Fabrication of Superhydrophobic Film on the Surface of Indonesian Bamboo Timber by TiO_2 Deposition and Using Octadecyltrichlorosilane as a Surface Modifier Agent

Diana Vanda Wellia*, Wulandari, Arifah Mustaqimah, Nurul Pratiwi, and Yulia Eka Putri

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Andalas, Campus Unand Limau Manis, Padang 25163, West Sumatra, Indonesia

** Corresponding author:*

email: nandadiana@sci.unand.ac.id

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Abstract: *The tropical bamboo has been widely used in modern society as a potential material for various applications. It is well known that bamboo has low durability due to its hydrophilic properties. To overcome this problem, the superhydrophobic surface on Indonesian bamboo timber had been successfully fabricated via hydrothermal deposition of an anatase TiO_2 and solution immersion of octadecyltrichlorosilane (ODTS), which exhibited a maximum water contact angle (WCA) of 155°. The as-fabricated superhydrophobic bamboo timber not only showed high mechanical resistance against the abrasion of SiC sandpaper but had also been proven to possess high chemical stability after immersion in acidic and basic aqueous solutions. Moreover, the superhydrophobic bamboo timber also demonstrated excellent self-cleaning and flame-resistance properties, in comparison to pure bamboo timber. It is believed that the strategy offered in this study can increase the utilization of bamboo timber for various purposes, especially as a self-cleaning material.*

Keywords: *superhydrophobic; TiO_2; bamboo; octadecyltrichlorosilane; self-cleaning material*

INTRODUCTION

Bamboo is a type of woody plant with a hole in the middle which belongs to the grass family (Gramineae), a sub-family of Bambusoideae, consisting of 121 genera and divided into approximately 1,662 species throughout the world [1]. They grow in various countries with various climates, from cold regions to hot tropics, most are located throughout East Asia, from Sakhalin at 51° N in Russia to North Australia, and west to the Himalayas and India [2]. Bamboo is one of the cellulose-based materials that is widely used due to its fast growth and abundant availability [3]. In 3–5 years, the anatomical structure of bamboo becomes stable and mature, resulting in good mechanical strength and utilization properties [4]. As it is widely known, all parts of bamboo have their own application, and the most favored is the bamboo stems [5]. In general, the bamboo stem is arranged in three sections: the outer layer with green color as the skin of the bamboo stem, the middle layer with brown color that is widely known as the bamboo timber, and the inner layer with yellow color [6].

According to the International Network for Bamboo and Rattan (INBAR), Indonesia accounted for 8% of the world exports of bamboo products in 2014 with a value of US$ 149 million, which ranked as the third largest producer and exporter country of bamboo products in the world. Almost 80% of total Indonesian bamboo usage was for construction material such as buildings, houses, interior and exterior decoration, bridges, scaffolding, ladders, walls, and flooring [7]. The most common Indonesian bamboo that has been reported for housing construction is betung bamboo (*Dendrocalamus asper*). The properties of betung bamboo is different than other types of bamboo, which has the potential to be developed into structural components for construction materials [8].

However, the nature of bamboo timber that consists of unique porous structures and a lot of hydroxyl groups on the surface, support absorbing water and moisture of the surrounding environments, which could later on affect the durability of bamboo products

[9]. Therefore, the most effective and appropriate way to improve the durability of bamboo timber is to modify the chemical properties of its surface.

In recent years, several approaches for the development and improvement of bamboo timber quality have been reported. Fabrication of a superhydrophobic system on the bamboo timber surface could be one of the promising approaches. Li et al. fabricated superhydrophobic bamboo timber by using the hydrothermal mineralization method to synthesize micro/nano $CaCO_3$ on the bamboo timber surface, then modified by fluoroalkylsilane (FAS) [10]. In another study, Jin et al. successfully prepared a durable, superhydrophobic, superoleophobic and corrosion resistant coating on the surface of bamboo timber by using (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane (FAS-17) as a modifier agent on rose-like ZnO nanoflowers coating [11]. By using the same method, Li et al. also studied the fabrication of durable, self-cleaning and superhydrophobic bamboo timber using the same modifier agent (FAS-17) on anatase TiO_2 film [12]. Based on those works, the deposition of nanoparticles of inorganic materials on bamboo timber plays an important role to improve the physical and chemical properties, like durability and stability. Furthermore, the contribution of the silane compound has been briefly reported as the modifier agent to fabricate the superhydrophobic system on the bamboo timber surface.

In this work, a similar approach was used to fabricate the superhydrophobic system on the surface of Indonesian bamboo timber by using the hydrothermal method through deposition of TiO_2 nanoparticles onto the surface to enhance the roughness of surface, followed by hydrophobization by octadecyltrichlorosilane (ODTS). Furthermore, the physical and chemical properties of the modified bamboo timber were determined and clarified by applying the self-cleaning approach.

