PHYSICAL PROPERTIES OF POLYVINYL ALCOHOL/CASSAVA STARCH COMPOSITE BIOPLASTICS WITH NANOCELLULOSE ADDITION FROM CASSAVA PEEL

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Abstract. This research was conducted to investigate the characteristics of bioplastics produced from a combination of polyvinyl alcohol (PVA) and cassava starch with the addition of nanocellulose filler derived from cassava peel. The basic bioplastic formula used was 5.4% PVA and 0.6% cassava starch. The treatment applied was the amount of nanocellulose added, namely 0%, 2%, 4%, and 6%. The composite bioplastics were made by casting method, followed by testing of physical properties including thickness, water vapour transmission rate (WVTR), and transparency. Bioplastic thickness was measured using a digital micrometer, while WVTR was measured using the gravimetric method. The transparency of the bioplastics was evaluated through measuring their transmittance using a UV-Vis spectrophotometer. The results showed that the addition of nanocellulose had no effect on the physical properties of bioplastics. Increasing nanocellulose concentration tends to increase the thickness and decrease the water vapour transmission rate of bioplastics. However, the addition of nanocellulose reduced the transparency of the bioplastics, especially at higher concentrations.

Keywords: bioplastics, nanocellulose, polyvinyl alcohol, tapioca, physical properties

A. Introduction

Global warming and the environmental crisis caused by the use of conventional plastics have driven the need to seek eco-friendly alternatives in the production of packaging materials. In this context, bioplastics present a promising solution as they can be produced from renewable resources and naturally degrade. One type of bioplastic that has gained attention for research is composite bioplastics made from polyvinyl alcohol (PVA) and starch.

PVA offers several advantages, including being resistant to oxidation, having high tensile strength, excellent bioplastic-forming capabilities, and good water solubility (1). The safety of PVA for food packaging is approved by the FDA and is considered a GRAS (Generally Recognized as Safe) material. Subchronic toxicity and genotoxicology studies also confirm that PVA is safe for humans when exposed through various routes of daily exposure (2).

Blending PVA with natural polymers is a good alternative to compensate for the lower mechanical properties of biopolymer products and the high cost of PVA. The PVA/starch blend has greater potential for use in disposable packaging products due to the abundance and low cost of starch raw materials. However, the presence of hydroxyl groups in PVA and starch makes the material hygroscopic, which can reduce its tensile strength. This weakness can be overcome by adding fillers as bioplastic reinforcements, such as nanocellulose, chitosan, kaolin, and carboxymethyl cellulose (3, 4, 5).

Cellulose is a naturally abundant material and one of the most common biopolymers on earth. The addition of cellulose in nanoscale (nanocellulose) to certain polymer matrices has been found to greatly improve their physical and mechanical properties (6). Nanocellulose can be produced from agricultural waste or by-products. One such by-product with the potential to be used as a source of nanocellulose is cassava peel.

The use of nanocellulose as a reinforcing filler for bioplastics is well-established. Nanocellulose-reinforced composites exhibit remarkable properties due to the nano-sized fillers, making them potential candidates to replace conventional synthetic polymer composites. The outstanding reinforcing ability of nanocellulose is attributed to its lightweight, high stiffness, and superior mechanical strength (7). The thermogravimetric analysis also shows an improvement in the thermal stability of PVA nanocomposites with the addition of nanocellulose as a filler (8). This study was conducted to examine the characteristics of bioplastics produced from a blend of PVA and cassava starch (tapioca) with the addition of nanocellulose fillers derived from cassava peels.

B. Methods

1. Material and Instrument

The materials used include cassava peels, sodium chlorite ($NaClO_2$), potassium hydroxide (KOH), polyvinyl alcohol (PVA), ethanol, polyethylene glycol (PEG) 400, and distilled water. The main equipment used includes a hot plate stirrer, water bath, thermometer, microwave, and high-velocity mixer.

2. Nanocellulose Extraction

The extraction of nanocellulose from cassava peels was carried out using an alkaline method following a modified procedure from Wicaksono et al. (9). The cassava peels were dried and ground into powder, then dewaxed to remove the wax layer on the peel surface. The fibers were then bleached with 5% $NaClO_2$ to remove chromophores, making the fibers whiter and degrading the lignin. Afterward, they were treated with 4% KOH at 80°C for 1 hour to dissolve the hemicellulose, residual starch, and pectin. The purified fibers were then subjected to mechanical treatment using a high-velocity mixer.

