The Effects of plasticizers and palmitic acid toward the properties of the carrageenan Film

Atmanto Heru Wibowo*, Oktaviana Listiyawati and Candra Purnawan
Department of Chemistry, Faculty of Mathematics and Natural Sciences, SebelasMaret University, Jl. Ir. Sutami 36A Surakarta 57126, Indonesia

*Email: aheruwibowo@staff.uns.ac.id

Abstract. Varied plasticizers and palmitic acid additive have been added in the carrageenan film. The film was made by mixing of the carrageenan and plasticizers (glycerol, polyethylene glycol, polyvinyl alcohol) with composition of 92:3, 90:6, 87:9, 84:12, 81:15 (%w/w) and in the presence of palmitic acid as additive with 1%, 2%, 3%, 4%, 5% of total weight. Casting method was used for the film molding and drying at 60°C with the oven for 12 hours. To investigate the effects of plasticizers and additive, some mechanical tests on film were performed. The test result concludes that plasticizers in the film decreased the tensile strength and increased the elongation break of the carrageenan film. The additive of palmitic acid decreased the tensile strength of the carrageenan film and also decreased the water absorbance of the film. The highest tensile strength of films made was with the formulation of carrageenan: PEG with composition of 92:3 (% w/w). The highest elongation break of the film was for carrageenan:PVA with the composition of 81: 15 (%w/w) and carrageenan:palmitic acid:PEG with the composition of 92: 3: 1 (%w/w). The lowest water absorption of the film was achieved for carrageenan:PVA:palmitic acid with the composition of 87: 3: 5 (%w/w).

1. Introduction
Carrageenan is the generic name for a family of high molecular weight sulfated polysaccharides obtained by extraction of certain species of red seaweeds [1]. This extracted carrageenan is a hydrocolloid composed from ester, sodium, potassium, magnesium, and calcium sulfate with a copolymer of 3,6 anhydrogalactosa. K-Carrageenan is a sulfated galactan polymer that is often used in the food industry and is expected to exhibit good adhesion on the surface of membrane filters via hydrogen bonding as well as electrostatic interactions [2]. The combination of gelatin and carrageenan also results in a hydrogel. Hydrogels are nothing but hydrophilic three-dimensional polymer networks capable of absorbing large amounts of biological fluids. Because of their relatively high water contents and their soft, rubbery consistency, hydrogel materials more closely resemble their physical properties to living tissue [3]. Some papers reported that carrageenan is suitable to be used for edible film or coating. Carrageenan-based coatings have been proven efficient to extend the shelf life of fresh-cut and fresh whole fruits, observed that carrageenan films present lower oxygen permeability than starch films. Moreover, carrageenan-coated strawberries presented lower weight loss and firmness loss when compared to starch-coated strawberries, probably reflecting a better moisture barrier of carrageenan coatings [4].

The plasticizer is added into the carrageenan film in order to increase the flexibility of the biopolymer film by reducing the intermolecular and intramolecular interaction within the polymer in
the film, decreasing brittleness and increasing the elasticity of the film. Some plasticizers have been added in the biopolymer film such as glycerol, polyethylene glycol, polyvinyl alcohol, and sucrose [5]. However, the addition of plasticizer with high concentration is able to reduce the functionality of the edible film such as the water vapor resistance and the mechanical properties [6]. The additive agent added into the film is common with highly lipophilicity or lipid. The addition of the lipid is able to increase the hydrophobicity of the film system. Lipid plasticizer that is commonly used for the edible film is glyceride, wax and a fatty acid such as stearic and palmitic acid due to the hydrophobicity and high melting point [7]. This study is aimed to investigate the influence of the plasticizer concentration and the fatty acid toward mechanical properties of edible film from carrageenan film. Besides, the fatty acid added into the carrageenan-based film is to increase the lipophilicity of the film to resist the water pass through where plasticizers used might be a lack of their lipophilicities. The addition of the palmitic acid into the carrageenan film together with the palmitic acid as long as the knowledge of the author has been not reported yet.

2. Methods

2.1. Materials
Carrageenan used for the study was kappa (κ) form obtained from PT. Bratachem (Solo Branch) for pharmaceutical, cosmetic, food, and other industries Solo, Indonesia). Plasticizers of glycerol, polyethylene glycol (PEG), polyvinyl alcohol (PVA) 98% were purchased from Bratachem (Indonesia), Merck (Germany), and Merck (Germany), respectively. The palmitic acid additive was obtained from PT. Bratachem (Solo Branch) for pharmaceutical, cosmetic, food, and other industries. Potassium chloride was obtained from Merck (Germany).

