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RESEARCH ARTICLE

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Structure and characterization of Chinese fir (*Cunninghamia lanceolata*) wood/MMT intercalation nanocomposite (WMNC)

Abstract With water-soluble phenol-formaldehyde resin as an intermediate, Chinese fir (*Cunninghamia lanceolata*) wood/montmorillonite nanocomposite (WMNC) was prepared through vacuum impregnation and characterized with XRD, SEM, FTIR and TG-DTA analyses. The XRD analysis indicated that the wood crystallinity of WMNC decreased, the MMT exfoliated and some nano silicate layers entered into the non-crystallized microfibrillar region of the wood cell wall. Wood structure is anisotropic and its impregnation is anisotropic. Due to the nonuniformity of the MMT organic modification, PF intercalation and wood impregnation, the MMT configuration and distribution in wood were diverse. The SEM graphs of WMNC showed that some silicate grains were blocked in the wood cell lumen, some silicate layers adhered to the inner surface of the wood cell wall, and some exfoliated MMT layers even penetrated the wood cell wall. The obtained hydroxyl of WMNC increased and its ether linking decreased. It was considered that MMT and wood interacted not only with hydroxyl bonds, but also involved some chemical linking. Compared with untreated wood and the PF-impreg, the pyrolysis process of WMNC changed; its starting decomposing temperature decreased and its pyrolysis weight loss at high temperatures greatly decreased. The WMNC indicated certain nanoeffects of the composition of the inorganic MMT nanolamellae.

Keywords Chinese fir wood, montmorillonite (MMT), water-soluble phenol-formaldehyde resin (PF), nano intercalation compounding, structure and characterization

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1 Introduction

Wood possesses many special properties such as beautiful grain, natural color, high strength-to-weight ratio, and good electricity and heat insulation; it can also be easily processed, glued or dyed. It is biodegradable, recyclable and environment-friendly. But as a biomaterial, it also has intrinsic defects such as easy decay, burning and deformation. With the change of forestry resources in China, juvenile wood and small-diameter wood are being produced more, and their usage has been largely limited by some specially evident and intrinsic shortcomings. Adding various heterogeneous materials to make wood composites has been an important method to improve wood. Montmorillonite (MMT) is very rich in China, and it is named as the clay with thousands of usage. Its nano lamella are highly rigid and plane-oriented, and they are good at obstructing the diffusion of water and heat. Due to its special structure, MMT has been widely used to prepare nano intercalated composites with high properties, which indicates very good application prospects. Wood itself can accommodate nano units such as nano particles, nano tubes, nano sticks and nano layers (Zhao et al., 2002, 2003). Based on the intercalation compounding theory, adding the inorganic MMT nano lamella may endow wood with a special structure, strength, dimensional stability, decay resistance, abrasion resistance, fire resistance, and other positive attributes. Chinese fir (*Cunninghamia lanceolata*) is an industrial plantation wood species of short rotation that has a high survival rate, preservation and productivity (Peng, 1999; Yu, 2000). But Chinese fir plantation wood is soft, low-strength, allows easy abrasion and is unstable, which greatly limits its utilization (Chen et al., 2000; Song, 2000). How to reasonably utilize Chinese fir wood, improve its usage value and realize its high efficient utilization are important problems faced by China's wood industries. In this study, a water-soluble phenol-formaldehyde (PF) resin was synthesized in advance; with the PF resin as an intermediate, wood/MMT

nanocomposites (WMNC) were prepared; the WMNCs were characterized with XRD, SEM, FTIR and TG-DTA analyses respectively.

2 Materials and methods

2.1 Materials and reagents

The clays used in this study were industrially purified and modified Na-MMT. The organic intercalation agent C_{18} was produced in the laboratory with hydrochloric acid and octadecylamine. The Chinese fir (*Cunninghamia Lanceolata*) wood came from Fujian province; it was air-dried, and its sample dimensions were 20 mm (L) × 20 mm (R) × 20 mm (T).

2.2 Preparation of organo-MMT (OMMT)

Organically modified MMT was prepared by the cation exchange of the Na-MMT with the organic ammonium salts C_{18} in distilled water. First, 5% powdery Na-MMT was fully dispersed into distilled water with mechanical stirring for hours. The C_{18} was prepared by mixing octadecylamine with hydrochloric acid solution, and the C_{18} solution of 1.5 CEC was added dropwise to the above Na-MMT suspension solution with vigorous stirring. The stirring was continued at 80°C for 1.5 h and the resulting white precipitate was collected in a Buchner funnel by suction filtration. The precipitate was repeatedly rinsed with a hot distilled water-ethanol (1:1) solution to remove the excessive intercalation agent, until no white precipitate was formed in the filtrate when tested with a drop of 0.1 N silver nitrate solution. The resulting product was then vacuum-dried to a constant weight. Finally, it was ground into fine particles, and a fraction passed through a 300-mesh-sift was collected by mechanical sieving. The final organophilic MMT was obtained and signified as OMMT.

