RESEARCH ARTICLE

Improvement of decay resistance of wood by *in-situ* hybridization of reactive monomers and nano-SiO_2 within wood

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Abstract: In order to improve the decay resistance of wood, we propose a novel method by *in-situ* hybridization of reactive monomers and nano-SiO_2 within wood porous structure to modify wood structure and chemical components. Glycidyl methacrylate (GMA), and polyethylene glycol-200 dimethacrylate (PEGDMA) were first mixed and then penetrated into poplar wood cell lumen by vacuum/pressure treatments, followed by *in-situ* hybridization under an initiation condition. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and transmission electron microscopy (TEM) observations described that the polymer-inorganic hybrid nanocomposite filled up cavities and tightly contacted the wood cell wall. Nano-SiO_2 particles were uniformly dispersed into the formed polymer within wood pores. Fourier transform infrared spectroscopy (FTIR) analysis suggested that the nano-SiO_2 probably chemical bonded to the polymer during the monomer polymerization. The derived wood-based polymer-inorganic hybrid nanocomposite exhibited remarkably improvement in decay resistance over the untreated wood as controls. Such treatment could potentially widen the wood applications with outstanding decay resistance.

Keywords: wood, porous structure, decay resistance, nano-SiO_2, organic-inorganic hybrid nanocomposite, reactive monomer

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1. Introduction

Wood is a renewable and degradable biopolymer composite, which has always been a popular material by human as its unique texture, higher heat insulation, and desired specific strength-weight ratio. It has a cellular structure mainly composed of three biopolymers, *i.e*., cellulose, hemicellulose, and lignin. Such structure could impart high tensile strength to wood with lower quality. As the biopolymers are easy to be degraded by microorganisms, wood is vulnerable to be attacked when exposed to fungi, especially at high humidity condition. When wood is surrounded by wet environmental condition, moisture could be easily absorbed by the biopolymer components as abundant hydroxyl groups. The components and moisture play an important role in the wood degradation as food and water for microorganism survival[1].

In addition, fast-growing wood is becoming more and more important as alternative to high quality wood to meet the people's need. However, such wood normally has low quality, which reversely limits the wide applications as structural materials.

In order to overcome the drawbacks of the low-quality wood, variety of methods has been employed, such as heat treatment, compression treatment, filling polymer and so on[2–4]. One of the most suitable technologies is using polymer to fill up wood porous structure so that water and microorganism could be rejected from wood substance as blocking of the paths[5–10]. Meanwhile, the polymer could share part of strength for wood, which improves the mechanical properties[11–12]. Many monomers are employed to produce polymer within wood cell lumen such as methyl methacrylate, styrene, vinyl acetate, acrylonitrile and so on[13–22]. However, these monomers are low-polar reagents that are hard to react with wood components, leading to poor compatibility between wood and polymer. Consequently, under such condition, the gaps could be potentially become the pathway of moisture and microorganisms to attack wood, resulting in dimensional instability and lower decay resistance[23–26]. Although several employed functional monomers such as glycidyl methacrylate, allyl glycidyl ether and anhydride showed good decay resistance and dimensional stability, the further exploration of other functional monomers is preferred, and such study is rarely reported[27–28].

Under such background, we employs several novel reactive monomers containing glycidyl methacrylate (GMA), polyethelyene glycol 200-dimethacrylae (PEG200DMA) and maleic anhydride (MAN) to modify the fast-growing wood, poplar in north of China. Nano-SiO_2 particles with C=C double bonds are also chosen as modifier to react with the monomers through *in-situ* hybridization. In theory, the groups of monomers and nano-SiO_2 are capable of copolymerizing under a certain thermal-catalyst condition, and simultaneously grafting onto wood matrix through chemical reaction of hydroxyl group and the epoxy group and/or cyclic anhydride group[4,6–7]. The PEG200DMA could potentially provide toughness to the cross-linked polymer and further extending to wood matrix for modifying the brittleness of wood-polymer composite. During the polymerization, nano-SiO_2 with C=C double bond chemically bonding to polymer chains could produce a cross-linking network that endows wood excellent durability. The preparation process and theoretical reaction of the resulted wood-based organic-inorganic hybrid nanocomposite can be demonstrated in the following scheme (Figure 1).

