Preparation and characterization of biodegradable film based on skin and bone fish gelatin

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Abstract. Biodegradable films can act as excellent oxygen, water, and lipid barrier. Gelatin is utilized extensively as a gelling agent, emulsifier, stabilizer, adhesives, viscosity agent, binder agent and film-forming agent. Fish gelatin as a film-forming agent has unique characteristics but varies depending on fish species. The study aims to characterize biodegradable film made using skin and bone fish gelatin with the addition of plasticizer. Gelatin of ocean fish, spotted oceanic triggerfish (Canthidermis maculata), and freshwater fish, tilapia (Oreochromis niloticus) were used. As a plasticizer, glycerol or sorbitol with concentrations of 0.25 and 0.5 % was added. Gelatin of spotted oceanic triggerfish resulted in film with higher tensile strength, whereas tilapia gelatin with glycerol produced biodegradable film with higher elongation and water vapor permeability. The best characteristics of biodegradable film made from gelatin of spotted oceanic triggerfish with 0.25% sorbitol.

1. Introduction
Biodegradable films have obtained attention because of their advantages over traditional synthetic films. Biodegradable films use renewable ingredients which are environmentally friendly. The films can act as barriers to gas, moisture, solute movement, aroma, and also can function as carriers of food antimicrobial and antioxidant agents [1]. Nevertheless, biodegradable films have some drawbacks, such as low physical and mechanical properties, lack of thermal resistance, and high cost compared to synthetic plastic films. Improving and developing excellent biodegradable films that can compete against plastic films has become research attention. Using waste product as film raw materials, not only benefits from less expensive by-products, but also reduces environmental pollution.

Gelatin as bio-macromolecule protein polymer has characteristics of colorless, translucent, brittle, edible, and flavorless. Gelatin is extracted from collagen tissue found in skin, bones, and connective tissue of various animal and fish by thermal hydrolysis [2, 3]. Commercial gelatin extracted mostly from porcine and bovine skin and bone, by-products of meat industries. Gelatin is one of functional biopolymers, owns good film-forming ability with good carbon dioxide and oxygen barrier properties, transparent, water-soluble, and highly extensible film [4, 5, 6]. Fish gelatin has gained increasing demand due to many socio-cultural, religious, and environmental reasons. Nevertheless, in general, fish gelatin films have lower mechanical properties than mammalian gelatin, lower oxygen...
permeability, and lower water vapor permeability [6, 7]. Moreover, fish gelatin properties vary depending on fish species, fish living environment, and gelatin extraction procedures.

The mechanical properties of gelatin films have been increased by using various plasticizers. The properties improved due to the decreasing of protein chains intermolecular forces. The reduced forces support the construction of strong covalent bonds in the protein network of the film or lead to the reduction of hydrophilic characteristic. Plasticizers intensify the flexibility of films and reduce the rigidity, and may assist in obtaining desirable mechanical properties [3, 8].

The aim of this research was to analyze the effects of different fish gelatin sources, and plasticizers on some properties of fish gelatin biodegradable film. Oceanic triggerfish (Canthidermis maculata) which is epipelagic fish inhabit tropical/subtropical oceans, and fresh water fish, tilapia (Oreochromis niloticus) were used in the study. Sorbitol and glycerol were used as plasticizers in an attempt to improve the characteristics of biodegradable film.

2. Method

2.1. Preparation of material

Fresh tilapia (Oreochromis niloticus) and triggerfish (Canthidermis maculata) skin and bone were obtained from small fish processing industry in Banda Aceh, Indonesia. The fish skin was cleaned from meat remnants with a knife and then washed and packed in plastic bags and stored at -24°C until further use. Frozen fish skin and bone were cut into small pieces (about 2-3 cm²). Then, the skin was thawed overnight in a refrigerator at around 4°C and used for extraction. All chemicals used were analytical grade.

