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ORIGINAL ARTICLE

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Preparation and characterization of urea-formaldehyde resin–sodium montmorillonite intercalation-modified poplar

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Abstract To improve its overall performance, fast-growing poplar was modified using the vacuum–pressure–vacuum impregnation method with a urea-formaldehyde resin–sodium montmorillonite intercalation as the modification solution. The results showed that considerable amounts of urea-formaldehyde resin and montmorillonites entered the poplar tracheid, and some entered the microporous wood. These substances formed bonds with the active groups in timber, causing reduced crystallinity in the amorphous region of the poplar, a decreased level of free hydroxyl, and an enhanced association with hydroxyl and ether bonds. The density, dimensional stability, and mechanical properties of poplar were markedly improved. The best results were obtained with 14% sodium montmorillonite and 20% urea-formaldehyde resin: the bending resistance, compressive resistance, and elastic modulus increased by 19.37%, 30.24%, and 50.06%, respectively. With elevated levels of sodium montmorillonite, the impact toughness and wear rate decreased.

Key words Poplar · UF resin/Na-MMT · Modified intercalation · Basic performance

Introduction

Poplar wood has a lot of advantages in terms of its fast growth and short cultivation time. However, its low density and its early and late woods display a large variation in properties. Currently, poplar is mainly used for making paper and wood-based panels. With the decreasing amount of natural hardwood resources available, new ways to use fully the fast-growing woods has become a hot research topic.

Thomas et al.,[1] Miyafuji and Saka,[2] and Saka and Ueno[3] modified fast-growing timber with inorganic materials. Xue and Zhao[4] used phenol formaldehyde (PF) resin–montmorillonite to modify fast-growing fir. Gindl et al.[5] impregnated spruce with melamine-formaldehyde; Donath et al. and[6] Ogiso and Saka[7] enhanced hinoki (*Chamaecyparis obtusa* Endl.) sapwood with silica sol. Furuno et al.[8] made changes to pine wood (*Pinus sylvestris* L. as a softwood species) by using low-molecular-weight PF resin. Xue and Zhao[9] and Lü and Zhao[10] modified Chinese fir with Ca-montmorillonite; Blokhina et al.[11] used an oligomer solution to alter wood. All these studies showed that the overall performance of softwood improved using these modification approaches.

In this study, the liquid-phase intercalation method was used to embed urea-formaldehyde (UF) resin into a sodium montmorillonite (Na-MMT) layered structure to form intercalated compounds. Then, these compounds were impregnated into poplar wood to create a poplar/UF–Na-MMT composite. This improved the performance of poplar wood, proving its potential for wide application.

Materials and methods

Experimental material

Eight-year-old poplar wood (*Populus euramericana* cv, "1-214") was collected from Yiyang, Hunan. The poplar was cut into $500 \times 80 \times 20$-mm^3 plates and dried to 8% moisture content. A low-toxicity UF resin (molar ratio of formaldehyde to urea 1.15, pH 7.1, viscosity 16.5 MPa·s; polyvinyl alcohol was used as a formaldehyde scavenger: free formaldehyde content 0.43 mg/l) with 52% solid content was made in house while Na-MMT (Jiangxi Gukang New Material, China), acrylamide, acrylic acid, acrylic amide, ammonium

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sulfate, and *N*,*N*-methylene bisacrylamide were all industrial products.

Na-MMT was soaked for 20 h to obtain a clay slurry. Then, it was made into a 30% solution and mixed with 30% acrylamide solution (w/w, 5:1). Appropriate amounts of acrylic acid, ammonium sulfate, and *N*,*N*-methylene bisacrylamide crosslinker were added and adjusted to pH 8. The mixture was stirred fully, polymerized at 80°C for 2 h, and then cooled to 50°C. UF resin was added according to the experimental design. The intercalation solution was then obtained after 30 min of stirring.

Impregnation process

Based on exploratory experiments, dried poplar was placed into an impregnation tank under a vacuum of 0.1 MPa. The UF–Na-MMT intercalation solution was injected under negative pressure. Then, normal pressure was restored for 2 h and then a pressure of 1.5 MPa was applied. After 6 h, the impregnation solution was removed and the tank was evacuated again for 0.5 h. Finally, the specimen was removed from the tank and dried to 8% moisture content to obtain UF–Na-MMT-modified poplar wood. The ratios of the impregnation solution for specimens 1–6 are listed in Table 1.

