Preparation and properties of arenga starch-chitosan based edible film

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Abstract. The main objective of this research was to prepare for edible film on the basis of arenga starch-chitosan. Carboxymethyl cellulose (CMC) was added to the blend and glycerol was used as a plasticizer. The tensile strength and water uptake of the film decreased with the increasing of glycerol content in the blend. Contrary, increasing glycerol content in the blend enhanced the elongation and swelling area of the film. The film C1, which has 6% of glycerol in the blend has a tensile strength of 124 KPa, elongation of 6.55%, swelling area of 21% and water uptake of 48%. The film C2, which has 10% of glycerol in the blend has a tensile strength of 58 KPa, elongation of 8.35%, swelling area of 32% and water uptake of 5%.

1. Introduction
An edible film could be defined as a thin layer of edible material which are commonly used for food packaging. Edible films are biodegradable and environmentally friendly. They have other advantageous related with their usage. They are able to extend the shelf life of food since they protect food from deterioration by microbial, oxygen, water and light. Furthermore, edible films also have been applied to control food contamination and enhance sensory perceptions [1-3].

Edible films are produced from renewable materials. The biopolymeric materials commonly applied to produce edible films are polysaccharides, lipids, proteins, or the combination of these components [4-7]. Although edible films have been used widely for coating of fresh fruits, vegetables, and processed foods, they have disadvantages in mechanical or barrier properties and are expensive. Research has shown increased concerning the preparation of edible films from diverse sources to produce films with different characteristics [8-11].

Polysaccharides which are frequently utilized for the preparation of edible films are agar, alginate, carrageenans, chitosan, gum, pectin and starch [3-4]. Amylose is responsible for the film-forming capacity of starch. Amylose starch films have flexible, oxygen impermeable, oil resistant, heat-sealable, and water soluble [12-13]. Chitosan-based edible films exhibit excellent mechanical properties and good oxygen and carbon dioxide permeability. Additionally, chitosan can form cohesive and compact transparent film which has a smooth contour with no pores or cracks on the film surface. Nevertheless, the chitosan based edible film has poor solubility in neutral solutions [14-16].

Blending more than one polysaccharide materials could improve film mechanical functionality. Edible films based on mixtures of many kinds of polysaccharides have been produced, such as chitosan-starch, chitosan-pullulan, CMC-rice starch, CMC-pea starch, starch-alginate and sago-alginate [17-19]. CMC are water-soluble heteropolysaccharides derived from cellulose which are often applied together with starches to enhance overall film quality and stability. The hydroxyl and carboxylic groups in CMC facilitate water binding and moisture sorption properties. Indonesian is
consuming arenga or sugar palm (*Arenga pinnata*) starch as their staple food in place of rice. Arenga starch also used as an ingredient in the preparation of cakes, noodles, and other dishes. It has high amylose content which can be used in forming excellent film matrix. Although the film formed was compact and rigid but it is a fairly brittle [20]. The main objective of this research was to prepare an edible film from arenga starch and chitosan. Carboxymethylcellulose (CMC) and glycerol were also added to the blend.

2. Materials and Methods

2.1. Materials

All chemicals were used are analytical grade from e-Merck. The arenga starch was provided by arenga starch home industries in Klaten, Jawa Tengah, Indonesia. Chitosan was supplied from PT Biotech Surindo, Indonesia.

2.2. Film preparation

Arenga starch (1.5 g) and CMC (1 g) were dissolved in 75 mL of distilled water, heated to 90°C and stirred for 24 h. Meanwhile, a mixture of chitosan and acetic acid at different concentration were prepared by stirring at room temperature for 24 h. This two mixture were then blended at different concentration for 1 h. Glycerol at various amount was then added, and the mixtures were stirred for a further 24 h. The sample solution at different volume was poured into casting tray followed by oven drying at 50-60°C for 7 h. The dry films obtained were peeled off and stored for further analysis.

2.3. FTIR Analysis

The spectra of the films were recorded at room temperature as KBr pellets on Shimadzu type FT-IR 8201 PC spectrophotometer. The light source of transmittance was in the range of 4000-500 cm$^{-1}$. The films were mounted directly in the sample holder.

2.4. Film thickness measurement

Film thickness was determined using a digital micrometer (Krisbow KW06-85) having a precision of 0.001 mm. Measurements were carried out at five different film locations, and the mean thickness value was used to calculate the mechanical properties of the films.