■ EXPERIMENTAL SECTION

Materials

All reagents were analytical grade and purchased from Sigma–Aldrich. Indonesian bamboo timber (*Dendrocalamus* asper) with a size of 20 mm × 20 mm × 4 mm was obtained from Universitas Andalas, Padang, Indonesia. The bamboo slices were washed in deionized water and acetone for 30 min, and dried in the oven at 80 °C for 24 h.

Procedure

Fabrication of TiO_2 particles on the surface of the bamboo timber via hydrothermal method

Two grams of ammonium fluorotitanate and 1.85 g boric acid were dissolved in 100 mL of distilled water under magnetic stirring for 15 min at 25 °C. The pH value of the mixed solution was adjusted to 2 by the addition of hydrochloric acid aqueous solution. Then, 75 mL of this adjusted solution was moved into a 100 mL Teflon-lined autoclave and the bamboo timber was subsequently placed into the reaction solution. The autoclave was placed in an oven at 90 °C for 5 h. Lastly, the sample was separated from the solution, washed with distilled water, and dried at 80 °C for 24 h in an oven [13].

Fabrication of superhydrophobic bamboo timber

Octadecyltrichlorosilane (ODTS) was used to modify the surface of the as-prepared bamboo timber as a layer with low surface energy. The bamboo timber that had a layer of TiO_2 nanoparticles was placed into sealed reactors, with different ratios of ODTS/ethanol solution (1:24, 1:9, 1:4, and 2:3) at ambient temperature for 5 h. Then, the samples were taken out from the reactor, followed by washing with ethanol and drying in an oven [14].

Characterizations

The structures of crystalline were analyzed by X-ray diffraction (XRD, PANalytical CubiX^3) with Cu Kα radiation (λ = 1.5418 Å) at a scan rate of 8 (°)/min ranging from 10° to 70°. The morphology of the samples was evaluated using a scanning electron microscope (SEM, JEOL JSM-IT-300) with 300×, 4000× and 6000× magnification. The chemical compositions of the bamboo timber with and without treatments were determined by energy dispersive spectroscopy (EDS, coupled with SEM instrument). FTIR spectra of the samples were recorded using FTIR (Perkin Elmer Company) in the range of 400–4000 cm^{-1}. The thermal properties of the samples (10 mg) were observed by TG-DTA (Perkin Elmer) from

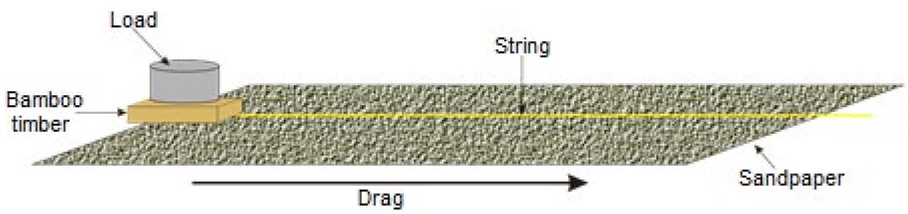

Fig 1. Scheme of the scratch test procedures

25 °C to 575 °C at a rate of 10 °C min^{-1}. The water contact angle (WCA) was captured at ambient temperature by digital microscope-1000× magnification with the droplet volume 5 µL and further analyzed by the image analysis software.

Physical and chemical stability tests

The mechanical stability of the modified bamboo timber was assessed by a scratch test. The procedures of this test were carried out by dragging the modified bamboo timber on the surface of 300 mm length of SiC sandpaper (1500 mesh) under 68 g of the load. The contact angle before and after the scratch test was measured. This analogical procedure is clearly illustrated in Fig. 1 [12]. The chemical stability was tested by measuring the static contact angle of the modified bamboo timber after immersion in the sulfuric acid (pH = 2) and sodium hydroxide (pH = 13) aqueous solution for 6 h, 12 h and 24 h.

Flame retardancy test

The flammability property was determined by counting the time that was used to quench the flame after the modified bamboo timber was burned with an alcohol burner.

Self-cleaning property test

In order to show the self-cleaning ability of the modified bamboo timber, the hydrophilic mud was used as contaminant specimens. The ability of water droplets to remove all of the contaminants on the surface of the modified bamboo timber was observed.

