The effect of combination of sugar palm fruit, carrageenan, and citric acid on mechanical properties of biodegradable film

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Abstract. Biodegradable film is a type of plastic material that can be degraded naturally and is usually made of organic material. The material commonly used is polysaccharides. The purpose of this study is to observe the effect of the combination of sugar palm fruit, carrageenan, and citric acid (CA) on the mechanical properties of the biodegradable films, such as tensile strength, elongation and film thickness. The experiment begins with dissolving the sugar palm fruit porridge and carrageenan with ratios of 1:0, 3:1, 2:1, 1:1 in water. The mixture was heated using a heater and magnetic stirrer at 80°C for 10 minutes. Glycerol and citric acid (CA) were added to the solution and stirred for 5 minutes. Each film solution was printed on a modified acrylic and, dried for 18 hours in an oven at 55°C. The formed film layer was then removed from the acrylic mold and inserted in a desiccator at 23°C for 1 hour. Then the film analyzed for its tensile strength, elongation using Dynamic Mechanical Thermal Analysis (DMTA), and thickness. The optimum result shown by sugar palm fruit and carrageenan ratio of 1:1 with 1% citric acid (CA).

1. Introduction

Biodegradable film is a type of plastic material that can be degraded naturally and usually made of organic material. In previous research, a bio plastic made of nata de cassava has a long stage because through the fermentation process to make nata with conditions that must be sterile because it involves bacteria [1]. Further research biofilm produced by adding lactate acid is not commonly used because of its expensive price [2]. Therefore, this research is a middle way that can utilize sugar palm fruit the availability is abundant and easy to obtain and use, carrageenan as a thickener, glycerol as a plasticizer which is easier and cheaper than collagen and addition of citric acid as a cross linker. The components of biodegradable film are sugar palm fruit and carrageenan as the main material, glycerol as a plasticizer and citric acid as a cross linker. The resulted films are expected to have better mechanical properties, such as tensile strength, elongation, and thickness.

2. Component of biodegradable film

The main components of the biodegradable film are grouped into three classes, namely hydrocolloids, lipids, and composites. Hydrocolloid compounds are very numerous in nature, one of which is the galactomannan polysaccharides commonly found in sugar palm fruit. The most often used hydrocolloid in biodegradable films are carbohydrates, especially starch. Sugar palm fruit has a high
content of carbohydrate, so it is a potential raw material in making a biodegradable film. The carbohydrates are mainly starch and galactomannan. The weakness of biodegradable film from carbohydrates is that it is easily torn, so it is necessary to add the plasticizer to strengthen the film produced. Also, it also needs the addition of cross linker, such as citric acid that forms a bond that inhibits recrystallization and retrogradation and increases the tensile strength of the film.

2.1. Sugar palm fruit
Sugar palm fruit has a high content of starch and crude fibber. In addition, the galactomannan polysaccharide compounds are also present. This carbohydrate can be utilized for raw materials in making a biodegradable film.

2.2. Carrageenan
Carrageenan is a polysaccharide extracted from several species of seaweed or red algae (Rhodophyceae). These natural polymers have the ability to form thermo-reversible gels or thickened solutions when they are added the salt solution, so they are widely used as gelling, thickening and stabilizers in various industries such as food, pharmaceuticals, cosmetics, printing, and textiles [3]. Carrageenan can also be used as a foodstuff coating or an edible film-forming agent [4].

2.3. Glycerol as plasticizer
The plasticizer is an additive added to the polymer to improve its performance by increasing ionic mobility and interaction between ionic and polar groups in the polymer chain [5]. One type of plasticizer used is glycerol. The addition of glycerol as plasticizer will reduce the density and force between substrate molecules (starch) with glycerol so that the thin layer formed is more flexible and smooth.

2.4. Citric Acid
Citric acid is a weak organic acid found in certain plant leaves and fruits. The chemical formula of citric acid is C₆H₈O₇. Citric acid (CA) has three carboxyl groups which will bind to the hydroxyl group (-OH) of starch and form an ester group. The bond inhibits recrystallization and retrogradation of the starch and increases the tensile strength of the formed film.

