MECHANICAL PROPERTIES OF MOSO BAMBOO TREATED WITH CHEMICAL AGENTS

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Abstract. Bamboo is a type of biomass material and has great potential as a bioenergy resource for the future in China. Surface chemical and thermal–mechanical behavior play an important role in the manufacturing process of bamboo composites and pellets. In this study, moso bamboo was treated by sodium hydrate solution and acetic acid solution. Surface chemical and dynamic mechanical properties of bamboo were determined using Fourier transform infrared spectroscopy and dynamic mechanical thermal analysis, respectively. Results showed that the main polar chemical groups of the outer layer of bamboo (OB) included hydroxyl group (O-H) and ester carbonyl (C=O). Some new polar chemical groups appeared on the inner layer of the bamboo surface (MB) such as aromatic ethers (C-O-C) and phenolic hydroxyl (C-O). The chemical group difference of OB and MB confirms that there was a waxy layer on the OB surface. Nonpolar chemical groups decreased and polar chemical groups increased on the OB surface when it was treated by acetic acid solution. The waxy layer of the OB surface was removed and the lignin structure was also destroyed by sodium hydrate solution. The general feature of thermal–mechanical properties with temperature was similar to cellulosic materials for OB, OB-NaOH

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(OB treated by sodium hydrate solution), and OB-acetic (OB treated by acetic acid solution). A lower storage modulus of OB-NaOH and OB-acetic was helpful to improve physical properties of bamboo pellets. There was an α transition (α_1) peaking at about 65°C for OB. The second major relaxation (α_2) occurred at 35°C. The α_1 and α_2 transition temperature of OB changed when it was treated by chemical agents. This information is very important for using bamboo to manufacture composites and pellets.

Keywords: Biomass, moso bamboo, surface chemical property, thermal-mechanical property, chemical treatment.

INTRODUCTION

Bamboo is a type of biomass material and has been widely cultivated in the west and south of China. Currently, bamboo resources are very abundant. The total area of bamboo is about 5 million ha and that of moso bamboo (*Phyllostachys heterocycla*) is about 3 million ha in China (Jiang 2002). Annual yield of moso bamboo is about 18 Mt, and it is widely used to produce furniture, flooring, and interior decoration materials. Bamboo, like wood and agricultural residue, is mainly composed of hemicelluloses, cellulose, and lignin. It has great potential as a bioenergy resource for the future in China.

The surface property is a fundamental characteristic of wood materials. Some information about the wood surface property is available. Cheng and Gu (2002) studied surface wettability of larch, birch, and oak. Cui and Du (2008) analyzed effects of surface property on *Pinus yunnanensis* wood treated by microwave plasma. Zhang et al (2008) studied surface dynamic wettability and free energy of poplar. Kathleen and Paul (1999) studied the surface property of wood with weathering. It is well known that surface property of wood material is affected by its chemical groups. Fourier transform infrared spectroscopy (FTIR) was found to determine functional groups of wood materials. Pandey (1999) studied chemical groups of softwood, hardwood, and wood polymers by FTIR. Yutaka and Makoto (2001) used FTIR to analyze chemical groups of degraded wood. Ohkoshi (2002) studied surface group changes in acetylated and polyethylene–glycol-impregnated wood using light irradiation by FTIR. Pandey and Pitman (2003) used FTIR to analyze chemical changes of scots pine sapwood and beech decayed by coniophora puteana, coriolus versicolor, and phanerochaete chrysosporium.

The dynamic mechanical properties are also an important characteristic of wood materials, and they affect physical properties of pellets. To compress from different materials, a natural binder or binding type of particles includes attractive forces among solid particles, interfacial forces, capillary pressure, adhesive and cohesive forces, mechanical interlocking behavior, and formation of solid bridges in the pellet formation process (Mahapatra et al 2010). It is also confirmed that bonding between particles is created mainly through solid bridges for corn stover and switchgrass pellets. The solid bridges between particles are made by natural binders in the biomass expressed during the densification process (Nalladurai and Vance 2010). Hemicelluloses and lignin are essentially natural binders in the bamboo components. Activating (softening) the natural binders using moisture and temperature in the temperature range of glass transition is very important and helpful to make durable particle–particle bonding of pellets. Dynamic mechanical thermal analysis (DMTA) is a type of thermoanalytical technique widely used to study the dynamic mechanical property of polymers or biomass materials. Yang et al (2009) studied thermal and viscoelastic properties of composites with different filler by DMTA. The glass transition and melting temperature did not significantly vary with filler content because chemical bonding did not occur at the interface between the matrix and filler. Sanchez-Cabezudo et al (2010) analyzed mechanical properties of poly (vinyl acetate) (PVAc)/epoxy thermasets as a function of the PVAc content through DMTA. The storage modulus-temperature curves were largely

