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Engineering of Cassava Stem Cellulose As a Filler for Manufacturing Plastic Biodegradable

Tika Febrianti[1*] , Irene Septiriana[1], Verananda Kusuma Ariyanto[1], Renaldy Rizky[1]

[1]Departement Chemical Engineering, University of Sultan Ageng Tirtayasa
Jl. Jendral Sudirman Km. 03, Cilegon, Provinsi Banten, Indonesia 42435

*Corresponding Author Email: *tikafebb@gmail.com*

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ABSTRACT

Biodegradable plastic is intensely researched in recently years. Out of many findings, one good finding suggests that lignocellulosic may prove to be one of the most useful alternatives to renewable environmental friendly sources. Cassava stems contain a 56.86 % cellulose. Cellulose from lignocellulosic material has a great impact to strengthen the mechanical properties of biodegradable plastic. Because cellulose has strong and stiff properties, it can be used to produce plastic film. The addition of glycerol helps to reduce the stiff properties of plastic film. This research is purposed to improve the use of cellulose from cassava stems to be a raw material of biodegradable plastic production. There are three methods to produce plastic film: hydrolysis, delignification, and casting of plastic film. IR spectra of biodegradable plastic results a cellulose and chitosan bonding because it has an ester group at wave number 2213 cm^{-1}. SEM analysis of the additional of glycerol cracks the surface of plastic. Degradation analysis shows the use of cellulose increases the degradation rate for bioplastic by losing the mass of sample in three weeks. Tensile strength of bioplastic is not qualified with the specification of conventional polymer but it has good elongation. Therefore, there are necessarily additional materials to increase the tensile strength of bioplastic.

Keywords: *cassava stems, cellulose, degradation, IR spectra, SEM,*

1. INTRODUCTION

Plastics are widely used in various human needs, ranging from household needs to industrial purposes. Generally, plastics are used as packaging. This is due to its elastic shape, light weight but strong, not easily broken, transparent, and waterproof. But plastic has also a negative impact. Plastic waste can pollute the environment because it takes hundreds of years to break down and produce dioxins when it is burned [1]. Based on these problems, an eco-friendly plastic alternative that is derived from biodegradable materials in the environment, available in the wild in large quantities, can produce similar products with synthetic plastic [2]. Development of biodegradable plastics is one solution to solve this problem.

Plants are easy to grow in Indonesia because it has a tropical climate. Cassava is a plant that is easily grown and found in almost all regions in Indonesia. Cassava has several parts that are very useful in life. However, cassava stem is only used a small part for replanting, most of which is waste.

Table 1 the composition of Cassava stem

Content	leaf	Stem	Root	Bark
Crude Protein	23,2	10,9	1,7	4,8
Crude Fiber	21,9	22,6	3,2	21,2
Eter Extractive	4,8	9,7	0,8	1,22
Ash	7,8	8,9	2,2	4,2
Extractive without N	42,2	47,9	92,1	68
Ca	0,972	0,312	0,091	0,36
P	0,576	0,341	0,121	0,112
Mg	0,451	0,452	0,012	0,227

Table 1 shows the composition contained in cassava. Cassava stem is generally composed of 56.86% cellulose, 12% hemicellulose and 23% lignin [4]. This research will be developed the utilization of cassava stem waste as producer of cellulose which used as raw material of biodegradable plastics. There are some methods to produce cellulose: hydrolysis and delignification. Cellulose is an unbranched glucose polymer that is connected by a β-1,4 glycoside bond forming a linear chain. This linear structure causes cellulose to be crystalline and insoluble [2]. In their research, the Isolation Study of Efficient α - cellulose from Waste Plant Stem Manihot Esculenta Crantz, Ketut, et al (2011), did a study of α - cellulose isolation process from cassava stem waste using variation of chemical solution in the delignification process (NaOH, Na2SO3, And Na2SO4). From this research, the chemical solution of the delignification process with the largest purity of α-cellulose was obtained by using 20% Na2SO3 solution, with the content of 88.90% [4].

