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IMPROVEMENT OF BIOPLASTIC CHARACTERISTICS FROM TAPIOCA WASTE BY USING TITANIUM DIOXIDE AS FILLER

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ABSTRACT

The use of conventional plastics that are difficult to decompose so that the accumulation of Plastic waste can cause various problems in the environment. One way to overcome this problem is to replace petroleum-based plastics with other materials that have similar characteristics but are made from renewable materials and have biodegradable properties so that they can decompose naturally in a relatively faster time. Cassava is a polysaccharide containing starch with a high amylopectin content but lower than sticky rice, namely 83% amylopectin and 17% amylose. Tapioca dregs are waste that rots quickly if not processed further. Therefore, efforts are needed to utilize tapioca waste. The addition of Titanium Oxide is very suitable as an antibacterial agent because it is economical, has good mechanical stability, thermal stability, absorbs ultraviolet light, has a photocatalytic effect, and has a large surface area, especially in the manufacture of Bioplastics. Titanium oxide as a filler in bioplastics from tapioca waste can improve the characteristics of bioplastics. In this study, the water resistance value of biodegradable plastics was the highest, namely 47.73%. Titanium Oxide as a filler affects the tensile strength of bioplastics from tapioca waste. The highest tensile stress was obtained at a percentage of 0.8307 MPa, the highest strain was obtained at a percentage of 0.0951%, and the highest modulus of elasticity was 11.4411 MPa. In the biodegradability test with a value of 47.77% with the addition of titanium oxide filler, it meets the requirements to be used as a basic material for biodegradable plastic.

Keywords: Bioplastic, Tapioca Waste, Glycerol, Titanium Oxide.

INTRODUCTION

One polymer material that is widely used in human life is plastic. Plastic is a synthetic polymer composed of monomers that are bonded or related to one another. Plastic is strong, lightweight, and practical so that it can be used as a packaging material for both food and others. The need for plastic is so great that it triggers environmental problems in the world, especially in Indonesia in the form of plastic waste. Plastic waste derived from petroleum raw materials is waste that is difficult to decompose by microbes in the soil. The increasing use of conventional plastics is one of the world's concerns. This is due to the characteristics of conventional plastics which are difficult to decompose so that the accumulation of plastic waste can cause various problems in the environment (Muharam et al., 2022).

One way to overcome this problem is to replace petroleum-based plastics with other materials that have similar characteristics but are made from renewable materials and have biodegradable properties so that they can decompose naturally in a relatively faster time. An alternative that can be used as a solution and meets these criteria is bioplastic. Bioplastic is an environmentally friendly biodegradable plastic made from natural materials such as starch. In the manufacturing process, bioplastics are added with a filler to improve the properties of bioplastics. So that the quality of this biodegradable plastic is expected to match the quality of conventional plastics on the market (Sari et al., 2019).

Bioplastics can be used as a substitute for conventional plastics because they are quickly degraded and environmentally friendly. One way to overcome environmental problems about plastic waste is to change the raw material of the plastic (Aulia Ramadhani et al., 2022). Until now, many bioplastic developments from natural materials have been carried out, for example from tubers. One alternative solution is through the development of biodegradable plastics, using thermoplastic starch. There are two main raw materials that can be used in making biodegradable plastics, namely animal products (chitosan) and plant products (starch and cellulose) (Puryati Ningsih & Ariyani, 2019).

One of the starch materials with cellulose that can be used is cassava tuber skin. Cassava peels have contents including tannins, peroxide enzymes, glucose, calcium oxalate, fiber, and HCN. The high starch content in cassava peels allows it to be used as a biodegradable plastic film as in the environmentally friendly plastic packaging used as the basis for its manufacture (Solekah et al., 2021).

Tapioca flour is made from the milling of cassava with the pulp removed. Cassava is classified as a polysaccharide containing starch with a high amylopectin content but lower than sticky rice, namely amylopectin 83% and amylose 17%. (Ardina, 2015). Tapioca pulp (tapioca waste) is one of the by products of tapioca factories which is often used as animal feed which has a low protein content and is used as raw material for the citric acid industry with a fermentation process. The waste is an organic waste that still contains a lot of carbohydrates, proteins, and sugars. In addition, it also still contains many sugar compounds such as sucrose, glucose, fructose, dextran, galactose, and nitric acid (Nurdiniah, 2017). This tapioca pulp is a waste that quickly decays if not processed further. Therefore, efforts are needed to utilize tapioca onggok.

