Application of modified starch on plastic bag bioplastic based on carrageenan from *Eucheuma cottonii* on mechanic and biodegradation properties

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Abstract. Types of polysaccharides such as carrageenan are potential materials used as biofilms. Modified starch is a material that can reduce the hydrophilic properties and increase the mechanical properties of bioplastics. The objectives of this study were to determine the effect of using carrageenan and modified starch on mechanical properties and biodegradation. The experiment was conducted using a completely randomized design factorial. The treatments applied were the concentrations of carrageenan (2 and 3 gram) and modified starch (0, 0.5, 0.7, and 0.9 gram). The results showed that the addition of high carrageenan increased tensile strength, water resistance but decreased elongation and slowed biodegradation. The addition of modified starch improves the mechanical properties but slowed the biodegradation.

1. Introduction

Plastic is a primary need today, because of its lightweight nature, however conventional plastic decomposition takes 300 to 500 years to completely decompose. Handling by burning is not a good solution because it will form dioxin compounds. One of the conventional plastic is a plastic bag. Plastic bags are plastics that are included in the type of Low Density Polyethylene (LDPE) plastic [1]. The solution to this problem is bioplastics.

Bioplastics are plastics whose polymers are made from natural and renewable materials and are easily biodegradable by microorganisms. Bioplastic has several components as its constituent. The main ingredients are components or basic materials that make bioplastics, while additional materials are materials used as materials to achieve the physical and mechanical properties formed, which consist of a plasticizer and a filler [2].

Types of polysaccharides such as carrageenan are potential materials used as biofilms. Carrageenan is a type of linear polysaccharide compound extracted from seaweed from the *Rhodophyceae* family. Biodegradable plastic bag based on carrageenan are able to produce bioplastics with characteristics that resemble conventional plastics. The plasticizer used is sorbitol, according to Putra *et al.* [3] the value of tensile strength and elongation in the use of sorbitol as a plasticizer is higher than that of glycerol. Sorbitol which is added as a plasticizer in bioplastics will increase elasticity.

The characteristic of bioplastic or plastic is its resistance to water. Carrageenan and sorbitol are hydrophilic due to the presence of a hydroxyl group and a sulfate group [4]. Bioplastics need the addition of hydrophobic materials. Modified starch is starch with modified thermoplastic characteristics, one of
which increases hydrophobic properties. In addition to hydrophobic properties, the addition of modified starch can also improve the mechanical properties of bioplastics. Modified starch is starch that has been modified by a chemical reaction [5].

The purpose of this study were to determine the effect of using modified starch and carrageenan from seaweed Eucheuma cottoni on mechanical properties and biodegradation and to determine the interaction of modified starch and carrageenan from seaweed Eucheuma cottoni to produce the best formulation of bioplastic plastic bags.

2. Materials and Methods

2.1 Materials

Tapioca starch, aquades, NaOH, HCl, acetic acid, ethanol, soil and Carrageenan from PT. Kappa Carageenan Nusantara, Pasuruan, Jawa Timur.

2.2 Research methods

Using Completely Randomized Design method – 2 factorials with 3 replications. The first factor is the addition of Carrageenan Concentration with 2 treatment levels (2 and 3 grams). The second factor is the addition of Modified Starch Concentration with 4 treatment levels (0, 0.5, 0.7 and 0.9 grams).

| No | Material     | Unit | Treatment |
|----|--------------|------|-----------|
| 1. | Carrageenan  | Gram | K2P1  2, K2P2  2, K2P3  2, K2P4  3, K3P1  3, K3P2  3, K3P3  3, K3P4  3 |
| 2. | Aquades      | mL   | 100 100 100 100 100 100 100 100 |
| 3. | Sorbitol     | mL   | 5 5 5 5 5 5 5 5 |
| 4. | Modified Starch | Gram | 0 0.5 0.7 0.9 0 0.5 0.7 0.9 |

