Effect of Polymer *In situ* Synthesized from Methyl Methacrylate and Styrene on the Morphology, Thermal Behavior, and Durability of Wood

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ABSTRACT: A novel fast-growing poplar wood, *Populus ussuriensis* Kom, was prepared into wood-polymer composite by the *in situ* polymerization of methyl methacrylate and styrene through a vacuum/pressure and subsequent catalyst-thermal process. scanning electron microscopy observation, FTIR, X-ray diffraction, dynamic mechanical analysis, and thermogravimetric/derivative thermogravimetric analysis indicated that the resulted polymer well filled up wood cell lumen in an amorphous form and reinforced wood matrix, which resulted in the improvement of glass transition temperature, storage modulus, and thermal stability of wood. The decay resistance and dimensional stability of wood were also improved. Such wood-based composite could be potentially used as reinforced material in construction fields. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Wood has been an essential material for human survival since the primitive state, for its wide abundance, renewable and environmentally benign nature, relative ease of working it, and outstanding strength-to-weight ratio. With the sci–tech progress, wood has been used for shelter, fuel, tools, boats, vehicles, bridges, furniture, engineering materials, weapons, and even raw materials for energy.[1] Now, wood is widely used in various corners of human life.

However, wood components are easy to be degraded by microorganisms, and susceptible to be damaged by fire as well as to dimensional change by water or moisture.[2,3] All these disadvantages limit the wider application of wood as high-quality material.

With the development of society, the consumption of wood has rapidly increased year-by-year. In contrast, however, the production of high-quality wood has fleetly decreased. Such prominent contradictions have driven researchers to look for alternate low-quality resources for value-added applications. To achieve these goals, suitable technologies are needed to improve attributes (e.g., mechanical properties, durability) of low-quality resources (especially wood of specific quality) in order to meet the end-use requirements.[4,5]

As we know, wood possesses porous structures consisting of various sizes of cell walls, which are mainly composed of bio-

polymers, i.e., 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.[6,7] However, some fast-growing wood have lower density and accordingly mechanical properties or unsatisfactory durability, which limit their value-added applications. Thus, modification of the cellular structure is regarded as one of the main effective way for value-added treatment of low-quality wood.[8] Several studies have reported that the above unfavorable behaviors of wood should be fundamentally ascribed to the presence of numerous hydroxyl groups (reactive sites) in the wood major components and various cell cavities (major paths for moisture movement) within wood.[9–11] Thus, blocking these reactive sites or plugging the cavities could not only make the wood more resistant to moisture, but also improve its durability and mechanical properties. Consequently, treatment on wood to modify its structure and thus improve its comprehensive properties has been carried out via physical or chemical impregnation, compression treatment, thermal treatment, and so on.[3] 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).[11] The scheme of process for WPC is shown in Figure 1. The resultant polymer can
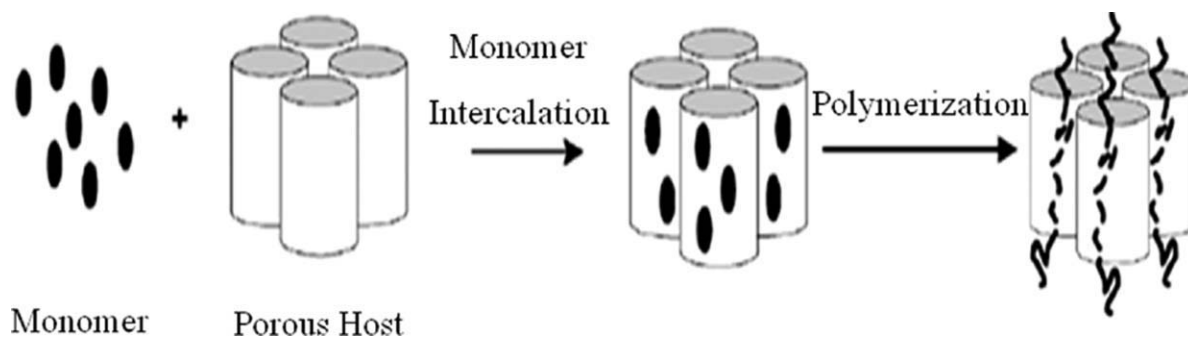
Figure 1. Scheme for preparation of wood-polymer composite from wood and monomer(s)

both strengthen the mechanical properties of wood and defer or stop wood matrix from being attacked by water or microorganisms.[12,13] Thus, such multifunctional treatment can help avoid the potential damage of leached preservatives from wood on environment,[14] deformation spring-back of compressed wood[15] and color change of heat-treated wood.[16] Consequently, it became an environmentally friendly way for wood modification.[17]