Glycerol is of the widely used plasticizers because it is quite effective in reducing internal hydrogen bonds, thus increasing the distance between molecules. Glycerol is a hydrophilic plasticizer, making it suitable for hydrophobic resins such as starch. For this reason, it is necessary to determine the optimal conditions for the best ratio of glucomannan to palm starch and the amount of glycerol to produce biodegradable plastics with good water resistance, tensile strength and elongation properties at the end of the tensile process.

Glycerol is the main component of all oils and fats, in the form of an ester called glycerol. A triglyceride molecule consists of one glycerol molecule bonded to three fatty acid molecules. Glycerol has many applications in the manufacture of household, industrial and pharmaceutical products. Today, the name glycerol refers to the commercially pure chemical compound known as glycerin (Purnavita et al., 2020)

The addition of TiO_2metal oxide is very suitable as an antibacterial agent because it is economical, has good mechanical stability, thermal stability, absorbs ultraviolet (UV) light, has a photocatalytic effect, and has a large surface area, especially in the manufacture of biodegradable plastics. Titanium Dioxide is a material that has several advantages including good optical properties, non-toxic, inert, good photocatalytic activity, low cost, abundant, insoluble in water, semiconductor at wide band gap, large surface area, photosensitive, environmentally friendly, high mechanical stability, dielectric properties, biocompatibility, high thermal strength and high chemical stability (N. Sari et al., 2019).

Bioplastics made from natural cellulose sources have the potential to produce void spaces due to their less stable polymer bonds. TiO_2 in bioplastics serves as a prevention of empty spaces, holes and cracks. These empty spaces, holes and cracks will affect the surface structure, heat resistance and weight loss of bioplastics. TiO because the addition of TiO_2 results in electrostatic interaction between the starch bond chain and TiO_2. Based on previous research, the amount of TIO_2 used as one of the bioplastic mixture ingredients is 7% of the total weight (Djonaedi et al., 2022).

RESEARCH METHOD

The experimental method is the method used in this research, namely the manufacture of specimens or bioplastic test samples from tapioca waste with titanium oxide filler TiO_2.

Research Tools and Materials

This research was conducted at the Chemistry Laboratory of Medan State University. The tools used in this research are: digital scales, memert oven, magnetic stirrer, filter, 10 x 20 cm mold, blender, measuring cup, stirrer, sieve, and Fourier Transform Infrared Spectroscopy (FTIR). The materials used were tapioca pulp waste, titanium oxide, glycerol, distilled water, and EM4 bacteria.

Research Variables

a. Independent variable: titanium oxide with variations of 0 gr, 1 gr, 2 gr, 3 gr, 4 gr.
b. Dependent variable (Response): Mechanical properties of bioplastics (tensile test value, water resistance, biodegradability test)
c. Control variables:
   - Waste type = solid (pulp)
   - Thickness of product object
   - Manufacture Method
   - Bioplastic lifespan
   - Test Method
   - Temperature and Ph
   - Solvent (diluent)

Research Procedure

Making bioplastics is done by mixing tapioca pulp waste that has been mashed and sieved with 100 ml of distilled water. Then 5 ml of glycerol solution was added as a plasticizer. After that, the bioplastic solution was homogenized using a magnetic stirrer with a rotation of 250 rpm until the solution thickened. Bioplastics were made according to the mixing of each material. The treatment was carried out at various concentrations of titanium dioxide 1 g, 2 g, 3 g, 4 g and 0 g (without the addition of titanium oxide) to determine the effect of the addition on bioplastics.

The bioplastic mixture was poured into a 10 x 20 cm glass mold. Oven dried for 2 hours and allowed to stand at room temperature for ± 7 days. The bioplastics formed were peeled off from the mold and stored in an airtight container. The bioplastic sheet was then tested for its characteristics.

