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Preparation and Characterization of Mechanical Properties Improved Bioplastics from Rice Bran with Varying Glycerol Volume

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Abstract

Bioplastics are plastics that we can get from biomass materials, such as corn, starch, corn husks, pea starch, and rice bran. This study aims to utilize cellulose from rice bran which has only been considered as agricultural waste, as an alternative material for forming bioplastics that can be widely applied. Rice bran added with 4% sodium hydroxide solution is called the delignification process, with heating for 3 hours at 90°C. Then the solid is dried. Subsequently, hemicellulose was removed by adding 0.2 M HCl, and heating for 3 hours at 90°C. Then the solid was dried, and the blanching process was carried out with H_2O_2. The process of making bioplastics was carried out by the phase inversion method with the fixed variables being 5 grams of cellulose powder, 5 grams of chitosan, 100 ml of 1% acetic acid, and the independent variables were the concentration of glycerol 3, 4, 5, 6, 7 ml. The results of the best swelling value was glycerol 3 ml with 40% with positive influence (R^2 = 0.9909). while the best tensile test was obtained from a 3 ml glycerol variable with a value of 9.55 MPa, for the best elongation was obtained from a 7 ml glycerol variable with an elongation value of 5.24%. While the biodegradation test with variations has a maximum biodegradation time of 17 days. As well as the FTIR Spectrophotometer test to test the wavelength and bonds between compounds in bioplastics such as CH, OH, glycerol, and acetic acid.

Keywords — bioplastics, cellulose, glycerol, phase inversion, rice bran.

1. Introduction

Indonesia is an agricultural country that has extensive agricultural land throughout western Indonesia to eastern Indonesia, farmers in Indonesia only mostly take their harvest, namely rice, we know there are harvests and there is rice harvest waste, namely rice bran, rice bran is a rice processing waste into the rice and its quality varies depending on the rice variety. Rice bran is a by-product of the rice mill in producing rice. Rice bran is part of the rice husk when the rice bleaching process is carried out. Rice bran is used as animal feed because it has a high nutritional content, the price is relatively cheap, easy to obtain, and its use does not compete with humans [1].

Rice bran production in Indonesia is quite high per year, reaching 4 million tons and each quintal of rice can produce 18-20 grams of bran. The rice milling process can produce milled rice of as much as 65% and milled waste of as much as 35%, consisting of 23% husk, bran, and rice bran as much as 10%. The bran protein ranges from 12-14%, fat about 7-9%, crude fiber about 8-13%, and ash around 9-12% [2].

Rice bran is a by product of rice milling which contains 16 – 32% (w/w) oil. The oil is widely used and very beneficial because it contains unsaturated fatty acids and antioxidants [3]. The utilization of rice bran use can increase the added value to and be a part of product diversifications of rice bran like lecithin from rice bran oil. [4].

Cellulose is a polymer with the chemical formula $(C_6H_{10}O_5)n$, n is the number of degree of polymerization that varies based on the source of cellulose it receives. Most of the cellulose fibers used for pulping have polymerization degree of 600-1.500[5].

Bioplastic is a type of plastic that is almost entirely of renewable materials, such as corn, such as starch, cellulose, and vegetable oil. The availability of basic materials in nature is very abundant with a various structures. This renewable material has excellent biodegradability so it has the possibility to be used as a bioplastic material [6].

Bioplastics are currently being developed for various applications, including plastic pipe, car interior, and mobile phones applications. Therefore, it is necessary to research the manufacture of bioplastics from rice bran flour using glycerol as a plasticizer and its characterization.

2. Materials and Methods

Materials used are Rice Bran, Chitosan, Glycerol, Sodium Hydroxide, Acetic Acid, Aquadest, Hydrochloric Acid, and H_2O_2.

Equipment used are Hot Plate Magnetic Stirrer, Thermometer, Porcelain Cup, Sieve, Glass Beaker, Flask, Erlenmeyer, filter paper, digital scale, glass bottle, pH meter, measuring pipette, glass funnel, burette, and sample glass bottles.

Analyzing bioplastics by analyzing water resistance tests is used to determine the resistance of bioplastics to water, biodegradation tests are used to determine the resistance of bioplastics to microbes. FTIR spectrometry tests are used to determine the wavelength and bonds between compounds. Tensile strength tests are the maximum tensile force that a plastic sheet can withstand during a measurement. The maximum strength in question is the maximum stress that can be achieved on the stress-strain diagram. This stress occurs because of the shrinkage phenomenon in the test object which continues until the test object breaks on activity tests, varying concentrations of glycerol.

