The Effect of Chitosan, Sorbitol, and Heating Temperature Bioplastic Solution on Mechanical Properties of Bioplastic from Durian Seed Starch (Durio zibethinus)

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ABSTRACT
Nowadays, bioplastics are often researched to substitute the conventional plastics because bioplastics come from raw materials that is very environmentally friendly and bioplastics is degradable. The purposes of this research are to know the characteristics of starch from durian seed and to know the effect of additional chitosan as filler, sorbitol as plasticizer, and variation of heating temperature bioplastic solution on mechanical properties of bioplastics. In process, the ratio between durian seed starch and chitosan are 7:3, 8:2 and 9:1 gram, while the concentration of sorbitol are 20%, 30%, and 40%. The heating temperature of bioplastic solution is varied at 70°C, 80°C and 90°C. Result of bioplastic FTIR shows there is incrcation of wave number N-H from 1570.06 cm⁻¹ to 1589.34 cm⁻¹ and O-H from 3352.28 cm⁻¹ to 3653.18 cm⁻¹. The characteristic of durian seed starch has water content 12.73%, ash content 0.51%, starch content 76.65%, amylopectin content 22.34%, amylose content 54.32%, protein content 11.61%, and fat content 0.61%. Optimum mechanical properties of bioplastic from durian seed starch occurs in heating temperature 70 °C with composition between durian seed starch and chitosan is 7.3 grams and sorbitol 20.0 grams.

Keywords: starch, durian, chitosan, sorbitol, bioplastic

I. Introduction
The necessities of plastic in industries especially as packaging are more increasing at this time. It happens because plastics are better than others like glasses and metals. Plastic is light, its making process is easy, and it is not fragile [1]. However, the raw material of conventional plastic that comes from petroleum is more decreasing and its characteristic is non-degradable. Another weakness of conventional plastic is migration of vinyl chloride monomer as constituent unit from Polyvinyl Chloride (PVC). That monomer is carcinogenic which is dangerous or harmful to human health [2]. Nowadays, bioplastic is often researched to substitute the conventional plastic because bioplastic comes from raw material that is very environmentally friendly and bioplastic is degradable.

Bioplastic is plastic that is degradable because its constituent compounds derived from plants like starch, cellulose, lignin, and also derived from animals like caseins, proteins, and lipids [3]. Starch can be a promising material for plastic raw material because its characteristics are universal, biodegradable, and has affordable price [4]. The using of starch as plastic raw material has a great potential because in Indonesia there are various plants producing starch [5].

One plant which can be taken its starch is durian fruit seed (Durio zibethinus). Durian seed is a part of durian fruit was not consumed by the public because its taste is slimy and itchy at our tongue. Even though if we look at the nutritional content, durian seed has potential as a source of nutrition. It has protein, carbohydrate, fat, calcium and phosphorus [6].

Starch-based bioplastics have deficiencies. Those are low mechanical strength and less resistant to water (hydrophilic) [7]. Therefore, additional material should be added to starch-based bioplastics in order that such deficiencies can be overcome. To improve the mechanical strength of starch, filler (reinforcing) in the form of metal and natural materials are usually added to the polymer matrix. Chitosan is a natural substance that is used as an amplifier. Chitosan also can reduce the moisture of plastics because it is not soluble in water [8]. Chitosan is a macromolecule which can be found in the shells of crabs, shrimps, and insects [9]. Selection of chitosan as an alternative to make environment-friendly plastic because chitosan has good biodegradation properties [10]. Chitosan is also added to increase the transparency property of bioplastics to be produced [11].

In the manufacture of bioplastic, starch requires additives to get the mechanical properties that are soft, resilient, and strong. For that, it needs to added a liquid or solid in order to improve the properties of plasticity. Substance that is added is called plasticizer [8]. In simple concept, plasticizer that is organic solvent with high boiling temperature is added to the resin which is hard or rigid, so that the accumulation of intermolecular forces in a long chain will decrease,
consequently the flexibility, softening, and elongation of the resin will increase [12]. Polyols such as sorbitol is a plasticizer that is good enough to reduce internal hydrogen bonds thereby will increase the intermolecular distance [13].

II. Methodology

2.1 Starch Extraction of Durian Seed

Starch that was used in this research of bioplastic was starch that was extracted from durian seeds. Durian seeds were obtained from merchants durian “Ucok Durian” located at Jalan KH Wahid Hasyim, Medan, Indonesia. Durian seeds that had been collected then were cleaned and peeled.

