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The composite wood by poplar wood impregnated with Na_2SiO_3-polyacrylamide hybrid solution

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Abstract

The Na_2SiO_3-polyacrylamide (PAM) inorganic/organic homogeneous hybrid was prepared by polymerization of acrylamide monomer in the presence of a water-glass solution. Then, the hybrid was introduced into pores of poplar wood by impregnation treatment, and composite wood was produced. The structure of the controlled and treated wood specimen was investigated by scanning electrode microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The thermal stability of the composite wood was evaluated by thermogravimetric (TG) and oxygen index. The results showed that the treated wood showed a lower weight loss and higher oxygen index when weight percent gains (WPG) of the composite wood reached 31.6%. Also, the composite wood showed improved bending strength, modulus of elasticity in static bending, and hardness, when compared with controlled samples.

Keywords: composite wood; hybrid solution; impregnation; Na_2SiO_3-polymer.

1. Introduction

Controlled chemical modification has been proven to be a promising way to improve wood properties [1]. A number of chemical substances, including inorganic and/or organic components, have been tested, and some have shown improvement in the mechanical properties and/or dimensional stability of wood [2]. It is reported that the bending, tensile and impact strength of beech and spruce wood decreased a little whereas compression strength increased [3], as a result of the impregnation of water-soluble salts. Furuno et al. [4] treated *Chamaecyparis obtuse* Endl wood with water glass and sodium silicate (SS). Then aluminum sulfate and calcium chloride solution were introduced [4]. The resulting wood showed high resistance to fungal and fire resistance, but displayed high water absorbency. Further improvement was manipulated by treating similar wood with SS, then with barium chloride, or boric acid and borax to form a water insoluble metallic silicate [5]. The treated wood showed moisture resistance and dimension stability, but had reduced bending strengths. Zhou et al. [6] impregnated SS and aluminum silicate into *Populus tomentosa* wood. The resulting material indicated an improved dimensional stability, fire resistance and decay resistance [6]. To reduce leaching of inorganic salts, some treatments were made by Na_2SiO_3 and/or silicon alkoxide using the sol-gel method [7, 8]. Also, organic monomers are used in wood modification by filling the capillaries, vessels and other void spaces after being polymerized in wood in order to increase the dimensional stability [9]. However, the expense of the monomer required to achieve an acceptable level of expected properties was too high. To address this problem, the hybrid and/or complex composites produced by blending inorganic and organic components were used. The composite of silica sol with styrene-acrylic emulsion, and that of silica sol with acrylate emulsion have been prepared and impregnated into poplar wood. The resulting composite wood material showed remarkable improvement in compression strength and water resistance [10, 11]. Soluble SS has been used as a reagent for wood modification by researchers, because of its unique chemical properties e.g., heat and chemical stability, polymerizing capability, and viscosity regulating ability. In order to improve the properties of SS, the homogenous solution of Na_2SiO_3-PAM hybrid was synthesized by *in vitro* polymerization. Then, the hybrid was introduced into pores of poplar wood. The structure and performances of as-formed composite wood were investigated.

2. Experiments

2.1. Materials

Poplar 72 (*Populus euramericaha cv. I-69/58*) was collected in the Huaining county of Anhui province in China, according to GB1929-91. The dried poplar timbers were cut in China into specific sample blocks with size according to GB1928-1929-91. The sample blocks were preliminarily dried in a ventilated oven at 103°C until a constant weight was achieved, and were then placed in the desiccator. Na_2SiO_3 with Na_2O/SiO_2=2.4 was provided by Beijing Letai Chemical industiral grade Co. (Beijing, China); acrylamide (AM) with analytical grade was purchased from Tianjin Fuchen Chemical Co. (Tianjin City, China); potassium persulfate (KSP)with analytical grade was provided by Beijing Chemical Co. (Beijing, China).

