Application of glycerol on bioplastic based carrageenan waste cellulose on biodegradability and mechanical properties bioplastic

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Abstract. The carrageenan industrial waste materials can be used bioplastic biodegradable production because has high cellulose content 71.38%. Bioplastics can easily degraded and flexible, it is necessary to add glycerol plasticizers, that can reduce internal hydrogen in intermolecular bonds that affected biodegradability and mechanical properties of bioplastics. This study aimed was to analyze the effect of glycerol application as plasticizers on bioplastics based carrageenan waste cellulose on biodegradability and analysis the best concentration of glycerol on bioplastics to get biodegradation standards and mechanical properties based on the review article. This research was experimental in testing biodegradability of carrageenan waste cellulose bioplastic with the addition of glycerol (1; 3; 5; 7% v/v) and review article on the mechanical properties of bioplastics and waste cellulose content. Experimental research used ANAVA data analysis and followed by DMRT. The results of this study were indicated that the glycerol has significantly effect (P <0.05) on the ability of biodegradation with the highest value of 39.20 ± 0.87% - 40.34 ± 0.78% for seven days at a concentration of 5-7%. Based on the review article, the concentration of glycerol on bioplastics cellulose that suitable with biodegradation standards and mechanical properties of bioplastics is 5%

1. Introduction
The nature of plastic that is not easily decomposed causes various environmental problems. Bioplastics is one of the solutions to the problem of environmental pollution caused by plastic. Bioplastics are one type of biodegradable packaging made from renewable biomass [1]. One of the materials that can be used as a basis for making bioplastics is cellulose derived from carrageenan waste. In the process of making carrageenan, waste produced between 65-70% of the weight of seaweed, even though the cellulose content can reach 71.38% [2] so that it can be used as bioplastics.

Bioplastics based cellulose are conveniently degraded but have weak hydrogen bonds due to the distance between the tenuous molecules, which causes bioplastics to be less solid and flexible. Therefore, it is necessary to add cellulose adhesives, one of which is chitosan. Chitosan can interact with cellulose polymer chains in the form of hydrogen bonds so that it can fill cavities between cellulose and make bioplastics stronger but not elastic, so glycerol needs to be added.

Glycerol is a material that can reduce the internal hydrogen bonds in the intermolecular bonds [3] and is amorphous [4]. This ability which causes glycerol is classified as a plasticizer, which can increase
bioplastic flexibility so that it can influence mechanical properties which include strength, flexibility and water resistance of bioplastic [5]. Glycerol is also amorphous, which will further facilitate the degradation process. Degradation is the ability of biodegradable films to decompose microbes, moisture and chemical factors present in the soil [4] so that the addition of glycerol will affect whether or not the bioplastic is degraded.

This study aimed was (1) to analyse the effect of glycerol application as plasticizers on bioplastics based carrageenan waste cellulose on biodegradability; (2) analysis the best concentration of glycerol on bioplastics to get biodegradation standards and mechanical properties based on the Artikel review

2. Methods
The method used was experimental and literature review. Experimental research was conducted at the Chemical Analysis Laboratory of the Faculty of Fisheries and Maritime, Universitas Airlangga, Surabaya in February-March 2020 and literature study in March-April 2020.

2.1 Bioplastic manufacturing
The process of making bioplastics starts from the process of separating cellulose in carrageenan waste. Waste sample powder is immersed in a 6% H2O2 solution which is heated for 1 hour at 70°C in a water bath shaker at a ratio of 1:3 w/v. Then washing with water to neutral pH and dried for 2-5 days. The cellulose obtained was weighed 30 grams and added 1 gram of chitosan, then given the treatment of the addition of glycerol (0; 1; 3; 5; and 7% v/v). The mixture is heated in 100 ml of distilled water and stirred for 30 minutes at 70°C. Then printed on a glass plate with a diameter of 7 cm and dried in an oven at 60°C for 1 hour. The formulation for making bioplastics is in Table 1.

