Bioplastic Properties of Sago-PVA Starch with Glycerol and Sorbitol Plasticizers

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Abstract. This study describes the making of sago starch bioplastics using glycerol and sorbitol plasticizers with the addition of PVA and chitosan filler. It purposes to compare the effect between the addition of glycerol and sorbitol plasticizers. Bioplastic samples of sago-PVA starch have been made from a mixture of sago starch and chitosan solution that had been dissolved with acetic acid, glycerol/sorbitol plasticizer, and PVA was printed and left in the air for 24 hours, then dried in the oven for 12 hours. Testing the mechanical properties of tensile strength refers to ASTM D882 then tearing strength testing based on method C in JIS K 7128 standard. In addition to testing mechanical properties, morphological tests were also referred to as the JSM-6390A standard and biodegradability tests were carried out qualitatively with DIN EN ISO standards 846, and this Water Uptake test was referred to the ASTM-D570-98 standard. This study found that the glycerol plasticizers have a better value than other comparable materials in biodegradation testing with a value of 82.38%. However, in tensile strength test, sorbitol has better value than other material, namely with the best tensile strength value of 16.12 MPa, 142.05% in elongation, tear strength of 12,729 kgf/mm, and water uptake value of 10.34%. Keyword: bioplastic, glycerol, sago starch, PVA, sorbitol

1. Introduction
Biodegradable plastics or commonly known as bioplastics are plastics that can be used like conventional plastics, but after they are used bioplastics can be easily discarded because they will break down decomposed by a microorganism. However, bioplastics still have disadvantages compared to conventional plastics, because it can be easily torn and not as strong as conventional plastics. So it needs a lot of research to develop the mechanical properties, morphology, and biodegradability of bioplastics as food packaging to replace conventional plastics. Bioplastics are made from compounds which can be found in plants such as starch, cellulose, collagen, casein, proteins or lipids found in animals [1]. Because starch is always available in large quantities and at low prices, starch is the most promising raw material in making plastics in the future [2]. One of the plants that have the potential to be a source of starch is sago (Metroxylon sp). Dry sago starch productivity reaching 25 tons/ha/ year, sago plants more than cassava which is only 1.5 tons/ha/ year, potatoes by 2, 5 tons/ha/ year and corn at 5.5 tons/ha/ year [3].

Sago is one of the types of palm plants in the wet tropical region which has a high carbohydrate content of 84.7 grams and 21.7 grams of amylose per 100 grams of sago. Based on the high carbohydrate and amylose content, sago has the potential to be a source of making starch-based bioplastics. Plastics which made from starch have isotropic, odorless, tasteless, non-toxic and...
biodegradable properties [4]. However, bioplastics which made from starch have the disadvantage that their mechanical strength (tensile strength) is still low [5]. The fact that starch as a bioplastic raw material has a high water absorption (hydrophilic), so it is resulted in the product being easily brittle (torn) [6]. Therefore, there is the addition of another material namely plasticizer which can reduce the fragility by its high intramolecular strength, preventing material during handling and storage [7]. Besides, to increase the strength and flexibility of starch bioplastics can be done by the addition of polyvinyl alcohol (PVA) [8]. Other researchers have modified the concentration of sorbitol PVA plasticizer on bioplastic synthesis which made from sorghum starch and chitosan with modified sorbitol PVA [9]. For the addition of plasticizers, one way to reduce the hydrophilic nature of starch bioplastics that cause bioplastics to become brittle is to add other biopolymers as hydrophobic filler [10, 11, 12]. Research on the effect of chitosan filler levels and glycerol plasticizer on the properties and morphology of sago starch-based bioplastics has also been conducted by previous researchers [13], so that in this research will describe the manufacture processing of sago starch bioplastics using glycerol and sorbitol plasticizers with the addition of PVA and chitosan.

2. Methodology

Material
The raw materials used in the research are from the Meranti Islands Riau local market, chitosan and polyvinyl alcohol (PVA) from CV. ChiMultiguna, aquades from the University of Riau's Natural Materials Technology Laboratory, glycerol and acetic acid from PT Bratako Chemika.

2.1. Making Bioplastic Samples
Sago-PVA starch bioplastic samples were made by mixing sago starch filtered with distilled water into a chitosan solution that had been dissolved with acetic acid, sorbitol plasticizer, and PVA. The mixture is stirred for 20 minutes using a magnetic stirrer by heating it on a hot plate at 80°C until it was homogeneous. After that, the mixture will be poured in a mold and allowed to stand for 24 hours in free air, then dried in an oven at 60°C for 12 hours. After bioplastics were released from the mold, bioplastics were ready to be tested for their characteristics and mechanical properties.