This paper deals with decay resistance of the modified wood by characterizing its microstructure and comparing the decay resistance of the wood-based organic-inorganic hybrid nanocomposite with common wood-polymer composites and unmodified natural wood.

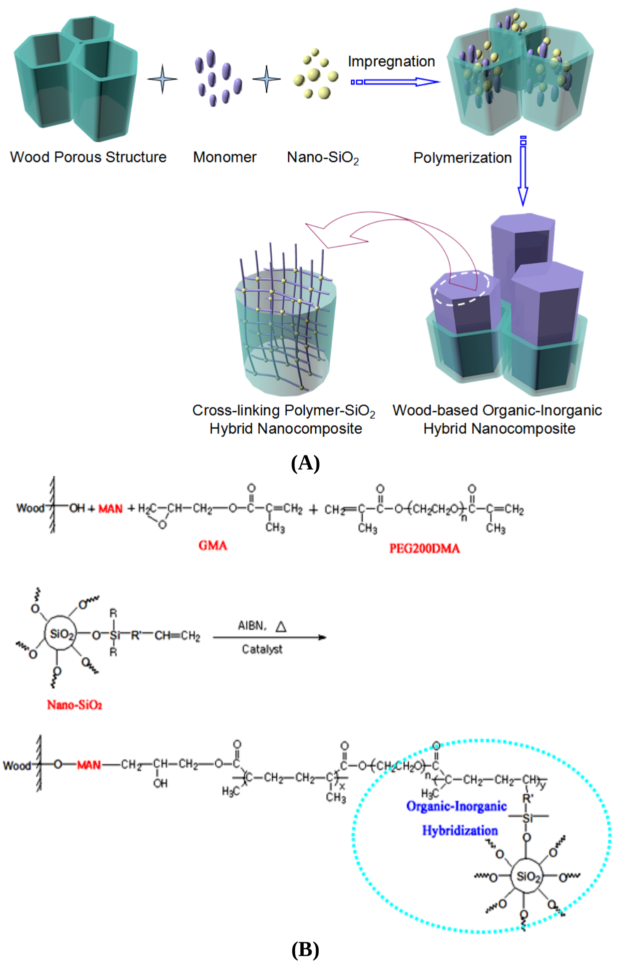


Figure 1. Schematic illustration to: **(A)** the preparation of wood-based organic-inorganic hybrid nanocomposite and **(B)** the mainly probable reaction mechanism.

2. Experimental Details

2.1 Materials

GMA (Nanjing Jiulong Chemical Industry Co., Ltd., Nanjing China), PEG200DMA (Yantai Yuntai Chemical Industry Co. Ltd., Yantai China), MAN and 2,2'-azobisisobutyronitrile (AIBN) (both of them purchased from Shanghai Chemical Reagent Factory, Shanghai China) are directly used without purification. The modified Nano-SiO_2 with 30 nm in diameter (Zhejiang Hongsheng Material Technology, Co. Ltd., Hangzhou China) is also used directly.

Poplar wood (*Populus ussuriensis* Kom) was brought from Maoershan plantation in Heilongjiang province of China. Samples of 20 × 20 × 10 mm^3 (Radial × Tangential × Longitudinal) were cut from the lumber and oven-dried at 105°C for 24 h, and then stored for further use. All %-data are, if not otherwise indicated, based on weight.

The vacuum/pressure equipment is self-made, and the ultrasonication equipment (HB-1990QT) with parameters of 100 W, 25°C is purchased from Dongguan Bixin Industry (Guangdong, China).

