Brightness, elongation and thickness of edible film with caseinate sodium using a type of plasticizer

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Abstract. The use of plasticizer could improve the flexibility, elasticity and friability of edible films. The characteristics of edible film made from caseinate sodium were influenced by the use of plasticizer types. The differences in material source and molecular weight of plasticizers type various result in the interaction of hydrogen bonds between water-protein-plasticizer molecules and further cause differences in the physical characteristics of edible films. The purpose of this study was to determine the effect of plasticizer types (glycerol, sorbitol and polyethylene glycol (PEG)) on the characteristics of edible films. The edible film characteristics observed were color L * (brightness), elongation and thickness. Data were analyzed with complete random design and repeated for three times. The use of plasticizer type affected the edible color value (L *) around 85.62-87.43 (close to white). However, the type of plasticizer did not affect the elongation and thickness of the edible film. The range of elongation and thickness of the edible film with the use of a type of plasticizer was around 15.96-16.22% and an average of about 0.15 mm. The color value of L * (brightness) of edible film using sorbitol plasticizers type was higher than that using glycerol and PEG. The characteristics of edible films using sorbitol plasticizers were better, compared to those using glycerol and PEG.

1. Introduction
Various food products have been produced from dairy products such as casein, fruit yogurt, curd, binahong pasteurized milk, kefir and edible film [1-6]. Edible film was a thin package for coating food. The use of Robertson's edible film is [7-8] able to extend the shelf life, carrier of important components, including vitamins, minerals, antioxidants, antimicrobials, preservatives and ingredients to improve the taste and color of the product. Edible film could be made by one of them from the basic ingredients of protein. Proteins that have been applied in the manufacture of edible films include collagen, gelatin, corn protein (corn zein), wheat protein (wheat gluten) [9], soy protein (soy protein), quinoa protein [10] whey [11-13] and casein [14-15]. Sodium caseinate was a casein which uses sodium hydroxide as a washing agent in processing. Sodium caseinate has been used in several food processing studies such as wrapping and edible films [16]. Sodium caseinate has a high molecular of weight and these results in the film forming characteristics of a strong film. Edible films that stand alone were very fragile. The fragility of edible films occurs because
of the stability of the film network. The stability occurs due to interactions between protein chains and is further strengthened by disulfide bonds, hydrogen bonds, hydrophobic bonds, and / or electrostatic interactions.

Reducing fragility in processing protein-based films was by adding plasticizers. The incorporation of plasticizer molecules in film processing can reduce the strength between the protein chains. Plasticizer molecules will insert and interact between monomer-monomer bonds. This condition results in elongation and flexibility with decreased elasticity, mechanical resistance, and other film inhibitory properties. [15] aimed that the characteristics of edible films are very much determined by the plasticizer. Plasticizer is an ingredient that was added in the formation of edible films. Some types of plasticizers that are often used in making edible films include glycerol, sorbitol and polyethylene glycos (PEG) [17-21].

The type of plasticizer could affect the characteristics of sodium caseinate films. Glycerol, sorbitol and PEG came from different sources having quantities, different molecular weight and composition [22]. Plasticizer could reduce intermolecular forces and increased film flexibility by widening molecular free space and reducing internal hydrogen bonds between polymer chains (sodium caseinate), the ability of plasticizers to reduce internal hydrogen bonds between polymer chains.

The use of the right type of plasticizer would affect the characteristics of edible film. This was the background of research on the physical characteristics of edible film made from sodium caseinate with the addition of a type of plasticizer.

2. Materials and methods

2.1. Research Material

The tools used are digital scales, Erlenmeyer, spatula, blender, pH meter, hot plate stirrer, thermometer, edible film mold, oven, micrometer (MDC-25M model, Mitutoyo, MFG, Japan), digital color meter test (T 135) and digital gauge HF 500. The material used is sodium caseinate (made in the biotechnology laboratory of Milk Processing Faculty of Animal Husbandry Unhas) and cold water used as a solvent. Glycerol, sorbitol, PEG and NaOH 1 N. In addition, plastic, aluminum foil and labels are needed.

2.2. Research design

This study used a complete 3X3 randomized design. The factors used were the type of plasticizer (glycerol, sorbitol and PEG).

2.3. Making Edible films

Sodium caseinate of 10% (w / v) mixed with cold water as much as 87% (w / v). Then the mixture is blended for 10 minutes to smooth and homogenize. Subtle mixture is added 1 N NaOH to pH 7-8. The mixture is then heated with a hot magnetic stirrer until the temperature reaches 90°C for 1 minute. On heating, a plastizicer (Glycerol, Sorbitol, PEG) of 3% (w / v) is added when the temperature reaches 40°C. After the cold edible film solution is poured into the mold as much as 15 ml and roasted at a temperature of 50°C for 8 hours.

