

Enhancement of physical, chemical, and mechanical properties of biocomposite for the fire resistant material application

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ABSTRACT

This study deals with the enhancement of physical and mechanical properties of oil palm empty fruit bunch fibers (OPEFB) for new fire resistant material application. Two flame retardants (organic and inorganic) were applied to improve the fire resistant capability of the produced fibers. The fire resistant capability was tested according to the ASTM D6413-99 method. Mechanical properties were characterized using a universal testing machine and the differential scanning calorimetry (DSC) was performed to investigate their thermal behaviors. The surface morphology of the produced fibers was observed using scanning electron microscopy (SEM). This study found that the fire resistant capability of the fibers can be improved by the addition of flame retardants. Thermal properties of the treated fibers can be enhanced compared to the untreated fibers. Mechanical properties inspection revealed that increasing the flame retardant concentration (0.5 to 1 M) can improve their tensile strength but started to decrease at a higher concentration (3 M). In general, the present work successfully performed the enhancement of non-woven OPEFB properties for foreseeable fire resistant material applications.

Keywords: Fire resistant; biocomposites; biomaterials.

1. INTRODUCTION

The demand for fibers produced from natural materials for numerous applications including automotive and aircrafts industries as well as consumer products has been dramatically increasing because of their ecological and economical features compared to synthetic fibers [1, 2]. Among these, automotive and aircrafts industries have been actively developing various natural fibers including hemp, kenaf, and sisal as well as bioresins. This is also a result of their high specific behaviors as well as providing lower prices compared to synthetic materials [3].

One major shortcoming for natural materials is poor fire resistance when interacting with fire. It has been established that the high cellulose content present in natural fibers can increase their flammability behaviors [4]. The burning process includes five steps such as heating, decomposition, ignition, combustion, and propagation. The flame retardancy of natural materials can be achieved by the disruption of the burning process at any of these stages. To improve fire resistance capability of natural fibers, it is necessary to the addition of some flame retardants delay the spread of fire after ignition [5-7]. Inorganic, organic, halogenated, and phosphorous compounds are the most widely used flame retardants materials [8]. In addition, the use boric acid, ammonium phosphates and borates, ammonium sulphate and chlorides, zinc chloride and borate, antimony oxide, sodium borate, and dicyanodiamide becomes an alternative as flame retardants [9, 10]. Several studies have been carried out to improve flammability properties of natural fiber/polymer composites. The use of flame

retardants such as ammonium polyphosphate (APP), magnesium hydroxide ($Mg(OH)_2$), zinc borate (Zb), and combination of APP with $Mg(OH)_2$ and Zb in sisal fiber/polypropylene (PP) composites was proven to improve flame retardancy and thermal stability of the composites without deterioration of their mechanical properties [11]. Another study also revealed that the combination of APP and Zb in polypropylene composites can improve fire behavior [12]. Alternatively, flame retardancy and thermal stability of intumescent polypropylene composites can also be improved by the addition of boron containing substances such as zinc borate (ZnB), borophosphate (BPO4), boron silicon-containing preceramic oligomer (BSi), and lanthanum borate (LaB) [13]. Moreover, it was also demonstrated that the addition of zinc borate (ZB) into intumescent flame retardant polypropylene composites (PP/IFR) containing ammonium polyphosphate (APP) and charring-foaming agent (CNCA-DA) can effectively improve the limiting oxygen index value and reduce the combustion performance of the composites [14].

Mechanism of flammability of composites using the flame retardants highly depends on the nature of the additives. It can act chemically or physically in the solid, liquid or gas phase. For instance, halogenated compounds can act as flame retardant by a vapour phase flame inhibiting mechanism through radical reaction [15]. When phosphorous compounds were used as flame retardant, they can act via the reduction of the formation of flammable carbon containing gases by increasing the conversion of polymeric

materials to a char residue during pyrolysis [15]. In general, common mechanisms of flame retardancy are by endothermic degradation, thermal shielding (solid phase), dilution of gas phase, and gas phase radical quenching processes. For instance, the use of magnesium and aluminium hydroxides can break down endothermically when subjected to high temperatures [16]. It is also possible to stop spreading of the flame over natural material by creating a thermal insulation barrier between the burning and unburned parts using intumescent additives [17]. Inert gases such as the use of carbon dioxide and water formed by thermal degradation can act as diluents of the combustible gases, lowering their partial pressure of oxygen, and slowing the reaction rate [18]. Moreover, chlorinated and brominated materials can undergo thermal degradation before releasing hydrogen chloride and hydrogen bromide.

