Chapter 1

The Utilization of Sorghum Rod Powder as Filler to Enchance Mechanical Strength In Bioplastics Synthesis

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Abstract. This research aimed to utilize sorghum as a filler rod using variations of sorghum starch-chitosan formulations-filler with 10 wt% glycerol as a plasticizer. The physical and mechanical characteristics of bioplastics then analyzed by using Low Density Polyethylene (LDPE) as a reference. Variation of sorghum starch-chitosan formulations used were 10:0, 9.5:0.5, 8.5:1.5, 7.5:2.5, 6.5:3.5 and 5.5:4.5 (w/w), variations of the addition of sorghum stem powder filler were 0.25:0.5:1 g with gelatinization temperature on 95 , stirring speed of 375 rpm and temperature drying in an oven was 60 for 11 hours. Starch granule was sieved in 63 micron and stirred for 35 minutes. The best conditions obtained by variation of formulation starch: chitosan 7.5:2.5 (g/g) with 0.25 g filler addition and best tensile strength test was13.9957 Kpa.

Keywords: bioplastic, filler, glycerol, modulus young, sorghum starch

I. Introduction

Bioplastic made from starch still has a low mechanical strength properties. When starch was combined with a filler, it will form a biocomposite, and will affect the properties of the composites formed [1]. The addition of filler from cassava powder was intended to produce the strengthen film and able to fill the air bubbles appear in the film [2].The filler would increase the mechanical strength of the starch. Rod sorghum is one of the materials that can be used as a filler which has a composition of sucrose (10 to 14.40% sorghum liquor), sugar reduction (0.75 to 1.35% sorghum liquor) and starch (209-1764 ppm [3]. Except the starch and the amplifier, glycerol was needed as a plasticizer which can increase the flexibility of bio-composites and produce bioplastic with optimal mechanical properties, morphology and biodegradability.

II. Materials and methods

A. Materials

The materials used in this research include: Sorghum flour, sorghum rod powder, Chitosan, Glycerol, distilled water, acetic acid. Analytical equipment used: Universal Testing Machine, digital calipers, and Fourier transform infrared spectroscopy (FTIR) brand Shimadzu 8400 to identify function groups.

B. Methods

This research was conducted to determine the effect of sorghum rod powder filler on the mechanical strength of bioplastics which will be analyzed. Where the ratio of starch and chitosan formulation is 10:0, 9.5:0.5, 8.5:1.5, 7.5:2.5, 6.5:3.5, and 5.5:4.5 (g/g).

While the addition of sorghum rod powder filler variation were 0.25, 0.5 and 1 (g). the speed of stirring used was 375 rpm. Glycerol concentration was 10% of the total dry weight from 10 grams of starch and chitosan, where the mixing stirring time was 35 minutes. After the stirring and mixing then followed by drying in an oven at 60℃ for 11 hours. The particle size of starch granules and sorghum rod powder filler used was 63 micron sieve escaped.

1) *Preparation of sorghum starch*

First sorghum washed and drained. After that sorghum dried in the sun until its gain constant weight. Then it was grinded with a soybeans grinding machine to become a sorghum flour. Afterwards dried sorghum flour back with the oven until its weight was constant. The dried sorghum flour was sifted with 63 micron sieve size and packaged in plastic bags to prevent any fungus or lice.

2) *Preparation of sorghum rod powder*

At first, sorghum rod was heated on the sun so that the water content of sorghum rod constant. Later, chopped the sorghum rod then grinded with grinder machine [5]. After becoming powder, then sieved with a 63 micron sieve size and packaged in plastic bags to prevent any fungus or lice.

