Mechanical and flame-retardant properties of oil palm empty fruit bunches

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**Abstract.** In this work we studied the mechanical and flame retardant properties of Oil Palm Empty Fruit Bunches (OPEFB). Currently, the use of OPEFB waste in Indonesia is not optimal and the amount of the waste continues to increase every year. In this study, we optimized the flame retardant properties of non-woven OPEFB fibers. The OPEFB fiber was modified by making it non woven and treated in situ by immersing it with a mixture of NaOH and CaCl\textsubscript{2} solution (flame retardant-1 treatment) and also a mixture of KOH and CaCl\textsubscript{2} solution (flame retardant-2 treatment). In addition, the treated fibers were investigated for surface morphology and tested for thermal and tensile strength tests. Provision of flame retardant treatment in non woven fibers can improve flame retarding and mechanical properties. The objective of this study was optimization of flame retardant treatment of OPEFB. Non woven fiber which was treated with the first flame retardant with a concentration of 3 M did not burn for 12 seconds. The vertical flame test showed that the burning time until the fiber runs out was slowed to 39 seconds. Fibers treated with NaOH and CaCl\textsubscript{2} with 3 M concentration also had the best tensile strength values of 8.13 MPa. In the morphology test, non-woven fibers with the first flame retardant treatment were better than non woven fibers with the second flame retardant treatment.

1. **Introduction**

Oil palm is one of the plantation products in Indonesia. The development of oil palm plantations in Indonesia is increasing every year [1]. Based on data from the Directorate General of Plantation in 2016, Indonesia is the largest oil palm producing country in the world. Almost every island in Indonesia has oil palm plantations, such as the islands of Sumatra, Java, Kalimantan, Sulawesi, Maluku and Papua. The area of oil palm plantations in Indonesia in 2016 reached 11.67 million hectares [2]. One part of oil palm is the Palm oil bunch (Figure 1) which consists of spikelet, stalk, and fruitlets. In the production of palm oil, only the fruit is taken to be processed into oil, while spikelet and stalk are not used so they will become waste. Generally spikelet and stalk are called Oil Palm Empty Fruit Bunch (OPEFB). This OPEFB is one of the oil palm industry wastes whose utilization is not yet optimal because OPEFB is piling up around the factory. To overcome this problem, it is necessary to process OPEFB into new material through breakthroughs and technological innovations, namely composite material engineering.
Composite is a new type of engineered material consisting of two or more materials where the properties of each material differ from one another both chemical and physical properties [3]. The use of OPEFB fiber which is one of the natural fibers in biocomposite products is an effort to reduce and utilize abundant OPEFB waste [3]. Biocomposite is a composite material which one of the constituents comes from nature. Biocomposites can also consist of natural polymers as matrices and natural fibers (biofibers) as reinforcement. Natural fibers are widely applied to composites for structural or semistructural components, such as building materials, construction materials, furniture or automotive components. Natural fibers have many advantages such as corrosion resistance, widely available in nature, light weight, strength and stiffness can be formed as needed [4]. Biocomposites should have superior mechanical and surface properties according to technological applications.

OPEFB contains cellulose, lignin, hemicellulose. Low lignin content will increase the char product produced [5]. Increased char formation during the combustion process is a good indication of flame retardancy (Salmeia et al. 2016). Therefore, it is necessary to do chemical treatment to remove lignin from the fiber, one of them by using NaOH. The addition of NaOH can remove impurities, lignin and hemicellulose from the surface of the fiber, so that it can expose the hydroxyl group to be modified. In addition, alkali groups can also act with hydroxyl groups and produce negative Oxygen ions (O-) [6].

Chemical treatment with alkali on natural fibers aims to eliminate hemicellulose, lignin, and other impurities. This treatment will cause the arrangement of fibers to form a more closed arrangement, thereby increasing the crystallinity of the fiber. So, this treatment can increase fiber rigidity [6]. This study aimed to obtain flame retardant treatment optimization on non woven fibers. Flame retardant treatment was soaking non-woven fibers with chemical solutions that can withstand fire [6].

