The Preparation of Agar-chitosan Film from *Gracilaria*

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Abstract: Packaging is one of the most important parts in maintaining the quality of food product. The film of agar-glycerol-chitosan has been prepared fromthe isolated agar of *Gracilaria*. The objective of this study is to investigate mechanical properties including the tensile strength, the young's modulus, the elongation at break,the functional groups by FTIR and the water solubility. The film was prepared by mixing agar, glycerol (20 %) and chitosan (0 %, 1 %, 2 %, 3 % and 4 %) at 60 ^{0}C and 600 rpm. FTIR showed that the interaction occurred in the film agar-glycerol-chitosan was hydrogen bonding. From the result, the more chitosan added to the agar-glycerol-chitosan film, the higher the tensile strength, the elongation at break, the young's modulus and the water solubulity.

1 INTRODUCTION

Packaging is one of the most important parts in maintaining the quality of food products. The most commonly used packaging is plastic, but the use of plastic causes some problems such as difficult to degradable in nature and environmentally unfriendly. Similarly, there is a concern using plastic as packaging which transfers plastic molecules to food. Hence, edible film is considered as one of alternatives for packaging food because it is environmentally friendly and safe for consumption.

Some biopolymers used as edible film and coating materials are polysaccharides, proteins and lipids (Susanne and Gauri 2002; Paula et al., 2014; Kwang et al., 2004). The biopolymers are available abundantly in nature and they can be easily and continuously obtained. Seaweed is one of potential resources of polysaccharides. For example alginate, agar, carrageenan, and vulvan. Agar is a derivative of the polysaccharide present in the cell wall red algae of Rhodophyceae class (Rafael,1995)which is widely cultivated in Indonesia.

Chitin is the main componen of the exoskeleton of crustacea like crabs and shrimps.Chitin is composed of a monomer unit N-asetil-D-glucosamine(2-acetamido-2-deoxy-Dglucopyranose) linear bonding β-(1→4) (Maher and Entsar, 2013). Chitin is white, hard, inelastic polysaccharide whichhas much nitrogen, and it is the main resources of pollutan in beach area.Chitosan is a derivative of chitin and it is the second most abundant polysaccharide after cellulose. Chitosan is a natural polysaccharide resulting from the deacetylation process ($COCH_3$ removal) of chitin. Generally, chitosan is added to a film to produce excellent biocompatibility film, forming ability and antimicrobial activity. The other advantage of adding chitosan is to decrease water sensitivity, increase mechanical and barrier of film (Lili et al, 2017).

2 EXPERIMENTAL METHOD

2.1 Isolated Agar

Agar was prepared by soaking *Gracilaria* overnight in a 200 ml NaOH 3%. After that, it was heated in a water bath for 3 hours at 50 ºC and then washed with deionized water. The process was followed by

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soaking *Gracilaria* twice in a H_2SO_4 0.025 % and deionised water for 2 hours. After that it was washed with 300 ml deionized water for 1.5 hours until pH 6-6,5. It was frozen, melted and dried for 24 hours at 60 ºC. Agar yield was determined as the percentage of dry weight by the following equation:

$$\text{Agar yield} = \frac{\text{Agardryweight (g)}}{Gracilaria\text{dryweight (g)}} x\ 100\ \% \qquad (1)$$

2.2 Film Preparation

Chitosan powder (1,2,3 and 4 g) was dissolved in a 100 ml acetic acid 0.2 M solution at 60 ºC and 600 rpm to produce chitosan solution. Agar powder (5 g) was dissolved in a 100 ml deionized water at 95 ºC and 600 rpm for 60 minutes. An amount of 20% of glycerol was added to the agar and chitosan solution as plasticizer. The agar-chitosan film was fabricated by mixing chitosan solution (1,2,3 and 4 g / 100 ml) and agar solution (5 g/100 ml) with a ratio of 1:1. The mixture was stirred at 60 ºC and 600 rpm for 60 minutes. An amount of film solution was distributed into the template for drying and casting for 24 hours at 40 ºC. The films were stored in a desiccator.