■ RESULTS AND DISCUSSION

Synthesis of Superhydrophobic Film on the Surface of Bamboo Timber

The superhydrophobic surface of Indonesian bamboo timber was successfully synthesized firstly by adding TiO_2 on the bamboo timber surface through the hydrothermal method followed by surface modification using ODTS. In the process of hydrothermal, the hydrolysis of $(NH_4)_2TiF_6$ occurred, which gradually changed the fluorinated titanium complex ions into titanium hydroxide complex ions in an aqueous solution (Eq. (1)) [14]. The resulted fluoro anions from this reaction were removed by boric acid as the fluoride scavenger (Eq. (2)). The H^+ ions in the solution were increased with the addition of HCl, that accelerated Eq. (2) to move forward. The obtained titanium hydroxide complex ions were further hydrolyzed to form TiO_2 nanoparticles (Eq. (3)). The reaction is described as follows [14]:

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

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

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

The bamboo surface consists of excess hydroxyl groups. The resulting TiO_2 nanoparticles strongly interacted with hydroxyl groups on the bamboo surface due to the presence of high energy and pressure inside the autoclave [14]. The presence of hydroxyl groups resulted in stable TiO_2 nanoparticles on the bamboo timber surface because of the electrostatic adsorption force. The trisilanol groups, resulted from the reaction between ODTS and ethanol will interact with the -OH group and then gradually absorb onto the TiO_2-coated bamboo timber surface (Fig. 2) [14].

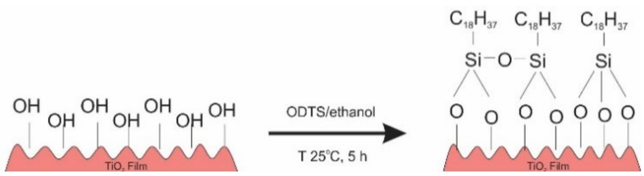

Fig 2. The reaction of superhydrophobic surface fabrication

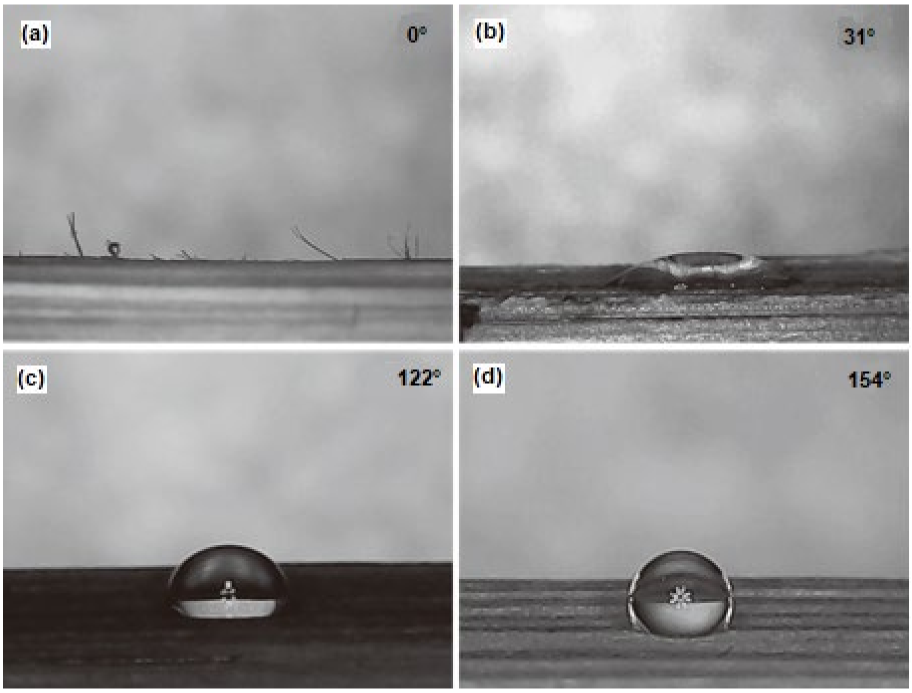

Fig 3. Digital images of the water droplets on the surface of (a) pure bamboo timber, (b) TiO_2–coated bamboo timber, (c) ODTS–coated bamboo timber, and (d) superhydrophobic bamboo timber

Surface Wettability

The WCA measurements were carried out to determine the chemical properties of the surface of the synthesized samples. Fig. 3(a) shows the photograph of water droplet behavior on the pure bamboo timber surface. Obviously, it demonstrated hydrophilic properties with WCA of 31°. In Fig. 3(b), the bamboo timber had been covered with TiO_2 which exhibited a superhydrophilic performance with WCA of 0°. This phenomenon was due to the excess of hydroxyl groups on the TiO_2 films surface that made the water spread out quickly on the surface of the bamboo timber [12]. On the contrary, when the bamboo timber was coated with ODTS, the surface properties became hydrophobic with a maximum WCA of about 122° (Fig. 3(c)). However, after the modification of ODTS on TiO_2-coated bamboo timber, the new surface exhibited superhydrophobic properties with WCA of 154° (Fig. 3(d)). The collaboration of surface roughness provided by TiO_2 and low-surface energy layer of ODTS had effectively trapped the air into interspaces of the bamboo timber surface, as the surface properties transformed into superhydrophobic [15].

