Application of Pectin Extracted from Cocoa Pod in the Production of Edible Film

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Abstract. Cocoa pod is lignocellulosic waste which contain cellulose, hemicellulose, lignin, pectin and other compounds. Pectin is a polymer of D-galacturonic acid linked by an α-1,4 glycoside bond. Some carboxyl groups in pectin compounds undergo esterification with methyl (methylation) to methoxyl groups. This compound is referred to as pectinic acid or pectin. Pectin in cocoa pod can be produced by extraction. The purpose of this research is to know the physical and chemical characteristics of pectin-based edible film from cocoa pod. This research is conducted in two steps. The first stage is the extraction of pectin from cocoa pod, and the second stage is the process of making edible film. Pectin extraction was performed by using 5% citric acid. The extracted pectin will be made into an edible film using glycerol as plastisizer. The glycerol treatments are 0%, 2%, 4%, 6%, 8%. The design used was Completely Randomized Design (CRD) at 5% significant level. The results showed that the addition of glycerol has significant effect on water content, thickness, color and water vapor transmission rate.

1. Introduction
The total area of cocoa plants in Indonesia according to Statistics data in 2017 is 1691,334 ha, with a total production of 688,345 tons. In West Sumatra the area of cocoa is 153,862 ha, and the total production is around 59,593 tons. Cocoa plants in West Sumatra are scattered in almost all districts / cities. The largest cocoa production centers in West Sumatra are Pasaman, Padang Pariaman, Agam, Lima Puluh Kota, Tanah Datar and West Pasaman. Indonesia.

The increasing the production area of cocoa plants can have a positive and negative impact. The positive impact is improving the country's economy. While the negative impact is the presence of waste produced from cocoa if it is not utilized properly can negatively affect the environment. Until now, the cocoa pod has not been optimally utilized. According to Riyadi [1] the increasing of cocoa production can trigger the level of agricultural waste in Indonesia. Cocoa pod is a potential lignocellulose waste because it contains the main components in the form of lignin, cellulose, hemicellulose and pectin. Cocoa pod is the biggest waste component of cocoa fruit, which is equal to 75% of the total fruit [2]. While pectin on cocoa pod is around 6-12% of its dry weight. Based on cocoa production data in Indonesia, the cocoa pod waste produced is 516.3 thousand tons / year, so there are 387. 225 thousand tons / year of cocoa pod potential which can be used to produce pectin. This pectin is widely used in the food industry as thickener, emulsifier, stabilizer and can be made edible film [3].

Pectin in the cocoa pod can be produced by extraction. The extraction process is the process of separating one or several materials from a solid or liquid. Separation occurs on the basis of different soluble abilities of each component in the mixture [4,5]. Several studies on extraction of pectin from cocoa skin have been carried out. Variables that influence the success of pectin extraction are time,
temperature, type of solvent and pH. Addition of acid solvents is used to hydrolyze protopectin to pectin. The use of citric acid as a solvent in the extraction process because the price is cheaper and easier to obtain. Citric acid is a weak organic acid. This acid is very well used in buffer solutions to control the pH of the solution, and can hold minerals in the extracted material so that it loses a little mineral. Chan and Choo [6] performed extraction of pectin from cocoa pod with citric acid at pH 2.5, concentration 1:25 (w / v), temperature 95°C for 3 hours.

According to Vriesmann's study [7], the extraction of pectin from cocoa pod with dilute citric acid at 95 °C, pH 3 for 95 minutes produced 9.0 g / 100 g pectin from dried cocoa pods. Whereas according to Chan and Choo's research [6], the extraction of pectin from cacao pod with citric acid solvent obtained the optimum temperature of 95°C for 180 minutes, pH 2.5 produced 7.62% pectin. According to Mierczynska, Cybulska, Zdunek [8], the extraction process can also determine the nature of pectin. The use of citric acid in the pectin extraction process is recommended because it is environmentally friendly and safe to use for the food industry. The pectin can later be made into edible film.

