Modification of Sago Starch-Based Bioplastic Using Citric Acid with Variation Plasticizers Glycerol and Sorbitol: Properties and biodegradability studies

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ABSTRACT

Bioplastic or biodegradable plastic is one of alternative replacement to conventional plastic that has the potential to harmful to the environment. One of the raw material that has the potential to be made into bioplastic is sago starch because it has ability to degraded. The general purpose of this research is to determine the characteristics of sago-based bioplastic by modified the citric acid, microcrystalline cellulose filler, plasticizer sorbitol and glycerol. The synthesis method is casting of starch, water, filler Micro Cristalline Cellulose (MCC) with varying plasticizer sorbitol and glycerol with composition of filler is (15-25 % w/w), composition of plasticizer (25–35 % w/w), and composition citric acid (3-9 % w/w). The results showed that the treatment with the addition of MCC fillers, plasticizers, and citric acid are contributed to the mechanical properties produced. In the best process conditions (20% w/w MCC filler, plasticizer sorbitol 30% w/w with citric acid 0.95% w/w) give result Tensile strength 15.84 MPa, Elongation 9.32%, Young's Modulus 171.2 MPa, Biodegradation 51.65%, and wavelength absorption 1722.51 cm^{-1}

Keywords: bioplastics, glycerol, sago starch, sorbitol

1. Introduction

The use of plastic as packaging materials have been selected for packaging material because it is robust (waterproof, light, and heat resistance), and the price is cheap [1]. However, the use of conventional plastics made from petrochemicals (material non-renewable) have quite a lot of limitations such as limited material, the nature of petrochemical products which are non-biodegradable or difficult to biologically degradation (takes too long times degradation), eco-contaminants [2].

Indonesia is the second largest plastic garbage after Chinese state [3]. Based on data from the United Nation Environment on Commemoration of World Environment Day (WED) 2018, is known that 10% of all human-generated waste is plastic; 500 billion plastic bags are used every year; 13 million tons of plastic empties into the sea every year; 17 million barrels of oil are used for the production of plastic each year; and 100,000 marine animals are killed by plastic every year. Therefore it is necessary diversion into bioplastics use conventional plastics to reduce environmental pollution as a result of plastic waste.

Bioplastics are polymers derived from natural starch material that is biodegradable (can be decomposed by microorganisms). Another advantage of the use of natural raw materials are the material properties can be updated (renewable), so that its presence can continue to be preserved and a high sustainability [4,5]. Some materials that can be used for the manufacture of bioplastics are starch, cellulose, chitin, chitosan and others. One potential plant which has the largest component of starch / cellulose is sago. Sago (Metroxylon sp) is a potential source of starch in Indonesia especially those in the province of Riau. Based on data from the Central Bureau of Statistics 2016 [6], acreage of sago palms in Riau province continues to increase from year to year that in 2011 the total area of sago palms in Riau Province amounted to 82.38 hectares and an increase up to 2015 reached 83.70 hectares with a total production of sago reached 366,032 tons of sago [6]. Sago starch consists of 27% amylose and 73% amylopectin [7]. Based on the composition of amylose and high productivity, sago has the potential to be used as the manufacture of starch-based bioplastic.

The aim of this experiment are to determine the characteristics of sago starch-based bioplastic with citric acid as modifier and sorbitol and glycerol as plasticizer. in this study a modification process was carried out by using citric acid as cross-linking agent (3-9 % w/w) and filler MCC (15-25 % w/w) with varying plasticizer sorbitol and glycerol (25–35 % w/w). The result shows that citric acid can use as cross-linking agent with absorption wavelength on the use of plasticizer sorbitol 1722.51 and 1728.29 cm-1 in the use plasticizer glycerol. Plasticizer sorbitol showed better results than the use of plasticizer glycerol in Tensile strength, Elongation Young's Modulus.