2.3 Making modified starch

100 grams of tapioca were mixed with 225 mL of distilled water, homogenized at room temperature for one hour. The next step is to add 5% acetic acid as much as 16% by weight of starch. The pH of the suspension was maintained at pH 8 by adding 3% NaOH at room temperature. Then left for 50 minutes, for the reaction. After that, the addition of HCl with a concentration of 0.5 N to pH 4.5. then, precipitation is carried out, after that washing with aquades and ethanol, filtered with watman paper. The starch was dried in an oven for 20 hours at 50°C. After drying, the starch is ground and sieved to reduce the molecules or refine the starch.

2.4 Making bioplastic

The modified starch according to the treatment concentration was dissolved into 100 mL of distilled water and then heated and homogenized to 85°C. Then add carrageenan and homogenize. After that, 5 mL of sorbitol was added to the solution and homogenized for 2 minutes and maintained at 65°C. Then the bioplastic is molded and then dried in an oven at 50°C for 24 hours.

2.5 Mechanical properties

2.5.1 Tensile Strength

Following ATSM D 882, the sample under test is cut to standard and both ends are clamped on the testing machine. The initial length is recorded and the tip of the recording ink is placed at position 0 on the chart. The start knob is turned on and the tool will pull the sample until it breaks and the tensile strength (F) and length after breaking are recorded [6]. The value is calculated by the equation:

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

\(\tau\) is tensile strength, F is the maximum applied load (kg), and A is the cross-sectional area (mm2).
2.5.2 Elongation
The percent elongation test was carried out on increasing the length of the bioplastic when the bioplastic broke [7]:

$$%€ = \frac{X_1}{X_0} \times 100\%$$

$X_1$ is the final length of the sample (cm) and $X_0$ is the initial length of the sample (cm).

2.5.3 Water resistance
The sample cut to a size of 2 x 2 cm, then the initial weight of the sample ($W_0$) is weighed. Put in a beaker glass containing 30 mL of distilled water for 3 minutes. The sample is removed and dried using a tissue, after which the final weight of the sample ($W_1$) is weighed [8].

$$swelling (\%) = \frac{W_1 - W_0}{W_0} \times 100\%$$

$W_1$ is the final weight of the sample and $W_0$ is the initial weight of the sample.

2.6. Biodegradation
Performed by soil burial test with soil that has a pH of 6 – 8 [9]. The sample was cut to a size of 2 x 2 cm and then weighed the initial weight, buried in the soil with a depth of 10 cm and weighed after being buried within a period of 7 days [3]. The value obtained is calculated by the formula:

$$ (%)lost weight = \frac{W_0 - W_f}{W_0} \times 100\%$$

$W_0$ is the initial weight of the sample and $W_f$ is the final weight of the sample.

3. Result and discussion

Table 2. Test results for bioplastic test parameters 2 gram carrageenan

| Parameters              | Carrageenan | Modified Starch |
|------------------------|-------------|-----------------|
|                        | 0 g         | 0.5 g | 0.7 g | 0.9 g |
| Tensile Strength (MPa) | 6.952       | -     | -     | 7.665 |
| Elongation (%)         | 37.67       | -     | -     | 40.33 |
| Water Resistance (%)   | 132.74      | 114.25 | 100.41 | 87.08 |
| Biodegradation (%)     | 62.58       | 59.59 | 58.59 | 58.10 |

Table 3. Test results for bioplastic test parameters 3 gram carrageenan

| Parameters              | Carrageenan | Modified Starch |
|------------------------|-------------|-----------------|
|                        | 0 g         | 0.5 g | 0.7 g | 0.9 g |
| Tensile Strength (MPa) | 10.537      | -     | -     | 8.702 |
| Elongation (%)         | 24.33       | -     | -     | 28.00 |
| Water Resistance (%)   | 121.56      | 93.33 | 87.14 | 77.39 |
| Biodegradation (%)     | 60.67       | 46.69 | 45.31 | 44.29 |
3.1 Mechanical Properties

