Bioplastic from Chitosan and Yellow Pumpkin Starch with Castor Oil as Plasticizer

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Abstract. This study has been conducted on bioplastic synthesis of chitosan and yellow pumpkin starch (Cucurbita moschata) with castor oil as plasticizer. The purpose of this study is to determine the characteristics of the effect of chitosan and starch composition of pumpkins against solvent absorption, tensile strength and biodegradable. The first stage of the research is the making of bioplastic by blending yellow pumpkin starch, chitosan and castor oil. Further, it tested the absorption capacity of the solvent, tensile strength test, and biodegradable analysis. The optimum absorption capacity of the solvent is obtained on the composition of Pumpkin/Chitosan was 50/50 in H₂O and C₂H₅OH solvent. Meanwhile the optimum absorbency in HCl and NaOH solvents is obtained by 60/40 composition. The characterization of the optimum tensile strength test was obtained on the 40/60 composition of 6.787 ± 0.274 Mpa and the fastest biodegradation test process within 5-10 days occurred in the 50/50 composition. The more chitosan content the higher the value of tensile strength test obtained, while the fastest biodegradation rate occured in the composition of yellow pumpkin starch and chitosan balanced 50:50.

1. Introduction
The use of plastic from petrochemical ingredients tends to increase. The Plastics have been used for various needs, such as food packaging, bottle drinks, and various household appliances and toys. Plastics from petrochemical raw materials can not be degraded either by the influence of solar radiation or microbial decomposers [1]. As a result, plastic waste from these products is also increasing along with the increasing use of plastic products, especially plastic as a packing material. Possible solutions to this problem have been given, such as recycling scrap plastic and burning plastic waste. Recycle plastic waste is difficult to obtain products with the same strength as plastic of origin because it is difficult to separate the plastic which is from the type of polymer. Burning plastic is also not a wise move, because it can cause air pollution due to the production of toxic gases, such as cyanide gas, chlorine, and carbon monoxide gas [2].

Other efforts continue to be encouraged is the synthesis of biodegradable plastics, namely strong plastic when used and immediately biodegradable or damaged when thrown away as garbage. In addition, the expected biodegradable plastic characteristics are that the resulting biodegradation product is not toxic to the environment. Synthesis of biodegradable plastics can be done through a number of alternatives, including copolymerization [3], biosynthesis [4], and poliblending between natural polymers and synthetic polymers [5-6]. Copolymerization is a chemical microstructure modification. This method has been able to create a variety of polymers as raw material for
biodegradable plastics, but considered less economical. Biosynthesis is a plastic synthesis by utilizing microbes. The disadvantage is that in addition to the resulting low yield of plastic is also difficult to regulate the resulting polymer chain structure, so the properties of plastic produced is usually difficult to control. The biodegradable plastic synthesis of highly economically viable prospects is through blending of natural polymers, in addition to being biodegradable in nature the polymer feedstock is readily available and renewable. A lot of very up-to-date research has been developed to ecologically friendly plastics through natural polymer blending. The environmentally friendly plastics through corn starch blending and thermoplastic chitosan have been synthesized [7]. The results show that the plastic film obtained has good thermal endurance, although the mechanical properties of polyblend are lower than the original chitosan. Furthermore, bioplastics can be obtained through blending of Polylactic acid and Poly-3-hydroxybutyrate [8]. The resulting polyblend show an increase in elongation at break. This characteristic is indispensable for plastic films, especially those used as food packaging.

Totally biodegradable plastics have been synthesized through blending of tapioca starch and chitosan with plasticizer from palm oil [9]. The results show that, in addition to being biodegradable, the polymer may be prepared in the form of films that can be used for food packaging. Other publication also reported the synthesis of poly (urethane-esters) of the lactone polyester prepolymer, and the resulting polymer is biodegradable [10]. Until now there has been limited publication about bioplastics from local raw materials of Aceh Province, such as pumpkin, taro, and others. Therefore, this research focuses on making bioplastic through blending of chitosan and starch from Aceh local raw material, that is from yellow pumpkin starch by using castor oil as natural plasticizer. The result of this research will contribute to the knowledge gap in the literature.

2. Experimental

2.1 Materials and equipment

The materials used in this study were yellow pumpkin starch, chitosan, castor oil, ethanol, sodium hydroxide pH 10, hydrochloride acid pH 5, acetic acid 5%, microbial Pseudomonas aeruginosa, nutrients agar (NA), Aquades, aluminum foil. The tools used in this research are glassware, hotplate, analytical scales, petri dish, tensile test equipment (IK Force Tester MCT-2150), needle, oven, spirit burner, laminar flow and autoclave.