3) *Synthesis of bioplastics*

Step for synthesis of bioplastics in this research follow the method from Weiping Ban [4] as follows: a mass of starch and chitosan with a ratio of 7.5: 2.5 (g/g) and the addition of fillers with a variation of 0.25 grams weighed using digital scales. Starch solution and chitosan solution made by adding distilled water in accordance with the amount of volume that has been calculated on a separate measuring cup. Hot Plate was turned on and set the temperature at 60^{o}C, sorghum solution in a 500 ml measuring cup was placed inside the hot plate, then chitosan solution was added to sorghum solution, and sorghum rod powder filler. After the hot plate was turned on, heat starch sorghum-chitosan solution mixture in hot plate for 35 minutes, after that added glycerol to starch sorghum-chitosan solution. Afterwards, bioplastics solution lifted and moved to the top of hot plate. Temperature and speed of hot plate set according to which will be used, it is on the T gelatination = 95℃ and the speed = 375 rpm. Then a magnetic stirrer was inserted into the solution and the hot plate was turned on. During stirring and heating the mixture, mixing temperature should be controlled at 95℃. After 35 minutes, the hot plate was turned off, a measuring cup containing the solution was removed from the hot plate, and then the solution was ignored a minute until reach the room temperature. Solution of 25 ml was poured into the mold, then placed it into an oven for drying at 60^{o}C for 11 hours. After drying in oven, the mold was removed and put into a desiccator (conditioned for 24 hours), after that, the plastic was released from the mold and stored in a zip lock bag, and plastic was ready to analyze. These steps were repeated for variations of comparison mass (g/g) sorghum starch to chitosan were 10: 0, 9.5: 0.5, 8.5: 1.5, 6.5: 3.5, 5.5: 4.5.

4) *Mechanical properties analysis*

Characteristics of the mechanical properties of a material was influenced by many factors, one of them was the ratio of starch-cellulose. Shown by the difference in the value of tensile strength, percent elongation, and Young's modulus which is diverge in every bioplastics. Sample of plastic film was tested by using Universal Testing Machine (UTM) INSTRON. The test was carried out by the standard of ASTM D 882-97 [6] and also test was executed at 23^{o}C, 50% humidity, and the cross head speed was 20 mm.min^{-1}.

5) *Water absorption analysis*

Bioplastic films water absorption test that conducted was refer to a method of making bioplastics [4].

6). *Density analysis*

By using a digital balance, weigh a mass, m (g) sample which will be tested. Then fill 5 ml of water and weighed sample into 10 ml measuring cup. After 15 minutes, note the new water volume (v). The actual plastic volume calculated by the difference between the final volume of water and its initial. Analysis of Function Groups by FTIR, samples iwas cut into small piece and crushed together with KBr until smooth to form pellets.

III. Results and Discussion

A. Result

Fig. 1. Shows the best results of bioplastic films which have physical and mechanical properties resemble wih conventional plastics LDPE (Low Density Polyethylene). The differences of structure, color, and level of mechanical strength on a sheet of bioplastics due to various factors, including the addition of a different filler ratio and imperfect stirring. The best conditions was obtained in starch: chitosan: filler formulation variations was 7.5: 2.5: 0.25 (g/g).

The test results of mechanical properties of bioplastics was shown in Table 1. Ratio starch-chitosan affects the characteristics of the bioplastic films, such as mechanical properties, physical properties, and biodegradability, so these need tests, and it aimed to get optimum conditions in the synthesis of bioplastics which resembles LDPE (Low Density Polyethylene). Testing of mechanical properties consist of tensile strength test, elongation, and Young's modulus. Testing of the physical properties consist of density test and solubility test, and other testing against bioplastic films such as FTIR.

Fig. 1. Bioplastic with ratio starch-chitosan-filler formulation7,5 : 2,5 : 0,25 (g/g).

Table 1. Result of Research Data Tabulation

Ratio of Starch: Chitosan: Filler (g/g)	Water Absorption (%)	ρ (g/mL)	Tensile Strength (kPa)	Elongation (%)	Young's Modulus (kPa)
10:0:0,25	11,11	0,389	0	0	0
9,5 : 0,5 :0,25	61,53	0,248	0,4675	11,75	3,97
8,5:1,5:0,25	79,61	0,468	4,4343	18,82	23,55
7,5:2,5:0,25	83,67	0,291	13,9957	10,8	129,36
6,5:3,5:0,25	89,33	0,254	11,4612	20,6	55,61
5,5:4,5:0,25	48,75	0,478	8,5285	8,59	99,26
Standard of LDPE [6]		0,9	$6{,}89 \times 10^3$-$24{,}13 \times 10^3$	225-600	$10^5 – 2{,}5 \times 10^5$

