



## Effect of Plasticizer Addition on The Characteristics of Chitosan-Alginate Edible Film

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**ABSTRACT.** The edible film of chitosan-alginate in this study showed characteristics of the physical and mechanical properties when various plasticizers of polyethylene glycol/PEG, polyvinyl alcohol/PVA, and glycerol were added into the origin film. It was also found that chitosan content in the edible film contributed to the change in the physical properties and the conductivity of the film. The general effect on the film because of the addition of plasticizers was the decrease of the tensile strength, the increase of the films' elongation, and the increase of the water vapor permeability (WVP). Among other plasticizers, PEG attracted the most attention in which it affected the most significant change on the properties. Meanwhile, the higher chitosan content in the chitosan-alginate film affected the increase of the tensile strength and the decrease of the elongation value, and the decrease of the WVP on the film. Characterization using FT-IR spectrophotometer showed that no chemical interaction was formed due to the mixing of alginate-chitosan in the film. Instead, only the physical blending of chitosan-alginate was formed in the edible film.

## INTRODUCTION

Nowadays, edible film is considered an important class of natural polymers owing characteristics to prevent water vapor movement, gas exchange, flavor loss, and lipid movement and to improve physical properties and as a carrier of additive substances (Hui, 2006). In general, edible film is composed of three main substances; hydrocolloid, lipid, and mixture. Alginate, that is one of the main substances of edible film, is classified in the group of hydrocolloid (Donhowe and Fennema, 1994) which is formed mainly from polymer of polysaccharide. It has thermoplastic characteristic for instance easily formed and molded when applied as film packaging. In the form of its salt, sodium alginate (Na-alginate) is water soluble, but calcium alginate is water insoluble with the rigid structure. Some reports about Ca-alginate for edible film have been published for decades up to now. The contents of the reports mostly are about the development and the modification of Ca-alginate film (Chen *et al.*, 2023b; Choi *et al.*, 2022; Karimi-Khorrami *et al.*, 2022; Rodrigues *et al.*, 2023; Santos *et al.*, 2022; Schöbel *et al.*, 2023; Zakaria *et al.*, 2023).

In the following stage of the development of alginate as an edible film, some additive substances such as putrescine (Zhong *et al.*, 2023) and montmorillonite (Zhang *et al.*, 2023) have been used to increase the properties of alginate film. Chitosan is one of the natural substances that is commonly used as filler for the edible film. The flexibility of the edible film is an important factor in why plasticizer addition is needed into the alginate substance. Besides, plasticizers have functions to protect a film from cracking and increase the permeability of gases and water vapor, and also to increase its solubility. The mechanical and physical properties of a film can be modified because of the cohesion and mechanical resistance reduction of the polymer chain (Lieberman and Gilbert, 1973). Glycerol, polyethylene glycol (PEG), and polyvinyl alcohol (PVA) are commonly known as additives for the film. The flexibility of the film due to the presence of polyols group such as glycerole and PEG can affect the structure of the edible film to be smoother. On the contrary, the addition of PVA plasticizer can improve the rigidity of an edible film (Lieberman and Gilbert, 1973).

Chitosan is classified as natural polysaccharides (hydrocolloids) through the deacetylation process. Some reports mentioned that chitosan is a good substance for edible film and membrane (Bouyer *et al.*, 2023; Castro-

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Muñoz *et al.*, 2023; Chen *et al.*, 2023a; Das *et al.*, 2023; Kong *et al.*, 2023; Soontarapa *et al.*, 2023). The cationic group of chitosan in the membrane structure has electrostatic interaction with anionic group for the formation of edible film. Besides, chitosan has strong, elastic, flexible properties that are required for the edible film. In this study, the hydrophobic property of chitosan is applied to the edible film in combination with alginate. This chitosan-alginate is then combined with some additive substances to obtain the best mechanical and physical properties of edible film.

## RESEARCH METHODS

FT-IR spectrometer used was from Prestige Shimadzu 8201 PC. Tension strength was from Pearson Panke Equipment LTD. Oven was from Barnsted International 3513-1. Some cups were standardized using ASTM E-96 for the measurement of water vapor permeability.

