Production and characterization of PVA/alginate composite filament with cellulose from oil palm empty fruit bunches

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Abstract. Cellulose is a renewable natural polymer that has abundant availability in the Earth and found in oil palm empty fruit bunches (OPEFBs). OPEFBs is one of the biomass produced from the crude palm oil industry. Cellulose fibers were isolated by alkaline treatment and bleaching. Cellulose from OPEFBs can be utilized as filament material by mixing it with polyvinyl alcohol (PVA) and alginate. In this work, OPEFBs cellulose/PVA/alginate composite filaments were produced by the wet spinning method with 9 wt% CaCl₂ as a coagulant solvent and characterized. The effect of composite formulation on mechanical, morphological, crystallinity, and thermal properties of filaments was observed. The observed result shows that the increasing cellulose concentration had excellent thermal stability, higher crystallinity, with the morphology of the surface became rougher than 0% cellulose filament. The addition of cellulose had a significant effect on the mechanical properties of filaments, increasing the tensile strength and decreasing the elongation of filaments.

Keywords: cellulose, composite, filament, OPEFBs, wet spinning.

1. Introduction
Indonesia is the world’s largest country that produces crude palm oil (CPO). There is an increase in CPO production per year, approximately 34.47 million tons of production in 2017 [1]. Oil palm empty fruit bunches (OPEFBs) are one of the biomass generated from CPO production. OPEFBs, in general, are utilized as compost for plantation sites. However, OPEFBs consist primarily of three biopolymers, namely cellulose (43-65%), hemicellulose (17-33%), and lignin (13-37%) [2]. Cellulose is known due to its abundant availability and excellent properties such as good mechanical properties, thermal
stability, biodegradability, and biocompatibility. Therefore, the utilization of OPEFBs as natural cellulose resources is potential for producing composite polymer-based products [3].

In previous work by Arnata et al. [4], the cellulose was successfully isolated from sago frond by alkaline chemical treatment and bleaching. Cellulose from agricultural biomass can be utilized as a composite material because of hydrogen bonding. Hydrogen bonding between cellulose chains causes entanglement of fibers with other materials [5]. Cellulose obtained further was mixed into PVA and sodium alginate to become filament. The filament is a widely used polymer-based product, especially in biomedical applications like surgical thread, scaffold, and wound dressing.

PVA is a widely used synthetic polymer with excellent biodegradability, biocompatibility, chemical resistance, and physical properties [3]. Meanwhile, alginate is a natural polymer with a long chain molecule that consists of two monomers, known as mannuronic acid (M) and guluronic acid (G). Alginate can form gel due to the cooperative binding of Ca$^{2+}$, Mg$^{2+}$, or any divalent cations and G-block regions of alginate. This ionic binding results in the formation of a specific structure called an “egg-box” structure. Accordingly, the proportion of M and G components in alginate is an essential factor for gel formation via the addition of divalent cations [6].

The objective of this work is to utilize cellulose from OPEFBs as a material for producing composite filaments and characterize the filaments produced. This work focuses on producing cellulose/PVA/alginate-based filament with a wet spinning method and CaCl$_2$ solution as a coagulant solvent. The spinning dope leaving spinneret submerged directly into the coagulant and filament was solidified [7]. The advantages of the wet spinning method are; easy to do and more economical.

2. Materials and methods

2.1. Materials

Cellulose fiber was obtained from OPEFBs supplied by PT Inti Indosawit Subur, Riau, Indonesia. NaOH and polyvinyl alcohol (PVA) were supplied by Merck, Inc. (Germany), sodium alginate was supplied by HiMedia (India). H$_2$O$_2$ and other chemicals used were the product with commercial grade.

2.2. Preparation of cellulose fibers

Cellulose fibers preparation was conducted as described in previous work with several modifications [4]. Dried OPEFBs cut to 0.5-1 cm length were heated in 10 wt% NaOH (1 gram fibers:20 mL NaOH solution) at ±95°C in 1 hour, then black liquor was separated, and fibers were washed with distilled water to neutral pH. After that, alkaline treatment followed by bleaching treatment was done in order to obtain bleached fiber. A 30 wt% H$_2$O$_2$(1 gram fibers:15 mL H$_2$O$_2$ solution) used for the bleaching process was conducted at ±95°C in 1.5 hours, then the fibers were washed with distilled water. The fibers were re-bleached with a mixture of 10 wt% NaOH and 30 wt% H$_2$O$_2$ solutions (the ratio of mixture 2:1) at ±95°C to more bleached fibers obtained. The resulting cellulose fibers were stored in the refrigerator.