2.2. Preparation of the Na_2SiO_3-PAM hybrid

In a typical synthesis process, 32 g of Na_2SiO_3 was dissolved in 68 g of distilled water in a three-neck bottle equipped by a stirrer and a condenser at 60°C. Then, 5.4 g of AM was added to the bottle. After fully stirring, 0.11 g of KSP was added and the temperature was elevated to 80°C. After reaction for 4 h, 0.82 g of N,N′methylene bis acrylamide as a crosslinking agent was injected and constantly stirred for 0.5 h. Finally, the bottle was cooled to room temperature, and the homogenous Na_2SiO_3-PAM hybrid solution, with 38.2 wt% solid content and 14.0 mPa·s of viscosity, was prepared.

2.3. Impregnation of poplar with Na_2SiO_3-PAM hybrid solution

Fast-growing poplar was impregnated by the hybrid solution according to a vacuum-high pressure impregnation process achieved by a SBK-450B instrument (Japan). Specifically, the fully dried and weighed samples were placed into a 5.0 l column tank with 15 cm diameter. Firstly, the tank was vacuumized to -0.09 MPa for 0.5 h. Then 4.5 l of the Na_2SiO_3-PAM hybrid with 38.2 wt% of solid content and 14.0 mPa·s of viscosity was sucked into the tank system under vacuum. Twenty min later, pressure in the tank was increased to 1.0 MPa. Keeping 1.0 MPa for 0.5 h and releasing the tank pressure to atmospheric, samples were taken out and fully dried. As a result, the treated samples reached 31.6 wt% of the average weight gain rate (WPG), compared with that of the controlled samples.

2.4. Structure characterizations

Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Bruker Vertex-70 FTIR spectrometer (Germany) equipped with a diffuse reflectance accessory. The completely dried samples (Na_2SiO_3-PAM hybrid, untreated and treated wood) were investigated and the spectra were acquired at room temperature for a total of 32 scans on a 400~4000 cm^{-1} wave number range; TG experiments were carried out using an instrument, STA449C DTA (Germany). Samples approximately 10 mg in weight were introduced into a quartz sample pan and heated from room temperature to 700°C at 10°C min^{-1} using nitrogen at a flow rate of 50 ml min^{-1} as purge gas; the oxygen index of the samples was tested by a JF-3 Oxygen Index Detector (China), according to the GB/T2406-93 Chinese standard. Controlled and treated wood pieces (120×10×0.5 mm^3 L×W×T) were used for each test, and fifteen tests were carried out for each group. The top of sample was ignited in a pyrex tube with 75 mm inner diameter and 450 mm height under an adjustable concentration of oxygen. The concentration of oxygen was averaged for each group, which was named as the oxygen index, when the sample can burn for 30 s.

2.5. Mechanical characterizations

The modulus of elasticity in static bending of the wood was measured according to GB1936.2-91 Chinese standard using Al-50kN test machine (Japan). The load was applied on two sites of 1/3 span of the sample block (300×20×20 mm^3 L×T×R), and the constant 3 mm min^{-1} deformation rate was applied to the controlled and treated specimens. The deformation value with applied force was recorded, and the modulus of elasticity in static bending of wood was calculated according to the formula: $E_w = \frac{23Pl^3}{108bh^3 f}$, where E_w is the modulus of elasticity in static bending of wood (MPa), P is the applied load (N), l is the distance between two supports (240 mm), b is the width of the sample (20 mm), h is the specimen thickness (20 mm) and f is the deformation value (mm). The value of the modulus of elasticity in static bending was averaged over 10 samples.

The bending strength of the samples was measured by a three-point bending test method adapted from GB1936.1–91 Chinese standard using Al-50kN test machine and applying a constant 3 mm min^{-1} deflection rate to the treated and control specimens of solid wood block (300×20×20 mm^3 L×T×R) until breaking occurred. Bending strength was calculated according to the formula: $\sigma_B = \frac{3F_{\max}L}{2bh^2}$, where σ_B is the bending strength (MPa), F_{max} is the maximum load (N), L is the distance between two supports (240 mm), b is the width of the sample (20 mm) and h is the specimen thickness (20 mm). Ten tests were carried out for each group.