Na-Alginate was obtained from Bratachem, Indonesia. Chitosan (with unlabeled DD) was obtained from the treatment of prawn crust in Lembaga Ilmu Pengetahuan Indonesia (LIPI). Polyvinyl alcohol, polyethylene glycol, calcium chloride, and acetic acid were pro-analysis grade from Merck, Germany.

### Fabrication of Film Ca-Alginate with Variation of Plasticizer Concentration

About 3.00 g Na-alginate, 0.14 g CaCl<sub>2</sub>, and 3% (w/w) of plasticizer (Glycerol/ PEG/ PVA) were mixed in 250 mL beaker glass and dissolved in 100 mL water. The solution was then stirred to homogenous alginate solution. About 1 g chitosan was added into 150 mL beaker glass and dissolved in the 100 mL 1% (v/v) acetic acid solution. The solution was stirred and heated at 60 °C to homogenous chitosan solution. Alginate with plasticizer and chitosan 96:4 (w/w) was mixed in 250 mL beaker glass and stirred at room temperature until homogenous solution was obtained. To form the film, the solution was then removed and coated uniformly to the glass plate (21.5 cm × 16 cm). The same procedure was repeated for plasticizer with weight percentages of 6%, 9%, 12%, and 15%. On the other hand, the film of Ca-alginate without chitosan was also made with the content of 15% (w/w) plasticizer. Films made were dried in the oven at 60 °C for ± 24 hours. The edible film was then loosed from the glass plate.

### Fabrication of Ca-Alginate Edible Film with Variation Concentration of Chitosan

About 3 g Na-alginate, 0.144 g CaCl<sub>2</sub>, and 15% (w/w) plasticizer (Glycerol, PEG, PVA) were mixed and stirred in 250 mL beaker glass and dissolved with 100 mL water until homogenous solution was obtained. Meanwhile, 1 g chitosan solution was prepared by dissolution in 100 mL 1% (v/v) at 60 °C. To the alginate mixture, the chitosan solution was added with the concentration of the same amount of plasticizer and with the weight ratio (w/w) of alginate solution: chitosan solution of 94:6, 92:8, 90:10, and 88:12 (w/w) in 250 mL beaker glass and stirred at room temperature until homogenous mixture obtained. To the glass plate 21.5 cm × 16 cm, thin film was made with a thickness 1 – 1.5 mm. In comparison, alginate film without chitosan was also made with the same amount of 15% (w/w) plasticizer. The film on the glass plate was dried at 60 °C for ± 24h and loosened from the plate.

### Tensile Strength and Elongation to Break of Ca-Alginate Film

Tensile strength and elongation to break were analyzed according to the ASTM D-638. Edible films of alginate composed of different % w/w of plasticizers were dumbbell-shaped with either a 25 mm/50 mm gauge length. The tensile strength was determined based on the [Equations \(1\)](#),

$$\sigma = \frac{F}{(T \times L)} \quad (1)$$

where:

$\sigma$  = tensile strength (MPa)

F = maximum force (Newton)

T = thickness (mm)

L = length (mm).

Elongation to break was determined using [Equation \(2\)](#),

$$\varepsilon = \left\{ \frac{(L_i - L_o)}{L_o} \right\} \times 100\% \quad (2)$$

where:

$\varepsilon$  = elongation to break (%)

$L_i$  = length after pulled (cm)

$L_o$  = initial length (cm).

