Preparation of Polyvinyl Alcohol/Cellulose Nano fiber Nanocomposite Isolated from Empty Oil Palm Fruit Bunches

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Abstract. This research was aimed to manufacture polyvinyl alcohol (PVA)/cellulose nanofiber (CNF) nanocomposite which was isolated from oil palm empty fruit bunches (OPEFB) through steam explosion method combined with a hydrolysis process involving HCl 10%. The isolation process was performed in 2 steps; α-cellulose isolation from empty fruit bunches fibers and then cellulose nanofiber isolation from α-cellulose which was hydrolyzed with acid using ultrasonicator and homogenized in rotational speed of 8000 rpm. The functional group and morphology of nanofibres cellulose were characterized. FT-IR spectrum resulted an absorptions for C=O group at wavelength of 1059.99 cm\(^{-1}\) which indicated a glycoside bond. Then, C-H group at 2900.94 cm\(^{-1}\) and O-H group at 3348.62 cm\(^{-1}\) were revealed to indicate the cellulose nanofiber. Moreover, TEM was used for morphological analysis and showing a decrease in fibres diameters after experiencing a chemical-mechanical treatment which lead to nanofibres with final diameter size of 20-30 nm. PVA/CNF nanocomposite with the percentage ratio of 80:20 gave a tensile strength of 17.41 Mpa and Modulus Young of 0.9 Gpa. Finally, the product was also morphologically analyzed with SEM and indicating an even distribution on the PVA surface.

Keywords: Steam Explosion, HCl 10% Hydrolysis, Cellulose Nanofiber, Empty Oil Palm Fruit Bunches, Nanocomposite, Polyvinyl Alcohol

1. Introduction
Oil palm is one of the commodities traded plantation crops, both for domestic and export industry. Indonesia has known to be the largest oil palm producer around the globe, with a total production of 130-176 million tonnes of Crude Palm Oil (CPO) annually by 17-26 million hectares of land area. According to Afriyanti (2015), this number already represents of 39-60% the world's palm. However, the production of palm oil in Indonesia is often associated with environmental issues that adversely affected the palm oil industry itself [1]. Based on Plantation Director General of the Ministry of Agriculture, Indonesia produced 29.3 million tons of CPO in 2014. Surely, a significant amount of waste is potential to be a threat to the sustainable use of CPO in Indonesia.

The OPEFB fibers are found to be multi cellular and ligno-cellulosic compound. Ligno-cellulosic biomass is generally consisted of cellulose (glucan), hemicelluloses (xylan and mainly arabinan) and lignin. However, a pre-treatment is needed to dissolve the non-cellulosic polysaccharides and improve the proportion of mass from cellulose in the biomass [2].
Steam explosion combined with acid treatment can effectively separate the cellulose nanofibers from non-cellulosic polysaccharides of lignocellulosic biomass, including hardwoods, softwoods, herbaceous residues, sugarcane bagasse and wheat straw, are becoming the most largely employed physic-chemical pretreatment for lignocellulosic biomass [3-5].

According to Roohani et al. (2008), PVA has good compatibility when added with filler in the form of nanocellulose so as to produce products (nanocomposite) that are environmentally friendly [6]. Thus, by adding nanofibre cellulose, the PVA-based film is expected to increase the mechanical properties of the resulting PVA film. Some research on edible film with the addition of nanocellulose from the fibers, it can improve the mechanical properties, the nature of the barrier, and the ability to aggregate with other particles [7, 8].

Mandal and Chakrabarty (2013), stated that the addition of nanofibriled cellulose for about 5% in the manufacture of PVA/nanocellulose nanocomposite is derived from sugarcane bagasse that showed a better thermal stability [9]. Bhatnagar and Sain (2005) in the manufacture of reinforced nanofibres composites stated that a polymer matrix/nanofibre cellulose was prepared from 10% of nanofibre cellulose showed an excellent reinforcing properties. The nanocomposite can be used in medical devices as conductor systems (drug delivery) which is biocompatible, where blood storage bags, and valves as reinforcement biomaterials. Due to the high strength and light weight of the resulting composite, it is potential to be used in the automotive sector [10].