2.3 Characterization

2.3.1 Spectra of Fourier Transform Infrared (FTIR)

Agar-chitosan films were measured by using an IRPrestige-21 Shimadzu - Japan to investigate the interactions of agar, glycerol and chitosan films. The sample was prepared by mixing the film and KBr with ratio of 100 : 1. The FTIR was operated with a wavelength of 400 – 4000 cm^{-1}, a resolution of 4 cm^{-1} and 100 scans.

2.3.2 Mechanical Properties

The tensile strength, the elongation at break and the young's modulus of the films (100 mm x 25 mm) weredetermined using a RTF-1350 Tensilon- Japan.

2.3.3 Water Solubility (WS)

The solubility of films in water (WS) is defined as the percentage of dry matter dissolved in water from the film dissolved after soaking in distilled water. The films were cut into a size of 25 mm × 20 mm and stored in a desiccator to obtain a constant weight. The specimen was weighed to determine the initial dry weight and placed in a glass containing a 50 mL of deionized water. The sample was maintained with a constant stirring for 2 hours, a temperature of 80 ºC and dried at 105 ºC until a constant weight was obtained. The percentage of total dissolved material is calculated as follows:

$$\text{WS} = \frac{\text{Initial dry weight (g)} - \text{Final dry weight (g)}}{\text{Initial dry weight (g)}} x\ 100\ \% \qquad (2)$$

3 RESULTS AND DISCUSSION

The agar yield from this research was 48 %. There are some factors that influence the isolation of *Gracilaria* including soaking time, temperature, extraction time and temperature (Mahdieh et al., 2013).With reference to Figure 1, the film was initially dark brown. It becomes brighter after the addition of glycerol 20% and chitosan 1, 2, 3 and 4%.

3.1 FTIR Spectroscopic Analysis of Film

FTIR spectral analysis of the agar film was performed to identify the nature of the functional groups present. From Figure 2, the peak at at 3556 $cm^{-1}$is attributed to OH stretching from hidroxyl groups (Babak and Fatemeh, 2012). The peak at 1184 $cm^{-1}$is attributed to stretching vibration C-O in C-O-H groups. The absorption at 1130 cm^{-1}represents stretching vibration C-O in C-O-C groups (Mayur and Sonal, 2010). In the chitosan spectrum the peak at 3371 cm^{-1}isassociated withstretching vibration N-H bending and hydrogen bonded hidroxyl groups (Lili et al, 2017).The peak at 1643 $cm^{-1}$and 1600 cm^{-1} representto amide II (N-H) and amide I (C=O) respectively (Lagaron et al.,2007).The wavenumber of the FTIR spectral of the film agar changed after the addition of 20% glycerol. It can be seen from 3603 cm^{-1} to 3317 $cm^{-1}$for OH stretching of the hydroxyl group , 1184 cm^{-1} to 1107 cm^{-1} for C-O of C-OH

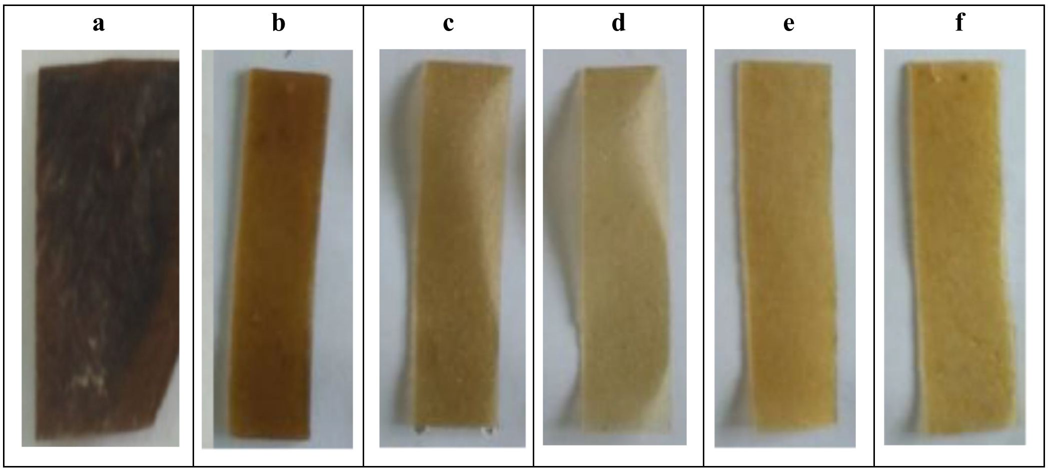

Figure 1 The Specimen of (a) Agar film, (b) agar-glycerol 20%, (c) agar-glycerol 20% – Chitosan1%, (d) agar-glycerol 20% - chitosan 2%, (e) agar-glycerol – chitosan 3% and (f) agar-glycerol – chitosan 4%.

