Wettability of Wood Pressure-treated with TiO_2 Gel under Hydrothermal Conditions

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TiO_2-treated acacia hybrid (*Acacia mangium x auriculiformis*) wood was fabricated by combined pressure-impregnation and hydrothermal post-treatment. The wettability and microstructure morphology, as well as the crystalline structure of the titanium dioxide (TiO_2) gels of the TiO_2-treated wood, were studied. Contact angle measurements of the blank wood and the TiO_2-treated wood indicated a significant increase in hydrophobicity, with contact angles of above 150° in treated samples. Furthermore, the water-resistant property of the treated wood was quite stable, even after immersion in boiling water. Field emission scanning electron microscopy (FE-SEM) results showed that the microstructure morphology and the size of TiO_2 gels on the wood surface were dependent on the pH of the post-treatment solutions. Additionally, the presence of amorphous TiO_2 gels was indicated by X-ray diffraction (XRD) analysis. The results of this study indicate that combined pressure-impregnation and hydrothermal post-treatment can create a hydrophobic wood-TiO_2 composite.

Keywords: Acacia hybrid wood; Contact angle; FE-SEM; TiO_2; Wettability; XRD

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INTRODUCTION

Wood is used extensively in many industries, including the architecture, textiles, construction, pulp and paper, and furniture industries. In general, the problem with using wood is its hygroscopicity, which results in high moisture adsorption. Moreover, the dimensional, mechanical, and thermal properties of wood depend on its moisture content (Rowell 2005). Reducing the hygroscopicity of wood is important in that it can improve dimensional stability and transform low-quality wood into a value-added product suitable for use in many applications. To resolve this problem, there are several methods available, such as impregnation with preservatives, heat treatment, and surface coating.

One of the typical techniques is the impregnation method, in which chemicals react with the most reactive groups of the cell wall of wood (Hill 2006; Bryne and Wålinder 2010). The main components of wood are cellulose, hemicellulose, lignin, and small amounts of extractives and inorganics. There are intermolecular forces acting between these constituents that may contribute to some of the unique characteristics of wood. It is evident that sorption and the consequent swelling are caused by the hydroxyl (OH) groups of cellulose macromolecules (Li 2002). The presence of these OH groups can promote the nucleation and growth of inorganic phases such as TiO_2 and SiO_2 on the wood surface (Li *et al.* 2010; Miyafuji and Saka 2001; Sun *et al.* 2010b; Tshabalala and Gangstad 2003; Tshabalala and Sung 2007; Wang *et al.* 2012), thereby producing wood-inorganic composite materials. In previous studies, TiO_2 has been used with wood to improve fire-resistance (Sun *et al.* 2010a), provide antibacterial qualities (Qin and Zhang 2012), increase decay protection (Shabir *et al.* 2013), prevent weathering (Mahltig *et al.* 2008; Rassam *et al.* 2011; Schmalzl and Evans 2003; Sun *et al.* 2012; Tshabalala *et al.* 2011), and improve dimensional stability (Sun *et al.* 2010b). These studies were largely focused on the enhancement of weather resistance, water resistance, and antimicrobial activity in wood using sol-gel processes or by surface coating using a hydrothermal method. The combination of pressure-impregnation of TiO_2 sol into wood, accompanied with hydrothermal post-treatment, to fabricate TiO_2-treated wood or wood-TiO_2 composites was rarely mentioned.

Acacia hybrid (*Acacia mangium x auriculiformis*) is a lower-grade, fast-growing wood abundantly available in Vietnam. In recent years, more acacia hybrid plantations have been established in Vietnam, and the large available quantity of this wood is primarily used for outdoor furniture production. The wood of acacia hybrid has poor dimensional stability and durability because of its very fast growth rate. In previous research, the dimensional stability of this wood has been improved by heat treatment (Tuong and Li 2010). In the present study, the wettability of acacia hybrid wood was reduced by pressure-treating the wood with TiO_2 gel under hydrothermal conditions. The goal was to study the effects of post-treatment conditions (mainly the pH of treatment solutions) on the water contact angles and the variability of TiO_2 morphology inside the treated-wood. In addition, the influence of immersion in boiled water on the wettability of the composites was also investigated.