2.3 Synthesis of water-soluble PF

The molar ratio of formaldehyde to phenol was 1.5:1. The melted phenol and sodium hydroxide was first added into a reaction pot with mechanical stirring. When the temperature decreased below 50°C, 80% of the total amount of formaldehyde was poured into the pot. In succession, the system was heated at an even rate and held at 50°C for 20 min, at 60°C for 50 min and at 70°C for 20 min. Then the remaining 20% formaldehyde was added into the reaction pot, and the system was steadily heated up to 90°C and left idle. One hour later, a sample of about 1 mL was taken from the pot to measure its water solubility. With the reaction going on, the interval to take samples was reduced. When water solubility reached about 3.5 times, the reaction was immediately stopped. PF was prepared, its main quality parameters were measured and it was later kept at low temperature.

2.4 Intercalation compounding of Chinese fir wood and PF resin

The above low-molecular-weight PF resin was blended with distilled water to prepare a PF water solution. The prescribed OMMT was added and its pH value was modulated; and the impregnating solution for wood was prepared. The impregnating treatment of wood was as follows: First, wood samples were vacuumed under negative pressure of 0.095 MPa for 30 min. Second, the impregnating solution was introduced in a vacuum container. After the samples had been soaked for the prescribed time, they were vacuumed again, and the negative pressure was maintained for 30 min. Then the samples were taken out from the impregnating solution and vacuumed again for several minutes to make the wood surface clear. After being air-dried for a while, they were cured at 120°C for 3 h, and the Chinese fir wood/MMT intercalation nanocomposites (WMNC) were obtained.

2.5 Measurements and characterization

All samples were ground with agate mortar into fine powder, and part which passed through100-mesh sieve was sifted out for the following analyses that were respectively performed at various conditions. 1) The XRD analysis: the XRD-6000 produced by SHIMADZU Corp. in Japan, continuing scanning, CuKα radiation ($\lambda = 0.154$ nm), radiation tube voltage of 40 kV, radiation tube current of 30 mA, 2θ scanning range from 1.5° to 40°, scan rate of 4° per min and scan step of 0.1°. 2) The SEM analysis: the Quanta 200 HV SEM produced by FEI Corp. in the U.S., and ion-spraying gilding in vacuum. 3) The FTIR analysis: the Tensor27 FTIR produced by Bruker Corp. in Germany, KBr wafer, scanning frequency of 32, resolution of 4 cm^{-1}, scanning range from 400 to 4000 cm^{-1}. 4) The TG-DTA analysis: the DT-60 thermal analyzer produced by SHIMADZU Corp. in Japan, air conditioner, air current of 100 mL/min, heating velocity of 10°C/min, temperature of 600°C, and samples of 6–9 mg.

3 Results and discussion

3.1 The XRD analysis of WMNC

The XRD patterns of the PF-impreg, the simple physical blend of PF-impreg and OMMT, and the WMNC were respectively depicted in Fig. 1. MMT possesses a layered crystal structure. According to Bragg equation $2d\sin\theta = n\lambda$, where d is the distance of silicate layers, θ is the diffraction angle, λ is the X-ray wavelength of

