

Property Improvement of Wood by Organic-inorganic Hybrid Polymer

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Abstract. Fast-growing wood plays an important role in addressing the contradiction between supply and demand of wood. However, the low-quality of fast-growing wood limits its wide applications as an alternative to high-quality wood. Consequently, we design organic-inorganic hybrid polymer as reinforcer to improve the mechanical properties and thermal stability of poplar wood. Poly(ethylene glycol) dimethacrylate (PEG200DMA) as an organic agent, tetraethoxysilane (TEOS) as an inorganic agent and γ -(methacryloxypropyl) trimethoxy silane (KH570) as a coupling agent were employed to form organic-inorganic hybrid polymer in wood via free radical polymerization and hydrolysis-condensation reaction, in order to impart the high toughness of polymer, and high thermal stability of inorganic matrix to wood. The modulus of rupture, compression strength, impact toughness and hardness of the resulted wood is remarkably increased by 61%, 57%, 140% and 221% over untreated wood, respectively.

1. Introduction

Wood has been a kind of raw material which is essential to human life since ancient times. It has been widely used in the fields of construction, transportation, interior decoration and sports equipment. However, in recent years, almost all the countries around the world have restricted timber cutting. At the same time, the supply of high-quality wood is limited. On the other hand, people's pursuit of the quality of life requires an increasing supply of wood. Sharp contradictions between supply and demand of wood have promoted the widespread cultivation of fast-growing species. Although the fast-growing wood has eased the contradiction to some extent, it has the inherent defects such as poor quality and poor strength. Consequently, it is difficult to substantially replace high-quality wood, and thus effective modifications are urgently needed to overcome the defects of the poor strength of the fast-growing wood[1-2].

The reported methods on wood modification include: 1) in-situ formation of polymer within wood to form wood-polymer composites to increase the strength of the wood[3-8]; 2) in-situ formation of

inorganic materials in wood to form wood-inorganic composites to improve the strength and thermal stability of wood[9]; 3) compression treatment to increase the strength of wood[10]. However, all these methods have certain fatal defects, and are difficult to make the modified wood being met the practical requirements. For example, 1) although the strength of the wood-polymer composite is significantly increased, the impact toughness is far lower than that of unmodified wood, suggesting brittleness; 2) the strength of wood-inorganic composites are normally less improved and brittle; 3) the strength of compressed wood are traditionally improved, but the thickness are easy spring-back in wet condition. Although the dimensional stability could be improved by impregnating formaldehyde-based resins, such treatment adversely results in significant reduction in the impact toughness of the modified wood. In other words, it can not simultaneously increase strength and impact toughness.

As organic-inorganic hybrid nanocomposite possesses the strength and toughness of the organic object and the rigidity, thermal stability and function of the inorganic object, indicating synergistic enhancement of the hybrid compounds in nanoscale, it becomes the fourth generation of new materials which are after one-component materials, composite materials and functional gradient materials. It has become a hot research topic in the field of materials science.

In this context, this study attempts to use functional monomers with flexible chain unit and polymerizable C=C double bond as the organic object, and tetraethoxysilane (TEOS) as the inorganic agent, and duplicate silane as the coupling agent, to form organic-inorganic hybrid polymer within the natural cell pores of wood. The purpose is to impart the high strength, high toughness of the polymer and thermal stability of the inorganicism to the untreated wood and accordingly form an integrated wood .

2. Experiments and materials

2.1. Test materials

Glycidyl methacrylate(GMA) (Shanghai Yuanji Chemical Co. Ltd.) and 2,2-Azobisisobutyronitrile(AIBN) (Shanghai Reagent 4 Factory) are analytical Reagents (AR). Poly(ethylene glycol) dimethacrylate (PEG200DMA) (Yantai Yunkai Chemical Co., Ltd.) is chemically purified (CP) agent. Tetraethoxysilane (TEOS) (Tianjin Komio Chemical Reagent Development Cente) is analytical reagent(AR). γ -(methacryloxypropyl) trimethoxy silane (KH570) (Nanjing Shuguang Chemical Group Co., Ltd..) is chemically purified agent. Laboratory chemical reagents such as hydrochloric acid(38wt), tetrahydrofuran, acetone, anhydrous ethanol, deionized water, are analytical reagent. All these chemical reagents can be used directly.

