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Application of Modified Starch on Carrageenan-Based Bioplastic's Cup From *Eucheuma cottonii* on Biodegradability and Water Resistance

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Abstract

Polysaccharides from carrageenan have potential as bioplastics that is resistance to waters (hydrophobic), alsocan be improved by using modified starch. Modified starch is a material that can reduce the hydrophilic properties of bioplastics. The objectives of this study were to determine the effect of modified starch application on carrageenan-based bioplastic's cup on biodegradability and water resistance and to determine the best bioplastic formulation for biodegradability and water resistance. This study was conducted using experimental methods in the biodegradation test and the resistance or swelling test. The experimental method in this study used a completely randomized design (CRD) at a significance level of 5% ($\alpha = 0.05$). The results of this study indicate that the addition of high modified starch can increase the water resistance of bioplastics but the addition of high modified starch will result in slower biodegradability..

Keywords: bioplastic, carrageenan, biodegradability, and water resistance

1. Introduction

Plastic is a packaging material that is widely used in various products and includes single-use packaging and produced worldwide in large quantities (Yamada *et al*., 2020). As a packaging, plastics are widely used because of lightweight, cost-effective, and durable (Tanksale *et al*., 2021). It can be made from synthetic or semi-synthetic organic materials (Verma *et al*., 2016). But currently studied that plastic is one of the main sources that cause problems in environmental pollution (Usha *et al*., 2011). One of the contributors to plastic waste that can cause waste is the use of plastic cups.

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Plastic cups are drinking cup made of plastic materials with lightweight and water-resistant properties. Plastic cups derived from *polypropylene* (PP) will be difficult to decompose by microorganisms because the carbon element forms complex and long chemical chains (Chintya and Rika, 2017). Reduction of plastic cup waste can be pursued with waste processing technology, recycling, and incineration. The countermeasure that is often done is to burn plastic waste. The use of this method has not been effective in solving problems that arise due to plastic cup waste. Burning plastic waste will produce toxic gases such as dioxins, furans, mercury and polychlorinated biphenyls which can increase global warming (Verma *et al*., 2016).

Based on these problems, there are some studies focusing on bioplastics. Reducing the use of plastic cups can be done by formulating materials that can decompose naturally. Bioplastic is an alternative way to use plastic packaging made from natural materials that is environmental friendly and easy to be degraded (Rahim *et al*., 2020).

Materials that often used to form bioplastics are derived from polysaccharides from carrageenan and starch (Coniwanti *et al*., 2014; Yuniarti *et al*., 2014; Susanti *et al*., 2015). Carrageenan is a natural material that can be used as a gelling agent during the production of bioplastics (Sari *et al*., 2021). Carrageenan is a group of galactose polysaccharides produced from the extraction of red seaweed. Carrageenan is a hydrocolloid compound that can be used in the manufacture of bioplastics (Maryuni *et al*., 2018). Carrageenan has a free hydroxyl group (OH^-) which is able to form hydrogen bonds with H2O so that carrageenan can be hydrophilic (Sulistyo *et al*., 2018). Red algae (Rhodophyta) such as *Kappaphycus alvarezii* and *Eucheuma cottonii* was known to produce carrageenan beside their ability of maintaining the fish quality (Nafisyah *et al*., 2015; Ermawati *et al*., 2015). While in this study the carrageenan was derived from *E. cottonii*.

Bioplastics made from natural materials have properties that are rigid and easily brittle, so they require *plasticizers* (plasticizers). *Plasticizer* is an organic material that has a low molecular weight and can be added to a product to reduce the stiffness of the polymer, while increasing the flexibility and extensibility of the polymer (Anita *et al*., 2013). Sorbitol is one of the *plasticizers* that is often used in the manufacture of bioplastics. Sorbitol is monosaccharide compound *polyhydric alcohol* a hydrophilic (Putra *et al*., 2017).