2.4. Measured Parameters

2.4.1. Edible film thickness. The measurement of film thickness using a micrometer (model MDC-25M, Mitutoyo, MFG, Japan). Thickness values were averages of measurements at five different places (i.e. each at the edge of a rectangle and in the middle [23].

2.4.2. The Elongation at break. Edible film was cut to the size of 8 cm x 3 cm. Edible film was clamped to the HF 500 digital gauge which is 1.5 cm in both sides. The value of edible film elongation was measured when the edible film is about to break up [23].

\[ E = 100 \times \frac{(d \text{ after} - d \text{ before})}{d \text{ after}} \]
Note: d before was the distance between the sample holder's clips before withdrawal, while d before was the distance between the sample holder's clips after the sample was withdrawn (until nearing breaking up) [21, 23].

2.4.3. The Color. The measurement of edible film brightness uses a digital color meter test (T 135). Brightness was symbolized by L *. The range of color values L * = 0 (black) to 100 (white). The instrument was calibrated with white standards (calibration values L * = 94.76, a * = -0.795, and b * = 2,200) [24-26].

2.5. Data analysis
The data were analyzed variantly with SPSS 18.0. If the analysis of variance showed the effect between treatments, Duncan's further tests [27] were performed.

3. Results and discussion
Edible film characteristics in general were transparent, flexible and not fragile [13]. Thickness, elongation and color of edible film could explain the characteristics of edible film related to its chemical structure. [28] argues that, the composition of the material and the exact process determined the characteristics of edible film.

The plasticizer requirement used as an elasticiser was stable, it was not degraded by heat and light, did not change the color of the polymer and did not cause corrosion [29]. Plasticizers commonly used in films include glycerol, sorbitol, xylitol, mannitol, polyethylene glycol (PEG) (with molecular weights 400 - 8000 g/mol), ethylene glycol, and propylene glycol. Generally, plasticizers were needed around 10 - 40% of the dry weight depending on the stiffness of the polymer used.

3.1. L Color* (Brightness)
The results of research on the color characteristics of L * edible film made from sodium caseinate with the use of a type of plasticizer are presented in Figure 1.

![Figure 1. Color L * edible film on various types of plasticizers.](image-url)

Note: Different ab on the same diagram show significant differences between treatments. (P<0.05); Color L * (0 - 100: black - white)
value of L*. Further test results showed that sorbitol type plasticizers gave the highest L* (brightness) color value compared to PEG and glycerol. However, the color value of L* edible film using PEG and glycerol is not different (the same). Sorbitol had a good solubility level, and could interact well with sodium caseinate ingredients. This is shown by the good dispersion of the sorbitol molecule in the edible film to interleave between the polymers. The difference in color values was influenced by the type of material used in making edible films and their interactions during processing. The same thing was stated by [21] that the difference in the color value of edible film made from mung bean protein was determined by the type of plasticizer (sorbitol, glycerol and PEG).

The distribution of the sorbitol molecule results in the strain of the sorbitol-sodium caseinate molecular matrix. The strength of edible film molecules using sorbitol was better or greater than PEG and glycerol, molecular strain conditions result in more easily penetrated light or directional light reflection and the resulting higher brightness color. While the edible film molecules that are less stretched cause light mixing or reflection of light in all directions and cause a slightly dull color value of L*. [20, 30] stated that an increase in the amount of polymer film will result in an increase in light diffusion. In this condition edible film would appear dull and blurry. Good light reflection was the reflection of light directed at the surface of an object. If the surface of the object reflects light in all directions, the surface of the object would be dull.

The comparison of brightness value of edible films from several studies that used basic materials and different types of plasticizers as follows: In the research of [31] which used a combination of casein and tapioca as raw material with PEG plasticizer produced an L* color between 50.97 - 79.11 which showed rather opaque color characteristics. [32] with the treatment of glycerol concentration had a bright L* color (87.23 - 88.89), a* greenish color (-0.215) - (-0.431) and b* reddish color (3.364 - 3.474). [33] the value of the brightness of edible films made from fro with the use of a PEG plasticizer is 79.489. While the use of sorbitol plasticizer has a brightness value that was equal to 82.487.

3.2. The elongation at break

The elongation characteristics of edible film made from sodium caseinate with a type of plasticizer are presented in Figure 2.

![Figure 2. The elongation of edible film on various types of plasticizers.](image)

The elongation was the change in maximum length at the time of stretching until the film sample was cut off. In general, the presence of plasticizer in a greater proportion would make the value of a film's elongation percent increase [21, 34].