The Structural Analysis

Fig. 4 shows the XRD patterns of the pure and the TiO_2-coated bamboo timber. In Fig. 4(a), the characteristic peaks at 15.2° and 21.5° that belonged to (101) and (002) crystal planes, respectively, represented the characteristic of the cellulose crystalline region from pure bamboo timber [14,16]. However, after the hydrothermal process

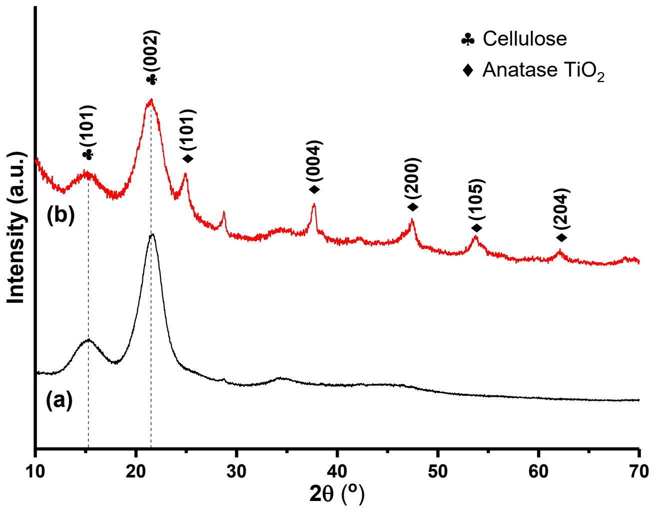

Fig 4. XRD Patterns of (a) the pure bamboo timber, (b) the TiO_2–coated bamboo timber

(Fig. 4(b)), several new diffraction peaks at 2θ values of 25.0°, 37.6°, 47.5°, 53.8° and 62.2° which corresponded to (101), (004), (200), (105), and (204) planes, respectively, were observed as the characteristic of anatase TiO_2 crystals (JCPDS cards: 21-1272).

The Functional Groups Analysis

The FTIR spectra of the pure bamboo timber, the bamboo timber modified by TiO_2 and the bamboo timber modified by both TiO_2 and ODTS (superhydrophobic bamboo) are shown in Fig. 5. The band at 3333 cm^{-1} (stretching vibrations of O–H groups) in Fig. 5(a) showed higher intensity than in Fig. 5(b, c), indicating that the OH groups were consumed by TiO_2 and ODTS. Respectively, the absorption peaks at 2924 cm^{-1} and 2853 cm^{-1} can be attributed to C–H symmetric and asymmetric stretching vibrations, representing the existence of the long-chain alkyl group from ODTS in the superhydrophobic bamboo [17] and the alkyl groups of cellulose, lignin and hemicellulose in the pure bamboo timber [18-19]. The spectra of superhydrophobic bamboo timber exhibited adsorption peak at 1033 cm^{-1}, which were attributed to the asymmetric stretching vibrations of Si–O–Si due to cross-linked chains between ODTS molecules [14]. Furthermore, the adsorption peaks at 959 cm^{-1} that only appear in the spectra of the TiO_2–coated bamboo timber and the superhydrophobic bamboo timber, corresponded to the vibration of Ti–O–Si [20]. Thus, we could deduce that the ODTS molecules had grafted on the TiO_2–coated bamboo timber surface.

Surface Morphologies and Chemical Compositions

SEM-EDX characterization was carried out to observe the surface morphology and determine the chemical composition of the elements on the surface of pure bamboo timber, TiO_2-coated bamboo timber, and bamboo timber modified by TiO_2 and ODTS (Fig. 6). The morphology of pure bamboo timber is shown in Fig. 6(a), the large pit like tunnel-shapes can be observed. Fig. 6(b) shows the morphology of TiO_2–coated bamboo timber, which showed that the surface of this sample is rougher compared with pure bamboo timber. This is because TiO_2 aggregation increased the surface roughness of the surface of the bamboo timber [14]. Fig. 6(c) presents the SEM image of TiO_2–coated bamboo timber with higher magnification. Clearly, TiO_2 aggregations covered the surface of bamboo timber in order to form a roughness surface. Fig. 6(d) demonstrates the SEM image of the superhydrophobic bamboo surface, which pointed out the combination structure of TiO_2 with the structure of the bamboo timber. Consequently, this structure led to air trapped within the grooves and later formed the superhydrophobic surface.