Chitosan is the second polysaccharide that is very abundant in nature after cellulose. Chitosan has good properties to be formed into plastic and has anti-microbacterial properties. This research was performed with the aim of obtaining biodegradable plastic film based on chitosan-cellulose with the addition of glycerol as plasticizer to obtain strong, non-rigid and flexible bioplastic.

2. METHOD

This research is performed for 5 months in Chemical Laboratory of Basic Chemical Engineering Faculty of Engineering UNTIRTA. There are some steps to make a biodegradable plastic: first step is a preparation of raw materials (chitosan and glycerol), followed by α-cellulose isolation from cassava stem waste, then continued with cellulose-blending chitosan and mechanical analysis, SEM, FTIR and biodegradation.

2.1 Materials and utilities

This research is using two kinds of utilities namely α-cellulose isolation from cassava stem waste device and chitosan-α-cellulose blending device. A-cellulose insulation devices are such as glassware, grater, filter and oven. Blending of chitosan-α-cellulose devices are using utilities such as glass equipment, magnetic stirrer, glass plate, and oven.

The materials are using such as chitosan, α-cellulose (from waste cassava stems), glycerol, Na_2SO_3, NaOH, H_2SO_4 and aquadest.

2.2 Isolation of α-cellulose from cassava stem waste

Cassava stem waste is debarked and shredded to become fiber. After that, it is dried in an oven at 100 ° C for 2 hours. For pre-hydrolysis treatment, weight 50 g of cassava fiber waste that has been dried. The process is further cooked with Na2SO3 solution (the ratio of the ingredients to the cooking liquor 1: 8) with a cooking solution concentration of 20%. Then the α-cellulose is separated from the cooking liquor and washed with water until it is clean. After washing, wet α-cellulose is dried in an oven with a temperature of 100 ° C. Then the resulting α-cellulose analysis is performed [4].

2.3 Plastic Film Making

For making plastic film, the first step is preparation the raw materials by varying (40%, 30%, 20% chitosan), (50% α-cellulose), and (10%, 20%, 30% glycerol). α-cellulose and chitosan are dissolved in 1% CH_3COOH solvent. The two materials are mixed into a homogeneous solution and added with glycerol due to its variations. Bioplastic is molded into glass plate with size 20cm x 20cm. Then bioplastic is dried in an oven with a temperature of 50 0C. Plastic film is formed and carried out mechanical testing, SEM, functional groups (FTIR) and biodegradation [5].

