

Synthesis of Nanofiber from Oil Palm Empty Fruit Bunches Cellulose Acetate for Bioplastics Production

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Abstract

The purposes of this research were to obtain nanometer-sized fiber with electrospinning method and to produce bioplastics with addition of diethylen glycol (DEG) plasticizer. This research was conducted through several stages, namely extraction of cellulose, synthesis of cellulose acetate, sythesis of nanofibers and production of bioplastics. In the production of nanofibers cellulose acetate, electrospinning method were used with concentrations of cellulose acetate (5, 10, and 15 %) and spinneret-collector distances (6, 8, and 10 cm) treatments. In the production of bioplastics, solution casting method was used with micro and nano fiber-sized cellulose acetate and addition of DEG plasticizer (0, 10, 20, and 30 %) treatments. The results of this research showed that the lowest nanofiber diameter of 134 nm was obtained on the cellulose acetate concentration of 10% and spinneret-collector distance of 8 cm. The best mechanical characteristic was obtained on bioplastic of nanofiber celulose acetate and the addition of plasticizer at the concentration of 10%. Its mechanical characteristics were tensile strength of 3.953 MPa and elongation of 18.56%.

Keywords: nano fiber, cellulose acetate, oil palm empty fruit bunches cellulose, electrospinning, bioplastics.

1.Introduction

Nanofibers are classified as fibers types at nanometer scale. Nanofibers in the textile world are defined as fiber which has diameter of 100-500 nm. Nanofibers can lead to a unique characteristic of material. Moreover, nanofibers also have advantages over bulk sized-fiber due to broad surface, porous structure, high elastic modulus, and high power of chemical reactions. Nanofibers have a potency to be used as filtration media (membran), fiber optics, drug delivery systems in the world of phamaceutical, tissue scaffolds in the medical world, and protective clothings (Subbiah *et al.* 2005). Formation of nanofiber can be done by several methods, such as multicomponent fiber spinning techniques, melt blowing, high pressure, homogenizer, ultrasonic waves and electrospinning. From several nanofiber synthesis methods, electrospinning is a simple technique that is capable to continuously produce fibers sized of 0,04-2 microns. Moreover, synthesis of nanofibers process is more flexible, efficient, and easy to control.

Nanofiber can be obtained from different types of polymers, either natural, semi synthetic or synthetic polymers. Nanofibers derived from natural polymers such as cellulose have been widely made and investigated by researchers, including from cassava bagasse (Wicaksono *et al.*, 2013). Cellulose is used as the main ingredient in the papermaking industry but as the development of technology, cellulose began to be used in various industries such as textiles, materials, bioenergy and others. The use of cellulose as raw material for synthesis of nanofiber will give great opportunity for developing new products.

Synthesis of nanofiber from cellulose using electrospinning, however, still has some obstacles. Research by Vallejos *et al.* (2012) revealed that synthesis process of nanofiber directly from cellulose has limitation in typical solvent and the result tend to form a gel. Electrospinning of cellulose derivatives such as cellulose acetate which is obtained from acetylation process of cellulose may overcome the problems. Cellulose acetate is processed by dissolving it in non-polar solvent, such as acetone, dichloromethane, chloroform and methyl acetate.

Cellulose acetate can be used as raw material for the production of nanofiber because it has resistency to chemical and thermal process, stable to thermal temperature and has a high tensile strength characteristic. Numerous researches have shown that cellulose acetate can be formed into nanofiber with electrospinning method. Kuzmenko (2012) has conducted synthesis of nanofiber carbon with electrospinning method from commercial cellulose acetate (*Sigma Aldrich*). Commercial cellulose acetate was obtained from wood cellulose. The excessive use of wood would have negative impact on the sustainability of the environment. In this research, therefore, cellulose acetate is produced from under-utilized biomass, namely oil palm empty fruit bunches. The resulted nanofiber cellulose acetates were used as raw material for the production of bioplastics using solution casting method with the addition of diethylen glycol plasticizer to increase the plasticity of bioplastics. The purpose of this research is to obtain nanometer sized fibers using electro spinning method and to use them as materials for

bioplastics with the addition of DEG plasticizer using solution casting method.

