

Research Article

Thermoplastic Cassava Starch-PVA Composite Films with Cellulose Nanofibers from Oil Palm Empty Fruit Bunches as Reinforcement Agent

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Thermoplastic starch-polyvinyl alcohol composite films were prepared by casting method with cellulose nanofibers as reinforcement agent and glycerol as plasticizer. The obtained cellulose nanofibers with a diameter of 27.23 ± 8.21 nm were isolated from oil palm empty fruit bunches (OPEFBs) by mechanical treatment. The addition of cellulose nanofibers until 3 wt% increased tensile strength and crystallinity of the composite films. In contrast, it decreased their elongation at break and water vapor transmission rate. Meanwhile, the addition of glycerol increased elongation at break and water vapor transmission rate of film matrix but lowers tensile strength of composite films.

1. Introduction

Petroleum-based packaging has caused serious environmental problems because it does not decompose easily in nature. In recent years, many studies on new bio-based materials for food packaging have been done in order to replace their nondegradable counterparts. Because of its low cost, biodegradability, and availability, starch is one of the most natural polymers attractively studied for application of food packaging. Starch is widely available in nature and a promising raw material for making biodegradable plastics. Starch is renewable, rapidly degraded in environment, and nontoxic [1]. Starch consists of amylose and amylopectin. Amylose is a linear polymer consisting of α -(1,4)-D-glucopyranose, while amylopectin is a highly branched macromolecule composed of both α -(1,4) and α -(1,6) glucopyranosyl linkages [2].

Thermoplastic starch (TPS) is produced through destruction of starch granular using shear forces at high temperature in presence of plasticizer. This process happens by breaking hydrogen bonds between the starch macromolecules, coinciding with a partial depolymerization of starch backbone [3]. In food packaging application TPS films have drawbacks,

that is, poor mechanical performance and high moisture absorption. Two approaches to overcome these disadvantages are addition of reinforcement agent and blending with other polymers.

Polymer blending is an important method to produce new materials that can meet with our needs. Polyvinyl alcohol (PVA) is a synthetic polymer which can be degraded naturally. PVA is also widely used in packaging industry because it is tasteless, odorless, nontoxic, dissolvable in water, and resistant to oil and fat. PVA has hydroxyl groups (-OH) in its structure which tends to form the intermolecular and intramolecular hydrogen bonds thereby increasing the integrity of mixture of TPS-PVA. It also has good capability for film forming [4].

Cellulose is a major component of plant and has played an important role in maintaining structure of plant cell walls. Cellulose is a linear homopolymer of β -D-glucopyranose units joined by (1 \rightarrow 4) glycosidic linkages [5, 6]. Cellulose nanofibers obtained from different treatment and different sources showed different properties [7–9]. We have succeeded to isolate cellulose nanofibers from OPEFBs by acid hydrolysis [5]. The addition of cellulose nanofibers as

reinforcement agent into TPS production has been studied by some researchers. Thermoplastic cassava starch was reinforced with cassava baggase cellulose nanofibrils [10]. Cellulose microfibrils from potato tuber cell waxy starch cellulose nanocrystals were also added to TPS films [2, 11]. All results showed that the addition of cellulose nanofibers increases the mechanical performance of TPS films.

In food packaging, vapor and gas permeability and migration of certain components are important issues [12]. Oxygen and water vapor can deteriorate food properties, so that the barriers to them are critical properties to consider in packaging materials. The hard diffusivity influences the gas diffusion through the film [2, 12].

In 2014 Indonesia produced around 29.24 million tons of crude palm oil (CPO) [13]. Each year, Indonesia produces a lot of OPEFBs as a byproduct of the palm oil industry. Therefore the use of OPEFBs as a nanosized reinforcement agent in the composite production is one alternative to improve the added value of OPEFBs.

This study is concerned with the production of TPS/PVA composite films with addition of cellulose nanofibers from OPEFBs as reinforcing agent and glycerol as plasticizer. In this study, cellulose nanofibers from OPEFBs were isolated by mechanical treatment using modification of ultrafine-grinder and ultrasonification. The effect of cellulose nanofibers content and glycerol on the properties of TPS/PVA matrix was evaluated by some analyses.