B. *Effect of starch-chitosan formulation and filler on mechanical properties of bioplastics*

In Fig. 2, It can be seen the influence of the ratio of starch-chitosan-filler to the tensile strength bioplastic films. Tensile strength is one of the test to determine the maximum stress of a material. The highest tensile strength values in the variation of starch-chitosan formulations and filler at 7.5: 2.5: 0.25 (g/g) is 13.9957 Kpa.

It can be deduced that with the addition of chitosan will be able to increase the tensile strength values in the sample of bioplastics. This is based on that the more chitosan given so that the better affinity which causes the chemical bonds of bioplastics increasingly strong and difficult to cut because it requires large energy to break the bond [4].

There is also a factor that can affect the value of tensile strength of bioplastic sample, it is sorghum rod powder filler. In this research, the tensile strength is affected by the starch-chitosan formulations and filler. The strong intermolecular forces in chitosan makes it difficult to interact with other components.

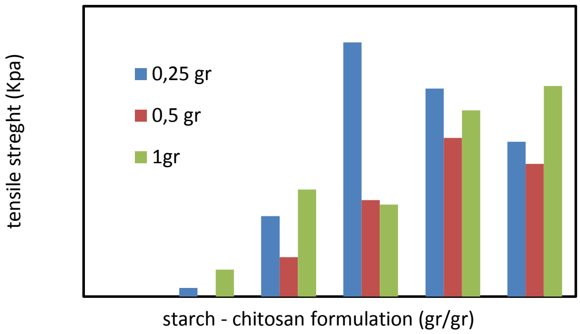

Fig. 2. The relationship between variation of starch: chitosan (g/g) and tensile strength of bioplastic with filler 0,25; 0,5; 1 gr.

Besides the combination of chitosan to starch are limited because chitosan is difficult to spread (dispersed), so that in addition of a lot of chitosan to the bioplastics solution, the value of tensile strength decreased due to the stronger intermolecular forces in chitosan makes it difficult to interact with other components.
Bioplastics which are made does not have the standards of LDPE tensile strength values. Percent extension is part of the mechanical properties which indicates elasticity or tenacity of a material when it is pulled up to break. Fig. 3 shows the effect of chitosan concentration against strains or percent extension of bioplastic films.

Based on the image, there is the best value of percent extension in the formulation 7.5: 2.5: 0.25 (g/g) with a value is 10.8%. It can be concluded that there are many factors that affect the value of the percent extension of bioplastics sample. One of them is the addition of chitosan factor which is proportional to the percent extension of the bioplastics sample.

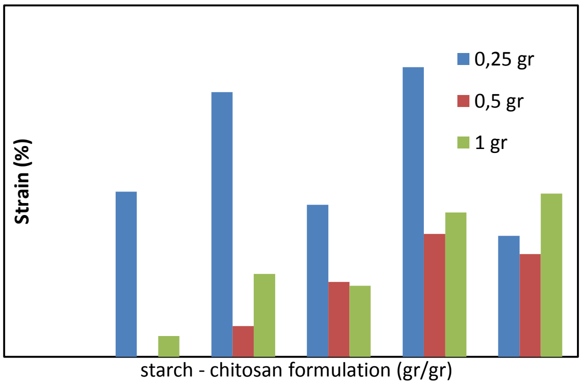

Fig. 3. The relationship between Variation of Starch : Chitosan (g/g) and strain of Bioplastic with filler 0,25; 0,5; 1 gr.

Young's modulus is obtained from the ratio between the tensile strength toward the percent extension (elongation at break). Young's modulus is often said as the size of the stiffness of a material.

Based on the Fig.3, It can be seen that the highest value for the Young's modulus is in the formulation of starch-chitosan-filler 7.5: 2.5: 0.25 (g/g) with a value is 129.36 kPa. Young's modulus values are vary greatly with the increase or decrease value by the formulation.

