MECHANICAL AND THERMAL PROPERTIES OF STARCH AVOCADO SEED BIOPLASTIC FILLED WITH CELLULOSE NANOCRYSTAL (CNC) AS FILLER AND POTASSIUM CHLORIDE (KCl) AS DISPERSION AGENT

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ABSTRACT

The development of bioplastics is currently in demand considering that was a substitute for the synthesis of plastic packaging with environmental consequences. Bioplastics are environmentally friendly because they are made from natural materials and can be degraded naturally. This study centers on the manufacture of bioplastic based on avocado seed starch with variations in the addition of cellulose nanocrystal (CNC) fillers using oil palm mesocarp fibers as raw material and the appended potassium chloride as dispersing agent. In this research, we analyzed the mechanical dan thermal properties of bioplastic including scanning electron microscopy (SEM), elongation at break (Eb), tensile strength (Ts), and thermal gravimetry analysis (TGA). The highest value of Ts was obtained at the appended of 2 wt.% of CNC and the appended 2 wt.% of KCl, while the highest value of Eb was obtained at 2 wt.% of CNC and 3 wt.% of KCl. Scanning electron microscopy showed uniformly distributed CNC granules filling the surface of the bioplastic. There are six phases of thermal gravimetry analysis. These results indicate that the addition of CNC and KCl will increase the mechanical and thermal properties of avocado seed bioplastic.

Keywords: Bioplastic, KCl, CNC, Avocado Seed, Mechanical Properties, Thermal Properties.

INTRODUCTION

The packaging industry mostly uses plastic, especially in food packaging. Food packaging must be made of natural and environmentally friendly materials. Bioplastics are a solution to the limited resources of petroleum-based polymers and environmental problems due to renewable sources which are of interest to current research.¹ Around 2.42 million tons will be reached from the production capacity of bioplastics in 2021 globally, approximately 48% of the volume intended for the packaging market, which is the major market segment in the industry of bioplastics.² Several biopolymers such as polysaccharides, proteins, and lipids have been used as polymeric matrices for the development of alternative biodegradable packaging because they are easy to obtain, renewable, low cost, and environmentally friendly.³ Starch (polysaccharide) is the most advantageous in the manufacture of bioplastics because of its transparency, non-toxicity, and cheap.⁴,⁵ Some of the starches that are often used in the production of bioplastics are potato starch, corn starch, cassava, and durian seeds. Avocado seeds can be used as a source of starch. Inadequate use of avocado seeds, usually when consuming avocados, the seeds are considered useless so they are simply thrown away. Whereas avocado seeds also have potential as a source of starch that contain comparatively high starch. In this study, starch from avocado seeds was used because the utilization of avocado seeds was not adequate and easy to obtain, so it has the potential to be used as starch in bioplastics. Usually, the mechanical properties of starch films are not good because they have low elasticity. To improve its characteristics, starch can be mixed with hydrophobic or water-resistant biopolymers such as glycerol. The addition of plasticizers in the mixture of biodegradable films is very important to prevent the cracking of the film layer due to high intermolecular forces.⁶ In addition to adding plasticizers, to increase the mechanical strength of bioplastics, it is necessary to add reinforcement/filler. Cellulose is a natural...
reinforcement that can be obtained from natural fibers. Natural fibers have been widely applied in various fields, especially as reinforcement/filler in bioplastics because they have many advantages, namely easy to obtain, inexpensive, can increase mechanical strength, and low density. One of the natural fibers whose utilization has not been adequate is palm fruit fiber. The fiber of Palm fruit is disposed of and generated from the palm oil manufacturing process which contains an average of 43-65% cellulose and an average of 13-35% lignin. Indonesia, especially North Sumatra, produces crude palm oil (CPO) of approximately 4.4 million tons every year. The abundant biomass outcome by oil palm with lignocellulosic content found in palm fruit fiber can be used in the production of cellulose nanocrystals (CNC) as bioplastic fillers. Utilization of oil palm fruit fiber has been carried out by Campos et al. (2017) as filler of nanocrystalline cellulose in cassava starch biocomposite with glycerol plasticizer produced a biocomposite with good mechanical strength at the addition of 6% (w/w) filler. Meanwhile, research by Nasution et al. (2018) on the outcome of adding nanocrystalline cellulose (NCC) from rattan waste as citric acid and as plaster as a co-plasticizer on the mechanical strength of sago starch biocomposites, showed that 3% nanocrystalline cellulose (NCC) and 30% citric acid have increased the tensile strength properties of biocomposites. However, the use of cellulose nanocrystals in bioplastics still has drawbacks such as the uneven distribution of cellulose nanocrystals, which affects the characteristics and properties of the resulting bioplastic products. According to research conducted by Silviana and Hadiyanto (2017) in the manufacture of bioplastics made from sago starch by reinforcing cellulose microfibrils from bamboo with the help of ultrasonic homogenizers produces bioplastic surfaces with randomly distributed pores. This indicates that mixing with the ultrasonication process has not had a maximum effect on the morphology of bioplastics. The addition of dispersing agents in the manufacture of bioplastics can be an alternative to producing bioplastics with good morphology and uniform distribution of fillers. Silviana and Rahayu (2019) conducted research on the manufacture of bioplastics based on sago starch and microcrystalline cellulose from bamboo and KCl as a dispersing agent to produce bioplastics with the highest tensile strength of 28,613 MPa with optimum conditions of microcrystalline 5% w/w cellulose filler and KCl concentration 3% w/w. The addition of KCl acts as dispersing agent reducing the time for making bamboo MFC solution to 1 hour in the course of the ultrasonication process. The homogenization process becomes more effective because K+ cations can stabilize the surface of the mixture. According to Zhang (2015), the addition of KCl as dispersing agent in the manufacture of bioplastics can reduce the homogenization time due to the influence of electrostatic forces. Based on this description, research will be conducted on the bioplastic characteristics of avocado seed starch produced by the addition of cellulose nanocrystal as filler from oil palm fruit fiber and glycerol as a plasticizer, and KCl as dispersing agent.

