Improved Applied Quality of Fast-Growing Poplar Derived by *in-situ* Formation of Itaconic Acid-Silica Sol Hybrid Polymer within Wood Hierarchical Cell Structure

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Poplar wood (*Populus euramericana* cv. "I-214") was impregnated by pulse dipping at 0.7 MPa to 0.8 MPa for 30 min with a catalyst $Ln \sim SO_4^{2-}/TiO_2$ —SiO₂, itaconic acid, and silica sol. Then, the modifier was cured within the wood micropores during *in situ* polymerization *via* kiln drying. The treated wood exhibited increased mechanical strength and decreased hygroscopicity. The modified samples were also characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The results from the FTIR analysis indicated that the itaconic acid and SiO₂ polymerized with the active groups of the wood cell wall. The TGA revealed that the crosslinking reaction between the modifier and wood enhanced the thermal stability of the composite. Lastly, the SEM results indicated the presence of the good interfacial adhesion in the wood modifier between the wood fibers and polymer.

Keywords: Wood; Itaconic acid; SiO₂; Esterification; In situ polymerization

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INTRODUCTION

Wood has been used for thousands of years due to its numerous favorable properties for building homes, bridges, fences, ships, and many other structures. Unfortunately, the sustainability of natural forests is now facing a severe challenge as demand is overcoming supply because of previous overexploitation (Dong *et al.* 2017). Accordingly, fast-growing wood is attracting increased interest from academia and relevant industries. Poplar, which is one of the most important species in the paper-making and timber industries (Chen *et al.* 2014a), has come into focus as a potential alternative to high-quality wood for wider applications due to its ability to grow quickly and its high value. However, despite its useful properties, poplar also possesses poor mechanical strength and unsatisfactory durability, greatly reducing its service life. In view of these reasons, there has been an increasing need and demand for alternative ways to utilize such abundant resources in value-added applications (Li *et al.* 2011).

At the same time, the interest in achieving an eco-sustainable economy and the development of biotechnology are stimulating a shift toward biobased processes. Different motivations are causing high interest in producing new biobased materials. First, the global depletion of petroleum resources and their uneven distribution around the world are encouraging the rational use of biomass as a renewable and ubiquitous resource. Additionally, the overwhelming usage of nondegradable plastics has caused serious ecological problems, further encouraging the development of new biodegradable materials

(Delidovich *et al.* 2015). Hence, the unique features of biomass-based materials have led to promising applications.

Itaconic acid (IA; also known as methylene succinic acid) is an organic, unsaturated dicarboxylic acid. In 1931, IA was discovered to be produced *in vivo* by the fungus *Aspergillus itaconicus*, which was descriptively named thereafter. To date, several other natural producers of itaconic acid have been identified, such as *Aspergillus terreus* (Calam *et al.* 1939), *Ustilago zeae* (Haskins *et al.* 1955), *Ustilago maydis*, and the yeast *Candida sp.* (Tabuchi *et al.* 1981). In 2011, mammalian immune cells were also discovered to be able to synthesize IA (Sugimoto *et al.* 2012).

The discovery of IA and its esters has received growing interest in relevant industries because of its potential role as a replacement for crude oil-based products, such as acrylic acid (Cordes *et al.* 2015). The chemical structure of IA, with its reactive conjugated double bonds and two carboxyl groups, enables IA and its derivatives to be used in a large variety of industrial applications, such as monomers and co-monomers for plastic polymer synthesis, as well as for resins and lattices (Willke and Vorlop 2001; Okabe *et al.* 2009). In addition to the main polymerization product, poly(itaconic) acid (PIA), several copolymers, such as styrene-butadiene-itaconic acid (SBIA) latex (Veličković *et al.* 1994), can also be prepared. Itaconic anhydride (IAn) can be used in the production of unsaturated polyester resins (UPRs) during substitution to maleic anhydride (Robert *et al.* 2011). As mentioned above, IA may also be used as a replacement for petroleum-based compounds, such as acrylic or methacrylic acid (MAA), forming methyl methacrylate (MMA) followed by polymerization to produce polymethyl methacrylate (PMMA) (Nagai 2001).