In WPCs, vinyl-type monomers are polymerized into solid polymer by free radical polymerization, which is superior over the condensation polymerization way 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 byproduct that must be removed from the final composite.[10] Another reason for such used method is that vinyl polymers have large range of properties from soft rubber to hard brittle solids depending upon the groups attached to the carbon-carbon backbone, which can endow wood with large range of properties. Some examples of vinyl monomers used in WPCs are styrene (St), vinyl chloride, vinyl acetate, methyl methacrylate (MMA), glycidyl methacrylate and acrylonitrile.[18–27]

In this study, monomers containing MMA and St were used to treat a fast growing poplar wood, *Populus ussuriensis* Kom, for theoretically the two most commonly monomers are capable of copolymerization under a certain condition. Although, several previous papers.[13,28–30] have reported the combination use of MMA and St for WPC, such treatment on poplar wood was rarely studied.[31,32] Thus, this study mainly focuses on the effect of such treatment on morphology, thermal behavior and durability of the poplar wood.

EXPERIMENTAL

Raw materials
All chemicals were purchased in China. All chemicals without purification: Initiator, 2,2′- azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Factory, Shanghai); analytical grade MMA and St (Tianjin Kermel Chemreagent, Tianjin). Poplar lumber (*Populus 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 before use. All %-data are, if not otherwise

indicated, based on weight. The impregnating equipment is self-made.

Preparation of WPC
AIBN as an initiator was dissolved in MMA/St (1:1 molar ratio) mixed solution to form 0.5% concentration. Poplar was impregnated into the solution under vacuum/pressure conditions (0.08 MPa for 20 min/0.8 MPa for 20 min).[1] Then, the treated wood samples were wrapped in aluminum foils and oven-dried at 80°C for 8 h[1]. The final sample was labeled as Wood-P(MMA-co-St) Composite (WPC for short). The conversion rate was calculated according to the following eq. (1):

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

where: w_p, w_d, and w_i is the weight of polymer impregnated wood, virgin and momonomer impregnated wood, respectively.

Morphology Characterization
Polymer distribution within wood and the morphology were demonstrated by environmental scanning electron microscopy (SEM) Instrument (QUANTA 200, FEI, Hillsboro). The end grain of sample was cut with a surgical blade and the sample was mounted on sample holder 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, Madison). 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 was separately ground into powders by a disintegrator and passed through a 100-mesh screen, and then followed by Soxhlet extraction with acetone for 24 h and subsequently dried to constant weight.

X-ray diffraction (XRD) tests were made with D/max2200 (Rigaku Corporation, Japan). The test parameters included Cu butt, 40 kV of voltage, 30 mA of current, 4°/min rotating speed, and a 0.02° step distance.

Thermal Behavior Analysis
Thermogravimetric analyzer (TGA Q500, Waters) instrument was used for the thermal behavior analyses. The TG test for 5–10 mg powders was done under continuous nitrogen flow, and the heat rate was 10°C/min, and the temperature range was from 35 to 670°C.

Dynamic mechanical analysis (DMA) test was made with a DMA242 analyser (NETZSCH, Waldkraiburg, Germany), and the test parameters (three-point bend test) included 60 μm of amplitude, 0.6 N of dynamic force, 10°C•min^{-1} of heating rate and 5 Hz of frequency. The size of wood sample for DMA test is $50 \times 3 \times 2$ mm^3 (radial (R) $\times$ tangential (T) $\times$ longitudinal (L)).

