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Fire-retardancy of Wood Coated by Titania Nanoparticles

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Abstract. Of late, the number of fire cases in Malaysia has been steadily increasing at a very alarming rate. One way to reduce the ability of fire ignition or spreading is by coating or doping the wood with a layer of fire-protected coating, or an insulating barrier, which is also known as Flame Retardant Coatings (FRCs). In this study, titania (TiO_2) is coated onto the surface of the wood to act as an FRC. The synthesis of TiO_2 was carried out by using the sol-gel method, while the coating process was done by the dip-coating method. FESEM images show that the surface of the wood has been fully covered by titania nanoparticles (TiO_2 NPs) in size range of 24 – 45 nm. From the TGA results, it was shown that the thermal stability of the wood has increased from 300 to 320 °C, with just by a merely coated layer of TiO_2 NPs. Flammability testing was carried out by a flame burner also shows that the coated wood is capable of reducing the flammability of the wood, where the coated wood required a longer time to be burned out. The flame spread test indicated that the coated samples managed to reduce the spreading of the flame, as compared to the uncoated sample. These initial results show the potential of the TiO_2 NPs as a good flame-retardant material.

INTRODUCTION

From 2010-2018, in Malaysia alone, more than 40,000 cases of fires involving building structures have been recorded, amounting to an average of 7,292 cases per year [1]. These fire cases continue to rise year after year, making it an extremely worrisome issue. These increases have a detrimental effect on the country as it involves the loss of property and housing tax, at the same time increasing the service cost incurred by the Government of Malaysia [2]. The Government of Malaysia, specifically the Fire and Rescue Department of Malaysia (FRDM), are finding ways and organizing various campaigns to increase public awareness on fire preventions. Hence, to overcome and reduce the number of fires each year, especially those involving structures, the government, FDRM, Energy Commission of Malaysia (ECM) and SIRIM have been carrying out various awareness campaigns to increase public awareness on fire preventions, such as emphasis on the usage of approved electrical appliances by SIRIM and ECM only, usage of fire retardant appliances, and measures to ensure all the electrical wiring is according to the specified specifications by ECM [3,4]. However, even with these campaigns, the numbers of fires are still not reducing. Apart from campaigns, improved measures, especially by combining knowledge and the technologies available, should be undertaken, such as introducing fire retardant coatings (FRCs) on combustible or flammable materials.

Fire is a manifestation of uncontrolled combustion which involves combustible materials that are found around us in buildings, workplace, and surrounding [5]. These combustible materials are commonly carbon-based and referred collectively as a fuel load [6]. A wide variety of fuels are available in different chemical and physical states [7]. These fuels can differ by the ease of fire ignition, the rate of fire development (flame spread), and the power that can be generated (rate of heat release) [5]. The concept of ignition in fires, known as a fire tetrahedron, consists of three main components (fire triangles) which are heat, fuel, and oxygen that surround the fourth element, which is the chemical chain reactions during combustion activity [8]. The ignition of fires occurs when all of these elements are linked and combined [9]. One way to prevent the occurrence of fire or reduce its likelihood is by protecting the flammable and combustible materials with an additional layer to improve its fire protection properties. The addition of fire-retarding materials to flammable and combustible materials will help to eliminate one of the elements in the fire tetrahedron concept during fires [10].

Conventionally, the surface of materials can be covered with a layer of the coated film, where the coated films used are mostly made up of conventional organic materials [11]. It is a known fact that organic substances

can easily act as a fuel because it is easier to ignite, melts, and drips that can cause severe injuries and damages when they are exposed to heat or fire [12]. Flame retardants (FRs) are one of the best approaches to minimize the likelihood of fire involving flammable and combustible materials [13]. FRs have become a class of chemicals which receive more and more scientific and public attention. FRs are a group of chemicals which are added or coated onto combustible or flammable material during manufacturing, such as wood, plastics, or textiles, to reduce the flammability properties of the substances [14]. To increase the effectiveness of FRs on a material, the particle size of FRs plays an important part, where FRs with the larger surface area will be able to provide a larger area to absorb the heat. Nano-pigments are one of the examples as they offer a high surface area for the optimum cover-up. According to Wang et al. [15], with increases in the surface area of non-combustible materials used as FRs, the flammability of substrate decreased due to the presence of nanoparticles (NPs) with a large surface area.