Material Characterization

a. FTIR Characterization

FTIR analysis is a fast and nondestructive, sensitive analytical technique that requires simple sample preparation, and the use of small amounts of chemical reagents and solvents. The working principle of FTIR is to recognize the functional group of a compound from the infrared absorbance performed on the compound. The absorbance pattern absorbed by each compound is different, so that compounds can be distinguished and quantified (Maryam et al., 2019). Tensile Strenght Characterization

The tensile strength test is a measure of the maximum force (pull) that an object can withstand when stretched or pulled before the film breaks or tears. The higher the force produced, the greater the tensile strength. Edible films that have high tensile strength will protect the packaged product from mechanical disturbances well. Composite tensile strength test The tensile strength and strain of the CU/epoxy composite were determined according to ASTM D882 standard.

b. Characterization of Water Resistance

The water solubility test has a process where the film that has been cut with a size of 2 x 2 cm is put into a cup and immersed into a distilled water solution for 2 hours. The film is taken and stored in a desiccator for 10 minutes. Then weighed to get the weight of the dry film after soaking. The water solubility test aims to predict the stability of the film against the influence of water itself.

c. Biodegradability Test Characterization

The biodegradable test is intended to test the time it takes for bioplastics to be degraded by decomposing bacteria. The testing process is carried out by cutting the bioplastic sample first with a size of 2 x 2 cm, and placing it into an aluminum cup. The next step is weighed with the mass of bioplastics before being treated with EM4. Then the bioplastic was sprinkled with EM4 solution as much as 20 mL and left at room temperature. Observed changes every day for 7 days by taking bioplastics once a week on an aluminum cup then aerated for 5 minutes then weighed again.

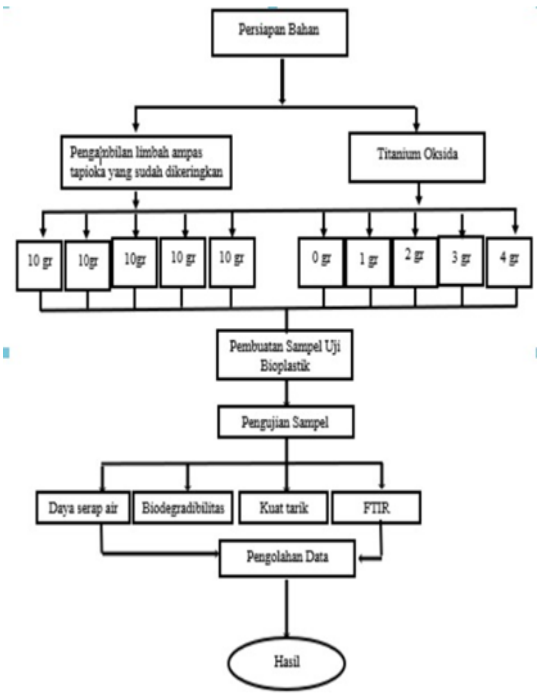

Figure 1. Research Flow Chart

RESULT AND DISCUSSION

Bioplastic Manufacturing Results

Based on the research that has been done, the results of making bioplastic tapioca waste titanium oxide as filler based on concentration are as follows:

Table 1. Comparison of Material Composition

No	Variations	Waste Tapioca (gr)	Glycerol (gr)	TiO_2 (gr)
1.	$0TiO_2$	10 gr	5 gr	
2.	$1TiO_2$	10 gr	5 gr	1 gr
3.	$2TiO_2$	10 gr	5 gr	2 gr
4.	$3TiO_2$	10 gr	5 gr	3 gr
5.	$4TiO_2$	10 gr	5 gr	4 gr

The resulting bioplastics are transparent, clear sheets, there is one smooth and rough surface, slightly stiff and there are small bubbles.

Mechanical Test Results

The mechanical test consists of tensile strength, strain, and modulus of elasticity.

1. Tensile Stress (Mpa)

The mechanical test consists of tensile strength, strain, and modulus of elasticity. Tensile strength measurement is useful to determine the amount of force achieved to achieve maximum pull on each unit area of the film to stretch or extend (Pratiwi et al., 2017).

The relationship between the variation of bioplastic samples from tapioca waste with titanium oxide filler to tensile stress is presented in graphical form in Figure 2.