Durability Evaluation

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.[33]

End-matched samples with dimensions of $20 \times 20 \times 10$ mm^3 (R $\times$ T $\times$ L) were prepared from each pair of control and treated Poplar. A minimum of five specimens were used for the test.[2] An incubator was filled with water to a depth of 50 mm. Test samples after autoclave of 30 min were placed on wood feeder chips with dimensions of $22 \times 22 \times 2$ mm^3 (R $\times$ T $\times$ L) in the incubator. Each incubator contained three wood samples, and each sample was placed on each wood feeder chip. The relative humidity inside the incubator was 80%, and the temperature was 28°C. 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 dimension of $20 \times 20 \times 20$ 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 time. The average value of five specimens for each kind of measurement was presented and drawn into curves in terms of volumetric swelling efficiency (VSE) versus immersion time.

The polymer loading was calculated according to the following eq. (2):

$$P_L = (w_p - w_d)/w_d \times 100\% \qquad (2)$$

where: P_L represents polymer loading.

The VSE was calculated by the following eq. (3):

$$VSE = (v_1 - v_0)/v_0 \times 100\% \qquad (3)$$

where v_1 represents the volume of samples after immersing in water for any time; and v_o represents the volume of samples before immersing in water.

The static contact angle was measured by contact angle instrument, JC2000A (Shanghai Zhongchen, Shanghai, China). The used liquid was water, and three drops of water were used to test different points on the cross section of each sample. Three duplicated samples were used under the same conditions for
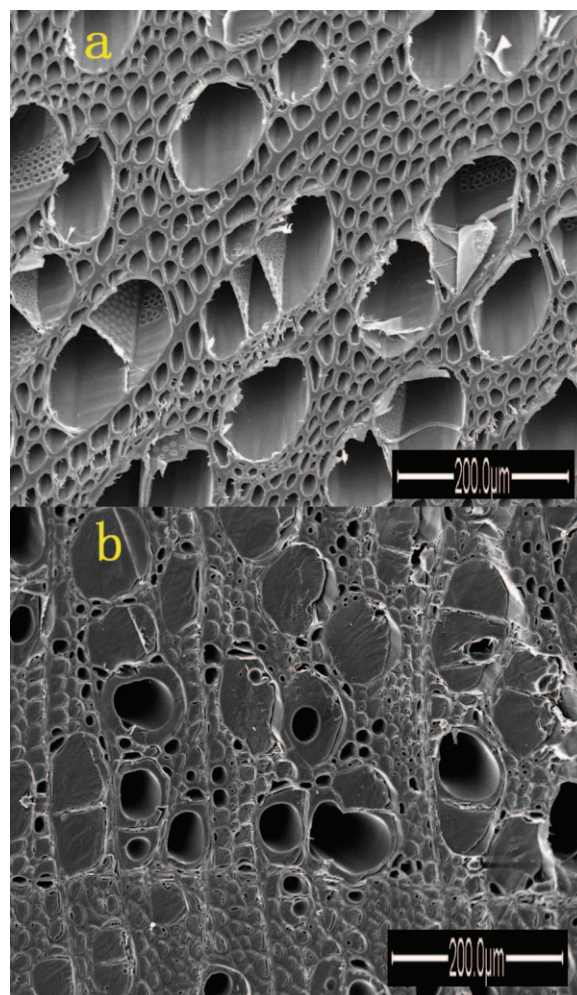
Figure 2. SEM morphologies of wood (a) and Wood-P(MMA-co-St) Composite (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

each TG, DMA and Water contact angle test, and the corresponding results curve was drawn on the basis of the mean values of each point.

RESULTS AND DISCUSSION

Polymer Loading

All the WPC samples were prepared according to the above processes, and achieved an average polymer loading of (37.54 $\pm$ 2.69) % and average conversion rate of (48.26 $\pm$ 2.02) %, indicating that the monomers successfully polymerized into solid polymer within wood. All the following experiments used the samples with the similar polymer loading, which guaranteed the effectiveness of property results of treated wood.

