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Improvement of water resistance and dimensional stability of wood through titanium dioxide coating

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Abstract

Moisture absorption and dimensional distortion are the major drawbacks of wood utilization as building material. In this study, poplar wood coated with a thin layer of titanium dioxide (TiO_2) was prepared by the cosolvent-controlled hydrothermal method. Subsequently, its moisture absorption and dimensional stability were examined. Scanning electron microscopy analysis revealed that the wood substrate was closely and entirely covered with the TiO_2 coat. Microscale features were visible despite masking of the ultrastructural features of the cell wall. To explore the effects of TiO_2 coating on the water-repellency and dimensional stability of wood, a 90-day water immersion test was carried out. Results showed that water absorption and thickness swelling of TiO_2-coated wood increase very slowly and minimally. Weight change after 90 days of water immersion was reduced to 20.5%, nearly one-tenth of untreated control wood, and that maximum cross-sectional relative swelling was only 1.2%. Specimens were conditioned for 3 months at 20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90% relative humidity (RH) to determine the effects of RH on moisture absorption and dimensional swelling of TiO_2-coated wood. There was no change in weight after 3 months of being exposed to humidity conditions below 60%, whereas there was linear weight increase above 60% RH, but the maximum change was less than 6%. Cross-sectional relative swelling was less than 0.3% below 60% RH but increased as RH exceeded 60%. The maximum change was approximately 3%. Anisotropic thickness swelling of wood was almost eliminated after coating. It is obvious that TiO_2 coating can act as a moisture barrier for wood and is an exceptionally strong water vapor-inhibiting shield under very humid conditions.

Keywords: coating; dimensional stability; titanium dioxide; water resistance; wood.

Introduction

Wood is a material sensitive to humidity because of the hydrophilic nature of its cell wall constituent polymers cellulose, hemicelluloses, and lignin. As a result, the moisture content (MC) of wood varies with the surrounding humidity and temperature changes. MC variation below fiber saturation point causes dimensional changes in wood. Undesirable dimensional changes lead to cracking and twisting, shrinkage and swelling, and cause important practical problems in wood utilization for building and construction. In addition, excessive moisture can result in fungal attack leading to color changes and – in the worst case – degradation. To obtain long-term service life, wood must have proper protection.

There are several approaches to improve water-repellency and dimensional stability of wood, including immersion-diffusion or vacuum-impregnation with preservatives, heating, brushing paint, and surface coating. One emerging technique is chemical modification, where chemicals such as anhydrides, isocyanates, alkyl chlorides, etc., react with hydroxyl groups, i.e., with the most reactive groups of cell wall polymers (Matsuda 1987; Hafizoğlu and Yildiz 1990; Rozman et al. 1997; Hill and Jones 1999; Chauhan et al. 2001; Chang and Chang 2002, 2003; Baysal et al. 2004; Kartal et al. 2007). For economic reasons and for simplicity, surface coating has long been preferred to modifications by chemical immersion (Denes et al. 1999; Magalhaes and Souza 2002; Tshabalala et al. 2003; Xie et al. 2008; Renneckar and Zhou 2009).

The primary function of any coating is to prevent moisture penetration, improve resistance to weathering, and maintain the natural appearance of wood. In recent years, the development of inorganic coatings on polymer surfaces has been fostered because of their excellent mechanical and thermal performance, optical behavior, and bacterial resistance. Barata et al. (2005) showed that cellulosic fibers act as efficient hydrophilic substrates for the nucleation and growth of inorganic particles in aqueous medium. Studies demonstrated that wood surface with its abundant hydroxyl groups is well suited for grown or deposit inorganic particles, such as silicon dioxide and titanium dioxide (TiO_2) (Schmalzl and Evans 2003; Tshabalala and Sung 2007; Chen et al. 2009). Tshabalala and Sung (2007) investigated sol-gel deposition of a hybrid inorganic-organic thin film on wood by means of a mixture of metal-organic precursors and reported its effect on weathering properties of wood surfaces. Chen et al. (2009) investigated the antifungal activity of TiO_2 photocatalytic reaction against *Aspergillus niger* for moist wood boards. Mahltig et al. (2008) described techniques to improve the properties of wood through the application of silica and other inorganic nanosols. The authors discussed the synthesis and modification of inorganic nanosols and methods of applying them to improve the mechanical properties of wood: (1) the use of modified silica sols for flame retardant, water-repellent, and antimicrobial properties; (2) the application of nanosols as protector of ThermoWood; and (3) as an additive for improving commercial wood lacquers.