1130 cm^{-1} to 1045 cm^{-1}for C-O in C-O-C. A new peak was not appeared in the spectrum which indicated that there was only hydrogen bonding between agar and glycerol.Similarly, there is a shift of wavenumber with the addition of 20% glycerol and chitosan 4%(Laura et al, 2016). They are from 3603 cm^{-1} to 3317 cm^{-1} indicating OH stretching of the hydroxyl group, 1184 cm^{-1} to 1107 cm^{-1}for C-O of C-OH, 1130 cm^{-1} to 1045 cm^{-1}for C-O in C-O-C.There was interaction between the functional group of O-H from polysaccharides and N-H from chitosan (Emma et al, 2016).The agar film with glycerol 20 % and chitosan 4 % its known that the FTIR results show a combination of the three constituent components without forming a new functional groups. the stretching OH of the hydroxyl group in film (3359 cm^{-1}) was higher than agar (3556 cm^{-1}) as well as chitosan (3371 cm^{-1}). This is due to inter and intra molecular hydrogen bonding interactions of all components (Lili et al, 2017).

3.2 Mechanical Properties

The mechanical properties of edible film from this research are show in Table 1.

Based on Table 1. film agar had the best mechanical properties with the tensile strength of 3.785 MPa, but the elongation at break was the lowest (0.199 %).

Table 1: Mechanical Properties of film agar, agar-glycerol agar-glycerol-chitosan

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation atBreaks (%)
Agar	3.785	1,993.31	0.199
Agar-glycerol (20 %)	0.029	4.173	9.805
Agar-glycerol (20%)-chitosan (1%)	0.184	2.927	8.449
Agar-glycerol (20%)-chitosan (2%)	0.276	22.743	12.792
Agar-glycerol (20%)-chitosan (3%)	0.413	38.946	16.857
Agar-glycerol (20%)-chitosan (4%)	0.759	48.836	19.168

The addition of glycerol decreased the tensile strength of film from 3.785 MPa to 0.029 MPa, increased the value of elongation at break from 0.199 % to 9.805 %. The tensile strength and the elongation at break of film increased after the addition of chitosan. The best mechanical properties of the edible film were found for agar-glycerol 20%-chitosan 4%.

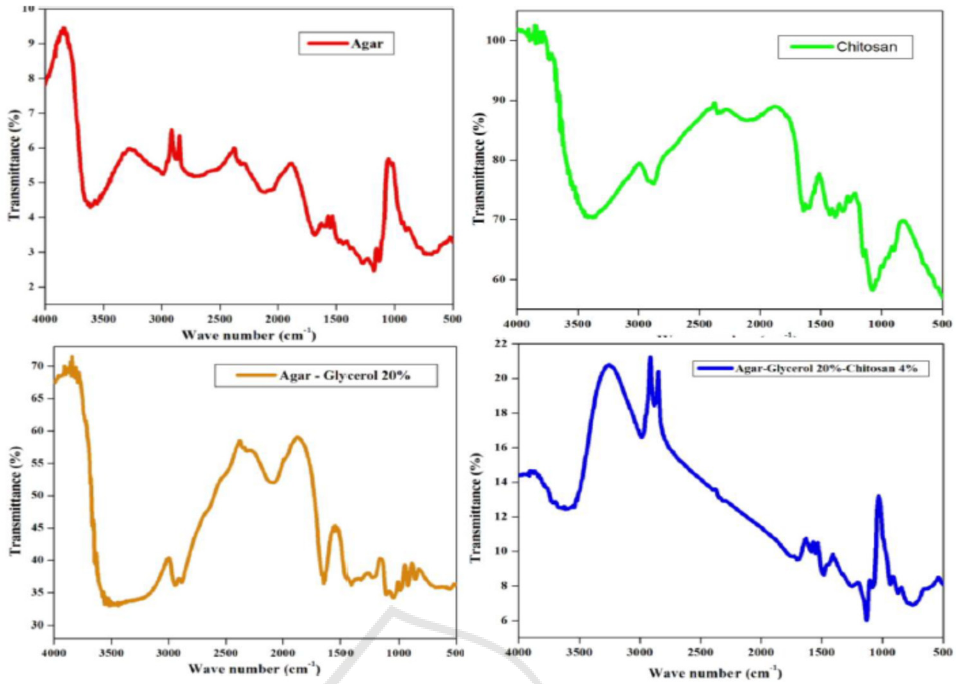

Figure 2: FTIR spectra of agar, chitosan, agar-glycerol 20 % and agar-glycerol 20 %-chitosan 4 %

