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Antiweathering properties of a thermally treated wood surface by two-step treatment with titanium dioxide nanoparticle growth and polydimethylsiloxane coating

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ABSTRACT

The weathering of thermally treated wood by light radiation and water is an important problem for the wood used in outdoor applications. In this study, a durable hydrophobic and UV-resistant layer was successfully formed on the surface of thermally treated wood at room temperature after *in situ* deposition of titanium dioxide (TiO_2) nanoparticles and a polydimethysiloxane (PDMS) coating. The morphology of the rutile TiO_2 nanoparticles formed on wood surface, varying from spherical (A-TiO_2) to acicular (B-TiO_2), was tunable by the reaction time between the precursors. Even though the deposited TiO_2 was proved to make the wood surface UV resistant, it was nondurable due to the poor leaching resistance. The successive coating by PDMS significantly improved the leaching resistance of TiO_2 nanoparticles due to the superior hydrophobicity of PDMS. Therefore, the degradation of wood components was reduced, and the removal of chromophoric products in the thermally treated wood was also hindered.

1. Introduction

Wood undergoes degradation in outdoor application due to the influence of numerous exterior conditions, among which ultraviolet light and water are regarded as the most important [1]. Energy provided by ultraviolet photons breaks chemical bonds in wood components and leads to the generation of reactive free radicals [2]. The exposure of wood surfaces to ultraviolet light causes photodegradation of lignin in the cell walls, resulting in changes in the wood color [3]. Additionally, the occurrence of surface discoloration, roughness and checking of exposed wood is accelerated by rapid changes in moisture content [4,5]. Considering this phenomenon, many attempts have been made to improve the weathering performance of wood or wood-based products by pretreatments such as thermal treatment [6], modifications using UV absorbers [7,8], adding water repellents [9] or covering with varnish coatings [10,11], among which thermal treatment has been particularly popular because it improves the dimensional stability and decay resistance of wood without adding any toxic chemicals. However, researchers found that thermal treatment still does not endow wood with resistance to ultraviolet radiation and moisture [12].

Recently, titanium dioxide (TiO_2) nanoparticles have received considerable attention in the material modification field because of their low toxicity and UV-shielding effect, with the rutile form of TiO_2 shown to be an effective ultraviolet protector for wood due to its high ultraviolet opacity and low photoactivity [13,14]. Rutile TiO_2 was usually added to coatings at different ratios to protect wood from photodegradation [15,16]. It can be successfully deposited on a wood surface by the hydrothermal method [17–19]. A room temperature method to improve the wood hydrophobicity was carried out by growing rutile TiO_2 hierarchical structures on the wood surface, controlling the direct hydrolysis and crystallization of $TiCl_3$ in a saturated NaCl aqueous solution [20]. However, these approaches appear to usually be unsuccessful in practical applications to wood surfaces because of the limited stability and durability of the TiO_2 layer. Without an appropriate design, the UV-shielding surface layers are prone to be damaged by moisture washing, leading to the loss of TiO_2 and undesired photodegradation of wood components. Accordingly, various nonpolar agents, such as oils, waxes, silanes and silicones, have been used to achieve water-resistant surfaces [21–24]. Among all of the waterproof agents, polydimethylsiloxane (PDMS) has attracted research attention as an industrial material because of its advantageous optical and hydrophobic properties [25]. Nakata et al. [26] developed a kind of TiO_2-PDMS composite film with rewritable wettability. However, the effect of the use of the combination of TiO_2 and PDMS on the weatherability of materials is still unknown.

Wood photodegradation is merely a surface phenomenon because

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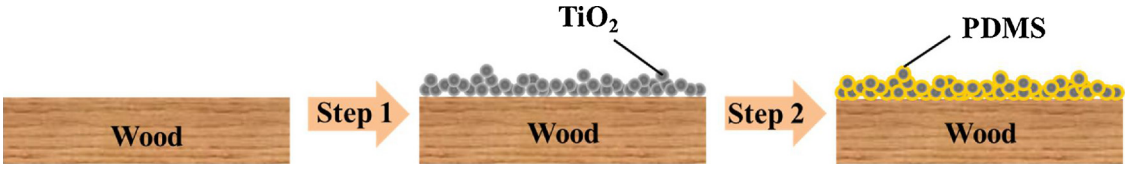

Scheme 1. Illustration of the two-step process for preparation of antiweathering thermally treated wood surfaces.

ultraviolet light cannot reach a depth of more than 75 μm into a wood surface [27]. Therefore, a surface-focused approach is needed to solve this problem by controlling ultraviolet light and water simultaneously. In this study, we present a simple surface modification method that can be implemented at room temperature on a thermally treated wood surface by using TiO_2 nanoparticles and hydroxyl-terminated PDMS, both of which are inexpensive and environmentally friendly. A durable antiweathering surface was achieved by the combined modification with TiO_2 and PDMS. Scheme 1 illustrates the two-step process of TiO_2 nanoparticles deposition and the coating of hydroxyl-terminated PDMS on the surface of thermally treated wood. The antiweathering performance of the as-prepared wood surfaces was investigated by using the untreated wood samples as controls.

