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Fabrication of Hydrophobic Indonesia Bamboo Modified by Octa Fluoro 1-Pentanol (OFP) Based on TiO_2 Thin Film for Self-cleaning Application

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ABSTRACT

The ultra-hydrophobic surface on Indonesia bamboo timber has been successfully prepared using OFP (2,2,3,3,4,4,5,5-octafluoro-1-pentanol) as a modifier agent. The hydrothermal method has been used to fabricate anatase TiO_2 film followed by OFP modification. Maximal water contact angle of 123° has been obtained for the composition of 10 mL of OFP and 15 mL of 2-propanol (B-T-OFP10). XRD analysis showed the existence of pure anatase TiO_2 film on bamboo timber, confirmed by EDS result. SEM image of a TiO_2-coated and a typical ultra-hydrophobic bamboo timber revealed irregular aggregates of spherical TiO_2 on the surface and compact ultra-hydrophobic surface, respectively. The optimum sample (B-T-OFP10) showed excellent mechanical stability, self-cleaning property, and flame retardancy compared to pure bamboo timber.

Keywords: TiO_2 thin film, Indonesia bamboo, bamboo timber, ultra-hydrophobic surface, self-cleaning.

INTRODUCTION

Bamboo is a source of renewable and widely available as natural material in Indonesia [1]. From the approximately 1,250 species of bamboo in the world [1, 2], about 140 species or 11% are native to Indonesia [1]. The reported work of Haryanto [3] introduced 11 genera and 35 species of Indonesia bamboo, which are distributed almost in every island (such as Sumatera, Java, Sulawesi, Kalimantan and Bali) [3]. This distribution affected the growth and the properties of Indonesia bamboo depending on its soil conditions, climate and geographical aspect [3]. Where generally the consequence of these factors provides that the Indonesia bamboos have an excellent elasticity and tensile strength (the external tensile strength c.a 2850 kg/cm and the internal tensile strength c.a 970 kg/cm) [4]. In fact, this excellent quality can be obtained from 2 to 5 years of the bamboo growth [4]. The other point of Indonesia bamboos are easy to cultivate, and no need special treatment [1, 3, 4]. Therefore, Indonesians have long utilized bamboo for construction of house building [5], furniture [6, 7], agricultural tools, flooring [8], handicrafts [9], musical instruments, pulp [10] and food [1].

Bamboo stem is composed of three parts: pith, bamboo timber, and bamboo skin [11]. Pith is the part of stick wall next to bamboo cavity which does not have vascular bundles. Bamboo skin is the outermost thin layer of the cross-section of stem wall, where no vascular bundles are present. Bamboo timber is the part of between peel and pith. Vascular bundles are visible cross the timber section [11]. The density of vascular bundles decreases from outer side of stem wall to inner side [12]. The bamboo timber can be further divided into three layers as shown in Figure 1. The outer part where vascular bundles are dense is called bamboo green, while the inner part where vascular bundles are rare is called bamboo yellow. The layer between bamboo green and yellow is called bamboo timber. If not indicated otherwise, the term "bamboo timber" in this study means the layer between bamboo green and bamboo yellow.

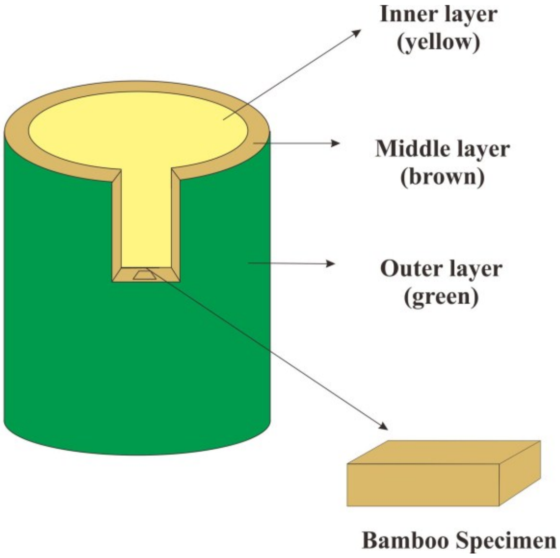

Figure 1. Illustration of bamboo timber

Bamboo can be used as an alternative to substitute wood beams [13]. However, when exposed in an outdoor environment, bamboo shows low decay-resistance if it is without protective treatment [14]. Fungi and insects will attack it and can be quickly degraded by acid rain, moisture, fire, air, sunlight, mainly shortens its service life and also reduces its value [15]. The main constituents of bamboo are lignin-cellulose, hemicellulose and which amount to over 90% to total mass. The elementary unit of a cellulose macromolecule is anhydro-d-glucose, which contains three hydroxyl (-OH) groups [14]. These hydroxyl groups form hydrogen bonds inside the macromolecule itself (intramolecule) and between other cellulose macromolecules (intermolecules) as well as with hydroxyl groups from moist air. Therefore, bamboo timber tends to absorb water and vapor in ambient conditions, which lead to reduce its quality, stability, and durability. To protect the economic value of bamboo products, it is necessary to develop a protective treatment for bamboo materials [16].