2. Experimental

2.1 Raw material

Raw materials used in this study are derived from sago starch Selat Panjang area, Kepulauan Meranti, filler to be used is Microcrystalline Cellulose (MCC), sorbitol and glycerol as plasticizer purchased from *PT. BRATACO Chemika*, and citric acid were purchased from *Putra Riau Bersama* (PRB) and distilled water

2.2 Equipment used

Analytical scale, volumetric flask, beaker glass, measuring cup, stir rod, oven, filter, mold glass, watch glass, heating mantle, condenser, three-neck flask, thermometer, hot plate. Equipment or instruments for characterization including testing of Fourier Transform Infrared (FTIR) in the Faculty of Mathematics and Natural Sciences University of Riau, testing the mechanical properties at the Faculty of Engineering, University of North Sumatra (USU) and testing of Scanning Electron Microscopy (SEM) at Indonesian Institute of Sciences (LIPI).

2.3 Research Variables

The variables used in this study consisted of a fixed variable and independent variables. Fixed variables in this study which is the ratio of starch: distilled water (1:20) [1], and gelatinization temperature (90°C) [8,10]. While the independent variable of the study is

- Citric Acid: 3, 6, and 9% (w / w starch)
- Sorbitol: 25, 30, 35% (w / w starch)
- Glycerol: 25, 30, 35% (w / w starch)
- MCC: 15, 20, and 25% (w / w starch)

2.4 Methods

This research through several stages:

2.4.1 Preparation Microcrystalline cellulose (MCC) Solution

MCC with a concentration of 15, 20, and 25% (w / w starch) was dissolved with 100g of distilled water and then stirred for 30 minutes using a mechanical stirrer at a temperature of 90°C to form a homogenous solution of MCC.

2.4.2 Manufacture of Bioplastics

10g of sago starch dissolve with 100 ml of distilled water into a beaker at room temperature (25°C), then a solution of MCC added, the mixture is stirred using a mechanical stirrer speed of 200 rpm, at 90°C (kept constant) for 30 minutes, after 20 minutes, sorbitol added with a concentration of 25%, 30%, and 35% (w / w starch) and then in the 25^{th} minute citric acid added at a concentration of 3%, 6%, and 9% (w / w starch).

Homogeneous mixture was keep settle ± 5 minutes. After that, the heated mixture was poured into a mold for 24 hours. After drying, the plastic film was released from the mold by lifting thin sheets of one side of the horizontal direction slowly until the entire surface of bioplastics apart from the mold. After that, bioplastics were ready to test the characteristics and mechanical properties. The procedure was repeated for variations in the levels of citric acid, sorbitol plasticizer levels, and levels of MCC filler, as well as plasticizers glycerol

3. Results and Discussion

3.1 Analysis of Fourier Transform Infrared (FT-IR)

In making sago starch bioplastics used citric acid which is expected to be a cross-linking agent. To be able to know the cross-linking reaction that occurs can be analyzed using the FT-IR method to identify the presence of a shift and expansion of the chains of which occur in polymer mixtures. The test results Fourier Transform Infra-Red (FT-IR) can be seen in Figure 1.