EXPERIMENTAL

Materials

All chemicals and solvents were supplied by Tianjin Baishi Chemical Industry Co., Ltd. and were used as received. Wood specimens were cut from three fast-growing acacia hybrid (*Acacia mangium x auriculiformis*) trees, each of which were 8 years old with breast high diameters (DBH) ranging from 19 to 22 cm. The samples were collected from Hoa Binh province, Vietnam. Approximately the same amount of heartwood was cut to prepare clear wood samples 10 mm (T) x 20 mm (R) x 30 mm (L) in size (where R represents the radial direction, T represents the tangential direction, and L represents the longitudinal direction) to fabricate the wood-TiO_2 composites. Samples were divided into four groups (Control, T1, T2, and T3), and each treatment group contained a total of 10 test samples. All samples were conditioned for three weeks at 20 °C and 65% relative humidity (RH) prior to impregnation with the TiO_2 sol solution.

Solution Preparation

A sol solution was prepared using tetrabutyl orthotitanate (TBOT) as the precursor and ethanol (EtOH) as the solvent. About 5 mL of TBOT was added, dropwise, to 200 mL of EtOH at ambient temperature. After stirring for 30 min, a light-yellow, transparent solution was obtained.

Additive solution for post-treatment *via* the hydrothermal process was prepared by dissolving sodium dodecyl sulfate (SDS) in distilled water. The concentration of SDS in this solution was 6.9 x 10^{-4} M. The different pH values of the additive solution were reached by the addition of acetic acid or sodium hydroxide.

Impregnation with Sol Solution

All samples in the three treatment groups (T1, T2, and T3) were impregnated with the sol solution. The impregnation process was carried out in a vessel under a pressure of 7 bar for 4 h at ambient temperature. After impregnation, the samples were removed from the impregnation vessel and excess solution was wiped from the sample surface.

Post-treatment

Impregnated samples were immediately transferred into three stainless-steel autoclaves filled with the prepared additive solutions associated with each of the three experimental groups (T1, T2, and T3). These autoclaves were held at 70 °C for 4 h in an oven. The pH values of additive solutions used to treat the samples in groups T1, T2, and T3 were 2, 6.5, and 9.5, respectively. Finally, the samples were removed from the autoclaves and ultrasonically rinsed with distilled water for 30 min before being oven-dried at 103 ± 2 °C overnight.

The weight-percent gains (WPG) of the samples were calculated according to the formula,

$$\text{WPG (\%)} = (m_1 - m_o)/m_o \times 100 \quad (1)$$

where m_o is the initial mass of the oven-dried sample and m_1 is the mass of the same sample after post-treatment.

Characterization Methods

The wettability of the TiO_2-treated samples and blank samples was evaluated by measuring the contact angle of distilled water. Pictures of water droplets on the wood surface were taken with a digital camera and imported into measurement software. The software is entitled Image processing and analysis in java (ImageJ) and included the Low bond axisymmetric drop shape analysis (LB-ADSA) plugin, which is free for download from the Internet. Each contact angle value reported was the average of five measurements.

The microstructure morphologies and the size of the TiO_2 gels formed in the treated samples were characterized by a field emission scanning electron microscope (FE-SEM, S-4800). Their crystal structures were analyzed by X-ray diffraction with a SIEMENS D5000 X-ray diffractometer.

RESULTS AND DISCUSSION

Water Contact Angle

The wettability of a material is measured by determining the contact angle of a liquid on its solid surface. By common definition, a surface is considered hydrophilic if the contact angle of water on its surface is smaller than 90°. Otherwise, it is classified as hydrophobic. Further, it can be considered super-hydrophobic if the contact angle of water on its surface is larger than 150°. In the present experiment, the wettability of TiO_2-treated acacia hybrid wood was evaluated by measuring the static contact angles of distilled water on the sample surfaces after 90 seconds of contact. The results are presented in Fig. 1, in which the contact angles of water on the sample surfaces were assessed as a function of the pH of the additive solution associated with the different treatment groups.