3. Materials and methods
The research was conducted in Instrumentation Laboratory, Chemical Engineering Operations Laboratory, Chemical Engineering Department, Diponegoro University Semarang.

3.1. Materials
The materials for this research were sugar palm fruit obtained from vegetable traders around Tembalang, carrageenan from CV. Karagenan Indonesia, while aquadest, glycerol, and citric acid from chemical store Indrasari Semarang.

3.2. Equipment
The equipment used in this work were basins, thermometers, ovens, acrylic plate, stopwatch, analytical scales (4 digits behind the comma), beaker glass, funnel, heater, and magnetic stirrer.

3.2.1. Fixed variables. Glycerol concentration: 40% (v/w) glycerol / sugar palm fruit – carrageenan and type of solvent: aquadest (total weight 125 gr)

3.2.2. Free variables. Mass ratio of sugar palm fruit to carrageenan for total weight of 5 gr: 1:0; 1:1; 2:1; 3:1 and citric acid concentration (w/w) (mass of citric acid per overall mass): 1% ; 3% ; 5%

3.3. Methods
3.3.1 Biodegradable film making. The biodegradable film was made according to modified methods of Adzaly [6]. First, a pulp of sugar palm fruit was made by cutting the fruit to small pieces to facilitate its destruction by using a blender. Then sugar palm fruit was blended by adding aquadest with a ratio of 1:1. A solution of sugar palm fruit-carrageenan was made by dissolving the pulp of sugar palm fruit and carrageenan in aquadest according to variable ratios in a measuring glass up to 125 ml. The mixture was heated using a heater and magnetic stirrer at 80°C for 10 minutes. Glycerol and citric acid were added to the solution and stirred for 5 minutes. Each film solution was casted on an acrylic plate, and dried for 18 hours in an oven at 55°C. The formed film layer was removed from the acrylic plate and inserted in the desiccator and kept at 23°C for 1 hour. The films were analyzed for thickness, tensile strength, and elongation.

3.3.2 The characterizations of a film. First, thickness analysis. It was conducted to determine the thickness of the film. The measurements were performed using a digital micrometer. Second, tensile strength analysis. The tensile strength of the film was measured at the time of elongation percentage measurement by the same procedure and equipment. Third, percent extension (elongation). The sample was cut into rectangular with the size of 12 cm x 2 cm. Then the sample was placed on the analyzer. The equipment was operated by stretching the sample until the film was broken and the final length of the film before it was broken was recorded.

4. Result and discussion

4.1. Effect of sugar palm fruit: carrageenan ratio and citric acid concentration on tensile strength

![Figure 1. Effect of sugar palm fruit: carrageenan ratio and citric acid (CA) concentration on tensile strength](image)

Figure 1 shows that the smaller the concentration of sugar palm fruit or the greater the concentration of carrageenan, the greater the value of tensile strength. This is due to more hydrogen bond in the film caused by the existence of carrageenan. An increase in carrageenan caused the formation of more hydrogen bonds between starch and carrageenan so the film would have greater bond density and stronger structures [7]. The optimum composition for the tensile strength is the ratio of sugar palm fruit: carrageenan 1:1 with the use of 1% of citric acid. The use of citric acid increases the strength of the film. This is due to the crosslinking formed between citric acid and carbohydrate that increases the value of tensile strength [8].
4.2. **Effect of sugar palm fruit: carrageenan ratio and citric acid concentration on % elongation**

![Graph of % Elongation vs Sugar palm fruit: carrageenan ratio](image)

**Figure 2.** Effect of sugar palm fruit: carrageenan ratio and citric acid (CA) concentration on % elongation

Figure 2 shows that the smaller concentrations of sugar palm fruit or, the greater the concentration of carrageenan increases the value of the elongation of the film. This is due to the increased water holding capacity of the resulted film matrix, so it is better and elastic. This result is similar that the greater the concentration of carrageenan increased the elongation of the film [9]. Increasing the concentration of citric acid affects the value of the elongation where the greater the concentration of citric acid decreases the elongation. The value of elongation in the addition of 1% citric acid slightly decreases compared to that without citric acid. This is due to the occurrence of crosslinking causing bonding between one polysaccharide molecule with other polysaccharide molecules, or even with glycerol [10]. Consequently, the matrix of the formed film becomes less elastic.