Wood and acid biopolymers have been used as constituents of innovative biocomposite materials that have exhibited remarkable properties for industrial bending, stamping, and flooring uses. However, for the past few years most of the early studies on IA applications focused on the synthesis of resins, and few reports are available in literature regarding wood modification.

Theoretically, IA can react with the hydroxyl groups in wood through esterification with $Ln \sim SO_4^{2-}/TiO_2$ -SiO₂ as the catalyst (Li *et al.* 2013). Furthermore, the conjugated structure of IA, which possesses high activity, greatly increases its reactivity with both wood and polymer matrixes, resulting in crosslinking or strong adhesion at the interface.

The impregnation treatment can be performed using mobile low molecular weight monomers, and then polymerization can be induced in wood *in situ*. A group of researchers has conducted a series of experiments on green wood impregnation (Chen *et al.* 2014b). A considerable body of evidence exists showing that chemical modification with certain reagents improves the mechanical properties of the modified wood, and the swollen cell walls that become filled with polymers enhance the dimensional stability of the wood.

Organic-inorganic treatment is an emerging method for modifying fast-growing wood materials by chemical reactions to achieve improved mechanical properties, durability, and even new functions (Trey *et al.* 2012; Merk *et al.* 2014; Li *et al.* 2016a, 2016b; Zhu *et al.* 2016). Silicon, which makes up approximately 25% of the earth's crust, is the second most abundant element after oxygen. Silicon is required for the formation of bones and connective tissue. In addition, silicates and most other silicon compounds are classified as being nontoxic (Mai and Militz 2004).

The ability to modify wood by applying a sol-gel process using a silica solution has been reported by several research groups. At the same time, these inorganic nanomaterials have been explored by incorporating them into polymers to improve their mechanical properties and thermal stability. In theory, chemically binding nano-SiO₂ to polymer chains could produce a crosslinking network that would endow wood with excellent durability. In addition, the sol-gel process could be used to finely control the morphology and distribution of the generated inorganic nanomaterials within the polymer matrix to tailor the properties of the integrated material (Maggini *et al.* 2012).

According to the aforementioned modifications in this study, as shown in Fig. 1, the *in situ* polymerization between IA, silica sol, and the active groups of wood was investigated. The mechanical properties of natural and modified wood were evaluated. Moreover, the reaction that occurred during modification was characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermal analysis (TGA), and scanning electron microscopy (SEM). The focus of the whole study was to characterize the mechanism of chemical modification using IA and SiO₂ from a chemical perspective.



Fig. 1. Schematic illustration to natural wood and the *in situ* modified wood: (a) three-dimensional (3D) natural wood; (b) 3D microstructure of (a) with aligned channels; (c) cell wall assembled from bundles of cellulose nanofibers with abundant hydroxyl groups; (d) 3D modified wood; (e) 3D microstructure of (d) with filled hybrid polymer; and (f) the organic–inorganic hybrid polymer with crosslinked polymer chains and inorganic nanomaterial well-defined in cell lumen and grafted onto cell walls

EXPERIMENTAL

Materials

The fresh poplar (*Populus euramericana* cv.'I-214') wood samples used in this study were obtained from Beijing, China. The initial moisture content of the wood ranged from 60% to 75% before impregnation. The IA was supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Nanosized neutral silica sol was prepared by Dezhou Jinghuo Glass Technology Co., Ltd. (Dezhou, China). All other chemicals were analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Catalysts Preparation- Preparation of SO₄²⁻/TiO₂

The typical synthesis of the SO_4^{2-} / TiO₂ solid acid catalyst was conducted according to a previous paper (Hino *et al.* 1979): first, 10 g of titanium sulfate (Ti (SO₄)₂) was dissolved in 90 g of distilled water under vigorous stirring. Then, aqueous ammonia (28 wt.%) was added dropwise to adjust the pH value of the above solution within the range of 9 to 10, and afterwards, a solid was slowly formed. After separating and washing the solid with deionized water, the obtained TiO₂ solid was dried at 100 °C for 24 h. Next, 2 g of TiO₂ was impregnated with 30 mL of 1 N sulfuric acid (H₂SO₄) for 2 h. The treated solid was evaporated at 80 °C until it was dried into powder. Then, the materials were powdered using a 100-mesh sieve and calcined in air at 500 °C for 6 h to prepare the final SO₄²⁻/TiO₂ catalyst.