The applications of NPs in coating industries have shown significant growth in recent years. This is due to the physicochemical properties of NPs itself, where NPs possess smaller particles size in the range of $0.1 - 100$ nm. The potential of NPs has been used to address many performance challenges presented by the expensive products in coating industries [16]. This is due to the appearance and usefulness of NPs that bring many advantages and opportunities to the coating industry [17,18]. Furthermore, the usage of NPs as coating materials can achieve higher opacity, promote better interaction between the coating and surface, greater durability from combustible and flammable materials, improve mechanical, thermal and electrical properties of the substrates [19,20]. A good example of NPs would be titania (TiO_2), where the fabrication of TiO_2 using various methods to produce TiO_2 NPs has been carried out to increase the efficiency of TiO_2 as a non-combustible filler [21]. The superior properties of TiO_2 NPs are shown when it is used as inorganic FR and for self-cleaning purposes. Due to strong oxidation power, non-toxic, environmental friendly, high photostability, chemical inertness, readily available in earth's crust and high thermal stability, TiO_2 NPs have been widely used as FR compared to others conventional FRs, such as halogenated, phosphorus, and nitrogen that can most likely be toxic to the environment eventually [22,23].

In this work, TiO_2 NPs were prepared and coated on the surface of the wood to act as a flame retardant. The physicochemical properties of the TiO_2-coated were to be determined by a few methods. Fire-retardancy of the TiO_2-coated was then tested by flammability testing using a flame burner.

MATERIALS AND METHODS

Materials

Commercial local plywood was purchased from Hang Seng, Taman Daya, Johor Bahru, Johor, Malaysia. The chemicals used; titanium (IV) isopropoxide (TTIP, 97%, Sigma Aldrich), anhydrous ethanol (99.84%, HmbG Chemicals), acetic acid (100.00%, BDH AnalaR), 3-aminopropyltrimethoxysilane (APTMS) and molecular sieve (Sigma Aldrich), were supplied by Pustaka Elit Sdn. Bhd and Permula Sdn. Bhd, Malaysia. All chemicals were used without any further purification.

Preparation of Colloidal TiO₂

The synthesis of TiO_2 colloidal suspension for usage as coating layers on the surface of the wood was carried out according to the method reported by Wang et al. [24] but with slight modifications. Prior to being used, ethanol (500 mL) was dried using a molecular sieve to prevent hydroxylation during the synthesis. The synthesis process involves two steps, wherein the first step (solution A), TTIP (8.88mL, 0.03 mole) was slowly added into 20 mL of dried ethanol while being continuously stirred to prevent oxidation of the chemicals. In the second step, another 20 mL of ethanol was mixed with 2 mL of distilled water and 5 mL of acetic acid to obtain a homogeneous solution B. After that; solution A was slowly added into solution B with vigorous stirring. The mixture was continuously stirred overnight at room temperature to allow polymerization to occur.

Pre-treatment of Plywood

The procured plywood was cut into sizes of 50 mm x 25 mm. Then, the woods were soaked in distilled water for 30 min before being sonicated for 30 min to remove any impurities [24]. Following that, the woods underwent a drying process at a temperature of 103 °C for 18 h [25]. The cleaned wood plates were then kept dried in a desiccator before undergoing surface modification. 3-aminopropyltrimethoxysilane (APTMS) was used to modify the surface of the wood to allow better interaction between the wood and TiO_2. The pre-

treatment process of the woods with APTMS was carried out based on the work of Chandren and Ohtani [26], but with slight modifications. APTMS (4.4 mmol) was dissolved in 100 mL of ethanol. Then, the sheet of wood was sprayed with APTMS solution and dried for one hour, followed by drying at 60 °C in the oven overnight before being used.

Coating of Wood's Surface with TiO_2 NPs via Dip-coating Method

The modified woods were dipped into the colloidal suspension of TiO_2 via dip-coating method. The process of dip-coating of the substrate in a colloidal solution of TiO_2 NPs was made every 30 seconds, and the dipping process was repeated for 5 times for every deposited layer to obtain multilayer coating [27]. Then, the TiO_2-coated woods were dried at room temperature for 24 h and followed by a curing process at 130 °C overnight [25]. The coated wood was denoted as CW, while the uncoated ones are denoted as UCW.