2.2. Instruments
The instrument used for the study is infra-red spectrophotometer from FT-IR IR prestige Shimadzu 8201 PC. Tensile strength measurement device is from Pearson Panke Equipment LTD and oven from Barnstead International 3513-1

2.3. Edible film casting with various plasticizers
Edible film formulation was divided based on the plasticizer used. Three kinds of carrageenan film with formulation glycerol plasticizer, PEG plasticizer, and PVA plasticizer. A film with glycerol was formulated by mixing 3 g κ-Carrageenan, 0.144 g potassium chloride and glycerol plasticizers with various concentrations (w/w) of 3%, 6%, 9%, 12%, 15%. A film with PEG was formulated by mixing 3 g κ-Carrageenan, 0.144 g potassium chloride and PEG plasticizers with various concentrations (w/w) of 3%, 6%, 9%, 12%, 15%. A film with PVA was formulated by mixing 3 g κ-Carrageenan, 0.144 g potassium chloride and PVA plasticizers with various concentrations (w/w) of 3%, 6%, 9%, 12%, 15%.

κ-Carrageenan, potassium chloride, and plasticizers were solved with 100 mL of distilled water and stirred until homogeny solvent of suspension-like achieved. The solvent was heated at about 80°C and exposed with homogeny thickness on the 21.5 cm × 16 cm glass plate until room temperature. Heating the film on the plate was done for 24 hours at 60 °C. The casted film was than stick off from the glass for the further test.

2.4. Edible film with palmitic acid additive
The influence of palmitic acid additive toward the character of the film was tried to select films with a plasticizer of the highest tensile strength value of tested film. The casting method of the edible film with the addition of palmitic acid is the same with above method. The addition of palmitic acid to the films is with various compositions of 1%, 2%, 3%, 4%, and 5% (w/w) palmitic acid.
2.5. Characterization of edible film
Films cast with various plasticizers and with the addition of palmitic acid were tested for some mechanical parameters such as tensile strength (TS), Young’s modulus with Pearson Panke Equipment LTD and elongation to break with Ruller. The swelling test was also done to investigate the resistance of film towards the water. Fourier Transform Infra-Red (FTIR) was also done to investigate the kind of mixture binding of the films.

2.5.1. Test of tensile strength (TS), % elongation to break and Young’s modulus
Tensile strength and elongation test is carried out based on ASTM D-638. The equations used for the tensile strength determination are listed as:

a. Tensile Strength value of the film is determined by formula (equation (1)).

\[ \sigma = \frac{N}{(T \times L)} \] (1)

Where:
\( \sigma \) = tensile strength of films (MPa)
\( N \) = force applied (N)
\( T \) = thickness of film (mm)
\( L \) = length of the film (mm)

b. Elongation value of the film is determined by equation (2).

\[ \{ \frac{(L_i - L_o)}{L_o} \} \times 100\% \] (2)

Where:
\( L_i \) = length of the film after test (cm)
\( L_o \) = length of the film before test (cm)

c. Young’s Modulus is determined by equation (3).

\[ E = \frac{\sigma}{\varepsilon} \] (3)

Where:
\( E \) = Rigidity of the film (MPa)
\( \sigma \) = Strength of drag force (MPa)
\( \varepsilon \) = Elongated film (%)

2.5.2. Swelling test of water
Swelling test is determined by equation (4).

\[ \text{Swelling Index} \% = \frac{W - W_o}{W_o} \times 100\% \] (4)

Where:
\( W \) = weight of edible film after water soaking (gram)
\( W_o \) = weight of edible film before water soaking (gram)
3. Result and Discussion

3.1. Carrageenan Edible Film with Variation of Plasticizer Concentration

The edible film of Carrageenan is with light brown color, rather a rough, a little bit oily with the thickness of 0.8 – 1.5 mm. Products of the edible film with the variation of plasticizers are showed in Figure 10.

![Figure 10](image)

(a) (b) (c)

**Figure 1.** Edible film of carrageenan with glycerol (a) with PEG (b) with PVA (c)

3.1.1. Tensile Strength Test

Figure 2 showed tensile strength value of film which was tested with ASTM D-638 standard method.