Preparation of Ln~SO4²⁻/TiO2-SiO2

First, 10 g of a mixture of Ti(SO₄)₂ and sodium silicate (Na₂SiO₃) were dissolved in 90 g of distilled water under vigorous stirring, and the molar ratio of Ti to Si was 25:1. Then, aqueous ammonia (28 wt.%) was added dropwise to adjust the pH value of the above solution within the range of 9 to 10, and afterwards a solid was slowly formed. After separating and washing the solid with deionized water, the obtained TiO₂–SiO₂ solid was dried at 100 °C for 24 h. An appropriate amount of lanthanum trioxide (La₂O₃) was dissolved in 2 mol/L H₂SO₄ to prepare a mixture solution, and the concentration of the La³⁺ ions was 0.07 mol/L. The TiO₂–SiO₂ was impregnated within the mixture solution for 2 h, and the ratio was 15 g TiO₂–SiO₂ per 100 mL of solution. Afterwards, the precipitate was evaporated and calcined using the same method used to prepare SO₄^{2–}/TiO₂ to obtain La³⁺~SO₄^{2–}/TiO₂–SiO₂.

Pulse Dipping of the IA and Silica Sol

The poplar logs chosen for impregnation were approximately 200 mm in diameter, and they were sawn to be 1000 mm in length. First, the fresh poplar was stabilized on a pulse-dipping machine (designed by the College of Materials Science and Technology, Beijing Forestry University, Beijing, China) with a clamping pressure of 17 MPa to 18 MPa along the longitudinal direction. Then, IA (10% w/w) and the $Ln \sim SO_4^{2-}/TiO_2 - SiO_2$ catalyst (0.45% w/w) were impregnated into one side of the log by pulse dipping at a pressure of 0.7 MPa to 0.8 MPa using a reciprocation pump. Hence, the tree growth was oriented along the pulse-dipping direction so that the tree sap and diluted modifier could flow out from the other side of the log. Gradually, the tree sap in the xylem was continually replaced by the original modifier for 30 min (Pu et al. 2009). After soaking, the impregnated wood pieces were sawn into blocks that were approximately 50-mm-thick (t) \times 120-mm-wide (r) \times 1000-mm-length (l) for kiln drying (designed by the College of the Materials Science and Technology, Beijing Forestry University, Beijing, China). The drying time was approximately 200 h. The pressure on the timber was 0.2 MPa. The drying kiln temperature was increased from room temperature to 135 °C (Chen et al. 2014b). Afterwards, the same steps were conducted to impregnate the wood using the silica sol.

Density and Mechanical Properties

The treated and untreated samples were prepared for mechanical property and dimensional stability testing, and the standards used are as follows: the method of testing in compressive strength parallel to grain of wood GB/T 1935 (2009), method for determining the wood density GB/T 1933 (2009), and method of testing in bending strength

of wood GB/T 1936.1. (2009). The average data of ten specimens for each kind of measurements were recorded.

Weight Percent Gain (WPG)

The WPG after pulse-pressure impregnation was calculated according to the formula below; the measurements were repeated using 10 samples,

$$WPG(\%) = \frac{m_2 - m_1}{m_1} \times 100\%$$
(1)

where m_1 is the oven-dry weight (g) of the untreated wood specimens with dimensions of 20 (l) × 20 (r) × 20 (r) mm³, and m_2 is the oven-dry weight (g) of the wood specimens after impregnation with the same dimensions.