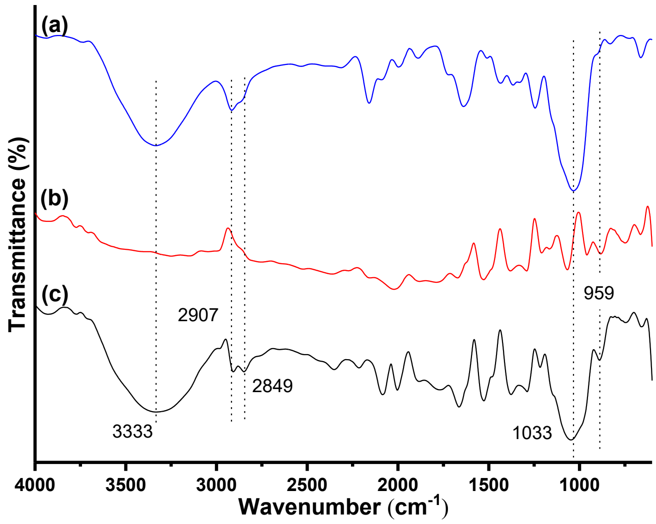

Fig 5. FTIR spectra of (a) the pure bamboo timber, (b) the TiO_2–coated bamboo timber, and (c) the superhydrophobic bamboo timber

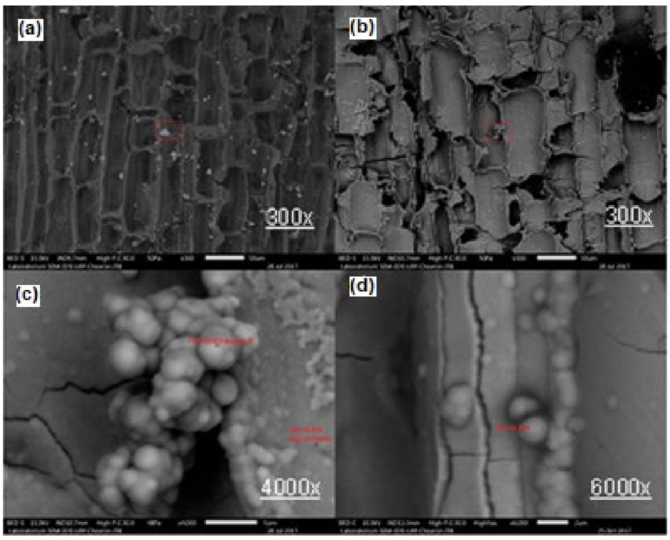

Fig 6. Images SEM of (a) pure bamboo timber (b) TiO_2-coated bamboo timber (c) high magnification for images b (d) superhydrophobic bamboo timber

EDS was performed to determine the chemical composition of the constituent elements on the surface of pure bamboo timber, TiO_2–coated bamboo timber, and bamboo timber modified by TiO_2 and ODTS. Fig. 7(a) shows the EDS spectrum of pure bamboo timber that is proven by the presence of the C and O elements. The existence of Ti and O elements are shown in Fig. 7(b), which indicated that TiO_2 had been coated on the bamboo timber surface. In Fig. 7(c), the EDS spectrum of bamboo timber modified by TiO_2 and ODTS is shown, which exhibited the peak of Si, F, Ti and O elements. The appearance of the Si element showed that ODTS had interacted on the surface of the TiO_2–coated bamboo timber. Furthermore, the peak of the F element was observed due to the excess of fluorine ions during the reaction involving TiO_2.

Thermal Stability

The TG/DTA analysis of pure bamboo timber, TiO_2–coated bamboo timber, ODTS-coated bamboo

