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The Effect of Additional Chitosan and Cellulose on The Performance of Bioplastic from *Manihot glaziovii* Starch

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A B S T R A C T

Manihot glaziovii has a starch content of 77.87 making it potential to be used as raw material for bioplastics manufacturing as a substitute for conventional plastics. It requires the addition of biopolymers (fillers) and plasticizers to overcome weaknesses against mechanical properties and water resistance. This study aims to determine the effect of filler variations on the quality of bioplastics to be compared with SNI No.7188.7:2016 using fillers addition in the form of chitosan and cellulose from newsprint and sorbitol as plasticizer were expected to improve the quality of the bioplastics. Melt intercalation methods are used with heating temperature of 60°C-80°C for 60 minutes and stirring speed of 500 rpm. The variation of cellulose combination for 30% chitosan (w/w starch) was 10%, 12%, 14%, 16%, and 18% while the variation of chitosan for 16% cellulose (w/w starch) was 20%, 30%, 40 %, 50%, and 60%. Based on the test results, the best characteristic value for the water absorption is 120.65%, biodegradability is 32.74%, tensile strength value is 15.72 MPa, WVTR value is 6.52 g/m2.hour, and elongation is 29.76%. From the test results, it can be concluded that bioplastics made from Manihot glaziovii starch have not been able to meet SNI No.7188:2016.

INTRODUCTION

Conventional plastic bags are still widely used among Indonesian people. Conventional plastic raw materials are synthetic polymers that can't decompose so it causes many environmental problems. Conventional plastics can be substituted with biodegradable plastics that have faster degradability times. Bioplastics are easily degraded because the basic material is natural biopolymers such as starch and cellulose [1].

Starch is a glucose homopolymer carbohydrate that composed of two fractions, that is amylose and amylopectin with a ratio of 1:3 [2]. Amylose is a linear natural polysaccharide with a helical conformation consisting of glucose residues linked by glycosidic α-1,4 bonds, while amylopectin has a branched structure and consists of α-1,4-glucans bonded to each other with α-1,6-glycosidic. In the manufacture of bioplastics, amylose can affect the compactness of the matrix while amylopectin can affect the stability of the bioplastic matrix that produced [3]. Starch is found in many tubers such as cassava, potatoes, corn, wheat and rice.

One type of cassava that can be used in the manufacture of bioplastics is rubber cassava. Rubber cassava has a starch content of 70-85% [4]. Rubber cassava is a type of cassava that can't be consumed by humans because the cyanide content that exceeds 50 mg/kg [5]. The higher amount of cyanide content in it, the higher starch content too [6].

The disadvantage of bioplastics when compared to conventional plastics is in their mechanical properties and resistance to water and moisture. Fillers are needed to make the matrix of bioplastic more strength. One of the fillers that is commonly used is chitosan. Chitosan is a natural carbohydrate polymer that can be found in the skeleton of crustaceans such as shrimp and crab.

Chitosan can form hydrogen bonds between chains with amylose and amylopectin in starch so can improve the mechanical properties of the bioplastics produce [7]. Chitosan is a multifunctional polymer that contains three types of functional groups, namely amino acids, primary and secondary hydroxyl groups so that chitosan has high reactivity [8].

Cellulose can also be used as a filler in the manufacture of bioplastics because it has a structure similar to chitin. Filler in the form of cellulose from newsprint is considered to increase the value of tensile strength, modulus of elasticity, thermal stability, and resistance to water [9]. The cellulose content possessed by newsprint has a long and strong linear structure, so it has a crystalline region and difficult to dissolve in water [1].

The addition of fillers in the form of chitosan and cellulose can make the resulting plastic rigid and easily broken, so plasticizers are needed as plasticizers. The addition of plasticizer volume is directly proportional to the percent of elongation produced [10]. Plasticizers can improve the quality of bioplastics because their molecules can penetrate starch grains and damage hydrogen bonds on the inside of starch with high temperatures and shear forces [9]. The more plasticizers added, the percent elongation will increase [11]. The types of plasticizers commonly used in mixtures in the manufacture of bioplastics are sorbitol and glycerol. Sorbitol has the advantage of minimizing oxygen permeability and can produce better tensile strength values when compared to glycerol [9].