The percentage weight gain was calculated as:

$$\mathrm{PL}(\%) = \frac{G_t - G_u}{G_u} \times 100 \quad (1)$$

where PL(%) is the percentage weight gain of the sample and G_t and G_u are the dry weights of the impregnated sample and the sample before impregnation, respectively.

The dry density and dry shrinkage ratio were evaluated according to national standard GB 1933–91 and GB 1932–2009, respectively. The samples were weighed using an electronic balance (AUY120, Shimadzu, Japan), the volume was measured by using Archimedes method, and the contour dimension was measured with an electronic digital caliper (D100, China).

Analysis and characterization

The phase composition and changes in the modified poplar were analyzed by X-ray diffraction (XRD; XD-2, China) with a Cu Ka radiation source at 35 kV and 20 mA; the poplar samples were cut from the middle of the tangential section of the poplar plates, and the scanning speed was set at 2° min^{-1}. The microstructure was observed by scanning electron microscopy (SEM; FEI Quanta 200, Holland) operated at 20 kV and 20 mA. The physical and chemical changes were characterized using a Fourier transform infrared spectrometer (FTIR; Nicolet 380, Japan) and carried out using KBr methods; the dry poplar samples were ground into 60 grit, mixed with suitable KBr, and then pressed into slices.

The mechanical properties were examined using a universal timber mechanical testing machine (WD-T). The hardness was measured according to GB1941–91, and the wear resistance was tested with a wear machine (JM-IV, China) consulting GB/T17657-1999(4·38); the weight loss was compared with per 200 r under the same grinding conditions.

Table 1. Ratio of urea-formaldehyde (UF) to sodium montmorillonite (Na-MMT) intercalation solution

Number	Na-MMT (%)	UF resin (%)
1	0	20
2	8	20
3	11	20
4	14	20
5	17	20
6	0	0

Sample 1 was impregnated with UF resin alone
Sample 6 was the original poplar

Results and discussion

Structure and characterization

The structure and basic characterization were analyzed with XRD, SEM, and FTIR.

XRD analysis

The XRD patterns of poplar and modified poplar samples are shown in Fig. 1. For poplar, the maximum peak of the cellulose crystal diffraction (100) occurred near the 17° diffraction angle, and an obvious trough was observed near 19.4°, which is a characteristic of the amorphous wood region. The most significant diffraction peak (002) of the cellulose crystal surface was near 23.4°, while a small diffraction peak (040) occurred near 35°.[12,13] However, the

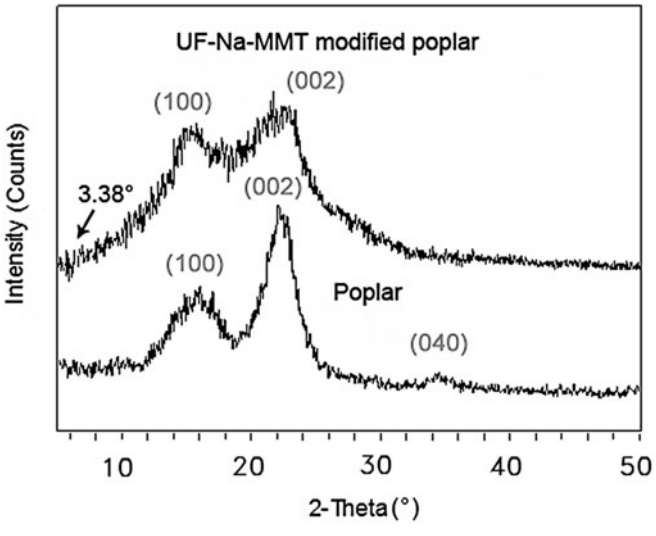

Fig. 1. X-ray diffraction patterns of poplar and urea-formaldehyde resin–sodium montmorillonite (*UF–Na-MTT*)-modified poplar

diffraction patterns greatly changed for the modified poplar wood. The trough at 19.4° elevated, the maximum diffraction peak (002) near 23.4° gradually passivated, and the diffraction peak for Na-MMT near 3.38° was not obvious. This indicated a significant increase in the layer spacing of Na-MMT or that the layers had peeled apart. This phenomenon is similar to the Ca-MMT-modified fir made by Xue and Zhao,[14] indicating certain structural changes of crystalline and amorphous areas for the modified poplar wood, which may be caused by the penetration of the stripped Na-MMT into the amorphous region of the poplar.

