Optimization of the Mechanical Properties of Bio-degradable Plastics from Chitosan with Acetic Acid Solvent

Ani Purwanti, Eka Sulistyaningsih, Wisnu Prayogo, Muhammad Yusuf
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Abstract— **Shrimp shell waste contains chitin which can be processed into chitosan. Chitosan can be utilized as an edible plastic. The film is expected to maintain food quality by resisting water vapour transfer as a preservative and maintaining odour. Edible plastics as food protectors are expected to have optimal mechanical properties. Chitosan films are brittle, so plasticizers are used to increase their flexibility. The mechanical properties of the film may change during storage time. The decline in film quality is expected to be fast enough to allow edible plastics for food wrapping. This study aims to determine the effect of glycerol addition and film storage time on the mechanical properties of edible chitosan film. From the results obtained, adding glycerol plasticizer produces films with thickness and elongation that tend to increase. In contrast, the tensile strength value increases and then decreases with the addition of glycerol. The optimal mechanical strength value was obtained in the film solution with glycerol at 0.3 mL/g chitosan with a maximum tensile strength of 200 kgf/cm^2 and a per cent elongation of 135%. The thickness of the film produced was 0.17 mm. The film produced in this study has met the standards of film mechanical strength (tensile strength and per cent elongation) based on the Japanese Industrial Standard (JIS). Meanwhile, based on the Indonesian National Standard (SNI), the tensile strength value produced in this study has yet to meet the SNI standard.**

Keywords— chitosan, edible film, tensile strength, elongation.

I. Introduction

Shrimp, with a brackish water habitat, has a body with 13 segments, and an outer skeleton covers the whole body called an exoskeleton. In Indonesia, shrimp is one of the main export commodities [1]. From the shrimp processing, waste is obtained in the form of a comb, namely the meat at the base of the head, which can be used to make shrimp paste. Much waste from shrimp heads and legs can be made into shrimp flour, often used as feed for cultured shrimp. In general, shrimp waste is wasted, disrupting the environment. The waste in shrimp shells contains as much as 25% chitin and has been used in several developed countries in the food, pharmaceutical, cosmetic, textile, biotechnology and paper industries [1]. Shrimp waste produced by Indonesia annually is around 300 thousand tons. Meanwhile, the chitosan that can be produced annually is 10 thousand to 19 thousand tons. The price of shrimp waste per kilogram is Rp. 5,000, while the selling price of chitin on the international market is US$ 10 per kilogram, and the selling price of chitosan is between US$ 15-40 per kilogram. From these economic considerations, processing shrimp waste into chitosan is considered profitable [2].

Chitosan contained in shrimp heads can be used in the fabric industry because it can increase the strength of dyes with properties that are not easily soluble in water [1]. In food technology, chitosan is used to make edible and degradable plastics (edible plastic) [3;4;5]. This plastic is expected to have the ability to protect food properly, including being able to withstand the transfer of water vapour and having selective permeability to certain gases. Besides that, this edible plastic can be a preservative and maintain the aroma to maintain the quality of food ingredients. In its use, edible plastic is expected to have optimal mechanical properties to function as a food protector against mechanical influences from the environment. Films formed from pure polymers are brittle, so a plasticizer is used to increase the flexibility of the film [6]. The mechanical properties of the film can change during storage time. The decline in film quality concerning film storage time will likely not occur too quickly to allow the use of edible plastics for food packaging. The mechanical properties of this film are affected by the length of storage of edible plastics.

The good mechanical properties of edible plastics allow them to last as long as they are used for food storage. This research on edible films made from chitosan was aimed at studying the effect of plasticizer content (glycerol) and the effect of storage time on edible plastics on the mechanical properties of edible plastics, namely tensile strength and elongation [7;8]. The type of material and plasticizer concentration influences the physical characteristics of edible films. The addition of glycerol to improve the mechanical properties will affect the thickness of the film produced, so it is necessary to optimize the addition of glycerol to the properties of the edible film [9].

Ani Purwanti is with Departement of Chemical Engineering, Institut Sains & Teknologi AKPRIND, Yogyakarta, 55222, Indonesia. Email: ani4wanti@akprind.ac.id
Eka Sulistyaningsih is with Departement of Industrial Engineering, Institut Sains & Teknologi AKPRIND, Yogyakarta, 55222, Indonesia.
Wisnu Prayogo is with Department of Building Engineering Education, Faculty of Engineering, Universitas Negeri Medan, Medan 20221, Indonesia. Email: wisnuprayogo@unimed.ac.id
Muhammad Yusuf is with Departement of Industrial Engineering, Institut Sains & Teknologi AKPRIND, Yogyakarta, 55222, Indonesia.