2. Materials and Methods

2.1. Production of Cellulose from Oil Palm Empty Fruit Bunches

Palm empty fruit bunches were cleaned from oil and shell. Then it was dried and cut with a length of 5-10 cm. Pieces of empty fruit bunches were dried until water content of 4-5%. Subsequently, 1 l HNO₃ 3.5% (v/v) were added to 150 g piece of empty fruit bunches and heated at 90 °C for 2 hours. The pulp was filtered and washed until the filtrate is neutral, then NaOH 17.5% (w/v) was added at temperature of 80 °C for 30 minutes. The pulp was filtered and washed until the filtrate is neutral, then it was purified by adding H₂O₂ 10% (v/v) and heated at 60 °C for 15 minutes. Cellulose was dried in oven at 100 °C for 6 hours.

Glacial acetic acid was added to the resulted cellulose at the ratio of 1:10 and stirred at temperature of 38 °C for 60 minutes. For activation process, 2 % sulfuric acid as catalyst was added and stirred at temperature of 38 °C for 45 minutes. For acetylation process, anhydride acetic acid with the ratio of glacial and anhydride at 3:2 was then added, and mixed at 38 °C for 45 minutes. Aquadest and acetate glacial at the ratio of 1:2 was then added and mixed at 50 °C for 30 minutes. The solution was centrifuged at 1500 rpm for 15 minutes, and then precipitated in aquadest. The precipitate was filtered repeatedly, and then it was dried at 55 °C (Bahmid *et al.* 2013)

2.2. Synthesis of Nanofiber Cellulose Acetate by Electrospinning Method

Cellulose acetate was weighed 5, 10, and 15 gram, and then was dissolved in 100 ml mixture of acetone: dimethylacetamide (2:1) solvent while stirred with magnetic stirrer at room temperature until cellulose acetate was dissolved completely. Nanofiber cellulose acetate was produced using electrospun (Figure 1). The initial step, polymer solution was put into a syringe at the volume of 10 ml, and then was placed on the syringe pump. Solution was flowed through syringe to spinneret. Spinneret metal tips were connected with positive pole from high voltage power source. Sheet aluminum plate was connected to negative pole as collector of nanofiber resulted from electro spinning process. Electric voltage used in this research was 6 kV and distances between spinneret-collector were set at 6, 8, and 10 cm. Electro spinning process was conducted at room temperature for 2.5 hours until nanofiber layers was formed at the surface of aluminum plate. Nanofiber cellulose acetate formed was analyzed for polymer structure with XRD and its morphology using SEM at the magnification of 2500-5000x.

