Manufacture of Bioplastic Composite Method of Blending Synthetic Polymer (PP) with Natural Polymers from Kapok Fiber (*Ceiba Pentandra*)

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In this modern era, the use of plastic materials has increased over time. This phenomenon affects the growth of plastic waste that causes the need for bioplastics as an alternative material. Therefore, the development of natural fibers utilizations like Kapok (Ceiba Pentandra) as bioplastics raw material becomes necessary. The bioplastic composites manufacture process by mixing Polypropylene (PP) synthetic plastic with natural polymers from Kapok fiber occurred in several stages: Kapok fiber isolation, cellulose acetate synthesis, cellulose acetate purification, and bioplastics manufacture. This study strived to determine the type of plasticizer and PP filler effects on the bioplastic composite characteristics. The production of bioplastic composites consisted of two types of plasticizers, namely 20 % glycerol and 40 % sorbitol, with mass variations of PP as filler (0 g, 1 g, 2 g, and 3 g). The results revealed that the addition of the type of plasticizer and the mass of the PP filler provided distinct impacts on the characteristics of the bioplastic composite. The soundest bioplastic composite retained with 1.0714 g/mL of density value, 5.7225 kPa of tensile strength value, 1.82 % of elongation, 3.1442 kPa of Young's modulus, 20.41 % of water absorption, and the mass degraded by 25.94 % gained from the addition of sorbitol plasticizer and 1 g of PP filler. In other words, the bioplastics have met the standard for plastic packaging for food and groceries based on Indonesian National Standard, ASTM and JIS.

1. Introduction

Plastic is a possible environmental hazard because of the difficulty in naturally recycling and decomposing it. Therefore, the use of biodegradable plastics or bioplastics is the way to solve these challenges. Bioplastics have biodegradable properties and can decompose up to 67 % within 2-3 weeks in activated sludge media for wastewater treatment. Bioplastics are environmentally friendly and degraded naturally in either anaerobic or aerobic conditions, depending on how they are generated. In addition, when bioplastics are disposed of in the environment, they do not leave poisonous compounds that might be hazardous to the organisms. Kapok fiber, with a cellulose concentration of 35-64 %, is one of the natural fibers with significant potential as the material for creating bioplastics (Rahmatullah et al.,2021). Besides, the kapok plant is perennial and abundant in Indonesia.

The development in boosting the strength of bioplastics can use fillers and plasticizers. PP has the potential to be used as a filler. PP contains hydrophobic, water-repellent, and high molecular weight properties whose main content are carbon and hydrogen (Jangong et al., 2020). Plasticizer types commonly used are glycerol and sorbitol. Glycerol becomes the most popular plasticizer material because the absence of glycerol makes the plastic sheet stiff and rigid. Sorbitol is a more effective plasticizer than chitosan in producing films with lower oxygen permeability (Asngad et al., 2020). Many researchers conducted related studies on bioplastics manufacture using cellulose as a raw material. Jannah et al. (2019) observed the influence of fillers and plasticizers on the mechanical properties of rice husk bioplastic cellulose. Jangong et al. (2020) conducted research to determine the effect of palm fiber (SPF) on the structural and optical properties of bioplastics

components (SPF/Starch/Chitosan/PP) to improve the mechanical properties and degradation performance. The previous research by Rahmatullah et al. (2022) determined the effect of the type and concentration of plasticizer on the characteristics of cellulose acetate-based bioplastics from kapok fiber. The novelty of this research is the use of natural fibers from kapok fiber with a combination of filler from PP and plasticizers of glycerol and sorbitol. This present work would like to investigate the effect of the plasticizer type and PP plastic filler on the characteristics of the bioplastic produced.

2. Methods

The materials of bioplastics manufacture employed in this present work were kapok plant (Indralaya Region), starch/tapioca flour (by PT Budi Strach and Sweetener Tbk), aquadest (by SMARTLAB, A-1078), alkaline water pH 8 (by PT Enagic. Co. Ltd.), Glycerol (by Merck), sorbitol (by Technical), sodium hydroxide (NaOH) (by Merck), glacial acetic acid (CH$_3$COOH (by Merck), PP (PT. Pertamina RU III), acetic anhydride ((CH$_3$CO)$_2$O) (by Merck), sulfuric acid (H$_2$SO$_4$) (by Merck).