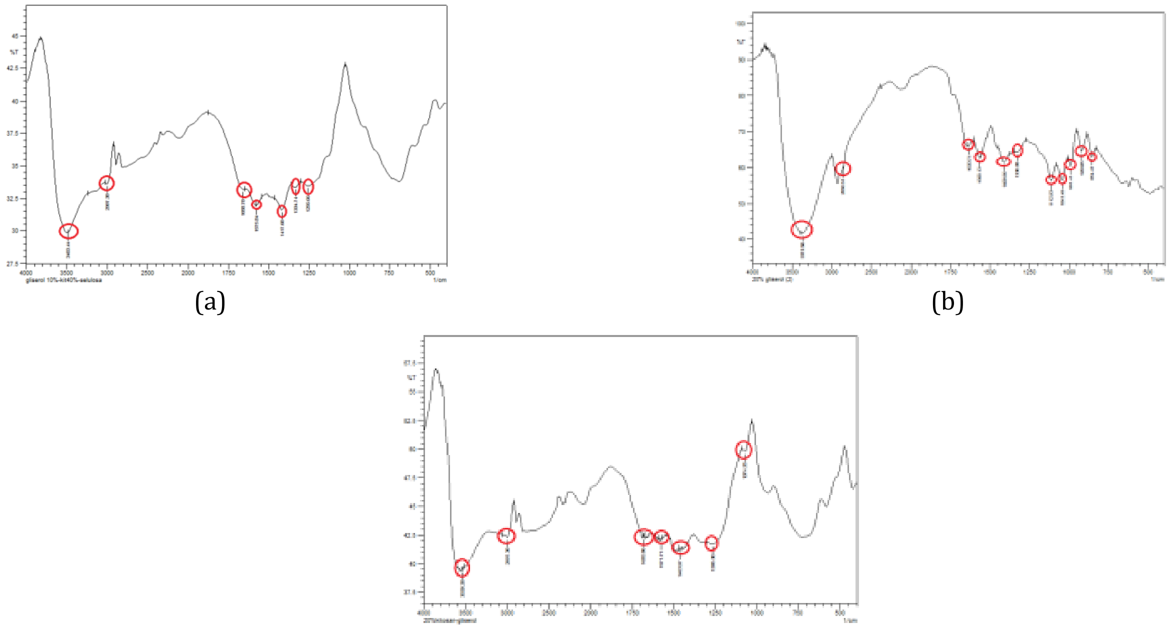
3. RESULT AND DISCUSSION

3.1 Isolation of cellulose from cassava sticks and plastic manufacture

Pre-hydrolysis and delignification are processes to isolate α-cellulose from cassava stem. Pre-hydrolysis is a process to break the holocellulose chain (cellulose, lignin and hemicellulose) and remove the hemicellulose in the cassava rod, while the delignification process is carried out in order to dissolve the lignin contained in the cassava stalk. From this process, α-cellulose analysis is performed by titrimetric method and cellulose yield is 55,27%. Plastic making is performed by casting method. It is done by dissolving, molding plastic and heating to remove solvent.

3.2 FTIR analysis

The FTIR analysis aims to determine the functional group characteristics present in the plastics. In this research, there are three biodegradable plastic products which are tested in BATAN by using IRPrestige-21 Shimadzu instrumen



(a)

(b)

(c)

Figure 1. Wave Clogging Function: (a). Plastic film with variation (Chitosan 40%, Glycerol 10% And Cellulose 50%) (b). Plastic film with variation (Chitosan 30%, Glycerol 20% And Cellulose 50%); (C). Plastic film with variation (Chitosan 20%, Glycerol 30% And Cellulose 50%.

Figure 1 shows the result of biodegradable plastic testing. On the graph there is the x-axis as a functional group wave number with units of cm-1 and y-axis represents %T. The compound group in the figure can be known by the wave number on the graph to be matched with the IR table of the Organic Compound. Figure 1 (a) is a FTIR graph of 10% glycerol, 1 (b) variation of 20% glycerol and 1 (c) variation of 30% glycerol. The three graphs produce a wave of functional group absorption that is read by FTIR. The first wave number absorbed is 3483.44 cm-1 in Fig. 1 (a), 3373.50 cm-1 in FIG. 1 (b), 3539.38 cm-1 in FIG. 1 (c) is an alcohol group (OH) , This proves that there is an alcohol group in the plastic which is one of the group of glycerol as a plasticizer. Based on FTIR analysis, it can be seen that there is a decrease of -OH wavelength as the addition of glycerol concentration. This is due to the plasticizer which has the ability to reduce the internal bond of hydrogen between polymer bonds and increase the distance between molecules [6]. This phenomenon is related to the hydrophilic behavior of glycerol and due to hydrogen bonds that is formed by hydroxyl groups of galactomannan and glycerol structures [7]. However, an increase in wavelength at 30% of glycerol occurs because glycerol does not interact well with chitosan and cellulose which cause the resulting physical properties are not optimal where glycerol can not act as an anti-plasticization agent, so the value of tensile strength and elongation produced is low.