2. Materials and Methods

2.1. Materials. Native cassava starch (Alini brand) with 99.5% purity was purchased from market. OPEFBs for obtaining nanofibers were supplied by PTPN VIII, Kertajaya, Lebak, West Java, Indonesia. Glycerol (commercial grade product), PVA (produced by Celvol™ Sekisui Chemical Co. Ltd), potassium hydroxide (KOH), and sodium hypochlorite (NaOCl) were used as received without any further purification.

2.2. Preparation of Cellulose Fibers from OPEFBs. Dry OPEFBs were cut to approximately 1 cm length and boiled with water at 100°C for 1 hour to remove impurities. Then, 50 g of cut OPEFBs were immersed in 1000 mL solution of KOH 6% for 12 hours at a room temperature and subsequently washed to neutral pH. Bleaching was done by soaking OPEFBs in 12% of hypochlorite solution for 5 hours at room temperature. The obtained cellulose pulp was then washed to a neutral pH and stored in a refrigerator prior to preparation of cellulose nanofibers.

2.3. Preparation of Cellulose Nanofibers from OPEFBs. The cellulose pulp was dispersed in water using a warring blender. Subsequently, the concentration of the pulp suspension was adjusted to 1-2% by adding water. The suspension was then passed 37 times through ultrafine-grinder (Masuko Co., Ltd) at 1500 rpm. Hereinafter the suspension was done with ultrasonification at 40% of amplitude for 30 minutes.

2.4. Preparation of TPS-PVA Nanocomposite Films. TPS-PVA composite films with addition of cellulose nanofibers were prepared by solution casting method. Cassava starch and PVA were mixed with the comparison of 4:1 and dissolved in water. The mixing was performed with stirring and heating up to 90°C for 10 minutes. In this step, the gelatinization of granular starch occurred. The suspension was added with glycerol as plasticizer (0 and 25 wt%) and cellulose nanofibers (0, 1, 3, and 5 wt%) and then stirred for 15 minutes. Subsequently, the material was molded in Teflon mold and dried in oven at 45°C for 48 hours. A series of TPS/PVA cellulose nanocomposite was coded as SPG-aNF-b, where SP stands for starch and PVA, G for glycerol, a for the percentage of glycerol, NF for nanofibers, and b for the percentage of nanofibers content.

2.5. Scanning Electron Microscopy (SEM) Observation. The morphology of obtained cellulose nanofibers was observed by SEM (SEM Zeiss EVOMA 10) operating at 16 kV. Thirty nanofibers for each sample in the SEM images were randomly selected and measured using ImageJ software. The average diameters of nanofibers were calculated.

2.6. Water Vapor Transmission Rate (WVTR). The WVTR was determined by the gravimetric with the modification method of ASTM E96 [14]. The nanocomposite film was cut to the size of 20 mm × 20 mm and conditioned in a desiccator for 24 hours. Then the film was laid on the surface of small container containing anhydrous CaCl₂. The sample was weighed and stored in the desiccator containing saturated KCl. The test was carried out at room temperature and RH in the desiccator of 70%. The WVTR was calculated by the following formula:

$$WVTR = \frac{\Delta m / \Delta t}{A}, \quad (1)$$

where WVTR is the water vapor transmission rate (g/m²/hour), Δm is the difference in mass of the container (mg), Δt is the difference in time, and A is area (m²).

2.7. X-Ray Diffraction. The test of X-ray diffraction (XRD) was performed using a XRD Bruker D8 with a radiation of K α Cu ($\lambda = 1.54060$). The sample with a diameter of 5 cm was placed on the sample holder and the analysis was performed on the operating conditions of 40 kV and 35 mA.

2.8. Mechanical Properties. The tensile tests were performed using universal testing machine (Instron). The nanocomposite film with a size of 45 mm × 20 mm × 40–50 μ m was clamped between the grips. Three measurements were conducted to characterize each sample at a crosshead speed of 3 mm/min.