Furthermore, durian seeds were cut, cleaned, and dried under the sun. Seeds that had been dried were blended with water at ratio 1 : 5 (w/v), then those were filtered. The filtrate was precipitated for 12 hours and the sediment was wet starch. Wet starch was dried in an oven with temperature 45 - 50 °C for 24 hours to obtain the dry starch. Dry starch was refined and sieved with 100 mesh sieve.

Starch durian seed was analyzed the water content, starch content, amylose content, amylpectin content, ash content, fat content, and protein content based on standard SNI-01-2891-1992, SNI-01-3194-1992, Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscope (SEM).

2.2 Manufacture Bioplastic and Testing Density, Water Absorption, Tensile Strength and Elongation at Break Bioplastic.

Durian seed starch and chitosan were weighed with a variation ratio 7 : 3, 8 : 2 and 9 : 1 of the total mass of starch and chitosan which were 10 grams. Starch solution was made by dissolving starch with distilled water (H2O). Chitosan solution was also prepared by dissolving chitosan which had been weighed before with a solution of acetic acid 1% wherein the ratio between chitosan and 1% acetic acid is 3 : 130 (w/v). Manufacture of bioplastic also added sorbitol as plasticizer with variation 20%, 30% and 40% of the total mass of the starch-chitosan. Glass beaker containing starch solution was placed on a magnetic stirrer hot plate while heated. Chitosan solution was then poured into a glass beaker containing starch solution. After 20 minutes, sorbitol was added to the solution and the solution was left up until the specific heating temperature bioplastic was achieved (temperature varied, T = 70 °C, 80 °C, dan 90 °C). Once the temperature was reached, the magnetic stirrer was turned off. Glass beaker containing a solution of bioplastic was cooled briefly before printing. The solution was poured into a mold bioplastic acrylic. The mold was then slowly put into an oven at temperature 45 °C for 24 hours. After the bioplastic was dry, bioplastic was removed from the mold and then stored in a desiccator. Bioplastic was ready to be analyzed.

Bioplastic that was successfully created was analyzed its tensile strength based on standard procedure ASTM D638-02a 2002, elongation at break based on ASTM D792-91 1991, Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscope (SEM).

III. Results And Discussion

3.1 Characterization of Durian Seeds Starch

The yield of starch extracted from the durian seeds is 20.58%, in which the starch in the form of powder and white with the particle size of 100 mesh. The chemical composition of durian seeds starch are presented in Table 1. Durian seeds starch is quite potential to be used as bioplastics due to starch contained in the starch extracted from durian seeds is quite high, that was 76.65%, with the ratio of amylose : amylpectin 22.34 : 54.32. There is a fairly large protein content in the durian seeds starch, it can induce browning reaction on bioplastics [14]. The presence of fat in the starch may form complexes with amylose thus granule surface enveloped by hydrophobic fat, it can inhibit the release of amylose from the granules during gelatinization [15]. But the fat content in the durian seeds starch is not high enough so it does not affect the gelatinization process.

<table>
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<tr>
<th>Component</th>
<th>Amount (%)</th>
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<tr>
<td>Starch</td>
<td>76.65</td>
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<tr>
<td>- Amylose</td>
<td>22.34</td>
</tr>
<tr>
<td>- Amylopectin</td>
<td>54.32</td>
</tr>
<tr>
<td>Moisture</td>
<td>12.73</td>
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<tr>
<td>Ash</td>
<td>0.51</td>
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<tr>
<td>Fat</td>
<td>0.61</td>
</tr>
<tr>
<td>Protein</td>
<td>11.61</td>
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</tbody>
</table>

3.2 Fourier Transform Infrared (FTIR)

The purpose of FTIR analysis is to identify the presence of hydrogen bonds that were formed in bioplastics. Fig. 1 below is the FTIR analysis result of durian seeds starch, chitosan, bioplastic from durian seed starch without chitosan and sorbitol, and bioplastic from durian seed starch with chitosan and sorbitol.
temperature variation on the mechanical properties of bioplastic.

3.3 Tensile Strength

The effect of increasing chitosan and sorbitol content and heating temperature solution of bioplastic on the tensile strength of bioplastics are shown in Fig. 2 and Fig. 3.

![Figure 2. The effect of increasing chitosan and sorbitol content on the tensile strength of bioplastics](image)

![Figure 3. The effect of increasing heating temperature of bioplastic solution on the tensile strength of bioplastics](image)

With the increasing concentration of chitosan and sorbitol cause the value of tensile strength of bioplastics is also increasing. Chitosan that was added in the starch solution is to fill and increase the density of bioplastics formed, so that it will increase the resilience of bioplastics on the testing of tensile strength. Addition chitosan can also undergo chemical bonding interactions with starch during the mixing process. Chemical bonds in the material can affect the mechanical strength, it is depending on the amount and type of chemical bonds (covalent bonds, hydrogen and van der walls) [17]. On the addition of chitosan, there are interaction between chitosan and starch suspension which are supported by the results of FT-IR showed an increase in wave numbers O-H groups and N-H groups on bioplastics. That increase are from interaction of the amyllose-amylopectin-chitosan. These hydrogen bonds increase the the value of tensile strength bioplastics.

