Dynamic mechanical properties and thermal stability of furfuryl alcohol and nano-SiO₂ treated poplar wood¹

Youming Dong, Xiaoyan Shen, Shifeng Zhang², Jianzhang Li

MOE Key Laboratory of Wooden Material Science and Application; Beijing Key Laboratory of Wood Science and Engineering; MOE Engineering Research Center of Forestry Biomass Materials and Bioenergy, College of Materials Science and Technology, Beijing Forestry University, Beijing, 100083 China

E-mail: zhangshifeng2013@126.com

Abstract. Wood polymer nanocomposites (WPNC) were prepared from the furfuryl alcohol and nano-SiO₂ using a method of vacuum impregnation. Dynamic mechanical properties in storage modulus and mechanical loss factor, as well as the thermal stability of the WPNC were evaluated. The interface interaction between the organic and inorganic compounds was also studied by the scanning electron microscope and energy dispersive X-ray spectrometer. The dynamic mechanical analysis showed the improvement in the storage modulus and mechanical loss factor of WPNC as a result of the strong interfacial interaction between the organic and inorganic matrix. Additionally, with an increase in nanoparticles content in the composites, the thermo-stability of WPNC improved significantly.

1. Introduction

As one of the most relevant raw materials and renewable resources in the world, wood is a continual, durable, beautiful, versatile, and cost-effective material, which has been used extensively for furniture and construction. Interest has recently peaked regarding the development of novel wood materials with comprehensive functions [1]. For example, wood polymer composites (WPCs) fabricated by the impregnation and polymerization of monomer or oligomer have an emerged as an important family of green composites [2]. The preparation of wood polymer nanocomposites (WPNC) via nano-treatment would be a hot point to combine the characteristics of organic polymers with those of inorganic nanoparticles.

As a commercially used WPC, furfurylation endows wood with high dimensional stability, stellar biological resistance, and environmental friendliness via the in-situ polymerization of furfuryl alcohol (FA) monomer [3-5]. FA is a hydrophilic organic liquid derived from furfural, which can be obtained from hydrolysis products of pentose-rich biomass [6]. Therefore, a variety of studies have been conducted to explore FA as an applicable hydrophilic nanoparticle dispersant and an in-situ polymerization precursor for preparing bio-based nanocomposites [6-8]. Generally, researchers...
postulated that the cross-link reactions of PFA via the electrophilic addition or Diels-Alder cycloaddition. During wood modification, PFA also forms covalent bonds with lignin [9].

Nano-SiO₂ is a form of common inorganic nanoparticles used regularly for reinforcing polymer properties such as high mechanical properties, flame resistance, and thermal stability [10, 11]. WPNC with nano-SiO₂ and urea-formaldehyde resin were utilized to augment wood properties [12]. The effect of nano-SiO₂ on the wood's properties and styrene acrylonitrile/nanoclay composites was evaluated. The results proved the hardness, thermal stability, and UV stability had improved by incorporating nanoparticles [10]. Hence, the combination of FA and nano-SiO₂ had the potential to use the virtues of FA and nano-SiO₂ for preparation of an innovative and eco-friendly high-performance WPNC. This organic-inorganic system would also have a synergistic effect on the wood's properties. WPNC were prepared by the in-situ polymerization of FA utilizing nano-SiO₂ as the particulate phase within poplar wood. The effect of nanoparticles on the physical-mechanical properties, morphologies, and crystallinity of the composites were evaluated in our previous study [13]. More detailed studies are needed for a true understanding of the nano-SiO₂’s effect on WPNC. In this work, the dynamic mechanical properties and thermal stability of WPNC are characterized in detail.

2. Experimental

2.1. Materials

Furffuryl alcohol (chemical purity 98.0%; Sinopharm Chemical Reagent Co., Ltd., China), nano-SiO₂ (particle diameter: 15 ± 5 nm; Shanghai Maikun Chemical Co., Ltd., China), maleic anhydride, and disodium tetraborate (analytically pure, Beijing Chemical Works, China) were used during these studies.