As can be seen in Fig. 1, the blank wood samples were hydrophilic, with an average contact angle of about 60°. In contrast, the TiO_2-treated wood samples exhibited more hydrophobicity than the blank wood samples. The samples post-treated with additive solution of pH 2 (group T1) had a greater contact angle than the samples post-treated with additive solutions of pH 6.5 (group T2) and 9.5 (group T3). The wood samples subjected to post-treatment with additive solution of pH 2 yielded a super-hydrophobic composite with a water contact angle of about 153.2°.

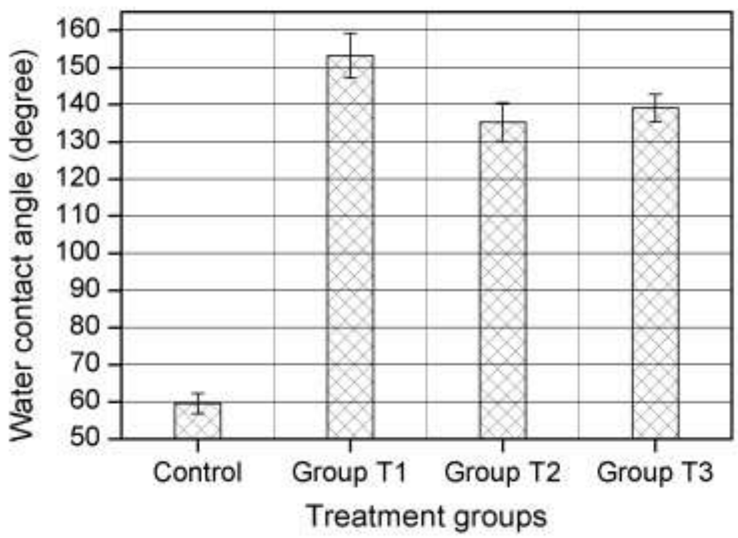

Fig. 1. Contact angles of water on treated and untreated wood sample surfaces

This increase in water contact angle suggests that the impregnation of TiO_2 gel into wood, accompanied with a hydrothermal post-treatment, is an efficient method to enhance the water repellency of acacia hybrid wood. To examine the permanency of this water resistance, wood samples from the treated groups T1, T2, and T3 were immersed in boiling water for varying durations. After 2, 4, 10, and 20 h of immersion, samples were removed and dried to a moisture content of 12% and their respective contact angles were measured.

The effects of boiling water immersion on the contact angles of wood composites are presented in Fig. 2. It is evident that the contact angles of TiO_2-treated wood decreased quickly in the first 2 h of immersion. However, all of the treated wood composite samples remained hydrophobic even after being immersed for 20 h. This is due to the interactions between the TiO_2 gels and the hydrocarbon chains of the wood (Li *et al.* 2010).

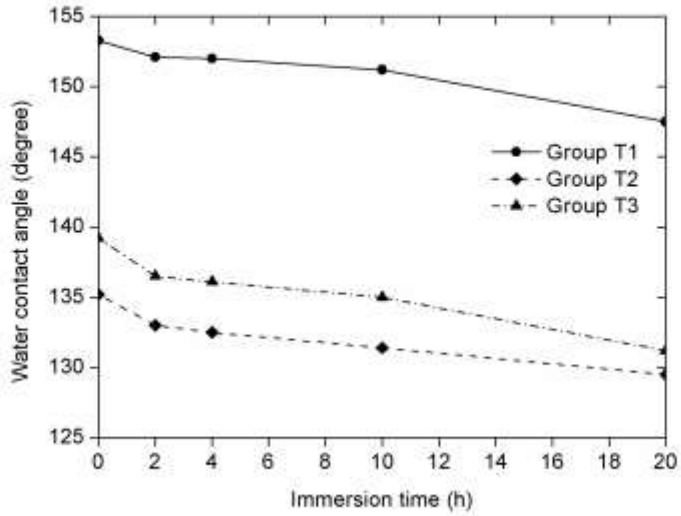

Fig. 2. Water contact angles as a function of water immersion time for TiO_2 gel/acacia hybrid wood composites

Microstructure Morphology of TiO_2

Figure 3 shows FE-SEM images of tangential sections of treated and untreated acacia hybrid wood. It is apparent that after impregnation and post-treatment, the TiO_2 gels were deposited onto the wood surface and were almost evenly distributed. However, the morphologies and the sizes of the titanium dioxide gels were not identical. In the samples of the T2 treatment group (pH=6.5), the titanium dioxide gel size was the smallest, at 0.113 μm. In samples of the T3 treatment group (pH=9.5), however, they were biggest, at 1.611 μm (Table 1).