One of the must-have properties of bioplastics is water resistance (hydrophobic). The filler that can be added to increase the hydrophobic properties of bioplastics is modified starch. Modified starch is starch that has been treated to produce better properties than before, besides that it will produce starch with the characteristics of a softer texture, high stability, and longer shelf life than unmodified starch (Yeh and Yeh, 1993).

2. Material and Methods

Material

The raw materials used in this study were carrageenan from PT Kappa Carageenan Nusantara (KCN) Pasuruan, Indonesia. The tapioca flour (Rose Brand), aquadest, sorbitol, 0.5N HCl, 3% NaOH, 96% ethanol, 16% acetic acid, Whatman paper no.93.

Methods

Process of Making Modified Starch by Acetylation

Starch was processed by the method of If'all *et al*. (2019). The initial preparation for the material is to prepare 100 g of tapioca flour dispersed into 225 ml of distilled water, stirred with a magnetic stirrer for an hour at room temperature. pH was maintained to 8 by adding 3% NaOH. Furthermore, 16% acetic acid was added by 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 that, 0.5 N HCl was added to pH 4.5 - 5. The next process was precipitation and washing with distilled water three times and ethanol once. Washing was carried out by pouring the suspension into a beaker glass and adding 50 mL of distilled water, stirring vigorously using a stirring rod and then filtering using whatman paper and *vacuum pump*, washing with distilled water was repeated three times. The washing steps with ethanol were carried out the same as washing with distilled water. Then drying in the oven at a temperature of 50˚C for 20 hours. The last stage is refining and filtering.

The Process of Making Bioplastic's Cup

Production of bioplastic as packaging refers to the method by Yanti (2020) which is modified on the concentration of the basic ingredients, the concentration of plasticizers, and the drying method. Dissolve the modified starch according to the treatment concentration that has been applied (0, 1, 2, 3 g) into 100 mL of distilled water, heated to a temperature of 85°C and stirring using a *hot plate* and a *magnetic stirrer*. Carrageenan (3 g) was added and stirred until homogeneous (Putri, 2019), it took about 15 min. After being homogeneous, 5 mL of sorbitol was added and stirred for 2 min while maintaining the suspension temperature at 60°C. The suspension was molded, allowed to stand at room temperature for 2 h and 50°C for 24 h (Rusli *et al*., 2017).

Table 1. Formulations of bioplastics

No.	Material	Unit	Treatment			
			P0	P1	P2	P3
1.	Carrageenan	g	3	3	3	3
2.	Modified starch	g	0	1	2	3
3.	Sorbitol	mL	5	5	5	5
4.	Aquadest	mL	100	100	100	100

Biodegradation Process

The biodegradation test refers to the method of Ashok *et al*. (2018) with slight modifications. The initial stage is cutting the sample with a size of 2 × 2cm, then weighing (W1). The bioplastic samples were buried in the soil with a depth of 8 cm for a period of 7 days. After that, the samples were cleaned and re-weighing (W2). The percentage value of the average mass reduction of the buried bioplastic is obtained through the following equation:

$$\text{Weight loss } (\%) = \frac{\text{W1} - \text{W2}}{\text{W1}} \times 100\%$$

$$\text{Perfect degradation time} = \frac{100\%}{\%\text{ lose weight}} \times \text{test time}$$

Note:
Biodegradation Test (%) = percentage of decomposition of the bioplastic
W1 = initial weight
W2 = final weight

Water Resistance Test

Water resistance test is aiming to determine whether the bioplastic is water soluble or not within a certain time and temperature. This test is used to determine the occurrence of bonding in the polymer and the degree or regularity of the bond in the polymer which is determined from the percentage increase in polymer weight after experiencing swelling. The process of diffusion of solvent molecules into the polymer will produce a bulging gel. The test begins by cutting the sample with a size of 2 x 2 cm, then weighing the initial weight of the