Characterization

The surface morphology and elemental composition of the coated wood were examined by field-emission scanning electron microscopy (FESEM, Hitachi SU8020) with accelerating voltage of 2 kV and ~16 mm of working distance, together with energy dispersion X-ray (EDX) to determine the surface chemical composition. The thermal stability was examined by a thermogravimetric analyzer (TGA, Pyris 1 PerkinElmer) with the furnace range of room temperature - 900 °C and the chemical functional groups were detected by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR, Spectrum One, PerkinElmer).

Fire Testing of the Coated Wood

The fire testing on coated wood was carried out according to the standard fire tests on the spread of flame, ISO 5658-2 [28]. Two types of tests were carried out, which were fire propagation [29] and surface spread of flame [30]. Both tests were carried out using a flame burner. Fire propagation provides a comparative measurement of the contribution to the growth of fire made by an essentially flat material, composite or assembly. The temperature comparison was made between the uncoated wood (reference wood) and the coated wood. The flammability of the samples was then compared through the ignitability and flame separation of the coated wood with the uncoated wood. Fire propagation test was carried out by exposing the surface of the coated and uncoated woods at a vertical position to the flame for 30 seconds with a minimum of two replicates for each sample, where the thickness must not be more than 50 mm. The mass, relative humidity, and the conditions were maintained for all replicates of the wood specimens. Time and distance were recorded for data analysis. Each sample was tested with a few replicates for accuracy purpose. Surface spread flame test was carried out by exposing the surface of wood (coated and uncoated) to the flame at a horizontal position for 300 seconds of flame exposure time. The distance of flame separation from the initial point of flame exposure, to the end of the flame spread, was recorded for data analysis.

RESULT AND DISCUSSION

Morphology of TiO_2-coated Wood by FESEM

Characterization via FESEM has been carried out to determine the surface morphology, while EDX was used for elemental identification. Figure 1 shows the FESEM images of the TiO_2 NPs-coated on wood, at different magnifications. At the magnification of 500 times, only the cracks of the wood can be seen. Upon further magnification to 120,000 times, the TiO_2 NPs can be seen agglomerated on the surface of the wood. The particle sizes of the TiO_2 NPs are in the range of 24.5 – 45.2 nm (inset of Fig. 1(b)), proving that TiO_2 NPs have been successfully synthesized and coated onto the surface of the wood.
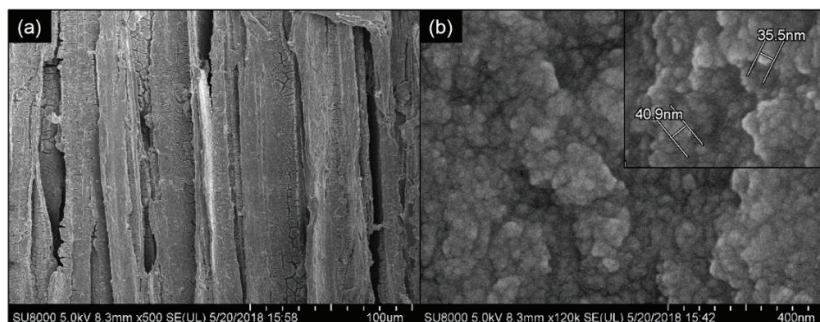
FIGURE 1. FESEM images of TiO$_2$ NPs-coated wood at different magnifications; (a) 500 times and (b) 120 000 times.