Morphology Characterization

SEM Observations. Figure 2(a) clearly showed the porous structure of Poplar with different sizes of pores, while Figure 2(b) showed that polymer was *in situ* synthesized within the wood pores under the suitable conditions and well filled up most cavities, indicating good distribution of polymer in the cross-section of wood.
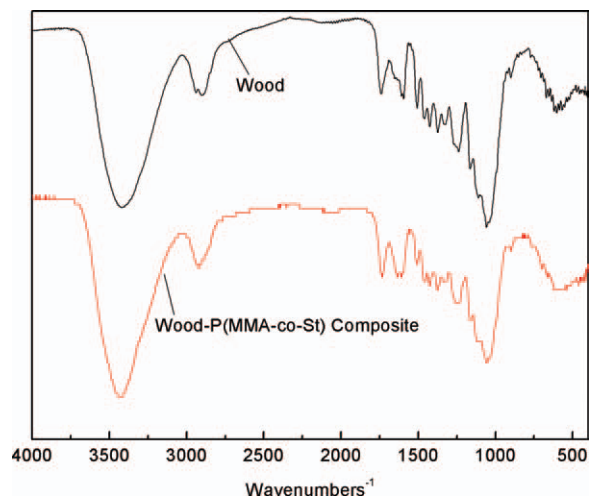
Figure 3. FTIR spectra of wood and Wood-P(MMA-co-St) Composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR Analysis. From Figure 3, it can be known that compared the spectra of both untreated Poplar and Wood-P(MMA-co-St) Composite, there is no obvious difference. It means that MMA and St mainly polymerized into polymer without chemical reaction with wood components. In other words, the resultant polymer most physically filled up wood cell lumens.

XRD behavior. The XRD curves of the unmodified Poplar and WPC were shown in Figure 4. As shown in the XRD pattern, the maximum peak of the WPC at $2\theta = 22.5°$ for the 002 side was lower than that of untreated Poplar, whereas its minimum wave trough value at $2\theta = 18.5°$ for the 101 side was higher than that of Poplar, indicating decreased crystallinity for the WPC. The relative crystallinity value of untreated Poplar and WPC was respectively calculated as 43.8 and 35.6% in terms of the Segal method [eq. (4)], which further demonstrated the decreased crystallinity of WPC. However, the 2θ diffraction patterns of Poplar and the WPC were generally similar, though there was little difference in the intensity, which represents the different value of relative crystallinity. It means that the crystalline structure of wood was not essentially changed after formation of polymer within wood. Consequently, the decrease of relative crystallinity of the WPC should be attributed to the resulted polymers mainly remaining as an amorphous form, which enhanced the proportion of amorphous components in the whole wood composites.

The relative crystallinity index is calculated according to the following formula:

$$C_r I(\%) = [(I_{002} - I_{am})/I_{002}] \times 100 \qquad (4)$$

where $C_r I$ is the percentage of relative crystallinity index; I_{002} is the maximum intensity of diffraction angle at about $2\theta = 22°$ for 002 side; and I_{am} is the dispersion intensity of non crystalline background at about $2\theta = 18°$ for 101 side.

Thermal Behavior Analysis
**Dynamic Mechanical Analysis.** From Figure 5(a), it can be known that the storage modulus (E') of Poplar and WPC were

generally decreased with temperature increasing within the testing range. However, the storage modulus of Wood-P(MMA-co-St) Composite was higher than that of Poplar within the testing range, which should be attributed to the reinforcement of polymer to wood.[1] Figure 5(b) shows the glass transition temperature of Wood-P(MMA-co-St) Composite and Poplar in terms of the mechanical loss factor (tanδ), for glass transition temperature approximately equaling to the temperature when tanδ reaches maximum on the curve of tanδ-T. The glass transition temperature of untreated wood (Poplar) was about 90°C, while the glass transition temperature of Wood-P(MMA-co-St) Composite was about 125°C. The increased glass transition temperature of the WPC should be also attributed to the reinforcement of polymer to wood by the polymerization of MMA and St in cell lumen.[1]

Based on the DMA analysis, it can be deduced that the polymerization of MMA and St reinforced wood matrix, which resulted in improvement of both the glass transition temperature and storage modulus of Wood-P(MMA-co-St) Composite over untreated wood.

TG Analysis. Thermogravimetric/derivative thermogravimetric (TG/DTG) test is one common way to analyze and characterize the thermal behavior of materials. Wood as a whole biomass material undergoes a complex thermal degradation process, which is greatly affected by its wood components. As we known, in thermogravimetric test, the major chemical components (cellulose, hemicellulose, lignin and extractives) degrade at different temperatures. Cellulose is highly crystalline, which makes it thermally stable. Hemicelluloses and lignin are amorphous and start to degrade before cellulose, which are regarded as the least thermally stable wood components.[34] To obtain information regarding the nature of WPC, the TG thermogram of WPC was compared with those of untreated poplar wood and cellulose.