2.2. Bioplastic Sample Testing
Tensile strength mechanical testing was done by referring to ASTM D882 and tearing strength testing based on method C of JIS K 7128 standard. Besides testing mechanical properties, morphological tests were also referred to JSM-6390A standard and biodegradability test was done qualitatively with DIN EN standard ISO 846, and this Water Uptake test referred to the ASTM-D570-98 standard.

3. Result and Discussion
Analysis of the characteristics of mechanical properties is aimed (purposed) to determine the best variable value of each of the sago / PVA starch ratio variables, glycerol/sorbitol, and chitosan. Analysis of the characteristics of mechanical properties was carried out by comparing the values of each tensile strength, elongation and elastic modulus. While the tear strength test has been carried out on samples with the highest tensile strength values.

3.1. Tensile Strength Analysis
Tensile strength is a measure of the amount of load or force that can be held before a sample is damaged or broken. The tensile strength is influenced by the plasticizer and reinforcement added in the bioplastic manufacturing process. Tensile strength is one of the most important mechanical properties of bioplastics because bioplastics which have high tensile strength will be able to protect the product they are packaging from mechanical interference.
Based on the figure 1 analysis of tensile strength above, the maximum tensile strength of bioplastics was obtained at a small percentage of plasticizer. The usage of plasticizers of more than 0.2% caused a decrease in tensile strength, it was related to the nature of glycerol and sorbitol which were easily bonded to molecules. So the more glycerol and sorbitol are used, the water content in bioplastics will increase and affect the tensile strength of the plastic because it will increase the flexibility of the plastic. That is because the plasticizer molecule will disrupt the compactness of starch, reduce hydrogen interaction and increase polymer mobility [13]. In general, glycerol has a higher ability than sorbitol to absorb water [14]. It is also known that the combination of starch and PVA is a hydrophilic polymer because they are both soluble in water so that PVA has a high ability to expand in water. It can be concluded that the addition of PVA to starch and the use of glycerol plasticizers make the hydrophilic properties of plasticizer increased compared to using sorbitol plasticizers. Therefore it is seen that bioplastics with sorbitol plasticizers have better tensile strength than glycerol.

3.2. Elongation Response Analysis

![Figure 2. Elongation Analysis Effect of glycerol and sorbitol plasticizers](image-url)
Along with the addition of plasticizer concentration, it will increase the percentage of bioplastic elongation, as shown in Figure 2. This increasing percent elongation when breaking up bioplastics has caused bioplastics to become more elastic. The increasing of elongation percentage has occurred as the result of plasticizers enable to reduce fragility and to increase the flexibility of polymer films by disrupting hydrogen bonds on adjacent polymer molecules. So, the intermolecular tensile strength of polymer chains has reduced [14, 16, 17]. Sorbitol and glycerol are plasticizers that are good enough to reduce internal hydrogen bonds so that they will increase intermolecular distances. The matrix in bioplastics becomes less dense and allows the movement of polymer chains when the film is pressed. The changes that occurred in the microstructure of starch encouraging plasticizer entry into the starch matrix. Plasticizer which has entered the starch molecule further reduced interaction between starch molecules (cohesion) by forming hydrogen bonds between hydroxyl groups in starch molecules with plasticizer molecules, thereby it has increasing bioplastic flexibility and the elongation percentage [17]. Also, sorbitol and glycerol, which are hydrophilic compounds, can soften the material and cause an increase in elongation percentages. So that increasing the concentration of plasticizer to a certain point can increase elongation. The addition of sorbitol is directly proportional to the percentage of strain or elongation meaning that the greater the addition of sorbitol, the greater the value of the percentage of strain or elongation [20]. From the results of this study, it can be seen that the elastic properties of sorbitol are better than glycerol so that the elongation value of plasticizer sorbitol is higher when compared to glycerol.

3.3. Tear Strength Analysis

Based on the test results, sorbitol plasticizer tear strength value was higher than glycerol, with the highest value of 12.729 kgf / mm. The factors that affect the strength of the tear were the composition of the composite and plasticizer. The addition of sorbitol as a plasticizer and starch-PVA ratio have increased the value of plastic elasticity which it would increase the value of tearing strength. If the highest tear strength value of sorbitol is 12,726 kgf / mm and glycerol is 9.32 Kgf compared to the SNI standard of 4.9 kgf / mm, then the test results have met the SNI bioplastic standards.

| Test No | Thickness (mm) | Max Load (gf) | Tear Strength (Kgf/mm) |
|---------|----------------|--------------|------------------------|
|         |                | Glycerol     | Sorbitol               | Glycerol | Sorbitol |
| 1       | 0.19           | 1690.0       | 2296.6                 | 8.71     | 12.088   |
| 2       | 0.21           | 1973.2       | 2448.3                 | 9.42     | 11.532   |
| 3       | 0.22           | 2113.6       | 2766.1                 | 9.39     | 12.729   |

