Physical properties of sago starch biocomposite filled with Nanocrystalline Cellulose (NCC) from rattan biomass: the effect of filler loading and co-plasticizer addition

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Abstract. Rattan biomass is an abundant bioresource from processing industry of rattan which contains 37.6% cellulose. The high cellulose contents of rattan biomass make it a source of nanocrystalline cellulose as a filler in biocomposites. Isolation of alpha cellulose from rattan biomass was being prepared by using three stages: delignification, alkalization, and bleaching. It was delignificated with 3.5% HNO₃ and NaNO₂, precipitated with 17.5% NaOH, bleaching process with 10% H₂O₂. Nanocrystal obtained through the hydrolysis of alpha cellulose using 45% H₂SO₄ and followed by mechanical steps of ultrasonication, centrifugation, and filtration with a dialysis membrane. Biocomposite was being prepared by using a solution casting method, which includes 1–4 wt% nanocrystalline cellulose from rattan biomass as fillers, 10-40 wt% acetic acid as co-plasticizer and 30 wt% glycerol as plasticizer. The biocomposite characteristic consists of density, water absorption, and water vapors transmission rate. The results showed the highest density values was 0.266 gram/cm³ obtained at an additional of 3 wt% nanocrystalline cellulose from rattan biomass and 30 wt% acetic acid. The lowest water absorption was 9.37% at an additional of 3 wt% nanocrystalline cellulose from rattan biomass and 10 wt% acetic acid. It was observed by the addition of nanocrystalline cellulose might also decrease the rate of water vapor transmission that compared to the non-filler biocomposite.

1. Introduction

Cellulose is the main component of plant cell walls and it is regarded as the most abundant natural resource. Cellulose has potential applications in the development of new high-performance materials with low environmental impact. Cellulose in particular size has large surface areas, relatively high strength and low density [1]. As a result, cellulose can be used to make green composite polymers [2], surfactant [3] and membrane [4].

Rattan biomass is the agricultural waste that can be used as a source of cellulose fiber for biocomposite. The high availability of rattan makes this natural resource can be engineered into a national technology product using a nanotechnology system [5]. Rattan consists of 37.6% cellulose, 41% hemicellulose and 22.6% lignin [6]. The cellulose content of rattan can be used as nanocrystalline cellulose. Based on the function of cellulose, it can be a reinforcement filler on biopolymer [7]. Reports have shown that cellulose as a filler has been done by Halimatuddahliana, et al. (2017) that made microcrystalline cellulose (MCC) from empty bunches of oil palm [8] and Harahap, et al. (2015) made nanocrystalline cellulose (NCC) from sugarcane bagasse [9]. NCC and MCC have potential as reinforcement in biopolymers.
Over the years, all people are concerned about environmental problems with conventional plastics. This is because the production of the petroleum-based plastics from non-renewable resources. Many researchers have been focused on materials that have properties comparable with those of the conventional polymeric materials. From this perspective, biocomposite based on starch are seen as the candidates to be developed as biodegradable materials.

Starch is a natural renewable polymer obtained from the variety of agricultural products like tubers and seeds. Among its advantages, starch is cheap, abundant and biodegrades quickly [10]. Biodegradable packaging can be produced from cassava starch [11], corn [12] and sago starch [13]. Sago starch has unique characteristics: it is easy to gelatinize and molded, availability as a renewable resource, cheap and has a high starch content of 82.94% [13]. Sago starch can be processed into thermoplastic starch or biodegradable plastic under the action of temperature and shearing action [13].

The bioplastic consisting of starch as an ingredient requires a mix of additives that are used to produce mechanical properties of soft, and resilient. The additives as plasticizer, co-plasticizer, and filler are typically used to be less rigid from starch [14]. Plasticizers such as glycerol are more commonly used because when processing there is no glycerol evaporate so that the mechanical process is easy to do. Acetic acid can be used as a plasticizer coating (co-plasticizer). The carboxyl group of acetic acid will make a strong hydrogen bond with the hydroxyl group of starch [13]. Tawakaltu, et al. (2015) reports the effect of acetic acid and citric acid modification on biodegradability of cassava starch bio-nanocomposite films [15].

Based on the explanation above, will research the effect of filler loading and co-plasticizer addition on physical properties of sago starch biocomposite.