4.3. **Effect of sugar palm fruit: carrageenan ratio and citric acid concentration on thickness**

![Graph of Thickness vs Sugar palm fruit: carrageenan ratio](image)

**Figure 3.** Effect of sugar palm fruit: carrageenan ratio and citric acid (CA) concentration on thickness

The thickness of the films, with or without an addition of citric acid, is almost the same. The thickness tends to increase the amount of sugar palm fruit decreases and a number of carrageenan increases. In the previous study, it was reported that the film thickness of the biopolymer was mainly affected by
starch concentration [11]. In this work, although the amount of sugar palm fruit decreases, the increase of the amount of carrageenan and citric acid increases the film thickness due to the total solid. Also, the thickness is also influenced by several other factors including the mixed water content after heating, the depth of the acrylic cast pool, the time and temperature in the heating process [12].

5. Conclusions
Based on its physical and mechanical properties, the ratio of carrageenan: starch of 1:1 and citric acid concentration of 1% are the best carbohydrate ratio and citric acid concentration, respectively, because the resulted film has the highest tensile strength, i.e. 3.91 N / mm². Meanwhile the ratio of sugar palm fruit: carrageenan at constant citric acid concentration has no significant effect on the film thickness.

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References
[1] Heru P dan Eli R.2011. Bioplastik Nata De Cassava Sebagai Bahan Edible Film Ramah Lingkungan. Jurnal Penelitian Saintek, Vol. 16, Nomor 2.
[2] Tuti I.S., Hotman P, Manurung, dan Fery Permadi.2008. Pembuatan Edible Film dari Kolang-Kaling. Jurnal Teknik Kimia, No. 4, Vol. 15.
[3] Campo V.L., Kawano D.F., Junior, S. 2009. Carrageenans: Biological Properties, Chemical Modifications, and Structural Analysis Carbohydrate Polymers. pp. 167-18
[4] Meyer R.C., Winter A.R. dan Weiser H.H. 1959. Edible protective coatings for extending the shelf life of poultry. Food technology. pp. 146-148
[5] Pradipta, I. M. D dan Johar M. 2012. Pembuatan Dan Karakterisasi Polimer Ramah Lingkungan Berbahan Dasar Glukomanan Umbi Porang. Prosiding Pertemuan Ilmiah Ilmu Pengetahuan dan Teknologi Bahan 2012. ISSN 1411-2213
[6] Adzaly, N. Z., Jackson, A., Villalobos-Carvajal, R., Kang, I., Almenar, E. 2015. Development of a novel sausage casing. Journal of Food Engineering. 152, pp.24-31
[7] Wu, Y., Geng, F., Chang, P.R., Yu, J., and Ma, X. 2009. Effect of Agar on The Microstructure and Performance of Potato Starch Film. Carbohydrate Polymers 76: pp299- 304
[8] Ghanbarzadeh, B, Almasi, H., and Entezami, A. A. 2010. Improving the barrier and mechanical properties of corn starch-based edible films:Effectofcitricacidandcarboxymethylcellulose. Industrial Crops and Products p7
[9] Irianto, H.E., Darmawan, M., and Mindarwati, E. 2006. Manufacture of edible film of the composite carrageenan, tapioca starch, and beeswax. Jurnal Penelitian Perikanan Indonesia 1(2): pp 93-101
[10] Lacroix Monique, Genevieve Delmas-Patterson, Ley Tien Canh. 2002. Crosslinked protein and polysaccharide biofilms. Patent WO 2001037683 A9
[11] Basiai, E., Debeaufort, F., Lenart, A.. 2016. Effect of oil lamination between plasticized starch layers on film properties. Food Chem. 195 p56
[12] Rahmansyah, H. 2015. Peningkatan Sifat Fisik dan Mekanis Edible Film Karagenan Melalui Penambahan Penaut Silang Kation Ca²⁺ dan Nanopartikel Karbon. Departemen Kimia. Fakultas Matematik dan Ilmu Pengetahuan Alam Institut Pertanian Bogor