Several studies have been conducted and reports that hydrophobic surfaces with high water repellency and low contact angle hysteresis (typically <10) could be one of the ways to protect the bamboo from the moist air [16]. Jingpeng et al. [14] prepared superhydrophobic bamboo timber with excellent chemical stability and flame retardancy. They prepared it by the hydrothermal deposition of anatase TiO_2 nanoparticles followed by octadecyltrichlorosilane (OTS) modification [14]. In another study, Jingpeng et al. [17] were successfully fabricated durable, self-cleaning and superhydrophobic bamboo timber surface using (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane $[CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3]$ (FAS-17) as modifier agent on TiO_2 anatase film [17]. Jingpeng et al. [18] also studied the fabrication of robust superhydrophobic bamboo using the same method and modifier agent (FAS 17) but different inorganic compound. Here, ZnO nanosheet was prepared to grow onto the bamboo surface [18]. Chunde Jin et al. [9] undertook another study that superhydrophobic surfaces could be synthesized from silver nanoparticles (Ag NPs) modified using fluoroalkylsilane compound resulting in a contact value of 155^0.

In this work, a similar approach was used to prepare protective surface on Indonesia bamboo using OFP (2,2,3,3,4,4,5,5-octafluoro-1-pentanol) as modifier agent. Crystalline structure and surface morphology were evaluated as well as mechanical stability, self-cleaning property, and flame-retardancy.

EXPERIMENT

Materials

All chemicals were used directly without further purification. Ammonium fluorotitanate, purchased from Sigma-Aldrich was used as Ti source; octa-fluoro-1-pentanol (Sigma-Aldrich) was used as the agent of hydrophobicity. Boric acid, 2- propanol, acetone, distilled water, hydrochloric acid, sulphuric acid, and sodium hydroxide were used as received. Bamboo timber slices (LxTxR) of 50 mm x 20 mm x 5 mm were rinsed in distilled water and then acetone for 30 min, and if completed, they were dried in an oven at 80°C for 24 h.

Procedure reaction

Synthesis of anatase TiO_2 nanoparticles on the surface of the bamboo timber via a hydrothermal method

In the fabrication process, ammonium fluorotitanate (2.0 g) and boric acid (1.85 g) were dissolved in 100 mL of distilled water under vigorous magnetic stirring. After vigorous stirring for 15 min at room temperature, the pH of the solution was then adjusted to 2 by dropwise addition of hydrochloric acid aqueous solution (1.0%). Seventy-five milliliters of the adjusted solution was transferred into a 100 mL Teflon autoclave. Bamboo specimens were subsequently placed into the reaction solution. The autoclave was kept in an oven at 90°C for 5 h. Finally, the samples were removed from the solution, washed with distilled water, and dried at 80 °C for more than 24 h in the oven [17].

Surface modifications for the hydrophobicity

In order to reduce the surface energy, the surfaces of the as-prepared bamboo based on TiO_2 ware chemically modified with 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFP). Typically, bamboo based on TiO_2 substrates were immersed in a mixed solvent of OFP and 2-propanol with various composition (v/v) of OFP:2-propanol (5:20; 10:15; 15:10; 20:5) for 12 h at 60^oC, and thoroughly rinsed. The obtained samples were marked as B-T-OFP5, B-T-OFP10, B-T-OFP15, and B-T-OFP20, respectively [19].

Characterizations

The crystalline structures were identified by X-ray diffraction (XRD). XRD pattern was collected using Rigaku Smartlab 3kV with Cu Kα radiation in the range from 10^o to 90^o. The morphology of the samples was observed by Scanning Electron Microscopy (SEM, JEOL JSM-IT-300). EDS supported in the SEM was used to determine the chemical compositions of the TiO_2-coated bamboo timber and as-prepared ultra-hydrophobic bamboo timber.

Product tests

The water contact angle (WCA) was measured manually at room temperature with a droplet volume around of 5 μL. An average of three measurements taken at different positions on each sample was applied to calculate the final WCA. The mechanical stability of the hydrophobic surface was evaluated by the scratch test. The scratch test was carried out on a homemade scratch tester: SiC sandpaper 1300 mesh served as an abrasion surface, with the hydrophobic surfaces to be tested facing this abrasion material. The surface self-cleaning property was determined by evaluating the capability of the water droplets brings the carborundum particles down. Flammability properties were examined by comparing the ability of the pristine bamboo timber and the ultra-hydrophobic bamboo timber in the presence of a flame using alcohol burner [14].