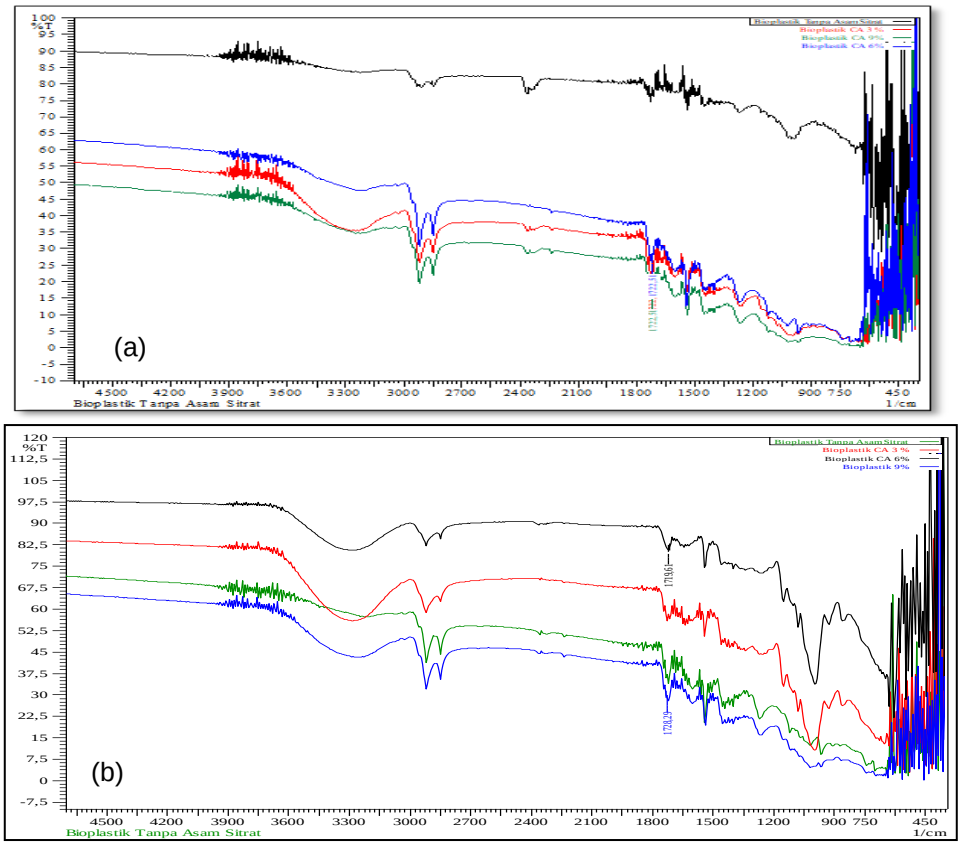

Fig 1. Bioplastics FTIR spectrum with Citric Acid Content Variation in plasticizer: (a) Sorbitol and (b) Glycerol

The results of FT-IR in Figure 1 (a) shows that the peak formed on citric acid levels 3, 6, 9% w / w is the wavelength 1722,51cm-1 while (b) is formed on the peak levels of citric acid 6 and 9 % w / w with a wavelength of 1719.61 cm -1 and 1728.29 cm-1.

It shows ester bond that has been formed in starch citrate in the presence of cross-linking agent is citric acid. Wilpiszewska and Czech [8] suggests the addition of citric acid causes the ester groups can be read at the peak absorption band 1720 cm-1 for a film of starch / citric acid esters and linked to a carbonyl group C = O (linking). This indicates that there has been a cross-linking bond which produces a new group that is an ester in the presence of cross-linking agent (citric acid). The more the concentration of citric acid addition show stronger absorption intensity and an increase in absorption area carboxyl group. The absorption intensity of widening and strong shows the influence of carboxyl groups contained in the citric acid to the resulting edible film. While on the citric acid content of 0% indicates that the absence of the ester group formed by bonding the carboxyl group of citric acid with the carboxyl group of the starch.

3.2 Mechanical Properties of Bioplastics

3.2.1 Anaysis of Tensile Strength

In general, the addition of plasticizer sorbitol and glycerol resulting bioplastic tensile strength increased to increase the concentration of 30%, but tends to decrease at the addition of plasticizers> 30% [9]. The addition of plasticizers determines the decrease in the value of tensile strength, this is because sorbitol and glycerol as plasticizers can reduce the energy needed by the molecule to move so as to increase its stiffness and increase the value of tensile strength. Plasticizer is a low molecular organic material that can reduce stiffness and improve polymers [10]