In accordance with the development of nano technology, oil palm empty fruit bunches can be used as materials for nanofibre cellulose. Bibin et al. (2010) produced nanofibre cellulose from pineapple leaf fibers with explosive vapor method (steam explosion) [11]. Cherian et al. (2008) described that the explosive vapor method is effective in separating nanofibre from biomass [12]. A further explanation from Bibin et al. (2010), nanofiber cellulose has a wide uses in biomedicine and biotechnology, such as drug delivery, wound dressings, tissue engineering and medical implants [11].

Based on those descriptions, researchers are interested in utilizing such materials as the development of science, by isolating nanofibre cellulose from oil palm empty fruit bunches (OPEFB) through explosive vapor (steam explosion) method and were hydrolyzed with HCl 10%.

2. Experimental method

2.1 Materials

Wheat straws were taken from fields. They were washed in order to remove any impurities and dried. Sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (\(CH_3COOH\)) Hydrolysed polyvinyl alcohol (PVA) (MW = 84,000-124,000 g/mol; 98-99%) and hydrogen peroxide (\(H_2O_2\)) were purchased from Sigma Aldrich and were pure without any further treatment.

2.2 Isolation of nanofibriled cellulose from OPEFB fibers

OPEFB fibers were minced into random size of around 1-2 cm. The OPEFB fibers were soaked in 2% solution of NaOH overnight and then treated with 12% NaOH solution (with ratio of 1:10) in an autoclave at pressure around 168 kPa for 4 h at 130 °C. This treatment reduced the amount of lignin from the fibers. The fibers were taken from the autoclave and the fibers were washed several times in distilled water until it was free of alkaline materials.

Steam exploded fibers were bleached using with a mixture of 17.5 % solution of NaOH and 7.4% acetic acid solution (ratio 1:1) and a mixture of (1:3) NaOCl solutions. Also, the steam explodes fibers were soaked in 8% of \(H_2O_2\) solution. The fibers were washed in distilled water after the bleaching treatment and then dried.

The steam exploded bleached fibers were treated with hydrochloric acid with the concentration of 10% and putted into sonicator for 3 h. Then, the fibers were washed in distilled water until the acid was removed. Finally, the acid treated fibers were suspended in water and stirred with a WiseTis HG-15D homogenizer for about 15 minutes until the fibers were agglomerated.
Then, as many as 9 g of PVA was dissolved into 100 mL of distilled water and heated at a temperature of 75 °C for 1 hour and stirred using a magnetic stirrer. Nanofibre cellulose was added with a variation of 0.5; 1.0; 1.5; 2.0; 2.5 by weight (w/w). Mixing was done by using a homogenizer with a rotation speed of 8000 rpm for 30 minutes. After that, it was mould using acrylic glass mold and dried in an oven at a temperature of 50 °C.

2.3 Characterization

2.3.1 Transmission Electron Microscopy (TEM). Transmission electron micrographs of nanofibre cellulose was recorded with a Philips CM 30 transmission electron microscope with a voltage acceleration of 75 kV. The nanofibrils were deposited from an aqueous dilute dispersion on a micro grid covered with a thin carbon film (200 nm). The deposited fibres were subsequently stained with a 2% uranyl acetate solution to enhance the microscopic image.

2.3.2. Fourier Transform Infrared (FTIR) spectroscopy. FTIR spectra of acid hydrolysis untreated fibers and nanofibrilated cellulose were measured using ABB 3000 FTIR spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and KBr/Germanium as beam splitter. FTIR spectra were collected at the mid-infrared region 4000-450 cm⁻¹ with a resolution of 8 cm⁻¹, using 32 scans for each sample.

2.3.3. Tensile strength. Tensile strength of samples was carried out by using a tensile test Gotech AL 7000 M with tensile speed of 10 mm/ min and a load of 2000 kgf. The specimen was clamped using griff on the device, then set up stress, strain and its unit. The data load (voltage) and stroke (strain) obtained can be used to calculate the tensile strength and elongation of each specimen.