Edible film is a thin layer of material that can be placed on the surface of food products to inhibit water vapor, oxygen and solids from food. Edible film can be used for food packaging, because it serves to extend the shelf life of food without causing an anaerobic state to maintain food quality. Edible films come from polysaccharides. The use of polysaccharides with a mixture of glycerol, will improve the quality of producing edible films produced [9]. The use of edible films has many advantages. One of its functions is reducing packaging waste associated with processed foods, because it is biodegradable [10]. The advantages of the film are, edible, natural and can maintain quality [11]. The functional properties of films are also determined by the characteristics of the constitution used, such as proteins, plasticizers or others that affect luster, characteristics, permeability, strength, flexibility and others [12, 13]. Film as an edible, inexpensive and renewable food packaging [14, 15]. In this research, edible films will be made from essential cocoa peel extract. The quality test of the edible film produced is the color test, thickness and water vapor transmission rate.

The purpose of this study was to determine the physical and chemical characteristics of pectin-based edible film from cocoa skin.

2. Materials and Methods

2.1. Materials
The material used in this study was cocoa pod Ferestero variety from Lubuk Minturun Padang, West Sumatra. INDONESIA, 5% citric acid, 90% alcohol, HCl, 95% ethanol, distilled water, pp indicator, NaOH, glycerol. This study will use tools such as 40 mesh filters, scales, measuring cups, rotary evaporators, 150 T screen fabrics, ovens, desiccators, pH meters, color test kits (calorie meters), glass for edible film molds bucket and several basins.

2.2. Pectin Extraction
Cocoa pod powder was weighed as much as 10 g, then put into a measuring cup and given citric acid solvent according to the variable ratio of ingredients and solvents, namely 1:25, the temperature (85 °C) with a pH of 3.2 and extraction time (120 minutes). Extraction uses a water bath. After the extraction process was filtered using a 90 T screen cloth, the filtrate was taken and heated using a rotary evaporator at a temperature of 60 °C for 15 minutes until the volume was half of the initial volume so that the filtrate became somewhat thick. Heating aims to evaporate water after extraction. Precipitation is carried out using alcohol whose purpose is to separate the pectin from the solvent. The filtrate is given alcohol with a ratio of 1: 2 and then left overnight until sediment occurs. After the sedimentation process, then filtering is carried out with screen 150 T. The filtrate is removed, while the filtered deposits are washed. Washing is done by rinsing using 96% alcohol to neutral pH. The deposits held on the screen cloth are inserted into the cup for drying in the oven at a temperature of 60-62 °C, then analysis of the pectin product [6, 16].

2.3. Edible Film Production
3 g of tapioca starch added as much as 50 ml of aquadest and glycerol according to the treatment. Then heated while stirring until gelatinization occurs (until the color is clear). Then add pectin little by little to prevent clumping. Pectin is added as much as 0.5 grams. After that it is heated to 70°C, then pour it into a mold measuring 20 x 20 cm. The next step is drying the dryer cabinet at 45°C for 24 hours. The treatment of adding glycerol is 0%, 10%, 20%, 30%. To see the effect of the use of glycerol in producing edible films, it was tested for color, thickness, rate of water vapor transmission [17].

2.4. Testing of physical properties
Edible films produced from cacao pod were tested by Hunter lab to see the color of edible films produced from each treatment [18]. Edible Film Thickness Test was performed using a micrometer thickness gauge [19]. Then compared the results for each treatment, while Measuring the Transmission Rate of Steam Water Edible Film is done by using the gravimetric method. The principle of action is to measure the amount of water vapor that can penetrate the edible film produced on moisture absorbing material (desiccant) that absorbs water vapor from outside the edible film [20]. The testing process is by weighing the cup with accuracy of 0.0001 g and placed in a room at 27°C, RH 97%. The day at the same time, then determine the weight added, then create an ant relations chart fig weight gain and time from WVTR values with the formula:

\[
\text{WVTR} = \frac{\text{Slope}}{\text{Sample area (m}^2\text{)}} \times \text{m}^2 \times 24 \text{ h}
\]

(96% RH, 27°C)

3. Results and Discussion

3.1. Pectin extraction
Observations made on the pectin extracted from cocoa pod (Figure 1) are water content, ash content, yield, pectin level, methoxyl content and color.