3.1.1 Tensile Strength

The highest tensile strength value is in K3P1 with a concentration of 3 grams of carrageenan and 0 grams of modified starch with a value of 10.537 MPa, while the lowest tensile strength value is in K2P1 with a concentration of 2 grams of carrageenan and 0 grams of modified starch with a value of 6.942 MPa.

| Source                      | Type III Sum of Squares | df | Mean Square | F      | Sig.  |
|-----------------------------|-------------------------|----|-------------|--------|-------|
| Corrected Model             | 21.934*                 | 3  | 7.311       | 7.084  | .012  |
| Intercept                   | 859.231                 | 1  | 859.231     | 832.540| .000  |
| Carrageenan                 | 16.096                  | 1  | 16.096      | 15.596 | .004  |
| Modified Starch             | .927                    | 1  | .927        | .899   | .371  |
| Carrageenan*                | 4.910                   | 1  | 4.910       | 4.758  | .061  |
| Modified Starch             |                         |    |             |        |       |
| Error                       | 8.256                   | 8  | 1.032       |        |       |
| Total                       | 889.422                 | 12 |             |        |       |
| Corrected Total             | 30.190                  | 11 |             |        |       |

The test results show that only at the concentration of carrageenan there were differences in treatment. The tensile strength values are not significantly different, there was a possibility in the treatment of adding a low concentration of modified starch so that the tensile strength values were obtained with an insignificant increase in value.

There are differences in tensile strength results when modified starch is added at different carrageenan concentrations. Carrageenan concentration of 2 grams, the addition of modified starch increased the tensile strength value, but at 3 grams carrageenan concentration the value decreased. According to Rizky [5], modified starch can increase the mechanical properties and the value of tensile strength at a concentration of 2 grams of carrageenan which increases with the addition of modified starch. The decreasing tensile strength test value may be caused by several factors. Mixing that is not homogeneous so that the insertion of the material into the matrix is not perfect, human errors, testing, the molding process and drying time in the oven due to the heating or drying process of bioplastics affect the shrinkage and removal of the water content of bioplastics.

Carrageenan with a higher concentration will cause the bonds between the molecules that make the bioplastics to increase, resulting in a more compact bioplastic. Carrageenan can bind water so that the lower the carrageenan which is given tends to form an elastic and soft gel, but the higher the carrageenan which is given tends to form a hard and stiff gel so that the force required to break the film is greater [10]. The yield of tensile strength increases with increasing concentration due to the interaction between carrageenan and modified starch which forms stronger hydrogen bonds and is difficult to break.

3.1.2 Elongation

The highest percent elongation value is in K2P4 with a concentration of 2 grams of carrageenan and 0.9 grams of modified starch with a value of 40.33%, while the lowest percent elongation value is in K3P1 with a concentration of 3 grams and 0 grams of modified starch with a value of 24, 33%.
The test results show that only at the concentration of carrageenan there is significant. The decrease in the percentage of elongation occurred due to an increase in the concentration of carrageenan. Increasing the concentration of carrageenan will increase the dissolved solids in the bioplastic. So that the higher the added carrageenan, the lower the percent elongation value because it will form a stronger and inelastic film matrix. Carrageenan with a higher concentration will increase the dissolved solids and form a stronger polymer chain. The matrix space will be filled and the movement of polymer molecules will be reduced [11].

Meanwhile, with the addition of modified starch, the percent elongation value increased. This is due to the presence of an acetyl group in modified starch which has more elastic properties than ordinary starch. This proves that as the concentration of modified starch increases, the percent elongation increases [5]. In addition, amylose in starch affects the formation of a strong gel, gel flexibility and film strength. While amylopectin is very effective in preventing the occurrence of broken granules due to gelatinization [12].