2.3.4. Thermal characterization. The DSC analysis by using a DSC-60 plus. With a sample size of 10.40 mg by using a metal cell Al and the reference sample and set the configuration on the sample and reference samples were placed on a heating with good thermal interaction, then heated slowly while increased thermal resolution.

2.3.5. Scanning Electron Microscopy (SEM) analysis. Microscopic observation using the SEM process was done on the fracture surface of the sample. Then, after the sample was cleaned with a blower, the sample was covered with gold and palladium in dionspater pressurized machine 1492 x 10⁻² atm, the sample was then inserted into a space (vacuum evaporator) pressure of 0.2 Torr using JSM-35C engine Shumandzu. Furthermore, the sample was irradiated with an electron beam-powered 20 kV in a special room so the samples emit secondary electrons and electrons that bounce can be detected by a detector reinforced with an electrical circuit that produced the image CRT(Cathode Ray Tube) for 4 minutes. Then, it was coated with a layer thickness of 400 Armstrong and putted in the specimen chamber to do the shooting. The photographs can be adjusted to the desired magnification.

3. Results and discussion

3.1 Morphology and chemical properties
The alkaline steam explosion treatment removed the materials like hemicelluloses, pectin, lignin and etc. The fiber surfaces changed after chemical treatment. These show the fibers surface roughness and individual fibers after the removal of the cementing material. In addition, acid hydrolysis treatment helps to eliminate excessive amount of lignin from the fibers. The particle size of fibers has reduced after chemical treatment and the average size of fibers are about 15-20 μm. Reduction of fibers size because of the dissolution of the non-cellulosic polysaccharide and it is clearly related with FT-IR data. Nanofibrilated cellulose after the final treatments are showed in Figure 1 (a-b). Agglomeration treatment using a homogenizer caused in defibrillation of the nanofibrilated cellulose from the cell wall and TEM images show separation of these nanofibers from the fiber bundles. The diameters of the
fibers were observed from the figure and the average size was determined using image processing software Image J. Most of the fibers sizes were found in the diameter range of 20-30 nm. Figure exhibits the distribution of nano-fiber diameter after final treatment. 20% of fibers have diameter between 20-30 nm. Over 15% of fibers has diameter between 10-20 nm and also the diameter of 40-50 nm. Around 14% fibers have diameter of 30-40 nm, but under 12% of fibers have diameter >50 nm.

**Figure 1.** TEM image of the cellulose nanofibrils at different magnifications: (a) 20000x and (b) 40000x.

**Figure 2.** Diameter distribution of cellulose nanofibrils after chemical and agglomeration treatments.

Figure 2 shows the size distribution of nano-dimensional fiber diameters after passing the final treatment. A total of 20% of the fibers with a diameter of 20-30 nm. Meanwhile, 17.89 and 16.84% respectively were 40-50 and a fiber diameter of 10-20 nm. For a fiber having a diameter of between 30-40, 50-60 and 60-70 respectively nm diameter size distribution was 13.68, 11.57 and 9.84%. Fiber having a diameter of > 70 nm, nanofiber distribution is 10.53%.
3.2 Fourier Transform Infrared (FTIR) spectroscopy

The FT-IR spectra are presented in Figure 3. Chemical constituent of fibers like cellulose, hemicelluloses and lignin has changed after the acid hydrolysis and agglomeration treatment. The absorbance peak is in area of 3348 cm\(^{-1}\) corresponds to the stretching vibration of OH and the peaks at 2916 cm\(^{-1}\) was assigned to the asymmetric stretching vibration of C-H lignin, cellulose and hemicelluloses.

The spectrum of nanofibrilated cellulose exhibited a trend difference from the acid hydrolysis untreated. The peak at 1715 cm\(^{-1}\) in the untreated fibers was attributed to the ester linkage of the carboxylic group of ferulic, the acetyl and uronic ester groups of hemicelluloses or and \(p\)-coumaric acid of hemicelluloses. However, the peak of nanofibrilated cellulose could not be found at 1715 cm\(^{-1}\). The peak at 1634 cm\(^{-1}\) was assigned to the bending mode of absorbed water or quite a few contributions from carboxylate groups. The peak at 1542 cm\(^{-1}\) was attributed to the stretching mode of the aromatic C=C came from aromatic ring of lignin and also the absorbance band at 1428 cm\(^{-1}\), observed in untreated fibers spectrum.

