Materials and Design 59 (2014) 233–240

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Morphological, thermal and dynamic mechanical properties of Cathay poplar/organoclay composites prepared by in situ process

Wang Wang, Yuan Zhu, Jinzhen Cao *

Department of Wood Science and Technology, Beijing Forestry University, Qinghua Eastroad 35, Beijing 100083, China

ARTICLE INFO

Article history:
Received 8 January 2014
Accepted 26 February 2014
Available online 6 March 2014

Keywords:
Wood/organoclay composite
In situ process
Intercalated structure
Thermal stability
Dynamic mechanical properties

ABSTRACT

In order to improve the thermal stability and dynamic mechanical properties of Cathay poplar (*Populus cathayana* Rehd.) wood, a kind of organoclay, that is, organo-montmorillonite (OMMT), was introduced into its structure via an in situ process by sequentially impregnating poplar wood with sodium-montmorillonite (Na-MMT, in concentrations of 1.0%, 2.0%, and 4.0%) and didecyldimethylammonium chloride (DDAC, in a concentration of 2.0%). Consequently, the wood/organoclay composites were prepared. The X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersed X-ray analysis (SEM-EDXA) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the morphological and chemical alterations of the composites. Also the effects of clay type and concentrations on the thermal stability and dynamic mechanical properties of the composites were studied. The results showed that didecyldimethylammonium ions were intercalated into the galleries of Na-MMT through cation exchange, partially separating the silicate layers. Thereafter, the inorganic Na-MMT transformed to OMMT during the in situ synthesis process, and the latter was successfully intercalated into the wood cell wall. The thermal degradation was alleviated in the wood/clay composites, among which the wood/OMMT composites exhibited the best thermal stability. According to dynamic mechanical analysis (DMA) results, the wood/OMMT composites showed an enhancement in energy storage and a diminution in energy dissipation compared to other groups. The improvements in the thermal stability and dynamic mechanical properties of the composites became more significant with the increasing clay content.

1. Introduction

Cathay poplar (*Populus cathayana* Rehd.) is one of the most important fast-growing wood species in China's 30 years of plantation history. However, its low density and mechanical properties limit its applications [1]. Therefore, many reinforcing fillers, such as silica sol and resins, have been introduced into poplar in order to improve these properties [2,3]. Montmorillonite (MMT), due to its superior swelling capacity, high surface areas and nanometer effect, is also considered as a suitable material for preparing reinforced wood composites [4].

MMT is a 2:1 layered silicates (or 2:1 phyllosilicates), namely, its two silica tetrahedral layers sandwich a central octahedral alumina layer. Introducing MMT into composites could improve the mechanical, dimensional, barrier and thermal properties [5,6]. The commonly used MMT can be classified into two types: natural MMT with a typical example of sodium-MMT (Na-MMT) and synthetic organo-MMT (OMMT). OMMT can be obtained by modifying natural MMT through cation exchange with quaternary ammoniums such as didecyldimethylammonium chloride (DDAC) [7] and cetyltrimethylammonium bromide (CTAB) [8]. Compared to Na-MMT, OMMT has better dispersibility due to its large interlayer spacing. "Dispersion" is the key point determining the performance of nanocomposites [9]. Therefore, the reinforcing effect of OMMT is much better than natural MMT.

According to previous investigation [10], the average diameter of cavities in wood cell wall is about 30–35 nm, while the thickness of a single silicate layer is approximately 1 nm. It implied that the clay intercalated wood composites could be expected. However, due to the agglomeration structure of silicate layers, natural clay such as Na-MMT is almost impossible to insert into wood cell wall. To exfoliate the agglomerated layers, it is necessary to increase the interlayer spacing by modifying the natural clay to organoclay. In our previous work, southern pine/OMMT composites were successfully fabricated, showing good dimensional stability and static mechanical properties [11]. However, the thermal stability and dynamic mechanical properties, which are also of great importance for organoclay reinforced wood composites. From these properties, we can learn the resistance to decomposition and deformation of

* Corresponding author. Tel./fax: +86 10 62337381.
E-mail address: caoj@bjfu.edu.cn (J. Cao).

http://dx.doi.org/10.1016/j.matdes.2014.02.059
0261-3069/

the composites under heating, and thereafter to predict the material state under high temperatures and ensure safety in use. Moreover, further information about the interaction between different components in the composites can be obtained by analyzing the rheology and viscoelasticity of the reinforced wood composites [12].

The effect of OMMT on the thermal stability and dynamic mechanical properties of wood/polymer composites and wood/plastic composites has been studied in some previous studies. Devi and Maji [13] modified simul wood with styrene–acrylonitrile (SAN) copolymer, glycidyl methacrylate (GMA) and OMMT. They found that the temperature of decomposition increased after introducing OMMT into the system, indicating the improved thermal stability of wood/SAN composites by adding OMMT. Park and Kim [14] added OMMT into wood flour/polyethylene (PE) composites, and found that the thermal stability and storage modulus of the reinforced composites increased. According to these researches, OMMT has positive effects on the thermal stability and dynamic mechanical properties of the wood-based composites by serving as a kind of thermal insulator and reinforcing filler at elevated temperatures. However, among all these studies, polymer or plastic was a necessity to introduce OMMT into wood, which makes OMMT only an auxiliary to the polymer. Therefore, it is of interest to test the possibility of improving the thermal stability and dynamic mechanical properties of wood by using OMMT without any intermediate.