Hygroscopicity

Rectangular specimens were prepared with dimensions of 20 (l) \times 20 (t) \times 20 (r) mm³, and the specimens were weighed after drying in an oven at 105 °C until the weight change was less than 0.02 g after 2 h. Then, the specimens were immersed in distilled water. After immersion, the excess water on the surface was removed by a soft cloth, and the weights and volumes of the specimens were measured during 72 h; the water uptake was reported as the weight gain/volume percentage. The measurements were repeated using 10 samples (Chen *et al.* 2014b).

Contact Angle Analysis

The water repellency of the wood surfaces before and after treatment was analyzed after conducting water contact angle measurements using a FTA 200 dynamic contact angle analyzer (First Ten Ångstroms, Portsmouth, VA, USA). Sessile droplets of distilled water (70 μ L) were deposited on the surfaces of the wood samples. The contact angles between each droplet and the sample surface were measured every 60 s.

X-ray Diffraction Instrument

The crystallinity of samples from the untreated and treated wood was evaluated by XRD using a Shimadzu diffractometer (model XRD 6000, Kyoto, Japan). The measurement conditions were as follows: CuK α radiation with a graphite monochromator, 30 kV voltage, and 40 mA electric current. The patterns were obtained within a 5° to 30° 2θ angular interval with a 0.05° step and a scan speed of 2°·min⁻¹. The degree of crystallinity was calculated as the ratio of the intensity differences in the peak positions.

Thermal Analysis

The thermal behaviors of the samples were evaluated using a TGA device (GDT-60, Shimadzu, Kyoto, Japan). Samples weighing approximately 8 mg were heated from 50 °C to 600 °C at a heating rate of 10 °C/min under an inert atmosphere of N₂ with a flow rate of 10 mL/min.

SEM Analysis

Scanning electron microscopy was used to characterize the elemental composition and morphology of the untreated and treated wood. Pieces were cut from the wood samples by ultramicrotome (EMUC7, Leica, Solms, Germany), coated with gold using a spraying instrument (Yulong Co., Ltd., Beijing, China), and observed with an electron microscope (S-3000N, Hitachi, Tokyo, Japan) with an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Density and Mechanical Properties

The density and mechanical properties are summarized in Table 1 (the data were averaged from 10 specimens). The air-dried density of the IA/SiO₂-treated wood increased 39.5%, and the oven-dried density increased 40.5%. Compared to the IA-treated and SiO₂-treated specimens, the IA/SiO₂-treated wood exhibited an improved bending strength 36.0% and a better compressive strength parallel to the grain 72.1%. These results coincided with the expectation that the composite modifier-treated samples would have much better mechanical properties than the single modifier-treated samples.

Properties	Natural wood	SiO ₂ -treated wood	IA/SiO2-treated wood
Air-dried density (g•cm ⁻³)	0.38 ± 0.029	0.49 ± 0.059	0.53 ± 0.058
Oven-dried density (g•cm ⁻³)	0.37 ± 0.033	0.47 ± 0.061	0.52 ± 0.039
WPG (%)	—	30.78 ± 3.65	48.22 ± 2.74
Bending strength (MPa)	75.54 ± 6.43	93.94 ± 7.96	102.70 ± 6.61
Compressive strength parallel to the grain (MPa)	43.57 ± 3.81	61.80 ± 5.73	74.99 ± 7.37

	Table 1. Mechanical	Properties of th	e Natural and	Modified Wood	d Samples
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Hygroscopicity

Lower moisture and water absorption is an indication of good shape stability. Data on the water uptake of the IA/SiO₂-treated wood are presented in Fig. 2.



Fig. 2. Water uptake curves of the natural and IA/SiO₂-treated wood

As shown, the final water uptake of the IA/SiO₂-treated wood decreased from 77.2% to 49.2%. This suggested that the IA/SiO₂ could effectively improve the water repellency of the base wood. Additionally, the wettability of the wood surface was studied by the contact angle of the water droplets, which is shown in Fig. 3. As was expected, the treated wood showed an increased contact angle compared with natural wood. This result was in good accordance with the result of the water uptake analysis given previously.