II. METHOD

This type of research is experimental, with the main raw material being shrimp shell waste (shrimp shells) which is processed into chitosan and then made into edible plastic, which is plasticized with glycerol. The research location and product quality analysis will be conducted at the Chemical Engineering Operations Laboratory, Institute of Science & Technology AKPRIND Yogyakarta, Laboratory at UGM Yogyakarta. The raw materials used to obtain chitosan in this study were shrimp shells, sodium hydroxide solution, and HCl solution. While the materials used to make edible plastic from chitosan are distilled water, acid solution, and plasticizer. Some equipment used to form plastics includes magnetic stirrers, vacuum filters, pans, and drying ovens. A desiccator (containing a saturated salt solution) will be used to research the effect of storage time on the mechanical properties of edible plastics.

III. RESULTS AND DISCUSSION

One of the quality parameters of the edible film made from chitosan is largely determined by its mechanical strength [10]. An edible film's mechanical properties can determine the packaging's flexibility. The lower the tensile strength value and the higher the elongation at break or elongation, the more chitosan edible film will be flexible. By having good mechanical properties, the quality of the packaging will be better. The total amount of solids influences the thickness of an edible film in the chitosan solution and the mould thickness during the printing process [11]. With the same mould, the formed edible film will be thicker if the volume of solution poured into the mould is more. In addition, the total solids with a greater amount will make the edible film thicker. The addition of glycerin affects the thickness of the edible film. The greater the amount of glycerin added, the thickness of the edible film increases because the total solids in the solution increase. The results of measuring film thickness for various chitosan compositions without adding glycerol in acetic acid solution can be seen in Table 1. Meanwhile, the results of the mechanical properties test of chitosan films for composition 0 can be seen in Table 2 below. Where K0: Sample without the addition of glycerol, K1: Sample with the addition of 0.2 mL/gram chitosan glycerol, K2: Sample with the addition of 0.3 mL/gram chitosan glycerol, K3: Sample with the addition of 0.4 mL/gram chitosan glycerol, K4: Samples with 0.5 mL/gram chitosan added glycerol, K5: Samples with 0.6 mL/gram chitosan added glycerol.

TABLE 1.
CHITOSAN EDIBLE FILM THICKNESS MEASUREMENT RESULTS

No.	Mass of Chitosan inside 150 mL Acetic Acid	Film Thickness (mm)
1.	0.5 gr	0.12 mm
2.	1.0 gr	0.15 mm
3.	1.5 gr	0.18 mm
4.	2.0 gr	0.20 mm

TABLE 2.
EDIBLE FILM MECHANICAL PROPERTIES TEST RESULTS FOR VARIOUS CONCENTRATIONS OF GLYCEROL IN EDIBLE FILM SOLUTIONS

No.	Sample Code	Film Thickness (mm)	Tensile Strength (kgf/cm^2)	Elongation (%)
1.	K0	0,12	225	55
2.	K1	0,14	201	120
3.	K2	0,17	200	135
4.	K3	0,21	185	116
5.	K4	0,23	160	110
6.	K5	0,25	125	101

The tensile strength values resulting from this study were then compared with the existing standard tensile strength values. It aims to be able to conclude whether the edible film produced meets the standards and is suitable for use or not. The standards that can be used include the Japanese Industrial Standards (JIS) and Indonesian National Standards (SNI). According to JIS, the maximum edible film thickness parameter value is 0.25 mm, the minimum tensile strength is 40 kgf/cm^2, and the minimum elongation is 70%. Meanwhile, according to SNI standards, tensile strength ranges from 251.87 – 3079.5 kgf/cm^2. When compared with the standard value, the edible film obtained has met the edible film standards according to JIS. Graph the relationship between the concentration of added glycerol (mL/gram of chitosan) and the film thickness used.