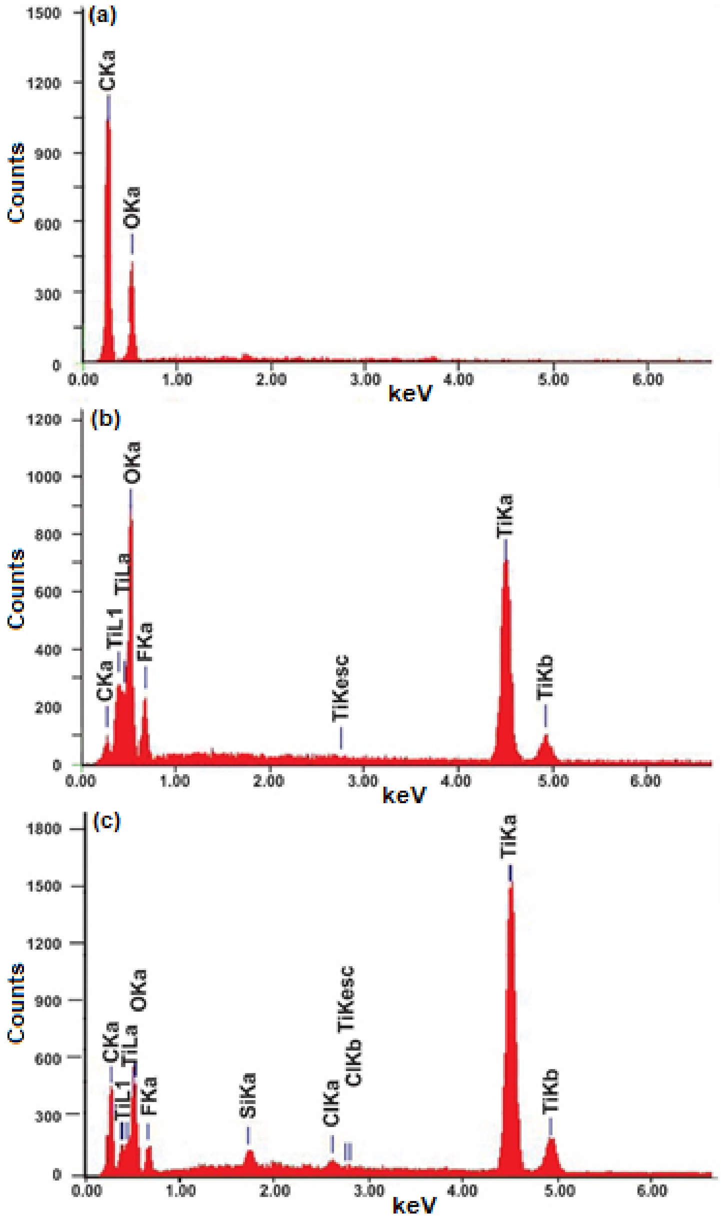

Fig 7. EDS spectrum of (a) the pure bamboo timber, (b) TiO_2–coated bamboo timber, and (C) superhydrophobic bamboo timber

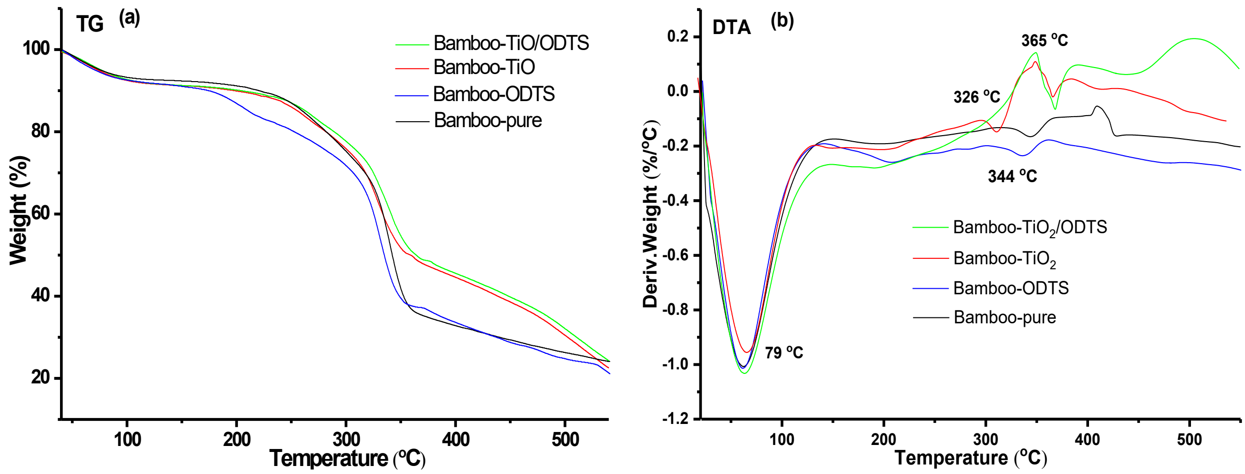

Fig 8. TG-DTA curves of superhydrophobic bamboo timber, TiO_2–coated bamboo timber, ODTS-coated bamboo timber, and pure bamboo timber

timber, and the bamboo timber modified by TiO_2 and ODTS were shown in Fig. 8. The TG curve (Fig. 8(a)) shows that all samples had a slight weight loss in the range of 60 to 80 °C due to the removal of the absorbed water before pyrolysis [21]. Thermal degradations were also shown in the range 180–250 °C, which is attributed to the partial degradation of hemicellulose [14]. The weight losses in the range of 250–380 °C were continuously due to cellulose and lignin degradation. Furthermore, all of the components of the four samples gradually degraded until the temperature reached 380 °C.

Corresponding to the weight losses of the TG analysis, the DTA curve (Fig. 8(b)) presented wide endothermic peaks at a minimum temperature of 344 °C for pure bamboo timber and ODTS-coated bamboo timber. On the contrary, the sharp endothermic peaks were present at a minimum temperature of 365 °C for the TiO_2–coated bamboo timber and the bamboo timber modified by TiO_2 and ODTS. The maximum degradation rates of TiO_2–coated bamboo timber and the bamboo timber modified by TiO_2 and ODTS were lower than of pure bamboo timber and ODTS-coated bamboo timber. This might be attributed to the TiO_2 coating on the surface of the bamboo timber, which inhibited the transfer of oxygen and heat [14].

The total percentage of weight losses during the whole process was about 57.91% for ODTS-coated bamboo timber, 50.04% for pure bamboo timber, 45.03% for the TiO_2–coated bamboo timber, and 44.72% for the bamboo timber modified by TiO_2 and ODTS. These results imply that TiO_2 plays a crucial role in thermal stability improvement.