0.154 nm, and n is the diffraction progression. If the interlayer spaces increase, the relating θ of the diffraction peak will decrease. When the interlayer spaces increase to a certain degree, the clay layers will be completely exfoliated, and the first grade diffraction peak within the XRD measure ranges will disappear (Kornmann et al., 2001). As seen from the figure, the characteristic diffraction peak of OMMT in WMNC at 3.38° of 2θ disappeared, which indicated that the interlayer spaces of MMT were greatly expanded or even the silicate layers were completely exfoliated. The skeleton substance of the wood cell wall is cellulose featuring a multiphase crystalline structure with the crystalline region and the amorphous region. There was no apparent boundary between the two regions, and the transition between them is gradual. Cellulose is of a unitary oblique crystal system with a distinct XRD pattern (Li, 2003). As shown in the figure, the PF-impreg had two wide diffraction peaks near 15.41° and 21.93°of 2θ and a small diffraction peak near 37.75° of 2θ. The peak near 21.93° of 2θ reflected the maximum diffraction of the 002 crystal plane of cellulose; the valley near 18° of 2θ was attributed to the amorphous region. The small peak near 37.75°of 2θ was due to the diffraction of the 040 crystal plane of cellulose. Because the glucose molecule plane in cellulose is parallel to the 002 crystal plane, the diffraction of the 002 crystal plane is stronger than that of the 040 crystal plane (Li, 2003). Compared with the PF-impreg's XRD pattern, the WMNC's XRD pattern had the following changes: the diffraction near 2θ from 16° to 18° intensified into a plateau from a valley of the PF-impreg; a small and sharp peak occurred near 2θ of 17°; the diffraction peaks of the cellulose 002 crystal plane near 2θ of 15.41° and 21.93° became dull; and the small peak of the cellulose 040 crystal plane near 2θ of 37.75° almost disappeared. All the above suggested that after the Chinese fir wood was compounded with MMT, its crystallinity degree decreased. It was concluded that MMT exfoliating occurred and some exfoliated nanolaminae were inserted into the cellulose amorphous region of the wood cell wall.

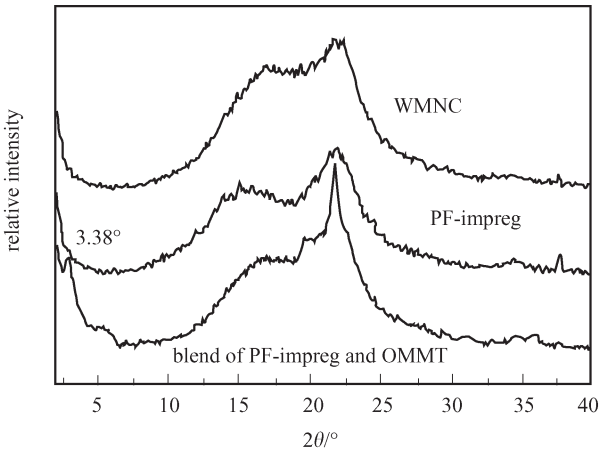

Fig. 1 The XRD analysis of WMNC

3.2 The SEM analysis of WMNC

To further explore WMNC structure and properties, SEM analysis was applied to investigate the MMT state and distribution in WMNC. Figure 2(a) is the cross section of WMNC, which indicated the adsorption and insertion of MMT nanolamella into wood pits and wood cell walls. Figure 2(b) shows the adsorption and insertion of MMT nanolamella into a wood pit. Figure 2(c) is the tangential section of WMNC, in which some MMT lamella were also big grains and were filled into the big spaces as wood cell lumens. Due to the nonuniformity of the OMMT modification, the PF intercalation and the wood impregnation, MMT morphology and distribution were very diverse in WMNC, and the big grains and free nanolamellae were in concurrence. The completely exfoliated nanolamellae were either closely adhered to the wood cell wall surface or inserted into the nanospaces in the wood cell wall. The exfoliated two-dimensional nanolamellae were of a high diameter-thickness space ratio. Their insertion or filling in of wood nanospaces were of a great orientation or selectivity, and their chances to enter wood microfibrillar spaces were small. They were mainly either filled into the big spaces as wood cell lumens, adsorbed by the wood cell wall surfaces or inserted into the wood pits. Based on MMT's dispersion state in a basic wood body, WMNC can be classified as one of the following three types: the conventional composite, the intercalated nanocomposite and the exfoliated nanocomposite (Lü et al., 2004, 2005). The nanocomposite types depend on the intercalation or exfoliation proportion of MMT.

With inorganic MMT filled into the microfibrillar spaces of wood cell walls, the compounding boundary between wood and MMT may disappear. Their combination is thus at the molecular level, which will undoubtedly most significantly improve rigidity of the wood cell wall and the dimensional stability, thermal and mechanical properties of wood. Through SEM analysis, it was found that the swelling and filling functions of PF resin and MMT strengthened the wood cell walls. There were much PF resins and a few MMT nanolamellae filled into the interfibrillar spaces, so the interfibrillar linking of the wood cell wall was enhanced. Some exfoliated MMT nanolamellae were very closely adsorbed by the wood cell wall surfaces. There might be some chemical linking between MMT nanolamellae and wood cellulose and hemicellulose. The MMT nanolamellae that entered instantaneous wood spaces were linked with the wood cell wall into a whole body, and they played a key role in improving wood. Further studies should be carried out to fully reveal the nano effects of inorganic MMT composition in WMNC.