One method that can be used in the manufacture of bioplastics is the melt intercalation method. This method allows phase inversion of solution to solids by evaporating solvent after printing on a glass plate. Solutions that were previously stable will experience instability at the phase change from solution to solid. Solidification begins with a change from the liquid phase to the two-liquid phase or commonly called liquid-liquid demixing and will form solids at a certain stage [12]. This method doesn't use inorganic solvents so that it doesn't cause waste that triggers environmental pollution. Another advantage of this method is that the process is quite simple, there is no chemical reaction that occurs and can increase the possibility of interactions that occur between bioplastic matrices and fillers as fillers.

Based on the description above, it's not yet known the optimal composition of the combination of chitosan and cellulose fillers in the manufacture of bioplastics. In this study, further review will be conducted on how the effect of adding chitosan and cellulose fillers from newsprint on the characteristics of bioplastics produced so it can be compared with Indonesian National Standard No. 7188:2016.

METHODES

The research was conducted at the Process Unit Laboratory, Bandung State Polytechnic with the melt intercalation method. The materials used in this study were: rubber cassava, chitosan, newsprint, and sorbitol. Variations are made on the addition of filler mass in the form of chitosan or cellulose with one made constant. The variation of cellulose combination for 30% chitosan (w/w starch) is 10%, 12%, 14%, 16%, and 18% while the variation of chitosan combination for 16% cellulose (w/w starch) is 20%, 30%, 40%, 50%, and 60%. The concentration of cellulose and chitosan variations is determined based on preliminary studies that have been conducted.

Raw Material Preparation

The preparation of raw material includes the manufacture of rubber cassava starch and pre-treatment of newsprint. Making rubber cassava starch begins with peeling the tubers then washed thoroughly, refine the tubers and added water with ratio (1:2). The next step is extracted the mixture using a filter cloth so that rubber cassava pulp and starch suspension are obtained. The starch suspension is precipitated until a wet starch precipitate is formed and then dried in the sun and sifted using a 100 mesh sieve.

The production of cellulose fibers is carried out using inkless newspaper. Newsprint is cut into pieces and then water is added and then extracted using a filter cloth. The pulp of wet newspapers are chopped and then dried in the sun. The dried newspaper is then mashed using a blender and sifted using a 100 mesh sieve.

Production of Bioplastics

The production of bioplastics begins with the dissolution of chitosan using 1% acetic acid. After that, starch gelatinization is carried out by mixing 10 grams of starch with 100 mL aquadest with a heating temperature at 60-80 °C and a stirring speed of 500 rpm. The dissolved chitosan was mixed into gelatinized starch and 5 mL of cellulose and sorbitol plasticizer were added. The mass of chitosan and cellulose is adjusted to the desired variation. After 60 minutes, the homogenization process can be stopped, and the solution can be printed using an acrylic mold measuring 20 cm x 20 cm x 20 cm x 20 cm x 20 mm. The sample is then dried using an oven with a heating temperature at 60°C until it dries completely and can be removed from the mold.

RESULT AND DISCUSSION

The rubber cassava starch used has a starch content of 77.87% with 19.74% amylose content and 58.09% amylopectin content.

Effect of Filler Mass on Water Absorption Test

A good bioplastic must have a low percentage value of water absorption. Because if the percentage of water absorption is high, it will make bioplastics easily damaged and soluble in water. The results of water absorption testing are shown in **Figure 1**.

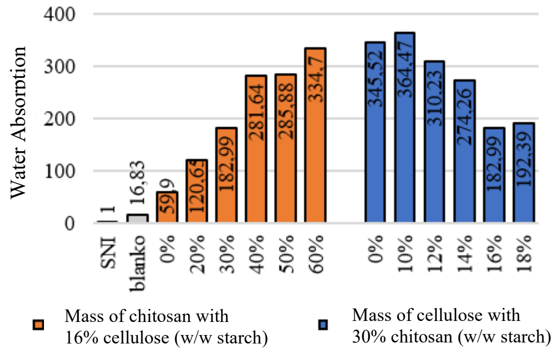

Figure 1. Water Absorption Percentage of Bioplastics

Figure 1 shows that the mass variation of chitosan with constant cellulose of 16% can affect the percentage of water absorption. The higher mass of chitosan, the higher percentage of water absorption will be produced. This is contrary to the nature of chitosan which is hydrophobic and insoluble with water. It also has three main types of functional groups, namely amino acids, primary and secondary hydroxyl groups where the hydroxyl groups (OH groups) are polar and hydrophilic [8]. This causes the occurrence of water absorption in bioplastics to get higher.