SEM analysis

SEM photographs can establish the microstructure of the material. An image of modified poplar wood is shown in Fig. 2a. Much granular material is gathered in the lumen (indicated by the arrows). This indicates that some Na-MMT existing in the timber pores is in the form of relatively large particles. Figure 2b shows a × 10 000 SEM image of the modified poplar and shows the attachment and insertion of the Na-MMT layer to the cell wall. The Na-MMT layer lamellae attached to, superimposed on, and tightly associated with the cell wall surface of the poplar (indicated by the arrow) suggest that Na-MMT can reach into small wood pores.

In fact, the macropores, pores, nanopores, and other multilevel pore structures of wood[15] resulted in different intercalation and infiltration for Na-MMT. Na-MMT displays a high selectivity and suitable orientation for intercalating and combining pores and nanopores of wood because the intercalation stripped of Na-MMT layers has a large radius/thickness ratio. Therefore, there will be different combinations during intercalation, which ultimately lead to multiple forms in composite timber, such as inserted, stripped, and granules. In addition, the combination between the fibers can be improved because the UF resin cannot only wet and fill the poplar cell walls, but can also form bonds with the polar groups in wood[16] due to the abundant active groups in the UF resin and the hydroxyl groups on the Na-MMT surface.

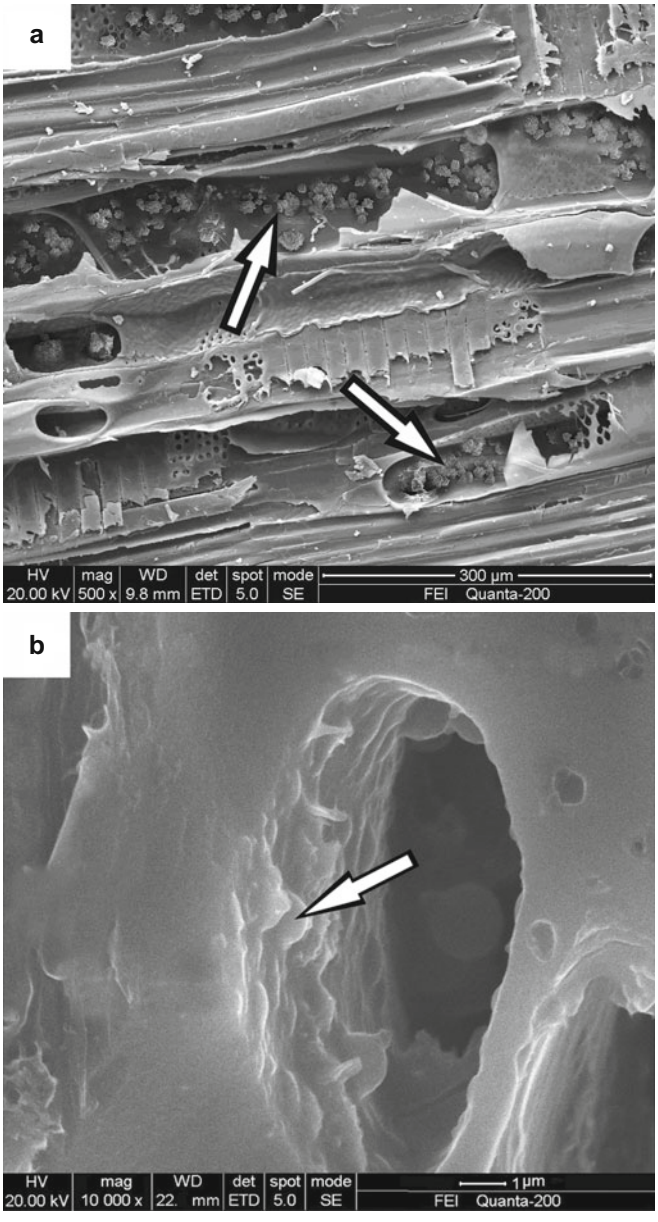

Fig. 2. Scanning electron microscopy images of **a** granular materials (*arrows*) gathered in the lumen of modified poplar of sample 4 and **b** attachment and insertion of the Na-MMT layer (*arrow*) to the cell wall of modified poplar