The wood species is *Populus Ussuriensis* Komarov, which was collected from Heilongjiang Maoershan Forest Plant. The size of the wood plates is 25 ×300×2000 mm³ (radial (R)×tangential (T) ×longitudinal (L)). After three-month adjustment at room temperature, the average moisture content of the wood plate reached 10.4 wt%. Then the specimens are dried at 105°C for 24h to form an average density of 0.35 g/cm³, and further stored for use afterward.

The experimental equipments and instruments include impregnation tank (home-made with size of 300mm × 600mm (inner diameter × high) and maximum pressure of 1.7 MPa), vacuum oven (DZF-6050 purchased from Shanghai Precision Instrument Instrument Co., Ltd.), WL-1 Particle Ball Mill (Tianjin Computer Room Equipment Factory), Atomic-force microscopy (AFM, NaioAFM, Nanosurf AG, Liestal, Switzerland) with tapping mode, QUANTA2000 Environmental Scanning Electron Microscope (ESEM) (FEI Company), Magna IR 560 Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet Company in US), D/max2200 X-ray diffraction instrument (Rigaku Corp., Tokyo, Japan) (XRD), and Thermogravimetric Analysis (TG/DTG, Q5000IR, TA Instrument, New Castle, Delaware).

2.2. Test methods

1) First, GMA and PEG200DMA were mixed into 100 mL tetrahydrofuran at a mass ratio of 20:1; and then, AIBN, which accounts for 0.5 % of the total mass of the monomer, was added, followed by KH570, which is 20 wt% of the total solution. The mixed solution was stirred for 15 min. Finally, the condensation reaction was cycled at 65~70 °C for 70min, followed by severe stirring at room temperature for 10 minutes. 2) At the same time, 0.3 M TEOS, 1.2 M deionized water, and a certain amount of 38 wt% hydrochloric acid to make the mixed liquid with pH = 3.5 were employed to react at 45 °C for 3h. 3) The above two kinds of solutions were mixed and stirred at room temperature for 30 minutes. Then, they were divided into two groups. One was poured into a glassware, which was sealed and saved it for 5 days (room temperature). Then the pre-reacted samples were stored at 30-35 °C for 2 days, and then at 45-50 °C for 2 days, and then at 70-80 °C for 1 day, and then at 105-110 °C for 1 day to form completely polymerized hybrid polymer for comparison. The other one was used to impregnate wood by the vacuum-pressure tank under the conditions of -0.8 MPa for 10min, followed by 0.8 MPa for 10min. After being wrapped in aluminum foil, the treated wood samples were stored at room temperature for 5 days, and then heated at 30-35 °C for 2 days, and at 45-50 °C for 2 days, and at 70-80 °C for 1 day, and at 105-110 °C for 1 day to finally obtain the wood-hybrid polymer composite. With the same steps, the above amounts of GMA, PEG200DMA and AIBN was mixed and impregnated into wood to form wood-polymer composite for comparison.

All the prepared samples were characterized by SEM, AFM, FTIR, XRD and TG/DTG (Thermogravimetry/Differential Thermogravimetry). Before FTIR and TG experiments, the polymer was extracted by THF for 24h.

The specimens' preparation and test methods for the properties evaluation were conducted according to the "national standard methods for testing wood physical and mechanical properties" (GB1928-2009). The size of the specimens for modulus of rupture measurement is 20mm × 20mm × 300mm (R × T × L), and the size of the specimens of the compression strength test is 20mm × 20mm × 30mm (R × T × L), and the size of specimen of the impact toughness test is 20mm × 20mm × 300mm (R × T × L). Each experiment was conducted in parallel for 5 times to obtain the mean value of the property.