Fig. 3. Contact angles of the natural and modified wood: (a) natural wood at 0 s; (b) SiO2-treated wood at 0 s; (c) IA/SiO₂-treated wood at 0 s; (d) natural wood at 60 s; (e) SiO₂-treated wood at 60 s; and (f) IA/SiO₂-treated wood at 60 s

The improved water-repellent properties of the modified woods were partly attributed to the fact that the grafting modification of the wood cell walls covered portions of the hydroxyl groups. Furthermore, the larger polymers formed by the IA/SiO₂ that remained in the lumen may have formed a barrier on the lumen face that decreased the water absorption to some extent. In addition, a tighter network may have been formed in the presence of IA/SiO₂.

XRD Characterization

The XRD was used to identify the intercalated structure of the wood. Figure 4 presents the curves of the natural and modified wood samples. The natural wood exhibited typical cellulose I diffraction angles of approximately 17° , 22.5° , and 35° , corresponding to the cellulose crystallographic planes of I_{101} , I_{002} , and I_{040} , respectively. After modification, the location of the peaks did not change, indicating that the ordered structure of the crystalline region on the remaining cellulose was not disrupted during modification (Zhao *et al.* 2007). However, the crystallinity degree of the modified wood decreased.

The drop in the crystallinity degree could be inferred from the results indicating that -COOH and Si-OH interacted with the cellulose in the form of hydrogen bonds or even covalent bonds after the removal of water. Simultaneously, ester groups could also be formed in the presence of IA, accompanied with self-crosslinking reactions of both the silica sol and IA. It seemed that_these reactions increased the size of the spaces between the cellulose in the amorphous region. As time passed, this caused the amorphous region to expand, resulting in a decrease in crystallinity (Fu *et al.* 2006).

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Fig. 4. XRD patterns of the natural and modified wood: (a) natural wood; (b) IA/SiO₂-treated wood; and (c) SiO₂-treated wood

However, the crystallinity degree of the IA/SiO₂-treated wood was slightly higher than that of the SiO₂-treated samples, possibly because the remaining IA in the IA/SiO₂-treated wood may have hydrolyzed the hemicellulose and lignin in the amorphous regions, which consequently increased the proportion of the crystalline region to some extent.

FTIR Analysis

To further investigate the probable chemical bonds among modified wood, the FTIR spectra are presented in Fig. 5. For natural wood, the broad bands at 3400 cm⁻¹ and 1050 cm⁻¹ were prominent, corresponding to –OH stretching and various polysaccharide vibrations (Horikawa *et al.* 2006; Devi and Maji 2012).



Fig. 5. FTIR spectra of the natural and modified wood: (a) natural wood; and (b) IA/SiO₂-treated wood

After the organic phase or the two phases had reacted within the porous wood structure, the peak at about 1650 cm⁻¹ (C=O stretching vibration) and 1150 cm⁻¹ (C-O-C asymmetric stretching of cellulose and hemicellulose) became remarkably reinforced, and at the same time, the new absorption peak appeared at 2850 cm⁻¹ (C-H symmetric stretching vibration of -CH₂). Such a phenomenon proved the successful introduction of IA into wood structure (Chen *et al.* 2014a). In addition, the presence of SiO₂ was manifest at 1250 cm⁻¹ (Si-O-C), 812 cm⁻¹ (Si-O), and 705 cm⁻¹ (Si-O-Si) (Gwon *et al.* 2010). This suggested the chemical hybridization of the organic and inorganic phases.

TG Analysis

A TGA was used to ascertain the thermal stability of wood. In Fig.6, the TG and DTG curves of the untreated and treated wood are compared.



Fig. 6 (A&B). Thermogravimetric analysis curves of the wood: (a) natural wood; (b) SiO₂-treated wood; and (c) IA/SiO₂-treated wood. A: TG curves; B: DTG curves

From the curves, the pyrolysis process of untreated wood was divided into four weight loss stages. The first step, from room temperature to 110 °C, was the dehydration process. When the temperature increased to 290 °C, the peak in the corresponding DTG curve was ascribed to the thermal degradation of the hemicellulose and regions of unstable cellulose. Then, the maximum weight loss of over 60% from 220 °C to 370 °C was observed as a result of the decomposition, oxidation, and combustion of cellulose, accompanied with the removal of small molecules such as CO₂, CO, CH₄, and CH₃OH. Afterwards, the samples continued to decompose at approximately 336°C, further ablating the molecular chains and oxidizing the lignin and residual carbon (Wu *et al.* 2011).

