WPC.

volume swelling efficiency achieved 14.5% after immersing in water for 6 h. When it immersed in water over 80 h, the VSE achieved about 15.2% and kept it for balance without great variation. The afore-mentioned results indicated that wood was easy to swell when it immersed in water due to its great abundant hydroxyl groups on wood components. While for Wood-P(MMA-co-St) composite, the volume swelling efficiency quickly achieved about 10% from about 4% after being immersed in water for the initial 80 h. After 80 h, its volume swelling efficiency retained about 10% for balance. For both the composites, their VSE reached maximum values within the initial immersing time of 80 h; while the VSE of Wood-P(MMA-co-St) composite was always lower than that of wood, indicating that the dimensional stability of the composite was higher than that of untreated wood. Based on the afore-mentioned SEM observation and FTIR analysis, it can be reasonably believed that the improvement of the dimensional stability of WPC was attributed to the water resistance of polymer and the physical block of polymer to wood components, both which prevented water from penetrating into wood cell walls. (Li et al., 2011c)

Contact angle

From Figure 5b, it can be known that the contact angle of wood quickly reduced from 68 to 0° within 20 s, indicating hydrophilicity available; while the contact angle of Wood-P(MMA-co-St) composite almost maintained 75° within 120 s, indicating a certain of water resistance. The difference should be also attributed to the block of polymer to wood pores coupled with the water resistance of polymer.

Conclusions

Poplar wood-polymer composite was successfully fabricated by *in-situ* thermoforming of copolymer from methyl methacrylate and styrene monomers within wood porous structure through a catalyst/thermal treatment. SEM observation shows that polymer converted from monomers filled up wood cell cavities, and tightly contacted wood matrix. FTIR analysis indicates that the resulted polymer physically filled up wood cell lumens. XRD analysis suggests that the resultant polymer mainly remained as an amorphous form within the cell lumen. The durability of WPC including decay resistance and dimensional stability was also remarkably improved over untreated wood. The volume swelling efficiency and the decay resistance of WPC in terms of weight loss against the brown and white decay fungus was improved by 5.2, 66.9 and 78.3%, respectively, over those of untreated wood. The static water contact angle of WPC was also remarkably reduced, compared with that of untreated wood. Such composite combined both advantages of wood and polymer is regarded as a promising friendly environmental material, which could be potentially applied in fields of construction, traffic, furniture and so forth.

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