3. Results and analysis

3.1. Microstructural morphology analysis

Figure 1a shows that there are nanoscale pores in the hybrid polymer and nanoparticles in the matrix. Figure 1b shows that the particle size in the hybrid polymer matrix is about 100nm, which is consistent with the structure of figure 1a. The structure should be ascribed to the fact that 1) the acidic hydrolysis condensation of ethyl silicate forms a granular spherical SiO₂, and the particle size can be controlled at the nanometer level when the conditions (pH, reaction time, etc.) are appropriate; 2) the particle size is linked by polymer chain, and the organic and inorganic objects are evenly combined on nanoscale to form organic-inorganic hybrid polymer. Figure 1c clearly shows that the polymer is densely packed in the wood cell lumen. Figure 1d further proves that the polymer in Figure 1c is combined with silicon-containing compounds, suggesting that the wood-based organic-inorganic composite is formed.

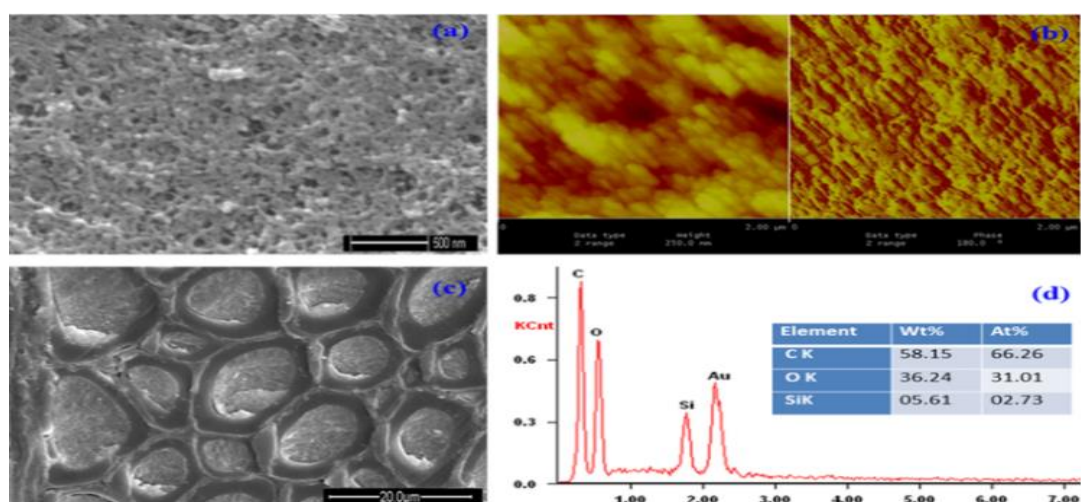


Figure 1. Microstructural topography of Hybrid Polymer and Wood-Hybrid Polymer Composite: (a) SEM morphology of Hybrid Polymer, (b) AFM morphology of Hybrid Polymer, (c) SEM photo of the Wood-Hybrid Polymer Composite, (d) the EDX mapping of figure(c).

3.2. Fourier transform infrared spectrometry (FTIR) analysis

Figure 2 proves that the hybrid polymer, untreated wood, wood polymer composite and the wood-hybrid polymer composite presents peaks at 3400cm^{-1} , 2960cm^{-1} , 2880cm^{-1} , 1730cm^{-1} , 1260cm^{-1} , 1160cm^{-1} corresponding to the stretch vibration of $-\text{O}-\text{H}$, $=\text{C}-\text{H}$, $-\text{C}-\text{H}$, $-\text{C}=\text{O}$, $-\text{C}(=\text{O})-$ and $-\text{C}-\text{O}$ (or $\text{Si}-\text{O}$) groups, respectively. The stretch vibration of wood-hybrid polymer composite at 1260cm^{-1} is more intensive than the that of wood-polymer composite and also untreated wood, suggesting $-\text{C}-\text{O}$ (or $\text{Si}-\text{O}$) groups formed in the hybrid polymer. In addition, same phenomena was observed at 1730cm^{-1} , suggesting that the polymer and hybrid polymer grafted onto wood components. In other words, the polymer can not only form chemical bonds with the wood component, but realize the connection of polymer chain with the inorganic component through $\text{Si}-\text{O}$ bond.

