

Effect of Glycerol Plastic Concentration on The Characteristics of Calcium Alginate-Based Edible Film

Fernandus Simanjuntak¹, Jamaran Kaban^{2}, Adil Ginting³*

^{1,2,3}Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jalan Bioteknologi No.1 Kampus USU Medan 20155, Indonesia

Abstract. Calcium alginate-based edible film has been made by way of immersion of sodium alginate into calcium chloride (CaCl_2) solution to form calcium alginate gel. In this case, using glycerol is a plasticizer with the variation of concentrations were 0%, 10%, 20%, and 30%. The characterization of edible films has been determined such as thickness, tensile strength, elongation, DTA, SEM, swelling, biodegradable and FT-IR analysis. Edible film characterization showed that with increasing glycerol plasticizer, thickness and tensile strength became greater, while elongation became lower. SEM analysis revealed that surface morphology became smoother and DTA analysis showed greater degradation temperature in the increase of glycerol. Characteristics of swelling showed that edible film without glycerol has to increase in weight with the addition of glycerol. The swelling value increased at the beginning of the measurement but increased after 10 interest. FT-IR analysis revealed that the stretching vibration form of the OH group changed from sharp to broad in the addition of glycerol. The biodegradable result showed an increase in the edible film weight and whole degradation after 21 days.

Keywords: Edible Film, Plasticizer, Glycerol, Characteristic, Calcium Alginate

Received [29 October 2019] | Revised [3 December 2019] | Accepted [28 January 2020]

1 Introduction

Alginate is one of the carbohydrates extracted from Sargassum, which has economic value. Until now, the alginate content of sargassum is still being used. (Alamsjah., et al 2011). Alginic acid is produced by extracting the brown algae (*Phaeophyceae*) and is widely used as a thermoreversible gelling agent and thickener in various industrial fields, as well as a suspending emulsifying and stabilizing agent. The alginate compound is commonly known as sodium alginate. Several countries such as Japan, China, and the United States had successfully commercially produced the alginates. Alginate is non-toxic and easily decomposed by microorganisms, so it can be widely used in various fields, especially in the textile (50%), food (30%), paper, pharmacy, and biochemistry industries. In addition, It has a role important

*Corresponding author at: Department of Chemistry, Faculty of Mathematics and Natural Sciences Universitas Sumatera Utara, Medan, Indonesia.

E-mail address: jamarankaban@yahoo.com

because it can be applied, to edible wrappers, enzyme immobilizers, and tablet coatings (Zhanjiang, 1990; McCromick, 2001; McHugh, 2003).

Edible packaging can be classified into two parts, such as to coat (edible coatings) and in form of sheets (edible films). These types of coating can be eaten with packaged products, as mass transfer inhibitors (eg moisture, oxygen, fat, and solutes) and/or as carriers of food ingredients or additives to improve food handling. The edible film can be produced from three types of materials, namely hydrocolloids (alginate, carrageenan, starch), lipids (wax, fatty acid), and the composite between hydrocolloids and lipids (Kinasih, 2010).

A plasticizer is an organic solvent in a simple concept with a high boiling point or a solid with a low melting point added to a resin such as PVC which is hard and rigid so that the accumulation of intermolecular forces in the long chain will decrease. Therefore, the chain members move easily, resulting in increased flexibility, softness, and elongation (Yadav and Satoskar, 1997). and materials that were hard and stiff will become soft at room temperature (Cowd, 1991). Plasticizers can decrease the melt viscosity, glass transition temperature (T_g), and product elasticity modulus without changing the chemical properties of the plastic material (Meier, 1990).

Glycerol is one of the most commonly used plasticizers in film making, due to its stability and compatibility with the hydrophilic chains of bio-polymers. The main function of glycerol is as a substance that serves to keep the softness and moisture.

The main function of glycerol is as a humectant and can also be used as a solvent (Bommardeaux, 2006).

2 Materials and Methods

2.1 Materials

In this study, the materials used were sodium alginate, glycerol, calcium chloride, aquadest, potato dextrose agar, *Aspergillus niger* sp. Fungus

2.2 Equipments

In this study, the equipments used were analytical balance, glassware, magnetic stirrer, caliper, screw thermometer, oven, and Petri dishes.