2.1 Synthesis of Cellulose and Celullose Acetate

Kapok fiber was prepared, then washed and dried in an oven at 100 °C to a constant weight. The dried kapok Kapok fiber was prepared, washed, and dried respectively in an oven at 100 °C until the weight was constant. The dried kapok fiber was delignified for 3 h at a temperature of 75 °C in a sodium hydroxide (NaOH) solution (3.4 M) as much as 12 % of the fiber mass. Then, the kapok fiber was filtered and washed with distilled water until the acidity was neutral. At 75 °C for 10 min, the delignified kapok fiber was bleached with sodium hypochlorite (NaOCl) solution (6.7 M) as much as 12 % of the fiber mass and mixed with distilled water (with the ratio between NaOCl and aquadest was 1:1). The kapok fiber was washed with distilled water until the acidity was neutral. The neutralized kapok fiber was dried to a constant weight in an oven with a temperature of 100 °C. The 10 g of kapok fiber cellulose was put into a three-neck round-bottom flask with 50 mL of glacial acetic acid and 0.5 mL of sulfuric acid. The mixture was stirred well for 3 min, covered with aluminum foil, and rest for 1 h. After 1 h, 50 mL of anhydrous acetic acid and 20 mL of glacial acetic acid was added to the mixture. Then, it was heated for 30 min at a temperature of 50 °C. The mixture then was left until the temperature dropped. The mixture was Poured in 50 mL of glacial acetic acid (7.1 M). Afterward, it was added 0.14 mL of sulfuric acid and reacted for 3 h at temperature 50 °C. After the reaction process is complete, the mixture was allowed to stand until the temperature drops and continues with the purification process.

2.2 Cellulose Acetate Purification and Bioplastic Production

The cellulose acetate synthesis solution was placed into a 1 L beaker, and 25 mL of distilled water was slowly added and stirred simultaneously. Then, another 500 mL of distilled water was added and stirred. The cellulose acetate solution was rested until it became a solid phase mixed with the solvent. Next, the cellulose acetate solution was filtered using a Buchner vacuum funnel and added with distilled water to obtain cellulose acetate solids. Then, it was washed and filtered using a Buchner vacuum funnel until neutral. The neutral cellulose acetate was dehydrated in an oven at a temperature of 100 °C to reach a constant weight and pulverized.
A total of 1.5 g of starch was dissolved in 9 mL of distilled water, heated for 15 minutes at 70 °C, and stirred continuously until gelatin was formed. 1 g of cellulose acetate was added to the starch solution. The solution then was stirred and heated at a temperature of 50 °C for 15 min (until it was thick and clear). At a temperature of 350 °C, the PP filler was melted in the plasticizer solution. Next, it was added to the cellulose acetate solution at a temperature of 100 °C. The bioplastic solution was molded in a petri dish covered with aluminum foil and rested to cool down into a room temperature. After it dried, a bioplastic sheet formed.

2.3 Bioplastic Characteristic Analysis

2.3.1 FTIR Analysis

The FTIR measures were conducted on a Perkin Elmer Spectrum One spectrometer coupled to an Auto Image light microscope. These analyses were performed on samples of starch bioplastic and composites bioplastics.

2.3.2 Tensile Strength, Elongation and DensityTest

Tensile tests were performed using the CMT-10 Computer Control Electronic Universal Testing Machine. Tensile strength and elongation were determined from the stress-strain curves, estimated from force-distance data obtained for the different and a strain rate of 2 mm/min at room temperature. All mechanical testing of bioplastics was conditional according to the standard method of ASTM-D638-14. The sample width of narrow section was 13 mm, length of narrow section was 57 mm, overall length was 165 mm, thickness was 3.5 mm and gage length were 50 mm. There are three specimens were tested for each sample.