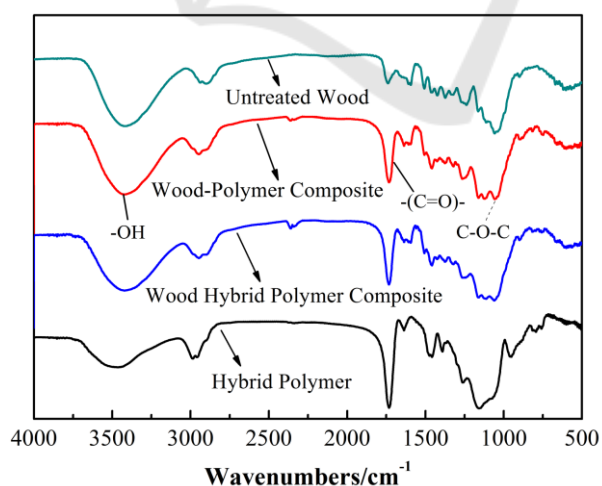


Figure 2. FTIR spectrogram of Untreated Wood, Hybrid Polymer, Wood-Polymer Composite and Wood-Hybrid Polymer Composite.

3.3. X-ray diffraction(XRD) analysis

Figure 3 shows that the hybrid polymer has no obvious crystal peak, indicating that it is an amorphous material. The untreated wood presents obvious peak at $2\theta=16.5^\circ$ and $2\theta=22.5^\circ$ assigned to the lattice plane of (101) and (002), respectively, which suggests crystal I form of the untreated wood. The wood-polymer composite and wood-hybrid polymer composite present similar peaks at $2\theta=16.5^\circ$ and $2\theta=22.5^\circ$, suggesting their same crystal form to that of untreated wood. However, their peaks are quite lower than those of the untreated wood, which should be ascribed to the fact that the amorphous polymer grafted onto wood components resulted in higher amorphous aggregation of the treated wood and thus decreased by the crystallinity of the wood-polymer composite and the wood-hybrid polymer nanocomposite. Such results proves the chemical grafting of the polymer onto wood components.