Table 1. Weight Percent Gain (WPG) and TiO_2 Gel Size under Different Treatment Conditions

Sample	pH value of post-treatment solution	WPG (%)	TiO_2 gel size (μm)
Group T1	2.0	5.8 (0.52) [a]	0.325 (0.070)
Group T2	6.5	7.5 (0.37)	0.113 (0.017)
Group T3	9.5	7.4 (0.44)	1.611 (0.491)

[a] Values in parentheses are standard deviations

In the samples of treatment group T2, titanium dioxide gels with a specific shape were not common (Fig. 3b). However, in the samples of treatment groups T1 and T3, many spherical gels were found (Figs. 3d, f). These results indicate that the pH of the additive solutions used in the hydrohermal post-treatment significantly affected the size of the TiO_2 gels formed on the wood surface. The micro/nano size TiO_2 gels deposited on the wood surface were the reason why the treated acacia hybrid wood displayed very high hydrophobic properties after impregnation with TiO_2 gel. The phenomena can be inferred by an explanation that the deposition of TiO_2 on the wood surface is capable of offering a secondary roughness, providing an air layer in order to prevent water drop penetrations into the lumina of wood (Hsieh *et al.* 2011).

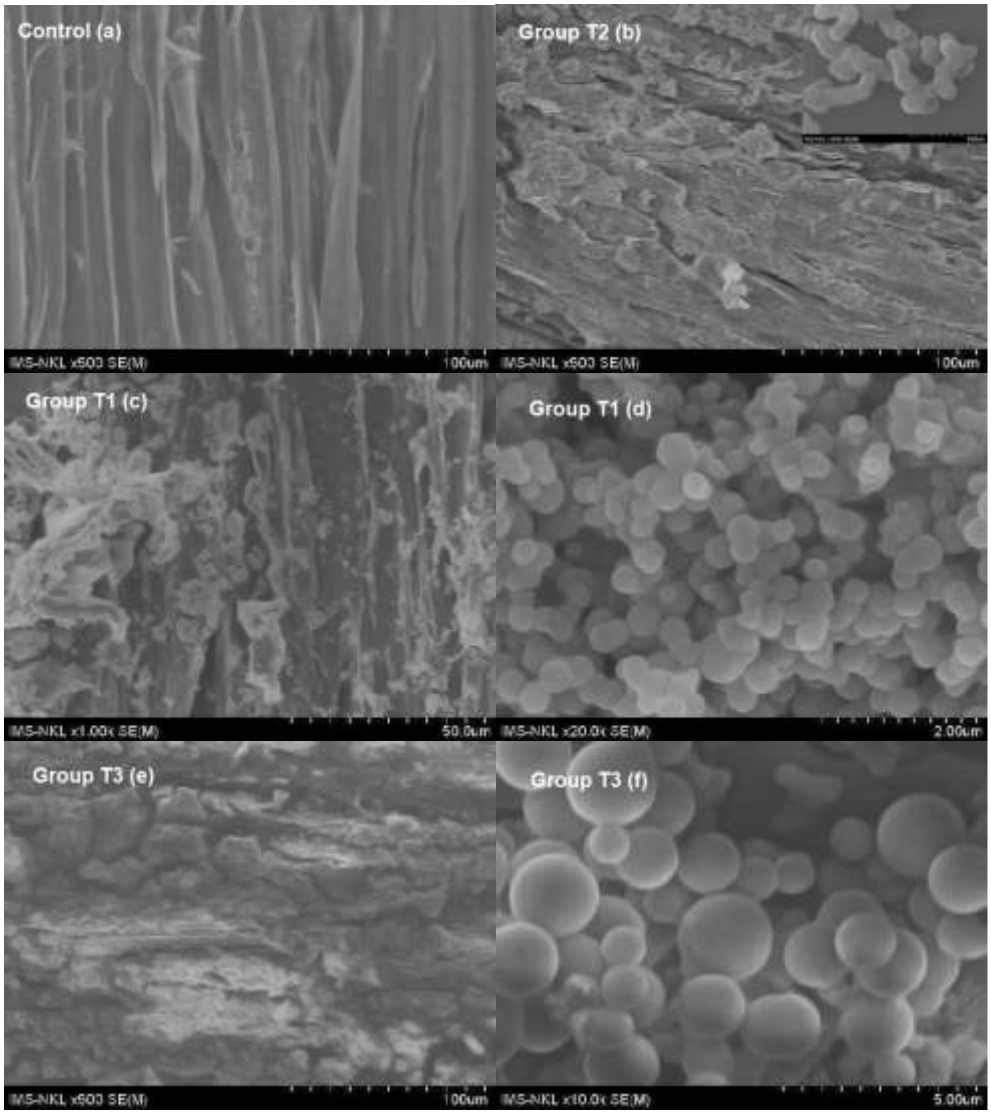

Fig. 3. FE-SEM images of TiO_2-treated acacia hybrid wood at different magnifications

X-ray Diffraction Analysis

To characterize the crystal structure of the TiO_2-treated wood, the XRD patterns of the treated and blank samples were collected from 2θ = 10 to 60° and are shown in Fig. 4.