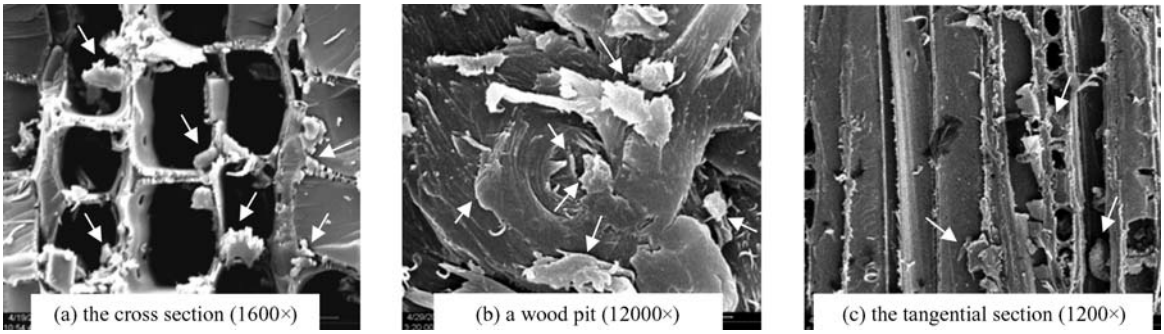

Fig. 2 The MMT distribution in WMNC

3.3 The FTIR analysis of WMNC

The molecular formula of MMT is $Na_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4 \cdot nH_2O$. MMT is a layered clay mineral with 2:1 type crystallite in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets linked by oxygen atoms (Giannelis et al., 1999). Wood, which is chiefly composed of three natural macro-molecules in cellulose, hemicellulose and lignin, has many hygroscopic groups as hydroxyl groups. Accordingly, hydroxyl bonds and some chemical linking may occur between wood and MMT. The FTIR analyses of Chinese fir wood, its PF-impreg and WMNC were respectively performed to investigate such linking in WMNC. Compared with untreated wood, both the PF-impreg and WMNC had wider and weaker adsorption peaks from 3200 to 3500 cm^{-1} which were ascribed to hydroxyl vibration; this indicated that their free hydroxyls decreased but their concluded hydroxyls increased (Ge, 1985; Nanjing Forestry University, 1990). Figure 3 was the FTIR difference spectrum of WMNC minus PF-impreg. Its adsorption peaks near 1042, 757 and 464 cm^{-1} were ascribed to vibrating Si-O-Si and Si-O-Al (Alexandre et al., 2000), which indicated the existence of inorganic MMT. Its adsorption peaks near 3300 and 1595 cm^{-1} were attributed to hydroxyl vibration, which indicated the increase of concluded hydroxyls; the obvious ether linking vibrating adsorption peaks from 1060 to 1300 cm^{-1} indicated the major increase of ether linking (Ge, 1985; Nanjing Forestry University, 1990; Li, 2003). The analysis showed not only hydroxyl bond linking, but also some chemical linking related to oxygen atoms possibly produced between MMT and wood in WMNC. Since most wood hydroxyls reacted or concluded, many properties of the PF-impreg and WMNC were improved.