Elemental analysis was performed via EDX. The spectrum in Figure 2 shows that TiO$_2$ NPs comprises titanium (Ti), oxygen (O), silicon (Si) and carbon (C). The carbon (C) detected are postulated to be from the wood, while the Si detected are due to the surface modification of wood by APTMS [31]. The EDX results further proved the successful coating of the wood with a layer of TiO$_2$.
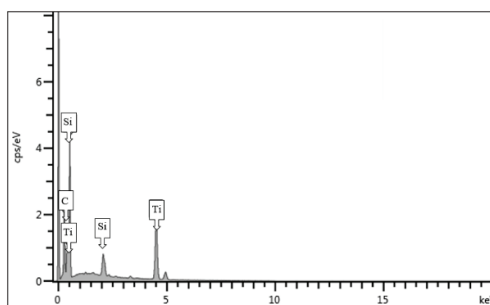
FIGURE 2: EDX spectrum of TiO$_2$ NPs-coated wood

Determination of Functional Groups by FTIR Spectroscopy

The functional groups on the surface of the wood for coated and uncoated wood were determined by FTIR-ATR and are presented in Figure 3. The FTIR spectrum of the uncoated wood is shown in Fig. 3(a). The band at 3394 cm^{-1} is attributed to the O-H stretch vibration of hydrogen-bonded hydroxyl groups or absorbed water [32], while the peak at 2912 cm^{-1} corresponds to the C-H stretching and a strong peak at 1027 cm^{-1} is due to the presence of C-O-C pyranose ring skeletal vibration of cellulose [33]. These two peaks are barely visible in the spectrum of the coated sample (Fig. 3(b)) as the formation of the TiO$_2$ layer covering the surface of the wood, hence decreasing the absorption of the peak [34]. The spectrum for the coated sample (Fig. 3(b)) shows a band at around 3394 cm^{-1}, which corresponds to the stretching vibration of hydroxyl groups [35,36]. Another peak observed in the spectra at 1641 cm^{-1} corresponds to the bending mode of hydroxyl groups [37]. These hydroxyl groups and adsorbed water are usually present on the surface of TiO$_2$ [38]. The characteristic vibration of the inorganic Ti-O stretch was also observed in the range of 690 to 450 nm [39].
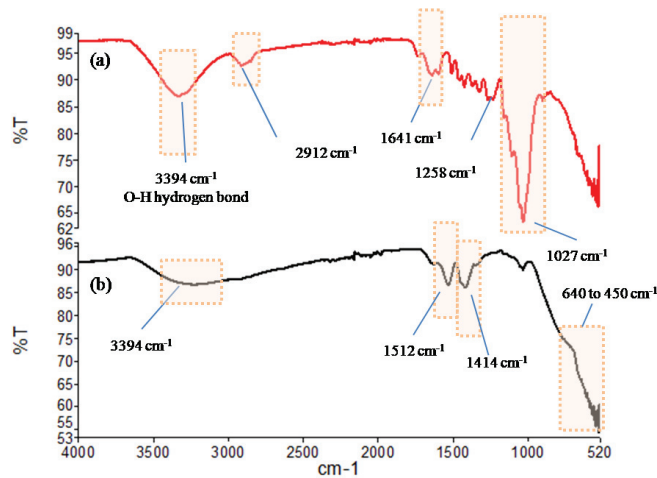
FIGURE 3. FTIR spectra of (a) uncoated wood and (b) coated wood

Thermal Stability and Flammability Performance Testing

The thermal stability of the TiO_2 NPs-coated wood was firstly tested via TGA, and the results are shown in Table 1. From the results, it is shown that for the coated wood sample 1 (CW-1), which has been coated with 2 mmol of TiO_2, the ignition temperature increased by about 5 °C, as compared to the reference temperature for the uncoated wood (UCW). As for sample 2 of the coated wood (CW-2) that has been coated with 5 mmol of TiO_2, an increase of 10 °C in the ignition temperature can be seen. These initial results show the potential of the TiO_2 NPs as a flame-retardant material.

**TABLE 1**: The flammability of the samples through TGA

Sample ID	Ignition temperature (°C)		Average
	1	2	
UCW-1	308.49 °C	308.81 °C	308.65 °C
CW-1	314.97 °C	311.19 °C	313.08 °C
CW-2	318.06 °C	318.24 °C	318.15 °C

Table 2 shows the results of flammability testing that has been carried out by exposing the wood samples to the source of fire or heat. The exposure times were carried out at intervals of 30 sec, 60 sec, 120 sec and over than 120 sec, with a constant flow of flame and constant distance between the source of flame to the target samples. From the results, it was found that sample 1 and 2 of the coated samples (CW-1 and CW-2, respectively) are capable of reducing the flammability of the wood. By exposing the uncoated wood (UCW) to the source of flame for as short as 1 min, the sample completely burned out, while CW required more than 2 min to be completely burned. In fact, after more 120 sec, the fire was self-extinguished where the fire was put out without using any external tool.