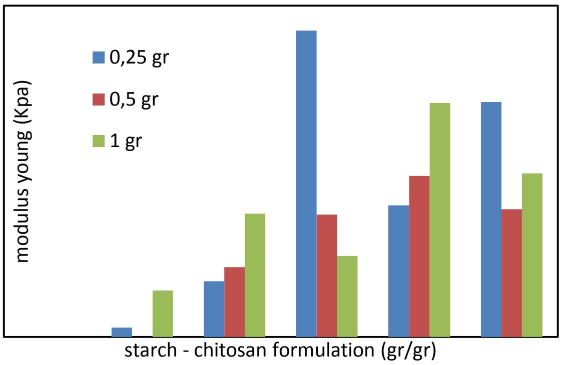

Fig. 4. The relationship between variation of starch: chitosan (g/g) and *Young's Modulus* of bioplastic with filler 0,25; 0,5; 1 gr.

C. *Effect of starch-chitosan formulation and filler on Physical Properties* of *Bioplastics*

The physical properties are properties that can be seen from the results and can change, for example, density, viscosity, and others. Physical properties test aim to determine the value of bioplastics solubility in water and the density of the bioplastics sample which is produced.

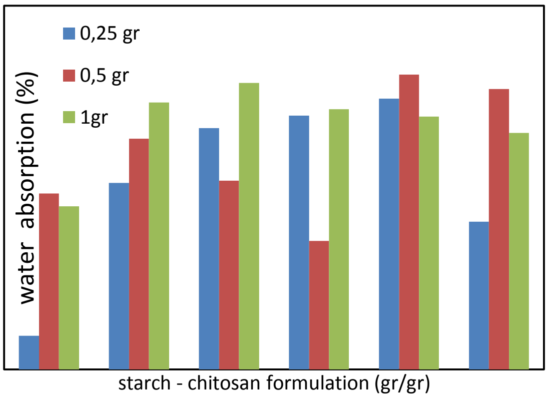

Fig. 5. **.** The relationship between ratio of starch : chitosan (g/g) and filler on water absorption of bioplastics

Based on Fig. 5, it can be seen that the best conditions on the water resistance test is in the formulation of starch-chitosan-filler at 6.5: 3.5: 0.25 (g/g) obtained in value at 89.33%. While for the value of the water resistance test that produces some water absorption is on starch-chitosan-filler formulations at 10:0:0.25 (g/g) obtained a value at 11.11%.

It can be concluded that the factors causing the high quality value of bioplastics sample against water absorption caused by the components. Chitosan with its hydrophobic characteristic is capable to give a great influence because they do not like water so it can modify the starch by grafting process or transplanting chitosan molecules into the starch molecules so chitosan is able to reduce the starch because of the hydrophilic characteristic.

Therefore the more chitosan given so the strength of bioplastic sample for absorption value will increase. Besides the addition of filler in the fabrication of bioplastic sample formulations are also able to affect the strength of the samples in the water absorption. Value test of the water resistance will increase along with adding the filler. In other cases, the addition of filler does not always increase the value of water resistance of bioplastic sample. There is also the fact that with the addition of filler then the value of the water resistance is reduced. It is based on other factors, for example in the process of drying in the oven, where sometimes there are technical problem that the death of the electrical energy from PLN's channel. It has consequences in drying the bioplastics samples which are uneven so the initial sample weight will be different from other bioplastics sample.

Density (mass/volume) is the physical properties of a polymer. The more tightly a material, the better mechanical properties where the plastic film which is produced has a good tensile strength. This bioplastic density was determined using the increasing of fluid in the measuring cup. Effect of chitosan concentration on the density can be seen in Fig. 7.