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sample (W_0). The sample was put in a beaker glass which had been filled with 30 mL of distilled water for 3 min. The sample was removed and waters that still attached to the surface of the bioplastic was removed with a dry tissue before final weighing (W_1).. The value of the weighing is entered into the equation (Illing and Satriawan, 2018).

$$\text{Water resistance (\%)} = \frac{W1 - W0}{W0} \times 100\%$$

Note:

Water resistance (%)	= percentage of plastic polymer swelling
W0	= initial weight
W1	= final weight

3. Result and Discussion

Effect of modified starch to biodegradability

Table 2. Result of biodegradation

Treatment	Carrageenan (g)	Aquadest (mL)	Sorbitol (mL)	Modified Starch (g)	Biodegradability (%) ± SD	Water resistance standard based on ASTM 5336 (day)
P0	3	100	5	0	$55.68^{b} \pm 4.32$	≤ 60
P1	3	100	5	1	$53.33^{b} \pm 6.03$	
P2	3	100	5	2	$49.26^{ab} \pm 7.15$	
P3	3	100	5	3	$42.75^{a} \pm 4.74$	

Table 3. Time of biodegradation

Treatment	Modified Starch (g)	Time of biodegradation (day)
P0	0	13
P1	1	13
P2	2	14
P3	3	16

The results of biodegradation test of bioplastics with the addition of the highest concentration of modified starch (3 g) has a value of 42.75%. Meanwhile, without adding modified starch the biodegradation value is 55.68%. The bioplastic's cup can be completely degraded within 13-16 days. These results indicate that the biodegradability of bioplastics with the addition of modified starch can meet the international plastic standard (ASTM5336). According to ASTM5336, the biodegradability time for PLA plastic from Japan and PCL from the UK takes 60 days to completely decompose.

The results of biodegradation test in this study indicate that higher addition of modified starch may cause the decreas on biodegradability. The decrease in biodegradability can be influenced by the hydrophobic nature of the modified starch. This hydrophobic nature can affect the activity of microorganisms in their ability to degrade bioplastics. This is in accordance with Hendrawati *et al*. (2015), hydrophobic properties can affect the water absorption ability of bioplastics and will affect the rate of degradation of bioplastics. Hydrophobic properties affect the activity of

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microorganisms because microorganisms need water for metabolism. The more addition of modified starch, the less water absorption. Such bioplastics will take a longer time to degrade due to the inhibition of degrading microorganisms.

Biodegradation in bioplastics can be influenced by temperature, humidity which determines soil pH, and microorganism activity (Marchelvam *et al*., 2019). The soil pH is very important because microorganisms can decompose bioplastics in soil. If the pH of the soil is in accordance with the activity of microorganisms, then its activity in degrading bioplastics will be optimal. According to Winkelmann *et al*. (1992), the optimum pH for soil microorganism activity produced by *Bacillus* sp. ranged from pH 6.5±7 or neutral pH. *Bacillus* sp. and *Pseudomonas* sp. can degrade bioplastics by breaking polymer chains into monomers (Udyani, 2017).

Effect of Modified Starch to Water Resistance

Water resistance tests on bioplastics can be used to determine whether the properties of the bioplastics produced are close to those of conventional plastics or not, one of which is water resistance. The water resistance of bioplastics can be done with a swelling test showing the ratio of bioplastic in the presence of water (Tan *et al*., 2020).

The lower percentage of water absorption means that the plastic properties are getting better, while the higher the percentage of water absorption means that the plastic properties will easily to be damaged (Coniwanti *et al*., 2014).