Figure 6 illustrates the thermogravimetric (TG/DTG) curves of wood, cellulose and WPC under a nitrogen environment at a heating rate of 10°C/min. Table I summaries the observations from the TG/DTG curves, including peak temperatures for the
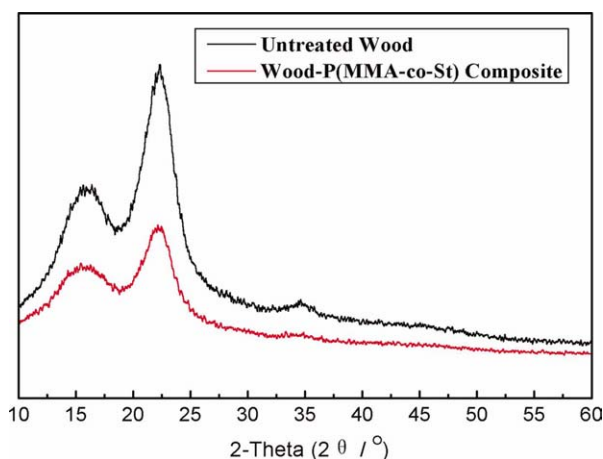
Figure 4. XRD patterns of untreated wood and Wood-P(MMA-co-St) Composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
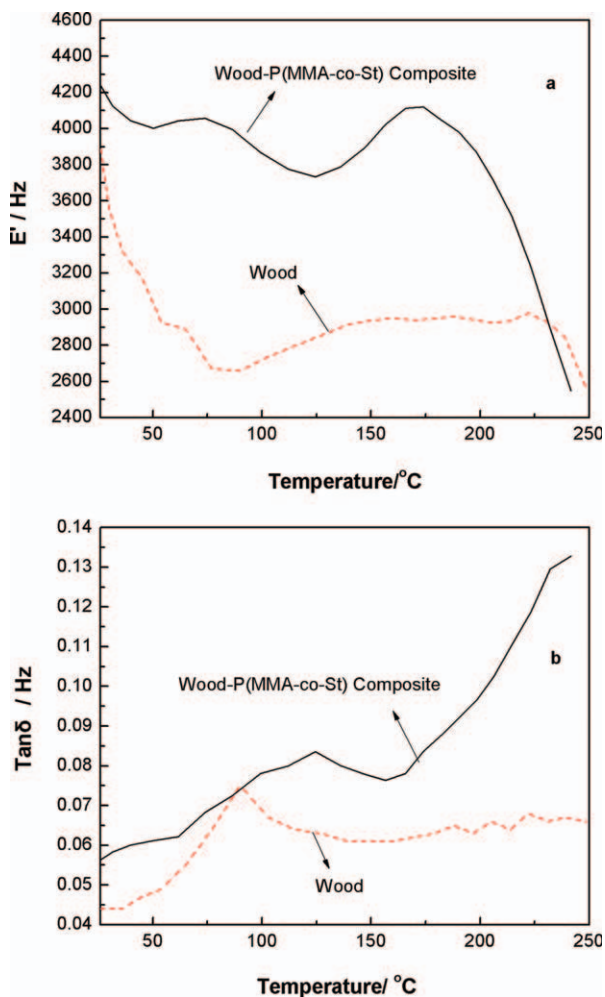
Figure 5. Storage modulus (E') and mechanical loss factor (tanδ) of wood and Wood-P(MMA-co-St) Composite versus temperature: Storage modulus (E') (a); Mechanical loss factor (tanδ) (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
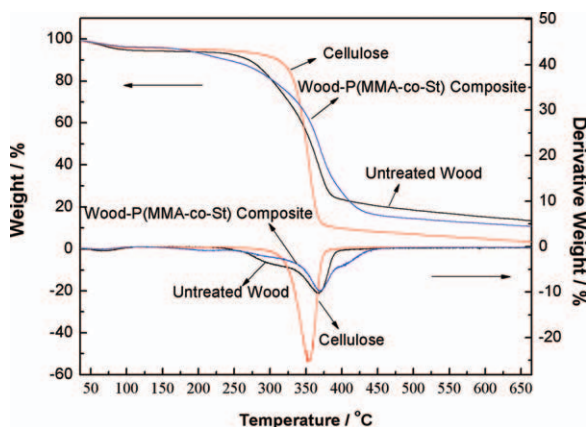
Figure 6. TG/DTG curves of untreated wood and cellulose as well as Wood-P(MMA-co-St) Composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of TG-DTG Data[a]