The average elongation of edible film in this study was made from sodium caseinate with the use of plastizicer types (sorbitol, glycerol and PEG) in the range of 15.96 - 16.22%. The elongation of edible
film in this study was still lower than that of edible film in [35] which uses whey and agar based ingredients with 35% sorbitol concentration. Average edible film elongation from [35] was 26.06 - 34.52%. While the elongation of edible film research [36] which used a combination of chicken leg skin gelatin and soy protein isolated with the use of glycerin as a plasticizer was 30.74%. [37] suggest that edible films that have a low elongation value indicate that the edible films were rigid and easily broken. Generally edible films that had a high tensile strength, had a lower elongation percentage.

The analysis of variance showed that the type of plasticizer had no significant effect (P> 0.05) on the elongation of edible films. This showed that the elongation of edible film made from sodium caseinate using glycerol, PEG and sorbitol plasticizer types was the same. A review of the average elongation of edible films in this study showed that glycerol type plasticizers had the highest elongation values compared to PEG and sorbitol.

The existence of the use of glycerol produces edible films with the highest level of elongation compared to the use of sorbitol and PEG. Glycerol had a hydroxyl group with a short chain so that if it binds with sodium caseinate, it will form solids or the number of matrices that cover the sodium casease cavity. [38] stated that the treatment of increased glycerol concentration resulted in increased edible film elongation. [39] states that glycerol can interact with polymers and form polymer-glycerol bonds. This bond will result in increased elasticity of the edible film. Hydroxyl group on the glycerol chain causes the formation of hydrogen bonds between the polymer and glycerol. These bonds replace the hydrogen bonds between polymers during the formation of edible films. Polyols like glycerol function as plasticizers. Plasticizer is able to reduce internal hydrogen bonds by increasing the free space between molecules, thereby reducing stiffness and increasing film flexibility.

The use of sorbitol in this study had lower elongation (15.96%). High or low elongation with the use of sorbitol was very dependent on the use of the basic ingredients. The elongation value was different in some edible film studies using sorbitol: whey dangke and carrageenan were 28-44% [20] and sukun_kitosan starch is 4.73-6.47% [40]. This is because sorbitol was a derivative of glycerol and the properties of both are almost the same. so that under these circumstances sorbitol is also able to produce edible films with a high average elongation. This was supported by the opinion of [28] which states that the use of plasticizers could be sourced from monosaccharides, disaccharides and oligosaccharides. The plasticizer served to reduce intermolecular forces in overcoming fragility and increasing elasticity.

3.3. **The thickness**

Thickness is the physical property of edible film. Edible film thickness affects the rate of water vapor, gas and other volatile compounds [41]. The results of research on the characteristics of the thickness of edible film made from sodium caseinate with various types of plasticizers are presented in Figure 3.

![Figure 3. Thickness of edible film on various types of plasticizers.](image-url)
Average addition of plasticizer types both PEG, glycerol and sorbitol provided the same thickness which was around 0.15 mm. The analysis of variance showed that the type of plasticizer treatment had no significant effect (P> 0.05) on the thickness of the edible film. This was presumably because the percentage of plasticizer types use (glycerol, sorbitol and PEG) did not change the amount of solids and composition of the ingredients. Some of the results of previous studies also produced edible film thickness values that were not different. [9] reported that the thickness of edible film made from whey dangke and keragenan did not statistically affect the thickness of edible film. [42] stated that the thickness of the edible film was very dependent on the composition, properties and content of the constituent polymers. [43] added that thickness was influenced by the nature and composition of the material used in making edible films.

The thickness of the edible film in the results of this study was greater than the edible film made from arrowroot starch with the addition of glycerol 30% which was around 0.08 mm [44], research of [45] made from apple pulp skin extract with the addition of glycerol concentration 10 - 30% which was around 0.015 - 0.020 mm and the thickness of the edible film in the study of [46] which uses a type of plasticizer on the basis of whey protein, which was between 0.13-0.14 mm. However, the thickness of the edible film in this study was thinner compared to the research of [47] on edible made from teak leaf extract with a glycerol concentration of 20% which is 0.18 mm.

The thickness of the edible film is more influenced by the type and composition of the material used. [48] showed that the thickness of the edible film increases with the concentration of the raw material. Furthermore, stated that the use of kimpul starch raw material which was incorporated with potassium sorbet showed that the thickness of the edible film produced ranged from 0.065 to 0.081 mm. The use of polysaccharides as the base material for edible films would provide thickness because it had a high viscosity. Here Viscosity was affected by the amount of solids in the solution of edible film raw materials. According to [48] showed that the thickness of the edible film increases with increasing concentrations of raw materials. The increase in the amount of solids in solution increases the viscosity of the edible film solution. Furthermore, [49] suggested the thickness of edible films is influenced by the nature and content of the constituent polymers.

4. Conclusion
The brightness value of edible film made from sodium caseinate was largely determined by the type of plasticizer. The use of glycerol as a plasticizer in the manufacture of edible films made from sodium caseinate gives better characteristics than sorbitol and PEG.

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