2.2 Preparation of WPC

Nano-SiO_2 was first vacuum dried at 105°C for 24 h and then dispersed into solution of GMA and PEG-200DMA (2:1 molar ratio), which gave 0.5% concentration of nano-SiO_2 in the solution. After that, the suspension was ultrasonically treated at 25°C for 30 min for evenly dispersion of nano-SiO_2. Then, MAN was further dissolved in acetone with 10% concentration. And AIBN was then dissolved in the above mixed monomers solution to form 1.0% (w/w). After that, the MAN solution was mixed with the above monomers solution, in which, MAN accounting for 6wt% of GMA and PEG200DMA. The mixed solution was further impregnated into wood samples under the vacuum/pressure condition of 0.08 MPa for 20 min followed by 0.8 MPa for 20 min[27]. Finally, the wood samples were oven-dried at 80°C for 8 h, followed by 110°C for 8 h after wrapping it in aluminum foil. The obtained samples were labeled as wood-P(GMA-co-PEG200DMA)-SiO_2 hybrid nanocomposite, wood-polymer-SiO_2 hybrid nanocomposite in short.

2.3 Characterization and Analysis

Scanning electron microscopy (ESEM) instrument (QUANTA 200, FEI Inc., Hillsboro USA) was used to characterize the morphology of the polymer within wood cell lumen. The location of nanoparticles in the wood was identified through X-ray composition analysis of the samples during the scanning process. The image of element Si, which is mainly from nano-SiO_2 for the wood-polymer-SiO_2 hybrid nanocomposite, was captured for analysis of the distribution. For TEM (Jeol USA, Inc., MA USA) observation, ultra-thin sections with a thickness of about 50 nm were microtomed at –80°C using a Leica Ultracut E cryo-ultramicrotome. FTIR spectra (KBr technique) were recorded with the instrument Magna-IR560 E.S.P (Thermo Nicolet Inc., Madison, USA).

2.4 Evaluation of Decay Resistance

This test was done according to the “Chinese forest industry standard-Laboratory methods for the toxicity test of wood preservatives on decay fungi (LY/T1283-02011)”, which is referred to the international fungal decay test, JIS K 1571-Qualitative standards and testing methods of wood preservatives[6].

A minimum of five wood samples were employed for the test. The specimens were first autoclaved for 30 min, and then placed on wood feeder chips with dimensions of 22 × 22 × 2 mm^3 (R × T × L) in an incubator with 3 samples. The relative condition is humidity of 80% and temperature of 28°C. The test was performed for 12 weeks. A brown decay fungus, *Gloeophyllum trabeum* (Pers. ex Fr.) Murr., and a white decay fungus, *Phanerochaete chrysosporium* Burdsall were employed in this test.

The polymer loading rate was calculated in terms of the following Equation 1:

$$R_m = (G_i – G_0) / G_0 \times 100\% \qquad (1)$$

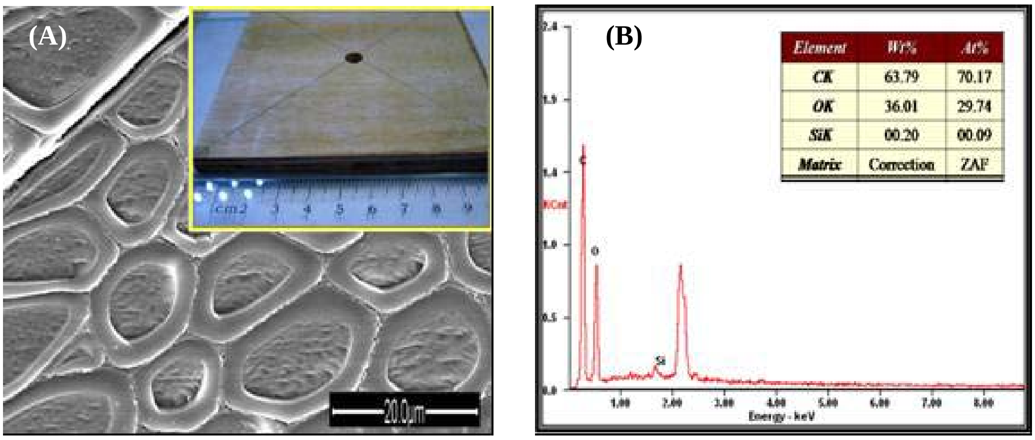
where R_m is polymer loading rate, G_i means weight of wood-based composite, and G_0 represents weight of natural wood.

The resultant wood-polymer-SiO_2 hybrid nanocomposite obtained a (70.5±2.3)% of weight percent gain. For comparison, wood-polymer composite was prepared with (72.9±3.1)% of weight percent gain.