The Brinell hardness was performed by GB/T1941-1991 standard. A 5.64±0.01 mm diameter steel ball was pressed into a tangential section of treated and control specimens of solid wood (70×70×50 mm^3 T×L×R) with 3~6 mm min^{-1} pressing rate until a depth of 2.82 mm. The moisture content of the wood with 20 mm×20 mm×20 m cut from cross section of the specimens was measured. The Brinell hardness was calculated according to the formula: *Hw=KP*, where *Hw* (N) was the hardness with wt% of moisture content of the wood, *K* was the coefficient named 4/3 with a pressed depth of 2.82 mm and P was the applied load (N).

3. Results and discussions

3.1. The SEM image of the Na_2SiO_3-PAM hybrid and the composite wood

Figure 1(A) shows the SEM images of the prepared Na_2SiO_3-PAM hybrid. It can be seen from the top-right image of Figure 1(A) that the inorganic Na_2SiO_3 and PAM polymer chain interacted and formed a continuous interface. The light part of the image was the Na_2SiO_3 phase, while the dark area was that of PAM. These two components interlinked each other with network as shown in inset of Figure 1(A), which was no obvious phase separation between the inorganic and organic components. When the hybrid solution was introduced into voids of poplar wood, the SEM pictures of the formed composite wood were shown as in Figure 1(B) and (C). The treated sample preserved the main structural features of poplar wood and the general morphological arrangement was not changed by the impregnating process. The hybrid filler mainly appeared as a deposit within the voids of the vessels and pits of the wood. The solid deposits partly occluded the pores of the wood structure and other apertures. Transverse scanning of the wood revealed

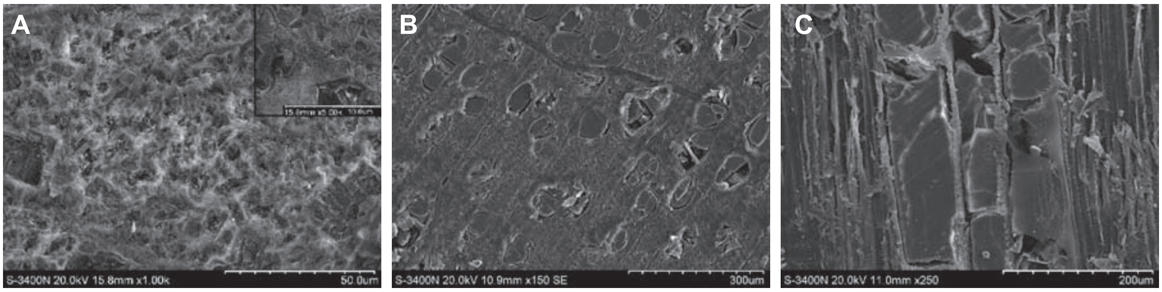

Figure 1 SEM pictures of the materials. (A) The prepared Na_2SiO_3-PAM hybrid (B) the transverse section of the treated wood (C) longitudinal section of the treated wood.

rod-shaped solid filler at the inside of most of the vessels. This solid filler followed the longitudinal direction. It did not cover the entire area of the cell walls of the vessels, but left some parts and bordered pits uncovered as in Figure 1(C).

3.2. The FTIR analysis

The FTIR spectra of the prepared Na_2SiO_3-PAM hybrid, the controlled and the treated poplar wood samples are presented in Figure 2. From Figure 2(A), the FTIR spectrum of the Na_2SiO_3-PAM hybrid showed a broad and overlapping peak within the range of 2750 cm^{-1} and 3750 cm^{-1}, which was assigned as the stretching vibration of -N-H bonds of PAM and -O-H bonds of Na_2SiO_3. Also, it covered bending vibration of -C-H bonds of PAM at about 2890 cm^{-1}. Moreover, another sharp peak around 1636 cm^{-1} was attributed to the vibration peak of -C=O bonds of PAM. Two very near and almost overlapping peaks around 1097 cm^{-1} and 1009 cm^{-1} resulted from the -Si-O bond of Na_2SiO_3 and the -C-N bonds of PAM, respectively. In addition, the peaks from stretching vibration of -Si-O and bending vibration of -Si-O-Si were shifted to 871 cm^{-1} and 761 cm^{-1}, respectively, [11]. This indicated that the inorganic Na_2SiO_3 and organic PAM formed the hybrid by Si-OH bond of Na_2SiO_3 and C=O and N-H bonds of PAM via hydrogen bonding. The FTIR spectra of the untreated poplar sample in Figure 2(B) showed the stretching vibration absorption of –O-H bonds at 3340 cm^{-1} and -C-H at 2893 cm^{-1} of cellulose and hemicellulose of the polar wood. In addition, the peaks