From the results of the research data that has been obtained, the results of the analysis of the thickness of the edible chitosan film without the addition of glycerol ranged from 0.12 mm - 0.20 mm, while for the edible film added glycerol had a thickness value of between 0.14 mm - 0.25 mm. The results of these measurements indicate a tendency to increase the average thickness of the edible chitosan film with the addition of glycerol. The mechanical properties of an edible film can be in the form of strength, hardness, stiffness, and plasticity [12].

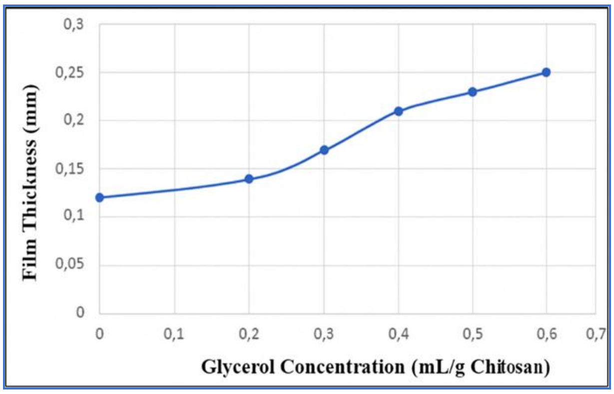

Figure 1. Edible Film Thickness Measurement

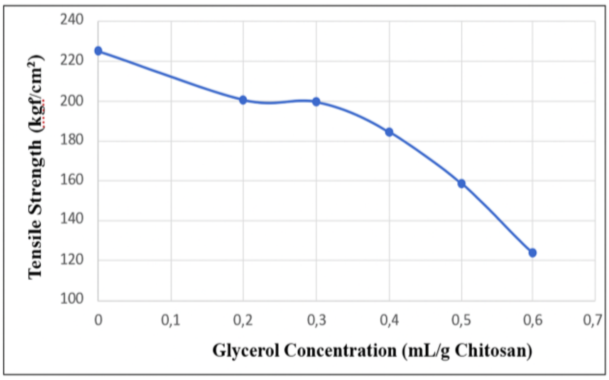

Figure 2. Graph of Edible Film Tensile Strength Measurement Results

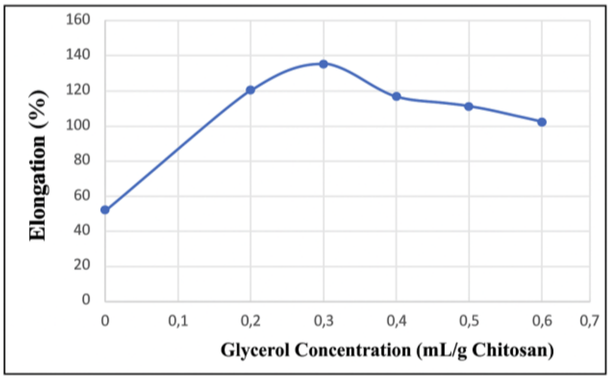

Figure 3. Graph of Edible Film Elongation Measurement Results

Tensile strength is an important parameter affecting the mechanical properties of edible films, defined as the maximum tensile stress of the sample before the sheet breaks. The tensile strength of chitosan edible film dissolved in acetic acid with the addition of glycerol has a tensile strength value that tends to decrease with increasing glycerol concentration. It is because adding glycerol reduces the intermolecular forces along the polysaccharide chain so that the formed film structure becomes smoother and more flexible [12]. Glycerol, a small hydrophilic molecule, can easily enter between the film's molecular chains and form amide hydrogen bonds with proteins. The mechanical properties of a film's tensile strength and elongation percentage are influenced by the number of carbon atoms in the chain and the number of hydroxyl groups present in the plasticizer molecule (glycerol) [13]. From the results of this study, the lowest tensile strength value was 125 kgf/cm^2, and the largest value was 225 kgf/cm^2. The measurement of the tensile strength of the edible film is the change in the maximum length experienced by the edible film when testing the tensile strength, which is seen just before the edible film breaks.

Meanwhile, the results shown in Figure 3 shows that adding glycerol concentration produces films with an increased per cent elongation [12;13]. However, from the data obtained, there is a maximum concentration of glycerol, which results in the maximum per cent elongation value. After this maximum value is reached, the percentage elongation decreases with the addition of glycerol concentration in the film. The elongation of the edible chitosan film dissolved in acetic acid without using glycerol (K0) was 55%. In comparison, the film made with the addition of glycerol had a per cent elongation value of 101% - 135%. Adding glycerol plasticizer can improve the mechanical properties of the edible film from chitosan so that the edible film will be more applicable. Increasing glycerol will produce an edible film with a higher elongation percentage. Due to an increase in the amount of glycerol, the strength of the intermolecular forces decreases so that the mobility between the molecular chains increases, which results in a higher percentage of film elongation.