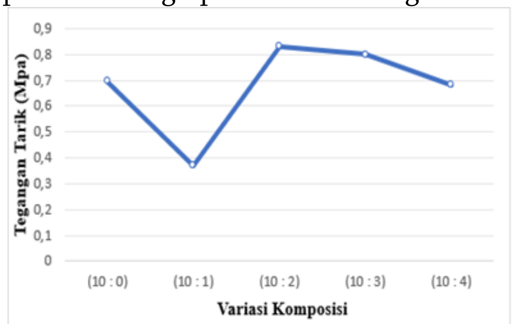

Figure 2. Relationship between composition variation and tensile stress

Based on the tensile stress graph in the figure, it can be seen that the best tensile stress value is obtained at a percentage of (10:2) which is 0.8307 MPa, while the lowest tensile stress value is obtained at a percentage of (10:1) which is 0.3717 MPa. It is in accordance with the standard value of tensile strength of bioplastic film of at least 4 kgF/cm2or 0.392 Mpa (JIS 2-1707).

2. Strain

The relationship between the variation of bioplastic samples from tapioca waste with titanium oxide filler to tensile strain is presented in graphical form in Figure 3.

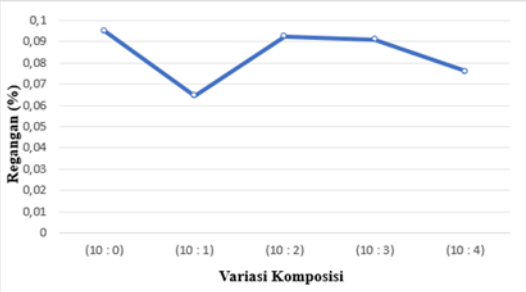

Figure 3. Relationship between composition variation and tensile strain

Based on the graph of strain results on variations in the composition of tapioca waste bioplastics with the addition of titanium oxide filler, the highest elongation value is in the sample (10: 0) with a value of 0.0951 and the lowest elongation value is in the sample (10: 1) with a value of 0.0646. This is due to the high flexibility of titanium oxide so that it can influence the elongation of the bioplastic sample.

3. Modulus of Elasticity

The relationship between the variation of bioplastic samples from tapioca waste with titanium oxide filler to the Modulus of Elasticity in the form of a graph in the Figure 4.

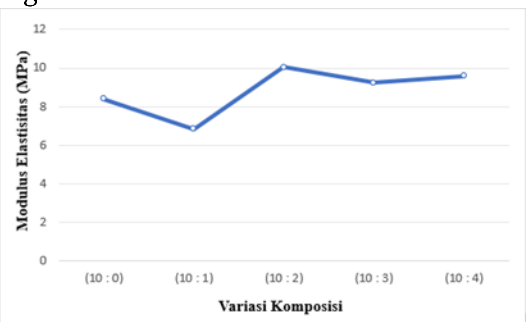

Figure 4. Relationship between composition variation and modulus of elasticity

It can be seen that each modulus of elasticity or young modulus in samples with variations of (10: 0); (10: 1); (10: 2); (10: 3);(10: 4) with a value of 8.4083 MPa; 6.8324 MPa; 10.0460 MPa; 9.2300 MPa; 11.4411 . Samples (10: 2) and (10: 4) have met the ASTM D882-12 standard with a minimum standard value of 10%.

The graph explains the data of the elastic modulus value, where there is an effect of the weight of titanium oxide with starch on the elastic modulus/young. This can occur due to the high tensile strength and the small amount of titanium oxide given to the sample which results in less elongation, so the young modulus value is high (Wahyudi et al., 2020).

4. Water Absorbency Test Analysis Results

The results of the water absorption analysis of bioplastics in this study can be seen in Table 2.

Table 2: Test Result Data of Water Absorbency Test.

Sample Name	W0	W1	%
$DS0TiO_2$	0,2575	0,4490	42,65
$DS1TiO_2$	0,3999	0,6155	35,02
$DS2TiO_2$	0,4233	0,8054	47,44
$DS3TiO_2$	0,3596	0,6373	43,57
$DS4TiO_2$	0,4080	0,7806	47,73

According to research by Rahmat et al (2014), titanium dioxide used as a biodegradable plastic material will reduce the moisture level of biodegradable plastics, because titanium dioxide is insoluble in water. In this study, the highest water resistance value of biodegradable plastics is $DS4TI0_{(2)}$ (47.73%) and $DS2TI0_{(2)}$ (47.44%) so it is very good to be used as biodegradable plastic, the higher the water resistance value of a bioplastic, the better the quality of the plastic so that the durability of the product to be packaged is also longer. On the other hand, the lower the water resistance of plastic, the greater the degradation and solubility of plastic in water, and the shorter the shelf life of packaged food products (Sri Wahyuni, 2018).