The absorption of the wave number 2858.51 cm-1 in Fig. 1 (b), 2997.38 Fig. 1 (a), 2007.38 cm-1 in Fig. 1 (c) is the absorption of the alkane group (CH) which is one groups present in cellulose, chitosan or glycerol. The absorption of wave number is 1566,56 cm-1 in figure 1 (a), 1568,13 cm-1 in figure 1 (b) and 1577,77 cm-1 in figure 1 (c), 1697,36 cm-1 is groups Amines are typical groups of chitosan. Chitosan is a glucosamine compound represented by the presence of O-H, NH2, and C-O amides, and CH 3 groups [8]. In addition, there is a 1256.66 cm-1 wave number in Fig. 1 (a), 1128.36 cm-1 in Fig. 1 (b), 1265.3 cm-1 in Fig. 1 (c) which is a spectrum strain group of ether CO derived from COC group bonds are present in cellulose and chitosan groups [9]. The absorption of wave number at 400-1000 cm-1 is a fingerprint or special characteristic of each biodegradable plastic product, because the fingerprint on each product is different.

Based on the FTIR analysis of the three bioplastic products, it can be concluded that in the presence of hydroxide (OH), carbonyl (CO) and ester (COO) groups, the plastic can be degraded [10]. In addition, of the wavelength reads no new functional groups have been formed, it can be seen that the resulting cellulose-chitosan-glycerol bioplastic is a physically blending process because no new functional groups are found so that bioplastic has properties such as its constituent components.

3.3 SEM analysis

SEM analysis aims to find out the microscopic structure of the resulting bioplastic surfaces. SEM analysis is performed at Polymer Technology Center Laboratory (STP), LIPI-Serpong using JEOL JSM-6510LA tool with gold coating and done magnification up to 20.000x.

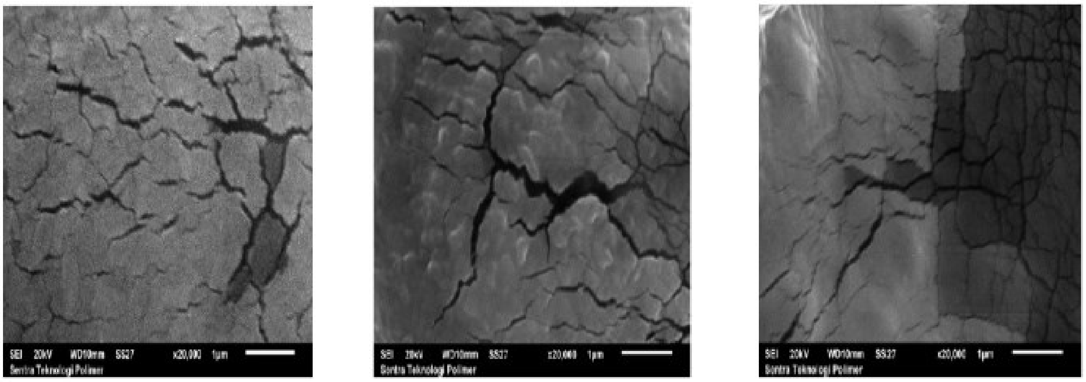


Figure 2. SEM Analysis (a). (Chitosan 40%, Glycerol 10% and 50% Cellulose) (b). (Chitosan 30%, Glycerol 20% And Cellulose 50%); (C). (Chitosan 20%, 30% Glycerol And 50% Cellulose)

Figure 2 shows SEM analysis of bioplastic samples with 20,000x magnification on 1 μm scale. The differences between the three variations are evident on the resulting bioplastic surfaces. In Fig. 2 (a) a sample with a variation of 10% glycerol, it is seen that the surface structure of the plastic exhibits considerable cracking and a subtle surface. However, in FIGS. 2 (b) and (c) the addition of 20% glycerol and 30% glycerol in sample, the surfaces are smooth. Cellulose, chitosan and glycerol are homogeneously distributed in bioplastic samples that are indicated by at least cracks of plastic samples formed. This rupture is caused by anti-plasticization behavior that is decreasing plastic property to polymer thus increasing tensile strength and reducing elongation and not optimal reaction that happened between cellulose, chitosan and glycerol. This is supported by Liu, et al (2013) suggesting that the addition of glycerol concentration is able to suppress anti-plasticization behavior by hydrogen bonding from the interaction between starch and glycerol [11]. The additional of glycerol will decrease stiffness property and increase elongation in the bioplastic sample, as evidenced by the decrease in the value of tensile strength and the increase in the elongation value along with the addition of glycerol concentration. So in this study, glycerol is able to improve the physical and mechanical properties of these biodegradable plastics.