2.5. Mechanical properties

Tensile strength and elongation of the films were determined using a material testing machine (RAY-RAN M500-50CT Testometric Rodhale England type DBBMTCL-5000 Kg Serial No. 36751) according to ASTM standard method D882-91 (ASTM D882-91, 1996). Film specimens, 6 cm x 0.4 cm were cut from each of film samples and were mounted between the grips of the machine. The initial grip separation and cross-head speed were set to 50 mm and 5 mm/min, respectively. The parameter determined were tensile stress (MPa) using equation 1 and elongation (%) using equation 2. The tensile strength was expressed as the force of film rupture, $F_{\text{max}}$ (N) divided by the cross-sectional area of the film, $A$ (mm$^2$), and the elongation was expressed as the tensile elongation of the film at rupture, $L_{\text{max}}$ (mm) divided by the initial length of film, $L_0$ (mm) (equation (1) and (2)).

$$\tau = \frac{F_{\text{max}}}{A}$$  \hspace{1cm} (1)

$$E = \frac{L_{\text{max}}}{L_0}$$  \hspace{1cm} (2)

2.6. Swelling area and water uptake

Pieces of films were cut and were soaked in distilled water for 24 h at room temperature. Swelling area and water uptake of the films were calculated by comparing the surface area or weight before and after soaking. Equation 3 was to calculated the swelling area ($S_a$) and equation 4 was used to
calculated the water uptake \((W_u)\), where \(L_1\) is the surface area before soaking, \(L_2\) is surface area after soaking, \(W_1\) is the weight before soaking, and \(W_2\) is the weight after soaking (equation (3) and (4)).

\[
W_u = \frac{L_2 - L_1}{L_1} \times 100\%
\]  

\[
W_u = \frac{W_2 - W_1}{W_1} \times 100\%
\]

\((3)\)

\((4)\)

3. Results and Discussion

3.1. Film preparation

In this studies, the blending of three polysaccharides, which are area starch, chitosan, and CMC, with the addition of glycerol as a plasticizer was carried out. The amount of each component was varied to find the most suitable composition which could give excellent mechanical properties. The thickness of the film was also modified. Initial attempts were made using a higher amount of a mixture of starch, CMC, and water than that of chitosan. The first attempt was carried out where the composition of the blend was 10.5 g of a mixture of starch, CMC, and water, 1.75 g of chitosan, 9 mL of glycerol and 50 mL of acetic acid. Nevertheless, the film has not formed yet.

The second attempts then performed with the additional amount of glycerol to the mixture. It was thought that additional amount of glycerol would produce films since glycerol are widely used as plasticizers which make the brittle films more flexible. The volume of the mixture that were poured into casting tray were varied (30, 40, 60 and 70 mL) to obtain a different thickness of the films (table 1). The results exhibited that films have been formed. However, they are brittle.

| Composition | Film A | Film B1 | Film B2 | Film B3 | Film B4 |
|-------------|--------|---------|---------|---------|---------|
| A mixture of starch, CMC and water (g) | 10.5 | 10.5 | 10.5 | 10.5 | 10.5 |
| Chitosan (g) | 1.75 | 1.75 | 1.75 | 1.75 | 1.75 |
| Glycerol (mL) | 9 | 10.5 | 10.5 | 10.5 | 10.5 |
| Acetic acid (mL) | 175 | 175 | 175 | 175 | 175 |
| Mixture volume (mL) | 50 | 30 | 40 | 60 | 70 |
| Film thickness (mm) | 0.504 | 0.147 | 0.493 | 0.514 | 0.567 |

The next attempts were made by changing the concentration of each component. Accordingly, a higher amount of chitosan than that of the concentration of a mixture of starch, CMC and water were applied. The concentration of glycerol was varied while the film thickness was the same (Table 2). The composition of the mixture was 0.175 g of a mixture of starch, CMC, and water, 1.75 g of chitosan, 0.105 (6%) or 0.175 mL (10%) of glycerol and 70 mL of acetic acid. The results revealed that rigid films have been produced. Hence, the FT-IR analysis and properties, such as tensile strength, elongation, swelling degree and swelling area, were then examined for these two films.

| Composition | Film C1 | Film C2 |
|-------------|---------|---------|
| A mixture of starch, CMC and water (g) | 0.175 | 0.175 |
| Chitosan (g) | 1.75 | 1.75 |
| Glycerol (mL) | 0.105 | 0.175 |
| Acetic acid (mL) | 70 | 70 |
| Mixture volume (mL) | 40 | 40 |
| Film thickness (mm) | 0.363 | 0.363 |
3.2. FTIR analysis
The FT-IR spectra of arenga starch-chitosan based films C1 and C2 are shown in Figure 1. The spectra show similar patterns. An absorption band at 3436 cm\(^{-1}\) for film C1 and 3443 cm\(^{-1}\) for film C2 appear. An extremely broad peak appeared between 3000-3600 cm\(^{-1}\) is the region of hydrogen-bonded hydroxyl groups associated with free, inter- and inter- molecular bound hydroxyl groups.