2.2. Fish gelatin extraction

Fish gelatin was extracted based on [9, 10] with some adaptations. The solution of 0.55N NaOH (1: 5 w/v) was used to soak fish skin and bone of triggerfish, whereas the tilapia was soaked in 0.77N NaOH for 1 hour. Then, for three times, using water (1: 5 w/v), the samples were washed, strained and then pressed. Subsequently, the triggerfish samples were submerged in 1.05 N HCl (1: 5 w / v) for 3 hours, and the tilapia sample in 0.59 N HCl for 1 hour. The samples were then washed three times with water (1: 5 w/v), strained, and pressed again. Next, distilled water (1: 4 w/v) were mixed with the samples in glass beakers and capped with aluminum foil, then extracted at 60°C for triggerfish and 66.8°C for tilapia in 3 hours by using a water bath. The samples were filtered using cheesecloth and the filtrate was dried in glass containers at 60°C for 72 hours.

2.3. Preparation of biodegradable film

Preparation of biodegradable film was carried out following [11, 12] procedures with some modifications. Gelatin of 3 g was dissolved in 100 ml of water and then stirred until homogeneous. Plasticizers (glycerol and sorbitol) were added with concentrations of 0.25% and 0.50% of the 100 ml water. The film solution then heated on a hot plate at a temperature of 45-50°C for 30 minutes, then added 0.1% corn oil and stirred for 5 minutes to obtain a good blend. Then 30 ml of the film solution was cast on rectangular teflon plates with a size of 13 cm x 18 cm and dried in an oven at 45°C for 15 hours. The film produced was released from teflon then stored for later analysis.

2.4. Film analysis and statistical analysis

The film thickness of 5 randomly selected spots on the film were measured by using a micrometer with 0.01 mm accuracy. Elongation and tensile strength at the breaking point were measured following the D882ASTM standard and by using Exceed Model E43 texture analyzer. A rectangular film of 4 cm x 1 cm was mounted between the two clamps of the machine at a specific initial distance, and the clamps moved at the rate of 10mm/min. Water vapor permeability (WVP) was measured following [13]. Statistical analysis was performed using Analysis of variance (ANOVA) to identify the effects of
3. Results and Discussion

3.1. Film thickness
The thickness of the fish gelatin biodegradable films was 0.10-0.15 mm with an average of 0.13 mm. The film thickness was thicker compared to the film of [8]. As in this research, using the same amount of 3 grams of gelatin in 100 ml water, their film thickness of fish skin gelatin containing clay nanoparticles were 60-70 micrometer. The film thickness is different allegedly due to differences in the amount of film solution used to produce the same film area. The findings of [14] show that barley bran protein-gelatin composite film thickness increased from 0.05 to 0.09 mm as gelatin content was increased from 1 to 4%. Film thickness went up along with the increase in the amount of solid in the film solution.

3.2. Tensile strength
Biodegradable film from triggerfish gelatin has higher tensile strength with a value of 2.34 MPa compared to tilapia gelatin film which is of 1.72 MPa (Figure 3.1). Atmaka et al. (2018) [15] produced a film using tilapia bone gelatin also show a low tensile strength of 0.58 MPa. Depending on the waters where fish live, the imino acid content of the fish gelatin may vary. Cold water fish derive gelatin which has lower imino acid content compared to warm water fish. Gelatin with lower imino acids of proline and hydroxyproline content possess low gel modulus and lower gelling temperature [7]. The triggerfish (Canthidermis maculata) is epipelagic fish inhabit tropical and subtropical oceans, often occur at an offshore island. Whereas tilapia, considered as warm water fish, is freshwater fish inhabiting rivers, lakes, ponds, and shallow streams, and less commonly found living in brackish water. Sutono and Pranoto (2013) [11] using a higher amount of black tilapia gelatin (8 grams vs 3 grams in this study) with the addition of 0.8% glycerol shows a film with a higher tensile strength of 3.08 MPa which presumably due to higher gelatin concentration used. Much higher film tensile strength of 17.3 MPa reported by Jiang et al. (2010) [16] using catfish gelatin. Lee et al. (2016) [17] also reported that film made of starfish gelatin had a high tensile strength of 19.61 MPa which increased more with the addition of vanillin.