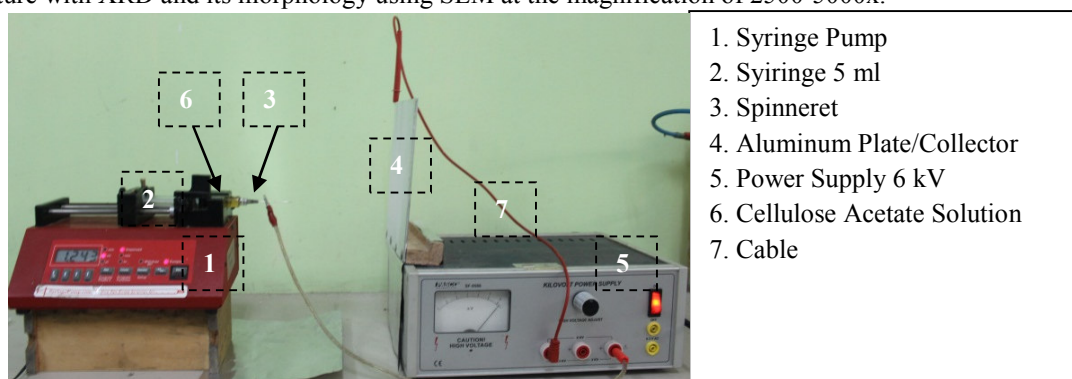


Figure 1 The configuration of electro spun

2.3. Production of Bioplastics

Production of bioplastics was conducted by solution casting technique. The resulted nanofiber cellulose acetate polymer was dissolved in acetone at the ratio of 1:15 at room temperature using magnetic stirrer for 1 hour until completely dissolved. DEG plasticizer was added to the solution at the concentrations of 0, 10, 20, and 30% , and then it was mixed for 1 hour until homogenous. Homogenous solution was poured on to a glass plate 15 x 17.5 cm, then was dried in oven at the temperature of 100 °C. After acetone solvent evaporated, bioplastics was separated from glass plate. Characterization of bioplastics was conducted for its mechanical properties, namely tensile strength and elongation (ASTM 882-97).

2.4. Characterization of Nanofiber Cellulose Acetate and Bioplastics

Morphology of nanofiber cellulose acetate was observed using Scanning Electron Microscope (SEM). Mechanical and physical characteristics of bioplastics were observed for its tensile strength and elongation.

2.5. Morphological Observation

Nanofiber cellulose acetate was placed on a plate, and then was coated with gold layer with coating time of ±30 seconds. Morphology of cellulose acetate was observed using SEM with voltage of 5-15 kV and magnification of 5000x.

2.6. Tensile Strength Test (ASTM 882-97)

Samples were prepared by cutting it to obtain specimens with size of 20x150 mm. Five pieces of each specimen were conditioned at a temperature of 23 °C and 50% humidity for 40 hours before testing. Tensile strength was measured using a Universal Testing Machine (UTM) 10 kN (250 N Load Cell) with a withdrawal speed of 5 mm/minute (for modulus of elasticity) and 50 mm/minute (for tensile strength) at a temperature of 22.7 °C and relative humidity of 52%.

Plastic tensile strength (tensile strength) was calculated using following equation:

$$\text{Tensile Strength (MPa)} = \frac{\text{Maximum of force (N)}}{\text{thick (mm)} \times \text{width (mm)}}$$

Elongation was calculated with the following equation :

$$\text{Elongation (\%)} = \frac{\text{final length at break} - \text{initial length}}{\text{initial length}} \times 100\%$$

3. Results and Discussion

3.1. Morphology of Nanofiber Cellulose Acetate

During the electrospinning process, the effect of solution concentration (5,10, and 15%) and distance of spinneret-collector (6, 8, and 10 cm) to diameter, morphology, and nanofiber structure were observed. The SEM results of samples are shown in Figure 2.

SEM images shown in Figure 2 (a-c) are the results of nanofiber cellulose acetate with solution concentration of 5% and spinneret collector distances (6, 8 and 10 cm). In image 2 (a-c), its is shown that the treatment conditions can not produce nanofiber cellulose acetate. The low solution concentration levels and the low electrical voltage cannot produce nanofiber cellulose acetate. Low solution concentration of cellulose acetate caused solution coming out from spinneret did not spin but it tends to form droplets attached to the collector. The low viscosity of solution caused solution easy to drop.

Different results are shown in Figure 2 (d-i) in which cellulose acetate concentrations were 10 and 15 % and distances of spinneret-collector were f 6, 8, and 10 cm. In Figure 2 (d-f), solution concentration of 10% can produce nanofiber, although there are some beads are resulted. At the solution concentration of 15%, the number of beads was decreased.

In addition to the effect on morphology of fiber, solution concentration also affect on nanofiber diameter. Figure 2 show that solution concentration of 10% has fiber diameter in the range of 134-252.7 nm, while solution concentration of 15% has fiber diameter in the range 248.9-644.3 nm. These results show that the increase in solution concentration, to some extent, will increase fiber diameter of nano fiber. The same phenomena also occurs in the research by Jun *et al.* (2003), in which an increase of solution concentration of PLA from 1% to 5% caused an increase in fiber diameter from 100-300 nm to 800-2400 nm. Likewise in the research by Zhang *et al.* (2005), fiber diameter of PVA increases from 87 nm to 246 nm along with an increase in solution concentration from 6% to 8%.