RESULT AND DISCUSSION

Synthesis of hydrophobic surface of bamboo timber

Precursors that used to form TiO_2 solutions were ammonium fluoro titanate and boric acid. Stirring process was done in water. In the initial solution there are a number of $[TiF_6]^{2-}$ ions, H^+ ions and H_2O molecules. All main reactions took place are as follows [17]:

$$[TiF_6]^{2-} + nH_2O \rightarrow [TiF_{6-n}(OH)_n]^{2-} + nH^+ + nF^- \ (n = 0\text{-}6) \quad (1)$$

$$H_3BO_3 + 4HF \rightarrow HBF_4 + 3H_2O \quad (2)$$

$$[TiF_{6-n}(OH)_n]^{2-} + (2 - n)H_2O \rightarrow TiO_2 + (4 - n)H^+ + (6 - n)F^- \quad (3)$$

The reactions above explained that the equation (1) is the hydrolysis reaction of $[TiF_6]^{2-}$ ions from $(NH_4)_2TiF_6$ precursor. The F^- ions produced in equation (1), then react with H_3BO_3 as express in the equation (2) to form fluoro complex compound and water. The further hydrolyzation of $(TiF_{6-n}(OH)_n]^{2-}$ ions in the equation (1) to form TiO_2 compound are express in the equation (3). In order to increase and speed up these reactions, the pH of the solutions was controlled through the addition of HCl to increase the number of H^+ ions. The anatase TiO_2 film is coated onto the bamboo surface using a hydrothermal process. In this hydrothermal process, hydrolysis of $(NH_4)_2TiF_6$ and condensation of hydrolyzed Ti occurs. Above the bamboo surface, there are excess hydroxyl groups. Ions $(TiF_{6-n}(OH)_n]^{2-}$ gradually yields nano-sized TiO_2 in the presence of high energy and pressure aid in the autoclave. Then obtained TiO_2 nano-scale that interact strongly with hydroxyl groups on the surface of bamboo. The presence of this hydroxyl group makes the position of TiO_2 nano-scale stable on the surface of the bamboo. Gradually, the TiO_2 nanoparticles are attracted to and join the preformed TiO_2 in the presence of an electrostatic adsorption force resulting in layered TiO_2 on the bamboo surface. The fluorine contained in 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFP) interacts with the -OH group is absorbed into the surface that has been coated with TiO_2 giving it a hydrophobic nature. The mechanism scheme of fabricating the TiO_2 film on the surface of bamboo timber and the illustration of fabricating the hydrophobic surface on TiO_2–coated bamboo timber are shown in Figure 2 and 3, respectively.

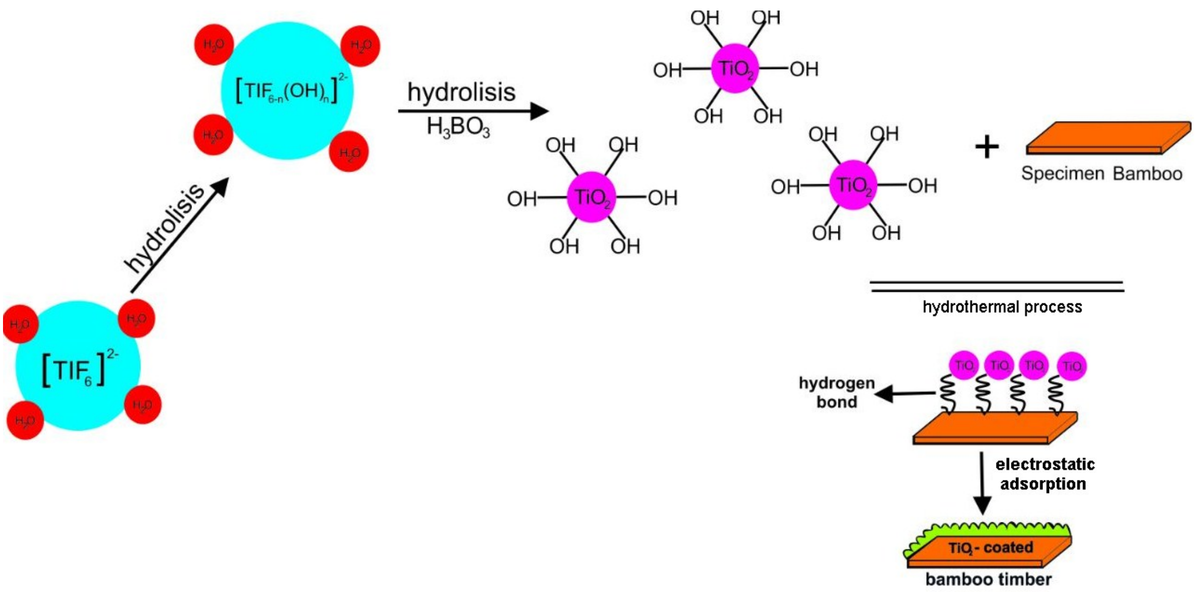

Figure 2. The mechanism of fabricating the TiO_2 film on the surface of the bamboo timber

