Application of Modified Starch in the Carragenan-Based Biodegradable Packaging from *Eucheuma cottonii* on Biodegradability and Mechanical Properties

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Abstract. The massive plastic production in Indonesia is an effort to meet the demand for the food packaging sector, which is nearly 40% of the total plastic demand. Plastics are not environmentally friendly because they are not degradable. Carrageenan-based biodegradable packaging in the form of bioplastic is an alternative, but it has disadvantages such as low resistance to water. Modified starch can be used to improve bioplastic characteristics. This research aimed to determine the application of modified starch in biodegradable packaging to its biodegradability and mechanical properties. This research is experimental which consists of primary parameters and supporting parameters. The independent variables used were modified starch (0, 1, 1.5, and 2 g). The experimental design used a completely randomized design (CRD) and data analysis using the Analysis of Variance (ANOVA) and the DMRT follow-up test. The results showed that the application of modified starch in biodegradable packaging based on carrageenan had a significant effect (p <0.05) on water resistance and the best test results were 2 g of modified starch (P3) with a water resistance value of 50.96% ± 4.86. Meanwhile, the results of biodegradability, tensile strength, and elongation were not significantly different.

1. Introduction

One of the factors of high plastic production is the effort to meet the demand for the food packaging sector which almost reaches 40% of the total plastic demand [1]. In 2015, plastic consumption in Indonesia reached 17 kg/capita/year. If in 2017 the population of Indonesia was around 261 million people, nationally the use of plastic reached 4.44 million tons [2]. Indonesia is ranked 2nd as the country that produces the highest plastic waste [3]. The amount of plastic waste that is quite high has a negative impact on environmental sustainability because it is difficult to degrade so that there is a buildup that pollutes the environment [4]. So the need for a solution such as the development of environmentally friendly biodegradable plastic.
Biodegradable packaging in the form of bioplastic is an alternative that has the potential to be developed by utilizing organic materials that can be degraded naturally. Bioplastics made from seaweed such as carrageenan are categorized into hydro colloidal plastics. When compared with other plastics, the category of hydro colloidal plastics has disadvantages such as low resistance to water, low mechanical properties in the absence of additional materials such as plasticizers. Carrageenan-based bioplastics need to be added with adhesives or fillers because they will produce less strong properties and low water resistance. This is caused by weak hydrogen bonds because the distance between the molecules is tenuous. Therefore, it is necessary to add adhesives to improve the mechanical properties of bioplastics.

The adhesive material that can be added to the bioplastic formulation is modified starch. One of the starches that can be used is tapioca flour, which has a fairly strong and transparent gel characteristic that is very supportive of fillers and adhesives [5]. However, tapioca flour has hydrophilic properties so it requires modification to produce a balance of hydrophilic and hydrophobic properties. Modification of starch is expected to change the molecular structure of starch that can be done physically, chemically, or enzymatically. Modification of starch aims to change the characteristics of gelatinization, gel formation, viscosity in the water medium, suspension stability due to the influence of heat, acid, and other processing processes.

2. Material and methods
This research was carried out at the Chemical Analysis Laboratory, Faculty of Fisheries and Marine Affairs, Material Physics Laboratory, Faculty of Science and Technology, Airlangga University, Surabaya from November 2020 to February 2021.

2.1. Material
The raw materials used include carrageenan from PT. Kappa Karrageenan Nusantara, tapioca flour, glycerol (C3H8O3), ethanol 96%, aquadest, sodium hydroxide (NaOH) 3%, hydrochloric acid (HCl) 0.5 N, and 5% acetic acid, Whatman paper No.93.

2.2. Method
The starch used is tapioca flour which is then modified by acetylation using acetic acid. 100 g of tapioca flour was dispersed into 225 mL of distilled water which was then stirred with a magnetic stirrer for one hour at room temperature. Furthermore, 16% acetic acid was added by the weight of the material used and allowed to stand for 1 hour. The suspension was maintained at pH 8 for 50 minutes by adding 3% NaOH at room temperature. After adding 0.5 N HCl to pH 4.5 - 5 for the reaction. The next process is washing and washing with aquadest three times and ethanol 96% once using a vacuum pump. Then the process of making Biodegradable packaging will be carried out.