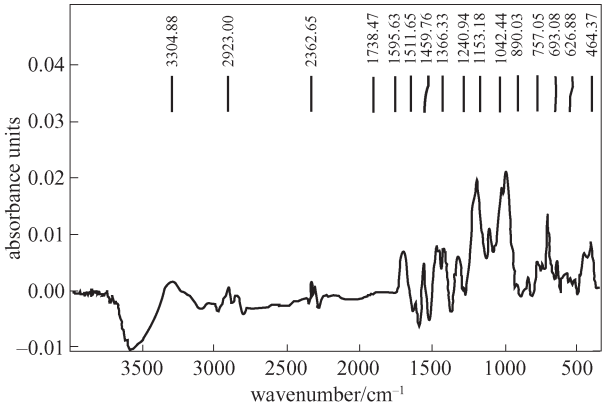

Fig. 3 The FTIR difference spectrum of WMNC minus PF-impreg

3.4 The TG-DTA analysis of WMNC

The TG-DTA analysis is an important method to evaluate material properties. The analysis results of Chinese fir wood and its PF-impreg and WMNC are shown in Table 1. Compared with the untreated Chinese fir wood, both its PF-impreg and WMNC had much better thermo properties. Their initial decomposing temperatures were a little decreased, but their pyrolysis weight losses at high temperatures were greatly decreased. Moreover, their heat decomposing processes were different, and their decomposing and carbonizing processes were also different. The heat decomposing process of Chinese fir wood can be classified into the following three stages (Hu et al., 1998; Hu et al., 2000; Xiao et al., 2002): The first stage is from 38 to 120°C, when there is mostly water loss and the weight loss percentage is small. Thereafter, the wood decomposes slowly, and its weight-loss and heat-decomposing velocity quickens at about 260°C. Decomposition mainly occurs from 270 to 370°C, and its peak temperature of the maximum pyrolysis velocity is about 365°C. The weight loss percentage at the second stage is about 60%, which is mainly due to cellulose decomposing and burning. The rest decomposes at the third stage after 370°C. In our study, the DTA diagram of the PF-impreg showed five peak temperatures at 67.02, 359.38, 431.43, 493.77 and 519.59°C respectively. Accordingly the PF-impreg's pyrolysis process could be classified into five stages. Similarly, the DTA diagram of the WMNC displayed four peaks

Table 1 The thermogravimetric analysis of Chinese fir wood and its PF-impreg and WMNC

pyrolysis course	Chinese fir		PF-impreg		WMNC	
	temperature/°C	weight loss/%	temperature/°C	weight loss/%	temperature/°C	weight loss/%
First stage	38–150	6.32	22–150	2.85	38–150	2.93
Second stage	190–370	61.04	160–390	32.32	160–391	34.84
Third stage	370–480	26.31	391–458	17.66	392–470	22.00
Fourth stage			458–519	12.64	470–598	20.80
Fifth stage			520–598	17.15		

with peak temperatures at 69.17, 356.27, 438.92 and 488.23°C. The weight loss from the WMNC's heat decomposing thus went through four stages.

The peak shape and peak temperature of the second and third stages of the WMNC's pyrolysis process corresponded with those of the PF-impreg. However, the WMNC's exothermic peak was stronger than that of the PF-impreg, and the maximum exothermic peak temperature of the former was higher. Compared with the PF-impreg, the WMNC had a much lower exothermic peak at the fourth stage, and then its decomposing velocity obviously slowed down. Compared with the WMNC, the PF-impreg delayed its decomposition at the fourth stage from 458 to 519°C; its exothermic peak was evidently stronger, and the weight loss of the fifth stage above 519°C was much bigger. After the third stage at about 450°C, the weight loss of the PF-impreg was obviously greater than that of the WMNC, and finally the total weight loss of the former was bigger. Although the mass fraction of MMT in the impregnating solution was small at about 3%, the heat decomposing process of the treated wood was changed. The thermo properties of high temperatures above 450°C were enhanced. This should be ascribed to the nanoeffects of the MMT nanolamellae in WMNC. According to the inherent structure of Chinese fir wood, its penetrability was significantly different, therefore its impregnating treatment always had great nonuniformity. In addition, the delamination and exfoliation of MMT were also uneven. All these could mean that thermo properties at the middle and low temperatures were not greatly improved. A further study should be carried out.

4 Conclusions

Because the interface area is relatively very small, it is very difficult to separately characterize or measure the interface properties of the different phases in composites. However, interface properties can be characterized by the improvement of the block composites or indirectly proven by advanced instruments.

1) The XRD analysis showed that the wood crystallinity of WMNC decreased, which indicated that partial MMT nanolamellae were exfoliated and entered into the microfibrillar amorphous region of the wood cell wall.

2) Because of the nonuniformity of the MMT modification, PF intercalation and wood impregnation, the size, shape and distribution of MMT were diverse in WMNC. The SEM analysis showed that some MMT filled in the big spaces as wood cell lumens, some MMT adhered to the wood cell wall surface and some MMT entered the wood cell wall. The uneven filling of MMT was due to the intrinsic anisotropic penetrability of wood.

3) The absorption peaks near 300 and 1595 cm^{-1} ascribed to –OH extending vibration of WMNC were stronger than those of the untreated wood and the PF-impreg, and WMNC's ether bond vibration from 1060 to 1300 cm^{-1} was much stronger. These indicated that WMNC had more concluded hydroxyls and its ether bonds greatly increased. Not only hydroxyl bonds, but some chemical linking might also exist between MMT nanolamellae and wood in WMNC.

4) The pyrolysis process of Chinese fir wood could be classified into three stages, while that of its PF-impreg and its WMNC could be classified as the fifth and fourth stages respectively. Due to the nanoeffects of inorganic MMT nanolamellae, adding only a few MMT could change the pyrolysis process of Chinese fir wood. Compared with Chinese fir wood and its PF-impreg, the WMNC had better thermo properties. Its starting decomposing temperature decreased and its pyrolysis weight loss at high temperatures greatly decreased.

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