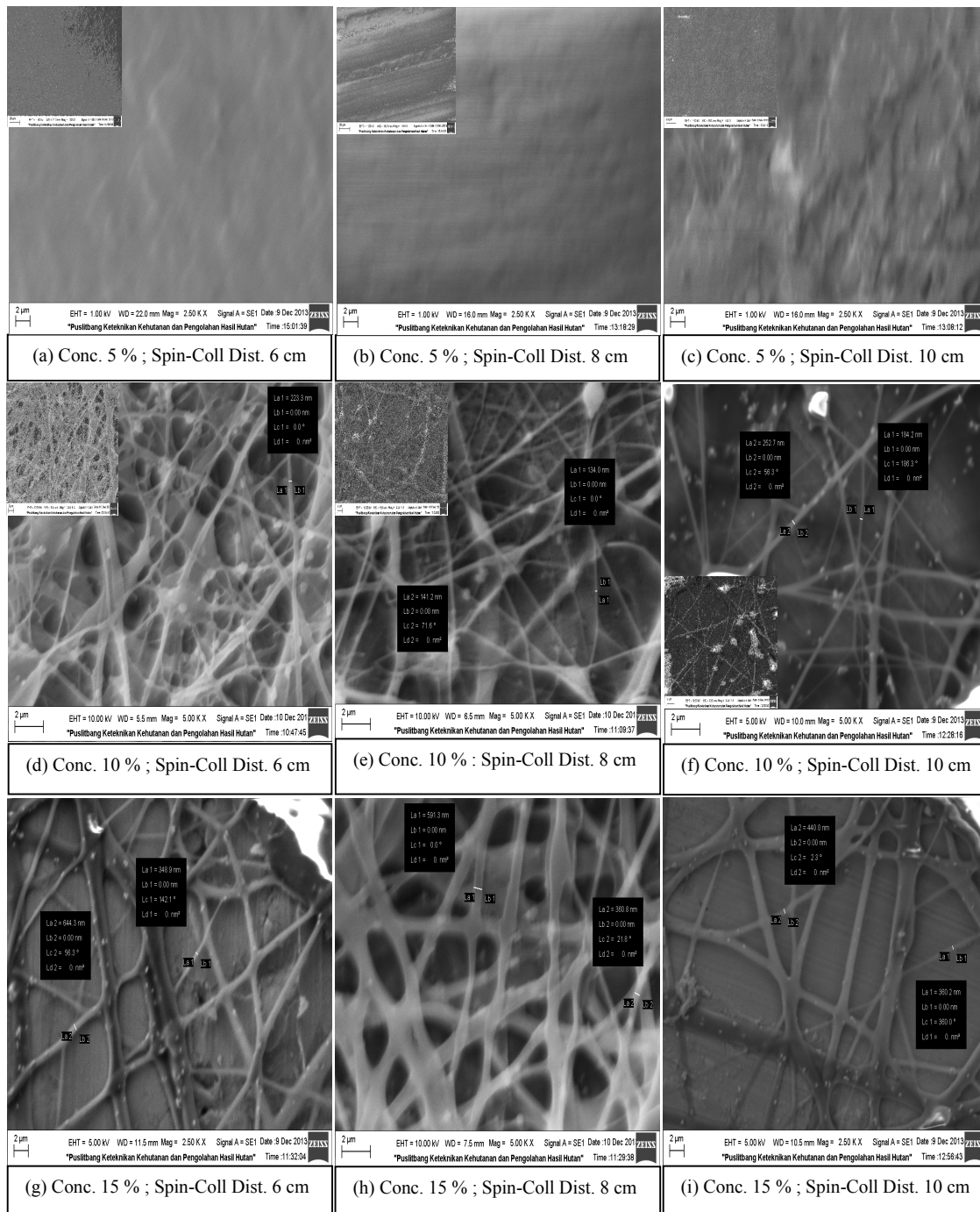


Figure 2 SEM image of cellulose acetate nanofiber

Distance of spinneret-collector affects the electric field strength and time which is required by solvent to evaporate before fibers reach the collector. Increasing the parameter reduces the radius of fiber. If the distance of spinneret-collector is too small, it will produce wet fibers collected in the collector (Andrady 2008).