| No. | Materials           | Unit | Treatment |
|-----|---------------------|------|-----------|
|     |         |      | P0 | P1 | P2 | P3 | P4 |
| 1.  | Carrageenan Waste  | Gram | 30 | 30 | 30 | 30 | 30 |
| 2.  | Aquades            | ml   | 100| 100| 100| 100| 100|
| 3.  | Chitosan           | Gram | 1  | 1  | 1  | 1  | 1  |
| 4.  | Glycerol (v/v)     | %    | 0  | 1  | 3  | 5  | 7  |

2.2 Biodegradation test
Biodegradation test is indicated by the degree of damage to bioplastics. Previously, the sample was weighed first as the initial mass (m0). After that, burial was carried out in the soil for 7 days. Bioplastic samples that have been buried are then dried and weighed. Then the re-weighing process is carried out as the value of m1 [6]. The percentage value of average mass reduction from buried bioplastics is obtained through the following equation:

\[ m\% = \frac{m_1 - m_0}{m_0} \times 100\% \]

2.3 Data analysis
The experimental method includes a biodegradation test using a Completely Randomized Design (CRD) and continued by Duncan’s Multiple Range Test. The data was analysis performed using the IBM SPSS statistics version 23.0 software. The reviews related to parameters that are not possible to obtain due to the existence of a pandemic were conducted a literature review using qualitative descriptive analysis.

3. Results and discussion
3.1 Results
This research produced bioplastics from carrageenan waste cellulose. The resulting bioplastics are circular with a diameter of 7 cm (Figure 1). The results of the Analyze of Variance (ANOVA) test
showed that the addition of glycerol concentration (0, 1, 3, 5, and 7%) significantly affected biodegradability. Meanwhile, in the DMRT follow-up test, it was found that the best concentration of glycerol in doing degradation was 7% with 40.3346 ± 0.78% biodegradation value. However, these results were not significantly different from the glycerol concentration of 5% with a biodegradation percent value of 39.203 ± 0.87% (Figure 2).

![Figure 1](image1.jpg)

**Figure 1.** Bioplastic Carrageenan Waste Cellulose with Addition of Glycerol.
Note: Letter notation (a) glycerol concentration 1%; (b) glycerol concentration of 3%; (c) glycerol concentration of 5%; (d) glycerol concentration of 7%.

![Figure 2](image2.jpg)

**Figure 2.** Comparison Graph of Bioplastic Percentage of Biodegradation with Different Glycerol Concentrations.
Note: Different superscript letter notations in the same column show comparisons between treatments are very significant differences (P <0.05). The same superscript indicates that between treatments were not significantly different (P> 0.05).
3.2 Discussion

The results of the analysis show that the addition of different glycerol concentrations in the bioplastic carrageenan waste cellulose significantly affects the ability of biodegradation, so increasing the glycerol concentration will further accelerate the process of bioplastic degradation. Biodegradation itself is a vulnerability of both organic and inorganic compounds to changes in material structure due to microorganism activity [7]. The high per cent value of biodegradation in bioplastics based carrageenan waste cellulose is also caused by the high content of cellulose in carrageenan waste.

According to Tan [8], cellulose is a polymer that is easy to interact with water and microorganisms and has a sensitivity to physicochemical effects, so it is easily degraded. In the results of research conducted by Fithriani [2]; Zulferiyenni and Hidayati [9] showed that the cellulose content in carrageenan waste reached 67.75-71.38%. The biodegradation process in cellulose bioplastics is due to the breaking of β-1,4-glycosidic bonds so that cellulose molecules are decomposed back into glucose molecules and degradation reactions occur in linear polymers that cause molecular weight loss and shortening of chain length [10]. The addition of glycerol to cellulose bioplastics will also increase the ability of degradation because glycerol can reduce the degree of crystallinity in cellulose, which will result in decreased bioplastic density [11].