2. Materials and methods

2.1. Materials

Samples with the dimensions of 70 mm (L) × 50 mm (T) × 5 mm (R) were machined from the air-dried sapwood of Finland Scots pine (*Pinus sylvestris* L.) lumber. The annual ring width of the Scots pine used in the experiment was 2.2 mm, and its air-dry density was 0.45 g cm^{-3}. Chemicals, including ammonium fluorotitanate, boric acid, hydrochloric acid, and absolute ethanol, were all of analytical reagent grade and were purchased from Beijing Lanyi Chemical Co. Ltd. Hydroxyl-terminated polydimethylsiloxane (PDMS) (Mw = 4200; d = 0.97 kg m^{-3}) was purchased from Alfa Aesar (China) Chemical Co. Ltd. Deionized water was used for all experiments.

2.2. Thermal treatment

All the specimens were preconditioned to achieve approximately 12% moisture content at 20 °C and 65% relative humidity in a conditioning room. Then, the specimens were thermally treated at 140 °C for 25 h in the steam atmosphere with a pressure of 0.7 MPa. Forty specimens were selected randomly to comprise the control group.

2.3. In situ deposition of titanium dioxide (TiO_2) on internal surface of wood

An aqueous solution was prepared by dissolving 8.0 g ammonium fluorotitanate and 7.4 g boric acid in 400 mL deionized water with vigorous magnetic stirring for 10 min at room temperature. Then, 1.0 wt% hydrochloric acid was added dropwise to adjust the pH of the mixture to 3 immediately to form treating solution A or after 25 h seasoning of the above solution to form treating solution B. Groups of wood specimens immersed in treating solutions A and B for 3 days were labeled A-TiO_2 and B-TiO_2, respectively. After immersion, all the specimens were washed with deionized water and dried at 60 °C for 48 h in a vacuum oven. The retained TiO_2 powders were collected from the reaction beaker to measure their crystal type after drying at 103 °C for 48 h.

2.4. Treatment of specimens with water repellent (PDMS)

Hydroxyl-terminated polydimethylsiloxane (PDMS) was coated on the surfaces of untreated and TiO_2-treated specimens (A-TiO_2 and B-TiO_2) at room temperature with a brush. The coating amount was 300 g m^2. Then, for all specimens, the coating was cured at 60 °C for 24 h.

2.5. Accelerated weathering test

The weathering performance of all of the wood specimens was tested in an accelerated weathering tester (QUV/Spray, Q-Lab Corporation) according to ASTM 154 (2004). The weathering cycle consisted of two periodic processes, the UV radiation stage at 60 °C for 8 h and the condensation stage at 50 °C for 4 h. In this test, the intensity of UV irradiation was 0.89 W m^{-2} at 340 nm. UVA-340 lamps were used to simulate the irradiation of sunlight in the critical wavelength region ranging from 365 nm to 295 nm. The lamps were calibrated every 500 h. Surface properties of the specimens were evaluated for different irradiation times (168, 336, 504, 672, 840, 1008 and 1176 h).

2.6. Characterization

2.6.1. Surface morphologies observed by SEM

Surface morphologies of the specimens were observed by scanning electron microscopy (SEM, Hitachi S3400, Japan) with an acceleration voltage of 5 kV.

2.6.2. Crystalline structures of TiO_2 characterized by XRD

The crystalline structures of the TiO_2 powders were identified by X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) operating with CuK_α radiation (λ = 0.154 nm) from 10° to 70° at a scanning rate of 2°/min. The accelerating voltage was set to 40 kV and the applied current was 40 mA.

2.6.3. Wettability of specimens by determination of WCA

The water contact angle (WCA) was determined to evaluate the wettability of the specimens using an OCA20 CA analyzer (Data Physics, Filderstadt, Germany).

2.6.4. Determination of chemical elements by XPS

The change of chemical elements on the specimens' surface was determined by X-ray photoelectron spectroscopy (Escalab 250 Xi, Thermo Scientific, USA) before and after the weathering test. The specimens were cut into slices (5 mm × 5 mm × 3 mm) and analyzed at pressures between 10^{-9} and 10^{-8} Torr with a pass energy of 29.35 eV and a take-off angle of 45°.

2.6.5. Surface color before and after accelerated weathering

The surface color of the specimens was measured using a chroma meter (Datacolour DF 110, Shenzhen 3NH Technology Co., Ltd, Shenzhen, China) according to the CIE LAB color system. The parameters, including L*, a*, and b*, were measured at six specific locations at intervals on the surface of each specimen and the average value was calculated. L*, varying from 100 (white) to 0 (dark), represents the lightness coordinate. Parameters a* and b* represent the red-green coordinate and yellow-blue coordinate, respectively. L*, a*, b*, and △E* were calculated using the following Eqs. (1)–(4).

$$\Delta L^* = L_t^* - L_i^* \quad (1)$$

$$\Delta a^* = a_t^* - a_i^* \quad (2)$$