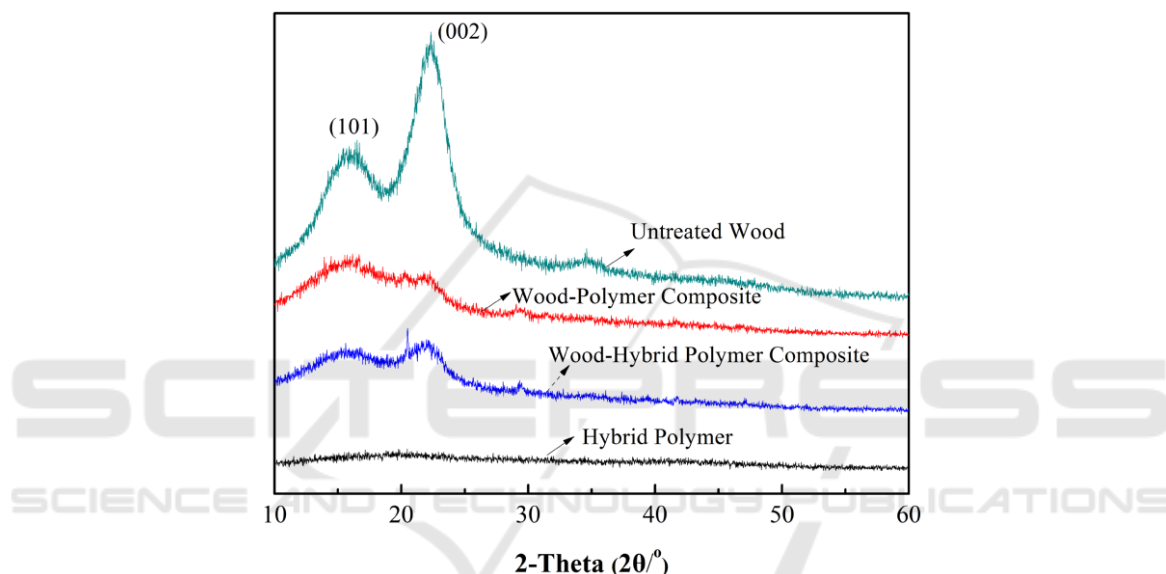


Figure 3. XRD spectrogram of Hybrid Polymer, Wood - Polymer Composite and Wood-Hybrid Polymer Composite.

3.4. Thermogravimetry and differential thermogravimetry (TG/DTG) analysis

Figure 4 shows that the hybrid polymer begins pyrolysis at 300°C , while the three wood materials begin to undergo obvious pyrolysis at 275°C , indicating that the wood materials are more likely to begin degradation than the hybrid polymer. The untreated wood and the wood-polymer composite present their maximum thermal decomposition temperatures at about 480°C , while the hybrid polymer and the wood-hybrid polymer composite are basically degraded at about 500°C , suggesting improved thermal stability of the wood-hybrid polymer composite due to its hybridization polymer formed in wood. In addition, in terms of the weight loss, the descending order is wood-polymer composite, untreated wood, wood-hybrid polymer nanocomposite and the hybrid polymer, indicating that the hybrid polymer improved the thermal stability of wood.

