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Fabrication of reversible thermoresponsive thin films on wood surfaces with hydrophobic performance

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ABSTRACT

The smart reversible thermoresponsive wood with hydrophobic performance was fabricated by depositing modified thermoresponsive coatings on wood surfaces. The modified composite films were prepared by entrapping thermochromic materials (TM) supported on the 3-Aminopropyltriethoxysilane (AEPT) into polyvinyl alcohol solution (PVA). All the samples possessed superior reversible thermoresponsive property, and the thermochromic response rate of TM-APTES/PVA modified wood was higher than the other samples. The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra demonstrated that the TM-APTES/PVA composite polymer films have been successfully settled onto wood surfaces. The scanning electron microscope (SEM) and pull-off test results proved that the modified wood possessed better dispersion stability of TM particles and stronger interfacial adhesion than TM/PVA coated wood. Furthermore, the surface properties of wood materials changed from hydrophilic to hydrophobic after chemical modification.

1. Introduction

As a natural and renewable biopolymer, wood has been extensively used in buildings, decorations, industries and other daily lives in virtue of its unique performances of the high ratio of strength to weight, esthetic, and amendment for indoor environment [1–3]. Whereas the wood supplies increase rapidly, many attempts have been made to create new functions for wood to meet market requirements and compete with other advanced materials [4–7]. Among them, the interest has recently arisen in the development of smart stimuli-responsive materials due to its potential applications as sensors, smart switches and energy storage [8–10].

The reversible thermochromic materials have become one of the most advanced materials in smart materials because of its fast response to temperature [11,12]. Due to the unique properties, reversible thermochromic materials are widely used in many fields such as molecular switch [13], temperature sensor [14,15], thermal relays [16] and intelligent coating [17,18]. As a novel type of smart material, the orthodromic reversible thermoresponsive wood was developed by coating wood substrates with transparent films. The evident advantage of the orthodromic thermoresponsive wood is that its color can be repeatedly changed with the changing temperature without destroying the naturally beautiful wood texture. However, the hydrophilicity of wood may limit their application [19].

The main substances of wood cell wall are cellulose, hemicellulose and lignin, making up approximately 97–99% of the total weight [20]. The hydroxyl and other oxygen-containing groups of wood cell wall polymers can attract and retain moisture through hydrogen bonding [21]. The moisture absorption of wood may cause dimensional changes of the composites and cause a serious problem to its durability and use value of the interfacial adhesion [22–24]. The chemical modification may make wood materials more dimensionally stable by reducing water sorption [25].

Binding of a functional group to wood surface via a covalent bond is a reliable method of modification of the wood substrate. Silane coupling agent is a chemical that functions at the interface to create a chemical bridge between the reinforcement and matrix [26,27]. That is, using its organofunctional group (Y) and hydrolysable groups (X) to form a stable link. Here, the schematic of organosilane bonded onto wood substrate is shown in Fig. 1. Three hydrolysable groups in silane coupling agent are expected to hydrolyze forming the Si—O—Si network structure, resulting into the preparation of structure [28–30]. At the same time, the organofunctional groups are chosen for reactivity or compatibility with the polymer, resulting into good contact with other

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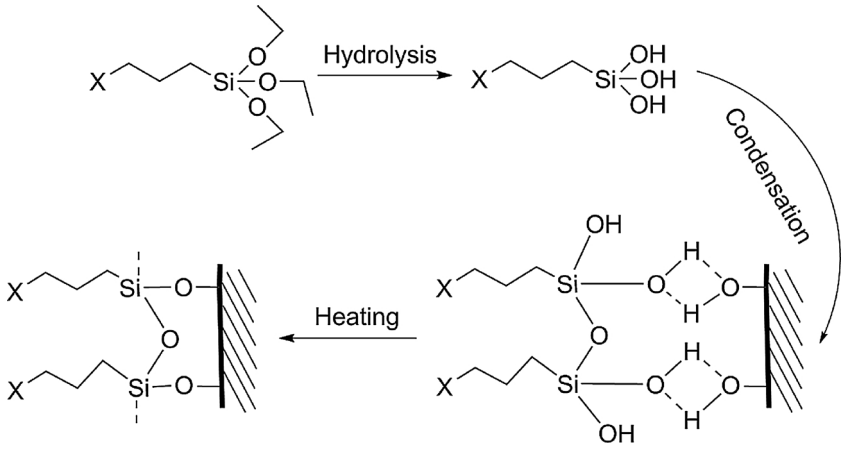

Fig. 1. The interaction reaction between organosilane and wood substrate.

phase [31–33]. As a kind of aminosilanes, 3-Aminopropyltriethoxysilane (APTES) may form the strong intra- and intermolecular hydrogen bonds with its amino group, meanwhile, possessing a strong affinity towards the hydroxyl groups of wood surface [34,35]. Although the interaction among thermochromic materials and wood surface can be reinforced by covalent bonds, the thermochromic materials may be destroyed by the tensile stress initiated from coating shrinkage during drying. Therefore, PVA was added to relieve the tensile stress and also serve as a transparent and environmental coating material [33,36].