Both films had a peak for amide I, illustrating C=O stretching/hydrogen bonding coupled with COO, which was a peak at 1638 cm\(^{-1}\) and 1641 cm\(^{-1}\) for films C1 and C2, respectively. Both films also had a peak at 1529 cm\(^{-1}\) for amide II, presenting the bending vibrations of N–H groups and stretching vibrations of C–N groups. Tongnuanchan et al. reported that films from fish skin gelatin containing glycerol had peaks at 1630 and 1538 cm\(^{-1}\) for amide-I and amide-II, respectively [21]. Hoque et al. presented similar spectra for cuttlefish skin gelatin film, where amide-I and II bands were found at the peaks of 1630 and 1539 cm\(^{-1}\), respectively [22].

Peaks at 2956, 2918 and 2849 cm\(^{-1}\) were shown when the film has more concentration of glycerols in film C2. These peaks represent the methyl, methylene symmetrical and asymmetrical and stretching vibration of the aliphatic C-H in CH\(_2\) and CH\(_3\) groups [23-24]. Both the methylene asymmetrical stretching bands at approximately 2853 cm\(^{-1}\) and methylene symmetrical stretching band near 2924 cm\(^{-1}\) were present in most lipids [23-24]. Film C2 had higher hydrophobicity properties than that of film C1, as evidenced by the peak appearances at 2849 and 2924 cm\(^{-1}\) which associated with hydrophobic interactions.

The band of O-H bending for the alcohols in film C1 that appeared at 1268, 1221 and 1190 cm\(^{-1}\) were shifted to 1272, 1228 and 1188 cm\(^{-1}\), respectively, with addition concentration of glycerols in film C2. A peak at 1030 cm\(^{-1}\) in film C1 for the C-H aromatic was shifted to 1045 cm\(^{-1}\) in film C2. An extra peak at 1021 cm\(^{-1}\) was shown in film C2. Other additional peaks were noticed in film C2. An additional peak at 1339 cm\(^{-1}\) which was associated with O-H bending of the primary or secondary alcohols appeared in film C2. A peak at 1458 cm\(^{-1}\) was shown in film C2, which was ascribed to C-H stretching and bending modes. Furthermore, a peak at 1158 cm\(^{-1}\) existed in film C2 which was attributed to C-O-C antisymmetric bridge stretching.

3.3. Film properties
Mechanical properties of films were characterized by assessing the tensile strength and elongation, which are main indicators of films strength and flexibility. The tensile strength can be ascribed to the cohesion between the matrices of the filmogenic polymer chains. The elongation is a measure of the plasticity of the film or a degree of the film’s capacity for stretching. The elongation is film capacity to enlarge to occur before its break [17, 25]. Table 3 presents that the mechanical properties of film C1 and film C2 varying according to the glycerol content. The film C1, which has 0.105 mL of glycerol.

![Figure 1. FTIR spectra of arenga starch chitosan-based films C1 and C2 with different concentration of glycerol.](image-url)
(6% of glycerol) in the blend has a tensile strength of 124 KPa, elongation of 6.55%, swelling area of 21% and water uptake of 48%. The film C2, which has 0.175 mL of glycerol (10% of glycerol) in the blend has a tensile strength of 58 KPa, elongation of 8.35%, swelling area of 32% and water uptake of 5%. The tensile strength results show that tensile strength decreased with the increasing of glycerol content in the blend. In contrast, elongation results show that elongation is increased with increasing glycerol content in the blend. Similar results were reported by other authors [20, 26]. Furthermore, the swelling area increased and water uptake decreased with increasing glycerol content in the blend.

| Properties          | Film C1 | Film C2 |
|---------------------|---------|---------|
| Tensile strength (Kpa) | 124     | 58      |
| Elongation (%)       | 6.55    | 8.35    |
| Swelling area (%)    | 21      | 32      |
| Water uptake (%)     | 48      | 5       |

Our results can be explained because glycerol act as a plasticizer. The addition of plasticizers makes the brittle films more flexible, and consequently less rigid and less strong. The glycerol interacts through hydrogen bonding with crystalline amylose and crystalline and amorphous amyllopectin when the temperature is increased and also during film storage at room temperature. As a result, matrix mobility increases, viscosity reduces and the material performs like a rubber [27]. Water uptake or water solubility is an important characteristic of edible films. Some applications may require water insolubility to enhance product integrity and water resistance [28]. Our results clearly demonstrated that films with a higher ratio of glycerol exhibited lower water uptake, indicating higher water resistance.

### 4. Conclusion

The arenga starch-chitosan based edible film have been successfully produced in the presence of CMC. The elongation and swelling area increased with increasing glycerol content in the blend, whereas the tensile strength and water uptake decreased with the increasing of glycerol content. Variation amount of the each component and the thickness of the film still need to be evaluated to produce the film with better mechanical properties.

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