3. Preparation of PVA/Starch – Nanocellulose Bioplastic

The bioplastic was prepared following a modified procedure from Wu et al. (10). A total of 5.4 g of PVA was dissolved in 46 mL of ethanol-H_2O (1:3 v/v) in a 100 mL beaker, followed by the addition of 0.6 g of starch. The solution was heated in a water bath at 80°C for 8 minutes. H_2O (4 mL) and 0.2 mL of PEG 400, along with nanocellulose, were added to the solution in the water bath for 2 minutes. The solution was poured onto a glass plate and allowed to dry at 50°C for 90 minutes. Nanocellulose was added according to predetermined treatments: 0%, 2%, 4%, and 6% (v/v).

4. Testing of Water Vapor Transmission Rate (WVTR)

The WVTR was tested using the cup test method. The bioplastic was tightly sealed over a petri dish containing silica gel. The petri dish was placed in a desiccator containing a saturated salt solution. The weight of the petri dish was measured every hour, and a regression line was drawn between time and weight increase. The water vapor transmission rate per unit of time (hour) was determined by dividing the slope of the regression line by the surface area of the bioplastic covering the petri dish.

5. Measurement of Thickness

The sample thickness was measured at three points using a micrometer, and the average thickness was calculated.

6. Measurement of Bioplastic Transparency Properties

The transparency of the bioplastic sample was analyzed using a UV-Vis spectrophotometer at a wavelength range of 300-650 nm.

7. Data Analysis

The data were analyzed using one-way ANOVA with α=5%.

C. Results And Discussion

1. Water Vapor Transmission Rate (WVTR)

The effect of adding nanocellulose into PVA/cassava starch composite bioplastics on the water vapor transmission rate (WVTR) is as follows.

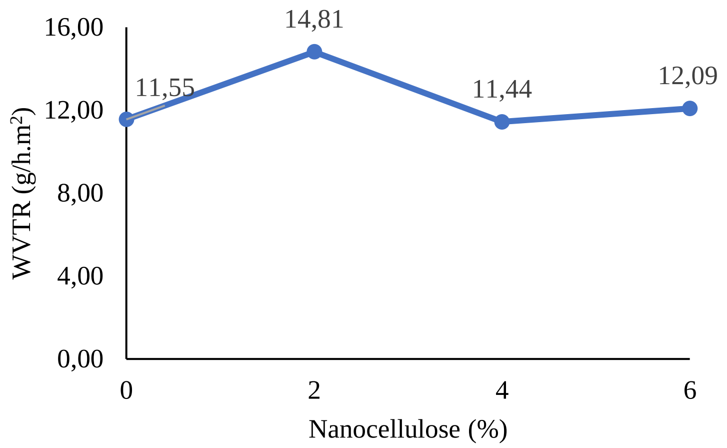

Figure 1. Effect of nanocellulose addition on the water vapor transmission rate (WVTR).

Figure 1 illustrates the relationship between the percentage of added nanocellulose and changes in water vapor transmission rate (WVTR), measured in $g/h.m^2$. The data shows that WVTR ranges from 11.44 to 14.81 $g/h.m^2$, depending on the concentration of nanocellulose used. Nanocellulose can enhance hydrogen bonding within the polymer matrix, which in turn strengthens the material's structure and reduces gaps that could serve as pathways for water vapor. At a certain concentration, nanocellulose acts as a filler, increasing the polymer network's density and reducing the water vapor transmission rate.

However, the graph shows that the addition of nanocellulose does not always result in a linear reduction in permeability. At the highest nanocellulose concentration (6%), WVTR reaches its peak value of 14.81 $g/h.m^2$. Statistical analysis indicates no significant difference in WVTR for bioplastics with the addition of nanocellulose. This may be due to the nanocellulose not being evenly dispersed and tending to interact with each other to form aggregates, thus reducing its efficiency in the polymer matrix (11). Such aggregation can create heterogeneity within the material, randomly affecting its properties, so the expected change in WVTR may not be significant. In this situation, the effect of nanocellulose diminishes because the filler is not evenly dispersed and does not form the network required to improve the barrier properties of bioplastics. The increased amount of nanocellulose can also lead to incomplete mixing during the manufacturing process, making the resulting bioplastic more heterogeneous (12).