In this paper, we prepared a novel reversible thermoresponsive wood with hydrophobic performance by a sample drop-coating method. The thermoresponsive properties, surface morphologies, wettability and bond strength of samples were investigated.

2. Experimental

2.1. Materials

Wood samples (radial section) of 50 mm × 25 mm × 5 mm were obtained from Harbin, China, Manchurian ash (Fraxinus mandschurica Rupr.). The wood specimens were oven-dried (24 h, 103 ± 2 °C) to constant weight after ultrasonically rinsing in deionized water, acetone and ethanol for 10 min, respectively. The ethanol (99.7%), acetone (99.5%) and polyvinyl alcohol (PVA) (alcoholysis 98.0–99.0%, model 1750 ± 50) were purchased from Tian jian Kaitong Chemical Reagent Co., Ltd. Thermochromic materials (TM) namely, 2′-chloro-6′-(diethylamino)-3′TR-2 (white powder), were manufactured by Chong Yu Technology Co., Ltd. 3-Aminopropyltriethoxysilane (APTES) was supplied by Sa en Chemical Technology (Shanghai) Co., Ltd. All of the chemicals were used as received without further purification.

2.2. Fabrication of APTES/PVA coated wood

Firstly the PVA solution was prepared by dissolving 4 g PVA into 100 ml deionized water at 75 °C for 2 h with magnetically stirring. Secondly 1.5 ml APTES was added into 8.5 ml alcohol solution, and then slowly added into 20 ml PVA solution under continuous stirring. Thirdly six separate experiments were set at 40 °C with different hydrolyzing time of 20 min, 25 min, 30 min, 35 min, 40 min and 45 min. Next, 1.0 ml above suspension was dropped onto the wooden substrates. Finally, the treated samples were placed in a 110 °C oven for 10 min to be dried.

2.3. Fabrication of thermoresponsive wood

To prepare coating solution, 0.35 g TM and 1.5 ml APTES were added into 8.5 ml alcohol solution stirred for 10 min at room temperature, and then slowly added into 20 ml PVA solution under magnetically stirring at 40 °C for 30 min. Next, 1.0 ml coating solution was dropped onto the wood surface. Then, the treated samples were dried in oven at 110 °C for 1 h. Finally, the TM-APTES/PVA modified wood was obtained. Furthermore, a named TM/PVA coated wood was also prepared for the purpose of comparison. The same experimental procedures were used except that the 1.5 ml APTES was absent.

2.4. Characterizations

The digital photos of the samples were obtained using a Nikon D7000 digital camera. A scanning electron microscopy (SEM, FEI Quanta200) was used to investigate the surface morphologies, the samples were glued onto a specific holder and were sprayed by gold to ensure the conductivity. The attenuated total reflectance of the Fourier transform infrared spectroscopy (ATR-FTIR) was recorded by the Nicolet Nexus 670 FTIR instrument in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. An OCA 40 contact angle system (Dataphysics, Germany) was used to measure the water contact angles (WCAs) by injected a 5 μl droplet of deionized water onto the surfaces of the samples at room temperature. The WCAs were measured at five different points for each sample and the average value was reported as the final contact angle value.

2.5. Color tests

The samples were placed into a DHG-9023A conditioning chamber (Jiangsu Jun Instrument Technology Co., Ltd.). The temperature sensor was calibrated to an accuracy of 0.1 °C, and the temperature was monitored at 200 s interval and increased in an interval of 1 °C. A digital camera was placed in a fixed position to record the whole process over a temperature range of 25–65 °C, and these records were imported to a computer. The Commission Internationale de L'Eclairage (CIE) L^*, a^*, and b^* values were measured by using the Adobe Photoshop CS6 software installed in the computer [19].

2.6. Response time tests

Response time test was measured according to the analysis of images captured by the camera. With the increase in temperature, the ΔE^* values increased from initial value to maximum value (Fig. 2a). As temperature continues to rise, ΔE^* values remain unchanged (Fig. 2b). Finally the ΔE^* values decreased from maximum value to initial value with the decreasing temperature (Fig. 2c). The response time Δt_1 was identified as the coloration time. Correspondingly, the response time Δt_2 was the bleaching time.