3. Results and Discussion

3.1 SEM Observations

Figure 2(A) describes that the resultant polymer tightly contact wood cell walls without obvious gaps, which proving the strong interaction between the two phases. Considering the structure and the probable reacting mechanism as shown in Figure 1, it could be reasonably believed that chemical interaction between the two phases plays an important role in the interaction. Figure 2 illustrates the electron microprobe analysis results of the wood-polymer-SiO_2 hybrid nanocomposite. Figure 2(A) shows the cross-section morphology of the composite and the inner photo is the real wood sample, and Figure 2(B) shows the captured Si element in the corresponding section of the sample. From Figure 2(B), it is seen that the middle lamella have the highest concentration of Si, implying that the nanofillers diffuse in the lamella.



Element	Wt%	At%
CK	63.79	70.17
OK	36.01	29.74
SiK	00.20	00.09
Matrix	Correction	ZAF

Figure 2. Electron microprobe analysis of wood-polymer-SiO_2 hybrid nanocomposite, **(A)** transversal face, and **(B)** Si elemental distribution.

3.2 TEM Observations

Figure 3 illustrates the transmission electron microscopy (TEM) analysis of the wood-polymer-SiO_2 hybrid nanocomposite, confirming that nanoparticles slightly aggregated at about 50 nm in diameter have been successfully dispersed in the polymer within wood cell lumen. Thus, it both contributes to enhance the mechanical properties of the wood[29], and improve the durability (dimensional stability and decay resistance) as well.

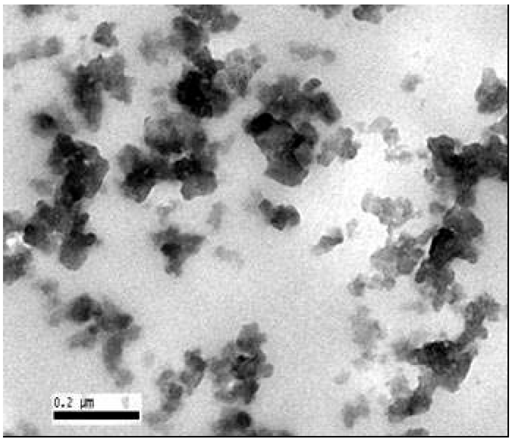


Figure 3. TEM morphologies of the wood-polymer-SiO_2 hybrid nanocomposite.

For the nanofiller, better dispersion behavior was observed, and better interactions of the organophilic nanofillers with the polymer substance were expected and achieved as proved by the following FTIR analysis in Figure 4.

3.3 FTIR Analysis

Figure 4 shows that there was an increased intensity in an absorbance peak at 1735 cm^{-1} corresponding to the carbonyl stretching vibration, 1060 cm^{-1} corresponding to the ether stretching vibration of the wood-polymer composite and wood-polymer-SiO_2 nanocomposite, respectively. This feature demonstrates the presence of MAN, GMA, and PEG200DMA[4–6]. The hydroxyl groups on the wood and the two wood-based composites peak at 3394 cm^{-1}, representing the stretching vibration. The peak of the later two samples is weakened in comparison to the untreated wood, indicating reaction occurring between the chemicals and wood substrates. The decrease of hydroxyl groups and the increase of carbonyl groups indicate the grafting of the monomer/polymer onto the wood matrix through the reaction of the cyclic anhydride of MAN/epoxy groups of GMA with the hydroxyl groups on wood, as shown in Figure 1(B). The C-O-C asymmetrical stret-