Mechanical and Chemical Stability

The scratch test was carried out to investigate the surface mechanical stability of bamboo timber modified by TiO_2 and ODTS. This investigation could represent the surface properties of the modified bamboo timber in order to survive in harsh conditions. The result showed that the WCA measurement of the modified bamboo timber before and after the scratch test were the same with WCA of 154° (Fig. 9). This result indicated that the modified bamboo timber had good mechanical resistance.

The chemical resistance test was carried out to analogize the corrosive environment. Fig. 10 exhibits the WCA of the modified bamboo timber towards immersing time. In acidic solution, WCA of the modified bamboo

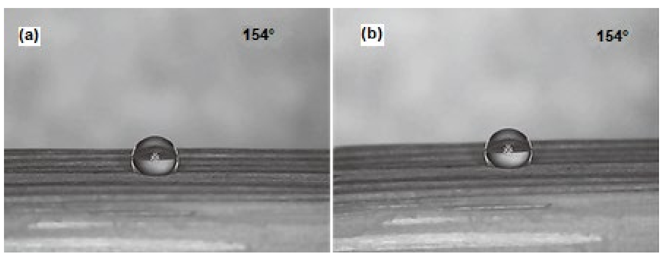

Fig 9. The water contact angle of superhydrophobic bamboo timber (a) before and (b) after the scratch test

timber decreased from 125° to 105° after being immersed for 6 to 24 h. The WCA also decreased from 120° to 95° after the modified bamboo timber was immersed in an alkaline solution for 6 to 24 h. The result shows that the obtained surface of modified bamboo timber was resistant in both acidic and alkaline conditions although the contact angle slightly decreased.

Flammability

In order to explain flammability properties, the pure bamboo timber and bamboo timber modified by TiO_2 and ODTS were burned with an alcohol burner and the time that needed to be burned was counted [14]. Fig. 11 shows digital photos of the pure bamboo timber and the modified bamboo timber when burned with the alcohol burner. The pure bamboo timber was heated with the alcohol burner for 3 sec and became ash in 60 sec (Fig. 11(a–d)). In contrast, modified bamboo timber was not covered with flames at 25 sec and then the flames extinguished itself at 30 sec (Fig. 11(e–h)). These phenomena showed that the modified bamboo timber was more fire resistant than the pure bamboo timber, so it has the potential to be applied as building material.

Based on a reported work, an efficient way to increase the fire-resistance of synthetic and natural cellulose-based substrates is by modifying the inorganic particles into the structure. In this work, the inorganic material used to improve the flame retardancy properties was TiO_2. It has been verified that the surface of cellulose-based substrates could be modified with TiO_2 as a fire-resistant agent by decreasing the release of total heat, the rate of mass loss, and the effective heat of combustion [14].

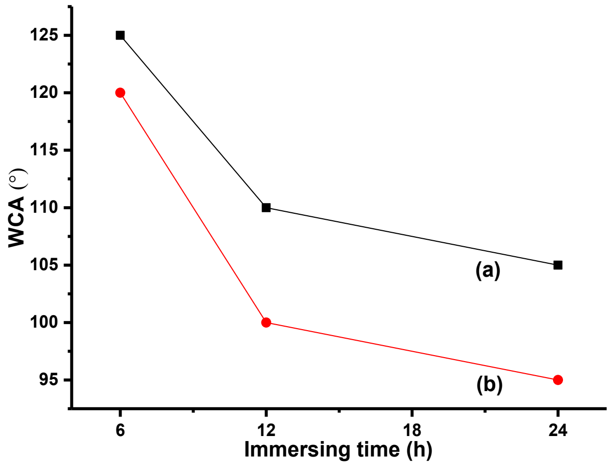

Fig 10. The water contact angle curve of superhydrophobic bamboo timber after immersing in (a) acid and (b) base solution