2.3 Research Procedure

As much as 2 g of Na-alginate was weighed on the analytical balance then dissolved into 100 mL of distilled water while stirring with a magnetic stirrer until evenly distributed and then left for 1 night. The alginate solution was then poured into a glass plate that had a cantilever and

kept for 60 minutes until the surface became flat. The glass plate containing the alginate solution was immersed into CaCl_2 0.1 M, then allowed to stand for 24 hours until the alginate solution was coagulated. After the coagulant formed, it was then immersed again into water and dried at 40°C to obtain a thin layer of a transparent edible film-based calcium alginate on a glass plate, then the obtained edible film-based calcium alginate was characterized using tensile testing, differential thermal analysis (DTA), scanning electron microscopy (SEM), swelling, biodegradable and fourier transform infrared spectroscopy (FTIR) In the same treatment, the preparation and characterization of edible films based calcium alginate were carried out using 10, 20 and 30% of glycerol as a plasticizer.

3 RESULT AND DISCUSSION

3.1 Thickness (mm)

The average thickness of the edible film derived from 2 g sodium alginate with variations in glycerol concentrations of 0, 10, 20 and 30% were 0.138, 0.158, 164, and 0.128, respectively.

Based on the result obtained that the addition of glycerol plasticizer affects the thickness of the edible film. This is due to the interaction between the OH group of glycerol and the OH group of calcium alginate. However, with the addition of a 30% glycerol plasticizer, the thickness of the edible film decreased. This is because the distance between the OH groups of glycerol and the OH groups of calcium alginate is getting closer so that the interaction between calcium alginate and glycerol becomes evenly and easily releases the water. According to McHugh (1993) Godras (2003) and Pieter (2007), the thickness of the film can also influence the rate of water vapor transmission, gases, and volatile compounds.

3.2 Tensile Strength and Elongation

Tensile strength is the ability of a material to withstand a pressure force to break. Elongation is the increase in the percentage of elongation that occurs in a material under pressure to break (Sperling, 2006).

The tensile strength and strain values of edible film-based calcium alginate and with the addition of glycerol as a plasticizer were 10, 20, and 30 presented in figure 1. Figure 1 showed that the specimen with the addition of glycerol as a plasticizer can increase the tensile strength of the edible film. Due to the nature of glycerol as a plasticizer is still in the polymer phase so that the intermolecular forces of the chain can still be maintained. Where the edible film-based calcium alginate with the addition of 30% glycerol has greater tensile strength compared to the addition of 10 and 20% glycerol, respectively. This is due to the external interaction between the molecules of glycerol and calcium alginate, resulting in high tensile strength. In contrast, elongation when glycerol was applied to the edible film-based calcium alginate, intermolecular

interactions occur, which causes a high elongation of 31.8%. However, the interaction between these molecules was disturbed by the addition of 10 and 20 % glycerol plasticizer, and the elongation percentage decreased to 7.18 and 9.60%, respectively. Meanwhile, the addition of 30% glycerol again experienced an increase in the interaction between the molecules on the edible film-based calcium alginate which caused the elongation to increase by 12.82%.

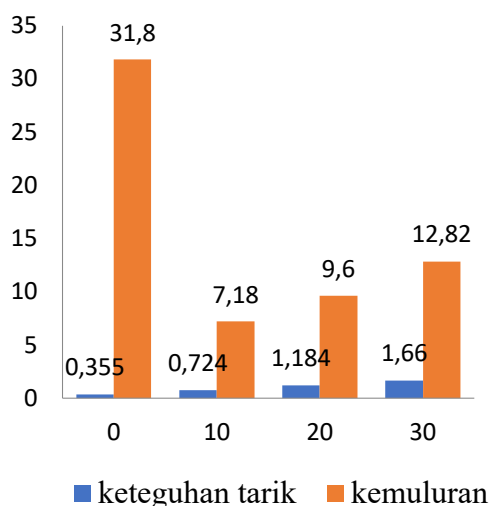


Figure 1. Histogram data of tensile strength and elongation

3.3 DTA (Differential Thermal Analysis)

DTA is to determine the thermal properties of a sample by measuring the temperature difference between the sample and reference material. Where the thermal analysis result obtained can provide information on changes in the physical properties of the samples, such as melting point and evaporation point, and also the occurrence of chemical processes that include polymerization, degradation, and decomposition (Wirjosentono, 1995).