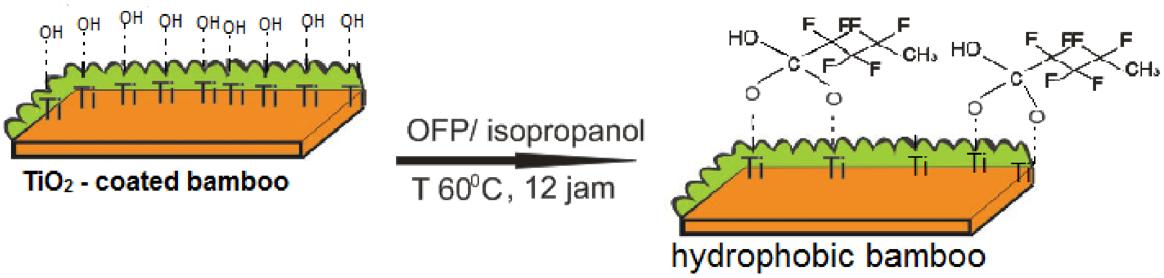

Figure 3. The illustration of fabricating the hydrophobic surface

Crystallinity, Chemical composition, and Morphologies

Characterization using X-Ray Diffraction was performed to find out the crystallinity and crystal size of the synthesis compound. In this study, the XRD characterization was done on pure and TiO_2-coated bamboo. Figure 4a shows emerging diffraction peaks at 15.65^0 and 21.71^0 indicating crystal phase of cellulose on pure bamboo [17]. This result proves that inside the bamboo contained cellulose [17]. Figure 4b shows the diffraction peaks at 2θ values of 15.69^0, 22.13^0, 25.06^0, 36.24^0 and 47.6^0 which are attributed to the anatase TiO_2 crystals (JCPDS cards: 21-1272), respectively. No other peaks are observed in the sample.

SEM/EDX was performed to determine the surface morphology and chemical composition of the constituent elements on the bamboo surfaces of pure bamboo, TiO_2-coated bamboo, and hydrophobic bamboo. Figure 5a shows a morphology on pure bamboo which is shaped like a tunnel and there are white spots around the tunnel. Figure 5b shows the morphology of TiO_2-coated bamboo, where the structure is rougher than pure bamboo. It is due to TiO_2 provides roughness on the bamboo surface and the particles become more tightly compacted. Figure 5c is an enlargement of the image b in which a sphere of bundles is visible on the bamboo. The spherical set gives a roughness to the surface of the bamboo. Figure 6a shows the EDX spectrum on a TiO_2-coated bamboo surface where the tops of Ti and O indicate TiO_2 particles were coated on the bamboo. Figure 5d shows the hydrophobic bamboo morphology in which the irregular spheres appear on the bamboo and the surface is denser.

The existence of OFP as modifier agent was evaluated by EDX result as showed in Figure 6b. That can be seen there are elements of F, Ti, O at the peak. The appearing element F^- indicates that it has attached to F^- on the surface where F^- contained in the OFP interacts with the -OH group absorbed on TiO_2 resulting in hydrophobicity.

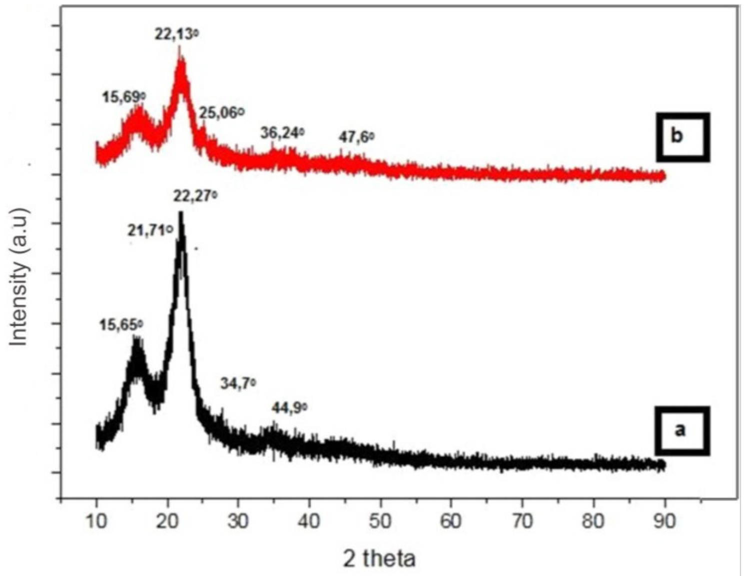

Figure 4. XRD Pattern of : (a) pure bamboo timber , (b)TiO_2–coated bamboo timber