SEM images in Figure 2 (d-f) show that increasing distance of spinneret-collector, will decrease the nanofiber density. Short distance between spinneret and collector causes spinning area of cellulose acetate flowing to the collector becoming narrower so that the fiber experienced compaction. On the other hand, Figure 2 (d-f) show that greater distance of the spinneret-collector will reduce the bead formation.

The production of nanofiber by electro spinning process is influenced by electrostatic forces and the viscoelastic behavior of polymers (Subbiah *et al.* 2005). The lowest diameter of 134 nm was produced at 10% solution concentration and spinneret-collector distance of 8 cm. The diameter of the resulting nanofiber has fulfilled the world trade standard for nanofiber (diameter less than 500 nm). Nanofibers have normally been produced and traded between 50-300 nm in diameter (Fong and Raneker 1999).

Figure 3 shows a comparative analysis between commercial nanofiber cellulose acetate (Sigma Aldrich)

produced at a solution concentration of 17%, and spinneret-collector distance of 25 cm, voltage 25 kV (Figure 3a), and the resulting nanofiber of this research at a solution concentration of 10%, spinneret-collector distance 8 cm, 6 kV voltage (Figure 3b). Commercial cellulose acetate nanofiber tends to be denser and more uniform in diameter (in the range of 300-1500 nm) compared to nanofiber in this research which was less dense with some beads but has a lower fiber diameter of 134 nm, as shown in Figure 3.

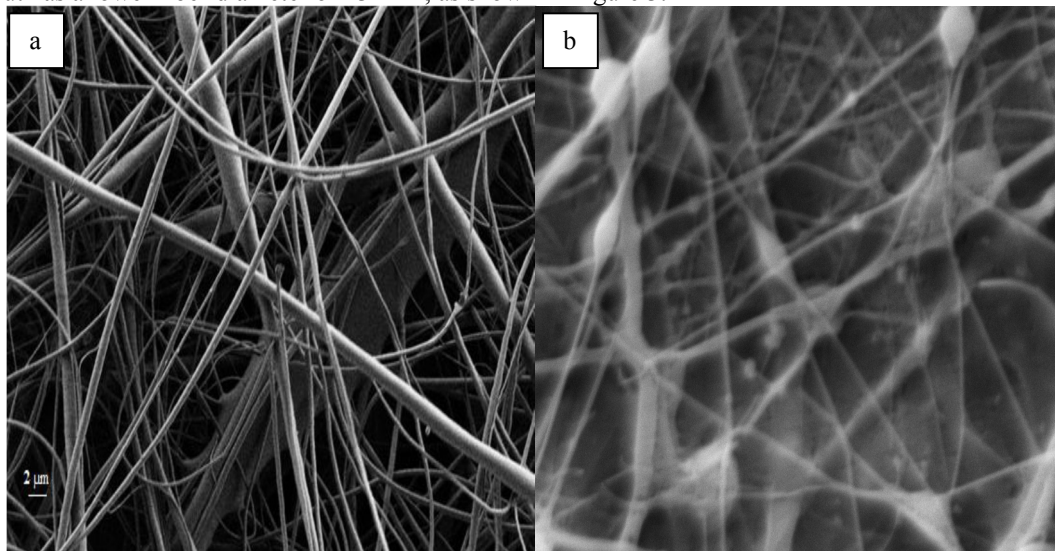


Figure 3 Nanofiber image of cellulose acetate (a) commercial (*Sigma Aldrich*) (Kuzmenko 2012) (b) from palm empty fruit bunches cellulose.

3.2. Crystallinity of Cellulose Acetate Nanofiber

X-ray diffraction can provide information about the structure of polymers, including amorphous and crystalline state. Polymers may contain crystalline regions which are randomly mixed with amorphous regions. X-ray diffractogram of crystalline polymers produce sharp peaks whereas amorphous polymers tend to produce a wide peak. X-ray scattering patterns also provide information about the configuration of the chain in the crystalline, crystalline size estimation and comparison with amorphous regions of crystalline regions (degrees of crystallinity) in the polymer sample.