The DTA analysis result indicated in Table 1 that the edible film with no glycerol has a lower melting point at 80°C. It means that the specimen begins to release the water vapor at 80°C and degraded at 520°C compared to addition 10, 20, and 30% glycerol plasticizers, the evaporation temperature increased to 100°C and the decomposition temperature decreased to 490 to 500°C. This is due to the interaction between the calcium alginate-based edible film with glycerol, in which glycerol has hydrophilic properties that can bind water, so it needs a higher temperature to release the water vapor.

In contrast, decomposition temperature is decreasing due to many organic matters being added to the edible film so that it will be adjusted to the coating material, namely the melting point will decrease.

3.4 SEM (Scanning Electron Microscope) Analysis

SEM analysis is to observe the surface morphology of the calcium alginate-based edible film such as fracture, indentation, and shape change (Matondang, 2013). The SEM analysis results are presented in figure 2 (a-d).

Figure 2. a showed that the surface looked at is rough due to the absence of glycerol plasticizer, and seen the calcium chloride loaded edible film because of incomplete washing. In addition, the small grains are still visible on the edible film which indicated that calcium chloride cannot interact with sodium alginate or the mixing is inhomogeneous and the surface is smoother due to the interaction of glycerol plasticizer with the calcium alginate edible film that was shown in figure 2. b. Otherwise, in figure 2. c, the presence of calcium chloride is no longer visible due to perfect washing led to the surface being smoother. Moreover, figure 2.d indicated that some lumps on the edible film surface due to incomplete washing with the results that there is still calcium chloride, and this less smooth surface may be due to saturation of the edible film that the glycerol plasticizer can no longer interact with the film till when washing the glycerol soluble in water.

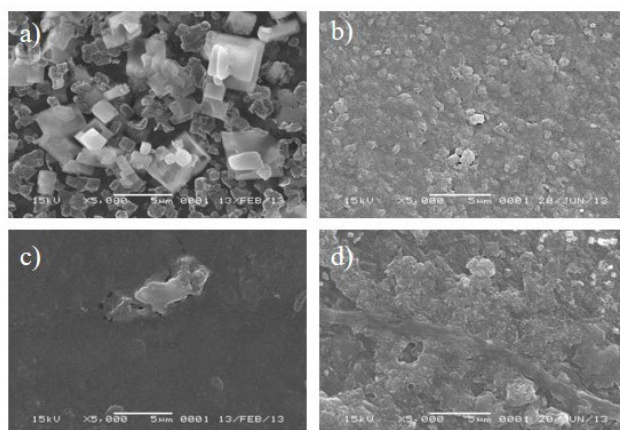


Figure 2. The morphology of calcium alginate-based edible film a). no glycerol, b).10% glycerol, c). 20% glycerol, d).30 % glycerol with 5000x magnification, respectively

Tabel 1. DTA (Differential Thermal Analysis) Test Results

Composition				
Sodium Alginate (g)	CaCl ₂ 0.1 M	Glycerol Plasticizer (%)	Melting Point (°C)	Decomposition Temperature (°C)
2	-	0	80	520
2	-	10	100	490
2	-	20	100	490
2	-	30	100	500

3.5 Swelling

Swelling is the increase in the volume of material upon contact with liquids, gases, and vapors. This test is carried out to predict the size of substances that diffuse through certain materials.

In the calcium alginate-based edible film with no glycerol, the weight gain was directly proportional to the increase in immersion time. On the other hand, the calcium alginate-based edible film with glycerol as plasticizer also increased in weight on the first immersion, but the longer the edible film was soaked, the weight of the edible film was lower. It can be due to the edible film no longer interacting with water molecules.

Based on the description above that the addition of glycerol as a plasticizer in the coating film will cause the edible film to be saturated till cannot be ionized and absorb the water was implemented in figure 3.