In the variation of cellulose mass with a constant chitosan of 30%, it can be seen that the higher percentage of cellulose used, the smaller percentage of water absorption produced. Cellulose has a long and strong linear structure so that crystalline regions are formed that are difficult to penetrate by water.

Overall, the percentage of bioplastic water absorption that is produced is still very high and not close to SNI 7818.7:2016. This is caused by various factors such as, the use of chitosan fillers, the type and content of starch and plasticizers that are used. Starch with a high amylopectin content will be more sensitive to water absorption.

Effect of Filler Mass on Biodegradability Test

The results of biodegradability testing on chitosan and cellulose composition variation are shown in **Figures 2 and 3**.

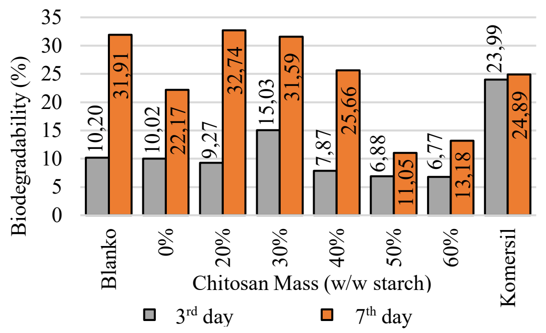

Figure 2. Biodegradability Percentage of Bioplastics on Mass Variation of Chitosan with 16% Cellulose (w/w starch)

Figure 2 shows that the addition of chitosan filler to the 16% cellulose mass makes the bioplastics produced tend to be strong and take longer to decompose. This is characterized by a tendency to decrease the percentage value of biodegradability as the amount of chitosan masses increases.

Chitosan has properties that are resistant to decomposing microorganisms contained in the soil so that the addition of chitosan mass can affect degradation time of the sample [13]. Chitosan can also form hydrogen bonds between chains with amylose and amylopectin in starch, making the resulting bioplastic matrix stronger and more difficult to degrade.

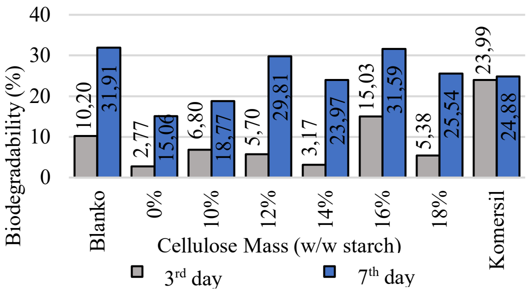

Figure 3. Biodegradability Percentage of Bioplastics on Mass Variation of Cellulose with 30% Chitosan (w/w starch)

Figure 3 shows that the higher percentage of cellulose added, the higher %biodegradability will produce. This indicates that the addition of cellulose can accelerate the degradation time of the resulting bioplastics. Cellulose is a natural polymer that can be easily degraded by the activity of microorganisms in the soil so when the cellulose content in bioplastics is high, the resulting degradation will be easier and faster.

Overall, the bioplastic that is produced will be completely degraded in the soil from week 3 to 5.

Quality of Bioplastic Products Based on *Water Vapour Transmission Rate* (WVTR)

Bioplastics with good quality must have a low water vapor transmission rate value, because if the water vapor transmission rate value is high, the pores owned by the bioplastic film are also large. The results of WVTR testing on chitosan and cellulose composition variation are shown in **Figure 4**.

In **Figure 4**, variations in the addition of chitosan mass with constant cellulose 16% tend not to significantly affect the WVTR value of the resulting bioplastics. There was no significant increase or decrease in the value of the test results. The slight increase of WVTR value occurs because chitosan has a polar group which causes high water vapor permeability while the decreased WVTR value occurs due to better solution homogeneity so that the bioplastic sample has a higher pore density.