Biodegradable fish gelatin film containing glycerol had lower tensile strength compared to the film that had sorbitol as a plasticizer (Figure 2). The results are in accordance with the findings of [8] who reported the similar behavior of the plasticizer in the gelatin film containing clay nanoparticles. The low tensile strength of films using glycerol may be due to the rise of glycerol matrix lubrication and lateral branches fluidity. Figure 2 shows that increasing concentration of glycerol to the fish gelatin biodegradable film caused an increase in tensile strength. In contrast with sorbitol, as the concentration increased, the tensile strength of the film decreased. [8] found that increasing both plasticizers, glycerol and also sorbitol, reduced the tensile strength of fish gelatin containing clay nanoparticles film. The decrease in tensile strength of the fish gelatin film may due to the crippling of gelatin structure by weakening the bonds through coming in between the lateral branches.
Figure 1. The tensile strength of fish gelatin biodegradable film based on the type of fish.

Figure 2. The tensile strength of fish gelatin biodegradable film as affected by the plasticizer.

3.3 Elongation

Figure 3 shows fish gelatin biodegradable film using glycerol had higher percent elongation than that using sorbitol. For both types of fish (triggerfish and tilapia) gelatin films, increased in glycerol concentration led to the increase of percent elongation. However, when sorbitol was used, mixed results were found, increasing sorbitol concentration induced a reduction in the elongation of tilapia gelatin film, in contrast, it caused a rise in the elongation of triggerfish gelatin film. The latter finding is in line with the results of Song et al. 2012 [14], using sorbitol in the porcine gelatin composite film. Plasticizers decrease intermolecular strengths and increase the movement of biopolymer chains which resulted in a decrease of brittleness and the increase of flexibility and strength of film [14]. Chemical and physical properties of gelatin vary with gelatin origin whereas, for fish species, the differences of derived gelatin are more significant [6]. The strength of the gel in gelatin affects the tensile strength of the edible film, the higher the strength of the gel, the higher the elongation of the edible film increases and the lower the tensile strength decreases.

Figure 3. Percent elongation of fish gelatin biodegradable film as affected by the type of fish and concentration and type of plasticizer.

3.4. Water vapor permeability

Triggerfish gelatin film containing glycerol had lower water vapor permeability (WVP) compared to that with sorbitol. On the contrary, tilapia gelatin based film using glycerol had higher WVP than that containing sorbitol (Figure 4). The difference may due to differences in gelatin properties which depend on fish species, fish living environment, and gelatin extraction procedures which render gelatin
with different composition of amino acid and distribution of molecular weight that will affect the interaction reaction [6].

Figure 5 shows that as the concentration of glycerol increased, the WVP of the film increased. Contrariwise, fish gelatin film WVP decreased as sorbitol concentration increased. These findings in accordance with that obtained by [8] who deduced that gelatin (bovine and fish-skin) films with sorbitol hold the minimum WVP and films with glycerol had the maximum, possibly because sorbitol is less hydrophilic than glycerol.

**Figure 4.** Water vapor permeability of fish gelatin biodegradable film affected by fish species and plasticizer.

**Figure 5.** Water vapor of fish gelatin biodegradable film affected by plasticizer concentration.

4. Conclusion
For both types of fish (triggerfish and tilapia) gelatin films, increased in glycerol concentration led to the increase of tensile strength, percent elongation and also water vapor permeability (WVP). Contrarily, increasing sorbitol concentration decreased tensile strength of triggerfish and tilapia gelatin films, and increased elongation of triggerfish gelatin film, but decreased elongation of tilapia gelatin film. Triggerfish gelatin film has a high tensile strength and percent elongation, with moderate water vapor permeability (WVP), in contrast with tilapia gelatin film which had low tensile strength, and high percent elongation also WVP.

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