The density test was conducted based on the procedure performed by Darni et al. (2017). A 10 mL of measuring cup was filled with 5 mL of water, and the bioplastic sample was put into the measuring cup for 15 min. Then, the new volume of water (v) was recorded, and the actual volume of bioplastic was calculated by dividing the final and the initial volumes of water. The density (ρ) of bioplastic was obtained with the Eq (1):

$$\rho = \frac{m}{v} \tag{1}$$

Where ρ was density (g/mL), m was mass (g) and v was volume (mL).

2.3.3 Soil burial degradation and water resistance test

The degradation process of cellulose acetate from kapok fiber used the loose soil as decomposer media with an acidity degree around pH 6-7. The degradation rate of the soil burial test was calculated from weight loss of the sample over time. The biodegradation weight loss was determined for seven days interval based on Eq(2):

$$Biodegradation\ (\%) = \frac{A1-A2}{A1} \times 100\ \% \tag{2}$$

Where A1 was initial mass (g), A2 was mass after testing (g).
In measuring water resistence of bioplastic, the initial bioplastic sample was weighed and the put into a container containing aquadest. The sample was taken out from the container every 10 seconds and weighed repeatly until obtained a constant final sample weight. The water absorbed on the bioplastic sample could be calculated by the following Eq(3) (Tamiogy et al., 2019):

$$Water\ (\%) = \frac{W - W0}{W0} \times 100\ \% \tag{3}$$

Where W0 was the initial sample weight (g) and W was final sample weight (g).

3. Results and Discussion

3.1. Characteristics of Bioplastic Products

The characteristics of bioplastics with FTIR (Fourier Transform Infra Red) aims to identify the functional groups contained in bioplastics based on the type of plasticizer and the mass of PP. The analysis of bioplastic functional groups result shows in Figure 1.
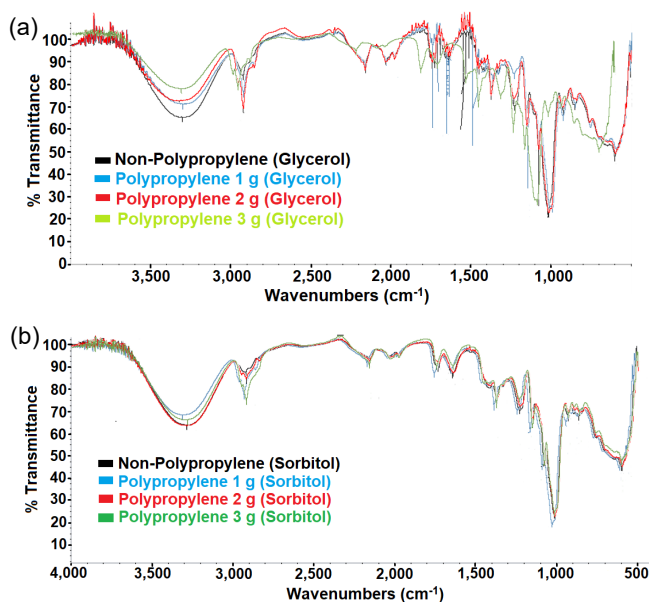

Figure 1: FTIR Test Results: (a) PP-Glycerol, and (b) PP-Sorbitol

Figure 1 revealed the spectrum of cellulose acetate-based bioplastic from kapok fiber with different characteristics determined by the added mass of PP. The wavenumbers on the mixture of cellulose acetate, starch, PP, and plasticizer (glycerol and sorbitol) did not indicate the formation of new groups. In conclusion,