FTIR analysis

Wood is composed of cellulose, hemicellulose, and lignin. The absorption peaks for cellulose include 2900, 1425, 1370, and 895 cm^{-1}; the infrared spectrum of hemicellulose is different due to the variance in the single sugar residue and other pendant groups.[17] However, the carboxyl group near 1730 cm^{-1} and the C=O stretching vibration peak of the acetyl group distinguish hemicellulose from the other major components.

Figure 3 shows the infrared spectra of poplar with and without modification. The two spectra exhibit obvious differences. The 3300–3050 cm^{-1} absorption peak present in the modified timber showed a reduced intensity and an enhanced broadness, which were mainly due to the decreased number of free hydroxyl groups. Meanwhile, the absorption peaks for the -OH stretching vibration near 3300 and 1590 cm^{-1} were augmented because of the associated hydroxyl group increase in poplar. In addition, the increased absorption peak intensity close to the ether bond at 1060–1300 cm^{-1} indicated that the modified wood gained a large number of ether bonds. More importantly, strong absorption peaks that belong to the Si-O-Si and Si-O-Al of montmorillonite appeared close to 1040 cm^{-1} and 462 cm^{-1} in the spectrum of the modified wood, indicating that some Na-MMT entered the modified wood. However, the presence of bond formation with the active groups in poplar at large scales remains to be investigated further.

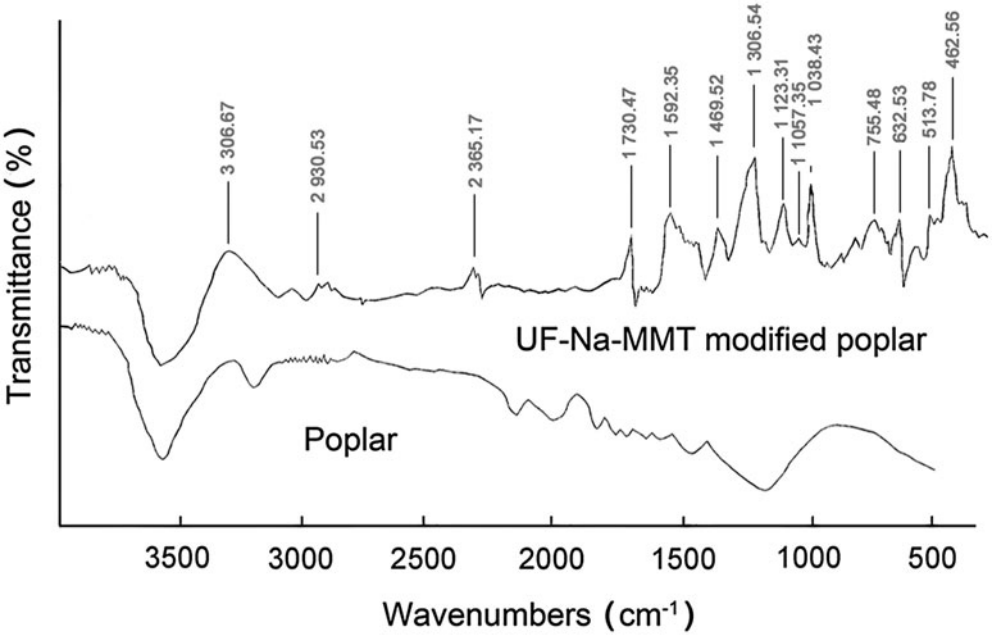

Fig. 3. Infrared spectra of poplar and modified poplar

Table 2. Effect of the dipping solution concentration on the dry density, weight gain, and shrinkage ratio