### Water Resistance

The test results show the amount of water absorbed. Low water absorption indicates high water resistance. This means that water absorption is thickly proportional to water resistance. The highest water absorption value is in K2P1 with a concentration of 2 grams of carrageenan and 0 grams of modified starch with a value of 132.2 %, while the lowest water absorption value is in K3P4 with a concentration of 3 grams of carrageenan and 0.9 grams of modified starch with a value of 77, 39%.

The decrease in water absorption with increasing concentration of carrageenan is due to carrageenan as a basic material carrying dissolved solids in the solution of making bioplastics which causes hydrogen bonds to form between molecules that make bioplastics. This results in reduced free water in the
resulting bioplastics. The low concentration of carrageenan in the bioplastic forming solution will increase the availability of free water that participates in the polymerization reaction [13].

The results of statistical analysis on modified starch showed that it had a significant effect on the 5% test level. The increase in water resistance is due to the modified starch having hydrophobic properties. The hydrophobic nature of modified starch due to the acetylation process using acetic acid is able to weaken the hydrogen bonds in starch, because the acetyl group in acetic acid causes more OH- groups of starch to be substituted by acetyl groups.

3.2 Biodegradation
The highest biodegradation value is in K2P1 with a concentration of 2 grams of carrageenan and 0 grams of modified starch with a value of 60.91%, while the lowest biodegradation value is in K3P4 with a concentration of 3 grams of carrageenan and 0.9 grams of modified starch with a value of 44.29%.

| Source                  | Type III Sum of Squares | df  | Mean Square | F      | Sig. |
|-------------------------|-------------------------|-----|-------------|--------|------|
| Corrected Model         | 1030.466*               | 7   | 147.209     | 3.750  | .014 |
| Intercept               | 67461.588               | 1   | 67461.588   | 1718.682 | .000 |
| Carrageenan             | 946.145                 | 1   | 946.145     | 24.104 | .000 |
| Modified Starch         | 72.988                  | 3   | 24.329      | .620   | .612 |
| Carrageenan * Modified Starch | 11.333               | 3   | 3.778       | .096   | .961 |
| Error                   | 628.031                 | 16  | 39.252      |        |      |
| Total                   | 69120.085               | 24  |             |        |      |
| Corrected Total         | 1658.497               | 23  |             |        |      |

The results of statistical analysis showed that only the carrageenan concentration treatment had a significant effect on the 5% test level. The test results show that the higher the concentration of carrageenan and modified starch, the lower the biodegradation value. This indicates that as the concentration increases, the ability of microorganisms to degrade will also increase.

Carrageenan can bind water and result in reduced free water content in the resulting bioplastics so that dissolved solids in bioplastics increase. Biodegradation has decreased because the modified starch has been substituted by an acetyl group which results in the modified starch having hydrophobic properties. The addition of biopolymers with hydrophobic materials, the level of damage to bioplastics to be degraded will be longer and the level of damage will be less [10].

Biodegradation is affected by the composition of the film. The high biodegradation value at carrageenan concentration of 2 grams and without the addition of modified starch was due to the hydrophilic nature of carrageenan. This is directly proportional to the water resistance value of bioplastic plastic bags where the highest water absorption is at a carrageenan concentration of 2 grams and without the addition of modified starch. The more hydrophilic the bioplastic, the easier it is to dissolve in the soil, because of the absorption of water, making it easier for microorganisms to accelerate the degradation process [8].

4. Conclusions
The application of the concentration of carrageenan and modified starch has an influence on the mechanical properties and biodegradation. Carrageenan and modified starch in each test show no interaction. The best formulation for tensile strength is carrageenan concentration of 3 grams and modified starch 0.9 grams. The best formulation for elongation is carrageenan concentration of 2 grams and modified starch 0.9 grams. The best formulation for resistance is 3 grams of carrageenan and 0.9 grams of modified starch. Meanwhile, the best formulation for biodegradation is carrageenan concentration of 2 grams and modified starch 0 grams.
5. References
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