The treated samples presented remarkable improvement of thermal stability. The maximum pyrolysis temperature of the treated wood reached 370 °C, which was significantly improved by 34 °C in comparison to that of untreated natural wood. In addition, the final weight loss of the treated wood was also improved when compared to natural wood. Both these enhancements could be interpreted to the synergistic effect resulting from the new network structure caused by the reaction between IA, SiO₂ and hydroxyl of wood (Gao *et al.* 2004; Zou *et al.* 2008; Tan and Cheetham 2011).

SEM Analysis

The SEM images of the natural and modified woods are presented in Fig. 7. The natural wood samples clearly exhibited a highly porous structure [Fig. 7(a)], and a film of the modifier covered the wood, forming a polymer layer. Compared to the single SiO_2 modifier [Fig. 7(b)], the polymer layer became prominently thicker when treated with IA/SiO₂ [Fig. 7(c)].





Fig. 7. SEM micrographs of the natural and modified wood: (a) radial section of the natural wood; (b) radial section of the SiO₂-treated wood; and (c) radial section of the IA/SiO₂-treated wood

This result correlated with the hypothesis that the participation of IA enhanced the penetration of the silica sol and consequently enabled higher polymer loading. The SEM studies provided evidence that strong interfacial adhesion in the wood modifier between the polymer and wood cell walls contributed to the above obviously improved physicochemical properties of the wood (Zou *et al.* 2008; Tan and Cheetham 2011).

Illustration of the Possible Reaction Mechanism

The possible reaction mechanism is shown in Fig. 8 as a simplified diagram. At first, the fresh poplar wood was impregnated with IA and silica sol by the application of the pulse-dipping pressure. During this process, the impregnated modifier could flow through the wood cells and wet the cell walls.



Fig. 8. Illustration of the reaction between the functional group of wood and impregnated modifier

First, IA participated as an *in situ* polymerization reaction. Esterification between IA and the –OH groups of the wood fibers provided additional anchor reaction sites for SiO₂. These sites enabled the formation of not only hydrogen bonds with the wood fibers but interactions with the unreacted –COOH groups of IA to form ester groups, and led to a tighter combination between the wood and modifier. Moreover, crosslinking occurred within IA due to the presence of double bonds; the crosslinking continuously expanded within the wood to form a kind of tight network structure.

Second, it was reasonable to assume that after being impregnated in the wood, the silica sol deposited on the fibers and prefilled the IA. At elevated temperatures, the polymerization process became faster. The Si-O-Si framework became spread out within the gel. In addition, the oligomers of the IA and Si-O-Si framework could react with each other as the -CO-OH and Si-OH groups formed CO-O-Si bonds. Additionally, the wood-OH groups could react with Si-OH groups to form hydrogen bonds, making the whole system more stable and hydrophobic.

Moreover, the modifier had the ability to fill the void spaces and the highly branched polymers inside the wood, which enhanced the mechanical properties (Lang *et al.* 2015).

CONCLUSIONS

- 1. Poplar wood (*Populus euramericana* cv. "I-214") was successfully impregnated with itaconic acid (IA) and silica sol. Impregnation occurred as the mobile low-molecular weight monomers diffused throughout the wide-bore capillary column system within the fast-growing poplar xylem, and then, polymerization was induced in the wood *in situ*.
- 2. The treated wood exhibited increased mechanical strength and decreased hygroscopicity. Such materials are expected to be usable for industrial bending, stamping, and flooring uses, depending on their physical properties.
- 3. The wood and modifier *in situ* polymerized within lightweight wood cell structure with high strength and excellent durability due to the formation of covalent bonds between the ester groups, wood hydroxyl groups, and silanol groups.

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