2. MATERIALS AND METHODS

2.1. Materials.

Raw OPEFB was obtained from the PTPN VIII, Bogor, Indonesia. An inorganic additive, $\text{Ca}(\text{OH})_2$ was prepared by reacting NaOH with CaCl_2 . For a comparison, an organic additive, $(\text{NH}_2)_2\text{CO}$ was also prepared. All additives were supplied by the Merck, Darmstadt, Germany.

2.2. Fiber fabrication.

Prior to treatment, OPEFB was soaked in tap water. When removing the binding components, it was necessary to replace the water with fresh water. Finally, the crude fiber was dried at room temperature for 2 d and then stored (see Figure 1(a)). To obtain pure OPEFB fibers (see Figure 1(b)), the samples were inserted into a fiber separator.



Figure 1. (a) Raw material and (b) produced OPEFB fibers.

2.3. Non-woven fabrication.

A weaving machine was used to make non-woven OPEFB fibers. It consists of an iron plate (20 cm in width and 50 cm in length). The plates moved vertically and the production of the non-woven OPEFB fibers was carried out at a speed of 1 m/min. Figure 2(a) illustrates the non-woven OPEFB fibers production using the machine and the produced fibers are shown in Figure 2(b).



Figure 2. (a) Non-woven OPEFB fibers production using the machine and (b) the produced non-woven OPEFB fibers

2.4. In-situ treatment.

In-situ treatment was conducted using a method proposed Zhao, Hu [19]. In this study, two flame retardant additives were

There are many shortcomings from the current methods of flame retarding natural composites for advanced material applications. They include the complexity of the treatment and deterioration of the mechanical of composites. Considering the aforementioned problems, this work aims to develop non-woven oil palm empty fruit bunch fibers (OPEFB) by inserting inorganic and organic flame retardants to improve both flames retarding and mechanical properties of the biocomposites. The use of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and urea ($(\text{NH}_2)_2\text{CO}$) as composites treatment technique to improve their flammability behaviors is relatively new, as very few studies could be found in scholarly literature. The experimental work presented here provides a new insight into evaluating the effect of flame retardant additives on the physical and mechanical properties of the produced non-woven OPEFB.

applied to the non-woven OPEFB fibers. They are (i) an inorganic additive, $\text{Ca}(\text{OH})_2$ obtained by reacting NaOH with CaCl_2 and (ii) organic material urea ($(\text{NH}_2)_2\text{CO}$). All additives were prepared at different concentrations of 0.5 M, 1 M, and 3 M before applying to the produced fibers. In the preparation, approximately 1 g of non-woven OPEFB fibers was dried in an oven at 105°C for 3 h and then soaked in a flame-retardant solution (1:10) before shaking for 30 min. Furthermore, the treated fibers were washed three times using 20 mL tap water. Next, the treated fibers were dried in an oven at 105°C for 6 h and stored in a clean plastic bag for further characterization.

2.5. Physio-chemical properties investigation.

Chemical compositions of the fibers were analyzed using TAPPI standard method. The lignin was investigated using TAPPI T222 om-88, and α -cellulose was analyzed using TAPPI T203 os-61. The length and diameter of the fibers used to make non-woven fibers were measured. To obtain the density properties, 20 samples of the non-woven OPEFB fibers were weighed using a balance.

2.6. Morphological study.

The surface morphological study was performed using the scanning electron microscopy (SEM) (JEOL JSM-6510LA model, Tokyo, Japan). A voltage of 20 kV with 800x magnification was applied during the scanning.