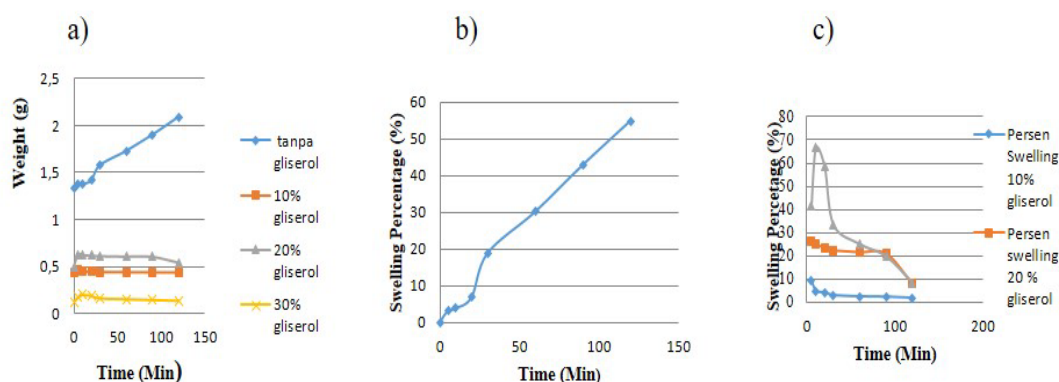


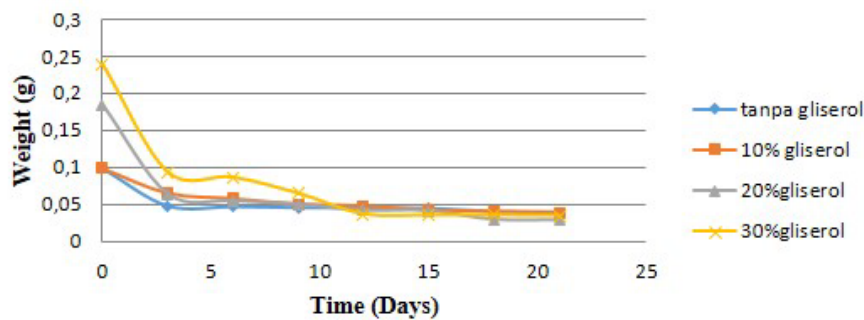
Figure 3. Swelling data of calcium alginate-based edible film

3.6 Biodegradable Edible Film

The biodegradable calcium alginate-based edible film data with no glycerol and 10, 20, and 30 % glycerol plasticizer on the variation of immersion time using *Aspergillus niger* sp were shown in figure 4. It can be seen that the decreasing weight of the edible film along increased the storage time of the film. The weight reduction of the edible film was indicated by the presence of black spots and a reduction in the weight of the coating film at a storage time of 21 days. It indicates that the *Aspergillus niger* sp. can break the polymer chains of the edible film into monomers.

Aside from that, the addition of 10, 20, and 30% of glycerol plasticizer is easily degraded compared to with no glycerol due to the glycerol can reduce the level of the brittleness of calcium alginate. Meanwhile, calcium alginate-based edible film with no glycerol is difficult to decompose because the polymer chains in the edible film are still strong and tight. Hence, it was hard to break. Furthermore, comparative data between calcium alginate-based edible film with

no glycerol and with the addition of glycerol showed that calcium alginate-based edible film



with glycerol can be used as an environmentally friendly plastic.

Figure 4. Biodegradable calcium alginate-based edible film data with no glycerol and 10, 20, and 30% glycerol.

3.7 FTIR (Fourier Transform Infra Red) Analysis

FTIR analysis is to determine the presence of several chemical bonds in organic compounds (Clark, 2004). The FTIR test results indicated in figure 5 show the band at 3446.10 cm^{-1} , which indicated the presence of the OH group, the band at 1577.13 cm^{-1} , which assigned a C=O bond, and the band at 1111.15 cm^{-1} , which showed C-O-C and -COOH.

In this case, there is an interaction between the oxygen from the hydroxy group on the glycerol and the hydroxy group on the calcium alginate-based edible film by forming a hydrogen bridge. From these results, they were found that the spectra of sodium alginate and the spectra of the calcium alginate-based edible films experienced different vibrations due to the formation of cross-links and chelate bonds on the calcium alginate-based edible film (Moe et al., 1996; Gong et al., 2012).

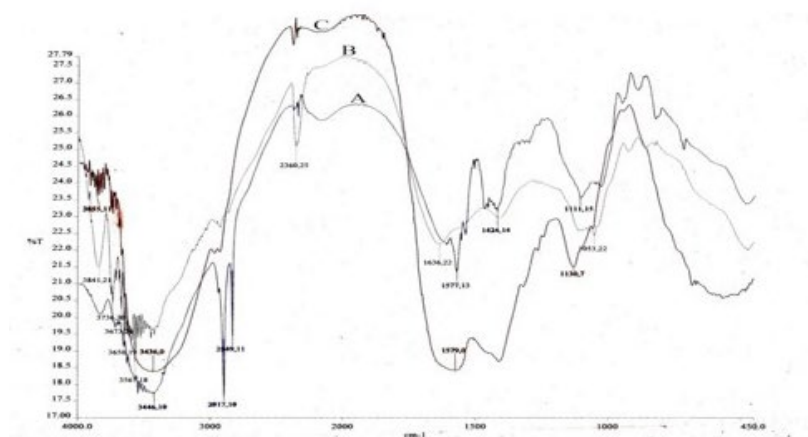


Figure 5. FTIR spectra of calcium alginate based edible film with no glycerol and 10, 20, and 30% of glycerol