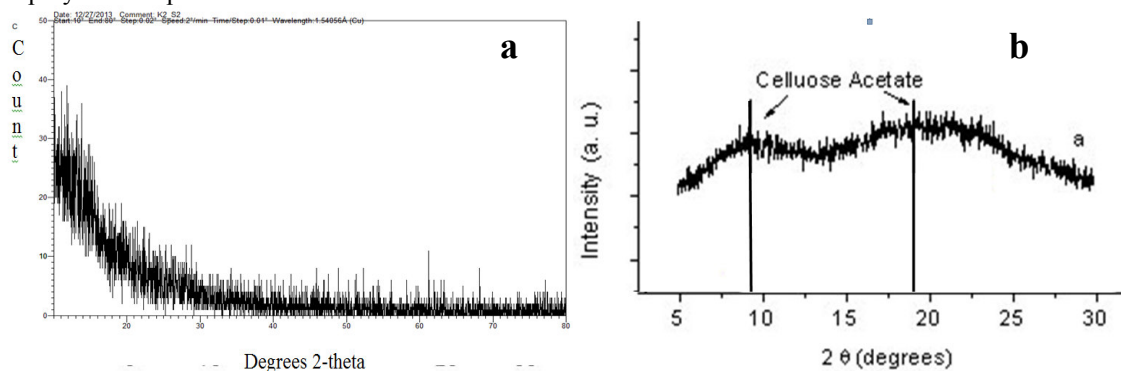


Figure 4. XRD characterization of cellulose acetate nanofiber (a) palm empty fruit bunches, (b) Cellulose acetate /DMAc/ Acetone-cellulose/LiCl/DMAc fiber (Park 2009).

Figure 4a shows the XRD profiles of nanofiber with the best process conditions at a concentration of 10% and spinneret-collector distance of 8 cm. Graph patterns show the XRD diffractogram of cellulose acetate nanofiber. Curve relation between intensity and 2θ shows that the peak is not a sharp and very high peak. It just looks like a noise. This indicates that the sample of cellulose acetate nanofiber has an amorphous structure and not having a regular molecular structure. Amorphous structure of cellulose acetate also was shown in Park's research (2009), as shown in Figure 4b. The curve does not show the presence of sharp peaks so that it can be said that cellulose acetate structure is amorphous.

3.3. Mechanical Characteristics of Bioplastic

Characteristics of cellulose acetate are rigid and hard that require the addition of plasticizer. Mechanical characteristic is one of the important factors for the selection of materials to be applied for a specific purpose. Measurements normally performed for mechanical characteristics are tensile strength and elongation.

Figure 5 shows that the values of bioplastics tensile strength increase following the addition of plasticizers DEG up to 10%. However, bioplastics tensile strength decreases with increasing concentration of DEG above 10%. The decrease in tensile strength is due to the large number of DEG that fills the spaces between the molecules of cellulose acetate polymer in the form of hydrogen bonding so that the distance between the polymer chains of cellulose acetate becomes tenuous. The higher the concentration of DEG was added, the higher the hydrogen bonds were formed, so that the bond strength of bioplastic sheet becomes weaker. The weaker molecular bonds on bioplastics causes the lower force required to break the bioplastics.