2.7. Thermal inspection.

The thermal behaviors of the proposed fibers were investigated using the differential scanning calorimetry (DSC) (DSC3+, Mettler Toledo, Greifensee, Switzerland). Approximately 10 mg of the sample was analyzed at temperature ranging from 30 to 450°C under a nitrogen environment with a scan rate of $10^\circ\text{C}/\text{min}$.

2.8. Flammability test.

Flammability test was performed using the hanging flame test. The treated fiber sample (0.1 g) was fabricated and then burned using a flame from a distance of 3 cm. The time to ignition of the fiber sample was recorded. The non-woven OPEFB was tested according to ASTM D6413-99. This test was performed by hanging a non-woven OPEFB fiber sample vertically (7.62 cm in width and 30.50 cm in length) above the burner in a fire test chamber. The flame from the burner was approximately 1.5 cm in height and the sample was 2.0 cm above the flame.

2.9. Tensile test.

For the purpose of mechanical testing, five samples were prepared with the dimensions 30.00 mm × 10.00 mm × 1.00 mm and a

gauge length of 10 mm. The tensile test was conducted using a Jinan WDW-20 (Ningbo, China). Additionally, p-value descriptive data was generated for all of the variables.

3. RESULTS

3.1. Fiber characteristics.

It is established that three principal chemical constituents of natural fibers are cellulose, hemicellulose, and lignin. The cellulose chains are arranged in parallel to form bundles, which are denoted microfibrils. Hemicellulose is a heterogeneous group of polysaccharides characterized by being short and branched. Lignin is a highly branched polymer composed of phenylpropane units organized in a complex three-dimensional structure. Table 1 presents the chemical composition of fibers including data obtained from this work.

Table 1. Chemical composition for different natural fibers [4].

Type of fiber	Cellulose (%)	Lignin (%)
OPEFB*	19.14 ± 0.08	55.09 ± 1.53
Flax	64 - 71	2 - 5
Kenaf	44 - 57	15 - 19
Jute	61 - 72	12 - 13
Hemp	70.2 - 77	3.7 - 5.7
Ramie	68.6 - 76.2	0.6 - 0.7
Abacca	56 - 63	7 - 10
Sisal	67.5 - 78	8 - 11
Cotton	85 - 90	07 - 16
Coir	36 - 43	41 - 45
Rice	28 - 48	12 - 16
Bagasse	32 - 48	19 - 24
Bamboo	26 - 43	21 - 31
Esparto	33 - 38	17 - 19
Coniferous	40 - 45	26 - 34

*obtained from the present study

In general, cellulose composition in the fibers was in the range of 19 to 90% depending on the fibers type as listed in Table 1. In addition, the listed fibers contained lignin ranging from 0.6 to 55% depending on the fibers type. In this work, OPEFB fibers contained moisture, α-cellulose, and lignin, of 7.95% ± 0.52%, 19.14% ± 0.08%, and 55.09% ± 1.53%, respectively.

It can be observed that the lignin content of OPEFB was higher compared to others as listed in Table 1. According to Dorez, Ferry [20], fibers with higher lignin content can contribute to their fire resistant ability. Lignin is known as a natural flame retardant owing to its phenolic backbones, which are able to produce a mass of char residue upon heating at elevated temperature [21]. This study also found that the cellulose content of OPEFB was lower compared to other fibers as tabulated in Table 1. In general, the cellulose content in natural fibers can be increased after processing treatments, due to the removal of non-cellulose residues of the fibers such as pectins and waxes.

Moreover, the dimensions of the produced fiber were 172.8 mm ± 48.2 mm (length) and 0.39 mm ± 0.08 mm (diameter). The produced fibers can be categorized as long fibers. In addition, the produced non-woven OPEFB fiber had a mass variance per unit area of 335.17 g/m² ± 27.39 g/m² and was assumed to be uniform as shown in Figure 2(b). Processing treatments can influence chemistry and structure of cellulose fibers with more variable properties compared to synthetic fibers.