**EXPERIMENTAL**

**Material**

The avocado seed used in this study was supplied by an avocado seller in HM. Joni Street, Medan, Sumatera Utara. Laboratory-grade chemicals were used for isolated cellulose nanocrystals. Oil palm fruit fiber waste used in this study was supplied by Palm Mill in Aceh Tamiang, Indonesia, and analytical grade glycerol was used for bioplastic preparation.

**Preparation of Cellulose Nanocrystal (CNC)**

Dried Palm Fruit Fiber was prepared as raw material. The dried fiber was blended to get 100 mesh size. The dried fiber was delignificated by using 1 liter of 10 mg NaNO₂ and 3.5% HNO₃ for 2 hours at 90 °C. The residue of the delignification process was washed until neutral and then followed by digesting process for 1 hour with 750 ml of 2% (w/v) NaOH and Na₂SO₄ at 50 °C. The digested fiber was bleached for 30 minutes by applying 250 ml of 1.75% (w/v) at boiling temperature with NaOCl solution. The residue was basted by applying 500 ml of 17.5% NaOH solution for 30 minutes at 80 °C. Then bleached again for 5 minutes by using 10% H₂O₂ solution at 60 °C. The resulting process called α-cellulose was obtained and neutralized by H₂O and dried in an oven. The cellulose hydrolysis process was obtained by using H₂SO₄ with a concentration of 50%. For 45 minutes each 1 gram of α-cellulose was combined in 25 ml of H₂SO₄ at 45 °C. The precipitated suspension was neutralized by H₂O and overnight it was permitted to settle. The precipitated suspension at 10000 rpm was centrifuged for 20 minutes to eliminate acid until a neutral pH was obtained. It was disseminated by using ultrasound for 10 minutes and dried in an oven at 60 °C.
Isolation of Avocado Seed Starch

100 grams of avocado seeds washed with water and then drained. Cut the avocado seeds with a size of 2 cm² and add 100 ml of water then blend until smooth. After smoothing, avocado seed pulp will be formed and the filtrate obtained is filtered and then allowed to stand for 1 hour to form a precipitate. Separated water with starch (sediment) is formed. The starch precipitate obtained was washed, then stirred, and deposited again for 1 hour. Drying in the oven, the obtained starch precipitates for 30 minutes at 70 °C. The starch obtained was milled and to obtain a uniform size, it was sieved with a size of 100 mesh.

Preparation of Bioplastic

Avocado seed starch and desired CNC were weighed with filler variations of 6:4, 7:3, 8:2, and 9:1 as much as 3 grams of dry weight total of nanocrystal containing starch-cellulose. CNC was put into a glass beaker with 75 ml of distilled water and KCl solution with concentrations of 0.1, 2, and 3% w/v was added. Then the solution was dispersed using ultrasound for 30 minutes. After 30 minutes, starch was added to the dispersed CNC-KCl solution. Added 30% glycerol and stirred until homogeneous. The solution was poured into molds, then dried at room temperature for 48 hours.