2. Method

2.1 Material

Rattan biomass was obtained from Kota Pinang, North Sumatera, Indonesia. Sago starch was being purchased by the local market. Sago starch particles were being screened by through a mesh size of 200. The chemicals, nitric acid (HNO$_3$), sodium nitrite (NaNO$_2$), sodium hydroxide (NaOH), sodium sulfite (Na$_2$SO$_3$), sodium hypochlorite (NaOCl), hydrogen peroxide (H$_2$O$_2$), sulfuric acid (H$_2$SO$_4$), glycerol and acetic acid were supplied by MERCK and used as received.

2.2 Production of Alpha Cellulose

Alpha cellulose was obtained from rattan biomass with a delignification process by using 3.5% nitric acid (HNO$_3$) at 90 °C. Followed by washing and filtering and digested with 2% w/v sodium hydroxide (NaOH) and sodium nitrite (NaNO$_2$). Bleaching was being treated by two steps. The first bleaching step was carried out with 1.75% sodium hypochlorite (NaOCl) at boiling temperature for 0.5h. Alkalization was being treated by 17.5% sodium hydroxide (NaOH) at 80 °C for 0.5 h. The second bleaching step was carried out with 10% hydrogen peroxide (H$_2$O$_2$) at 60 °C for 1h.

2.3 Production of NCC

The alpha cellulose derived from cellulose was hydrolyzed using 49% sulfuric acid (H$_2$SO$_4$) and stirred at high-speed for 45 min at 45 °C. The white suspension was diluted with distilled water and allowed to settle overnight. The clear top layer was being decanted, and the remain of a cloudy white layer was being washed by distilled water and centrifuged at 10000 rpm for 25 min at several times to remove the solvent and other organics soluble. The white precipitation was diluted with distilled water and dispersed by ultrasonication for 10 min. The suspension was dialyzed using activated dialysis tubing for 96 hours. NCCs were dried in vacuum oven at 25 °C until the water was evaporated.

2.4 Production of Biocomposite

Biocomposite films were being based by a solution casting and evaporation process. The variation amount of NCCs (1, 2, 3, 4 wt% of starch) was dispersed into the 95 ml of distilled water under continuous stirring at 1000 rpm for 15 min. After that designated weights of 10 gr of sago starch were mixed and stirred for the complete dissolution of starch. Glycerol content based on starch was being
fixed by 30 wt% and Acetic acid with the variation amount (10, 20, 30, 40 wt% of starch). Starch, glycerol and acetic acid were mixed and heated at 70 °C for 30 min with stirring until the mixture gelatinized. The water was evaporated at room temperature overnight after that solution poured into an acrylic mold. The Film formed uniformly and removed smoothly.

2.5 Characterization
2.5.1. Density. The density of biocomposite has been investigated by the standard of ASTM D792-91 on film with size approximately 5x5 cm. The film’s mass was measured using analytical balance. The Density calculated as follows:

\[
\text{Density} = \frac{\text{mass (gram)}}{\text{volume (cm}^3\text{)}}
\]  

(1)

2.5.2. Water Uptake. Water uptake was investigated by cutting film with size approximately 2x2 cm and then weighed the mass. The film put into a container filled with distilled water for 24 hours. After immersion in water, a film was removed from the water and weighed to measure the wet weight. Water uptake calculated as follows:

\[
\text{Water Uptake} = \frac{\text{Wet Weight-Dry Weight}}{\text{Wet Weight}} \times 100\%
\]  

(2)

2.5.3. Water Vapor Transmission Rate (WVTR). The Film to be tested in the mouth of a porcelain bowl with an inside diameter of 7 cm, an outside diameter of 8 cm and a depth of 2 cm which contained 10 gram of silica gel. The edges of the porcelain bowl and film covered with wax or insulation. The porcelain bowl inserted into the jar that containing 40% sodium chloride (NaCl) (w/v). Water vapor diffuses through the film will be absorbed by silica gel and will add weight to the silica gel. The condition of the water vapor transmission rate of equilibrium is reached by 7-8 hours. The films were weighed periodically every 1 hour. The data obtained made linear regression equation and WVTR values can be determined by the equation:

\[
\text{WVTR} = \frac{\text{linear slope for the change in weight of a jar (g/hour)}}{\text{Surface Area (m}^2\text{)}}
\]  

(3)

3. Results and Discussion
3.1 The Effect of NCC Content and Acetic Acid Addition on the Density of Biocomposites
The density of the biocomposite shows in Figure 1. The density increased considerably with the filler and co-plasticizer content, at 3 wt% NCCs and 30 wt% acetic acid addition, the biocomposite was showed an optimum value of 0.26 gram/cm³. The improvement indicated that nanocrystalline cellulose (NCC) is evenly distributed causing and increase the density of the biocomposite structure [16,17]. At 4 wt% NCC loading, a slight decrease in the density was observed, it indicated that nanocrystalline cellulose (NCC) formed aggregates that reducing the effectiveness of biocomposite density [14,18].