3. Results and Discussion

3.1. Morphology of Cellulose Nanofibers from OPEFBs. Based on the analysis, the contents of cellulose, hemicellulose, and

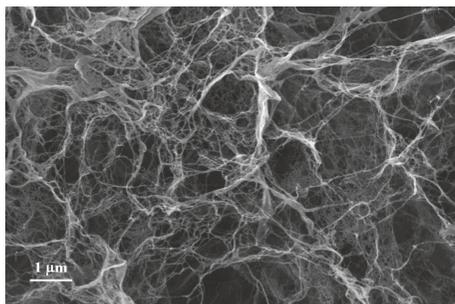


FIGURE 1: SEM image of cellulose nanofibers from OPEFBs isolated by mechanical treatment.

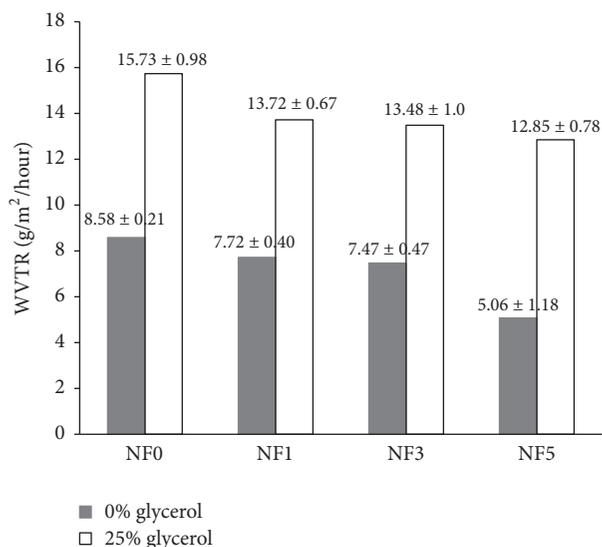


FIGURE 2: Water vapor transmission rate of TPS-PVA cellulose nanocomposite films.

lignin of OPEFBs used in this study were 52.28%, 20.7%, and 27.02%, respectively. After bleaching and alkali treatment for preparing cellulose fibers, the chemical contents of pulp were 76.53% of cellulose, 17.66% of hemicellulose, and 5.81% of lignin. The lignin content was lower compared to the lignin content in OPEFBs. It showed that the delignification and bleaching processes succeeded in reducing the lignin and hemicellulose significantly. The cellulose fibers obtained were reduced in size mechanically to nanoscale using combination of ultrafine-grinder and ultrasonicator. Figure 1 shows the SEM image of the cellulose nanofibers produced. The cellulose nanofibers produced from OPEFBs have the diameter of 27.23 ± 8.21 nm.

3.2. Characterization of TPS-PVA Nanocomposite Films

3.2.1. Water Vapor Transmission Rate (WVTR). The WVTR of TPS-PVA cellulose nanocomposite films can be seen in Figure 2. The addition of cellulose nanofibers lowers the WVTR. It might be caused by the cellulose nanofibers which made the changing of the lanes of the direct diffusion of

TABLE 1: Crystallinity of TPS/PVA cellulose nanocomposite films.

Sample	Crystallinity
SPG0NF0	26.3
SPG0NF1	28.2
SPG0NF3	32.7
SPG0NF5	37.8
SPG25NF0	21.8
SPG25NF1	27.8
SPG25NF3	30.5
SPG25NF5	35.3

the water molecule into the composite become tortuous (tortuous path); thus they blocked the water vapor to pass through the film [15]. The film without the addition of the glycerol shows that the WVTR is lower compared to the film with the glycerol. The glycerol is hydrophilic that can improve the hygroscopic properties so that it has the ability to absorb the water from air around the material and to increase the WVTR of the material.

3.2.2. X-Ray Diffraction (XRD). The X-ray diffraction profiles and crystallinity of nanocomposite films can be seen in Figure 3 and Table 1, respectively. The film without the addition of glycerol has a higher degree of the crystallinity compared with the film using glycerol. Chen et al. [16] reported that PVA exhibited an obvious diffraction peak at 19.4° . In Figures 3(a) and 3(b), all peaks in tapioca starch were not observed and all diffraction patterns seem very close to that of PVA; even in a nanocomposite film, starch content was four times more than the PVA. This might be because of the destruction of crystalline structure of starch granules caused by the gelatinization during the mixing process with PVA at 90°C for 10 minutes.