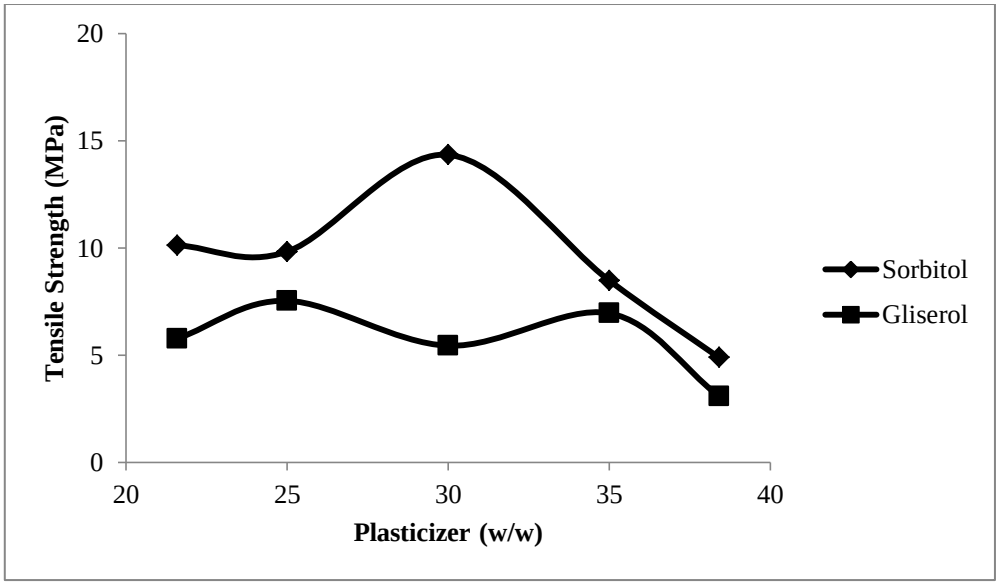

Fig 2. Tensile Strength Value of Bioplastic with MCC filler 20% (w / w), Citric Acid 6% (w / w) and Plasticizer Sorbitol Glycerol

The addition of excess sorbitol / glycerol causes the molecules of the plasticizer in the solution to interact by forming hydrogen bonds in bonds which can reduce the energy needed by the molecule to move so that the stiffness decreases causing a decrease in tensile strength [9,11]. This is also in accordance with Lubis's research [1] that the addition of sorbitol plasticizers into the mixture increases the tensile strength to an additional concentration of 25 w / w% and decreases to an additional concentration of 40%. Tensile strength grades of bioplastics obtained by using plasticizer sorbitol ranged from 4.9 to 15.84 MPa and a glycerol plasticizer ranges from 2.41 to 9.34 MPa.

3.2.2 Analysis of Elongation

Increase *plasticizer* sorbitol and glycerol resulting bioplastic elongation tends to increase. Starch is a natural polymer in the form of granules which can not be processed into a thermoplastic material due to strong intermolecular and intramolecular hydrogen bonds. Plastizicer molecules will disrupt the cohesiveness of starch, lowering the intermolecular interactions and increase the mobility of the polymer, so that the presence of water and plasticizers, such hydrogen bonding can be decided. Furthermore, resulting in increased elongation and tensile strength decrease due to increased concentrations of plasticizer [11]