Excessive cellulose content will cause the plastic film to become more heterogeneous. This heterogeneity results in imperfect blending, weakening the bonds between starch-cellulose and glycerol. Additionally, the water vapor barrier capability is influenced by the hydrophilic nature of the film's components and the added nanocellulose. The presence of a plasticizer, in this case PEG 400, is hydrophilic, thus increasing the risk of a higher WVTR value. This condition was also observed by Wahyuningsih et al. (13) in PVA-based films with glycerol plasticizer and added nanocellulose derived from pineapple leaf fibers. This increase in WVTR is due to the plasticizer's hydrophilic nature, which stretches the existing hydrogen bonds. This hydrophilic nature is important to note as it can trigger the growth of microorganisms on the surface of bioplastics during storage (14).

2. Film Thickness

The effect of adding nanocellulose into the PVA/tapioca starch composite bioplastic on the film thickness can be observed in Figure 2.

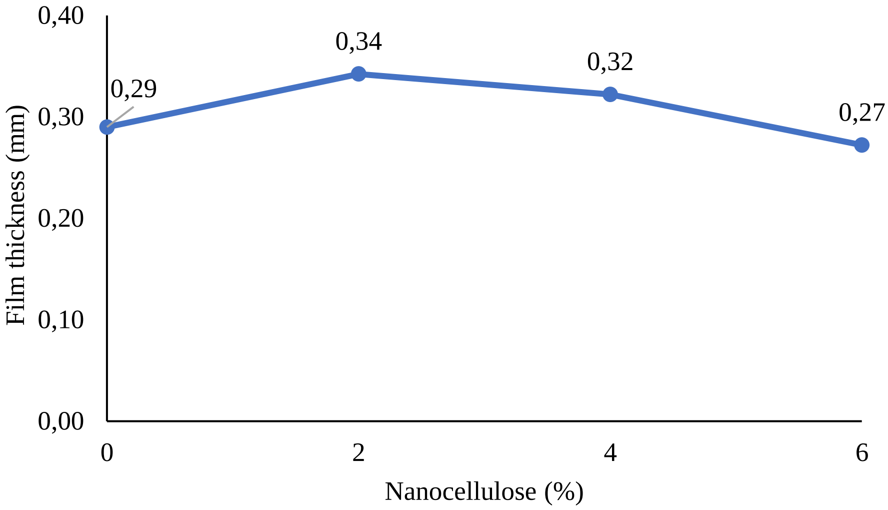

Figure 2. The effect of adding nanocellulose on film thickness.

Figure 2 shows the variation in thickness at different nanocellulose concentrations (0%, 2%, 4%, and 6%). The thickness ranges from 0.27 mm to 0.34 mm, with the highest value observed at a 2% nanocellulose concentration (0.34 mm) and the lowest at a 6% concentration (0.27 mm). However, statistical tests did not reveal any significant differences. The addition of nanocellulose does not exhibit a consistent trend in terms of increasing or decreasing thickness. There is an increase in thickness at the 2% concentration, followed by a decrease at the 4% and 6% concentrations. This indicates that an increase in nanocellulose concentration does not necessarily correlate with an increase in thickness. This phenomenon was also observed by Huang et al. (15) in cassava residue cellulose nanofibril/cassava starch composite films with the addition of cellulose nanofibrils from 0 to 0.5 g. The nonlinear variation in thickness may also be influenced by relative humidity, which leads to a swelling effect in the film matrix (16).

3. Film Transparency

The effect of adding nanocellulose into the PVA/tapioca starch composite bioplastic on the transparency properties of the bioplastic can be observed in Figure 3.