Samples prepared under different hydrothermal post-treatment parameters (mainly the pH of the additive solution) exhibited distinct differences in their characteristic peaks. Figure 4 shows that the diffraction peaks located at 16 and 22.6° of 2θ were assigned to the peaks of cellulose crystal planes of 101 and 002, respectively (Li 2003). In general, no crystalline phases of TiO_2 were found in the spectra of any treated samples. This indicates that the TiO_2 deposited in the wood samples with hydrothermal post-treatment at 70 °C for 4 h was amorphous in structure.

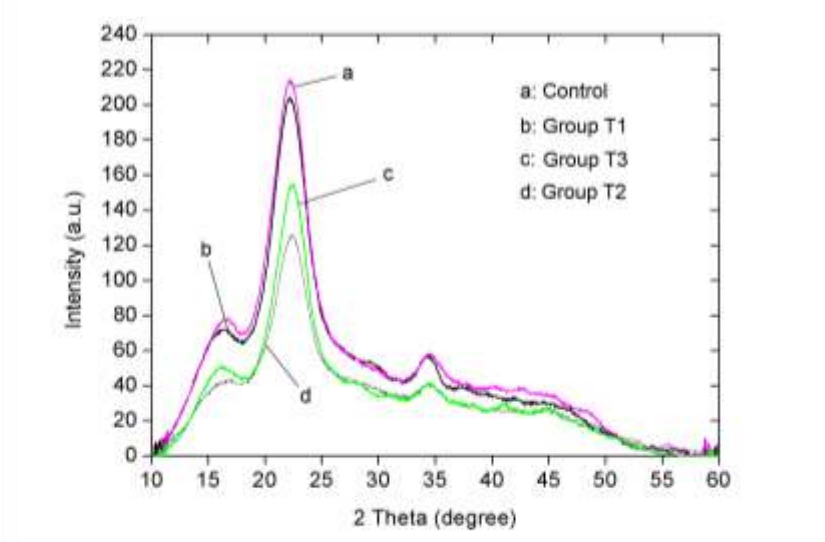

Fig. 4. XRD patterns of different wood samples

CONCLUSIONS

1. The wettability of TiO_2-treated acacia hybrid wood was less than that of the blank wood. Furthermore, the treated wood had a water contact angle above 150°, indicating that it was extremely hydrophobic.
2. The hydrophobic properties of the composites developed *via* TiO_2 treatment remained stable after immersion in boiling water.
3. FE-SEM images indicate that the pH of post-treatment solutions had a significant effect on the microstructure morphology of TiO_2 gels deposited on the wood surface.
4. The TiO_2 gel within the composites was amorphous in structure, as determined by XRD analysis.
5. Combined pressure-impregnation and hydrothermal post-treatment proved to be an effective method for fabricating TiO_2-treated wood or wood-TiO_2 composites with low wettability. Further studies are necessary to clarify the moisture adsorption behavior, dimensional stability, resistance to biological deterioration, and UV resistance properties of TiO_2-treated acacia hybrid wood.

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