### Water Vapor Permeability

Water vapor permeability was determined based on ASTM E-96 for explaining water vapor transmission rate testing. A cup was filled with distilled water until air space between edible film of alginate on the top of cup and the surface of water was about 0.75" to 0.25". This cup was then sealed to prevent vapor loss as tight as possible prior to the initial weight was taken. Weighing was then done periodically over time until results become linear. Water vapor permeability (WVP) was determined by Equation (3),

$$WVP = \frac{(\text{slope} \times \text{thickness})}{(A \times P)} \quad (3)$$

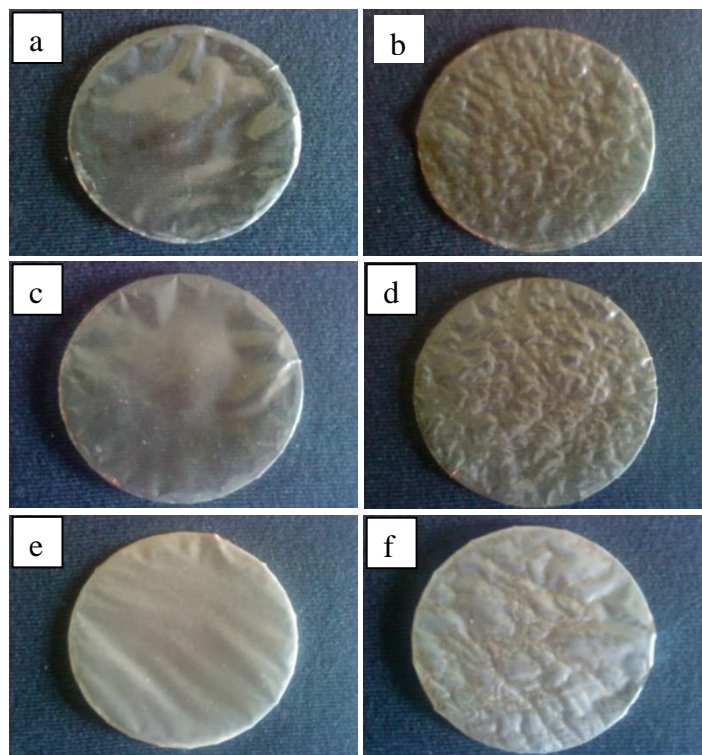
where:

Slope = b, from linear integration

Thickness (mm),  $A = (1/4) \times \pi \times D^2$  (m<sup>2</sup>),  $P = \text{atm}$ .

### RESULTS AND DISCUSSION

In this study, the discussion was written based on the data obtained from the measurement and focused on the physical and mechanical change of the edible film. The physical appearance of the alginate film was shown in Figure 1. The addition of CaCl<sub>2</sub> onto the Na-alginate initiated the exchange of Ca<sup>2+</sup> ion to the Na<sup>+</sup> ion. Generally, it occurred due to the gel formation as the effect of the presence of di or trivalent ions. Figure 1 showed the appearances of the Ca-alginate film at different compositions of plasticizers.



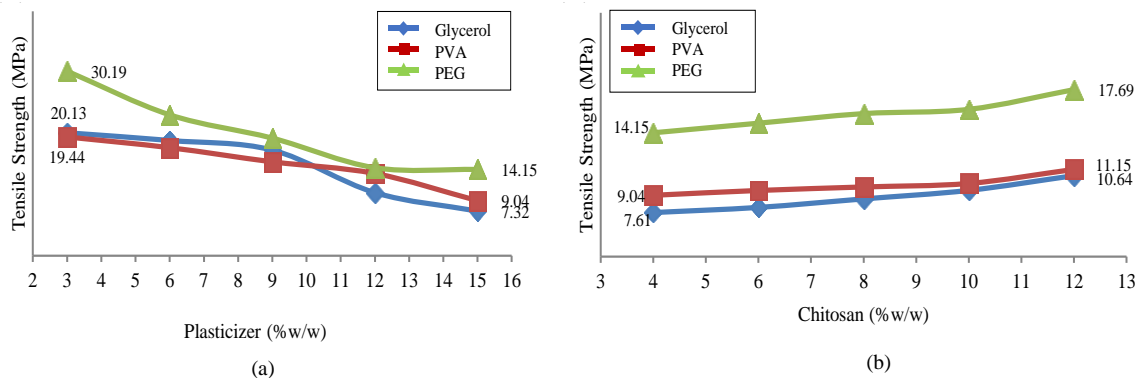
**Figure 1.** (a) Edible film alginate without chitosan and with glycerol, (b) with chitosan and glycerol, (c) without chitosan and with PVA, (d) Edible film alginate-chitosan plasticizer PVA, (e) with chitosan and PVA, and (f) with chitosan and PEG.