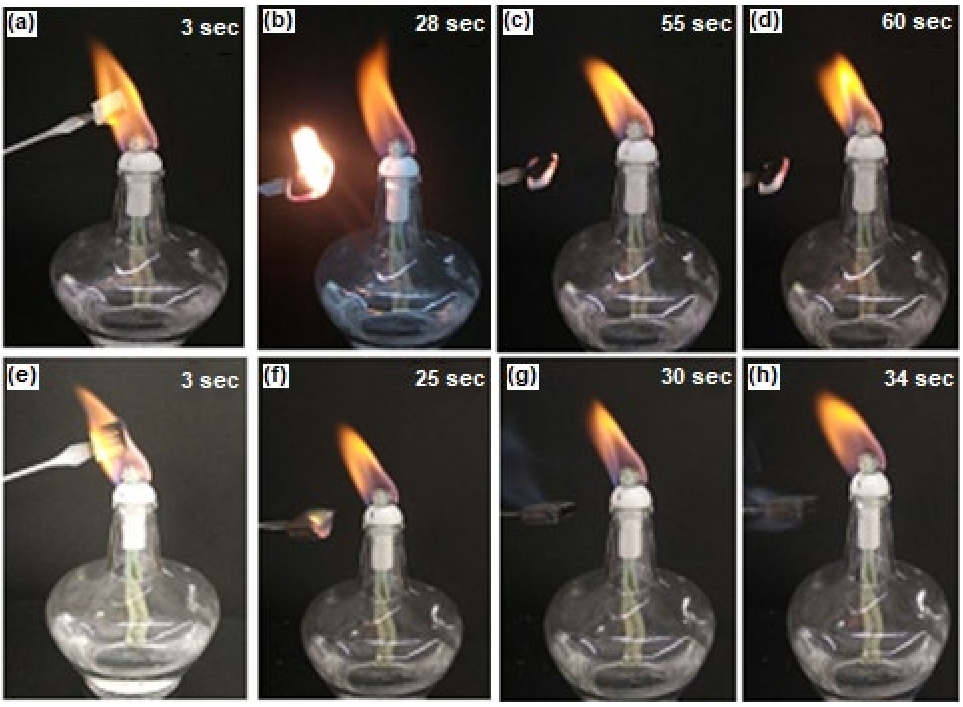

Fig 11. Flammability test of (a-d) pure bamboo timber, and (e-h) superhydrophobic bamboo timber

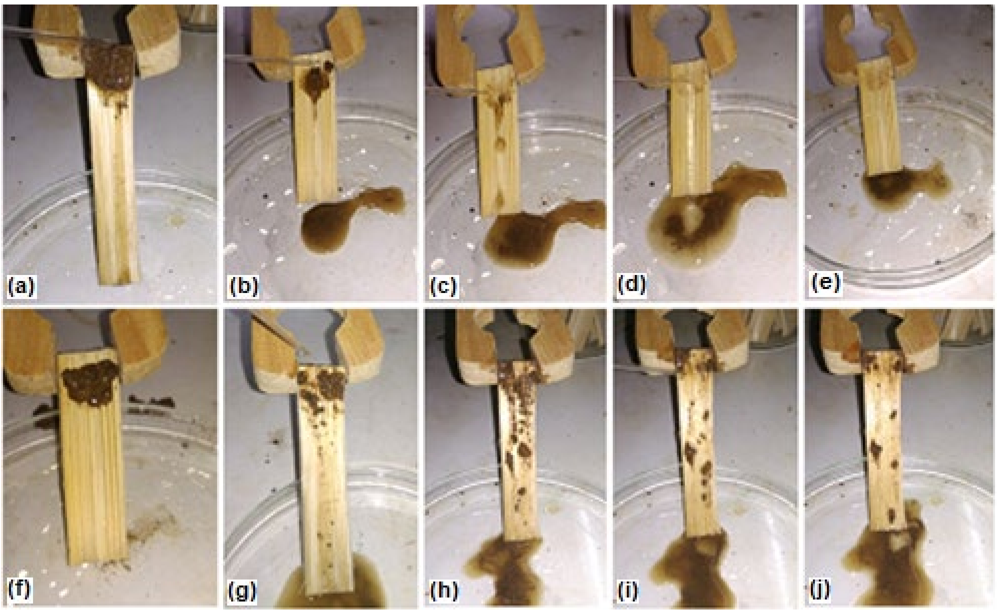

Fig 12. The self-cleaning property test of (a-e) superhydrophobic bamboo timber, and (f-j) pure bamboo timber

Self-Cleaning Property

Fig. 12 shows the process of a self-cleaning system on the pure bamboo timber surface and bamboo timber modified by TiO_2 and ODTS. The procedures of this test were performed by applying the contaminants on the surface of the pure and modified bamboo timber, and then the surface was washed with water. As shown in Fig. 12(a–e), the contaminants were removed easily on the surface of modified bamboo timber by rolling action of a water droplet and then reached a completely clean surface. However, in a similar procedure, the contaminants on the pure bamboo timber surface were not as easily removed as the modified bamboo timber (Fig. 12(f–j)). From the experiments, it can be concluded that the self-cleaning ability of the modified bamboo timber was better than pure bamboo timber. This is because of the nature of the superhydrophobic surface that causes water to be pass easily while carrying the impurities.

■ CONCLUSION

The superhydrophobic film on the surface of Indonesian bamboo timber with a maximum contact angle of 154° has been successfully fabricated through hydrothermal deposition of TiO_2 combined with octadecyltrichlorosilane (ODTS) modification. This special wettability was contributed by high surface roughness and low surface energy due to an anatase TiO_2 deposition and a monolayer coating of ODTS, respectively. The treated Indonesian bamboo timber not only exhibited superhydrophobic surface but also mechanical and chemical outstanding stability as well as self-cleaning and flame retardancy properties.

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