The OMMT particles are difficult to disperse in water, which is the major obstacle in preparing the wood/OMMT composites. Na-MMT would be able to form a stable suspension in water, thus it could be easily introduced into wood. However, the enhancing effect of Na-MMT on the composites is much weaker than that of OMMT. Therefore, in this study, we tried to combine the advantages of both OMMT and Na-MMT by using an in situ process. First, Na-MMT suspension was used to impregnate Cathay poplar wood (*Populus cathayana* Rehd.) and then DDAC was successively introduced to modify Na-MMT to OMMT. The objective of this study was to confirm the formation of OMMT during the in situ process and evaluate the thermal stability and dynamic mechanical properties of Cathay poplar/OMMT composites.

2. Materials and methods

2.1. Experimental materials

Cathay poplar with an air-dry density of 0.38 g cm^{-3} and an average growth ring width of 0.6 cm was collected from Baoding, Hebei province, China. After air-drying, the lumber was cut into samples of 50 (L) × 10 (T) × 3 (R) mm^3. Before impregnation treatment, wood samples were oven-dried at 103 °C to constant mass, m_1 (g).

Na-MMT was purchased from Zhejiang Hongfeng Clay Chemical Co., Ltd., Huzhou, China. The mean interlayer distance of Na-MMT is 1.459 nm with a cation exchange capacity of 90 mmol per 100 g. The Na-MMT particles were dispersed in deionized water with three different concentrations (1.0, 2.0 and 4.0 wt%, respectively), followed by ultrasonic dispersion for 30 min (40 kHz, 600 W). The average particle size of Na-MMT suspension was 726 nm as tested by a Laser Particle Analyzer (DelsaTM Nano C, Beckman coulter, USA). The modifier used in this study was DDAC with 70% concentration (Shanghai 3D, Bio-chem Co., Ltd., Shanghai, China), which was diluted with deionized water to 2.0% prior to experiments.

2.2. Preparation of wood/clay composites

The modification of wood included two steps. In the first step, wood samples were impregnated with prepared Na-MMT suspensions by the vacuum-pressure process. Wood samples were exposed to vacuum at −0.1 MPa for 30 min at first, and then pressure at 2 MPa for 60 min. After the Na-MMT impregnation, samples were taken out from the treating cylinder, wiped with tissue paper, and then oven-dried at 103 °C to constant mass, m_2 (g). In the second step, DDAC with 2.0% concentration was impregnated into wood samples by using an initial vacuum at −0.1 MPa for 20 min at first and a pressure level at 0.5 MPa for 30 min thereafter. Then, the samples were immersed in DDAC solution (2.0%) at 75 °C for 10 h, followed by oven-drying at 103 °C to constant mass, m_3 (g). The weight percent gains (WPGs) of each impregnation steps and the total WPG after the two steps were calculated according to Eqs. (1)–(3).

$$\mathrm{WPG}_1\ (\%) = \frac{m_2 - m_1}{m_1} \times 100 \tag{1}$$

$$\mathrm{WPG}_2\ (\%) = \frac{m_3 - m_2}{m_1} \times 100 \tag{2}$$

$$\mathrm{WPG}_T\ (\%) = \frac{m_3 - m_1}{m_1} \times 100 \tag{3}$$

where WPG_1 is the weight percent gain of the first step, WPG_2 is the weight percent gain of the second step, and WPG_T is the total weight percent gain after the two-step treatment. The treatments of different groups are shown in Table 1. In order to characterize the properties of OMMT, DDAC modified OMMT was prepared by blending Na-MMT (20.0 g), DDAC (6.5 g) and deionized water (73.5 g) in a ball-mill for 2 h at a speed of 250 rpm. Then, the OMMT was dried and ground to pass through a 60-mesh sieve before characterization.

2.3. Characterizations

X-ray diffraction (XRD) analysis was used to investigate the crystalline structures of clay. Wood samples were ground to pass through a 60-mesh sieve and then oven-dried before analysis. The XRD studies were performed with an X-ray 6000 (Shimadzu, Japan) machine using Cu Kα (λ = 0.154 nm) radiation at a scanning rate of 2°/s and 2θ ranged from 2.5° to 10° with the rotation speed of 30 rpm.

The evaluation of the clay distribution in reinforced wood composites was made by scanning electron microscope (SEM, Hitachi S-3400) coupled with energy dispersed X-ray analysis (EDXA). For SEM analysis, the transverse and tangential surfaces of wood samples were observed at an acceleration voltage of 15 kV. Fractured surfaces of the samples were coated with gold. The distribution and the atomic percentages of carbon, oxygen, silicon and chloride elements in wood cell wall were investigated by using SEM-EDXA.

Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical changes happened during the in situ process. Samples were ground to pass through a 100-mesh sieve, and FTIR spectra were recorded by using a KBr pellet in an FTIR spectrophotometer (Bruker Vertex 70v, German) in transmission mode within the range of 4000–400 cm^{-1}.

The thermogravimetric analysis (TGA) was performed on a Netzsch STA-409 TG instrument to examine the thermal degradation behaviors of different samples. Approximately 6 mg of milled samples was placed in an aluminum crucible with a diameter of 5 mm. The temperature of the apparatus was programmed from 30 to 600 °C at a heating rate of 10 °C/min while the samples were continually flushed in atmospheric nitrogen with a flow rate of 60 mL min^{-1}.

The temperature-dependent dynamic thermomechanical properties were tested by using a dynamic mechanical analyzer