NaOH solution mixed with CaCl₂ can produce Calcium hydroxide (Ca(OH)₂) and NaCl. Calcium hydroxide (Ca(OH)₂) has a flame retardant function. Ca(OH)₂ can be decomposed into calcium hydroxide and water when heated. Water and CaO can help stop fires during combustion [6]. In this study, we prepared a Ca (OH)₂ emulsion from a mixture of alkaline solution and calcium hydroxide. Ca (OH)₂ can be slightly soluble in water. NaOH and Ca (OH)₂ react with hydroxyl groups in OPEFB fibers to form -O-Na + and -O-Ca₂ + OH-, thus producing -O- on the surface of the fiber [6].

Dissolved Ca(OH)₂ is used continuously during this process and causes Ca(OH)₂ to dissolve continuously. Insoluble Ca(OH)₂ is stored on the surface of the fiber through hydrogen bonds between -OH of Ca(OH)₂ and -O of the fiber. Thus, during the combustion process Ca(OH)₂ insoluble and -O-Ca₂ + OH- on the surface of the fiber can be stored with CO₂ in the air to form calcium carbonate (CaCO₃) [6].

CaCO₃ can be decomposed into CaO and CO₂ when it burns. CaO will stick to flammable surfaces, which can prevent the spread of combustion. CaO can also absorb gas, smoke, and residual melt resulting from incomplete combustion. Thus, the burning will stop immediately. The more CaCO₃, the better the biocomposite resistance to fire [6].

To the best of our knowledge, optimization of OPEFB flame retardant properties based on NaOH + CaCl₂ Molar variation have so far never been reported elsewhere. We point out that such analysis is necessary if the material will be applied for bulletproof vessels since burning effects may occur in the process. Our work also highlighted the mechanical properties of OPEFB, specifically non-woven OPEFB to various bundles.
2. Methods

OPEFB fiber is made into non-woven fiber as shown in Figure 2 with a size of 30 x 30 x 1 cm with a mass of 30 g (modified fiber). Then a solution of sodium hydroxide was made and mixed with calcium chloride (first flame retardant solution) and potassium hydroxide solution mixed with calcium chloride (second flame retardant solution). Each flame retardant solution was made with 3 concentrations, namely 0.5 M, 1 M, and 3 M. After that the modified fibers were immersed in each of the 1st solution and the 2nd solution for 30 min at room temperature. The fibers were then dried in the oven with a temperature of 100 °C for 6 hours.

\[
\text{NaOH (s) + CaCl}_2 \ (\text{aq}) = \text{Ca(OH)}_2 + \text{NaCl} \\
\text{KOH (s) + CaCl}_2 \ (\text{aq}) = \text{Ca(OH)}_2 + \text{KCl}
\]

![Figure 2. Non woven fibers from OPEFB](image)

The next step was testing the fiber samples that were treated with flame retardant. The fiber was made as shown in Figure 3 and tested to be fire-resistant based on the ASTM D6413 standard (vertical test) based on time (Figure 4). Samples were burned for 12 seconds and time was recorded until the samples burned out.

![Figure 3. Flame retardant treatment](image)

In addition to the burning test, micro-sample testing was also carried out, namely thermal analysis using Differential Scanning Calorimetry (DSC) of the Perkinelmer type DSC 4000 brand to determine
thermal characteristics, mechanical tests to determine the tensile strength value using Universal Testing Machine (for Tensile Strength test), and surface morphology test using SEM.

3. Results and Discussion

3.1. Flame test

In this study, flame test, tensile strength, thermal analysis and fiber surface morphology data were obtained. For the flame test using the ASTM D1230 standardization, the data is shown in Table 1. From the table it can be analyzed that the time of the flame in the long flame test to burn out was non woven fiber with the first flame retardant treatment of 3 M concentration. In accordance with ASTM D1230, the sample was burned for 12 seconds, then the flame time was measured until the sample was burned out [7]. The optimum flame time of 39 seconds was the time required for the sample to burn out along 15 cm. During combustion, -O, Ca2+ , -OH react with CO2 and CaO will be produced. When CaO is formed and attached to flammable surfaces, continuing can prevent the burned surface from spreading. CaO can also absorb gases and fumes produced from flammable polymer surfaces [6].

| Molar  | Time of fire (seconds) | KOH + CaCl₂ | NaOH + CaCl₂ |
|--------|------------------------|-------------|--------------|
| 0.5    | 5.00                   | 10.00       |
| 1      | 17.00                  | 16.67       |
| 3      | 18.00                  | 39.00       |