Characterization of Bioplastic

Ts and Eb tests were tested according to ASTM D882-02 standards by Instron UTM in the Polymer Laboratory, Chemical Engineering of the Faculty of Engineering at Universitas Sumatera Utara. SEM test was performed using an SEM machine model (HITACHI TM 3000) in Integrated Research Laboratory, Universitas Sumatera Utara. SEM images were captured with a magnification of 1000x.

RESULTS AND DISCUSSION

Effect of Addition of Cellulose Nanocrystal (CNC) Palm Fruit Fiber and Potassium Chloride (KCl) on Tensile Strength Starch Avocado Seed-Based Bioplastic

Figure-1 below shows the tensile strength of starch avocado seed-based bioplastic against the addition of cellulose nanocrystal cellulose (CNC) and potassium chloride (KCl).

![Fig.-1: The Effect of the Addition of Cellulose Nanocrystal (CNC) Palm Fruit Fiber and Potassium Chloride (KCl) on Tensile Strength (Ts) Starch Avocado Seed-Based Bioplastic](image)

Based on Fig.-1, avocado seed starch bioplastic with the appended CNC and KCl has the highest Ts value with the appended 2% CNC and the appended 2% KCl with a value of 1.79 MPa. While the lowest Ts value of 0.19 MPa was obtained with the appended 4% CNC and the appended 0% KCl. Figure-1 also shows that the Ts increase as the appended cellulose nanocrystal (CNC) increases from 1% to 2%. This is because cellulose nanocrystals have hydrophilic properties so there is an interaction between solid hydrogen bonds between the starch matrix and the filler to produce good mechanical strength. With the appended of 3% cellulose nanocrystal (CNC), there was a decrease in the Ts value, but with the appended of 4% cellulose nanocrystal (CNC), the Ts value increased. This is due to fluctuating data variations. It can be seen that a uniform error bar with the appended of 3% and 4% cellulose nanocrystal (CNC) can be considered a decrease in Ts value. The decrease in Ts at the addition of 3% and 4% CNC was caused by the addition of excessive filler which could damage the bond between the matrix and filler, thereby reducing the ts value.
of bioplastics. The appended of KCl only acts as a dispersing agent for cellulose nanocrystal (CNC) giving significant results on the Ts of bioplastics. Potassium chloride (KCl) aids the dispersion of cellulose nanocrystals (CNC) in bioplastics. This can be supported by the SEM results in Fig.-2.

![Fig.-2: Analysis of Bioplastic Fractures (a) without KCl (b) with KCl using Scanning Electron Microscopy (SEM) with 1000x Magnification](image)

Figure-2 shows the results of the analysis of bioplastic fractures (a) without KCl and (b) with the addition of KCl. Figure-2(a) shows a rough surface and holes. Empty holes are formed due to the weak interaction between filler and matrix. Ooi et al. (2013) also stated that the formation of holes on the surface of bioplastics was due to the lack of strong interaction between the matrix and filler. Meanwhile, Fig.-2(b) shows uniformly distributed CNC granules filling the surface of the bioplastic. The appended of KCl as a dispersing agent gave a nice effect. KCl can be ionized into K+ and Cl-. K+ cations can stabilize bioplastic solutions so that they can disperse cellulose nanocrystals (CNC) well. Even dispersion of CNC can increase the tensile strength (Ts) of bioplastics. Silviana and Rahayu (2017) reported that the addition of KCl was able to reduce the formation of craters or air bubbles on the surface of sago starch bioplastics.

**Effect of Addition of Cellulose Nanocrystal (CNC) Palm Fruit Fiber and Potassium Chloride (KCl) on Elongation at Break (Eb) Bioplastic Avocado Seed Starch**

Figure-3 shows the impact of at break (Eb) elongation of avocado seed starch bioplastic on the appended cellulose nanocrystal (CNC) and potassium chloride (KCl).

![Fig.-3: Elongation at Break (Eb) of Bioplastic Avocado Seed Starch-Based with CNC and KCl as Dispersant Agents](image)