Modified tapioca flour was dissolved in 100 mL of distilled water which was then heated to a temperature of approximately 85°C while stirring using a magnetic stirrer and hot plate. Then 3 g of carrageenan was added and stirred until homogeneous. It was allowed to stand at 60°C and then 5 mL of glycerol was added. The suspension was molded and allowed to stand for 2 hours at room temperature and then in an oven at 50°C for 48 hours. After drying, it is cooled in an open space until the temperature is the same as room temperature. After that will be tested.

2.2.1. Experimental design
The research used in this study was a completely randomized design (CRD) with 4 treatments and 5 replications design, obtained 20 research units. The independent variables used were modified starch (0, 1, 1.5, 2 g).
2.2.2. Biodegradation Test
The first step is to prepare a sample with a size of 2 x 2 cm and weigh the sample as the initial mass (W0) which is then buried in the soil for 7 days. After that, it was weighed again as the final mass (W). The following calculations are carried out in biodegradability testing:

\[
\text{Weight Loss (\%) } = \left(\frac{W_0 - W}{W_0}\right) \times 100\%
\]

\[
\text{Perfect Degradation Time (Day) } = \frac{100\%}{\text{Weight Loss (\%)}} \times \text{Test Time}
\]

2.2.3. Water Resistance Test
The water resistance test begins with cutting the sample with a size of 2 cm x 2 cm, then weighing the initial weight of the sample (W0). The sample was put in a beaker glass which had been filled with 30 mL of distilled water for 3 minutes. After 3 minutes the sample was removed and the water that was still attached to the surface of the bioplastic was removed with a dry tissue. The final weight (W1) was then weighed. The value of the weighing is entered into the equation. Furthermore, the water absorbed by the sample is calculated by:

\[
\text{Swelling (\%) } = \left(\frac{W_1 - W_0}{W_0}\right) \times 100\%
\]

2.2.4. Tensile Strength Test
The tensile strength test is the maximum stress that a material can withstand when it is pulled or stretched, tested referring to the American Standard Testing Method/ASTM (1993) using the MPY testing machine [6]. Sheets of film size 2.5 x 15 cm with humidity (RH) 50% for 48 hours. The Instron device is mounted on an initial grip separation of 50 mm, a crosshead speed of 50 mm/minute and a load cell of 50 kg, and is measured using the formula:

\[
\tau = \frac{F_{\text{maks}}}{A}
\]

2.2.5. Elongation Test
Elongation Percentage Test (elongation measured using Universal Testing Machine Auto Strain brand Yasuda Seiki which is based on the elongation of the film at break. The equation for tensile strength or elongation is as follows:

\[
\text{Elongation (\%) } = \left(\frac{A - B}{B}\right) \times 100\%
\]

2.3. Analysis Data
Data analysis using the Analysis of Variance (ANOVA) and the DMRT follow-up test.

3. Results and discussion
3.1 Results
Biodegradable packaging is printed like mica plastic packaging for dry food that is transparent. Parameters in this study consisted of Main Parameters and Supporting Parameters. The main parameters are Biodegradation Test and Water Resistance Test. While the Supporting Parameters are the Tensile Strength Test and Elongation Test based on the best results from the Main Parameters.
### Table 1. The Results of Parameter Tests on Biodegradable Packaging Compared with ASTM D-6002 and the JIS Food Packaging Industry Standard (Japanese Industry Standard)

| Parameter                        | Treatment | Standards |
|----------------------------------|-----------|-----------|
| Perfect Degradation Time (Day)   | P0: 15    | 60        |
|                                  | P1: 16    | ASTM D-6002 |
|                                  | P2: 17    |           |
|                                  | P3: 17    |           |
| Water Resistance (%)             | 132.78    | ≤ 70      |
|                                  | 112.46    |           |
|                                  | 92.76     |           |
|                                  | 50.96     |           |
| Tensile Strength (MPa)           | 3.3       | > 0.39 JIS |
|                                  | -         | (Japanese Industri Standard) |
| Elongation (%)                   | 49.5      | < 10 Very bad |
|                                  | -         | > 50 Very Good |
|                                  | -         |            |
|                                  | 53.4      |            |

**Figure 1.** Value Average Percent Loss of Weight Biodegradable Packaging
Figure 2. Biodegradable Packaging Swelling Percentage Chart
Note: Different superscript letter notations in the same column showed a very significant difference between the differences (P < 0.05). However, the same superscript letter indicated that the treatments were not significantly different (P > 0.05).