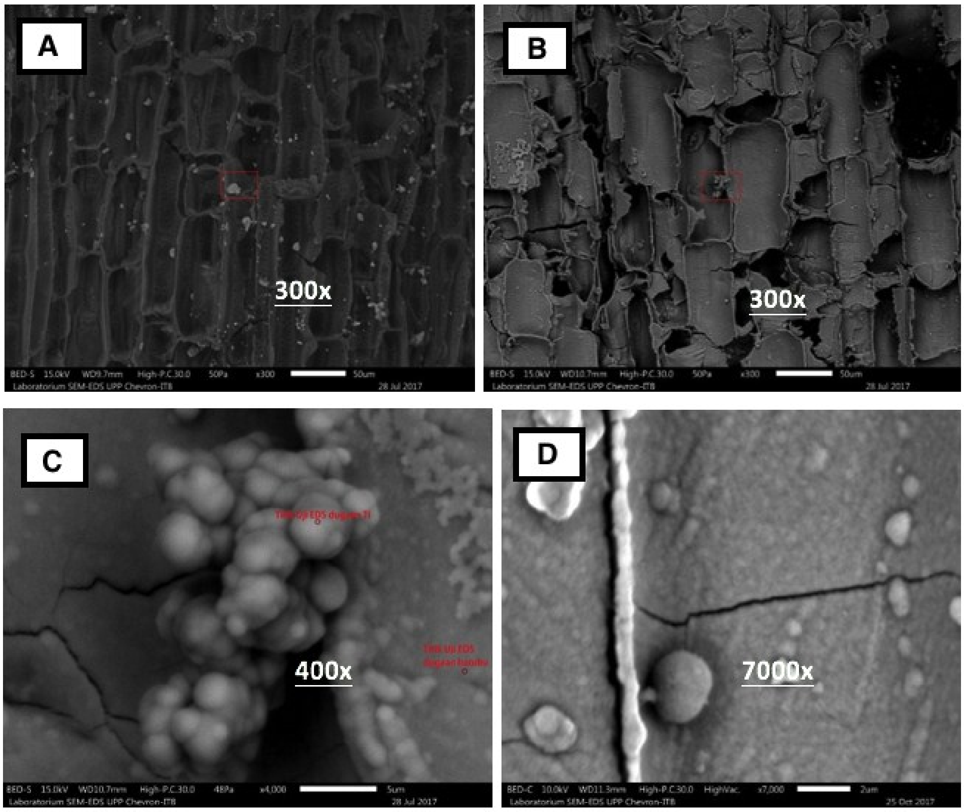

Figure 5. Images SEM of (a) pure bamboo timber, (b) TiO_2-coated bamboo, (b) TiO_2-coated bamboo with higher magnification, (d) ultra-hydrophobic bamboo