the bioplastic production was a mixing process without any reaction to the constituent materials, and the bioplastic products still possessed their constituent's properties, such as elastic, decomposable, and hydrophilic. (Melani et al., 2017). The addition of 1 g, 2 g, and 3 g of PP to the glycerol resulted in 3,299.43; 3,318.84; and 3,280.84 cm^{-1} of wavenumbers, while the addition of the same PP to sorbitol resulted in 3,299.46; 3,286.95; and 3,285.90 cm^{-1} of wavenumbers respectively. These results was an indication of a hydroxyl group (O-H). The hydroxyl group signified the presence of polymer, glycerol, and sorbitol compounds (Lopes et al., 2018). The wavenumbers from the addition of 1 g, 2 g, and 3 g of PP to the glycerol plasticizer were 2,921.27; 2,918.85; and 2,918.18 cm^{-1}. Then, the wavenumbers of the addition to the sorbitol plasticizer were 2,918.28; 2,918.77; and 2,919.58 cm^{-1}. These results signified the presence of C-H groups from cellulose acetate. The C-H functional group was the cellulose acetate framework with a wavenumber range of 2,800-3,000 cm^{-1}. This value also indicated the characteristic of PP as the filler of bioplastic composite. Finally, the band of PP was 2,800-3,000 cm^{-1} (Siregar, 2016). The glycerol sample wavenumbers for the addition of 1 g, 2 g, and 3 g PP were 1,630.97; 1,630.94; and 1,640.72 cm^{-1}. On the other hand, the sorbitol sample wavenumbers were 1,641.99; 1,641.96; and 1,643.43 cm^{-1}. These results indicated the presence of C-C groups of starch. A spectrum of starch appeared at a wavenumber of 1,640-1,949 cm^{-1} representing the presence of C-C bonds (Salinas-Jasso et al., 2021). The wavenumber of the glycerol samples for every PP addition were 1,235.04; 1,232.18; and 1,232.14 cm^{-1}, while the wavenumber sorbitol samples for every PP addition were 1,230.25; 1,297.7; and 1,232.48 cm^{-1}. These results were the indication for the presence of C-O ester groups. The wavenumber of 1,000-1,300 cm^{-1} marked the C-O ester group. The existence of the C-O functional group implied that bioplastic could degrade well and easily decompose in the soil. The C-O ester was included in the hydrophilic group because water molecules could cause microorganisms in the environment to penetrate the bioplastic matrix and decompose the bioplastic (Salinas-Jasso et al., 2021).

3.2. Density and Water Resistance of Bioplastic Products

Figure 2a shows the density of cellulose acetate-based bioplastics from kapok fibers increased when the higher mass of PP was added to each type of plasticizer. The density value of the bioplastic products ranged from 0.833 -1 .50 g/mL, where the lowest density value was from a glycerol-type plasticizer without PP. Sorbitol plasticizer type bioplastic with a mass of 3 g PP has the highest density value. The type of plasticizer and PP mass significantly influenced the density value of the resulting bioplastic. Darni et al. (2017) supported this statement by mentioning that the higher material density indicated the denser the molecular structure of the materials. The density of bioplastics with the type of plasticizer sorbitol and 3 g of PP with a mass of 1,500 g/mL gave the highest density value for bioplastics that met the SNI of conventional plastic (0.95 g/cm^3) and ATSM standard of bioplastics (1,4 g/cm^3). Figure 2b shows the effect of the type of plasticizer and PP mass on the water absorption of bioplastics. This test aimed to determine the ability of bioplastics to absorb water. The water absorption capacity of the bioplastic produced is anticipated to provide the lowest possible value. The high value of water absorption capacity caused the bioplastic to be easily damaged (Purnavita et al., 2020). The water absorption value for sorbitol bioplastic still fluctuated with the addition of PP, while the water absorption of glycerol bioplastic tended to increase. This happened because the mixture of cellulose acetate, starch and PP filler was not dispersed homogeneously in the cellulose acetate solution. It affects the irregular bioplastic matrix that causes large porosity of cellulose acetate then bring greater water absorption. This condition is supported by Tamiogy et al. (2018). The value of bioplastics was still fluctuating due to the inhomogeneous mixing between starch and cellulose. Inhomogeneous mixing of bioplastics also created a volume of empty voids between particles that could accommodate water between the particles. There was a capillary channel connecting the empty space, the surface of the composite that was not covered with adhesive, and the depth of penetration of the adhesive to the particles (Nuryati et al., 2020). The lowest water absorption value for sorbitol bioplastic was obtained by adding 2 g of PP (12.87 %), and the one for glycerol bioplastic the addition of 1 g PP was 13.98% by adding 1 g of PP. These findings met the Indonesian National Standard with a maximum water absorption value of 21.5%.
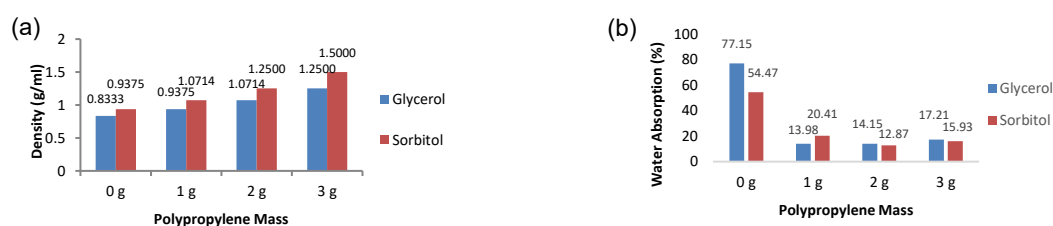