In this study, an analysis was carried out on the effect of storage time on the mechanical properties of biodegradable plastic made from chitosan using a desiccator containing a saturated salt solution. Biodegradable plastic films, including those based on chitosan, are designed to degrade in the environment. However, this characteristic also means that their mechanical properties may change over storage time, affecting their functionality, particularly for applications such as packaging. Relative humidity is one of the most influential environmental factors on the mechanical properties of chitosan films. Chitosan-based plastics are hydrophilic, meaning they readily absorb water. When the film absorbs moisture from the environment, water molecules interact with the polymer chains. Water can act as a plasticizer, increasing the flexibility and elongation of the film [14].

Increased humidity can lead to an increase in elongation and a decrease in tensile strength of chitosan films. These changes in water content also occur during plastic storage [15]. From the research results, data were obtained as shown in Figure 4 below.

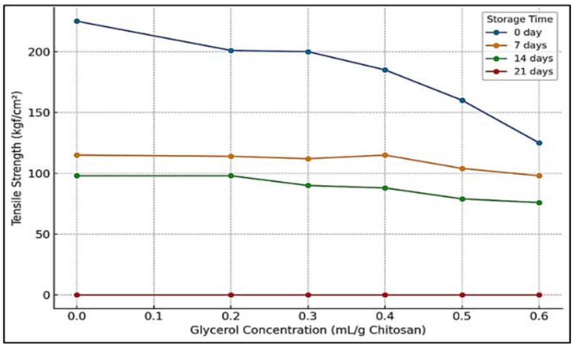

Figure 4. Effect of Glycerol Concentration on Tensile Strength at Different Storage Times

From the experimental results, it was found that during storage from 0–21 days, there was a decrease in the tensile strength of the plastic, and at 21 days of storage, the plastic could no longer be tested for tensile strength; therefore, the test result was recorded as 0 kgf/cm². A significant decrease in tensile strength occurred during storage up to 7 days and up to 21 days.

The effect of storage time on the tensile strength and elongation of biodegradable films is, in general, that the tensile strength of biodegradable films (particularly those based on biopolymers such as chitosan) tends to decrease over storage time. This is caused by the intrinsic degradation processes of the material. Such degradation can be in the form of hydrolysis, where polymer bonds break due to reaction with water (especially in humid environments) [16;17]. The breaking of polymer chains reduces the structural integrity of the film, ultimately lowering its ability to withstand tensile loads [18;19].

Over storage time, the elongation of biodegradable films also tends to decrease. This is also consistent with the experimental results, from the obtained data the plastic at 21 days of storage could no longer be measured for elongation because it became easily torn; therefore, the measurement result was recorded as having 0% elongation. This is consistent with the literature review, where several mechanisms are involved, including the migration of the plasticizer glycerol from the polymer matrix of the plastic, causing the film to become stiffer and more brittle, thus reducing its elongation [20;21].

IV. CONCLUSION

Adding glycerol plasticizer produces edible films with thickness and elongation values that tend to increase. In contrast, the tensile strength values increase and then decrease with the addition of glycerol. The optimal mechanical strength value was obtained from the composition of the film solution with glycerol of 0.3 mL/g chitosan with a maximum tensile strength of 200 kgf/cm^2 and a per cent elongation of 135% with a film thickness of 0.17 mm. The films produced in this study met the film mechanical strength standards (tensile strength and per cent elongation) based on the Japanese Industrial Standard (JIS). Meanwhile, based on the Indonesian National Standard (SNI), the tensile strength values produced in this study did not meet the SNI standards. This study confirms that storage time markedly decreases the tensile strength and elongation of chitosan-based biodegradable films, primarily due to hydrolytic degradation, structural rearrangements, and plasticizer migration. After 21 days, the films lost their flexibility and became unsuitable for mechanical testing. The results provide valuable insights for the development of biodegradable packaging, underscoring the importance of stabilizing plasticizers and controlling storage conditions to maintain the functional performance of films during their intended shelf life.

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