The absorbance bands at 1542 and 1428 cm\(^{-1}\) has significantly changed before the chemical treatment. The peak at 1542 cm\(^{-1}\) is very small and intensity of the absorbance band at 1428 cm\(^{-1}\) has significantly declined in nanofibrilated cellulose assigning to partial removal of lignin. The intensity of the peak at 1251 cm\(^{-1}\) has dramatically decreased after treated with the mechanical and chemical treatments attributing the removal of hemicelluloses. Some of non–cellulosic polysaccharides like hemicelluloses and lignin have removed from the fibers because of the alkaline treatment and bleaching process. The characteristic absorbance bands for all of lignin were not found in the spectrum of the nanofibrilated cellulose. The removal of lignin was occurred after the chemical treatment like alkaline treatment. In addition, the non-cellulosic polysaccharides can be also removed by acid treatment.

![FT-IR spectra of nanofibrilated cellulose and untreated fibres.](image)

**Figure 3.** FT-IR spectra of nanofibrilated cellulose and untreated fibres.

3.3 Analysis of Mechanical Properties of PVA nanocomposite / NFC

The test for mechanical properties of nanocomposite polyvinyl alcohol/ Nanofiber cellulose with a variety of tested through analysis of the tensile test at room temperature using a load of 1 kN at a speed of 10 mm/ min. The average thickness of the resulting nanocomposite films is 0.1 -0.2 mm. Where also the length of the nanocomposite PVA/ NSS of 80 mm and a width of 20 mm. The tensile strength of nanocomposite PVA/ NFC is displayed in Table 1.
Table 1 and figure 4 shows that the addition of the nanocomposite filler affects the results of its strength. Minimum tensile strength occured in variations of PVA/ NFC (10: 0.0) with the value of its strength was 5.68 MPa and a Young's modulus of 0.4 GPa. The maximum tensile strength variation occurred in PVA/ NFC (8.0: 2.0) with 17.41 MPa and a Young's modulus of 0.9 GPa. However, the tensile strength began to decrease with the addition of cellulose nanoserat weight by 25%.

From the results of tensile strength, it can be seen that weight variation of PVA/ NFC (8.0: 2.0) (w/w) is a variation with the most severe kind because it can increase the tensile strength and Young’s modulus of the nanocomposite produced. The increase in tensile strength of the resulting nanocomposite may be caused by the rigidity of the chain attached to nanofiber cellulose (due to the strength of hydrogen bonds and the inter molecular force on cellulose itself) and homogeneous distribution of the polymer and nanofiber cellulose high compatibility between the fiber and the matrix more aided by a high interfacial surface area. Nanofiber hydrogen bonding between cellulose and PVA matrix causes an increase in the tensile strength of the resulting nanocomposite. However, the increasing amount in weight gain with 2.5% cellulose nanofiber effect tensile test for impairment and Young's modulus. This is probably due to the dilution effect or tendency of agglomeration of nanometer-sized particles are very active [9].

**Table 1. Mechanical Properties of PVA Film and nanocomposite PVA /NFC.**

| PVA nanocomposite composition/ Nanofiber Cellulose (w / w)% | Tensile Strength (MPa) | Young’s Modulus (GPa) |
|------------------------------------------------------------|------------------------|-----------------------|
| PVA + NFC (10: 0.0)                                         | 5.68                   | 0.4                   |
| PVA + NFC (9.5: 0.5)                                         | 8.09                   | 0.6                   |
| PVA + NFC(9.0: 1.0)                                          | 10.88                  | 0.7                   |
| PVA + NFC (8.5: 1.5)                                         | 14.51                  | 0.8                   |
| PVA + NFC(8.0: 2.0)                                          | 17.41                  | 0.9                   |
| PVA + NFC (7.5: 2.5)                                         | 15.83                  | 0.8                   |