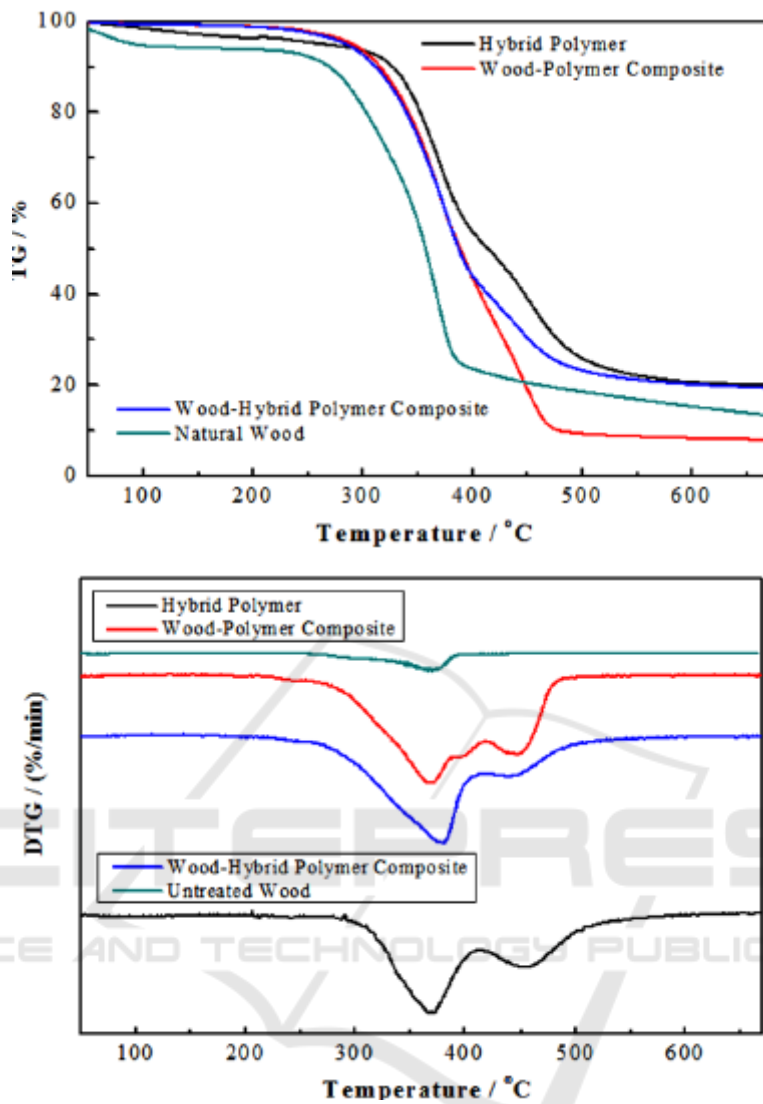


Figure 4. TG/DTG curves of Hybrid Polymer, Untreated Wood (i.e., Natural Wood), Wood-Polymer Composite and Wood-Hybrid Polymer Composite.

Table 1. Comparison of mechanical properties of untreated wood and other two wood materials.

Mechanical properties The name of the specimen	The modulus of rupture (Tangential section)		The compression strength (Rift grain)		The impact toughness (Tangential section)		The hardness (Tangential section)	
	The absolute value (MPa)	Multiple (Compared to the material)	The absolute value (KJ/m ²)	Multiple (Compared to the material)	The absolute value (KJ/m ²)	Multiple (Compared to the material)	The absolute value (N)	Multiple (Compared to the material)
Untreated Wood	57.47	—	39.2	—	35.23	—	1752	—
Wood-Polymer Composite	90.82	1.58	56.1	1.43	99.34	2.82	5072	2.89
Wood-Hybrid Polymer Composite	92.36	1.61	61.6	1.57	84.62	2.4	5619	3.21

*The polymer quality of all kinds of wood composites accounts for 70~ 100% of the quality of wood materials. The test data is the mean of 5 parallel test results. The hardness number is the pressure value when the head is pressed at depth of 2.81mm under the wood surface. The size of the specimen is about 50 × 50 × 20 (mm) (L × R × T).

3.5. Performance analysis

According to the data shown in table 1, the modulus of rupture, compression strength, impact toughness and hardness of the resulted wood is remarkably increased by 61%, 57%, 140% and 221% over that of untreated wood, respectively. The results should be due to the hybrid composition of the polymer and the inorganic object, which makes the molecular chains into stereo cross-linked form, and accordingly improves the mechanical properties of wood. Interestingly, the thermal stability of the hybrid wood is also improved. This consistence should be ascribed to the formation of the hybrid polymer within wood that presents in cross-link form, which in turn contributes to enhanced stability of the polymer as reinforcer of wood. The strong hybrid polymer consumes more energy of the external loading and heating, enabling simultaneously improved mechanical properties and thermal stability of wood.

4. Conclusions

- 1) The organic-inorganic hybrid polymer is produced in wood pores, and the wood-hybrid polymer composite is synthesized by organic-inorganic hybrid technology. Among them, the inorganic moiety is evenly distributed in the polymer matrix *in situ* formed within wood cell lumen, and the nanoparticle size is around 100nm.
- 2) The succeeded composition of the hybrid polymer and wood obviously improves the thermal stability of wood with enhancement of maximum pyrolysis temperature of about 20 °C over untreated wood. And the modulus of rupture, compression strength, impact toughness and hardness of the resulted wood is remarkably increased by 61%, 57%, 140% and 221% over untreated wood, respectively.

Author contributions

Jie Wei, Ruo Zhao, Zhixing Yang, Baoxuan Liu, Jing Dong and Yongfeng Li designed the experiment. Jie Wei, Ruo Zhao and Zhixing Yang performed the whole experiments. Jilong Fan, Changkai Wang and Yun Sun helped to do some experiments. Baoxuan Liu and Canghai Li provided the wood materials for the whole experiments. Jie Wei, Xiaoying Dong and Yongfeng Li wrote the paper. Everybody comments on the final manuscript. Jie Wei, Ruo Zhao and Zhixing Yang contributed equally to this work. Baoxuan Liu, Jing Dong and Yongfeng Li are corresponding authors.

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