![Figure 2](image)

**Figure 2.** The effect of plasticizer toward tensile strength in the carrageenan film

Figure 2 showed that all kind plasticizers with increasing concentration of 3% to 15% (w/w) decreased the tensile strength of the film. This result indicated that the plasticizer as the common basic property of plasticizer just afford the elasticity but not simultaneously increased the tensile strength. The tensile strength obtained from the film was around 4.418 - 1.308 Mpa with glycerol, 5.725 – 1.942 Mpa with PEG and 4.297 – 2.5 Mpa with PVA. Plasticizers behaved on the film as an agent which changes the
mechanical property of the film and decreased the cohesion and mechanical resistant of the chain polymer [8]. Plasticizers also caused internal hydrogen bonding strength and reduced the polymer intermolecular bonding strength which reduced the strength of the strain-brake strength of the film. This bonding change within the film was showed on the infrared spectrum, in which intensity of OH group become wide after components blending to form a film. Plasticizer dispersed in the carrageenan was depended on the concentration added. More plasticizers added, the strength of intermolecular bonding decreased as more plasticizers filled between the carrageenan-film layers.

3.1.2. Elongation to break test
Elongation to break test was done following ASTM D-638 standard. Figure 3 showed the percentage of elongation of the Carrageenan with varied concentration.

![Figure 3](image-url)

Figure 3. Effect of plasticizer and concentration toward % elongation of carrageenan film

Figure 3 showed that increasing concentration of plasticizer 3% to 15% (w/w) increase also the elongation value. Elongation value obtained was 6.25% – 12.5% with glycerol, 5.88% - 15.38% with PEG and 5.55% - 21.43% with PVA. The phenomena of the change of tensile strength were also similar to the elongation value, in which reducing the strength of hydrogen bonding and intermolecular force was the cause of the strain-brake force and the increase the flexibility of the film. The present of the plasticizer randomized the structure of film molecule which affected to the reduce of the film matrix rigidity. The increase of plasticizer will also increase the elongation value.

3.1.3. Young Modulus Test
Modulus Young Test was done following the ASTM D-638 standard. Young modulus value of the film was obtained from the calculation of tensile strength divided by elongation to break. Figure 4 showed the modulus young of the film with the concentration of the plasticizer.
Figure 4 showed that Youngs modulus value of film tended to decrease with the increase of plasticizer concentration added. Young Modulus obtained of test on the film was 70.688 – 10.464 Mpa with glycerol, 97.364 – 12.627 Mpa with PEG and 77.423 – 11.666 Mpa with PVA. The increase of plasticizer concentration added (3% - 15% (w/w), the rigidity of the material tend to decrease. This was due to the role of the plasticizer to increase the elasticity of film.

3.2. The effect of the additive concentration of palmitic acid
The effect of palmitic acid as an additive agent was tested toward the film which has the highest tensile strength of each plasticizer. The aim of the test on the film with high elongation is to investigate the ability of the film to protect the product from the mechanical accident. From the physical figure of figure 5, white granules with thickness 0.8 – 1.5 mm appeared on the surface. This seemed that the lipophilicity difference was still a problem. The carrageenan film products with the variation of palmitic are shown in figure 5.

Figure 5. Edible film of carrageenan with palmitic acid and glycerol (a) with palmitic acid, PEG and glycerol (b) with palmitic acid, PVA, and glycerol (c)
3.2.1. Tensile Strength Test
Figure 6 showed the effect of the palmitic acid additive on the tensile strength of the film.

![Image of tensile strength graph]

Figure 6. Effect of the tensile strength of the carrageenan film at various palmitic acid concentration

Figure 6 showed that the tensile strength of the film tended to decrease as palmitic concentration from 1% to 5% (w/w) increased. The tensile strength obtained with the palmitic acid additive was 4.111 – 2.074 Mpa for glycerol plasticizer, 2.9 – 1.533 Mpa for PEG plasticizer, and 3.745 – 1.785 Mpa for PVA plasticizer. According to Yang and Paulson (2000), the addition of fatty acid causes the decrease of tensile strength value of the film. The decrease in the tensile strength causes the film more fragile or broken.

3.2.2. % Elongation Test
Figure 7 showed the result of elongation test after addition of palmitic acid toward Carrageenan film.