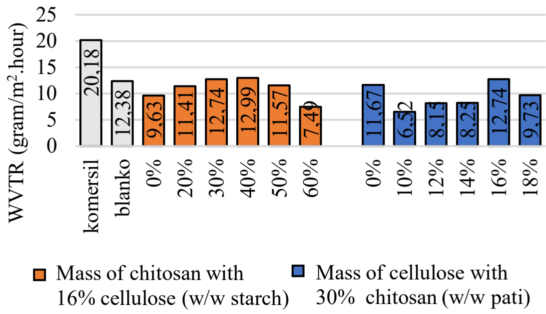

Figure 4. *Water Vapour Transmission Rate* (WVTR) Percentage of Bioplastics

The WVTR value of cellulose mass variations with 30% constant chitosan (blue graph) tends to increase in value as the cellulose mass increases. Ideally, the addition of cellulose fiber from newsprint can increase the resistance of bioplastics to moisture so that it can reduce the WVTR value. The increase in WVTR value can occur due to low homogeneity of the solution. However, when compared to blank bioplastics, bioplastics with the addition of cellulose filler have a lower water vapor transmission rate (WVTR) so it is proven that the addition of cellulose from newsprint can reduce the rate of water vapor transmission in bioplastics.

When viewed as a whole, the resulting bioplastics have a lower WVTR value compared to commercial bioplastics with the 7188.7:2016 SNI standard. This indicates that all the bioplastics produced have a smaller pore density so that they have better quality than commercial bioplastics in terms of water vapor transmission rate (WVTR).

The Effect of Filler Mass on the Tensile Strength of Bioplastics

The tensile strength value is one of the parameters of the mechanical properties of bioplastics. The higher the tensile strength value, its means the quality of the resulting bioplastic is better. Tests for tensile strength and elongation values were carried out on several selected samples based on the percentage of water absorption and adjusted to research needs. The results of testing the tensile strength values are shown in **Figure 5**.

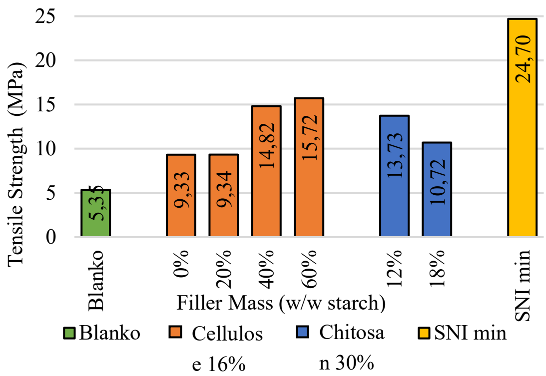

Figure 5. Tensile Strength Percentage of Bioplastics

In **Figure 5**, Bioplastics without the addition of filler (blanks) have a lower tensile strength value compared to bioplastics using fillers, both in the mass variation of chitosan and in the mass variation of cellulose. This shows that the use of chitosan and cellulose fillers can improve the quality of the bioplastics produced in terms of tensile strength.

At a constant mass of 16% cellulose filler (orange graph), the value increases with the addition of chitosan mass. Chitosan can improve mechanical properties because it can form interchain hydrogen bonds with amylose and amylopectin in starch [7].

In the variation of cellulose with 30% constant chitosan (blue graph), there is a decrease in the tensile strength value of bioplastics with 18% cellulose when compared to 12% cellulose. Ideally, the addition of cellulose mass can increase the tensile strength value because the high fiber content can fill the space in the bioplastic matrix. The discrepancy that occurs can be caused by a decrease in the level of homogeneity of the solution due to the addition of cellulose mass. The low homogeneity of a mixture can affects the tensile strength value due to the uneven distribution of bioplastic components [14]. Overall, the bioplastics produced cannot meet No. 7188:2016 SNI standard.

The Effect of Filler Mass on Bioplastic Elongation

Testing of break elongation on bioplastics was carried out to determine the ability of bioplastics to elongate optimally. The results of the elongation test are shown in **Figure 6.**