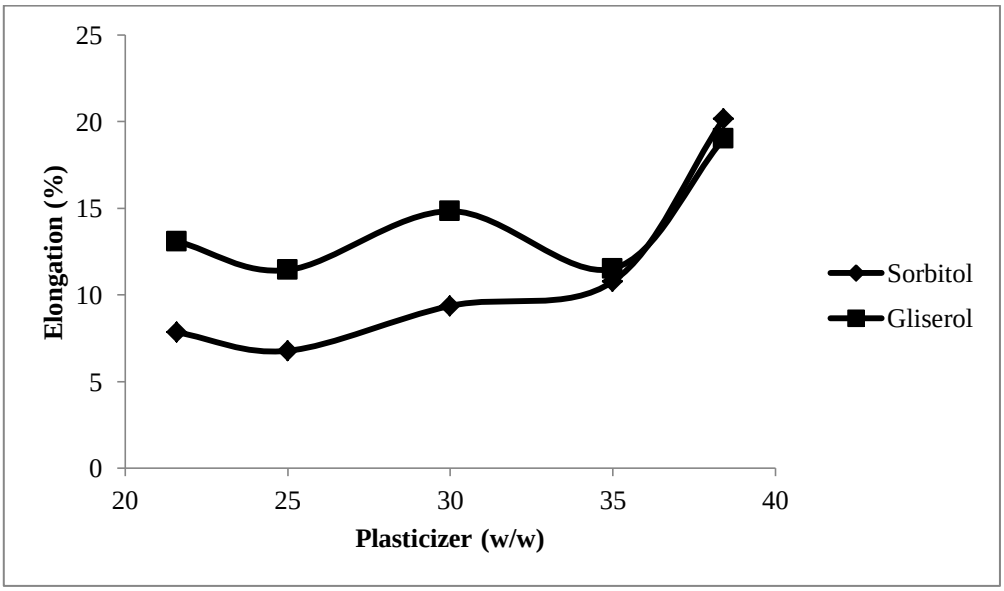

Fig 3. Elongation Value of Bioplastic with MCC Filler 20% (w / w) and Citric Acid 6% (w / w) with Plasticizer (a) Sorbitol (b) Glycerol

The addition of the plasticizer also can reduce the activation energy for the movement of molecules in the matrix. The reduction in the movement of molecules can lead to increased elastic power of bioplastics or edible film, resulting in increased concentrations of plasticizer up to a certain point can raise the value of the elongation [11]. Bioplastics elongation value obtained using plasticizer sorbitol ranged from 5.77 to 22.81% and a plasticizer glycerol ranges between 8.79- 20.56%.

3.2.3 Analysis of Young's modulus

Young's modulus or so-called modulus of elasticity is a measure of the stiffness of a material that can calculate the amount of tensile strength divided by the elongation at break. Young's modulus can also be regarded as a measure of the stiffness of a material. The more rigid material, the Young modulus values possessed by the material will be even greater. Young modulus value obtained from the comparison between the tensile strength of the percent extension

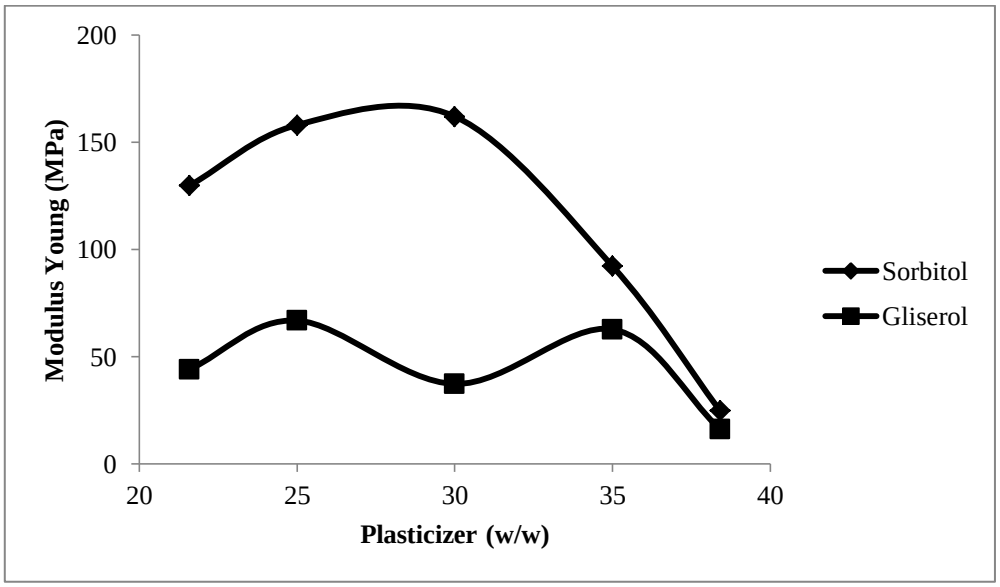

Fig 4. Young's Modulus Value Calculation Results Results Testing Model with MCC Filler 20% w / w and Citric Acid 6% w / w with Plasticizer (a) Sorbitol (b) Glycerol

Young's modulus value of bioplastics obtained by using plasticizer sorbitol ranged from 18.98 to 179.72 MPa and glycerol plasticizer ranges from 11.79 to 107.81 MPa. Based on test data results of this study showed that young modulus value is directly proportional to the value of tensile strength and elongation is inversely proportional to the value.