![Image of elongation graph]

Figure 7. Elongation of carrageenan film after addition of palmitic acid
The figure 7 showed that the increase of the palmitic acid concentration from 1% to 5% (w/w) tended to decrease the elongation value. The elongation value of film with palmitic acid was 16.67%–7.143% with glycerol plasticizer, 18.18% - 6.25% with PEG plasticizer and 16.67% - 5.26% with PVA plasticizer. Palmitic acid seemed to hinder the interaction of carrageenan molecule in the film.

3.2.3. Youngs Modulus Test
Figure 8 showed the correlation of Young Modulus Test of the film after addition of palmitic acid.

![Figure 8](image_url)

Figure 8. The Young modulus value of the film after the addition of palmitic acid.

Figure 8 showed that the lowest Youngs modulus value of the film after the palmitic acid addition was with the composition of film 3% PEG and 4% palmitic acid. The Youngs modulus value of the film was 24.661 – 29.035 Mpa with glycerol plasticizer, 15.952 – 24.524 Mpa with PEG plasticizer and 22.466 – 33.935 Mpa with PVA plasticizer. The addition of palmitic acid from 1% to 5% (w/w) is generally able to increase film elasticity.

3.2.4. Swelling test
The swelling test was done to investigate the interaction between polymer and uniformity of bonding within polymer which is determined by percentage of weight increase after swelling. Diffusion of the solvent molecule into polymer causes the swelling of the polymer. Figure 9 showed that the swelling test (swelling index) of the film in the present of varied palmitic acid.
Figure 9. The effect of palmitic acid concentration toward swelling index (%) of the film.

Figure 9 showed that 5% palmitic acid in the film affected the best water resistant toward other additions. Swelling index (%) of film with various concentration of palmitic acid was 94% - 81% for glycerol plasticizer, 94% - 80% for PEG plasticizer, 96% - 77% for PVA plasticizer. Palmitic acid in the film decrease the swelling index as hydrophilicity of the palmitic acid hindered water diffusion into the film.

3.3. Analysis of Film Structure
Structure analysis of the film is aimed to investigate the content and interaction of functional group in the film. IR spectra of the film are showed in figure 9.

Figure 10. IR Spectra of carrageenan film with glycerol (black), carrageenan (pink), PEG (red), palmitic acid (green)

Figure 10 showed that hydroxyl group of the film at about 3400-3450 cm\(^{-1}\) was seen from carrageenan, plasticizer and additive (plasticizer glycerol, PEG, and PVA). C-H stretch of glycerol at 2945.30 cm\(^{-1}\), PEG at 2920.23 cm\(^{-1}\), PVA at 2902.87 cm\(^{-1}\), sulphate ester at 1219 – 1259 cm\(^{-1}\),
glycosidic at 1035 - 1072 cm\(^{-1}\) (for all carrageenan). 3,6-Anhydro D-galactose bond at 910–925 cm\(^{-1}\). D-Galactosa-4 sulfate at 844 – 846 cm\(^{-1}\). C=O Carbonyl on glycerol at 1627.92 cm\(^{-1}\), PVA at 1635.64 cm\(^{-1}\). S=O group at 1219.01 cm\(^{-1}\) for glycerol, PEG at 1163.08 cm\(^{-1}\), PVA at 1035.77 cm\(^{-1}\). O-H stretch of glycerol at 3419.79 cm\(^{-1}\), PEG at 3444.87 cm\(^{-1}\), C-O ester stretch of glycerol at 910.40 cm\(^{-1}\), PEG at 1062.78 cm\(^{-1}\), PVA at 923.90 cm\(^{-1}\). The additional of glycerol, PEG, PVA and palmitic acid are aimed for the development of carrageenan film on mechanical properties and water resistant where the IR spectra showed just the physical interaction between additive and matrix in the film occurred.

4. Conclusion
Almost all plasticizers in the carrageenan behave to reduce tensile strength and Young modulus properties and increase the elongation value of the film (3% and PVA 15%). Increased concentration of palmitic acid in the film decrease the tensile strength, % elongation and Young modulus of the carrageenan film. The best composition of film that affords the value of swelling index, tensile strength, elongation and Young modulus is obtained for the film (3% glycerol, 1% palmitic acid and 3% PEG, 1% and 4% palmitic acid) and the best value of swelling index of film is obtained for the film (5%palmitic acid and PVA plasticizer). Palmitic acid is able to be used together with a plasticizer to increase the water resistant of the carrageenan film.

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