TABLE 2: The flammability of the samples through the flame test by exposing the samples to the source of fire for different duration

Sample	Exposure time (sec)			
	30 sec	60 sec	120 sec	>120 sec
UCW	Ignited	Ignited	Completely burned	Out of fuel source (wood completely burned)
CW-1	Not ignited	Ignited	Not completely burned	Self-extinguished
CW-2	Not ignited	Ignited	Not completely burned	Self-extinguished

Figure 4 shows the images of the wood samples after being exposed to the flame. In Fig. 4(a), it was shown that sample UCW was completely burned after 120 sec of exposure time. While in Fig. 4(b) and (c), samples CW-1 and CW-2 were not completely burned, and the fire was suppressed by self-extinguishing after 120 sec of exposure to the flame.
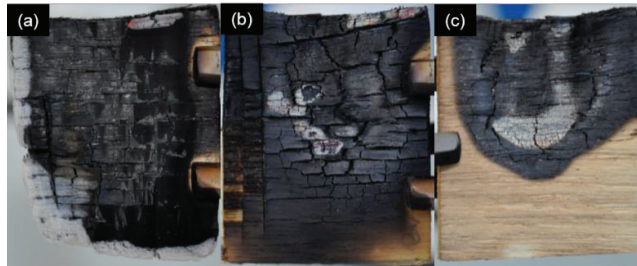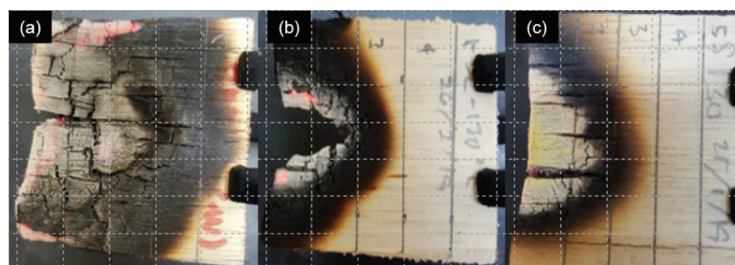

FIGURE 4. Images of the wood samples; (a) UCW, (b) CW-1, and (c) CW-2 after undergoing flame test by exposing the samples to the source of fire for different duration

The results of surface spread flame test that was carried out by exposing the wood samples to the flame for 300 seconds at the horizontal position are shown in Table 3. The separation area was calculated based on the spread area through the sample grids shown in Fig. 5. In Fig. 5(a), it can be seen that the separation of burned area for UCW's samples covered 32 out of the 35 grids marked, making the total burned area of 91.4%. As for sample of CW-1 (Fig. 5(b)), 15 out of the 35 grids have been burned, resulting in 42.9% of burned area. 37.1% burned area was obtained for sample CW-2 (Fig. (c)), where 13 out of the 35 grids were burned. By continuously exposing flame to the initial position, the results of flame separation show that sample CW-1 and CW-2 have a smaller burned area as compared to the uncoated sample (UCW). This indicates that the coated samples managed to reduce the spreading of the flame, as compared to the uncoated sample.

TABLE 3: Results of the surface spread flame test

Sample	Exposure time = 300 seconds
	Percent burned (%)
UCW	91.4
CW-1	42.9
CW-2	37.1

FIGURE 5. Images of the wood samples after undergoing the surface spread flame test; (a) UCW, (b) CW-1, and (c) CW-2

CONCLUSION

Based on the results obtained from the characterization and flammability testing, it was shown that TiO_2 NPs had been successfully coated onto the surface of the wood. From the thermal stability studies by using TGA, it was shown that the coated wood results in the increase of the ignition temperature. The flammability testing, which was carried out by exposing the wood to the source of fire, also showed that the coated wood is capable of reducing the flammability of the wood, as a longer time was required for the wood to be burned out as compared to uncoated wood. The flame spread test indicated that the coated samples managed to reduce the spreading of the flame, as compared to the uncoated sample. These initial results show the potential of TiO_2 NPs a good flame retardant, which can be further exploited for better use.

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