![Figure 1. Pectin extracted from cocoa pod](image)

The results of the analysis of water content, ash content, pectin content, yield, methoxyl content and pectin yield can be seen in Table 1.
Table 1. Pectin Analysis Result

| Parameter                  | Content | Indonesian Standard (SNI) |
|----------------------------|---------|---------------------------|
| Moisture content (%)       | 9.26    | Maks 12                   |
| Ash (%)                    | 4.42    | Maks 12                   |
| Yield (%)                  | 3.75    | -                         |
| Pectin content (%)         | 66.15   | -                         |
| Metoxyl Content (%)        | 3.94    | 5.03                      |
| Color (°Hue)               | 23.21   | -                         |

Pectin of cocoa pod from this study meets SNI standards. According to Chaichi et al. [21], pectin has good properties for edible films, and is an alternative used as a strong and biodegradable packaging material, because pectin is safe to use for food ingredients as packaging, stabilizers, gel formers and more [22].

3.2. Observation of Edible Film
Edible film produced from pectin with the percentage of glycerol addition can be seen in Figure 2.

![Figure 2. Edible films from cocoa pectin with the use of glycerol (0%, 2%, 4%, 6%, 8%)](image)

Observations made on the edible film produced were water content, thickness, color and water vapor transmission rate (Table 2). The results of data processing using Completely Randomized Design at a significant level of 5%. It can be seen that there is significant effect of the addition of glycerol to the moisture content, thickness, and Water Vapor Transmission Rate (WVTR). The higher the percentage of glycerol, the higher the water content. Determination of water content in this study aims to determine the quality of pectin obtained. Water content is one of the important parameters that determine the durability of food products and is related to the activity of microorganisms during storage. Products that have high water content are more easily damaged because these products can be a conducive medium for the growth of microorganisms. Products with low water content are relatively more stable in long-term storage than products with high water content. The results showed that the water content of edible film ranged from 2.34% -5.02%. Increasing the concentration of glycerol will...
increase the water content of the edible film produced. This is because glycerol is hydrophilic. Glycerol has a hydroxyl group which can form hydrogen bonds and when drying water is difficult to evaporate, so the water content will increase.

| Glycerol content (%) | Moisture Content (%) | Thickness (mm) | Water Vapor Transmission Rate (g/m²) |
|----------------------|----------------------|----------------|-------------------------------------|
| 0                    | 2.34<sup>a</sup>     | 0.0330<sup>a</sup> | 0.744<sup>a</sup>                  |
| 2                    | 3.32<sup>b</sup>     | 0.0336<sup>b</sup> | 0.773<sup>b</sup>                  |
| 4                    | 3.91<sup>c</sup>     | 0.0342<sup>c</sup> | 0.825<sup>c</sup>                  |
| 6                    | 4.67<sup>d</sup>     | 0.0351<sup>d</sup> | 0.874<sup>d</sup>                  |
| 8                    | 5.02<sup>e</sup>     | 0.0364<sup>e</sup> | 0.892<sup>e</sup>                  |

Thickness is directly proportional to the use of glycerol in the manufacture of edible films (Table 2). Thickness affects the water vapor transmission rate, tensile strength and elongation of edible film. The thickness of the edible film produced by the treatment of glycerol concentration was 0.0330 - 0.0364 mm. The thickness of edible film in the results of this study is thinner compared to the results of several edible film studies with different ingredients. The thickness of the film can change due to structural changes caused by the swelling of the hydrophilic matrix of the film caused by the addition of plasticizers, because the higher the treatment concentration of glycerol increases the thickness of the edible film. This is because the higher the treatment the concentration of glycerol will increase the total solids in the solution. Increasing the total amount of solids in the solution causes the thickness of the edible film to increase. This occurs because an increase in the amount of solids in the solution results in more polymers making up the matrix of edible film [23].