3.4 Strong Pull and Elongation Analysis

The tensile strength and elongation analysis is performed at the Center for Chemistry and Packaging (BBKK), East Jakarta. This analysis is performed using ASTM D882 standard reference. Figure 3 shows the value of tensile strength for variation of glycerol concentration with constant cellulose content on the manufacture of biodegradable plastic. Tensile strength value for 10% glycerol variation is 0.854 Mpa, 20% glycerol is 0.287 Mpa and 30% glycerol is 0.133 Mpa.

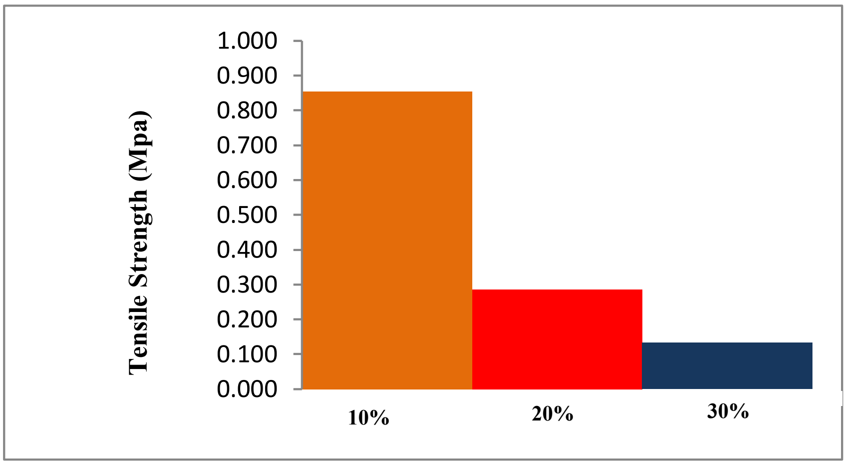


Figure 3. Effect of glycerol concentration with Cellulose constant on tensile strength (tensile strength)

In this study, the additional of glycerol concentration followed by reduction of chitosan concentration. The additional of glycerol concentration influences the value of the tensile strength of the plastic, which is shown in Fig. 3 that if the more glycerol concentration and the reduction of chitosan concentration, the tensile strength value will decrease.

This change in mechanical properties is related to the interaction of chitosan, cellulose and glycerol. If the concentration of chitosan is greater, the more hydrogen bonds present in the plastic film so that the chemical bond in the plastic will be stronger and more difficult to break. This statement is supported by research Nugroho, et al., 2015, mentioned that if the concentration of chitosan is greater, the physics changes in the more homogeneous plastic and the structure is compact, with these characteristics of course the tensile strength will be greater. Pamilia, et al., 2014, stated that the addition of chitosan and glycerol concentration is related to the chitosan-cellulose-glycerol interaction wherein the greater the chitosan concentration the more hydrogen bonding there is to the role of glycerol as a hydrogen bond breaker to improve the stiffness properties of plastic films [12]. The value of tensile strength obtained is not more than 1 MPa, this is thought to occur due to the lack of cellulose role in increasing the expected tensile strength value because the cellulose produced is only 55.27%. The highest value of tensile strength was observed at concentration of 10% glycerol / 40% chitosan.