dependent on the morphology of samples, and the glass transition temperature of PVAc and of the epoxy phase in the blends were different from those of the neat polymers. Stelte et al (2011a) investigated thermal transition of amorphous polymers in wheatstraw using DMTA. The key transitions attributed to softening lignin were found at 53, 63, and 91°C for moist samples of wheatstraw, extracted straw, and spruce, respectively.

Despite the fact that previous research is very helpful in understanding surface chemical and dynamic mechanical properties of biomass materials, bamboo is different from other biomass materials. There is a waxy or silicious layer on the bamboo surface, affecting the property of interfacial conglutination between bamboo particles and adhesive in the manufacturing process of bamboo composites. Adsorption, spreading, and permeability simultaneously occur when adhesive is introduced to the bamboo surface. The waxy or silicious layer on the bamboo surface prevents adhesive from permeating into bamboo, which causes poor bonding strength of bamboo composites. Liu et al (2012) found that the glass transition of wax on the surface of bamboo materials probably overlapped with the higher temperature of hemicelluloses. The softening and subsequent flow of the waxes at lower temperature result in the formation of weak boundary layers that are responsible for the low physical properties of bamboo pellets compared with wood pellets. In this study, moso bamboo was treated by sodium hydrate and acetic acid solution. The surface chemical and dynamic mechanical properties were determined by FTIR and DMTA, respectively. The aim of this study was to investigate the change of surface chemical and dynamic mechanical properties and provide a guideline for the manufacturing of bamboo composites and pellets.

MATERIALS AND METHODS

Material

Moso bamboo was used in this study. The initial moisture content of samples was about 6.13%. Bamboo materials were cut off to a sample size of 17.5 mm (longitudinal) × 2.2 mm (radial) × 7.2 mm (tangential). Samples were respectively treated using 2% sodium hydrate solution and 2% acetic acid solution for 30 min. Then they were dried using a drying oven under rigidly controlled conditions of temperature (105°C) for 8 h. They were removed from the drying oven and placed into a desiccator to cool to room temperature. They were weighed using a precision digital balance (0.0001 resolution). All samples were returned to the drying oven at 105°C for 2 h and were cooled and weighed. When mass variability of all samples was less than 0.2%, the final mass (W_1) was recorded. All samples were placed into the conditioning room at 27°C and 65% RH to equilibrate the moisture content. After samples were conditioned for 10 da, mass (W_2) was weighed and moisture content of samples was calculated based on the mass change. Then, the moisture content of samples was about 8.0%.

Testing Surface Chemical Property of Bamboo

FTIR was conducted on a Thermo Nicolet (Thermo Electron Corp., Madison, WI) spectrophotometer to test some functional groups present on the sample surface. Scans were run at a resolution of 4 cm^{-1}, and each sample consisted of 64 scans recorded in absorbance units from 4000-750 cm^{-1}. The spectra were obtained using attenuated total reflectance. The sample surfaces were analyzed in contact with a ZnSe crystal with a 45° angle of incidence. Five replicate samples were analyzed in this research.

Testing Dynamic Mechanical Property of Bamboo

The dynamic mechanical properties were tested by means of DMTA (Q800; TA-instruments, New Castle, DE) using a single cantilever grip. The viscoelastic region (strain directly proportional to stress) was determined by performing a strain sweep. Specimens were measured in their exact dimensions, immediately fixed in

the grip, and cooled to −50°C using liquid nitrogen. Measurements were conducted between −50 and 150°C with an amplitude of 5 μm at a frequency of 1 Hz. The storage modulus (E') and loss factor (tanδ) were used to determine the transition of amorphous polymers. A minimum of two samples were tested, and data from the first run were used when they were shown to be in accordance with the second run.