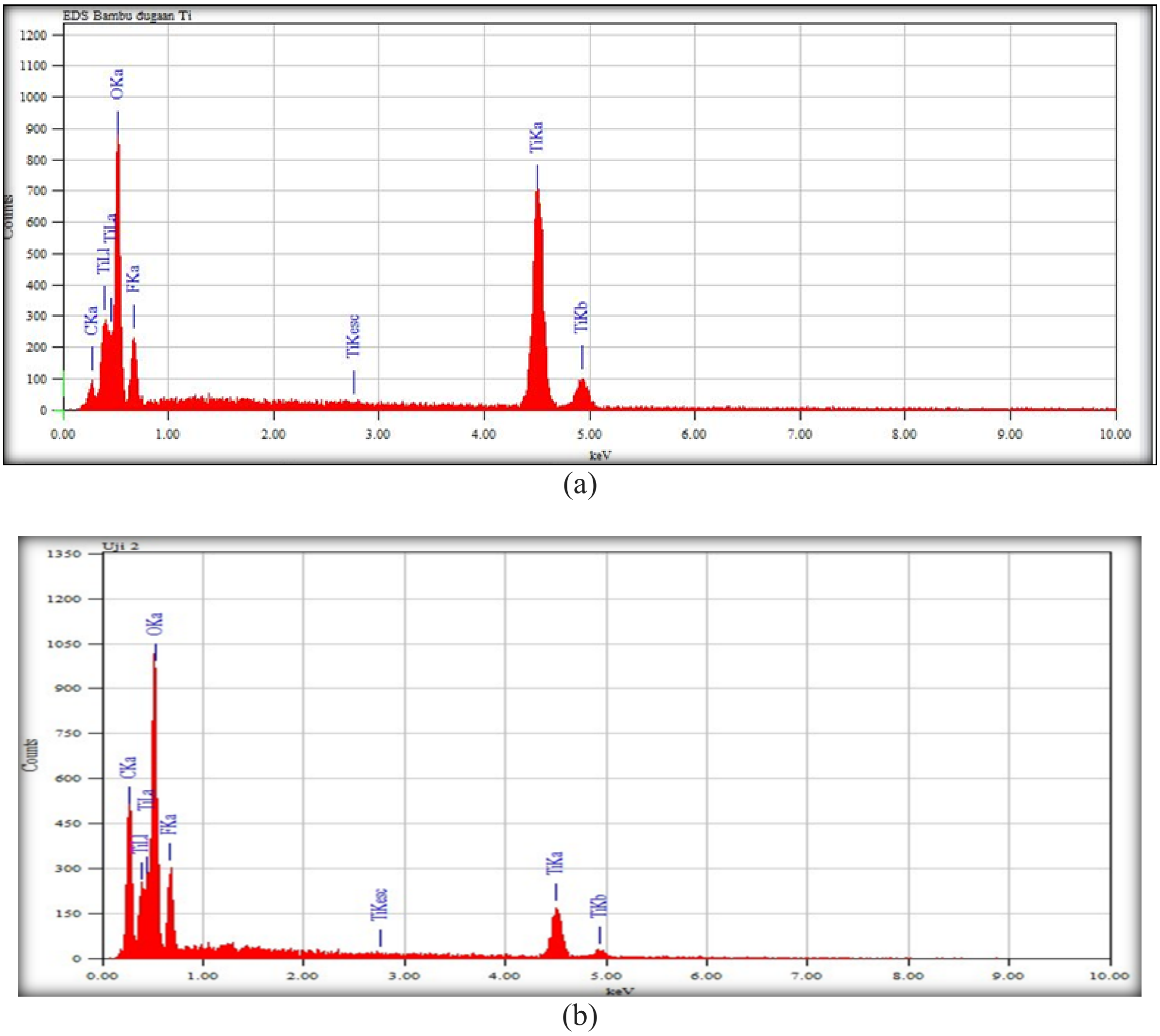

Figure 6. (a) EDX pattern of the TiO_2-coated bamboo and (b) ultra-hydrophobic bamboo

Surface wettability

The contact angle measurements of water droplets on the surface of as prepared bamboo timber were performed to evaluate the surface wettability properties such as hydrophilic, superhydrophilic, hydrophobic, ultra-hydrophobic and superhydrophobic. Figure 7 shows photographs of water droplets on the surface of the pure bamboo timber, TiO_2-coated bamboo timber, OFP-coated bamboo timber and ultra-hydrophobic bamboo timber. Figure 7a shows that the WCA measurement of the pure bamboo timber is 15^0 and demonstrates that the surface wettability property of this substrate is the hydrophilic. This type was developed because inside the pure bamboo timber contains hydroxyl groups [17]. Figure 7b shows that the water directly spread out on the surface of the TiO_2-coated bamboo timber and achieves the WCA of about 0^0. This phenomenon was attributed to the abundant hydroxyl groups on the surface of the TiO_2-coated bamboo timber, which developed the superhydrophilic surface on this substrate. On the contrary, Figure 7c shows that the OFP-coated bamboo timber could achieve a maximal WCA of about 70^0 and develops a hydrophobic property, to a certain extent. But, modification of TiO_2-coated bamboo timber with the OFP monolayer, that shows in Figure 7d exhibited an excellent hydrophobic property. This substrate reaches a maximum WCA of about 123^0 and could be classified into the type of ultra-hydrophobic surface. This phenomenon could be explained that the self-assembly of TiO_2 film and OFP layer respectively providing the surface roughness and lowering the surface energy so that a significant amount of air is trapped into the interspaces or cavities of the ultra-hydrophobic bamboo timber. Therefore, this modified bamboo timber cannot be wetted by a water droplet and induces ultra-hydrophobicity [14, 20].

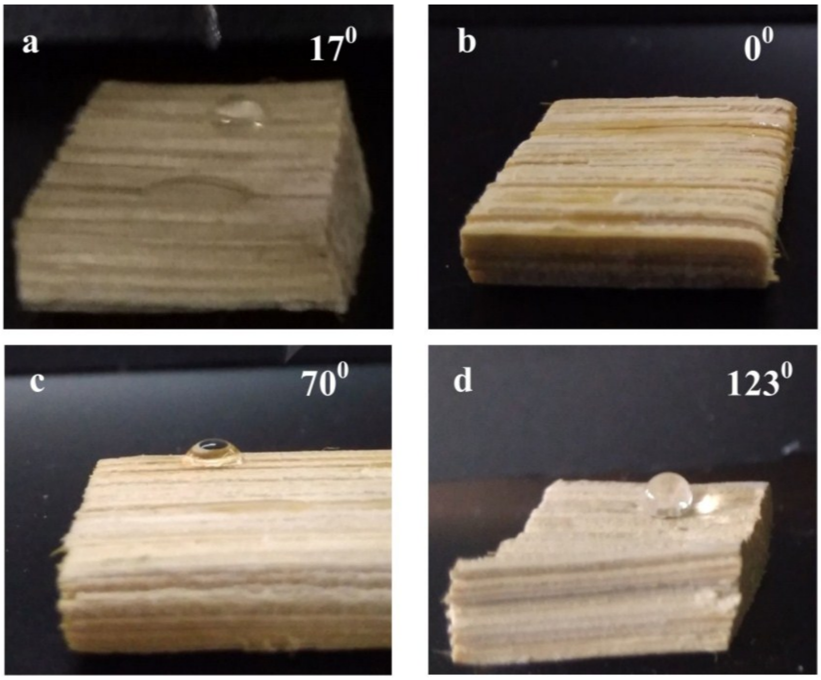

Figure 7. WCA of *(a)* pure bamboo timber, *(b)* TiO_2-coated bamboo timber, *(c)*OFP-coated bamboo timber, *(d)* ultra-hydrophobic bamboo timber