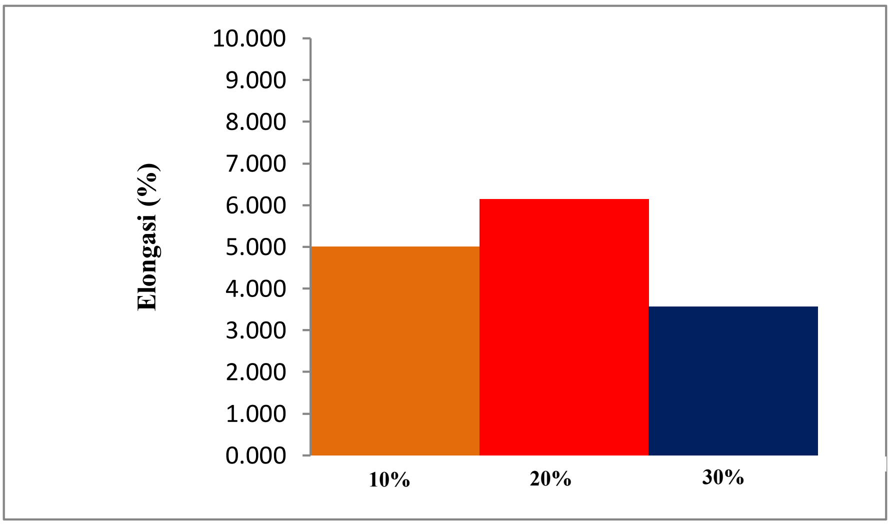


Figure 4. Effect of glycerol concentration with constant cellulose level to %-elongation.

In addition to tensile strength (tensile strength), this study also performs %elongation analysis. The value of this elongation is as one type of deformation. Deformation is the size change that occurs when the material is styled. Figure 4 shows the effect of glycerol concentration on elongation value. From figure 4, elongation values are obtained at 10% glycerol concentration of 5%, 20% glycerol by 6.14% and 30% glycerol at 3.57%. Glycerol has a strong interaction force with the polymer in the chitosan-glycerol cellulose so that the glycerol molecule diffuses into the polymer chain. Wardhani, 2012, mentions that glycerol molecules in polymers will affect the mobility of chains that can improve the plastic properties of polymers to the extent of chain compatibility [13]. It appears that the greater the concentration of glycerol, the greater the elongation value. However, there is a decrease of elongation value at 30% glycerol / 20% chitosan concentration with an elongation value of 3.57%. This is thought to occur because the addition of glycerol concentration exceeds the chain compatibility limits so that glycerol resides in its own phase outside the chitosan-cellulose phase. These conditions can cause intermolecular intermolecular degradation between polymer chains.

3.5 Biodegradation Analysis

The data and observations in the form of the loss of the third mass of bioplastic are shown in Table 2. Table 2 shows the results of the analysis in the form of reduction of sample mass after 3 weeks of landfilling. In the table, it appears that the addition of glycerol affects the ability of biodegradation of plastic samples. The more the amount of glycerol is added, the less mass of the sample. This means that the more glycerol the more easily bioplastic decomposes to the environment. This happens because cellulose and chitosan with glycerol are so bonded that it decreases the crystallinity of the polymer or the polymer structure becomes more amorphous which triggers the microorganisms in the soil to break and break down the bond more easily.

Table 2. Biodegradable Analysis Data with constant cellulose levels Information:

Plastic film	Mass loss (%)
Sample 1	0.2401
Sample 2	0.339
Sample 3	0.3772

Sample 1 = 50% Cellulose, 10% glycerol, 40% Chitosan
Sample 2 = 50% Cellulose, 20% glycerol, 30% Chitosan
Sample 3 = 50% Cellulose, 30% glycerol, 20% Chitosan

The level of polymer biodegradation is influenced by the corresponding polymer structure, the polymer with amorphous structure more easily degraded by microorganisms [5]. The biodegradation analysis that has been done shows that the bioplastic produced is environmental friendly bioplastic.

4. CONCLUSION

Cassava stalk is generally composed of cellulose in this research is 55,27 %. The resulting bioplastics have characteristics of physical properties with elongation values that have met the specifications (5%, 6.14% and 3.57%) but the tensile strength score has not met the specification (less than 1 MPa). The functional groups present in this cellulose bioplastic are alcohol groups, amine groups, ester groups, alkane groups and ether groups. Cellulose-chitosan bioplastics can decompose into environmentally meaning bioplastics.

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