The hydrothermal method was employed to construct organic or inorganic nanocomposites efficiently (Marques et al. 2006) as it is inexpensive and flexible. Our previous research has demonstrated that TiO_2 coating can be synthesized on wood surface through the cosolvent-controlled hydrothermal method (Li et al. 2010). To further understand its effect on water absorption and its ability to inhibit dimensional change, a 90-day water immersion experiment and 3-month humidity conditioning experiment were carried out separately. The goal was to determine how TiO_2 coating improves water resistance and dimensional stability of wood.

Experimental

Raw materials

Wood specimens from air-dried poplar wood (*Populus ussuriensis* Kom.) were cut into a size of $20\times20\times20$ mm^3 (long., tang., and rad.). The chemicals, including tetrabutyl orthotitanate (TBOT), sodium dodecyl sulfate (SDS), and anhydrous ethyl alcohol (EtOH), were supplied by the Shanghai Boyle Chemical Co. Ltd., Shanghai City, P.R. China.

TiO_2-coating by the cosolvent-controlled hydrothermal method

The synthetic conditions, under which TiO_2 coating grew on wood surface, were as follows: 5 g of TBOT was firstly dissolved in EtOH in a 200-ml glass beaker with an even agitation and transferred into a Teflon-lined stainless steel autoclave. No water was allowed to enter in all operating processes. Wood specimens were placed in the TBOT alcoholic solution. The reactor was sealed and heated at 110°C for 6 h. After heating and cooling, the reactor was opened and a solution of 9.1×10^{-4} mol l^{-1} SDS (pH 10) was added. The reactor was then sealed again and re-heated at 60°C for 4 h, after which the treated wood specimens were collected and finally dried at 45°C over 24 h. To quantify the TiO_2 grown on wood surface, some specimens were oven-dried and weighed before and after reaction. The surface morphology of specimens was characterized using the FEI Quanta 200 scanning electron microscopy (SEM) operating at 12.5 kV.

Long-term water immersion test

The specimens were placed separately in chambers containing distilled water of 20 ± 2°C with a stainless steel mesh cover in accordance to the Chinese national standard GB1934.1-2009 ''Testing methods for physical and mechanical properties of wood''. The specimens were weighed and measured after 1, 2, 4, 8, 10, 20, 30, 40, 50, 60, 70, 80, and 90 days of immersion.

Humidity conditioning test

Moisture absorption behavior was tested by exposing the TiO_2-coated wood specimens to different humidity levels (20%, 30%, 40%, 50%, 60%, 70%, 80%, and 90%) at 20°C. Relative humidity (RH) was achieved by means of selected saturated aqueous solutions in desiccators. Each specimen was weighed to the nearest 0.001 g and measured to the 0.001 mm, and was then grouped and placed accordingly in conditioning desiccators. Absorption equilibrium was attained in 3 months after which the specimens were weighed and measured again.

Computational parameters

Weight percentage change, thickness swelling, and cross-sectional relative swelling were calculated to evaluate the water absorption and dimensional stability of wood.

$$\text{Weight change: } WC(\%)=\frac{W_1\text{-}W_0}{W_0}\times100\%$$

where W_1 is weight of the specimen after treatment (water immersion or humidity-conditioned) and W_0 is weight of the specimen before treatment.

$$\text{Thickness swelling: } TS(\%)=\frac{L_1\text{-}L_0}{L_0}\times100\%$$

where L_1 is dimension of the specimen after treatment (water immersion or humidity-conditioned) in mm and L_0 is dimension of the specimen before treatment (oven-dried dimension) in mm.

Cross-sectional relative swelling is the sum of thickness swelling in radial direction and in tangential direction in %.

Results and discussion

Visual and SEM observation of TiO_2 coat on wood surface

The anisotropic surface appearances of wood and its microstructures have already been well described in previous studies. Therefore, the discussion in this paper will be limited to the surface and structural changes of wood due to TiO_2 attachment. Figure 1 presents photographs of untreated control and TiO_2-coated wood. The thin coating is light-transmitting and there were no essential changes in the macroscopic appearance of the wood surface.