2.3. Preparation of cellulose suspension

Isolated cellulose fibers were diluted in distilled water to a concentration of 2%. The suspension was suspended using a blender in five minutes. After that, the suspension was ultrasonicated at 80% amplitude in 30 minutes in order to get more homogenous cellulose suspension.

2.4. Production of cellulose/PVA/alginate

Composite filaments were produced by the wet spinning method, as described in previous work with several modifications [8]. Cellulose/PVA/alginate solutions were prepared on a dry weight basis (4 grams dry materials diluted in 100 grams of distilled water). The composition of the solution was described in Table 1. The solution preparation firstly was conducted by diluting the cellulose suspension in distilled water. Then alginate was added and stirred at 1400 rpm speed in 20 minutes until well-mixed. Subsequently, PVA was added and stirred with the heat at 90°C, 1500 rpm speed in
40 minutes until well-mixed. Also, the solutions were degassed at 200 rpm speed for removing the rest of the bubbles. The prepared mixtures were spun using a syringe pump into a 9 wt% CaCl₂ coagulant bath. The speed of spinning was 0.33 mL s⁻¹ with a needle inner-diameter of 2.5 mm. The filaments that already spun and coagulated, then soaked into distilled water for 10 minutes and followed by drying at 55°C for 30 minutes.

**Table 1.** The formulation of cellulose/PVA/alginate solution.

| Sample | Composition (%) |  |
|--------|-----------------|---|
|        | Cellulose       | PVA | Alginate |
| C0     | 0               | 50  | 50       |
| C5     | 5               | 47.5| 47.5     |
| C10    | 10              | 45  | 45       |
| C15    | 15              | 42.5| 42.5     |

2.5. **Characterizations of cellulose/PVA/alginate filaments**

2.5.1. **Morphology of cellulose fibers and filaments.** The morphological cellulose fibers and filaments were observed using Scanning Electron Microscope EDX EVO MA10. The specimens were coated by platinum and performed at 20.0 kV voltage. The size distribution of cellulose diameter was measured using ImageJ software at 54 spots.

2.5.2. **Fourier transmission infrared spectroscopy (FTIR) analysis.** Five grams of cellulose fibers were prepared using the KBr pellet. FTIR spectra were recorded using Bruker Tensor 37 at absorbance mode with a resolution of 2 cm⁻¹. The analysis was performed at the range of 400-4000 cm⁻¹ wave number.

2.5.3. **Crystallinity degree.** The analysis was performed by X-Ray Diffractometry (XRD) using Shimadzu XRD7000 with the radiation of Kα Cu (λ=1.54060). samples were cut to powder-sized and placed on the holder. The operating conditions were carried out at 40.0 kV voltage and 30 mA current in the region of 20 from 10° to 80°. The degree of crystallinity was calculated from diffraction profiles as the ratio of the area under the crystalline diffraction peaks to the total area under the curve.

2.5.4. **Thermal properties.** The thermal properties of cellulose and filaments were determined by Thermogravimetric analysis (TGA). Thermograms were obtained using Perkin Elmer TGA4000 between 25 and 500°C at with nitrogen as purge gas at flow rate 20.0 mL min⁻¹.

2.5.5. **Mechanical properties.** The analyses consisted of tensile strength and elongation at break. All samples were analyzed using Universal Testing Machine Instron 3369 series. The tested samples previously were pre-conditioned for one day at room temperature, a test length of 50 mm was used for fibers at a speed of 5 mm min⁻¹. Three measurements were conducted in each sample.