Sample ID	The first stage Peak temp./°C	The first stage Mass loss/%	The second stage Peak temp./°C	The third stage Onset of degradation/ °C	The third stage Peak temp./ °C	The third stage End of degradation/ °C	The third stage Mass loss/%	The fourth stage Onset of degradation/ °C	The fourth stage Peak temp./ °C	The fourth stage End of degradation/ °C	The fourth stage Mass loss/%	The fifth stage Peak temp./ °C	The fifth stage End of degradation/ °C	The fifth stage Mass loss
Untreated Wood	70	3.5	240	265	290	325	25.7	325	365	390	75.4	–	–	86.8
Cellulose	70	3.1	–	–	–	–	–	312	350	370	87.3	–	–	96.7
WPC	70	2.7	205	265	290	325	29.5	325	373	384	68.1	405	440	89.3

[a]The range of temperatures within which degradation occurs was estimated from the DTG curves and the mass loss percentage was read from the TG curves.

Table II. Decay Resistance of Untreated Poplar Wood and the Modified Wood

Sample ID	Gloeophyllum trabeum (Pers. ex Fr.) Murr.		Phanerochaete chrysosporium Burdsall	
	Weight loss/%	Change/%[a]	Weight loss/%	Change/%[a]
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

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

onset of degradation, the main degradation and end of degradation, and also mass loss in each step.

In thermogravimetric test, dehydration process is a common behavior in the samples, in which 3–5% of adsorbed water is removed. Table I and Figure 6 showed that the dehydration process happened at the range between 70 and 110°C for all the three samples with mass loss from 2.7 to 3.5%. The lowest mass loss of 2.7% for WPC indirectly presented its relatively higher resistance to wood over another two samples. The peak temperature of the second degradation for untreated wood and WPC appeared at 240 and 205°C, respectively, which corresponded to the decomposition of hemicelluloses. The relative lower peak temperature of WPC was caused by the effect of polymer on hemicellulose. For the third thermal degradation, both Poplar and WPC showed same behaviors at the temperature range from 265 to 325°C with peak temperature at 290°C. Such information implied that there was no evident reaction occurring between lignin and polymer. The fourth thermal decomposition step mainly corresponded to the degradation of cellulose. Compared to cellulose, both untreated wood and WPC showed higher thermal degradation, which should be attributed to the crosslink of cell wall components. WPC presented slightly higher peak temperature and lower mass loss over untreated wood, which should be due to the effect of polymer on the degradation of wood components. The previous researches proved that the peak degradations of PMMA and PSt mainly occurred at the range between 360 and 450°C, which corresponded to the polymer chain scission.[35–38] Such polymer chain decomposition produces monomers and oligomers, resulting in the mass loss of polymers. The decomposition peak of WPC at 405°C further validated the effect of polymer on cellulose. Over 440°C, all the three samples almost completed the thermal decomposition. The different mass loss of residues among the three samples represented the difference of components. In conclusion, the total difference of TG curves of WPC and Poplar demonstrated the effect of polymer on wood components, which endows WPC with tendency of potentially improved thermal stability.

Durability Evaluation
Decay Resistance. Table II showed that the decay resistance of WPC in terms of weight loss against the brown and white rot fungus was respectively improved 66.88 and 78.30% over those of untreated wood, indicating that the wood after polymer treatment gained improved decay resistance. The in situ formed polymer excluded water and moisture to access wood cell wall, which

resulted in insufficient moisture content within wood cell wall for the survival of most decay fungi.[39] Moreover, the polymer physically blocked the microorganisms to access the wood components, which also contributed to the improvement of decay resistance of WPC.[2,39-41] However, as the content of lignin was lower than that of holocellulose, the value of decay resistance for both Poplar and WPC against the white rot fungus was corresponding higher than those against the brown rot fungus.