Figure 2 shows the SEM images of the microscale features of TiO_2-coated wood at different magnifications. A continuous coating covered the entire surface, including fiber cells,

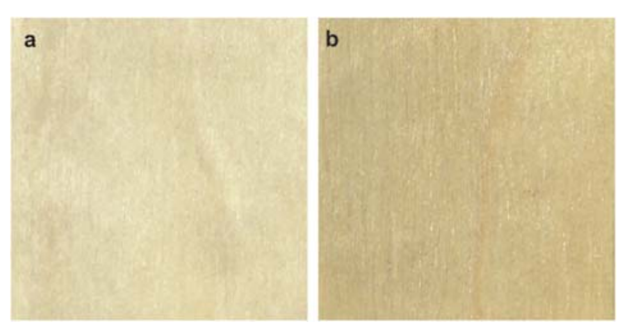

Figure 1 Images of (a) untreated control and (b) TiO_2-coated wood.

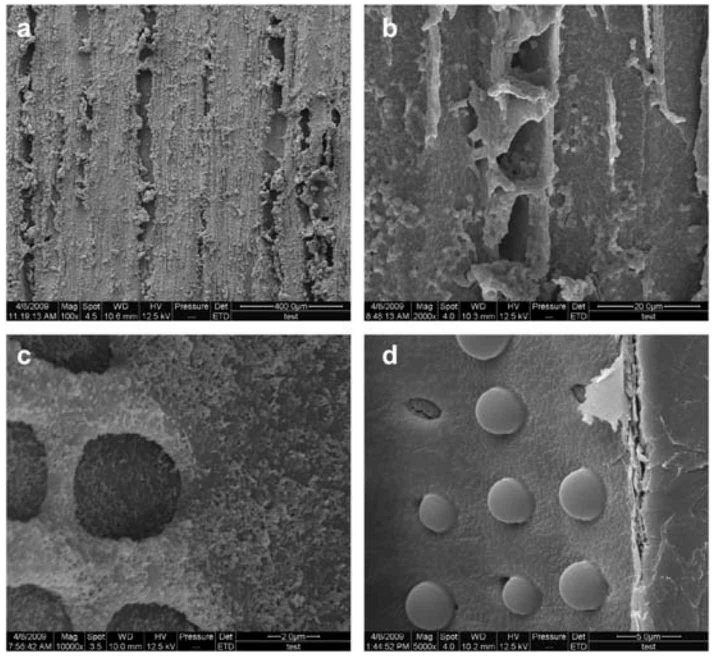

Figure 2 SEM images of TiO_2-coated wood at different magnifications. (a) Low-magnification image (100×, scale bar 400 μm), whereas (b, c, and d) high-magnification images (2000×, scale bar 20 μm; 5000×, scale bar 5 μm; 10 000×, scale bar 2 μm). (b) Lumen surface and ray cells with the film masking the exposed surfaces. (c) The vessel-ray cross-field pits in radial section. (d) The intervessel pits in tangential section.

vessel walls (Figure 2a), ray cells (Figure 2b), vessel-ray cross-field pits (Figure 2c), and intervessel pits (Figure 2d). A number of slippery TiO_2 spheres approximately 300–600 nm in diameter was dispersed evenly on the thin coating. Strong attachment of the TiO_2-coating to the wood surface was deduced when no significant loss of titanium was found after vigorous washing of the specimens. Typically, the TiO_2-coating represented 20% or more of the wood weight.

Long-term water immersion test

As presented in Figure 3, there was a significant decrease in water absorption after 3-month water immersion of TiO_2-coated wood. With an initial mean moisture content (MC) of 8.3%, the weight of the specimens increased as dipping time was extended. The maximum weight percentage change of TiO_2-coated specimens only reached 20.5% after 90 days of soaking, whereas that for untreated control wood specimen can absorb up to 220% water. Water absorption of TiO_2-coated wood can be reduced to almost 11-fold of that of untreated control, which is similar to the results of other chemical treatments or modifications. Yalinkilic et al. (1998) reported that sugi wood treated with boron-vinyl monomer has water absorption levels 13-fold less than untreated wood. Baysal et al. (2004) found that furfuryl alcohol and borates treatment can reduce water absorption of wood by 10 times compared with untreated wood.

Regression analysis conducted to assess the relationship between change in weight and water immersion time (Figure 3) revealed a quadratic equation with a good correlation ($R^2=0.988$). This allows the prediction of long-term water immersion behaviors based on soaking time.

