Improving Physical Properties of Polyvinyl Alcohol Film through The Addition of Nanocellulose Prepared from Palm Oil Solid Waste

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Abstract. Cellulose from the palm oil solid waste (oil palm shells and stems) be isolated and used as a filler material in a biodegradable plastic, in order to improve its mechanical properties. Polyvinyl Alcohol (PVA) is a biodegradable polymer and compatible for nanocellulose fillers, where its mechanical properties can reach the same level as the conventional plastic. In this study, nanocellulose has been successfully prepared from the oil palm shells and stems with acid hydrolysis method and applied as a filler for PVA/nanocellulose film composite. The characterizations include Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry (DSC) and mechanical properties (tensile and elongation). The FTIR and DSC analysis confirm the improvement of the mechanical properties after the addition of nanocellulose, where the tensile strength reaches 14.64 kgf/mm² with the optimal thermal ratio at 203.5°C. Nevertheless, the addition of 20% nanocellulose reduces the value of tensile strength and elongation.

1. Introduction

Indonesia is the largest palm oil producing country in the world. However, a large quantity of palm oil production also results in an equally proportionally enormous solid waste, found in the form of oil palm empty fruit bunches, shells, stems, fibers, and etc. [1]. The solid waste contributes to the release of organic pollutant to the environment. In order to overcome the problem, solid waste can be taken as biomass resources. The solid waste, including the palm shells and stems, can be processed into biomass material due to their high fiber contents. Cellulose, hemicellulose, and lignin are the three major components of the fiber. The cellulose content in palm shells can reach up to 26.27%, followed by the hemicellulose and the lignin that respectively give 12.61% and 42.96% [2]. Palm stems are the likewise, having a high content of cellulose, hemicellulose, and lignin. On the other hand, natural fibers are the main composites, consisted of cellulose fibrils, which can be found in the lignin matrix [3]. Agricultural wastes such as shells, stems, coconut husk, coconut shell, and oil palm empty fruit

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bunches, can be taken as natural fiber resources, which make them to be very abundant and diverse. Nowadays, the natural fiber has been widely developed for its use as fillers and reinforcement in composite films, owing to its renewable and environmentally friendly properties.

This study evaluates the effect of the addition of fibers in polyvinyl alcohol (PVA) composites, where the fibers are from palm oil nanocellulose. PVA is a polymer with a molecular weight of 26,300-30,000, a melting point of 180-190°C, degree hydrolysis of 86.5-89%, and biodegradability [4]. Due to the stated properties it has, PVA has been widely utilized as a promising alternative for packaging. It is also due to the fact that PVA is easy to shape, resistant to oils and fats, and high in tensile strength and flexibility. However, PVA has a weak property against high humidity. The ambient water can be absorbed, causing the PVA film to experience a decrease in tensile strength and tear strength and an increase in elongation. According to Roohani et al. [5], PVA exhibits high compatibility with nanocellulose fillers, where the composites are found to be environmentally friendly. Thus, the addition of cellulose nanofiber in PVA-based films is expected to improve the mechanical properties of the final product [6].

Previous studies have reported the use of acid hydrolysis in the preparation of nanocellulose. Xiong, et al. [7] has successfully obtained cellulose nanofibers (with the size of 10-65 nm) through an acid hydrolysis method employing strong acid, namely sulfuric acid Moreover, Tang and Liu [8] reported that the addition of high cellulose nanofibers (> 40% by weight) in a PVA-based film, can increase its mechanical strength by up to 50%. This study aims to determine the effect of the nanocellulose addition to the mechanical and thermal properties of PVA-based film composites.

2. Methodology

2.1. Preparation of cellulose isolation
Palm oil solid waste (oil palm shells and stems) was shredded to a size of 1-5 mm. Then the sample was washed and dried in an oven (24 h, 60°C). Next, 10 g sample was put into a solution of 300 mL NaOH 0.5 M and simultaneously evaporated at 80 ºC. After that, the sample was washed 3 times, filtered, and dried in an oven at 60 ºC for 5 h. The product of this procedure is cellulose.

2.2. Preparation of nanocellulose
6 grams cellulose, obtained from the oil palm shells and stems, was mixed in 180 mL formic acid 50%. The mixture was hydrolyzed at 90 ºC and 400 rpm for 4 h. After that, it was washed with distilled water 3 times and centrifuged for 20 minutes. The nanocellulose pellet was collected from the centrifuge tube and dried in an oven at 70 ºC.