Research Procedures

The manufacture of cellulose powder is done by drying rice bran at 150°C. After drying, 50 grams of dry bran are taken and 1000 ml of 4% NaOH is added while heated at 90°C for 3 hours. The results obtained were carried out by the process of removing hemicellulose to prevent the cellulose from becoming brittle, adding 500 ml of 0.2 M HCl, heating and stirring at 90°C for 3 hours, Filtering, taking the solid, washed until neutral, and adding 10% adding10 ml. Fixed variations Glycerol 5 ml, Cellulose 5 grams, 1000 ml aqua dest, Chitosan 5 grams, Meanwhile for the independent variable glycerol 3, 4, 5, 6, 7 ml. Spectrophotometer AnalysisInfrared Fourier Transport was carried out to determine the wavelength and bonds between compounds. AnalysisTensile Strength Tester is conducted to determine elongation and tensile strength. In testing the water resistance, water is added to the measuring cup for 2 hours. In the biodegradation test, the soil was added to a large cup with variations of 0, 10, and 17 days.

3. Results and Discussion

This discussion includes the results of the analysis carried out in the research on making bioplastics.

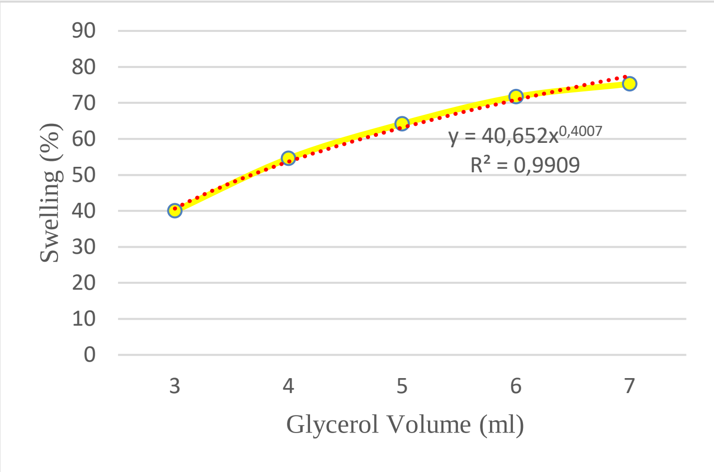


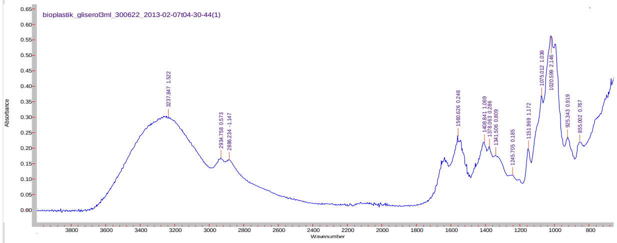
Figure 1. The results of the water resistance test for variations in glycerol volume

Figure 1 - shows that $y = 40.652x^{0.4007}$ with $R^2 = 0.9909$ where x = glycerol volume and y = percentage of swelling. The best water resistance test (% swelling) was obtained for samples containing 3 ml of glycerol.

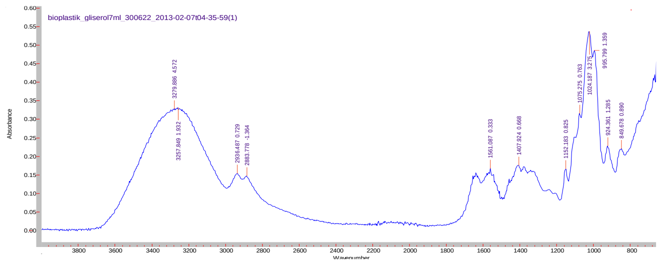
A water resistance test is carried out to determine how much the material absorbs water. In plastic, it is expected that very little water is absorbed or the absorption of the material to water must be low. The use of chitosan mainly beacuase of its water resistance. This is widely practiced because chitosan is hydrophobic.

The water resistance test was carried out to determine the occurrence of bonds in the polymer and regularity of the bonds in the polymer. The process of diffusion of starts from inserting the sample into a polymer solvent which will then produce a bulging gel. The nature of the resistance of bioplastics to water is determined by the swelling test, namely the percentage of swelling of the film by the presence of water. [7].

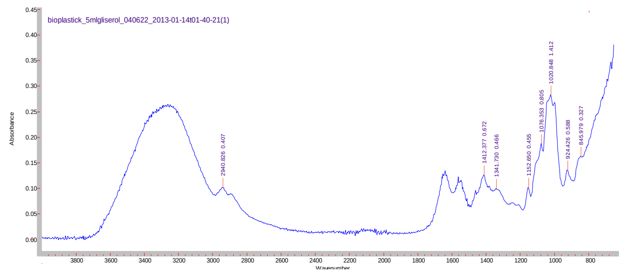
This research was conducted with the Phase Inversion process. In this study, 5 grams of chitosan were used, 5 grams of rice bran cellulose, 1% acetic acid, and varying volume of glycerol 3, 4, 5, 6, 7 ml.