RESULTS AND DISCUSSION

Surface Chemical Property

Chemical Group Difference of Outer and Middle Bamboo. The functional groups of outer bamboo (OB) and middle bamboo (MB) are shown in the FTIR spectra in Fig 1a. For OB, the main absorbance at 2910 and 2850, 1710, 1470, and 1070 cm^{-1} was attributed to C-H stretching vibration of saturated alkane, C=O stretching vibration of ester carbonyl, C-H deformation, and O-H stretching vibration of aromatic ether, respectively. For MB, there was a strong broad O-H stretching absorbance at 3350 cm^{-1}. The absorbance at 2910 cm^{-1} was a prominent C-H stretching. In the fingerprint region (from 1800-800 cm^{-1}), some important information on various functional groups was present in MB. The absorbance at 1740 cm^{-1} was attributed to C=O stretching vibration in hemicelluloses. The bands from 1600-1450 cm^{-1} were caused by aromatic skeletal vibration in lignin. The absorbance at 1370 cm^{-1} was C-H bending of cellulose or hemicelluloses and that of 1230 cm^{-1} was C-O stretching of phenolic hydroxyl groups in the lignin. The absorbance at 1160 and 1030 cm^{-1} was attributed to C-O-C stretching of cellulose or hemicelluloses and C-O stretching of cellulose, hemicelluloses, or lignin, respectively (Li 2003).

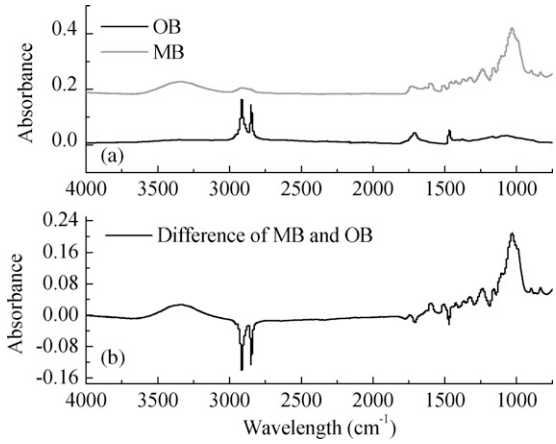

Figure 1. (a-b) Chemical group difference of outer bamboo (OB) and middle bamboo (MB).

The chemical groups of bamboo surface can be classified into nonpolar and polar functional groups, respectively. The nonpolar functional groups increase hydrophobicity of bamboo, but the polar functional groups can increase hydrophilicity of bamboo. Urea–formaldehyde resin (UF) and phenol–formaldehyde resin (PF) are the two main types of wood adhesives for the Chinese wood industry. There are some polar chemical groups in UF and PF molecular structure. Some polar chemical groups of bamboo materials and adhesives can chemically join, which improves bonding strength of bamboo composites. The more polar chemical groups on the bamboo surface, the stronger the bonding strength is of bamboo composites. According to Fig 1a, the main polar chemical groups of OB include hydroxyl group (O-H) and ester carbonyl (C=O). Some new polar chemical groups appear on the MB surface such as aromatic ethers (C-O-C) and phenolic hydroxyl (C-O). The chemical group difference of OB and MB is shown in Fig 1b. The more saturated alkyl (C-H) on the OB surface also confirms that there was a waxy layer on the OB surface. It was found that the number of all polar chemical groups on the MB surface was more than that on the OB surface, especially hydroxyl groups and aromatic ethers. The less polar chemical groups of the OB surface were possibly influenced by the fact that they were covered by a waxy layer.

Chemical Groups of Outer Bamboo Surface Treated by Different Chemical Agents. The functional groups of OB, OB-acetic, and OB-NaOH are shown in the FTIR spectra in Fig 2a. It was found that the main chemical groups of OB and

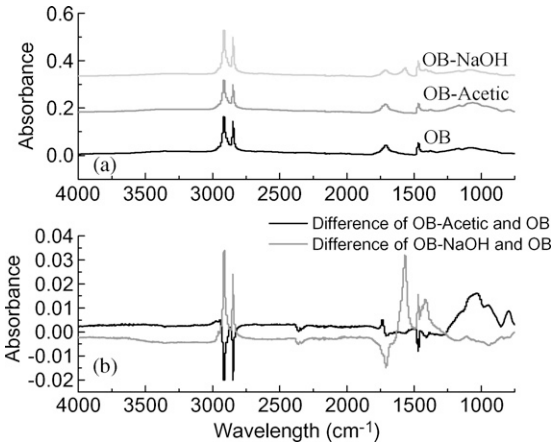

Figure 2. (a-b) Chemical groups of outer bamboo (OB) treated by different chemical agents.