Mechanical stability

The mechanical stability of as prepared bamboo timber was examined through a scratch test by using SiC sandpaper (1500 mesh) as an abrasion surface. The methodology of the scratch test was adopted from reported work of Jingpeng et al. [17]. The WCA measurement was used to describe the abrasion effect on the surface of ultra-hydrophobic bamboo timber. Figure 8a and 8b presents the WCA comparison of before and after the scratch test, where the result shows that the WCA of ultra-hydrophobic bamboo timber was slightly decreased from 123^0 to 111^0 after the scratch test. It indicates that the ultra-hydrophobic bamboo has good mechanical stability.

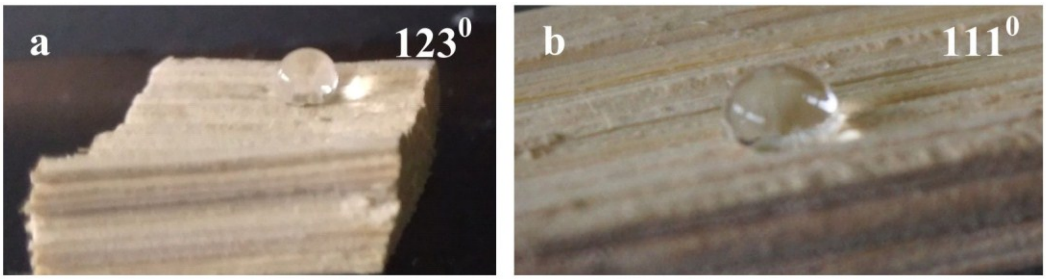

Figure 8 The WCA comparison of ultra-hydrophobic bamboo timber *(a)* before the scratch test, *(b)* after the scratch test

Self-cleaning ability

The self-cleaning ability were evaluated by seeing how easy the contaminant on the surface of the bamboo substrates removed with the water droplets [17]. Figure 9 shows the demonstration of the self-cleaning process on the surface of pure bamboo timber and ultra-hydrophobic bamboo timber, which was captured by a well-resolution digital camera. In this process, the contaminants were placed on the surface of pure bamboo timber and ultra-hydrophobic bamboo timber, and then the contaminated surface was rinsed with a little amount of water. The result of this demonstration describes in Figure 9(a-d), where the contaminant on the surface of pure bamboo timber was hardly removed by loading of water droplets. Whereas the contaminant on the surface of ultra-hydrophobic bamboo timber, that shows in Figure 9(e-h), were easily to remove in a similar procedure. It can be concluded that the ultra-hydrophobic bamboo timber has an excellent self-cleaning ability than the pure bamboo timber.

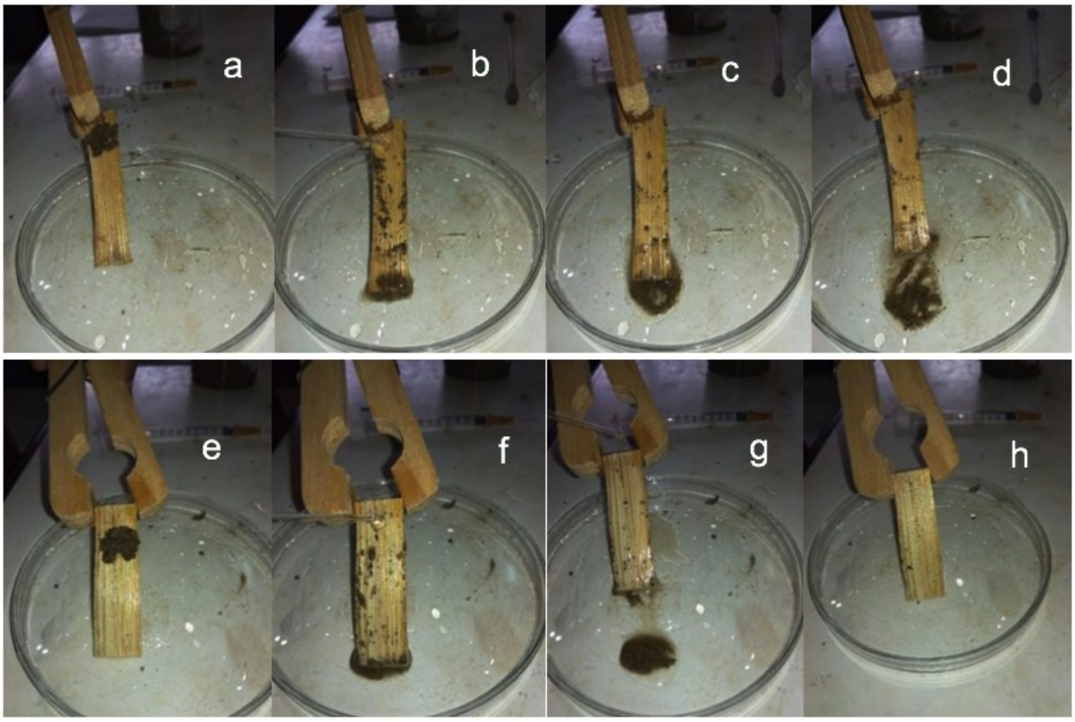

Figure 9. The demonstration of the self-cleaning process on the surface of: (a-d) pure bamboo timber, (e-h) ultra-hydrophobic bamboo timber