Table 1 shows the thickness swelling in radial and tangential orientations, and the cross-sectional relative swelling of untreated control wood and TiO_2-coated wood during the 90-day water immersion test. There were minimal changes in thickness swelling of TiO_2-coated wood. In addition, anisotropicity of wood in thickness swelling was almost eliminated. Thickness swelling increased slightly during the first 96 h and approached equilibrium until the end of the test. This indicates that TiO_2 coating effectively improves long-term dimensional stability of wood soaked in water.

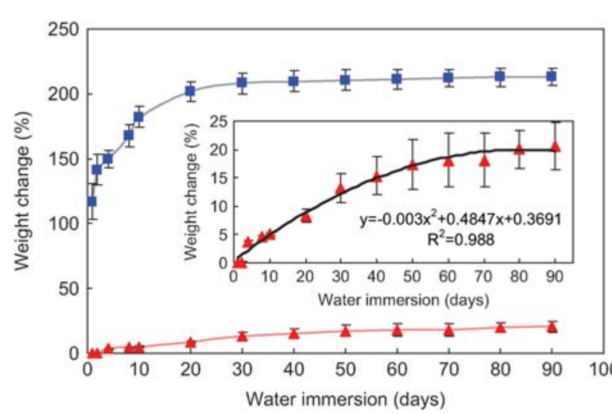

Figure 3 The weight percentage change of untreated control (square symbols) and TiO_2-coated wood (triangle symbols) during 90 days of water immersion test.

Table 1 Thickness swelling (TS) in radial and tangential directions and cross-sectional swelling of untreated control and TiO_2-coated wood during 90 days of water immersion test.

Swelling types of samples		Time (days) 1	2	4	8	10	20	30	40	50	60	70	80	90
Control	Radial TS (%)	2.57	3.11	3.63	3.91	4.17	4.60	4.70	4.75	4.75	4.75	4.75	4.75	4.75
	Tangential TS (%)	5.81	6.44	6.83	7.03	7.15	7.21	7.28	7.35	7.37	7.39	7.40	7.40	7.40
	Cross-sectional (%)	8.38	9.55	10.46	10.94	11.32	11.81	11.98	12.10	12.12	12.14	12.15	12.15	12.15
TiO_2-coated	Radial TS (%)	0.14	0.36	0.39	0.44	0.59	0.74	0.75	0.64	0.38	0.31	0.31	0.31	0.31
	Tangential TS (%)	0.11	0.30	0.32	0.38	0.57	0.46	0.43	0.40	0.49	0.52	0.52	0.52	0.52
	Cross-sectional (%)	0.25	0.66	0.71	0.82	1.16	1.20	1.18	1.04	0.87	0.83	0.83	0.83	0.83

Table 2 Equilibrium moisture content (EMC) of the untreated control and TiO_2-coated wood moisture-conditioned for 3 months between 20% and 90% RH.

EMC	Relative humidity (RH) 20%	30%	40%	50%	60%	70%	80%	90%
Control (%)	4.4	5.6	7.1	8.9	10.7	12.5	15.6	19.8
TiO_2-coated (%)	5.0	5.1	5.1	5.1	5.3	6.7	9.0	10.6

Humidity conditioning test

The weight and tangential and radial dimensions of the untreated control and TiO_2-coated wood were recorded after conditioning tests at various RHs. The equilibrium moisture content (EMC) of untreated control and TiO_2-coated wood are listed in Table 2. The EMCs of untreated control are bigger than those of TiO_2-coated wood. Maximum EMC of the former is close to the fiber saturation point, whereas that of TiO_2-coated wood is approximately 10%.

Figure 4 shows the weight percentage change of untreated control and TiO_2-coated wood due to water vapor absorption under different RH conditions for a period of 3 months. There was no significant change in the weight of TiO_2-coated specimens in humidity conditions below 60% RH but there was a linear increase above this point. Maximum weight change was approximately 6%, suggesting that TiO_2 coating can greatly decrease water vapor absorption even throughout a 3-month humidity conditioning test.

All thickness swelling values in the radial orientation were less than 1.0%; those in tangential orientation were from 0.05% at 20% RH to 2.3% at 90% RH. Thickness swelling showed an indistinct anisotropicity, if any.