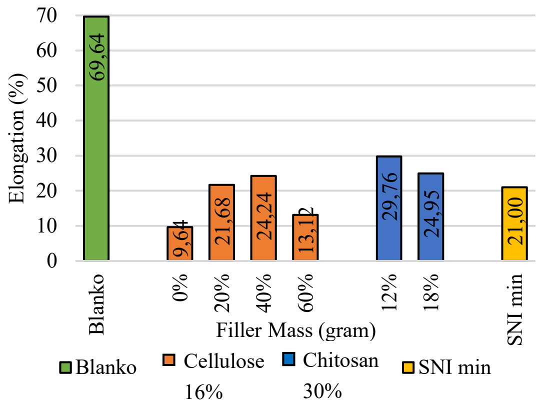

Figure 6. Elongation Percentage of Bioplastics

In **Figure 6**, Bioplastics without filler (blanks) have a higher elongation value compared to bioplastics with variations in the addition of filler. This can happen because blank bioplastics do not add reinforcing materials such as chitosan and cellulose. Blank bioplastics only consist of a mixture of starch and sorbitol as a plasticizer. The plasticizer will penetrate the starch granules and break the hydrogen bonds inside the starch so that the resulting elongation value will be much higher.

In the variation of chitosan mass with 16% constant cellulose (orange graph), the value increases up to 40% chitosan mass and decreases at 60% chitosan mass. Ideally, the addition of chitosan mass can reduce the elongation value because the additional mass of chitosan will make the intermolecular bond distances smaller so that the resulting bioplastic will be harder and stiffer.

In variations in the mass of cellulose with a constant chitosan 30% (blue graph), there is a decrease in the percent elongation in the mass range of 12% to 18% cellulose. This shows that the addition of cellulose mass as a filler can reduce the elongation value of bioplastics. Cellulose has a high crystalline area and a regular structure and has molecules with very long and strong bonds that can make bioplastic products hard and stiff which results in a decrease in elongation [1].

Overall, the highest elongation value in the bioplastics produced complies with No. 7188:2016 SNI standard.

Functional Group Analysis of Bioplastic Products Using Fourier Transform Infrared Spectroscopy (FTIR)

Functional group analysis is carried out to identify the functional groups contained in a polymeric material which in this case is bioplastic. The results of functional group analysis were carried out on variations in the composition of 20% chitosan with constant cellulose 16% which is a bioplastic with the best absorption and biodegradability results.

In **Table 1**, it can be known the molecular structure of bioplastics based on the results of FTIR characterization. From these results obtained seven types of absorption bands. The absorption band of 3429.43 cm^{-1} indicates a carboxyl bond (OH) which indicates the presence of a hydrogen bond. The OH bond may indicate the role of sorbitol in bioplastics. The absorption band of 2922.16 cm^{-1} indicates the presence of standard chitosan compounds while the absorption band is 1082.07; 1159.22; 1242.16 cm^{-1} indicates the presence of ester bonds (CO) from starch. The absorption band of 1595.13 cm^{-1} shows an amine bond (N-H) which indicates the addition of chitosan in the manufacture of bioplastics, where N-H is a component of starch-chitosan. This is in accordance with research conducted by Saputro, et al using chitosan filler and produced an infrared spectrum in starch with absorption bands of 2877.79 cm^{-1} and 1026.13 cm^{-1} where the shifts are not much different from bioplastics in this study [15].

Based on these results, it is evident that the resulting bioplastics can be indicated as biodegradable plastics that have degradability capabilities due to the presence of carboxyl (O-H) and ester (C-O) bonds.

Table 1. Bioplastic Molecular Structure Wavelength

Peak	%T	Wave Number (cm^{-1})	Molecular Structure
1020,34	54,096	1300-1000	Ester (C-O)
1082,07	55,449	1300-1000	Ester (C-O)
1159,22	57,861	1300-1000	Ester (C-O)
1242,16	72,5	1300-1000	Ester (C-O)
1595,13	57,863	1650-1550	Amina (N-H)
2922,16	52,795	3000-2700	Stretch C-H
3429,43	40,835	3700-3500	Carboxyl (O-H)

CONCLUSION

The composition of chitosan and cellulose fillers from newsprint can affect the quality of the bioplastics produced. Based on SNI No.7188: 2016 and the value of the SNI-standard commercial bioplastic test results, it was found that the bioplastics produced met the standards on the percent elongation value, percent biodegradability and water vapor transmission rate (WVTR) value and could not meet the standards on the value of water absorption and tensile strength value.

The non-fulfillment of bioplastic standards on the percentage of water absorption and tensile strength values is caused by the amylopectin content in rubber cassava starch which is higher than the amylose content so that the use of rubber cassava starch as a raw material for making bioplastics is not recommended.

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