Flame retardancy

The flame retardancy test was performed to see the response of the sample to fire, where the methodology of this scenario was adopted from the reported work of Jingpeng et al. [14]. Figure 10 shows the digital photographs of the pure bamboo timber and the ultra-hydrophobic bamboo timber when burned on the alcohol burner. As shown in Figure 10(a-d), the pure bamboo timber caught fire at 3 s, being burned and covered with flame for 28 s and finally become ash in 60 s. On the contrary, as shown in Figure 10(e-h), the ultra-hydrophobic bamboo timber caught fire at 3 s, then being burned and slightly covered with flame for 25 s, and then the flame gradually quenched itself in 30 s. Those results proved that the ultra-hydrophobic bamboo timber has good flame retardancy compared to pure bamboo timber, so it provides a potential for being used for other great application such as an alternative reinforcement material in functional constructions.

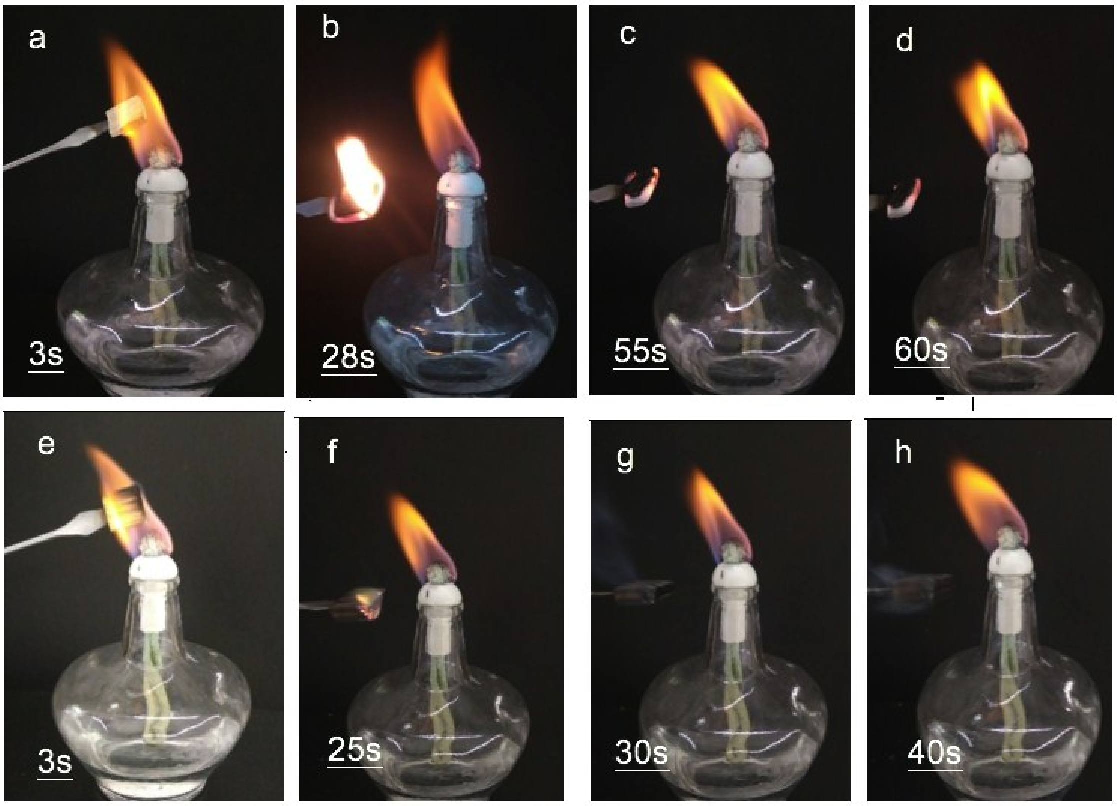

Figure 10 Flammability test on: (a-d) pure bamboo timber, (e-h) ultra-hydrophobic bamboo

CONCLUSION

Ultra-hydrophobic surface on Indonesia bamboo timber with maximal water contact angle of 123^o (B-T-OFP10 sample) has been successfully prepared by hydrothermal deposition TiO_2 anatase film followed by 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (OFP) modification. It was attributed to high surface roughness and reducing surface free energy due to TiO_2 deposition and OFP assembly, respectively. The obtained hydrophobic surface has good mechanical stability as well as self-cleaning property and flame retardancy compared to untreated bamboo.

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