Figure 2: (a) Density of Bioplastic Products, and (b) Water Absorption of Bioplastic Products

3.3. Tensile Strength, Elongation, and Young's Modulus of Bioplastic Products

The tensile strength values of bioplastics of each type of plasticizer and PP mass that are shown in Figure 3a were in a range of 0.3065-9.8100 KPa. Referring to the JIS (Japanese Industrial Standard) standard, plastic for food packaging categorized as biofilm has a minimum tensile strength of 0.039 KPa. The highest tensile strength value of bioplastic was obtained from sorbitol plasticizer with a mass of 0 g of PP (without PP), which was able to restrain a load of 9.8100 KPa. The glycerol bioplastic plasticizer with a mass of 2 g of PP possessed the lowest tensile strength value and could only restrain a load of 0.3065 KPa. The tensile strength value of PP bioplastic with glycerol as a plasticizer fluctuated since its mass decreased to 1 g and increased again to 2 g. This phenomenon occurred because of the inhomogeneous cellulose acetate mixing process with starch, plasticizers, and fillers in bioplastics production. It is in line with the finding of Tamiogy et al. (2018). They discovered that the value of bioplastics fluctuated due to inhomogeneous mixing between starch and cellulose. The occurrence of fluctuations in the yield value of bioplastics was due to the difficulty of dissolving PP with natural polymer materials at temperatures below 300 °C so that PP became solid again. This condition was in agreement with Tamiogy statement that the solubility properties of polypropene were insoluble at room temperature. The elongation percentage (Figure 3b) is slightly different for each type of plasticizer and PP mass. These differences happened because of differences in the composition of the bioplastics produced. The elongation percentage values ranged from 1.29 to 1.82. The elongation percentage value in the sorbitol bioplastic sample experienced the optimum point at the addition of 1 g of PP mass, and the glycerol bioplastic sample experienced the optimum point at the addition of 2 g of PP. According to Jangong et al. (2020), adding up to 50 % of polymer materials is likely to eliminate the original material elasticity with the existence of the fillers. Simultaneously, smaller elasticity leads to more extensive elongation of the bioplastic. The research obtained 1.82 % as the highest percentage of elongation by adding sorbitol with 1 g of PP. The percent elongation value of bioplastics is close to the ASTM standard for bioplastics (3 %). The addition of 0 g of PP (without PP) to sorbitol results in the smallest elongation percentage (1.29 %). The elongation percentage of bioplastics added with glycerol tends to be lower than sorbitol plasticizers because the mobility of glycerol plasticizers is lower than that of sorbitol plasticizers. The finding was in line with the statement of Jannah et al. (2012). They found that the elongation percentage of polymeric materials relies on the mobility of the molecular chains of a polymer. The Young's modulus of bioplastics (Figure 3c) in each bioplastic sample was achieved the highest Young's modulus value were obtained from the plasticizer sorbitol with a mass of 0 g of PP about 7.6046 kPa. The lowest value of Young's modulus is 0.1781 kPa in sorbitol plasticizer with a mass of 2 g of PP. Young's modulus value of bioplastic still does not meet the standards of SNI, ASTM, and JIS. Young's modulus declines with the increase of PP mass. The decrease in the value of Young's modulus occurs because the tensile strength has a smaller value than the elongation making the value of Young's modulus small. It is in line with Jannah et al. (2019) that the growth of tensile strength increases of Young's modulus because the tensile strength and Young's modulus are comparable.
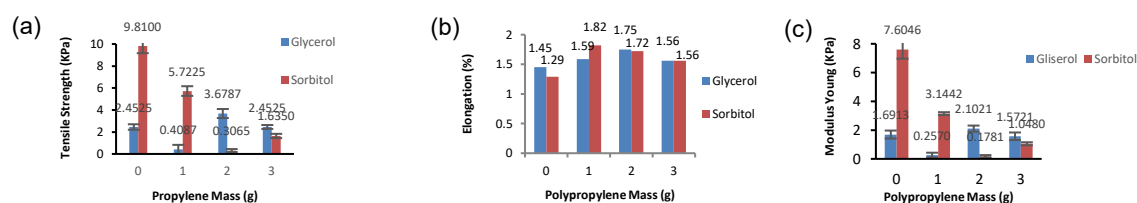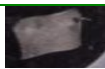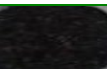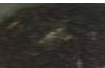