3.3 Analysis Biodegradation

The biodegradability is often used in synonym with compostability. A biodegradable plastic is the one in which degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi or algae. This takes place in two-steps: (i) degradation/ de-fragmentation initiated by heat, moisture or microbial enzymes and (ii) is biodegradation [10]

During the process of biodegradation, the large molecules of the substance are transformed into smaller compounds by enzymes and acids that are naturally produced by micro-organisms. Once the molecules are reduced to a suitable size, the substances can be absorbed through the organism cell walls where they are metabolized for energy [10]

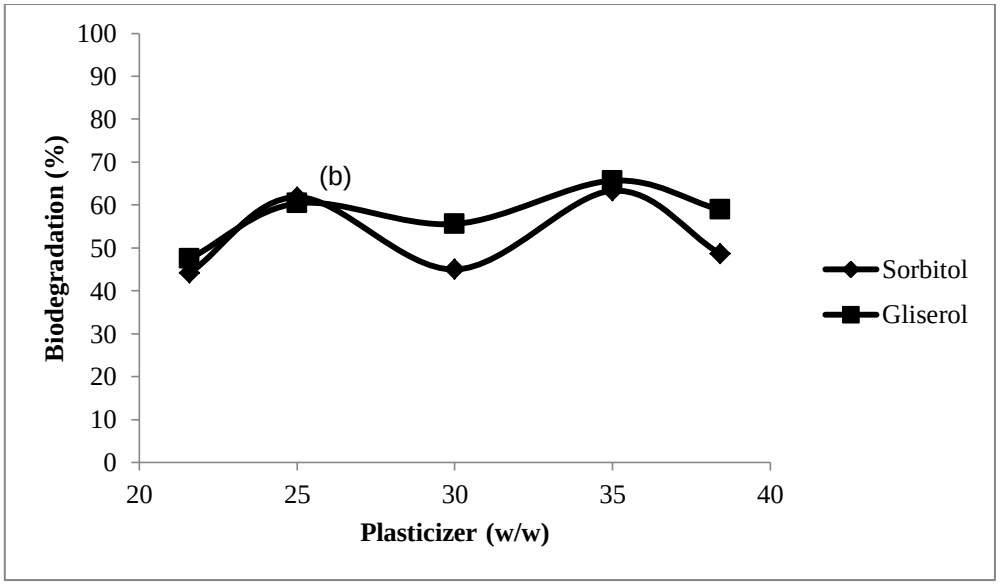

Fig 5. Biodegradation Value Calculation Results Results Testing Model with MCC Filler 20% w / w and Citric Acid 6% w / w with Plasticizer (a) Sorbitol (b) Glycerol

The biodegradation value increases with increasing levels of plasticizer. This happens because the plasticizer that donates the OH group is a hydrophilic group so that water molecules can cause microorganisms present in the environment to enter the bioplastic matrix. So that the absorption capacity of water by bioplastics increases and results in a faster degradation process [4, 10, 12]. Biodegradable bioplastics value obtained by using plasticizer sorbitol ranged between 32.5% - 63.33% and a plasticizer glycerol ranged between 41.08% - 65.68%.

3.4 Scanning Electron Microscope (SEM)

The morphology structure of polymer blends was a very important characteristic to understand many properties of polymer blends, especially the mechanical properties [9]