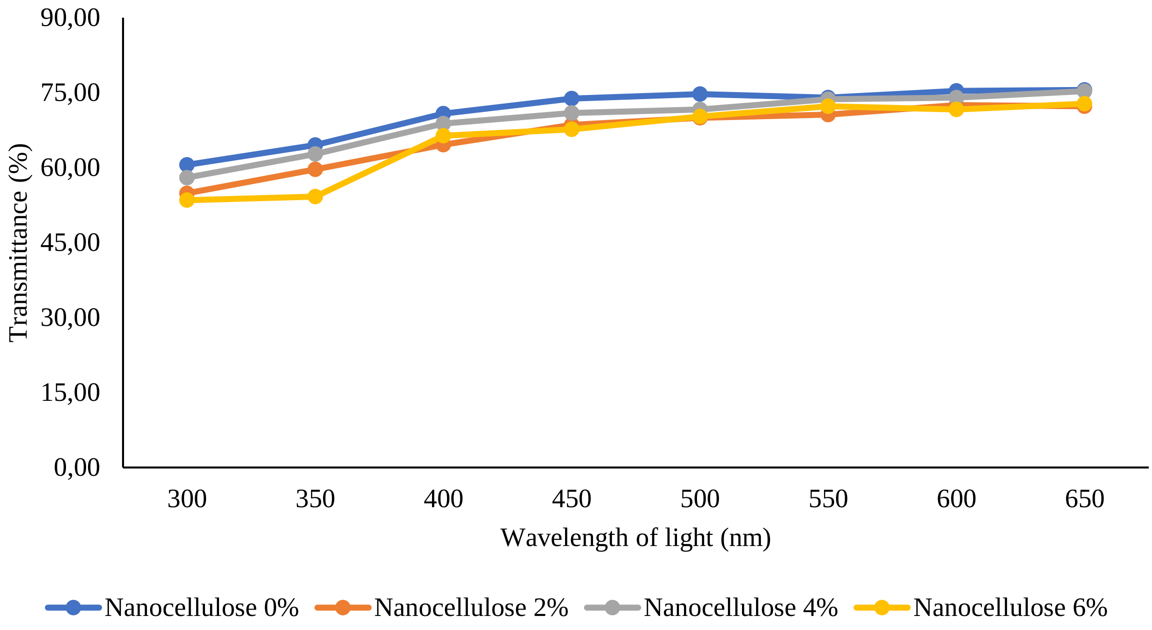

Figure 3. The effect of adding nanocellulose on film transparency.

The addition of nanocellulose to PVA (Polyvinyl Alcohol) and cassava starch composite bioplastics is known to affect the material's transparency. Bioplastic transparency is generally measured by transmittance values, which represent the percentage of light that can pass through the material at various wavelengths. Based on the research results, increasing the nanocellulose concentration in bioplastics tends to reduce transparency. This is due to the presence of nanocellulose particles that cause light scattering, making the material more opaque. At low nanocellulose concentrations, transparency remains relatively high; however, an increase in concentration up to 6% results in a significant decrease in light transmittance. Additionally, this reduction in transparency can also be attributed to cross-linking between nanocellulose particles, which obstruct light beams from passing through the film matrix (17).

Moreover, bioplastic transparency is also influenced by light wavelength. Data shows that increasing nanocellulose concentration leads to a reduction in transmittance, particularly at lower wavelengths (300-450 nm), which fall within the ultraviolet spectrum. At higher wavelengths, around 600-650 nm (visible light spectrum), bioplastics containing nanocellulose still show a slight increase in transparency, though it remains lower compared to bioplastics without nanocellulose. This suggests that the optical properties of bioplastics are greatly influenced by the particle size distribution of nanocellulose and its interaction with light at specific wavelengths.

The addition of nanocellulose reduces the transparency of the film. However, on the other hand, the ability of nanocellulose to block UV rays provides a beneficial property. This ability is necessary to prevent or slow down the oxidation of proteins, lipids, vitamins, or pigments. These characteristics are directly related to the shelf life of food by preventing color changes, undesirable taste, loss of aroma, and nutrients while preserving the organoleptic properties and nutritional content of packaged food (18).

D. Conclusion

Based on the research findings, it can be concluded that the addition of nanocellulose had no significant effect on the physical properties of the bioplastics. An increase in nanocellulose concentration tended to increase the thickness and decrease the water vapor transmission rate of the bioplastics. However, the addition of nanocellulose reduced the transparency of the bioplastics, particularly at higher concentrations.

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