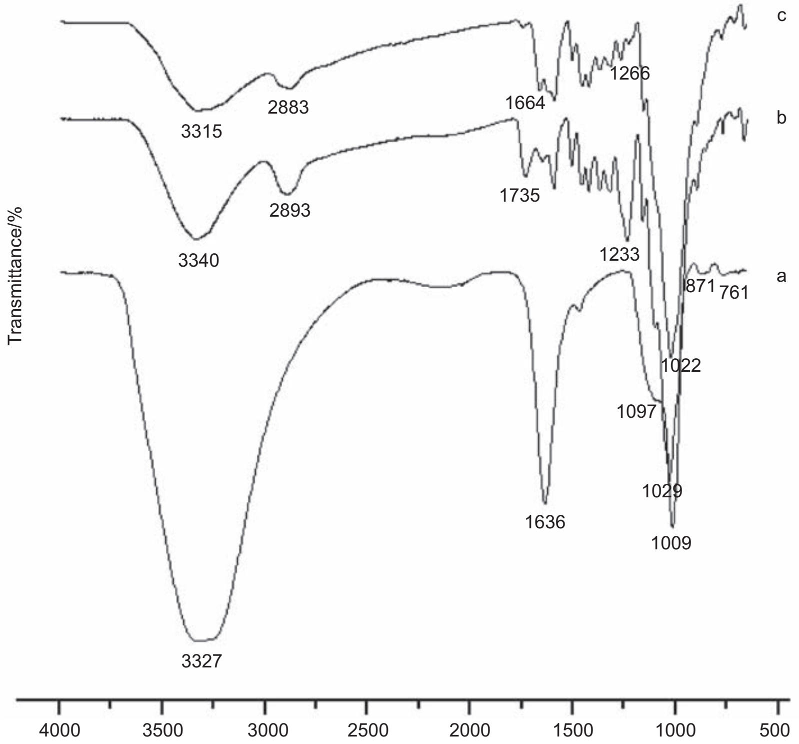

Figure 2 FTIR spectrum of the specific material. (A) The prepared hybrid (B) untreated poplar (C) treated sample.

from the stretching vibration of –O-CH and –-C-O-C were shown at 1233 cm^{-1} and 1029 cm^{-1}. In comparison, the spectra of the treated sample in Figure 2(C) indicated that the strong adsorption peak of hybrid at 3327 cm^{-1} became weak, resulting from the interaction of -N-H and –O-H bonds of the hybrid with –O-H and C=O bonds of the cellulose and hemicellulose in wood. Also, the peak of C=O in Figure 2(C) became little and weak at 1664 cm^{-1}, which was the result of the peak shifts of C=O bond of the hybrid and the C=O bond of the wood. Moreover, the peaks of –O-CH and –C-O-C of the wood were shifted from 1233 cm^{-1} and 1029 cm^{-1} to 1266 cm^{-1} and 1022 cm^{-1}, respectively in Figure 2(C), due to the influence of Si-O- bonds of the hybrid. Therefore, the results of FTIR indicated that the composite polar wood was formed as result of the groups of the hybrid interaction with that of poplar.