2.3. Preparation of PVA composite films
PVA crystals (1.5 g) were dissolved in 15 mL distilled water, and the mixture was heated at 80 ºC for 2 h and left to cool down. Nanocellulose was added into the PVA mixture with the w/w (of PVA) ratio variations of 1%, 5%, 10%, and 20%. The mixture was stirred for 2 h [9]. Then, it was poured onto a mold (Petri dish) for 48 h at the ambient temperature until the plastic (film) can be removed.

2.4. Characterizations
Fourier Transform Infrared (FTIR) analysis was carried out with electromagnetic radiation within the wavelength region of 0.75–1,000 µm. For palm oil solid waste (oil palm shells and stems), the functional group analysis was carried out with Shimadzu Prestige FT-IR 6400 at 4000–400 cm⁻¹. Analysis of the tensile strength and elongation of the samples was carried out with HT-8503 Computer Type Universal Testing Machines. Prior to the tensile strength analysis, the samples were cut according to ASTM-D638 standards. The analysis conducted by pinning both ends of the sample to a tensile testing machine, then the tool pulled the sample to break, and the data of tensile strength and elongation were recorded after the breaking. The thermal analysis was performed by Differential
Scanning Calorimetry (DSC), using a Shimadzu DSC-60 type Detector tool. The sample analysis was carried out at the range of 20–200 °C with a heating rate of 10 °C/min.

Table 1. Composition of composite film with fixed variable of 1.5 g PVA

| Sample code | Nanocellulose (%) |
|-------------|-------------------|
| PVA         | 0                 |
| Shell1      | 1                 |
| Shell2      | 5                 |
| Shell3      | 10                |
| Shell4      | 20                |
| Stem1       | 1                 |
| Stem2       | 5                 |
| Stem3       | 10                |
| Stem4       | 20                |

3. Results and discussion

3.1. Morphology of the PVA/nanocellulose composite

FTIR spectrum of PVA film (without filler), as shown in Figure 1, indicates the presence of hydroxyl groups at 3528 cm⁻¹. It also suggests the hydrophilic properties of the PVA, which can be associated with its affinity with water. The absorbance peak is observed at 1741 cm⁻¹, associated with the presence of ketone functional group (C=O). Meanwhile, the presence of C=C aromatic rings can be observed at 1568 cm⁻¹. The results of the FTIR analysis can be seen in Figure 1, where the wavelengths of each functional group are presented in Table 2 [10].

The FTIR analysis is also carried out for PVA/nanocellulose composites filled with the nanocellulose from oil palm shells and stems. The FTIR spectra of the PVA/nanocellulose composites exhibit a similar pattern with the PVA film spectrum, indicating the absence of chemical reaction during the composite preparation. However, shifts of wavelength are observed in the composites spectra, which can be ascribed to the presence of hydrogen bonds and ester bonds. Those interactions...
are responsible for the improvement of the adhesion properties between the fillers and the PVA polymer matrix.

Table 2. Interpretation of IR spectra in pure polyvinyl alcohol nanocomposites

| Wavelength (cm\(^{-1}\)) | Bond  | Functional Group         |
|--------------------------|-------|--------------------------|
| 3600 – 2000              | O – H | Alcohol, hydrogen bond   |
| 3000-2800                | C-H   | Alkane, aromatic rings   |
| 1760-1690                | C = O | Keton, Ester             |
| 1600 – 1500              | C = C | Aromatic rings           |

3.2 Thermal properties of the PVA/ nanocellulose composite

DSC analysis of PVA/ nanocellulose composite shows the transition sequence of the thermal properties of the polymer, namely melt onset, \(T_g\) and \(T_m\). As can be seen in Table 3, melt onset temperatures of PVA films were obtained between the range of 67.81 to 200.3 \(^\circ\)C, the \(T_g\) temperatures were between the range of 52.58 to 157.8 \(^\circ\)C and \(T_m\) temperatures were between the range of 187.7 to 203.5 \(^\circ\)C. It can be observed that the higher transition glass temperatures (\(T_g\)) were given by the PVA/ nanocellulose composites. It can be ascribed to the presence of strong bonds between the matrix (PVA polymer) and the filler (nanocellulose from oil palm shells and stems). Higher \(T_g\) contributes to a longer reaction required to change the materials from glassy to rubbery, thus indicating an increase of stability.