Figure 5 presents the differences in cross-sectional relative swelling between untreated control and TiO_2-coated wood after various RH, whereas Figure 6 shows cross-sectional relative swelling of TiO_2-coated wood as a function of RH. Changes were minimal in humidity conditions below 60% RH but increased visibly above 60% RH. The maximum weight change was less than 3%, which is nearly 1/20 of that of untreated control wood.

Reductions in water absorption and thickness swelling could be responsible for the decrease in crosslinking efficiency of wood after TBOT and SDS addition and TiO_2 coat

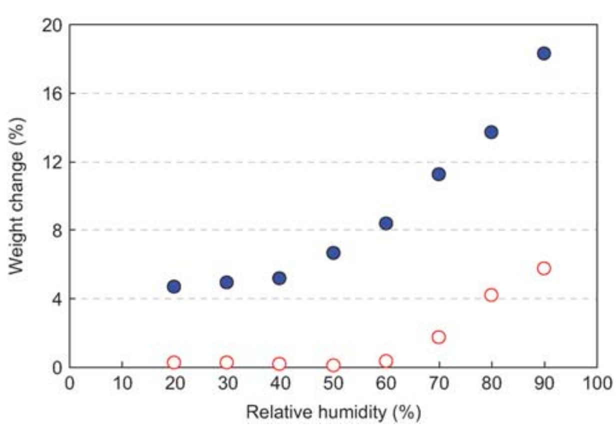

Figure 4 The weight percentage change of untreated control (solid circle symbols) and TiO_2-coated wood (open circle symbols) due to water vapor absorption under different RH conditions for a period of 90 days.

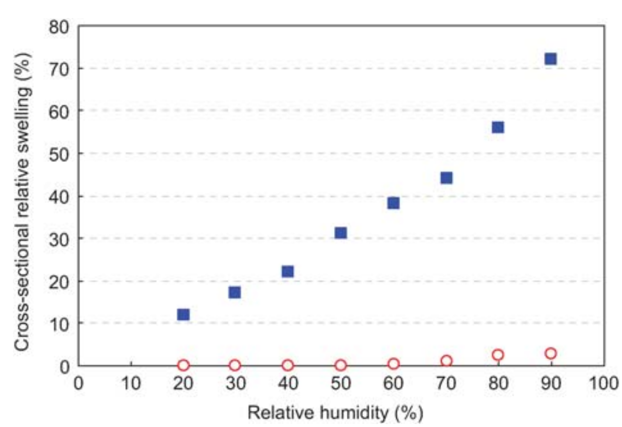

Figure 5 Differences in cross-sectional relative swelling between the untreated control (solid square symbols) and TiO_2-coated wood (open circle symbols) due to water vapor absorption under different RH conditions for a period of 90 days.

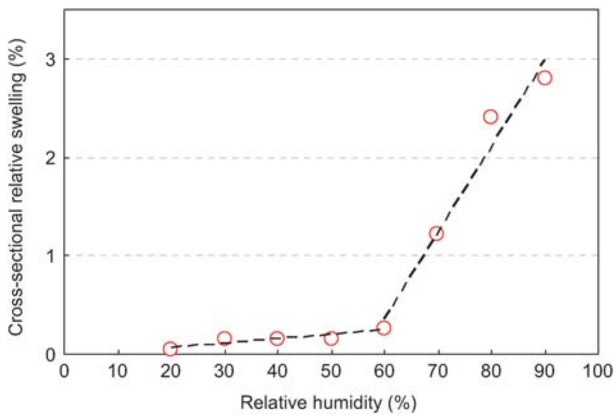

Figure 6 Cross-sectional relative swelling of TiO_2-coated wood due to water vapor absorption under different RH conditions for a period of 90 days.

formation, which have hydrophobic and shielding effects on wood surfaces. TiO_2 can play a section-sealing role in blocking water when used to cover surfaces on wood fiber walls, vessel lumens, and other void spaces, thus resulting in less water penetration.

Conclusions

Formation of TiO_2 nanostructures on the surface of solid wood was achieved by the cosolvent-controlled hydrothermal method. Results showed that thin TiO_2 coating can remarkably decrease water absorption and prevent dimensional swelling of wood. The improved water-repellent characteristics of wood surfaces resulting from this simple method can create new functional features and be useful for wood protection mainly for wood constructions in exterior use.

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