Both Figures 3(a) and 3(b) exhibit that increasing cellulose nanofibers content made differential peak at 22.5° more obvious gradually. Meanwhile, the addition of glycerol gave the changed diffraction pattern of nanocomposites. It means that the crystalline structure of nanocomposites strongly was influenced by PVA, glycerol molecules, and cellulose nanofibers.

The final crystallinity of materials depends on the ability of the chain to form crystals, as well as on the mobility of the chain. With glycerol content the crystallinity of starch films decreases due to the decrease of intra- and intermolecular interactions of the starch-starch chain [17]. Meanwhile, with increasing cellulose nanofibers, the crystallinity of TPS-PVA composite films increased.

According to Savadekar et al. [18], the existing crystallinity in the cellulose nanofibers also helps improve the crystallinity of the TPS-PVA nanocomposite films. The higher percentage of crystallinity of the nanocomposite film makes the film stronger, because of the compact and orderly structure. This affects the tensile strength of the composite film.

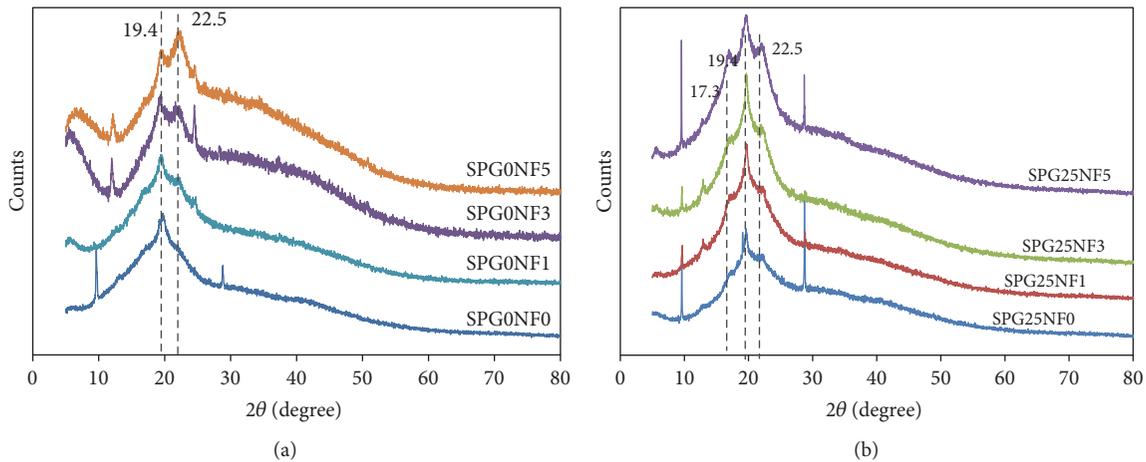


FIGURE 3: XRD Profiles of TPS/PVA cellulose nanocomposite films (a) without glycerol; (b) with glycerol.

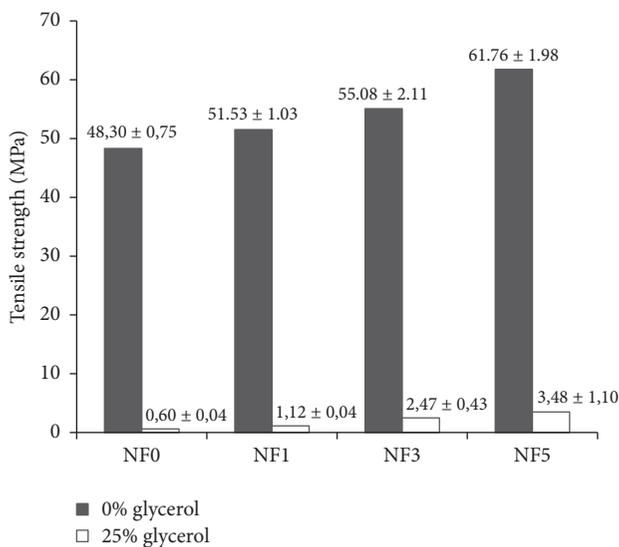


FIGURE 4: Tensile strength of TPS/PVA cellulose nanocomposite films.