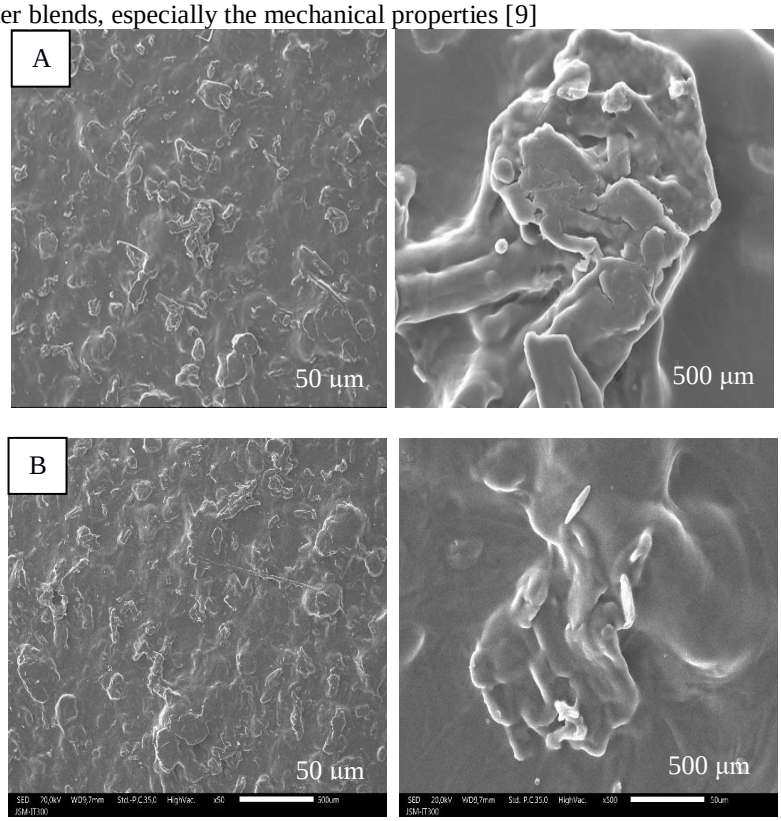

Fig 6. *Scanning Electron Microscope* (SEM) of Bioplastic

Scanning Electron Microscope SEM results show a rough and uneven structure. In Figure 6 shows that

SEM results with a magnification of 50-1000 μm can be seen the presence of agglomeration or accumulation of MCC fillers in several edible film points in both types of plasticizers. Agglomeration of the starch matrix can result in uneven distribution of added fillers which causes large agglomerates to form in the filler particles. When the level of agglomeration increases, the interaction between filler and matrix becomes weak. In addition, a decrease in tensile strength can also be caused by the inability of the charger to support evenly distributed voltage from the matrix, so that the strengthening mechanism by the filler does not occur well [13]

4. Conclusions

1. Citric acid as cross-linking agent with the levels of 3% w / w, 6% w / w starch and, 9% w / w starch can result in the absorption wavelength on the use of plasticizer sorbitol 1722.51 and 1728.29 cm-1 in the use plasticizer glycerol
2. Increasing the number of sorbitol 25-35% w / w to increase the value of elongation is 5.77 to 22.81%, ie 40.28 to 58.01% water uptake and also increases the value of the biodegradation of 32.35 to 63.33%. But inversely proportional to the value of tensile strength and Young's modulus decreased, namely from 4.25 to 15.84 and 18.98 to 179.72 MPa MPa.
3. The addition amount of glycerol can increase the value of elongation and degradation to the value of 11.44 to 20.56% and from 41.08 to 65.68% and inversely proportional to the tensile strength decreased from 2.41 to 9.34 MPa, Young modulus with a value of 11 , 79 to 107.81 MPa and water uptake with a value of 28.57 to 58.65%
4. Plasticizer sorbitol showed better results than the use of plasticizer glycerol in Tensile strength, Elongation Young's Modulus. whereas glycerol plasticizers have a better biodegradation than sorbitol. Nevertheless, the results obtained from the two plasticizers were almost the same / not significant differences. The optimum value in operating condition filler 20% w / w, plasticizer sorbitol 30% w / w with citric acid 0.95% w / w give result Tensile strength 15.84 MPa, Elongation 9.32%, Young's Modulus 171.2 MPa, Biodegradation 51.65%, and wavelength absorption 1722.51 cm-1. Whereas the optimum value in operating condition filler 25% w / w, plasticizer glycerol 25% w / w with citric acid 3% w / w give result Tensile strength, Elongation, Young's Modulus, Biodegradation and wavelength absorption respectively 9.34 Mpa, 8.79%, 8.79%, 107.81 Mpa, 65,68%, and also 1719.61 and 1728.29 cm-1

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