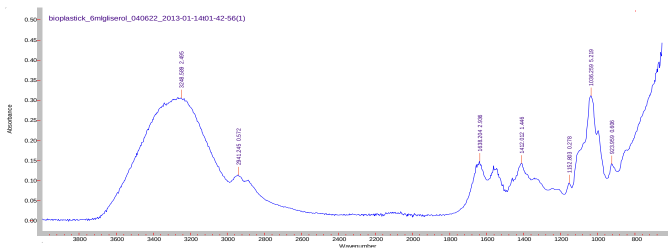
3 ml



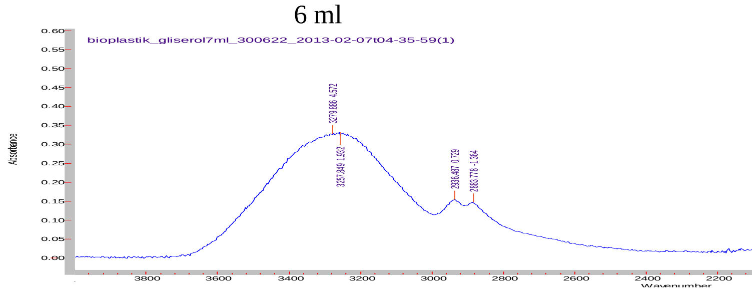
4 ml



5 ml



6 ml



7 ml

Figure 2. Glycerol Variable FTIR Test Results

As the data shown in **Figure 2**, several peaks (absorption peaks) that appear in the FTIR spectra of bioplastics indicate that in the analyzed bioplastics there is more than one type of bond (functional groups). The results of the identification of the types of functional groups related to the FTIR spectrum band are read at certain wave numbers as shown in Figure 2. it shows that samples show the same absorption band, while for the 3 ml glycerol samples. The observed absorption band is only bound to another absorption band. In this test, it was found that the CH alkane with a weak absorption band with a wavelength of 2934 cm^{-1} is a CH stretching region which indicates the presence of starch and glycerol which also has a CH group. Relevant to the absorption band close to 2934 cm^{-1} is a characteristic of the CH functional group. At a wavelength of 2934 cm^{-1} there is a sharp absorption band with weak intensity, namely the carboxylate OH functional group. indicating the presence of acetic acid. Wide absorption band with weak intensity at a wavelength of 3200-3500 cm^{-1} there is a vibration peak where in this absorption area there is also an NH stretching group (amine group). This the indication of gelatin, that the stretch absorption at a wavelength of 3000-3700 cm^{-1} on the left of the CH absorption, several functional groups such as OH, CH, C=O, NH, and aromatic CH are the spectra found in commercial gelatin, but the NH stretching peak was not found because it was covered by the H stretching bond peak of OH. The CO functional group of COC with a sharp absorption band and strong intensity is in the fingerprint region with a wavelength of 1075 cm^{-1}. At a wavelength of 1150 cm^{-1} there is a weak CO functional group from CHO with a sharp absorption band, both of which show the presence of a starch functional group as evidence that the absorption band 3200-3500 cm^{-1} there is also starch, and the OH bond also indicates the presence of a glycerol functional group. At a wavelength of 1640-1820 cm^{-1} showed that there was a functional group of carbonyl compounds, namely C=O (amide) with a sharp absorption band and a weak intensity indicating the presence of a gelatin functional group. The characteristics of the resulting film in terms of functional groups indicate that the main component of bioplastics is a cellulose polymer. This is indicated by the characteristic functional groups, namely the OH, CH and CO groups. This functional group is a characteristic functional group for cellulose [8].

The Tensile Strength and Elongation Tests aims to determine the mechanical properties of rice bran bioplastic with variations in glycerol. The tests of mechanical were carried out at a rubber research center, using the L&W Tensile Strength Tester. Figure 3 shows the results of the tensile strength test.