The following are the results of the water resistance test on bioplastic's cup:

Low temperature

Table 1. The water resistance test of bioplastic's cup at low temperature

Treatment	Carrageenan (g)	Aquadest (mL)	Sorbitol (mL)	Modified Starch (g)	Water Resistance (%) ± SD	Water resistance standards based on Japanese Industry Standard (%)
P0	3	100	5	0	93.35[c] ± 20.79	≤ 70
P1	3	100	5	1	72.64[b] ± 11.56	
P2	3	100	5	2	74.04[b] ± 13.39	
P3	3	100	5	3	48.86[a] ± 9.67	

Room temperature

Table 5. The water resistance test of bioplastic's cup at room temperature

Treatment	Carrageenan (g)	Aquadest (mL)	Sorbitol (mL)	Modified Starch (g)	Water Resistance (%) ± SD	Water resistance standards based on Japanese Industry Standard (%)
P0	3	100	5	0	127.05[b] ± 13.77	≤ 70
P1	3	100	5	1	135.80[b] ± 12.64	
P2	3	100	5	2	93.22[a] ± 9.64	
P3	3	100	5	3	71.33[a] ± 13.01	

High temperature

Table 6. Glass bioplastic water resistance test at hot temperature

Treatment	Carrageenan (g)	Aquadest (mL)	Sorbitol (mL)	Modified Starch (g)	Water Resistance (%) ± SD	Water resistance standards based on Japanese Industry Standard (%)
P0	3	100	5	0	99.14[a] ± 30.36	≤ 70
P1	3	100	5	1	131.22[a] ± 23.24	
P2	3	100	5	2	98.56[a] ± 27.17	
P3	3	100	5	3	97.13[a] ± 22.98	

The water absorption capacity test of bioplastic's cup with addition of modified starch obtained the least absorption at 48.86% at low temperatures (4˚C) and the highest absorption was 135.80% at room temperature (25˚C). The test results on bioplastic's cup using a high temperature of 80°C also resulted in a fairly high water absorption compared to low temperatures and room temperature. The higher water absorption will produce bioplastics with lower water resistance. This statement is in accordance with Illing and Satriawan (2018), the lower water absorption will produce bioplastics with higher water resistance, while higher water absorption will result in lower water resistance in bioplastics and swelling of the sample will occur. Bioplastics derived from starch have a weakness, namely their resistance to water, so it is necessary to add hydrophobic materials.

The addition of modified starch in this study aims to improve the properties of bioplastic's cup, one of which is water resistance. The starch modification process using acetylation method can be done by adding acetic acid which can weaken the hydrogen bonds in starch. Acetic acid containing an acetyl group can

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cause the abolition of the OH group so that the water absorption ability will be lower (López *et al*., 2011). Thus the use of modified starch by acetylation can increase the hydrophobic properties of starch.

Damage to bioplastics is characterized by bioplastics that look soft and eventually break. Bioplastics that are in hot water will initially appear warped, then return to their original state after a while and will eventually break. Meanwhile, at high temperatures, the bioplastic will melt. At first the heated bioplastic will harden and then at a certain temperature will melt (Nurviantika *et al*., 2015). The results obtained in this study indicate that the addition of modified starch will increase the water resistance of bioplastic's cup. The increase in water resistance was due to the modified starch having hydrophobic properties. Modified starch is hydrophobic because the modification process in starch can produce smaller starch (Panjaitan *et al*., 2019). According to Rahman (2007) that an amorphous area is an area that is less dense and tenuous so that in the end it can be easily penetrated by water and easily absorbs water.

4. Conclution

The application of modified starch to bioplastic's cup based on carrageenan from *Eucheuma cottonii* has a significant effect on the biodegradability and water resistance of the bioplastic. The best level of biodegradation is 55.68% while the lowest is 42.75%. The best results of water resistance are 48.86% with an initial temperature of 4°C, 71.33% with a temperature of 25°C, and 97.13% with an initial temperature of 80°C. The best formulation for the biodegradability of bioplastic's cup is the addition of 0% modified starch with a biodegradability value of 55.68%. Meanwhile, the best formulation for water resistance is 3 g of carrageenan with the addition of 3 g of modified starch with a water resistance value of 48.86% at low temperature, 71.33% at room temperature, and 97.13% at high temperature.

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