![Figure 1. The Effect of NCC Content and Acetic Acid Addition on the Density of Biocomposites](image-url)
As shown in Figure 1, at 30 wt% acetic acid addition, biocomposite has a high-density value because the acetic acid will increase the physical interaction that allows the formation of hydrogen bonds into more chains of starch which increases the density of the biocomposite. When the acetic acid percentage increased to 40 wt%, acetic acid will loosen the bonds between molecules in biocomposite, reducing the stiffness of the biocomposite structure that can reduce the density of biocomposite [19,20]. The mechanism of acetic acid and cellulose interaction show in the Figure 2 [20]:

![Acetic Acid and Hydrogen Bond](image)

**Figure 2. Mechanism of Acetic Acid and Cellulose Interaction**

The distribution and dispersion were being supported by scanning electron microscope (SEM) of bioplastic and biocomposite that showed the surface of the matrix is more smooth and coherent. It shows that nanocrystalline cellulose (NCC) has been uniformly distributed on the sago starch matrix. As co-plasticizer agent, the acetic acid has good interface bondage with the filler and matrix as shown in Figure 3.

![SEM Bioplastic and Biocomposite](image)

**Figure 3. SEM (1000x) of Bioplastic (a) and Biocomposite (b)**

3.2 The Effect of NCC Content and Acetic Acid Addition on the Water Uptake of Biocomposites

Figure 4 shows the water uptake of biocomposites with NCCs and acetic acid addition. The addition of NCCs led to a decrease in water uptake, which attributes to the formation of a cellulose nanoparticle network that prevented swelling of the starch and therefore water uptake as well. At 4 wt% nanocrystalline cellulose (NCC) addition, the water uptake biocomposite increased due to the agglomeration of nanocrystalline (NCC) cellulose and the presence of amorphous zones in nanocrystalline cellulose (NCC) making it easier for water to diffuse into the biocomposite that increasing the properties of water uptake [21,22]. At 30 wt% acetic acid addition, the biocomposite water uptake becomes increased. The increased percentage of water uptake is due to an increase in the concentration of co-plasticizer, this is thought to cause the bonding that occurs between the plasticizer, and the polymer becomes brittle when exposed to water [23].
3.3 Water Vapor Transmission Rate (WVTR)

The water vapor transmission rate is the important parameter for packaging film materials on biocomposite. Table 1 shows the water vapor transmission rate of bioplastic and biocomposite which is calculated by according to the equation (3).

### Table 1. Water Vapor Transmission Rate of Bioplastic and Biocomposite with 3 wt% NCC and 10 wt% Acetic Acid Addition

| Sample         | WVTR (g/m².hour) |
|----------------|------------------|
| Bioplastic     | 10.33            |
| Biocomposite   | 5.61             |

The diffusivity and solubility of water molecules in the film matrix will affect the water vapor transmission rate [24]. Starch is hydrophilic, and hence it has high WVTR. The high WVTR is decreased by the presence of dispersed phase of NCC into the starch biopolymer matrix [14]. Biocomposite has better dispersion and lower aggregation of NCCs particles contributing to generating a barrier for the passage of water molecules evoking a decrease in WVTR [24]. On the other hand, NCC was well dispersed and covered by the matrix, suggesting that the introduction of NCC into the starch and plasticizer films resulted in improved adhesion between the NCC and the polymer matrix [25]. This result was supported by the morphology image as seen in Figure 3b.

4. Conclusion

The density value increases with NCC and acetic acid additions. Furthermore, the addition of NCC content decreases water uptake of biocomposites. Contrary from NCC content addition, an increases in water uptake value was being reported by the acetic acid addition. It observes that the addition of nanocrystalline cellulose might also decrease the rate of water vapor transmission that compared to the non-filler biocomposite.

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