From Figure 1, it can be seen that there was a clear change at the surface of the film. The plasticizer used, as well as the addition of chitosan, affected the physical surface appearance of the film. PEG plasticizer affected the film to be harder and more rigid. Meanwhile, the other plasticizers (PVA and glycerol) led to a smoother and

more elastic edible film. The surface film was seen smoother when PVA was added into the film. On the other hand, the surface of the film was coarser when PEG was added into the film. In general, the addition of chitosan modified the film surface to be coarser due to homogeneity of the chitosan in the alginate film and the nature of chitosan. Meanwhile, the nature of the plasticizers added into the film generally caused the film surface to be smoother. Functional groups of the plasticizers can modify the structure interactions of the film that affected the physical appearance of the film.

### Tensile Strength Test

The tensile strength test of the edible film was done according to the standard of ASTM D-638. The result of the tensile strength of the alginate chitosan film with various concentrations of plasticizer was shown in Figure 2a and the tensile strength of alginate-chitosan film with various concentrations of chitosan was shown in Figure 2b.



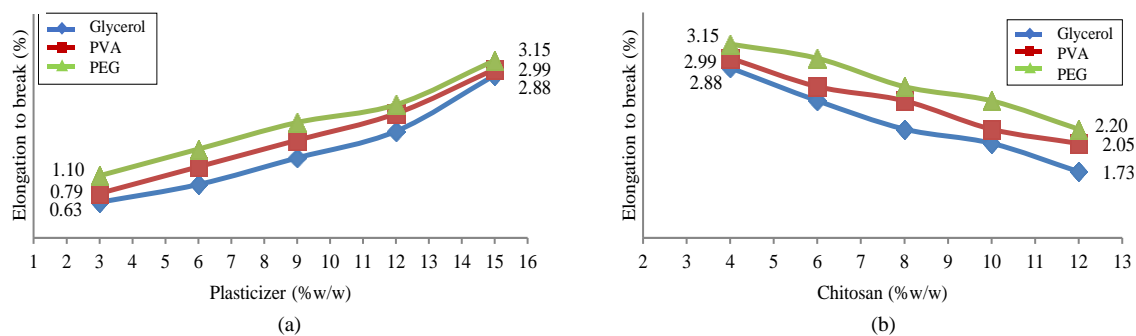
**Figure 2.** (a) Tensile strength of alginate-chitosan with various plasticizer concentrations (% w/w) and (b) tensile strength of alginate-chitosan film with various chitosan concentrations (% w/w).

Figure 2a showed that increasing the plasticizer concentration to 3%, 6%, 9%, 12%, and 15% (w/w) in the chitosan concentration of 96:4 (w/w) caused a decrease in the tensile strength of the alginate-chitosan film. It was due to the increase of plasticizer concentration and the interaction force of the polymer matrix in the alginate-chitosan weaker. As a consequence, the tensile strength of the film decreased. Besides, the increase in the plasticizer number might reduce the intermolecular and intramolecular-hydrogen bonding of the polymer chain followed by the increase in polymer mobility and also migration of water vapor (Rodrigues *et al.*, 2006).

The tensile strength data (Figure 2b) showed that the increase of chitosan concentration from 96:4, 94:6, 92:8, 90:10, and 88:12 (w/w) in the 15% (w/w) plasticizer concentration affected the increase of the tensile strength of the films. A higher chitosan content in the film resulted in a higher structural strength of the film compared to the only alginate structure. The interaction strength between chitosan and alginate was higher than the interaction of only alginate in the film.