Obtained from Guangxi province of China, the untreated and treated wooden specimens of the sound sapwood of fast-growing poplar were cut into a size of 3 (Radial) × 8 (Tangential) × 60 (Longitudinal) mm³. The specimens were oven-dried at 105°C to achieve a consistent weight. Afterward, they were sorted into four groups: A, B, C and D. Group A, B, and C were treated with 30 wt% FA solutions containing 0, 1.0 and 2.0 wt% nano-SiO₂, respectively. Group D was untreated, and used as the control group.

2.2. Preparation of wood polymer nanocomposites

The nano-SiO₂ swelled in an FA water solution (30%) and sonicated for 20 minutes. Then 2 wt% maleic anhydride and 4 wt% di-sodium tetraborate was added to the solution to complete the impregnation. Next, the specimen were immersed into solutions under a vacuum pressure of 0.095 MPa for 30 minutes, and soaked under the atmospheric pressure for 2 hours. After the impregnation, the specimens were wrapped with aluminum foils, placed at the room temperature for 12 hours, and then oven-cured at 100°C for another 12 hours. The aluminum foil was removed, and the specimens were then oven-dried at 105°C until a constant weight was obtained. After the treatment, the wood percentage gain (WPG) was calculated using to the following equation:

\[
WPG (%) = \frac{W_1 - W_0}{W_0} \times 100
\]

In the equation, \(W_0\) and \(W_1\) are the oven-dried weights of a specimen before and after treatment, respectively.

2.3. Measurements

The morphological features of WPNC and the distribution of nanoparticles were examined using the Hitachi S-4800 scanning electron microscope, which was equipped with an energy dispersive X-ray spectrometer (SEM-EDX, Japan). The tangential sections of treated and untreated wood samples were mounted on conductive adhesives, sputter-coated with gold, then observed at an accelerating voltage of 15 kV.
The Dynamic Mechanical Analysis (DMA) of the untreated and treated specimens was conducted using the NETZSCH DMA 242 (Germany) in the dual cantilever-bending mode. The specimens were scanned over a range of 40 to 225°C, at an increased rate of 5°C/minute, and a frequency of 2 Hz. Five replicates were conducted.

The thermal stability of the untreated versus treated specimens were evaluated by TGA by using a Q50 TGA analyzer (TA Instruments, USA) at a constant heating rate of 10°C/minute from a room temperature to 600°C under the flowing nitrogen atmosphere.

![Figure 1. FE-SEM observations of (a) untreated wood, (b) FA-treated wood, (c) FA-treated wood with 1.0% SiO2, and (d) FA-treated wood with 2.0% SiO2 and their relative EDX spectrum of the elements.](image)

3. Results and discussion

3.1. SEM-EDX analysis

The prepared WPNC was dark brown due to the conjugated structure derived from the aliphatically linked poly-FA. The average WPG was 78.11%. The morphological features of WPNC examined by SEM-EDX are shown in figure 1. It was noticed that, in the untreated wood, the avulsed lamellar structure of the cell wall can clearly be discerned (figure 1a). However, these details depicting the cell wall's division was absent in the FA-treated wood (figure 1b) due to the polymerization of FA on the vessel cell walls. In the FA/SiO2-treated wood (figure 1c), the cluster aggregation of nano-SiO2 was invisible. Additionally, most of the nanoparticles were clearly covered by the FA polymers, exhibiting a highly desirable combination of organic and inorganic compounds that could have an effect on the properties of the WPNC. When SiO2 was increased, the cluster aggregation would become larger (figure 1d). In the EDX spectrum, no silicon was present in untreated poplar wood and FA-treated wood, while the distribution of silicon was obvious in the FA/SiO2-treated wood. In the third part in figure 1c, the EDX spectrum suggested that the Si element evenly distributed onto the wood's cell.
walls. In addition to the silicon, a sodium signal in the FA-treated wood and FA/SiO2-treated wood was present, which had resulted from the addition of disodium tetraborate in the furfurylation process.