3. **Results and discussions**

3.1. **Characterization of OPEFBs cellulose fibers**

Based on the analysis, cellulose, hemicellulose, and lignin contents of raw OPEFBs were 45.37%, 15.46%, and 17.80%, respectively. There was an increase of cellulose content to 90.83% after alkaline treatment and bleaching steps, whereas the hemicellulose and lignin contents became 8.92% and 1.85%, respectively. These results showed that alkaline treatment and bleaching were succeeded in reducing the lignin and hemicellulose contents significantly. The alkaline solvent used for treatment, namely NaOH solution. Lignin degradation occurred due to the fact that the hydroxyl ions of NaOH catalyze the breakage of aryl ether linkages in the lignin and set free the soluble sodium...
phenolates in the liquid [9]. Hemicellulose also degraded because of the sensitivity of alkaline solution [4]. Bleaching was carried out in order to decolorize cellulose fiber by the degradation of chromophore groups in lignin. Perhydroxyl ion decomposed from H$_2$O$_2$ chemical reactions has the role of bleaching agent [10]. The change of visual appearance of OPEFBs during the process can be seen in Figure 1.

![Figure 1](image1.png)

**Figure 1.** The change of visual appearance of (a) raw OPEFBs, (b) alkaline treatment OPEFBs fiber, and (c) bleached OPEFBs fiber.

FTIR spectra in Figure 2 exhibited chemical composition, particularly the functional groups after alkaline treatment and bleaching. Three notable peaks used as the indicator of lignin removal effectiveness, namely peaks at 1720, 1509, and 1267 cm$^{-1}$. The peak at 1720 cm$^{-1}$ attributed ester linkages of carboxylic groups of the ferulic and p-coumaric acids in lignin or acetyl and uronic groups of hemicellulose vibrations. The last two peaks at 1509 and 1267 cm$^{-1}$ respectively attributed the vibrations of C=C aromatic linkages of lignin and C-O stretching of hemicellulose and lignin [11]. Based on FTIR spectra, it showed no peaks appear at three peaks of 1720, 1509, and 1267 cm$^{-1}$. The absence of those peaks indicated lignin and hemicellulose degradation have effectively succeeded. The factors that affect the elimination of hemicellulose and lignin are solution concentration, pH, stirring, time, and temperature of the process [4].

![Figure 2](image2.png)

**Figure 2.** FTIR spectra of the obtained cellulose fibers from OPEFBs.

The morphology and diameter size of cellulose fibers were observed using SEM. The picture of SEM observation was analyzed by software for measuring the diameter size of fibers. Measurement
was conducted at 54 spots. Hence, the results generated the size distribution of fiber diameter histograms that can be seen in Figure 3b with the highest frequency at range from 5.267 to 6.842 μm. Because of strong hydrogen bonds, cellulose commonly agglomerate after diluted in water. Ultrasonication was performed in order to the cavitation effect produced from ultrasonic waves caused the intermolecular collision, so the more homogeneous suspension and uniform size of fibers can be obtained [12].

Figure 3. The SEM image of (a) OPEFBs cellulose fibers with the magnification of 250x and (b) histogram of the size distribution of fibers.

Figure 4 exhibited the x-ray diffraction pattern of isolated cellulose fibers from OPEFBs. This pattern showed three peaks at 2θ = 16.18°, 22.56°, and 35.56°, which indicated that obtained cellulose was cellulose I [13]. The crystallinity degree of cellulose in this work was 56.89% compared to the previous work by Lisdayana et al. [14] showed the crystallinity degree of OPEFBs cellulose fibers with the similar method was 56.78%.

Figure 4. X-ray diffraction pattern of OPEFBs cellulose fibers.
TG curve (in Figure 5) exhibited the weight loss of cellulose fibers occurred after they were heated up to 500°C. Thermal degradations occurred two times. An initial weight loss was detected from 25.4 to 87.92°C due to the moisture evaporation of fibers. Then, second weight loss was cellulose degradation, which happened from 300 to 400°C. Similarly, the previous work by Reddy et al. [15] was about the initial cellulose degradation that begins from 300°C.

![TG curve of OPEFBs cellulose fibers](image)

**Figure 5.** TG curve of OPEFBs cellulose fibers.

3.2. Morphology of cellulose/PVA/alginate filaments

The morphology of produced filaments by the wet spinning method was observed using SEM (in Figure 6). Based on the images, the filament without cellulose generated smoother surface and cross-section than filaments with cellulose added. The higher cellulose concentration contributed to a rougher surface and cross-section of filaments. From 5% cellulose to 15% cellulose, there was the morphological difference in which the 15% cellulose filament was rougher instead of 5% and 10% cellulose filaments. The addition of cellulose formed an entangled network that participates more effectively on the structure of filaments so that there was a significant differentiation between no cellulose and cellulose-added filaments [16].
3.3. Thermal properties of cellulose/PVA/alginate filaments