OB-acetic were similar. However, there was a new absorbance at 1560 cm^{-1} when OB was treated by acetic acid solution. The absorbance at 1560 cm^{-1} was attributed to aromatic skeletal vibration in lignin. This also confirmed that the waxy layer of the OB surface was partly removed by acetic acid solution. The chemical group difference of OB, OB-acetic, and OB-NaOH is shown in Fig 2b. The absorbance at 2910 and 2850 cm^{-1} (C-H stretching vibration of saturated alkane) and 1470 cm^{-1} (C-H deformation) decreased for OB-acetic, which belonged to nonpolar chemical groups. Some polar chemical groups increased such as C=O stretching vibration of ester carbonyl (1710 cm^{-1}), C-O-C stretching of cellulose or hemicelluloses (1160 cm^{-1}), and C-O stretching of cellulose, hemicelluloses, or lignin (1030 cm^{-1}). The nonpolar chemical group decrease and polar chemical group increase both improved the interfacial conglutination between bamboo material and adhesive and the bonding strength of bamboo composites. For OB-NaOH, absorbance at 2910 and 2850 cm^{-1} increased. The lignin structure was possibly destroyed by the sodium hydrate solution, which resulted in the phenomenon. On the bamboo surface (OB), lignin content was the greatest compared with other chemical compositions (cellulose and hemicelluloses). Jiang et al (2006) also found that cellulose and hemicellulose content on the bamboo surface (OB) was obviously lower than that of lignin, and the hemicellulose content in the OB was lower than that in the MB. The increase of absorbance at 1570 and 1470 cm^{-1} (aromatic skeletal vibration in lignin) further confirmed the phenomenon that the waxy layer on the OB surface was partly removed by sodium hydrate solution.

Dynamic Mechanical Property

Storage Modulus. Figure 3 shows the storage modulus of OB treated by different chemical agents. The general feature of storage modulus variation with temperature was similar to previous research on wood materials (Eiichi et al 2003). The substantial decrease of storage modulus implied that bamboo materials underwent a glass-to-rubber transition in the entire temperature range. The storage modulus decrease was caused by the fact that kinetic energy of material molecules was very low in this temperature condition with only the motion of some small units such as side chains and branched chains (Jiang and Lu 2009). The lesser decrease of storage modulus can be attributed to crystallization or ordering of the molecules (Georget et al 1996). For OB, the storage modulus gradually increased after 70°C. The probable reason is that moisture content of samples decreased with temperature increase. In the previous research, it was found that the bamboo with

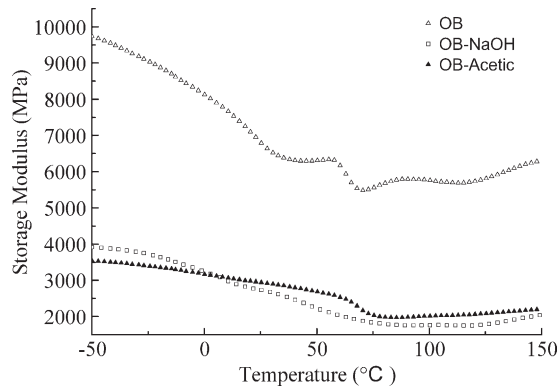

Figure 3. Storage modulus of outer bamboo (OB) treated by different chemical agents.

the lower moisture content had a higher storage modulus (Liu et al 2012). Kelley et al (1987) also found that glassy modulus decreased with water content increase. In general, water is only introduced into the amorphous region of the bamboo cell wall. Because the amorphous region is viscoelastic and its storage modulus is much lower than that of the crystalline region of the cellulose microfibrils, the swelling of bamboo usually involves a decrease of storage modulus unless a crosslinking structure is formed (Eiichi et al 2003). Loss factor (tanδ) gives the information on the glass transition, whereas storage modulus determines its relevant stiffness (Kim et al 2005). The storage modulus of OB, OB-NaOH, and OB-acetic indicated that bamboo stiffness decreased when it was treated by chemical agents. The stiffness of bamboo particles plays an important role in pellet formation. After bamboo particles are compressed to pellets, some bamboo particles undergo elastic deformation and elastic recovery. The greater the stiffness of bamboo particles, the bigger the elastic recovery, which results in a more easily destroyed natural binder of bamboo particles. The physical properties of bamboo pellets can be affected by its stiffness. In preliminary work, physical properties, including durability and fine, were compared with bamboo pellets manufactured using different moisture content of bamboo particles. Bamboo pellets manufactured using bamboo particles with higher moisture content had better physical properties, probably because of the lower storage modulus of bamboo particles. The research also further confirmed that bamboo pellets probably had better physical properties when the bamboo particles were treated by chemical agents.