3.4. Water Uptake Analysis

Water uptake is often also referred to as water absorption, where bioplastics are expected to have low water absorption. RSM analysis results have shown the effect of process variables on the response of water uptake. The effect can be seen from the coefficient of the quadratic equation from the water uptake model in the form of a variable code.
Figure 3. Analysis of Water Uptake Plasticizer glycerol and sorbitol

Figure 3 shows that increasing plasticizers tend to produce water uptake values that are directly proportional, this is because the nature of glycerol and sorbitol are hydrophilic to increase water absorption [21]. Based on figure 3 can be seen that the value of sorbitol water uptake is better when compared with glycerol. Sorbitol plasticizer has a lower ability to bind water compared to glycerol [14], this is likely to cause a lower percentage of water uptake sorbitol plasticizer compared to glycerol. Also, it is influenced by the addition of polyvinyl alcohol (PVA) in this study, it is known that the combination of starch and PVA is a hydrophilic polymer because they are both soluble in water so that PVA has a high ability to expand in water [15]. It can be concluded that the addition of PVA to starch and the usage of glycerol plasticizers have made increasing of hydrophilic properties of plasticizer comparing to use sorbitol plasticizers.

3.5. Biodegradable Analysis

Figure 4. Biodegradable analysis of the effects of glycerol and sorbitol plasticizers
Biodegradability aims to find out how long it takes bioplastics to biodegrade in the environment. Figure 4 shows that the more plasticizer additions, the easier and faster the bioplastics to be degraded. It was caused by the effect of glycerol and sorbitol plasticizers which accelerated the degradation time and weight reduction of the sample. Glycerol and sorbitol have hydrophilic properties which are easily soluble in water. Bioplastics with glycerol plasticizers are more easily degraded because glycerol is more soluble in water compared to sorbitol as well as the addition of PVA to starch causes glycerol hydrophilic properties to increase.

3.6. Morphological Analysis of Bioplastics

Bioplastic morphology test was directly shown by SEM (Scanning Electron Microscopy). SEM testing was carried out to determine the shape and surface structure of bioplastic samples.

Picture 1. Morphological analysis of bioplastic glycerol plasticizers

Picture 1 shows the surface of the bioplastic scanning electron microscopy (SEM) test results, it can be seen the agglomeration or buildup of material components at one point. Agglomeration in PVA can result in an unequal distribution of the added filler so that the results of bioplastic sample analysis are not optimal. This was supported by the theory which stated that an increase of particle size of the filler would be made causes the formation of large agglomerates in the filler particles. When the agglomeration rate increases, the interaction between the filler and the matrix becoming weak. Also, the decrease in tensile strength can be caused by the inability of the charger to support the evenly distributed voltage transfer from the matrix, so that the mechanism of reinforcement by the presence of fillers did not occur properly [22].

In Picture 1 b, it can also be seen that the distribution of fillers was not evenly distributed and filler clumping occurs, it can result in the low mechanical properties of bioplastics that were produced due to the filler buildup so that interactions do not occur between the filler and the matrix. In the picture above a large crater that is likely an air bubble. This shows the uneven distribution of glycerol on the surface of the plastic film. Bubbles were spread on the surface of the film very much. The bubble caused the surface of the film mildly smooth.
The results of SEM bioplastic analysis with the best mechanical properties is at 4% filler content, and the amount of sorbitol plasticizer 3% were tested to measure the distribution of fillers using SEM, the results as shown in the picture above. From the picture 6, it can be seen that the distribution of fillers is not evenly distributed and filler clumping occurs which can result in the low mechanical properties of bioplastics produced, due to the buildup of fillers so that interactions between the filler and the matrix do not occur. Better compatibility and mixing techniques are needed, such as using ultrasonic processing to increase filler distribution [15].

4. Conclusion
The results obtained from this study are that glycerol plasticizers have better values in biodegradation testing, while sorbitol has better values in others. Glycerol plasticizer has the best value of 82.38% in the biodegradation test, while sorbitol with the best tensile strength value is 16.12 MPa, 142.05% in elongation, tear strength is 12.729 kgf/mm, and water uptake value is 10.34 %. This is related to the hydrophilic nature of glycerol and sorbitol, glycerol has a higher ability than sorbitol to absorb water so that glycerol is more hydrophilic compared to sorbitol. It is also known that the combination of starch and PVA is a polymer that is hydrophilic because both are soluble in water so that if the plasticizer is mixed with starch-PVA will increase the ability to expand in water.

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