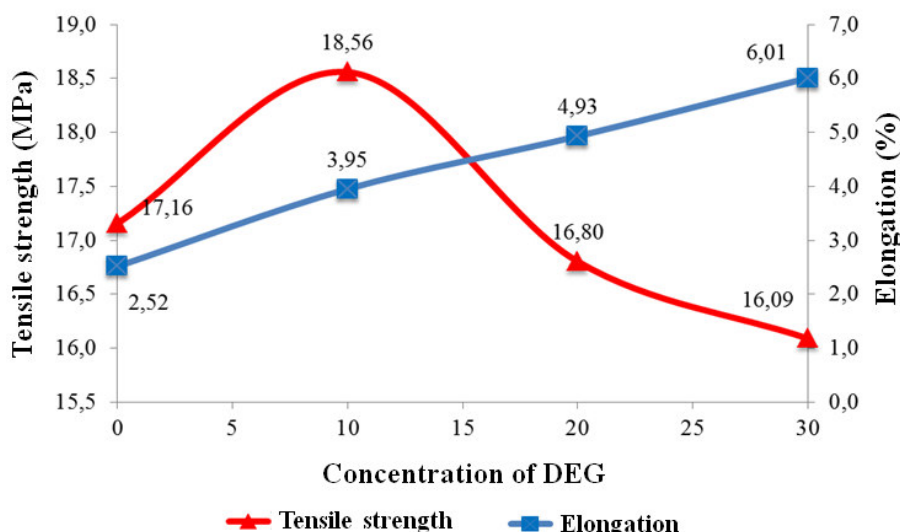


Figure 5 The effect of plasticizer (DEG) concentration on tensile strength and elongation of bioplastics

Elongation characteristic of bioplastics is in opposite to the tensile strength of bioplastics. The elongation of bioplastics increases with increasing concentration of DEG (Figure 5). The addition of plasticizers aims to improve the bioplastic characteristic that are hard and stiff. The increase in elongation is caused by the increasing number of hydrogen bonds formed by plasticizers which fills the pores in bioplastics. The higher the hydrogen bonding also increases the viscoelastic response. This causes the bioplastics becoming more flexible, soft, and elastic.

Bioplastics with the best mechanical characteristic was obtained at the addition of DEG concentration of 10% (tensile strength of 18.56 MPa and elongation of 3.95%). This type of bioplastics has strong mechanical characteristic, plastic, and does not readily absorb water. Comparison of mechanical characteristic of bioplastics in research with other types of bioplastics and conventional plastics can be seen in Table 1.

Table 1. Comparison of mechanical characteristic for PHA, PVC, polystyrene (PS), LDPE, and *nanofiber cellulose acetate* (NCA).

Parameter	PHA ^a	PVC ^b	PS ^b	LDPE ^b	NCA ^c
Melting Point (°C)	168.72	170	210	220	170 ^d
Tensile Strength (MPa)	0.12	20	42	10	18.56
Elongation (%)	7	-	2.4	19	3.95
Density (gcm ⁻¹)	0.97	1.38	-	0.915	1.04
Modulus of Elasticity (GPa)	-	0.03	2.5	0.25	0.68

^a[Brand *et al.* (1990)] Poly-β-hidroksialkanoat (PHA) ; ^b[Harrison *et al.* 2004] polyvinyl chloride (PVC), Polystyrene (PS) and *low density polyethylene* (LDPE); ^cNanofiber cellulose acetate from palm empty fruit bunches; ^d[Roganda *et al.* 2013] The thermal characteristic of cellulose acetate

Compared with other types of bioplastics (PHA) and conventional plastics (PVC, PS, and LDPE), bioplastics in this research has a higher tensile strength than PHA and LDPE plastic but lower than the PVC and PS. Based on these characteristics, bioplastics produced in this research resembles PVC in term of its tensile strength of 20 MPa (Table 3). The melting point of cellulose acetate is approaching that of PVC namely between 170-240 °C (Roganda *et al.* 2013), while PVC has a melting point of 170 °C. PVC plastic can normally be used as food packaging.

4. Conclusions

The conclusions of this research are as follows:

1. Process of electrospinning solutions of cellulose acetate with a concentration of 5% does not produce nanofiber
2. Process of electrospinning solutions of cellulose acetate concentration of 10% at a distance of 8 cm spinneret-collector produce nanofiber with the lowest diameter of 134 nm.

3. Nanofiber cellulose acetate has an amorphous structure
4. The best mechanical characteristics of bioplastics made of cellulose acetate nanofiber from oil palm empty fruit bunches was obtained at a concentration of 10% DEG plasticizer, namely tensile strength of 18.56 MPa and elongation of 3.953%.

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