With the increasing concentration of sorbitol, it can lower the tensile strength of bioplastics produced. The addition of sorbitol can also increase the absorption intensity of the O-H group on bioplastics. This is because the sorbitol has functional groups O-H [18]. But as a plasticizer, sorbitol molecules will slip between amyllose-amylopectin-chitosan chains and can weaken the interaction between that polymer.
thus prevent the formation of rigid structures and also soften the polymer matrix [19].

There was an effect of raising the heating temperature of bioplastics solution on tensile strength value in bioplastics. The rising heating temperatures could cause the decreasing value of tensile strength of bioplastics. This can be caused by the influence of higher temperatures that can cause intermolecular bonds in starch chains becoming more weak. The hydrogen bonds between amylose chains undergo the formation of the bond. Then further heating will break glycoside bonds (bonds between monomers) in amylose. Based on research Haryanti, et al., 2014, increasing the heating temperature can cause depolymerization in amylose chain, the straight chain amyllose fatty and become shorter, thus decreasing amyllose content [20]. Reduced levels of amyllose is influential in the process of making bioplastics, which amyllose was important instrumental in the formation gel and can produce the compact thin layer (film) [21]. So that by the reducing of amyllose content has impact on the decrease of the cohesiveness of bioplastics formed and the decrease value of tensile strength.

3.3.2 Elongation at Break

The effect of increasing chitosan, sorbitol content, and heating temperature solution of bioplastics on the elongation at break of bioplastics are shown in Fig. 4 and Fig. 5.

The addition of chitosan resulted in a decreased value of elongation at break. The amount of filler chitosan causes decrease the intermolecular bonding distance so that plasticizer molecules are in a separate area outside the polymer phase [22]. Decreasing bond distance is due to the increasing number of hydrogen bonds formed between molecules of chitosan with amylose and amylopectin. It makes bioplastics become increasingly rigid and less elastic.

Increasing the concentration of sorbitol can cause the elongation at break value of bioplastics to be increased. This is because sorbitol as the plasticizer has a quite low molecular weight when compared to polymeric compounds such as starch and chitosan, so with the addition of the sorbitol would increase the free volume of the polymer and the available sufficient space for the movement of polymer molecules [23].

The increasing heating temperature of bioplastic solution cause the value of elongation at break increases. That is because the heat that is given causes an increase in the kinetic energy of the molecules in which the molecules vibrate and create a free volume to allow larger molecular chains rotation [19]. Addition of sorbitol has been increasing the free volume of the polymer, then the increase in temperature will more increase the free volume, so that the elongation at break value of bioplastics is increasing.

3.4 Scanning Electron Microscope (SEM)

The purpose of the SEM analysis was to observe the morphology of fracture surface of the bioplastics, whether all components of bioplastics has been mixed homogeneously.
Scanning electron microscopy of fracture of bioplastic samples using a magnification of 5000x are presented in Fig. 6. When we compared differences in the structure of fracture of bioplastic in Fig. 6 (a) and Fig. 6 (b), it can be seen that bioplastics in Fig. 6 (a), bioplastics with the filler chitosan and plasticizer sorbitol have more dense and compact structure because the chitosan as a filler has been distributed homogeneously in the bioplastics that fills empty spaces in bioplastics, thus it is increasing the density of bioplastics. Homogeneity structure of bioplastics is one indicator that can indicate improvements in the value of the mechanical strength of the bioplastics [24]. This supports the results of this research that an increase in tensile strength of bioplastics is caused by the increasing concentrations of chitosan which has been distributed homogeneously.

IV. Conclusions
The addition of chitosan was able to increase the tensile strength of the bioplastics value because of increasing in hydrogen bonding between chitosan-amyllose-amylopectin chains. But it made bioplastics to be compact and rigid, so that the elongation at break value of bioplastics decreased. The opposite effect was provided by sorbitol. Sorbitol could increase the free volume between the polymer molecules, so it increased the elongation at break value of bioplastics. Sorbitol would weaken and soften the structure of bioplastics so that it lower the tensile strength value of bioplastics. Increasing the heating temperature of bioplastic solution caused the tensile strength value of bioplastic decreased and the value of elongation at break increased.

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