Based on the chemical reaction, the two samples used of KOH and NaOH produced the same compound, Ca(OH)₂. The compound Ca(OH)₂ dissolved in water and in 30 min a precipitate occurred. The hydroxyl group in the fiber reacted with Na + and Ca(OH)₂. The dissolved OH ion from Ca(OH)₂ binds with positive Na to NaOH which reacts with the hydroxyl group on the fiber surface to become -O-Na +. However, dissolved Ca(OH)₂ can also react with hydroxyl groups in fibers and O ions were formed. Therefore, CaO was formed and coated the surface of the fiber. While Ca(OH)₂ which was not dissolved was left on the fiber and discarded during the soaking process. The same process also occurs when KOH and CaCl₂ are mixed. KOH and NaOH are strong alkaline. One thing that distinguishes it is the radius of the atom, its molecular weight and electronegativity which are chemical characteristics. Element K has all three chemical properties which are greater than Na. The distance between the lattice in the OPEFB molecule group has a size corresponding to Na so that Ca(OH)₂ resulting from the reaction of NaOH with CaCl₂ can fill in the blanks and interstices in the fiber. Meanwhile, K has a larger atomic radius, so that the bonds formed a curvature which results in brittle fibers, and Ca(OH)₂ formed was wasted. In addition, electronegativity between Na and OH is lower than K and OH. This also results in the process of forming a bond between K and OH in the fiber faster than Na and OH. Chemical process that takes place too fast can make the bond become not strong.

3.2. Tensile strength test

The tensile strength of non-woven fiber and bundle fibers are shown in Table 2. Based on Table 2, non-woven fibers produced lower tensile strength values than bundle fibers. This was because the connection of knits between fibers in non-woven fibers breaks first, so that the bundle fiber has a higher tensile strength.
Table 2. Tensile strength of OPEFB fiber with flame retardant treatment

| Repetition | Non-woven Tensile strength (MPa) | Bundle Tensile strength (MPa) |
|------------|----------------------------------|-----------------------------|
| 1          | 5.45                             | 34.11                       |
| 2          | 3.27                             | 34.11                       |
| 3          | 6.55                             | 25.59                       |
| 4          | 7.39                             | 27.06                       |
| 5          | 4.73                             | 34.11                       |
| Average    | 5.48                             | 30.99                       |

Tensile strength of non-woven OPEFB fiber with flame retardant treatment in different concentrations is shown in Table 3. Based on Table 3, non-woven fibers treated with NaOH + CaCl$_2$ 3 M showed the most optimum tensile strength values. Meanwhile, treatment with KOH + CaCl$_2$ solution produced tensile strength values that tend to be constant. Tensile strength is the optimum pressure a material can accept [8]. Tensile strength is the result of maximum force quotient with a material cross-sectional area. When compared with controls, fibers treated with flame retardant had a higher average value. As in the previous explanation, the flame retardant treatment with NaOH + CaCl$_2$ solution has a stronger bond than KOH + CaCl$_2$ with fiber so that the tensile test results of NaOH treatment were more optimum. Therefore, the NaOH + CaCl$_2$ 3 M treatment was chosen as a flame retardant treatment of OPEFB non-woven fibers in subsequent biocomposite manufacturing.

Table 3. Tensile strength of non-woven OPEFB fiber with flame retardant treatment

| Molar | KOH + CaCl$_2$ Tensile strength (MPa) | NaOH + CaCl$_2$ Tensile strength (MPa) |
|-------|--------------------------------------|----------------------------------------|
| 0.5   | 1.22                                 | 1.55                                   |
| 1     | 1.36                                 | 4.50                                   |
| 3     | 1.62                                 | 8.13                                   |

3.3. Analysis of thermal properties

In Figure 5, 6, 7 showing the DSC plot, the DSC graph shows endothermic and exothermic transitions at variable temperatures. Differential Scanning Calorimetry (DSC) thermal analysis is used to determine the response of non-woven fiber OPEFB with flame retardant treatment to heat. Based on the results, sample with flame retardant-1 showed an endothermic curve with an onset temperature of 54.69 ºC and a peak of 88.82 ºC. In this phase, the absorption of heat energy from the environment to the system occurs with an enthalpy change of 383.28 J/g to the end set of 104.17 ºC followed by the release of H$_2$O into the environment. The next phase was the glass transition between the endothermic endpoint of 104.17 ºC and the exothermic onset point of 241.30 ºC. This phase was the starting point of melting in the form of rubber. Next was the exothermic phase where the system released energy from the system to the environment with enthalpy changes of -133.36 J/g to the end set of 321.15 ºC which is called the carbonization phase. After this phase was passed, the fiber experienced activation at 321.15 ºC. Meanwhile, non-woven fibers with KOH + CaCl$_2$ solution showed an endothermic curve with an onset temperature of 38.88 ºC with a peak of 66.47 ºC with the system absorbing energy from the environment of 73.88 J/g to an end set of 96.65 ºC. When compared, the sample curve of flame retardant-1 had a higher endothermic end set point. This explains that sample of flame retardant-1 needs more energy to burn out than control sample and flame retardant-2 sample, so it is in accordance with the results of the vertical burning test that the time of sample flame retardant-1 burned out was slowed down to 39 seconds.
Figure 5. Control sample