3.2. Flammability behaviors.

Flammability behaviors of the treated (with the inorganic and organic flame retardants) and untreated fibers are presented in Table 2. It was found that the duration needed for the untreated fibers to burn was 4.0 s ± 2.65 s. For Ca(OH)₂ without washing, their durations needed for the treated fibers to burn were 11.0 s ± 2.0 s, 18.7 s ± 3.1 s, 36.7 s ± 4.2 s at additive concentrations of 0.5 M, 1 M, and 3 M, respectively. After washing, the corresponding values were shorted into 7.7 s ± 2.5 s, 9.3 s ± 3.1 s, and 15.3 s ± 4.0 s. When (NH₂)₂CO without washing was applied, their durations needed for the treated fibers to burn were 5.7 s ± 1.5 s, 13.8 s ± 2.1 s, and 36.3 s ± 7.8 s at additive concentrations of 0.5 M, 1 M, and 3 M, respectively. After washing, the corresponding values were shorted into 5.3 s ± 1.2 s, 13.0 s ± 3.6 s, and 34.0 s ± 6.0 s. The proposed additives can prolong durations needed for the fibers to burn. Although durations needed for the treated fibers to burn can be decreased by washing, their values were still longer compared to untreated fibers.

Table 2. Duration needed for the proposed fibers at different treatments to burn.

Treatment		Concentration of additive		
		0.5 M	1 M	3 M
Ca(OH) ₂	w/o washing	11.0 s ± 2.0 s	18.7 s ± 3.1 s	36.7 s ± 4.2 s
	w/ washing	7.7 s ± 2.5 s	9.3 s ± 3.1 s	15.3 s ± 4.0 s
(NH ₂) ₂ CO	w/o washing	5.7 s ± 1.5 s	13.8 s ± 2.1 s	36.3 s ± 7.8 s
	w/ washing	5.3 s ± 1.2 s	13.0 s ± 3.6 s	34.0 s ± 6.0 s

In this case, when NaOH and CaCl₂ were reacted, Ca(OH)₂ formed on the surface of the fiber and the washing with water caused it to dissolve into ions. Previous work found revealed that Ca²⁺ ions can increase the fire resistant ability [22]. The results of this study indicated that Ca(OH)₂ and (NH₂)₂CO can enhance the anti-flammability ability of the produced fibers. This result can be explained by the fact that Ca(OH)₂ can serve as an additional protective material when exposed to heat from fire by forming char intumescence [23]. Several reports have shown that a flame retardant that contains nitrogen produces incombustible gases and dilutes with oxygen to form a protective layer during heating [23]. The lignin content in the fiber helped with the formation of char during thermal decomposition of the fiber and was apparently able to increase the anti-flammability ability [20, 24]. However, lignin to cellulose ratio above 1:2 causes the char to be reduced [25].

3.3. Thermal properties.

Figure 3 shows that all curves had almost the same tendency in the form of endothermic reactions when the temperature was below 150 °C. The most interesting aspect of this graph was the large peak for Ca(OH)₂. It was possible that these results were because of some inorganic materials decomposing during the endothermic reaction and increasing the fire retardancy effect. The endothermic reaction that occurs was generally a process of removing water when the sample was exposed to heat [26]. The increase in the endothermic curve indicated the absorption of heat [27].

It was also found that the onset temperature increased from 42.5 °C (untreated) to 54.69 °C (treated with Ca(OH)₂). Also, the enthalpy of the system increased from 58.1644 J/g (untreated) to 383.2803 J/g (treated with Ca(OH)₂). Calcium alkoxide was grafted onto the surface of the OPEFB fiber and caused fire retardation [19]. In accordance with the current results, previous research has shown that inorganic salts can affect thermal properties [28]. The ion layer on the fiber can produce more carbon residue, which can reduce the amount of heat released [22].

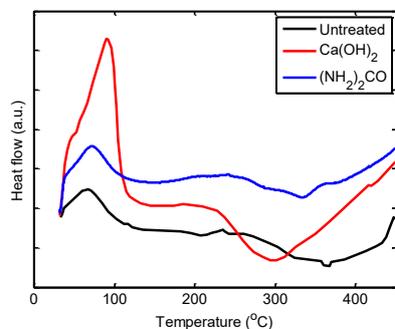


Figure 3. DSC curves for all treated and untreated non-woven fibers.