### Elongation to Break Test

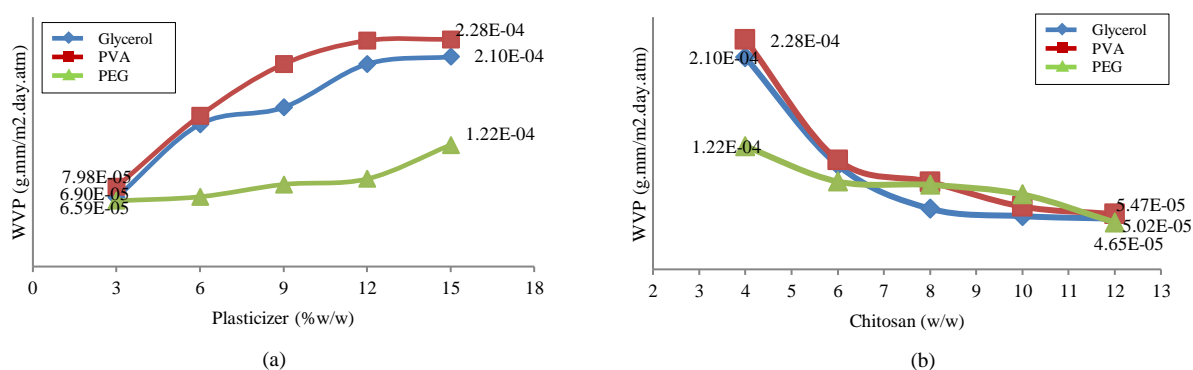
Elongation to break test of alginate-chitosan film in the various plasticizer and chitosan concentrations according to the ASTM D-638 was seen in Figure 3a and 3b. The result of the elongation break from Figure 3a showed that the increase of plasticizer concentration of 3%, 6%, 9%, 12%, and 15% (w/w) at the concentration ratio of alginate chitosan 96:4 (w/w) caused by the increase of the elongation to break of the film. Besides, the increase in plasticizer concentration affected the reduction of intermolecular and intramolecular hydrogen bonding of the chain. As a consequence, the flexibility and the percentage of elongation to break of the film increased. As shown in Figure 3b, the increase of chitosan concentration 96:4, 94:6, 92:8, 90:10, and 88:12 (w/w) in the 15% (w/w) plasticizer concentration caused the reduction of the elongation to break of the alginate-chitosan film. It was due to the increase of synergic interaction force in the polymer matrix in the film.



**Figure 3.** (a) Elongation to break alginate chitosan film in the various plasticizer concentrations and (b) Elongation to break alginate chitosan film in the various chitosan concentrations.

### Water Vapor Permeability

Water vapor permeability was determined according to the ASTM E-96. The result of the water vapor permeability of the film with various concentrations of plasticizer and chitosan was seen in Figure 4a and 4b.



**Figure 4.** Water vapor permeability of alginate-chitosan film in the various concentrations of (a) plasticizer and (b) chitosan.

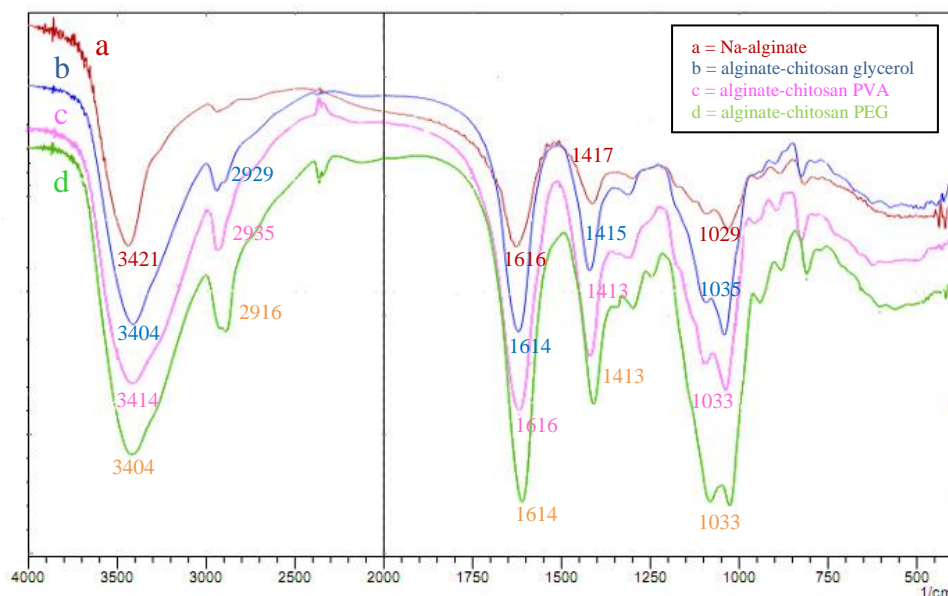
The increase in the number of the plasticizer content in the film caused the water vapor permeability to increase (Figure 4a). It was due to the decrease of intermolecular and intramolecular hydrogen bonding of the polymer chain regarding the addition of plasticizer. Furthermore, plasticizer weakened the intermolecular hydrogen bonding between the closest polymer chain. Besides, the increased mobility of the polymer chains due to the reducing intra and inter-hydrogen bonding caused the increase in water vapor permeability.