Figure 6. Sample of flame retardant-1

Figure 7. Sample of flame retardant-2
3.4 Morphology Analysis

Observation of micro morphology using SEM aimed to determine the micro surface structure of OPEFB fiber samples coated with flame retardant. Based on the images shown in Figure 8a, 9a, and 10a, the difference in the surface in micro is not yet apparent because it only used a magnification of 20 x. However, a darker color difference was observed in the control fibers compared to the flame retardant treatment fibers. At 100 x magnification as shown in Figure 8b, 9b, and 10b, visible differences began to appear on the surface. Based on Figure 9b and 10b, it appears that the fiber with the flame retardant treatment contains white grains which do not appear in Figure 10b. Likewise with Figures 9c and 10c which show that there are white granules lining the OPEFB non-woven fibers, whereas Figure 8c does not show any white coating on the fibers. This shows that the flame retardant treatment with both solutions affected the surface structure of the fibers. The microstructure of white granules which were seen in SEM observations are indicated as Ca(OH)_2 layers resulting from the chemical reactions of sample of flame retardant-1 and sample of flame retardant-2.

![Figure 8. Analysis of morphology using SEM of non-woven OPEFB fiber control sample with magnification of 30 x (a), 200 x (b), 100 x (c), and 800 x (d)](image-url)
4. Conclusion
In this study, we found that non-woven OPEFB fibers with flame retardant treatment of NaOH + CaCl$_2$ 3 M solution had the optimum flame retardant ability with 335 g/m$^2$ non-woven fiber OPEFB fibers. This was evidenced by the results of the flame test and DSC where there was an increase in the thermal properties of the fiber. The mechanical properties in the form of tensile strength values in fiber with NaOH + CaCl$_2$ 3 M solution showed the most optimum compared to KOH + CaCl$_2$ solution. Variation in the concentration of non-woven fiber OPEFB 18% flame retardant treatment was the optimum variation as a bullet proof material shown with the lowest depth of bullets in the biocomposite and optimum impact strength.
References

[1] Badan Pusat Statistik 2016 Statistik Kelapa Sawit Indonesia (Indonesian Palm Oil Statistics). Direktorat Jendral Perkebunan

[2] Direktorat Jendral Perkebunan 2016 Statistik Perkebunan Indonesia (Indonesia Plantation Statistics) www.ditjenbun.pertanian.go.id

[3] Suryadi G 2017 Kajian mikrostruktur, sifat termal, mekanik, dan permukaan biokomposit berpenguat tandan kosong kelapa sawit (Study of microstructure, thermal, mechanical and surface characteristics biocomposite reinforced oil palm empty bunches) [Thesis] Bogor (ID): Bogor Agricultural University (IPB)

[4] Sapuan 2017 Composite Material. United States: Elsevier Inc

[5] Dorez G, Ferry L, Sonnier R, Taguet A, Cuesta M 2014 Effect of cellulose, hemicellulose and lignin contents on pyrolysis and combustion of natural fibers Journal of Analytical and Applied Pyrolysis 107 pp 323-331

[6] Zhao WJ, Hu QX, Zhang NN, Wei YC, Zhao Q, Zhang YM, Dong JB, Sun ZY, Liu BJ, Li L, Hu W 2017 In situ inorganic flame retardant modified hemp and its polypropylene composites. Royal Society of Chemistry 7 pp 32236-32245 doi:10.1039/c7ra04078d

[7] ASTM D1230-10 Standard Test Metod for Flammability Apparel Textiles

[8] Istiyono E 2006 Kajian Sifat Mekanik Bahan yang Mengakami Anilisasi Jurnal Penelitian Saintek 11(1) pp 56-68