3.4. Mechanical properties.

Figure 4 shows that the tensile strength of the non-woven OPEFB was influenced by washing and concentration. It was found that the tensile strength of the untreated fibers was 4.7±1.29 MPa. It can be observed in Table 3 that the tensile strengths of the fibers treated with Ca(OH)₂ without washing increased at additive concentration up to 1 M before decreasing to reach below-untreated fibers at an additive concentration of 3 M. After washing, a similar pattern was also observed but with lower value at an additive concentration of 3 M.

For the fibers treated with (NH₂)₂CO without washing, their tensile strengths can be increased up to 6.94 ± 1.58 at 1 M additive concentration. The value becomes to decrease when the fibers were treated with (NH₂)₂CO at an additive concentration of 3 M. A similar pattern was also observed for the fibers treated with (NH₂)₂CO with washing but at higher additive concentration, the values are higher compared to untreated fibers. It suggests that the addition of (NH₂)₂CO onto the fibers can improve their tensile strength although after washing treatment.

3.4. Morphology.

SEM images of the untreated and treated fibers are shown in Figure 5. Before the treatment, it was exhibited that no agglomerated solid particles observed on the surface of the

4. CONCLUSIONS

The present work was aimed to evaluate physical and mechanical properties of non-woven OPEFB for new fire resistant applications enhanced by the addition of organic and inorganic flame retardant additives. An increase in the concentration of the fire resistant improved the anti-flammability ability of the fibers.

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composite fibers. Conversely, after treatment with Ca(OH)₂ as shown in Figure 5(b), solid particles (white dots) were observed covering almost all parts of the surface-treated fiber. It is suggested that these solid particles were likely Ca(OH)₂ and CaCO₃, which can be formed when exposing with O₂ in the air [19].

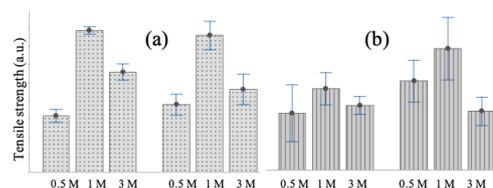


Figure 4. Tensile strength of the non-woven OPEFB (a) with washing and (b) without washing

Table 3. Summary the tensile strength of the fibers at different treatment.

Treatment		Tensile strength (MPa)			
		Concentration			
		0 M	0.5 M	1 M	3 M
Ca(OH) ₂	w/o washing	-	4.94 ± 2.60	5.33 ± 1.94	3.60 ± 1.37
	w/ washing	-	4.60 ± 2.01	7.79 ± 0.56	3.35 ± 2.45
(NH ₂) ₂ CO	w/o washing	-	5.71 ± 1.44	6.94 ± 1.58	3.64 ± 1.70
	w/ washing	-	4.37 ± 1.75	7.58 ± 1.41	5.58 ± 1.28

Similar surface properties were also observed when the fibers were treated with (NH₂)₂CO as shown in Figure 5(c). Agglomerated solid particles (white dots) can be found on the surface fibers. Solid particles present in the surface of the fibers treated with (NH₂)₂CO can be attributed to the (NH₂)₂CO salts, which were also confirmed to function as a fire inhibitor [29]. In general, findings of this study support previous works [30-35].

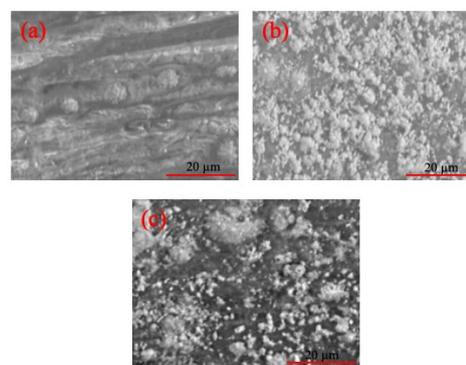


Figure 5. SEM images of the OPEFB fibers of (a) untreated, (b) treated with Ca(OH)₂, and (c) treated with (NH₂)₂CO.

The thermal properties of the treated fibers can be improved compared to the untreated fibers. Mechanical properties of the fibers were affected by the addition of flame retardant additive depending on the type and concentration of the additives.

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