Table 3. Results of DSC analysis of polyvinyl alcohol nanocomposites

| Sample     | Melt onset (\(^\circ\)C) | \(T_g\) (\(^\circ\)C) | Melt peak \(^{TM}\) |
|------------|-------------------------|----------------------|---------------------|
| PVA        | 84.35                   | 52.58                | 203.48              |
| shell 1%   | 80.11                   | 54.50                | 201.45              |
| shell 5%   | 67.81                   | 63.07                | 119.12              |
| shell 10%  | 82.52                   | 58.31                | 201.76              |
| shell 20%  | 88.76                   | 64.83                | 201.49              |
| stem 1%    | 71.69                   | 54.16                | 201.44              |
| stem 5%    | 77.90                   | 53.63                | 187.73              |
| stem 10%   | 83.13                   | 56.99                | 203.50              |
| stem 20%   | 200.39                  | 157.81               | 201.50              |

The stated results can also explain the thermal characteristics of the composite. Below the \(T_g\), the polymer is found to be fragile and nearly rigid. It is due to the fact that the polymeric chains are locked in a circular and irregular position. Whereas, when the temperature is above the \(T_g\), the rigid and glassy properties are removed, transforming the polymer to be more elastic. As an addition, \(T_g\) depends on the preparation process, structures, bonds, and molecular weight of the materials. Meanwhile, for \(T_m\), samples received constant heating, thus causing a stronger vibration. Eventually, it allows the sample to decompose, where the bonds between the chains are broken, thus reducing the heat resistance of the sample and reaching the melting point. It is important to study the thermal properties of a sample in order to obtain the information pertaining to the preparation process and the maximum storage temperature (below the melting temperature of the sample).

3.3 Mechanical properties of the PVA/ nanocellulose composite

As shown by Figure 2, the tensile strength of the composites increases along with the increase of the nanocellulose filler content, either from the oil palm shells or stems. For the addition of nanocellulose from oil palm shells of 1%, 5%, and 10%, the tensile strength values are 7.5, 11.29, and 13.5 kgf/mm\(^2\). Meanwhile for nanocellulose from oil palm stems, with the same % weight ratio, the tensile strength...
values are 8.21, 14.64, and 13.93 kgf/mm$^2$. The increase of tensile strength is owing to the closer
distance between particles after the addition of nano fillers (< 10%) [11]. Nevertheless, the addition of
20% nanocellulose, from either oil palm shells or stems, results in a decrease of tensile strength. It can
be ascribed to the reduction of the nanocellulose particle homogeneity in the mixture, where in fact,
the mixing process was carried out with the same conditions and treatments [12].

![Figure 2. Effect of filler contents on the tensile strength of the PVA/ nanocellulose composites](image2)

![Figure 3. Effect of filler contents on the elongation of PVA/ nanocellulose composites](image3)
Elongation is defined as an extension of a film, measured from the initial time until the film breaks [13]. The elongation analysis results can be seen in Figure 3, where the addition of the filler affects the elongation. For nanocellulose from the oil palm shells, the addition of 1%, 5%, and 20% gives 237.56%, 226.24%, and 171.6% elongation, respectively. Meanwhile, with the same variations, the addition of nanocellulose from the oil palm stems gives 245.52%, 93.52%, and 179.96% elongation, respectively. The clearly observable decrease of elongation with the addition of 20% nanocellulose can be ascribed to the distribution of nanocellulose particles that occupy the pores of the composites, allowing a tighter filler network arrangement and a closer distance between fillers. The obtained values increase the strength of the composites but reduce the elongation.

4. Conclusion
Nanocellulose has been successfully prepared from palm oil solid waste (oil palm shells and stems) and applied as a filler for PVA/nanocellulose film composites. DSC analysis suggests better thermal properties by the increase of Tg in PVA film after the addition of nanocellulose, either from oil palm shells or stems. It is ascribed to the presence of strong bonds of hydrogen and ester between the matrix and the filler, confirmed by the FTIR spectra profile. These bonds are also responsible for the improvement in mechanical properties, indicated by the increase of tensile strength value. The addition of nanocellulose filler improves the mechanical properties (up to 245.52 kgf/mm²), with the optimal thermal ratio at 203.5°C. However, the homogeneity of the nanocellulose distribution is reduced by the addition of 20% nanocellulose, resulting in a drawback in the tensile strength. The addition of 20% nanocellulose also results in the reduction of elongation due to the formation of a tighter filler network arrangement and a closer distance between fillers. This study, in conclusion, provide evidence that the nanocellulose that is prepared from palm oil solid waste can be effectively used as a filler to improve the mechanical properties of PVA film.

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