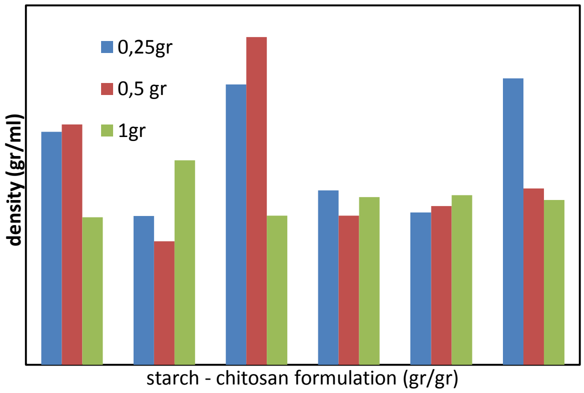

Fig. 6. The relationship between variation of starch: chitosan (g/g) and filler on density of bioplastics

Based on Fig. 6, it can be seen that there are the best conditions obtained from a density test ofbioplastics sample. Best condition on the formulation of starch-chitosan-filler are 7.5:2.5:0.25 (g/g) with values obtained at 0.291 (g/ml). From the result is density test of a bioplastics sample can be concluded that there are various factors in influencing the density of a bioplastics sample. This is based on the more dense molecular structure of the material, it will be stronger.

D. *Fourier Transfer Infra-Red (FTIR) analysis*

Based on the results of functional groups bioplastic samples test at various ratios of starch-chitosan, obtained the information several peaks appear. The emergence of a lot of peak indicates that in bioplastics there are many types of functional groups. Based on IR spectra bioplastics formulation of starch-chitosan-filler 7.5:2.5:0.25 (g/g) there is also a hydroxyl group (-OH) on the absorption area from 3567.04 to 3446.79 cm^{-1}, this group shows the breaking point. There is a group (C-OH) the absorption area is at 1078.02 $cm\text{-}^{1}$ and there is also a amide group (C=0) the absorption area is from 1651.42 to 1561.43 cm^{-1}. And to the lowest point at 779.63 cm^{-1} the absorption area is phenyl group. The difference lies in the lowest point that there are group (C-Cl) for the variation of 10:0: 0.25 and phenyl group for variation of 7.5: 2.5: 0.25.

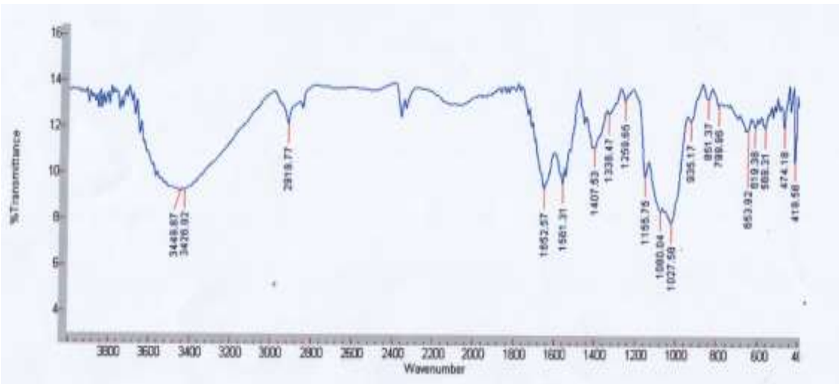

Fig. 7. Bioplastic FTIR Spectrum with Ratio Starch-Chitosan-Filler 6,5 : 2,5 : 0,5 (g/g)

IV. Conclusions

Characteristic of bioplastic that have resembled with LDPE is obtained on the starch: chitosan formulation variations 7,5 : 2,5 (g/g) with the addition of 0,25 g filler. The best tensile strength as mechanical strength characteristic of bioplastic film is 13,9957 Kpa.

List of Notation

Sym.	**Definition**	**Unit**
τ	Tensile Strength	MPa
F_{max}	Maximum Strain	N
A	Wide of Surface	(mm^2)
ε	Percent Elongation	%
L_1	Length of Bio Film	mm
L_0	Initial Length Film	mm
σ	Tensile Strength	MPa
W	Sample Weight	G
W_0	Int. Sample Weight	G
ρ	Density	g/ml
m	Sample Mass	g
v	Volume	ml

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