Number	Dry density (g cm^{-3})	Weight gain (%)	Dry shrinkage ratio (%)	
			Tangential	Radial
1	0.412	18.68	5.43	3.67
2	0.467	28.30	4.87	2.94
3	0.501	37.63	4.19	2.73
4	0.538	47.80	3.46	2.58
5	0.547	50.27	3.64	2.33
6	0.364	0	7.83	4.12

Mechanical properties

Weight percentage gain and dimensional stability

The density of a material has a great impact on its performance, and its dimensional stability is related to its application. During modification, the weight percentage gain is directly correlated with the density, and it also reflects the infiltration of the modification solution and the dosage. Table 2 lists the dry density, shrinkage rate, and weight gain of the different specimens. As shown in Table 2, the density and weight gain quickly increases as the amount of Na-MMT is increased; however, this rate of increase slows down for large amounts of Na-MMT. At the same time, the tangential and radial shrinkage rate was clearly reduced compared with the unmodified wood (specimen 6). Thus, modification improved the dimensional stability. Moreover, specimens 4 and 5 exhibited similar dry densities and percentage weight gain. Considering the cost of raw materials, the ratio for specimen 4, i.e., 20% UF resin and 14% Na-MMT, seems most beneficial.

Improved dimensional stability may occur because of the entrance of UF–Na-MMT intercalation compounds into the tracheids, and wood cell cavities under negative pressure and high pressure. Hydroxyl group exists at the surface of both Na-MMT and UF resins.[18] Some of these form stable chemical combinations with poplar, strengthening the cell cavities and tracheids, reducing deformation, and enhancing hydrophobicity. Meanwhile, others adhere and deposit on the tracheids, lumen, and cell wall of poplar, thus blocking water-exchange channels at a certain level, decreasing the water absorption, and augmenting dimensional stability.

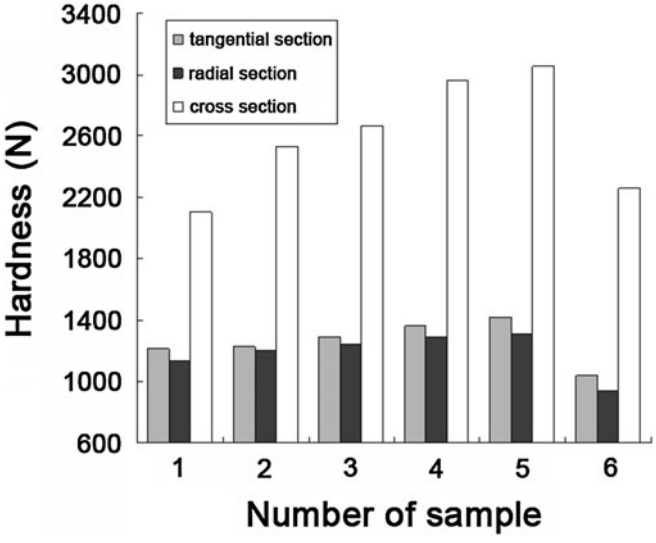

Fig. 4. Hardness of modified and unmodified poplar samples (see Table 1 for definition of the six sample types)

Hardness and wear resistance

The hardness changes for the tangential, radial, and cross sections of different samples are shown in Fig. 4. Compared with the original material (sample 6), all treated poplars