2.2 Methods

2.2.1 Preparation of pumpkin yellow starch. Pumpkin fruit is firstly cleaned and separated from the hard skin and seeds. Then, it is washed using water to remove the fruit juice which is located in the middle of the pumpkin fruit. The next process is the pumpkin fruit is cut in small piece and adding enough water. Then it is blended until it becomes mush. The yellow pumpkin pulp that has been obtained is then filtered and allowed to stand for 50 minutes, to get the precipitate. After sterilizing for 50 minutes, the sediment still mixes with the water is filtered back so as to obtain wet starch deposition. The wet starch deposition is dried by an oven to obtain starch which is ready for use as a bioplastic feedstock.

2.2.2 Bioplastic synthesis. Bioplastic synthesis was performed by weighing chitosan and yellow Pumpkin starch with varying predetermined mass (Table 1). Then the chitosan is dissolved into 5% acetic acid while stirring with a magnetic stirrer. The same thing is also applied on yellow pumpkin starch until all the starch dissolves. Both solutions are mixed in a beaker and added with 15% of castor oil. After the sample begins to form the gel, the sample is poured into the mold and dried over the hotplate at 75 ° C until all the solvents evaporate and plastic films are obtained.

2.2.3 Tensile test. Bioplastic samples were cut to lengths of 4 cm and 1 cm wide. The measurement condition is a tensile velocity of 100 mm / min with a maximum load of 500 N. The sample is clamped
Table 1. Experimental Design on Bioplastic Synthesis

| Code | Chitosan/starch (%) | Chitosan mass (g) | Starch mass (g) | Total mass (g) |
|------|---------------------|-------------------|----------------|---------------|
| CP46 | 40/60               | 0.56              | 0.84           | 1.40          |
| CP55 | 50/50               | 0.70              | 0.70           | 1.40          |
| CP64 | 60/40               | 0.84              | 0.56           | 1.40          |

on a tensile test apparatus, and runs the apparatus according to a predetermined condition until the sample is disconnected. Repeated procedure above for each sample is done 3 times tensile test. Recorded tensile test results are presented in the form of tables between tensile strength and extension. The magnitude of the breaking strength of a material depends on the amount of loading applied and the cross section of the material itself according to the following formula:

\[ \sigma = \frac{F}{A} \]  

(1)

where \( \sigma \) = strength (Mpa), \( F \) = load at break (N), \( A \) = the cross-sectional of the polymer material (mm\(^2\)). While Young Modulus determined using the following formula.

Young Modulus (Mpa) = \( \frac{\sigma}{\varepsilon} \)

(2)

where \( \varepsilon \) = elongation at break, \( \Delta L \) = the difference between the length at break, and \( L_0 \) = the initial length.

2.2.4 Solvent uptake test. This test is based on the method performed by Pimpan, et al., 2001. Plastic is cut to the size of 1.0 cm x 1.0 cm. The plastic that has been cut is then weighed with an analytical balance sheet. The plastic is put into a 10 ml beaker filled with 5 ml solvent, then sterilized in room temperature. Every minute, the plastic is taken, the solvent on the plastic surface is wiped with a tissue, then weighed. The absorption capacity of the solvent is calculated using the following formula:

Solvent uptake = \( \frac{W - W_0}{W_0} \times 100\% \)

(3)

where: \( W_0 \) = weight of dry sample while \( W \) = weight of sample after immersion in the solvent

2.2.5 Biodegradation test. Bioplastic samples were cut to 1 x 1 cm size then sterilized using UV light in the laminar flow for 20 minutes. Sterilized bioplastic samples were incorporated into the biodegradation medium then incubated for 5, 10, 15 and 20 days

3. Result and Discussion

3.1 Bioplastic film

Bioplastic film obtained in this study is shown in Figure 1, which is a colored plastic film from light yellow to orange. The resulting of film color depended greatly on the composition of the pumpkin starch and chitosan. The color of bioplastic with a composition of at least 40% chitosan looks darker than the other two variations of bioplastic variation. This is influenced by the pigment base yellow pumpkin starch. The appearance of color pigment caused by starch used has not undergone bleaching and purification process.
Figure 1. Film bioplastic from pumpkin yellow starch and chitosan: (a) CP46, (b) CP55, (c)CP64

3.2 Solvent uptake.
Solvent uptake test is carried out to determine the resistance of a bioplastic sample to some type of solvent. The lyophobicity test is performed by weighing the bioplastic mass before and after dissolved into the solvent. The solvents used in this study were H\textsubscript{2}O, C\textsubscript{2}H\textsubscript{5}OH, HCl, and NaOH. The observed results of the solvent absorption by bioplastics are shown in Table 2.

| code | composition | Quantity absorption(%) |
|------|-------------|------------------------|
|      | chitosan/starch | H\textsubscript{2}O | C\textsubscript{2}H\textsubscript{5}OH | HCl (pH=5) | NaOH (pH=10) |
| CP46 | 40/60       | 13.903 | 0.258 | 22.032 | 19.451 |
| CP55 | 50/50       | 8.833 | 0.214 | 11.333 | 12.047 |
| CP64 | 60/40       | 9.628 | 0.485 | 10.771 | 9.914 |