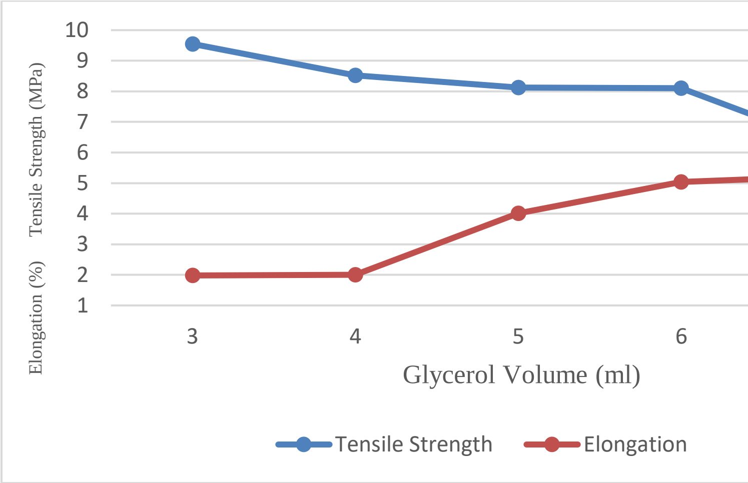


Figure 3. Glycerol Variable Tensile Strength and Elongation Test Results

From **Figure 3** it can be seen that the effect of increasing the volume of glycerol on the mechanical properties of the resulting bioplastics is the opposite properties between elongation and tensile strength. The tensile strength results decreased as the glycerol concentration

3 ml (0 Day) 	3 ml (10 Day) 	3 ml (17 Days) 
4 ml (0 Day) 	4 ml (10 Day) 	4 ml (17 Day) 
5 ml (0 Day) 	5 ml (10 Day) 	5 ml (17 Days) 
6 ml (0 Day) 	6 ml (10 Day) 	6 ml (17 Days) 
7 ml (0 Day) 	7 ml (10 Day) 	7 ml (17 Day) 

Figure 4. Biodegradation Test Results for Varying Glycerol Volume

increased. Bioplastic with glycerol 3 ml tensile strength value 9.55 MPa, glycerol 4 ml tensile strength value 8.52 MPa, glycerol 5 ml tensile strength value 8.12 MPa, glycerol 6 ml tensile strength 8, 10 MPa. and glycerol 7 ml tensile strength 6,11 MPa.

The addition of glycerol concentration as a plasticizer affects the tensile strength of bioplastics. The greater the glycerol added, the lower the tensile strength. Increasing the concentration of glycerol as a plasticizer. results in interactions by forming hydrogen bonds in with the polymers, causing the bonds between biopolymer molecules to decrease. This causes a decrease in the tensile strength of bioplastics with the addition of too high a plasticizer. The addition of excessive glycerol will be able to reduce the intermolecular tension that composes the film matrix so that the bioplastic is getting weaker to mechanical treatments. The addition of plasticizer volume can increase film moisture because the film is hygroscopic. This can affect the decrease in bioplastic macromolecular bonds. [9].

Biodegradation testing aims to determine the rate of bioplastic degradation so that it can be estimated how long it will take for bioplastics to decompose. The biodegradation test was carried out by a soil burial test. Bioplastic samples are buried with soil by maintaining a stable temperature and soil moisture. Then, the bioplastics buried in the soil were visually seen for bioplastics with time variations. The biodegradation test using the soil burial test method shows several weaknesses. Bioplastic samples in the form of films are difficult to control during testing. The cause of the reduced mass fraction of bioplastics cannot be determined thoroughly whether it is caused by microorganism activity or degradation by water absorption into bioplastics. Therefore, controlling the temperature and humidity of the soil used needs to be kept stable. This biodegradability test was carried out on bioplastic samples with the best mechanical properties.

The size of the plastic sample covered with soil is 20 x 10 cm as shown in figure 4. The soil used is sourced from a trash can. Tests were carried out on ten samples of bioplastics. The results of bioplastics are seen with variations in days as in figure 4. The results of the bioplastic test concluded that the lower the volume of glycerol added, the faster the bioplastic sample decomposes in the soil. This result is in according with other study in which the increasing addition of glycerol volume, caused the percentage value of the degradation of biodegradable plastic will be smaller along with the heavier content of chitosan [10].

4. Conclusion

From the experimental results and data analysis, the conclusions that can be drawn are:

1. From the results of the regression analysis, it was found that the glycerol volume did not affect the heating time. The correlation value for the glycerol volume and heating time was 0.857.
2. The best the water resistance at 75.29% was obtained for sample containing 5 grams of chitosan and 7 ml of glycerol.
3. The FTIR results show that variation of glycerol volume and the length of heating time did not induce the formation of new functional groups at the wavelength that was read in the starch mixture. It can be concluded that the bioplastic production process is a mixing process without a reaction involving the ingredients.
4. The best tensile strength of 9.55 MPa was obtained for sample containing 3 ml of glycerol, while the best elongation of 5.24% was shown by sample with 7 ml volume of glycerol.
5. Test biodegradation of plastic film in soil concluded that plastic film was degraded within 17 days in the soil so this plastic film is categorized as eco-friendly plastic film

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