TGA measurements were performed in order to understand the effect of cellulose addition on the thermal stability of filaments. Thermal stability can be determined from the residue of filament after heated at 500°C. Table 2 showed a tendency of increasing residue weight with increasing cellulose concentration. This indicated that the addition of cellulose fiber could improve the thermal stability of filament. The enhanced thermal stability was obtained due to a strong hydrogen bonding between the hydroxyl groups of cellulose fibers and PVA/alginate matrix [17]. However, the residual weight decreased at 15% cellulose. It might be caused by the lack of homogeneity of the cellulose in the composite filament.

Figure 6. SEM images of cellulose/PVA/alginate filaments.
TGA thermograms of all composite filaments that can be seen in Figure 7 showed similar patterns. There were three main weight loss regions. The first region occurred below 150°C due to the evaporation of water. The second region (200-400°C) was due to the structural degradation of composite filaments by decomposition of the glycosidic units, while the third region occurred above 400°C, probably due to the cleavage backbone of PVA nanocomposite films or the decomposition of carbonaceous matter [3][17].

### 3.4. Crystallinity of cellulose/PVA/alginate filaments

The x-ray diffraction patterns and crystallinity degree can be seen in Figure 8 and Table 3, respectively. The pattern of PVA/alginate (C0) filament has a peak at $2\theta = 19.6^\circ$, while the increasing cellulose concentration generated a peak at $2\theta = 22.7^\circ$ and made more obvious gradually. The peaks appeared due to strong interaction of hydrogen bonding and Van der Waals influenced among hydroxyl groups in cellulose and PVA/alginate matrix so that tight crystalline structures were formed [18]. From the table, the increasing cellulose concentration also increased the crystallinity degree of filaments. The higher percentage of crystallinity helped to enhance the composite filament to be stronger because of the orderly compact structure [19]. Therefore, this influenced the tensile strength of filament.

### Table 2. Residual weight of cellulose/PVA/alginate filaments after heated up to 500°C.

| Sample | Residue (%) |
|--------|-------------|
| C0     | 29.347      |
| C5     | 32.684      |
| C10    | 33.686      |
| C15    | 30.663      |

![Figure 7. TGA thermograms of cellulose/PVA/alginate filaments.](image)
3.5. Mechanical properties of cellulose/PVA/alginate filaments

Figure 9 showed tensile strength and elongation at break of cellulose/PVA/alginate, in which filaments with no cellulose had lower tensile strength compared to other filaments with cellulose added. The tensile strength of no cellulose filament was 37.93 MPa, whereas the value increased 21.3% to 48.22 MPa for filament with 15% cellulose. This indicated the addition of cellulose fibers improved the tensile strength of composite filaments due to the formation of strong hydrogen-bonded occurred interfacial adhesion between the PVA/alginate matrix and cellulose fibers [20].

PVA is a polymer that has flexibility [3]. The elongation of filament with no cellulose added is higher than other filaments with cellulose. Otherwise, the increasing cellulose concentration decreased the elongation of filaments. This result was indicated by the stiffness effect given by cellulose fiber. Strong hydrogen bonding caused tight network formation, so the elongation was decreased.

Table 3. Crystallinity of cellulose/PVA/alginate filaments.

| Sample | Crystallinity (%) |
|--------|-------------------|
| C0     | 24.56             |
| C5     | 29.31             |
| C10    | 46.76             |
| C15    | 49.96             |

Figure 8. X-ray diffraction of cellulose/PVA/alginate filaments.
4. Conclusions and suggestions

4.1 Conclusions
The production of composite PVA/alginate and isolated cellulose from OPEFBs succeeded through a wet spinning method and CaCl$_2$ solution as a coagulant solvent. The addition of cellulose affects the characteristics of filaments. The increasing cellulose concentration generates the filament with rougher morphology due to the formation of the entangled network between cellulose fibers and PVA/alginate matrix. Strong hydrogen bonding of cellulose contributes to high crystallinity, excellent thermal stability, and tensile strength but decreases the elongation of filaments.

4.2 Suggestions
For the next research, regenerated cellulose or nanofiber/nanocrystal cellulose can be developed into composite filament production in order to increase the homogeneity of the solution so that smoother filament can be produced.

5. References
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