3.3. The TG analysis

The thermal behavior of the controlled and treated wood specimens in a nitrogen atmosphere was presented through the TG curves in Figure 3. The curve of the controlled specimen in Figure 3(A) showed that the main decomposition occurred at the range of 250–380°C, resulting in a mass reduction of 65.13%. This weight loss was mainly due to releasing combustible gases during the heating of the poplar wood. When the temperature was above 380°C, the weight loss became slow, mainly from the release of the remaining combustible gas. The weight loss rate attained 76.54% when the temperature was 650°C. In comparison, the weight loss of the treated sample in Figure 3(B) occurred at heating, due to releasing some small molecules of PAM. The obvious weight loss occurred at temperatures between 200°C and 320°C, leading to mass reduction of 41.93% at 320°C. This weight loss was mainly ascribed to the release of combustible gases of the wood and partly decomposition of PAM. The weight loss slowed down when the temperature was higher than 320°C. When the temperature was 650°C, the total weight loss of the composite wood was 56.25%, 20% lower than that of the controlled one. This indicated that the silicate inorganic components in the hybrid can endure higher temperatures and can hopefully improve the thermal stability of poplar wood.

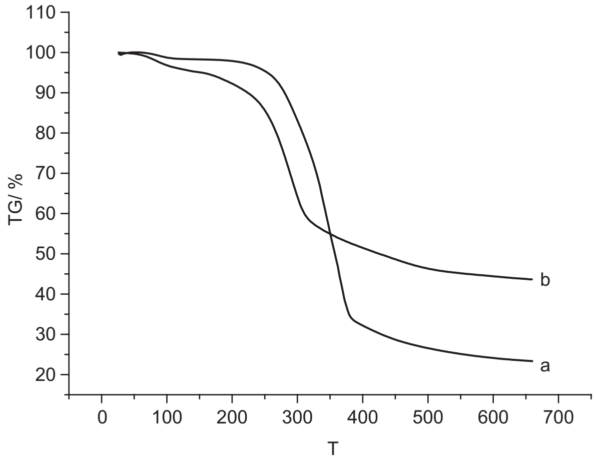

Figure 3 TG curve of the samples. (A) untreated wood (B) treated wood.

In order to indicate the thermal property of the samples further, the oxygen index of controlled wood and treated wood were investigated. The results showed that the controlled specimen was easy to burn at the atmospheric oxygen concentration. The average oxygen index was 21.7%. However, the treated sample was less combustible. It can not be burned with an oxygen concentration <50%. The average oxygen index of the composite wood was 50.3%. The increased oxygen index further indicated that the composite poplar wood showed improved thermal property and was less flammable.

3.4. The mechanical properties of the samples

The measured bending strength, elastic modulus and hardness of the materials are shown in Table 1. From Table 1, the bending strength of the controlled specimen was 64.43 MPa, while that of the treated specimen was 71.62 MPa. The modulus of elasticity in static bending of the treated wood was 10.37 GPa, increased by 18.2% compared with that of the controlled wood, 8.77 GPa. The measured hardness of samples in Table 1 indicated that the radial, tangential and cross sections of the treated wood were 3.40, 3.46 and 6.16, respectively, which were increased by 15.6%, 12.7% and 26.2%, respectively, compared with the corresponding direction of the controlled wood. Consequently, the treated poplar wood showed improved mechanical properties, due to the impregnation of Na_2SiO_3-PAM hybrid within the voids of the vessels and pits of the wood.

4. Conclusions

In conclusion, Na_2SiO_3-PAM hybrid solution was prepared and has been introduced into poplar wood. SEM pictures showed that the solid deposit partly occluded the pores of the wood structure and other apertures. TG and oxygen index methods indicated that the treated poplar wood showed an improved thermal property. The mechanical properties investigation showed that the bending strength, modulus of elasticity as

Table 1 The mechanic properties of composite wood.

Materials	Bending strength(MPa)	Modulus of elasticity in static bending(GPa)	Hardness		
			Radial	Tangential	Cross
Treated wood	71.62	10.37	3.40	3.59	6.16
Controlled wood	64.43	8.77	2.94	3.06	4.88

well as the hardness of radial, tangential and cross section of composite wood improved. The fast-growing poplar, treated by Na_2SiO_3-PAM hybrid solution, showed some improved mechanical properties.

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