Elongation at break (Eb) is obtained when the maximum elongation (max strain) of the bioplastic film is stretched until the maximum tensile strength (max stress) is obtained. Based on Fig.-3, it can be inferred...
that the effect of adding filler in the form of cellulose nanocrystal (CNC) and the appended potassium chloride (KCl) on Eb has the highest elongation at break value with the appended 4% cellulose nanocrystal (CNC) with the appended of KCl 3% of 19.39%. Meanwhile, the lowest Eb value was obtained with the appended 2% cellulose nanocrystal (CNC) with the addition of 0% KCl of 10.84%. It can be seen (From Fig.-3) that the decrease in Eb occurred with the addition of 2% cellulose nanocrystal (CNC). Cellulose nanocrystals (CNC) which have a fairly high crystallinity cause stiffness when added to bioplastics. The interaction between cellulose nanocrystal (CNC) with starch and glycerol is also limited due to the stiffness of the CNC it limits the movement of the polymer chains and breaks intermolecular bonds and reduces the elongation value at break.18 Then the value of Eb was augmented by the addition of 3% and 4% cellulose nanocrystal (CNC). The increasing number of fillers resulted in a decrease in the interaction between cellulose nanocrystal (CNC) and starch. According to Fazeli and Simao (2018), the difference in polarity between materials can reduce the tensile strength properties thereby increasing the elongation properties at the break.21 The addition of KCl has a significant effect in bioplastics on the elongation value at the break. The elongation at break value continued to increase with the increase in the amount of KCl dispersing agent in the bioplastic. The increase in Eb was due to KCl which has a high osmotic pressure so that it stabilizes the solution and spreads cellulose nanocrystal (CNC) evenly so that strong interactions are formed between starch, glycerol, and cellulose nanocrystal (CNC) molecules. This interaction will reduce the stiffness of the bioplastic, thereby increasing the flexibility and mobility of the bioplastic.18

**Thermal Gravimetry Analysis (TGA) of Bioplastic**

Thermal analysis was carried out on bioplastic samples of avocado seed starch and 30% glycerol, bioplastics of avocado seed starch with the appended 2% cellulose nanocrystal (CNC), and bioplastics with the appended 2% cellulose nanocrystal (CNC) and 2% KCl. The results of these samples can be seen in Fig.-4.

![Fig.-4: Thermal Gravimetry Analysis of Bioplastic](image)

**Table-1: Weight Loss Data of Bioplastic**

<table>
<thead>
<tr>
<th>Weightloss (%)</th>
<th>Temperature (°C)</th>
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<tbody>
<tr>
<td></td>
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<td>351</td>
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<td>60</td>
<td>382</td>
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TGA results showed that all samples started to lose weight from 5-80%. Starch bioplastics have several phases of the decomposition process. In the first phase, the process of dehydration occurs. The moisture content of the bioplastics was evaporated at a temperature of 63-200°C for starch bioplastics, starch + CNC
bioplastics, and starch + CNC + KCl bioplastics. At this stage, volatile matter compounds are lost, and the process of thermal decomposition occurs due to water evaporation. At a temperature of 220-330°C, a lignocellulosic thermal decomposition process occurs in starch bioplastics, starch bioplastics + CNC, and starch bioplastics + CNC + KCl with a weight loss percentage of 10-60% where the weight loss occurs due to the decomposition of cellulose nanocrystals. At a temperature of 330-460°C, the thermal decomposition process occurs in starch bioplastics, starch bioplastics + CNC, and starch bioplastics + CNC + KCl where weight loss occurs due to the decomposition of glycerol as a plasticizer and the decomposition of bioplastics into charcoal. The final stage is at a temperature of 460-500°C, thermal decomposition occurs in starch bioplastics, starch bioplastics + CNC, and starch bioplastics + CNC + KCl where the weight loss reaches 90% due to the decomposition of charcoal (charcoal), where the decomposition of charcoal (charcoal) is caused by volatile compounds and oxygen which diffuse into the charcoal (charcoal) thereby burning the charcoal (charcoal). Nurul et al. (2016) also mentioned in their research that T50% (the temperature at which 50% weight loss occurs) is at 250°C and 310°C, respectively for sweet potato and potato bioplastics. Based on Table-1, starch bioplastics with the appended of 2% cellulose nanocrystal (CNC) at high temperatures, had great thermal stability due to weight degradation appealed to bioplastics with starch and starch bioplastics with the appended 2% cellulose nanocrystals (CNC) and 2% KCl.

CONCLUSION
The appended of CNC to bioplastics improves the mechanical properties and thermal properties of bioplastics. The best value from bioplastic Ts analysis was 1.79 MPa at the appended 2% CNC and the appended 2% KCl. The best Eb value was 19.39% with the appended 4% CNC and the appended 3% KCl. The appended of 2% CNC at high temperatures, has great thermal stability due to heavy degradation compared to bioplastics with starch and starch bioplastics with the appended 2% CNC and 2% KCl in accordance with TGA results.

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CONFLICT OF INTERESTS
All authors have no conflicts of interest to declare.

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All the authors contributed considerably to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The author's research profile can be verified from their ORCID ids, given below:

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