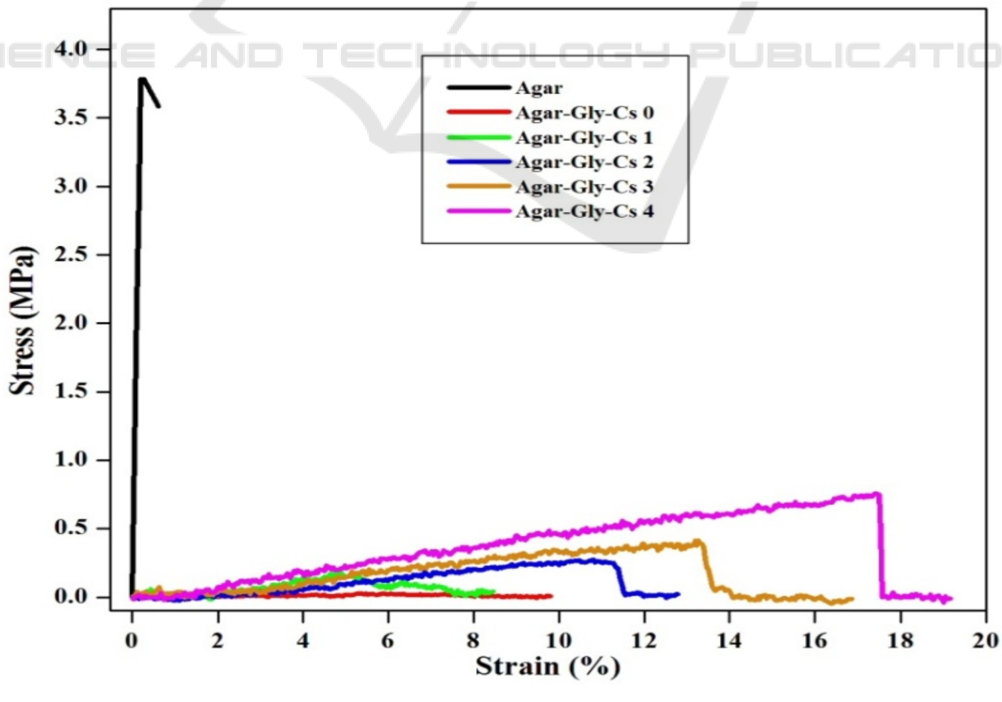

Figure 3:The tensile strength of agar, agar-glycerol 20 %, agar-glycerol 20 %-chitosan 4 %

3.3 Water Solubility (WS)

Based on Table 2,the solubility of film increased by the addition of chitosan. This is due to chitosan highly soluble in water. However, agar forms gel in water.

Table 2: Water solubility (WS) of agar, agar-glycerol, agar-glycerol-chitosan

Sample	Water Solubility (%)
Agar	9.84
Agar-glycerol 20 %	88.19
Agar-glycerol 20%-chitosan 1%	69.57
Agar-glycerol 20%-chitosan 2%	80.02
Agar-glycerol 20%-chitosan 3%	85.58
Agar-glycerol 20%-chitosan 4%	87.78

For food packaging application, low solubility filmisneeded in order to maintain the integrity of structures to cover vegetables andfruits. However, high film solubility can be preferred for films to wrap candy (Lili et al, 2017)

4 CONCLUSIONS

In summary, it has been shown from this reseach that the result from the isolation of *Gracilaria* is 48%. FTIR spectral indicates that there is hydrogen bonding in the film agar-glycerol-chitosan. The more the concentration of chitosan added to the filmagar-glycerol-chitosan, the tensile strength, the elongation at break, the young's modulus and the water solubility increase.

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