4 Conclusion

Edible film calcium alginate with concentrations of 0%, 10%, 20%, and 30% glycerol plasticizer has the following characteristics: 1. The thickness of the film is obtained between 0.120 – 0.164 mm, where the tensile strength increases with the addition of glycerol, and elongation decreases with the addition of 10%, for concentrations of 20% and 30% the elongation price increases. 2. DTA analysis showed an increase in temperature at the time of the release of water vapor, SEM analysis showed a smoother surface, and the swelling test showed an increase in the initial immersion but then a decrease in weight. Meanwhile, the biodegradable test showed the presence of film decomposition on day 21. 3. FT-IR analysis on calcium alginate edible film with the addition of glycerol gave a wider stretching vibration peak of the OH group at 3436.0 cm⁻¹, while the edible film without glycerol showed a sharp OH stretching vibration at 3567.18cm⁻¹.

References

- Alamsjah. A., 2011. Study of Alginate and Chlorophyll Content of *Sargassum* sp. at different harvest ages. Faculty of Fisheries and Marine Universitas Airlangga. Surabaya. pp 121-122.
- Bombardeaux. J. 2006. Glycerin Overview. Australian Department of Agriculture and Food.
- Cwod, MA 1991. Polymer chemistry. Bandung Institute of Technology. Bandung
- Godras J. M, Kartini DS, Pujiasturi, Djagal WM 2003. Development of Biodegradable Film from Marine Products Biopolymers. In the Journal of the National Seminar and PATPI Annual Meeting; The Role of Indushi in the Development of Indonesian Food Products, Yogyakarta.
- Gong, H., Liu, N., Chen, J., Han, F., Gao, C., and Zhang, B., 2012. Synthesis and Characterization of Carboxymethyl Guar Gum and Rheological Properties of its Solution, Carbohydrate Polymers Vol . 88, Page 1015-1022.
- Kinasih, DN, Prasetyaningrum. A, and Wardhani.FDN 2010. Characteristics of Bioactive Edible Film from Composite Alginate and Beeswax as Biodegradable Food Packaging Materials. Chemical and Process Engineering Seminar. Semarang, Indonesia. Diponegoro University, Semarang.
- McCormick, Ed. ALI. 2001. AlginateLifecasters gold. Food and Agriculture Organization of the United Nations, Rome.
- McHugh, Dennis, J., 2003. Basic Principles of Membrane Technology. Knever Academic Publisher Dordrecht.
- Mieir, L, in R. Gachter and H. Muller (eds). 1990. Plastic Additives Handbook. Hanser Publishers. Munich. German.
- Moe ST, Draget KI, Skjak-Break G, and Smidsord O, 1996. Alginates. In: AM (Ed). Food Polysaccharides and Thai Application. P. 230-265. Marcel Deker Inc. New York.

- Matondang TDS, 2013. Production of biodegradable plastic packaging from maleic anhydrous grafted polypropylene with palm sago starch as filler. Thesis. Universitas Sumatera Utara. Medan.
- Tong, H., Xia, F., Feng, K., Sun, G., Gao, X., Sun, L., Jiang, R., Tian, D and Sun, X., 2008. Structural Characterization and in Vitro Antitumor Activity of a Novel Polysaccharide Isolate from the Fruiting Bodies of *Pleurotus Ostreatus*. *Bioresource Technology*, Vol. 100, Page 1628-1686.
- Wirjosentono, B. 1995. Analysis and Characterization of Polymers. USU Press, Medan.
- Yadav, GD and DV Satoskar, 1997. Kinetic of Epoxidation of Alkyl Ester of Undecylenic Acid. Comparison of Traditional Route vs. Ishii-Penturello Chymistry, *JAACS*. 74(4). Page 397-407.
- Zianjiang. F. 1990. Training Manual of Gracilaria Culture and Seaweed Processing in China. China's Regional Seafarming Development and Demonstration Project.