The results of this study indicate the highest percentages of biodegradation with glycerol 5%-7% can degrade bioplastics respectively by 39.20 ± 0.87% - 40.334 ± 0.78% has met the ASTM D-6002 standard which explains that 60 day is the time needed to degrade bioplastics 100% [12]. Also, the yield is much higher in biodegradation level when compared to LDPE and HDPE packaging, whose degradation ability only reaches 75.3% for 120 days [13]. The high biodegradation ability of bioplastic cellulose carrageenan waste with the addition of glycerol can also affect the mechanical properties of bioplastics such as water resistance, per cent elongation and tensile strength.

Tensile strength is the maximum stress that can be achieved by the film to survive before breaking [14]. The application of glycerol in bioplastic based cellulose will affect the tensile strength because glycerol aims to reduce the molecular bonding power of cellulose so that the flexibility of bioplastics is increased [6]. In the research of Hidayati [4], at a glycerol concentration of 1.25% the tensile strength value was 13.7 MPa while at the glycerol concentration 5% the tensile strength value was 124.2 MPa, while at a concentration of 7% it was worth 120 MPa [15], so the higher the concentration of glycerol can reduce the tensile strength. These results indicate that at a concentration of 5% glycerol produces tensile strength under SNI standards of packaging materials which range from 24.7-302 MPa [16].

The decrease in tensile strength due to glycerol is reducing intermolecular hydrogen can also weaken the intermolecular attraction of adjacent polymer chains, it causes the tensile strength of bioplastics to be reduced and stiffness decreases resulting in decreased tensile strength [17]. The addition of glycerol also affects the per cent lengthening of bioplastic based cellulose.

Per cent elongation is the change in length from a specimen to termination due to the applied force [18]. Several studies have been conducted to determine the effect of the addition of glycerol on bioplastic based cellulose to the per cent elongation of Hidayati [4] stated that the addition of 1.25% glycerol to bioplastic cellulose of solid waste seaweed had an elongation per cent value of 63.18%, while a 5% concentration was worth 79.58%. The results of the study are under SNI standard packaging materials with elongation per cent values of 21-220% [16] Another study was also carried out by Nafiyanto [19] who stated that an increase in glycerol concentration > 2.5% will increase the per cent elongation to a certain point.

The increase in per cent elongation value due to glycerol will lie between the biopolymer chains so that the distance between chitosan and starch increases. This increase will cause the hydrogen bond between chitosan and starch to be reduced so that it is replaced by the interaction of hydrogen between chitosan-glycerol and glycerol-starch (Figure 3.) thus bioplastics become more elastic [19].
Increasing the concentration of glycerol in bioplastic based cellulose also affects the nature of water resistance. Water-resistance is intended to determine the extent to which bioplastics are resistant to water by calculating the per cent of bioplastic swelling by the presence of water [20].

In the research of Hidayati [4], the resistance of water to cellulose bioplastics with the addition of 1.25% glycerol which is 54.4%, while the addition of 5% water resistance reaches 98.4% for one week. Nafiyanto's research [19] also states that the greater the volume of glycerol added will increase the per cent water resistance. According to SNI standard packaging materials, the hydrophobicity value is 99% [16], so the concentration of 5% glycerol in the Hidayati [4] almost meets these standards.

The increase in the value of water resistance with increasing glycerol concentration is due to the presence of three hydrophilic hydroxyl groups found in glycerol which are responsible for their solubility in water [21]. Glycerol has many -OH groups so that it can bind to water through hydrogen interactions which reason bioplastics to have a high absorption.

Based on the literature review of previous studies on the mechanical properties of bioplastic based cellulose with the addition of glycerol, it should be stressed that the concentration of 5% glycerol suitable with the SNI mechanical properties standards namely the tensile strength value of 24.7-302 MPa, elongation per cent 21 -220%, and 99% hydrophobicity [16]. Also, the concentration has a high degradation ability that is 39.20 ± 0.87% within seven days.

4. Conclusion
The application of glycerol to bioplastic based carrageenan waste cellulose has a significant effect on biodegradability. The highest degradation rates were at glycerol concentrations of 5% and 7% with a value of 39.20 ± 0.87% - 40.34 ± 0.78%. Based on the Artikel review conducted that, the best glycerol concentration on the ability of biodegradation and mechanical properties of bioplastics was 5%.

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