The thickness determines the resistance of the film to the rate of displacement of water vapor, gas, and other volatile compounds. Edible films are relatively resistant to the transfer of oxygen and carbon dioxide, but are less resistant to water vapor [23]. The thicker the edible film produced, the higher the ability to inhibit the rate of gas and water vapor, so that the product's storage power will be longer. However, if it is too thick it will affect the appearance and taste / texture of the product when eaten. The thickness of the film is also influenced by the thickness of the edible film usually less than 0.25 mm [24]. Thin edible film is suitable for coating candy, lunkhead or sausage so it doesn't feel rough when eaten / chewed.

Water Vapor Transmission Rate (WVTR) is a constant rate where water vapor permeates through edible film at certain temperatures and relative humidity. The average water vapor transmission rate of the edible film produced is 0.744 - 0.892 g / m² / hour. Glycerol affects edible film, which increases permeability to water vapor [17]. This shows that the height of the glycerol concentration treatment can increase the water vapor transmission rate. This is because the water vapor transmission rate is related to the hydrophilic properties of the materials used in making edible films [25, 26]. Glycerol also has hydrophilic properties which cause an increase in the water vapor transmission rate. This is in line with previous research that glycerol and cassava starch have a high ability to bind water resulting in a high value of the water vapor transmission rate. The water vapor transmission rate increases with increasing plasticizers added to edible films. Addition of glycerol (starch-glycerol) to the manufacture of edible films will increase permeability of vapor and oxygen, thereby increasing water resistance [27]. Films from pectin are waterproof, and can be used as food packaging [28].

3.3. Correlation between Glycerol and Color Value of Edible Film
The color of edible film greatly influences the appearance and appearance of packaged products. The brighter the edible film, the better the quality of edible film. The thicker the edible film produced, the higher the ability to inhibit the rate of gas and water vapor, so that the product's storage power will be longer (Figure 3).
Figure 3. Correlation between Glycerol and Color Value of Edible Film

Note: L (brightness value) = 0 (black) to 100 (white),
a = -60 (green) to +60 (red),
b = -60 (blue) to +60 (yellow).

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Measurement results in an L value that states the brightness parameter, while the color values a and b are chroma coordinates. The color of edible film can affect the appearance of packaged products. Edible films can provide clear or dull / opaque colors. The brighter the color, the better the appearance of the packaged product. The color and transparency of edible films are two indices that have a significant overall appearance and consumer acceptance [29].

The use of glycerol affects the appearance of edible film [10]. The measurement of edible film color in this study uses a hunter system with measurements of L (0 = black, 100 = white), a (-60 = green, +60 = red), and b (-60 = blue, +60 = yellow). The average color of edible film produced by the treatment of glycerol concentration is the color value L * (23.62 - 24.78), color a * (4.23 - 4.81) and color b * (5.72 - 6.32). The addition of glycerol affects the value of the edible color of the film produced, the higher the addition of glycerol, the higher the value of the edible color of the film produced.
The color of edible film produced tends to be brown, this is because the color of pectin used as raw material for making edible films also has a brown color. But the brown edible film produced is not dull, still clear (transparent) [10]. Glycerol provides a slightly different color for edible film for each edible film produced. The more the addition of glycerol concentration, the L value (brightness) decreases. Pectin with glycerol will be dispersed. The color of edible film depends on the color of the basic material used. The brightness of edible film will affect the packaged product. The brighter the color, the better the appearance of the product being packaged. The brightness of edible film will affect the use of edible film in packaging applications in food products [29].

4. Conclusion
From the research that has been done, it can be concluded that: The use of glycerol has a significant effect on water content, thickness, water vapor transmission rate and color of edible film, and Duncan's further test is significantly different in each treatment; From the results of the analysis of edible film, the value of water content was 2.3%-5.02%, thickness of 0.0330-0.0364 mm, water vapor transmission rate of 0.744-0.889 g / m² / hour, color L * (23.62 - 24.78), a * (4.23 - 4.81), b * (5.72 - 6.32). It can be stated that Edible films produced from pectin with the addition of glycerol have good quality and can be used as packaging material. Further research is needed regarding the application of edible films from pectin to packaging in food products, variations in the use of glycerol and the addition of antimicrobial compounds in the manufacture of edible films so that they can extend the shelf life of food products.

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