![Figure 2](image.png)

**Figure 2.** Dynamic mechanical analysis of untreated wood (Control) and treated wood with FA and 0, 1.0%, and 2.0% nano-SiO2. (a): storage modulus (E'); (b): mechanical loss factor (tan δ).

### 3.2. Dynamic mechanical analysis

After the specimen were treated with FA and 0, 1.0%, and 2.0% nano-SiO2, the dynamic mechanical properties such as the storage modulus (E’) and mechanical loss factor (tan δ) as a function of temperature are shown in figure 2. Figure 2(a) depicts E’ of the specimens. With the increase in temperature, E’ of control group was found to decrease due to the heightened chain mobility of the wood cell wall components [14]. The steep decrease appeared when E’ neared the glass transition temperatures of wood (~150°C). It was noticed that the higher E’ was represented by the specimens treated with FA. The first steep decrease of E’ value appeared at about 60 ~ 80°C, due to the glass transition temperature of PFA is 80°C [6]. The onset of the E’ value increased according to the fluctuation in SiO2 content. When the content of SiO2 was 1.0%, the E’ values improved (9256 MPa) considerably compared to the control (7602 MPa) and FA-treated wood (8658 MPa). This improvement in E’ values for FA/SiO2-treated wood samples may be related to the better interface interaction among PFA, nano-SiO2, and wood components, which allowed better stress transfer at the interphase between organic and inorganic compounds [14]. Additionally, WPNC became more rigid when SiO2 was added due to the rigidity property of the nano-SiO2 [15]. Overall, a similar changing trend of both 1.0% and 2.0% SiO2-treated wood samples was observed.

The ratio of the loss modulus in relation to the storage modulus is measured as the mechanical loss factor (tan δ). Figure 2(b) depicts the variation of tan δ as a function of temperature for both the control and treated wood fragments. When compared to the control groups, the tan δ variation of FA-treated wood samples changed significantly. Due to the higher WPG, PFA played the most vital role in the wood polymer composites. It is interesting to realize that the FA- and FA/SiO2-treated wood samples may be related to the better interface interaction among PFA, nano-SiO2, and wood components, which allowed better stress transfer at the interphase between organic and inorganic compounds [14]. Additionally, WPNC became more rigid when SiO2 was added due to the rigidity property of the nano-SiO2 [15]. Overall, a similar changing trend of both 1.0% and 2.0% SiO2-treated wood samples was observed.

The ratio of the loss modulus in relation to the storage modulus is measured as the mechanical loss factor (tan δ). Figure 2(b) depicts the variation of tan δ as a function of temperature for both the control and treated wood fragments. When compared to the control groups, the tan δ variation of FA-treated wood samples changed significantly. Due to the higher WPG, PFA played the most vital role in the wood polymer composites. It is interesting to realize that the FA- and FA/SiO2-treated wood samples displayed two distinct peaks, however they cannot be detected for the control samples in the tan δ curves. The peaks of tan δ for FA-treated wood samples were about 80°C and 150°C, while the peaks for FA/SiO2-treated wood samples appeared at about 90°C and 175°C. It was indicated that the peaks shifted to the higher temperatures. Due to the slip of PFA, the molecular chains decreased with the nano-SiO2 content. As a result of the barrier between nanoparticles, this phenomenon also implied the strong interphase interaction between the nanoparticles and PFA [14, 15].