Figure 3: (a) Tensile Strength of Bioplastic, (b) Elongation of Bioplastic, and (c)Young's Modulus of Bioplastic

3.4. Biodegradation of Bioplastic Products

The degradation of the burial soil test was calculated from the weight loss of the sample over time (Table 1). The weight loss calculation measures the biodegradability of polymers directly. The weight loss percentage of bioplastics without the addition of PP and composite bioplastics is shown in Table 1.

The weight loss of the two samples increases with the increase number of days. The maximum % weight loss without the addition of PP were 75 % and 89 % while with the addition of PP 47 % and 63 % for the glycerol and sorbitol bioplastic samples. It was observed for a month. These results show the % weight loss of bioplastics without the addition of PP is greater than composite bioplastics. This phenomenon due to the microorganisms are not easy to attack PP composite bioplastics (Amin et al., 2019). The Indonesian National Standard requires that biodegradable plastics degrade after 60 days. Based on these results, both plastics degrade rapidly and can be considered as biodegradable materials.

Table 1: Biodegradation of Bioplastic

Type of Plastisizer	Day 1	Day 7	Day 14	Day 30
		(weight loss)		
Glicerol without PP	0 %	21 %	36 %	75 %
Glicerol with 2 g PP	0%	10 %	22 %	47 %
Sorbitol without PP	30 %	38 %	47 %	89 %
Sorbitol with 2 g PP	19 %	31 %	33 %	63 %

4. Conclusions

The results of bioplastic composite by mixing PP synthetic plastic with natural polymers from kapok fiber show that the addition of different plasticizer types (glycerol and sorbitol) and PP fillers mass give different effects on the characteristics of the bioplastic composite products. The addition of PP plastic fillers provides better advantages than bioplastics without the addition of PP plastic fillers, such as in the density, tensile strength, elongation, Young's modulus, and water resistance values. However, bioplastics with PP fillers have a weakness in bioplastic biodegradation compared to non-PP bioplastics. The most promising bioplastic outcomes were bioplastics with the addition of sorbitol plasticizer and 1 g of PP filler with 1.0714 g/mL of density value, 5.7225 kPa of tensile strength value, 1.82 % of elongation, 3.1442 KPa of Young's modulus, 20.41 % of water absorption and 25.94 % of mass degradation. These results indicate that bioplastics have fulfilled the standard for plastic packaging for food and groceries based on Indonesian National Standard, ASTM and JIS.

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