As seen in Figure 4b, the increase in the number of chitosan in the alginate film caused the reduction of the water vapor permeability. Chitosan is classified as natural hydrophobic substance with higher water resistance. In general, a lower water vapor migration through film means a better edible film to maintain the lifetime of the packed product. The stronger networking structure of the film caused the increase in the film lifetime due to water vapor migration through the structure.

### FT-IR Characterization

Figure 5a shows IR spectra of Na-alginate at 3421 cm<sup>-1</sup> of (OH), 1616 cm<sup>-1</sup> (C=O), 1417 cm<sup>-1</sup> (O-Na), and 1029 cm<sup>-1</sup> (C-O). Plasticizers of glycerol, PVA, and PEG (-OH-NH<sub>2</sub> vibrations) were seen with wavenumbers at 3404 cm<sup>-1</sup>; 3414 cm<sup>-1</sup>; 3404 cm<sup>-1</sup>, respectively. C-H stretching was seen at wavenumbers 2929 cm<sup>-1</sup>; 2935 cm<sup>-1</sup>; 2916 cm<sup>-1</sup>. C=O vibrations were seen at 1614 cm<sup>-1</sup>; 1616 cm<sup>-1</sup>; 1614 cm<sup>-1</sup>. C-H bending was seen at wavenumber 1415 cm<sup>-1</sup>; 1413 cm<sup>-1</sup>; 1413 cm<sup>-1</sup>. C-O vibrations were seen at 1035 cm<sup>-1</sup>; 1033 cm<sup>-1</sup>; 1033 cm<sup>-1</sup>. Figure 5a showed the presence of O-Na vibration. Figures 5b, 5c, and 5d showed the presence of -NH<sub>2</sub>, C-H stretching, and C-H bending. This proved that the substance characterized in Figure 5a was pure Na-alginate and substances characterized in Figure 5b, 5c, and 5d were edible films with various plasticizers. As observable in the FTIR

spectra, it can be concluded that the interaction of additive, alginate, and chitosan in the film occurred due to physical blending.



**Figure 5.** FT-IR Spectra of Na-alginate (a) and alginate-chitosan with different plasticizers of glycerol (b), PVA (c), and PEG (d) in correlation with %T.

## CONCLUSION

The addition of glycerol, PVA, and PEG plasticizer affected the mechanical physical properties of the edible film of Ca-alginate. Increasing plasticizer concentration led to the reduction of tensile strength and water vapor permeability and an increase in the elongation to break value. The increase in chitosan number affected the physical and mechanical properties of Ca-alginate film, such as the increase in tensile strength, the decrease in water vapor permeability, and the decrease in elongation to break value.

## CONFLICT OF INTEREST

There is no conflict of interest in this article.

## AUTHOR CONTRIBUTION

All authors confirm responsibility for study conception and design, data collection, analysis and interpretation of results, and manuscript preparation. All authors reviewed the results and approved the final version of the manuscript.

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