3.2.3. Mechanical Properties. The tensile strength of TPS/PVA cellulose nanocomposite films can be seen in Figure 4. The tensile strength of neat TPS/PVA film was 48.3 MPa. Obviously, the addition of cellulose nanofibers improved tensile strength of TPS/PVA films. With increasing cellulose nanofibers content up to 5%, tensile strength of TPS/PVA films without glycerol improved 28% from 48.30 MPa to 61.76 MPa. Both matrix TPS/PVA and cellulose nanofibers as filler have identical chemical nature, that is, hydroxyl groups. Therefore, a good affinity between them could happen, causing the formation of strong hydrogen bonded percolation cellulose nanofibers network at their interfaces and giving reinforcement effect. The increase of tensile strength due to the addition of cellulose nanofibers indicates that interfacial adhesion between TPS/PVA as polymer matrix and cellulose nanofibers occurred.

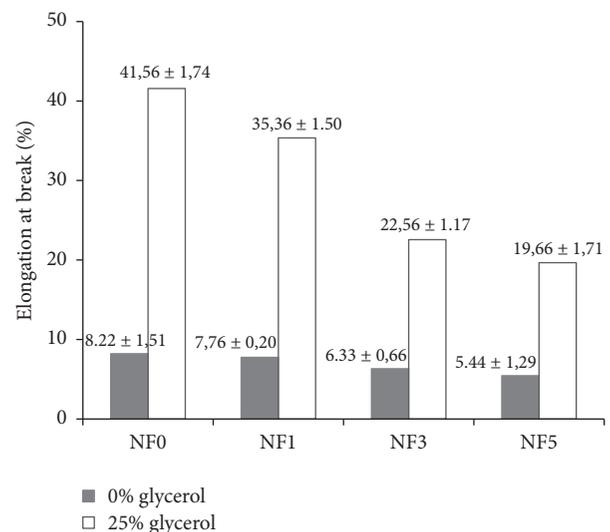


FIGURE 5: Elongation at break of TPS/PVA cellulose nanocomposite films.

Figure 4 exhibits that there is a difference in the tensile strength between nanocomposite films with glycerol and the films without glycerol. Glycerol reduces the inter- and intramolecular forces of the polysaccharide chain so that the film structure becomes more flexible [19]. The addition of glycerol caused tensile strength to decrease significantly. These results were supported by the results of X-ray diffraction analysis.

Figure 5 shows that with increasing cellulose nanofibers content the elongation at break decreased. The film without the addition of glycerol has the lower elongation value compared to the film with the addition of glycerol. The presence of the plasticizer in TPS can interrupt the formation of double helices from the amylose with the branch of amylopectin; then it reduces the interaction between the molecules of amylose and amylopectin; thereby it increases the flexibility of film [20].

4. Conclusion

The isolation of the cellulose nanofiber from OPEFBs succeeded mechanically with the size of 27.23 ± 8.21 nm. The cellulose nanofibers showed good reinforcement in the nanocomposite films of TPS-PVA. The addition of the cellulose nanofibers lowered the WVTR, but the addition of glycerol increased the WVTR of the composite films. The film without glycerol had the better tensile strength, but it lowered the elongation at break of the film and made the film not elastic. The addition of cellulose nanofibers also lowered the elongation at break of the film. The film crystallinity was more increasing with increasing cellulose nanofibers content. The film with glycerol had the lower crystallinity compared to the film without glycerol.

Conflicts of Interest

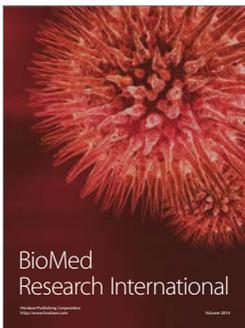
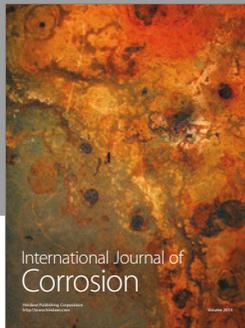
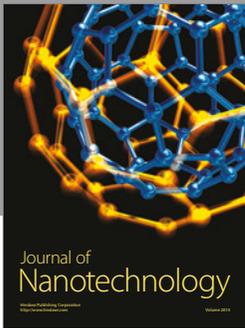
The authors declare that they have no conflicts of interest.

Acknowledgments

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