Figure 3. Tensile Strength Chart of Biodegradable Packaging
3.2 Discussion

The packaging of the biodegradable formula with the addition of modified starch resulted in the lowest percentage of biodegradation reaching 41.62% ± 7.4. The more addition of modified starch, the lower the percentage of biodegradation. The decrease in the percentage of biodegradation is thought to be due to the addition of modified starch which has hydrophobic properties. This is the same as the research results of Hartatik et al. (2014) which states that as the addition of hydrophobic chitosan increases, the level of damage to bioplastics is degraded longer and the level of damage is less [7].

Based on the International standard (ASTM) so that the time required for the film to be degraded (biodegradation) for PLA plastic from Japan is 60 days to decompose 100% or completely. PLA or polylactic acid (PLA) is a bioplastic or organic plastic which is a type of plastic made from vegetable oil, corn starch, pea starch, and microbati. In this study, the time used was 7 days with an average biodegradation percentage value of around 41.62% ± 7.4 – 45.71% ± 3.5 and a complete degradation time of 15-17 days. These results indicate that the biodegradable packaging in this study met the criteria for the degradation of bioplastic films. Biodegradable packaging contains hydrophilic materials which will make it easier for decomposing bacteria to colonize. Bacterial colonies will stick to the surface of the bioplastic and form a biofilm, then the bacteria will break down complex polymers into simpler ones so that they can accelerate the degradation process [8].

The packaging of the biodegradable formula without the addition of modified starch resulted in the highest swelling value reaching 132.78% ± 30.85 (P0). The greater the concentration of carrageenan, the greater the level of water absorption, this is caused by carrageenan which has more hydroxyl (OH) groups so it tends to be higher in absorbing air [9]. Carrageenan is hydrophilic in the presence of a free hydroxyl group (OH) capable of forming hydrogen bonds with H2O as a solvent. In addition, carrageenan contains sulfate esters which are also hydrophilic and in the sulfate ester group, there is sulfite (SO3-) which can bind to water. The addition of plasticizers can also increase the water absorption of the film because it has hygroscopic properties that affect the mechanical properties of the bioplastic and contribute to the reduction of the close intermolecular strength. The greater the addition of modified starch, the swelling value in the biodegradable packaging will decrease.

The biodegradable packaging formulated with the addition of 2 g of modified starch had the lowest swelling value of 50.96% ± 4.86. Based on the Japanese Industrial Standard (JIS), the swelling value of bioplastic material is 70%, so that P3 meets the standards which have the lowest air absorption properties and the highest air resistance compared to other treatments. The lower the water absorption, the better the plastic properties, while the higher the water absorption, the plastic properties will be easily damaged [10]. This was due to the addition of modified starch which had better hydrophobic properties when compared to non-modified starch. Therefore, more and more modified starch is added to the packaging.
of the biodegradable formulation so as to increase its ability to air resistance. The hydrophobic nature of modified starch is due to the acetylation process using acetic acid which is able to make hydrogen in starch, because the acetyl group in acetic acid causes more OH- groups to be substituted by acetyl groups [11]. The ability of bioplastics to absorb water can also be seen in the morphological structure of the film which has many cavities that function to absorb water content [10].

The results of the analysis showed that the increase in the concentration of modified starch had no significant effect on the tensile strength of the biodegradable packaging, the graph of the tensile strength results showed an increase between P0 and P3 with the tensile strength values of 3.3 MPa and 3.48 MPa respectively. The value of tensile strength that is not significantly different is expected because the addition of starch is still low so it does not have a significant increase in the value of tensile strength. The greater the concentration of modified starch, the more modified starch is formed so that the elongation value of polymeric materials depends on the mobility of the polymer molecular chains that the elongation of polymeric materials depends on the mobility of the polymer molecular chains [15]. This can explain the higher elongation value of glycerol compared to other plasticizers such as bioplastic sorbitol because the mobility of glycerol plasticizers is higher than that of sorbitol plasticizer [16]. Glycerol enters into the amyllose intermolecular or between modified starch hydrogen and carrageenan, it will disrupt the modified compactness, reduce intermolecular interactions, and increase mobility so as to increase elongation [17].

4. Conclusion
The results showed that the application of modified starch in carrageenan-based biodegradable packaging had a significant effect (p < 0.05) on water resistance and the best test result was 2 g of modified starch (P3) with a percent water resistance value of 50.96% ± 4.86. While the results of biodegradability, tensile strength, and elongation showed no significant difference.

5. References
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