### 3.3. Thermal stability analysis

The thermal degradations of the controlled and treated wood samples were examined by the thermogravimetry (TGA). Figure 3 shows the TGA scans of each sample. The TGA data confirmed a lowered decomposition temperature and an increased char formation for the treated wood samples, particularly for the treated wood sample with 2.0% SiO2. The temperatures at the 20%, 40%, 60%, and
80% weight losses occurred, and the residual weights at 600°C as representative of thermo-stability are listed in table 1. It was apparent that the thermal stability of the FA- and FA/SiO$_2$-treated samples were improved when compared against the control samples. Specifically, the thermal stability of the nano-SiO$_2$ incorporated samples increased with the rise of the nanoparticle content. When the content of nanoparticles was 2.0%, the residual weight at 600°C was subsequently increased by 18.45% when compared with that of the FA-treated wood sample. This result indicates that the thermo-stability of the composites was significantly improved by the incorporation of nanoparticles. The main reason for the spike in thermal stability is the fact that the inorganic matrix could promote the formation of the self-insulating char on the wood surfaces and the heat transfer is inhibited [16]. Lastly, this result also suggested that a strong interface interaction between organic and inorganic matrix existed.

Figure 3. Thermogravimetric curves of control and treated wood samples with FA and 0, 1.0, and 2.0% SiO$_2$.

| Sample        | Temperature of decomposition in °C at different weight loss (%) | RW% at 600 °C$^a$ |
|---------------|-----------------------------------------------------------------|-------------------|
|               | 20%                 | 40%               | 60%               | 80%               |                  |
| Control       | 321.78              | 361.50            | 384.20            | 564.28            | 19.60             |
| FA            | 314.39              | 346.50            | --                | --                | 35.51             |
| FA+1.0%SiO$_2$| 314.45              | 346.95            | 509.47            | --                | 36.91             |
| FA+2.0%SiO$_2$| 319.85              | 354.87            | --                | --                | 42.06             |

$^a$RW refers to the residual weight.

4. Conclusion
The dynamic mechanical properties and thermal stability of WPNC treated with FA/SiO$_2$ were decidedly improved due to the secure interface interaction between PFA and nanoparticles. The storage modulus and softening temperature of WPNC rose with the increase of the SiO$_2$ content. When the content of SiO$_2$ was 1.0%, the onset of the storage modulus could be improved by 21.8% compared to that of the control sample. Additionally, the inorganic nanoparticles in WPNC can potentially improve its thermo-stability by fostering the self-insulating char formation in wood, and inhibiting the heat transfer. The combination of organic and inorganic materials can improve the thermal properties of wood and expand the wood’s application.

References
[1] Qin C and Zhang W 2012 Mater. Lett. 89 101
[2] Deka B K and Maji T K 2012 Polym. Bull. 70 403
[3] De Vetter L, Pilgård A, Treu A, Westin M and Van Acker J 2009 Wood Mater. Sci. Eng. 4 30
[4] Lande S, Westin M and Schneider M 2008 Mol. Cryst. Liq. Cryst. 484 367
[5] Venås T M and Rinnan Å 2008 Chemometrics Intellig. Lab. Syst. 92 125
[6] Guigo N, Mija A, Zavaglia R, Vincent L and Sbirrazzuoli N 2009 Polym. Degradation Stab. 94 908
[7] Pranger L and Tannenbaum R 2008 Macromolecules 41 8682
[8] Ahmad E E M, Luyt A S and Djoković V 2012 Polym. Bull. 70 1265
[9] Nordstierna L, Lande S, Westin M, Karlsson O and Furo I 2008 Holzforschung 62 709
[10] Devi R R and Maji T K 2013 J. Taiwan Inst. Chem. Eng. 44 505
[11] Li J Z, Furuno T, Zhou W R and Yu Z M 2005 J. Wood Chem. Technol. 25 257
[12] Shi J, Li J, Zhou W and Zhang D 2007 Frontiers of Forestry in China 2 104
[13] Dong Y, Yan Y, Zhang S and Li J 2014 BioResources 9 6028
[14] Islam M S, Hamdan S, Talib Z A, Ahmed A S and Rahman M R 2012 Composites Sci. Technol. 72 1995
[15] Peng Z, Kong L X and Li S D 2005 Synth. Met. 152 25
[16] Merk V, Chanana M, Keplinger T, Gaan S and Burgert I 2015 Green Chem. 17 1423