Loss Factor. Figure 4 shows the loss factor (tanδ) of OB treated by different chemical agents. The loss factor (tanδ) corresponded to two major transitions for all samples. The α_1 and α_2 transition peaking of OB were at about 65 and 35°C, respectively. The α_1 transition was mostly linked to the glass–rubber transition of lignin, and the α_2 transition was attributed to the glass–rubber transition of hemicelluloses. Lignin has a glass transition in the range of 60-200°C, depending on the moisture content and measuring technology (Salmen 1984, 1990). Olsson and Salmen (1997) showed that the α_1 transition of moist wood usually occurs between 60 and 95°C because of the glass–rubber transition of lignin. Hemicelluloses have a glass transition of between −23 and 200°C, depending on the moisture content (Kelley et al 1987). Results showed that the α_1 and α_2 transition temperature of OB changed when it was treated by chemical agents. The α_1 transition peak of OB-NaOH shifted to the higher temperature compared with OB. However, the opposite trend occurred for the α_2 transition peak. This phenomenon can be attributed to the natural wax layer. The α_2 transition of wax probably overlapped with the higher temperature of hemicelluloses for OB. Stelte et al (2011b) found that the α_2 transition peak of straw occurred at about 40°C. The softening and the subsequent flow of waxes at lower temperatures is problematic because it has been shown to inhibit adhesion between bamboo particles in fuel pellet production. This results in the formation of weak boundary layers that are responsible for the low compression strength of bamboo pellets.

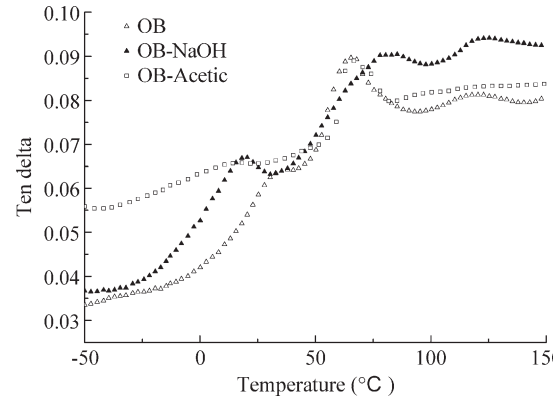

Figure 4. Loss factor (tanδ) of outer bamboo (OB) treated by different chemical agents.

CONCLUSIONS

The main polar chemical groups of OB include hydroxyl group (O-H) and ester carbonyl (C=O).

Some new polar chemical groups come up on the MB surface such as aromatic ethers (C-O-C) and phenolic hydroxyl (C-O). The chemical group difference of OB and MB confirms that there is a waxy layer on the OB surface. Nonpolar chemical groups decreased and polar chemical groups increased on the OB surface when it was treated by 2% acetic acid solution. The waxy layer of the OB surface was removed and the lignin structure was destroyed by sodium hydrate solution. The wax removal of OB is very significant to the manufacturing process of bamboo composites and pellets.

The general feature of thermal–mechanical properties with temperature is similar to cellulosic materials for OB, OB-NaOH, and OB-acetic. The substantial decrease of storage modulus in the entire temperature range implies that the bamboo materials underwent a glass-to-rubber transition. A lower storage modulus of OB-NaOH and OB-acetic was helpful for improving physical properties of bamboo pellets. The loss factor (tanδ) corresponded to two major transitions. There was an α transition (α_1) peaking at about 65°C for OB. The second major relaxation (α_2) occurred at 35°C. The α_1 and α_2 transition temperature of OB changed when it was treated by chemical agents. The α_1 transition peak of OB-NaOH shifted to the higher temperature, but the opposite trend occurred for the α_2 transition peak. This information is very important and significant for manufacturing bamboo composites and pellets.

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