Based on the data in Table 2, the lowest absorption capacity of H\textsubscript{2}O and CH\textsubscript{3}COOH solvents was produced by bioplastic films at a 50/50 composition. While the lowest absorption capacity of HCl and NaOH solvents is produced by 60/40 bioplastic film. This is due to the basic nature of chitosan that is hydrophobic, so that in a balanced composition between starch and chitosan cause molecular interactions that can decrease the hydrophilic nature of starch [11]. In the HCl and NaOH solvents, the highest adsorption capacity of the solvent is produced by the film on bioplastic variations in which the more yellow squash starch content. It is caused by hydrophilic amylose so easily soluble in water, strong base solution, slightly soluble in dilute acid [12].

3.3 Tensile test
The tensile strength of the film is a specific strength obtained from the maximum pull before breaking/tearing. This measurement is to determine the magnitude of force required to reach the maximum pull point on every surface area of the film. The result of tensile strength test from bioplastic of pumpkin starch can be seen in Table 3.

| No  | chitosan/starch | Tensile strength (Mpa) | Elongation (%) | Young modulus (Mpa) |
|-----|-----------------|------------------------|----------------|---------------------|
| 1   | 40/60           | 6.787 ±0.274           | 13.451 ±3.709  | 6.093               |
| 2   | 50/50           | 2.912 ±0.470           | 13.278 ±4.413  | 2.176               |
| 3   | 60/40           | 2.563 ±1.055           | 7.285 ±1.135   | 5.263               |

Based on the data in Table 3, the tensile strength of bioplastic samples is influenced by the variation of the composition of yellow pumpkin starch and chitosan, where the highest tensile strength
is found in the composition of starch/chitosan 40/60 of 6.787 Mpa. While the lowest tensile strength is in the 60/40 composition of 2.563 Mpa. Based on the results of this tensile test, it showed that the composition of chitosan is very influential on the increase value of tensile strength bioplastik starch pumpkin produced. This is due to the greater chitosan composition that encourages the formation of hydrogen bonds with stronger starch molecules [13].

Young modulus is the ratio between the tensile strength at break of the extension. The lower the modulus of young value the more elastic the bioplastic samples are tested and vice versa if the higher the modulus of young value the less the elasticity value and the tensile strength value is very high [14]. Bioplastic samples with the best elasticity are 50/50 compositions of 2.076 MPa. This is triggered by the peak stress on the strain at break (mm), the lower the peak load and the value of the strain value at breaks are greater the more elastic the bioplastic is produced. The graph of tensile test results by using the tool IK Force Tester MCT-2150 can be seen in Figure 2.

![Figure 2. Tensile test graph, (A) CP46, (B) CP55 and (C) CP64](image)

Based on Figure 2, the value of young modulus is greatly influenced by the chitosan content in the bioplastic film. The higher the chitosan content the modulus young value is also higher. The plastic film of the results of this study is better with the results achieved by publication on the manufacture of plastic films of corn starch and chitosan with a composition of 50/50, resulting from a modulus young value of 105 Mpa [15]

3.4 Biodegradation test
Biodegradation test is done by incubating bioplastic film in culture medium of pseudomonas aeruginosa. The film is incubated within a period of 5 days to 20 days. The surface of the biodegradation film at various time ranges is presented in figure 3. Based on figure 3, it is seen that the sample began to change after 5 days incubation in pseudomonas aeruginosa media. After 10 days of incubation seen in the media there has been a change of color, especially films with more starch content. After a 30-day biodegradation process, the film has been totally biodegradable, where the film is difficult to separate from the media due to damage. Films with larger starch content are easier to biodegradable. This is due to the presence of glucosidic bonds in the amyllose and amylopectin units. The existence of this bond causes the starch molecules more easily biodegraded through hydrolyzed mechanisms.
Figure 3. Biodegradation film: a = CP46 sample, b= CP55 sample, c = CP64, where the number of 0, 1, 2, 3, and 4 refers to before biodegradation, after 5 days biodegradation, after 10 days biodegradation, after 15 days biodegradation, and 20 days biodegradation.

4. Conclusion

Bioplastics of yellow pumpkin and chitosan have been successfully synthesized by polblending pathway and its can be printed in the form of thin films. The resulting film has a biodegradable characteristic for 20 days incubation in the medium of pseudomonas aeruginosa. The mechanical properties of bioplastics are highly determined by the composition of starch and chitosan, where the higher the chitosan content, the value of tensile strength and modulus of young increases. The adsorption capacity of water solvent, hydrochloric acid and sodium hydroxide is higher with the increase of starch content in plastic composition.

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