VSE. Figure 7(a) showed the variation of VSE of Poplar and WPC with time. For Poplar, the VSE achieved 14.5% after
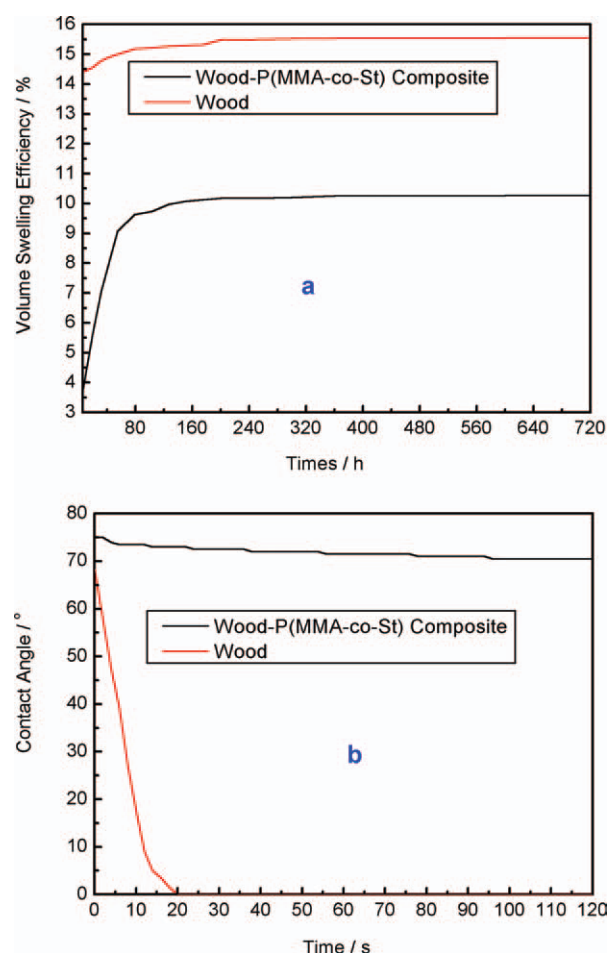
Figure 7. The curves of VSE versus times (a) and contact angle versus times (b) for wood and WPC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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. These results indicated that wood was easy to swell when it immersed in water due to the availability of great abundant hydroxyl groups on wood components. Although for Wood-P(MMA-co-St) Composite, the VSE quickly achieved about 10% after being immersed in water for the initial 80 h. After 80 h, the VSE maintained about 10% for balance. For both the composites, their VSEs reached maximum values within the initial 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 above SEM observations and FTIR analysis, it can be concluded that both the block of polymer to wood components and resistance of polymer to water contributed to the higher VSE of WPC.

Contact Angle. From Figure 7(b), it can be known that the contact angle of Poplar quickly reduced from 68 to 0° within 20 s, indicating large hydrophilicity available; while the contact angle of Wood-P(MMA-co-St) Composite almost maintained 75° within 120 s, indicating a certain of hydrophobicity, which is in agreement with the VSE results. The difference of contact angles should be also ascribed to the block of polymer to wood pores coupled with its resistance to water.

CONCLUSIONS

Poplar WPC was successfully fabricated by thermoforming of polymer from MMA and St *in situ* wood porous structure through a catalyst-thermal treatment. SEM observations and FTIR analysis indicated that the polymer well filled up wood cell lumens without reaction with wood components. XRD analysis suggested that the polymer mainly remained as an amorphous form within the cell lumen. DMA analysis demonstrated that the polymer reinforced wood substrates, which rendered WPC both improvements of glass transition temperature and storage modulus. TG/DTG test showed tendency of potentially improved thermal stability of WPC in comparison to untreated wood. The durability of WPC including decay resistance and dimensional stability was also remarkably improved over untreated wood. The VSE and decay resistance of WPC in terms of weight loss against the brown and white rot fungus was respectively improved 5.2, 66.88, and 78.30% over those of untreated wood. The static water contact angle of WPC was also higher than that of untreated Poplar. Such composite combined both advantages of wood and polymer can be regarded as a promising friendly environmental material which can be potentially wide used in fields of construction, traffic, furniture, and so forth.

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