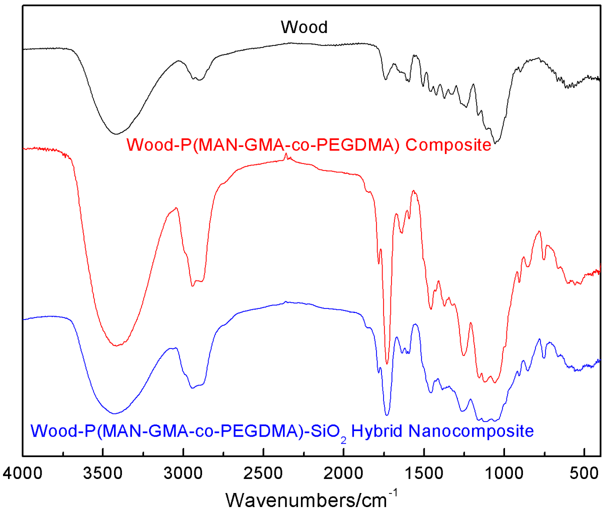


Figure 4. The FTIR spectra of wood, wood-polymer composite, and wood-organic-inorganic hybrid nanocomposite.

ching vibrations peaking at 1164 cm^{-1} show a visible enhancement as evidence of the reaction between GMA/PEG200DMA copolymers with the hydroxyl groups on wood, resulting in polyethers[5,7]. Compared with wood-polymer composite, only the peak at 1060 cm^{-1}~1260 cm^{-1} representing the stretching vibration of Si-O bond in wood-polymer-SiO_2 nanocomposite become slightly wider, indicating chemical bond produced between polymer and nano-SiO_2. Consequently, it can be concluded that the resultant polymers exhibit a chemical interaction with the wood components and nanofillers, and contribute strength and durability to wood matrix, which can be further supported by property testing.

3.4 Decay Resistance

Table 1 presents the decay resistance of the wood-P(GMA-co-PEG200DMA)-SiO_2 hybrid nanocomposite when exposing to microorganisms attack. Comparing the control natural wood, the weight loss of the modified wood against the brown and white decay fungi is improved by 95.84% and 97.43%, respectively. This indicates that the modified wood possesses remarkably improved decay resistance. The cross-linked hybrid polymer tightly contact wood matrix, resulting in moisture that makes microorganisms hardly accessible to the wood cell wall. Moreover, the probably chemical grafting of hybrid polymer onto wood may also change the wood chemical components, which results in irrecognition by the microorganisms. Both factors contribute to the enhanced decay resistance of our modified wood[8]. Thus, the organic-inorganic hybridization inspired from wood porous structure is an effective way to modify wood for excellent decay resistance.

Table 1. Comparison of decay resistance of wood-organic-inorganic hybrid nanocomposite and unmodified wood against brown rot fungus (*Gloeophyllum trabeum* (Pers. ex Fr.) Murr.) and white rot fungus (*Phanerochaete chrysosporium* Burdsall)

Fungus Species	Brown Fungus [*Gloeophyllum trabeum* (Pers. ex Fr.) Murr.]		White Fungus [*Phanerochaete chrysosporium* Burdsall]	
Sample	Weight Loss/%	Change*/%	Weight Loss/%	Change*/%
unmodified wood	79.28(3.91)	—	27.61(1.34)	—
wood-P (MAN-GMA-co-PEGDMA) -SiO_2 hybrid nanocomposite	3.30(0.19)	95.84	0.71(0.05)	97.43

*change is a comparison of modified wood to unmodified wood

4. Conclusions

From the structural characterization and property test of the new wood-P(MAN-GMA-co-PEGDMA)-SiO_2 hybrid nanocomposite, we can reasonably draw conclusions as follows: (i) monomers and nano-SiO_2 reacted within wood cell lumen via *in-situ* hybridization, and the resultant polymer tightly interact with wood cell wall without obvious gaps; (ii) the nano-SiO_2 is well distributed in the polymer, aiding in the interaction between polymer and wood; (iii) the strong interaction remarkably improved the decay resistance of our modified wood as it is having quite lower weight loss compared to that of unmodified wood. Such way could be extended to modify other wood species and potentially broaden the wood applications.

Author Contributions

Dong X Y, Zhuo X, and Liu C contributed equally to this work. Li Y F and Dong X Y designed the experiment. Dong X Y, Zhuo X and Liu C carried out experiment of preparing wood-based composites. Wei J and Zhang G measured the properties of composites. Pan R T performed the characterizations. Dong X Y, Zhuo X, Liu C and Li Y F wrote the paper. Everybody comments on the final manuscript.

Conflict of Interest and Funding

No conflict of interest was reported by the authors.

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