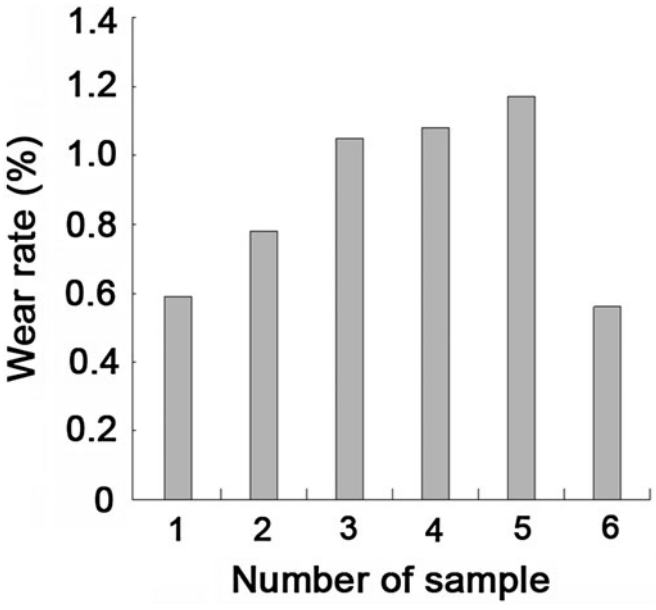

Fig. 5. Wear rates of modified and unmodified poplar samples

displayed improved hardness. In addition, higher hardness was observed in UF–Na-MMT treated poplar than the untreated sample. This is because UF resin and Na-MMT filled in the pores of poplar, forming hard three-dimensional structures, and thereby enhancing the hardness after solidification. Figure 4 also shows that the hardness for the cross section of modified timber was far higher than the hardness for the tangential and radial sections. This is because the UF–Na-MMT modification solution mainly penetrated into the conduits in the longitudinal direction from the cross section, keeping the relatively larger Na-MMT particles in the vessels.

The wear rates of samples are shown in Fig. 5. All samples exhibited higher wear rates than the original material (Sample 6), indicating that the wear resistance of all samples decreased after impregnation treatment. The reduced wear rate agreed with the increased amounts of UF–Na-MMT supplemented. This is because the Na-MMT and water-soluble UF resin impregnation solution entered the cell wall and cell cavity of the poplar sample, potentially forming hydrogen bonds. Combined with the relatively higher rigidity and strength of Na-MMT, the brittleness increased in modified wood, affecting the wear resistance. A comparison of different samples revealed that Sample 2 had the lowest hardness, Sample 5 had the highest hardness, and Samples 3 and 4 had comparable levels of hardness. Considering the percentage weight gain and dimensional stability, the treatment ratio used for sample 4 is the most appropriate.

Bending resistance and elastic modulus

The modified poplar had an increase in density and an improvement in its mechanical properties. Table 3 shows the mechanical properties of poplar wood for different UF–Na-MMT intercalation solutions. As shown in Table 3, the mechanical properties of the modified materials all improved significantly compared with the unmodified wood. There was a 19.37% increase in bending resistance, a 30.24% maximum increase in the parallel compressive resistance, and a 50.06% increase in elastic modulus, but the impact toughness decreased by 15.15%. This is because the bonding of the modification reagent with the poplar fiber and the increased deposition of UF–Na-MMT modification reagent on the cell wall enhanced the ability of the cell wall and fiber to resist external force. However, the montmorillonite itself has a high hardness, and the plasticizing effect of UF resin on poplar fibers can make the material more brittle, resulting in a lower toughness.

Table 3. Effect of the dipping solution concentration on mechanical properties of poplar samples

Number	Parallel compressive resistance (MPa)	Bending resistance (MPa)	Elastic modulus (GPa)	Impact toughness ($kJ \cdot m^{-2}$)
1	56.59	87.13	9.47	30.56
2	59.72	89.82	10.85	29.83
3	62.45	95.78	11.06	28.74
4	67.11	97.55	11.63	27.01
5	68.17	98.37	13.25	27.55
6	52.34	82.41	8.83	32.47

Conclusions

The properties of fast-growing poplar can be improved with UF–Na-MMT combined modification solution through a vacuum–pressure–vacuum impregnation process. Montmorillonite can effectively penetrate into the poplar and adhere or tightly bind to the surface of the wood fibers and cell wall. Some Na-MMT can enter the amorphous region and form bonds, leading to reduced crystallinity. The modified wood showed a decrease in free hydroxyl and an increase in association with hydroxyl and ether bonds.

In comparison with the original material, the modified fast-growing poplar wood exhibited improved dimensional stability, density, bending resistance, compressive resistance, and elastic modulus. However, it also showed an increase in brittleness and a decrease in impact wear rate and toughness. The most effective ratio for the treatment solution was 14% Na-MMT and 20% UF resin.

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