**Figure 4. Stress-Strain Graph of PVA and PVA nanocomposite / NFC.**

### 3.4 Thermal degradation analysis by DSC

Thermal analysis for PVA/ NFC nanocomposite is passed using instrumentation tool Differential Scanning Calorimetry (DSC). Variations used for thermal analysis was a PVA/ NFC nanocomposite with minimum variation in the tensile test, namely PVA/ NSS (10: 0.0) and PVA/ NFC nanocomposite
with optimum variation in the tensile test, namely PVA / NSS (9.5: 0.5) using the initial temperature of room temperature at 28 °C to 500 °C.

Figure 5. Spectra DSC nanocomposite PVA / NFC variation (10: 0.0)% and 8.0: 2.0%.
In a variation of PVA/NFC (10: 0.0) DSC thermal test conducted in laboratory tests on PTKI. The result was obtained in the form of a peak that indicates an element that occurs endothermic and exothermic for the initial peak that appears to happen is marked peak endothermic reaction occurs at temperatures 96.47 °C and 300.31 mcal require heat stability which is a transition temperature ($T_g$), the second peak appears still state at a temperature endothermic 190.15 °C and heat stability 51.66 mcal require a crystallinity point ($T_c$), the third peak is still a state of endothermic and occurs at a temperature of 327.15 °C and 785.57 mcal require heat stability, the fourth peak is still in a state where there is endothermic at a temperature of 428.23 °C and 65.62 mcal require heat stability is the melting point ($T_m$) and peak last appeared in an exothermic temperature 472.82 °C and a heat of 56.73 mcal issued a decomposition temperature ($T_d$), the nanocomposite material starts to break down.

In the variation of (8.0: 2.0)% for the DSC test obtained similar results with minimum variation, in the form of five peaks which appeared after treatment. Peak began to appear in an endothermic area at a temperature of 101.48 °C and requires a heat stability at 471.23 mcal which is a transition temperature ($T_g$) the second peak appears in an endothermic at a temperature of 189.75 °C and requires a heat stability of 35.93 mcal is crystallinity point ($T_c$), the third peak appears in an endothermic at a temperature of 314.65 °C and requires a heat stability at 635.61 mcal, fourth peak appearing in an endothermic at a temperature of 447.30 °C and requires stability amounted to 100.79 mcal heat is melting point ($T_m$), and a fifth peak appears in an exothermic temperature of 483.83 °C and removing the heat of 65.72 mcal a decomposition temperature ($T_d$).

3.5 Scanning electron microscopy (SEM) analysis

Morphology analysis by SEM using ZEISS tool, with a magnification of 500 and 1000 times. Based on morphology analysis demonstrates that the pure PVA nanocomposite has a smooth and homogeneous surface, this is caused by the PVA nanocomposite filler was not filled by nanofiber cellulose or other material that may affect the morphology of the nanocomposite surface so the surface looks more even and smooth.

In the PVA/ Nanofibre cellulose nanocomposite with a ratio of (8.0: 2.0) after the tensile test showed that nanofibre cellulose was evenly distributed on the surface of the PVA, homogeneous and smooth, so that the surface morphology is dominated by the morphology of cellulose fibers bond together between the fiber. This occurs because the cellulose fibers of nanometer-size physically interacting with PVA resulting nanocomposite surface is flat, homogeneous and produce the optimum value of the tensile test.

![SEM morphological analysis results PVA / NFC (8.0: 2.0)%: (a)500x (b)1000x.](image_url)
4. Conclusion
Based on the research conducted, it can be concluded that Polyvinyl Alcohol/ Cellulose Nano fiber Nanocomposite was successfully isolated from the Oil Palm Empty Fruit Bunch (OPEFB). The FTIR analysis confirmed that the cellulose was completely joined the PVA, indicated by the presence of broad O-H group. Moreover, it is obvious that the composite resulted was in a nanometer scale with the average diameter of 20-30 nm. In term of mechanical properties, the nanocomposite with the ratio PVA: CNF of 80:20 promotes the optimum tensile strength and young modulus.

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