5. Biodegradability Test Analysis Results

Table 3. Biodegradability Test Result Data

Sample Name	W0	W1	%
UB0TiO_2	0,2748	0,1485	45,96
UB1TiO_2	0,3406	0,1895	44,36
UB2TiO_2	0,4648	0,2541	45,33
UB3TiO_2	0,3890	0,2084	46,42
UB4TiO_2	0,4110	0,2147	47,77

From the table it can be seen that the highest value is found in the UB4TI0 2sample with a value of 47.77%. For SNI of Biodegradation based on SNI 7188.7: 2016, Degradability is a function of susceptibility to changes in chemical structure due to changes in physical and mechanical properties that encourage the degradation of a product or material. The SNI of degradation is > 60% for 1 week (National Standardization Agency, 2016).

6. FTIR (Fourier Transform Infra Red) Spectrophotometer Analysis Result

Analysis of the samples by FTIR was carried out to identify the presence of functional groups in the biodegradable plastics. FTIR spectra of biodegradable plastics with starch-glycerol mixture and biodegradable plastics with starch-glycerol- $Ti0_2$ mixture as shown in the figure several peaks (absorption peaks) that appear in the FTIR spectra of bioplastics indicate that in the bioplastics analyzed there is more than one type of bond (functional group). The results of identifying the types of functional groups related to the FTIR spectrum bands that are read at certain wave numbers as shown below.

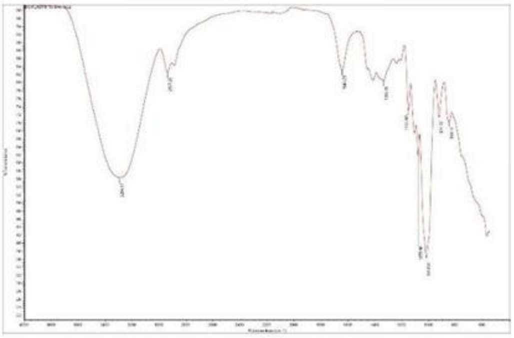

Figure 5. IR spectra results of Bioplastic Analysis from Tapioca Waste without TiO_2 by FTIR spectroscopy

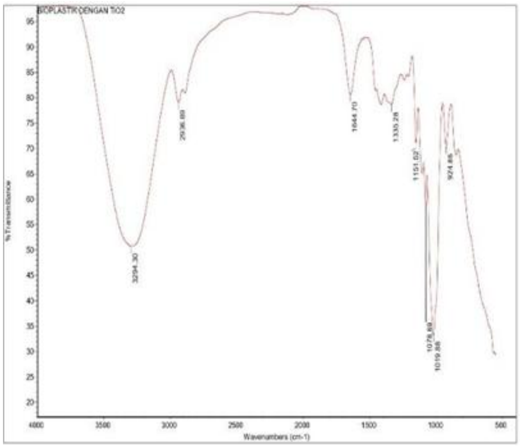

Figure 6. IR spectra results of Bioplastic Analysis from Tapioca Waste with TiO_2 by FTIR spectroscopy

Based on the results of FTIR absorption of biodegradable plastics above, the peaks obtained can be seen in Table 3 below:

Table 4. Functional group analysis of biodegradable plastics

Code Sample	Wavelength (cm-1)	Function group
Without TiO_2	3294.17	O-H
	2937.2	C-H
	1643.79	C=O
	1335.18	C-O ester
	1018.92	$\boldsymbol{\beta}-\mathbf{1},\mathbf{4}$ Gikosidik
With TiO_2	3294.30	O-H
	2936.89	C-H
	1644.70	C=O
	1335.28	C-O ester
	1078.69	$\boldsymbol{\beta}-\mathbf{1},\mathbf{4}$ Gikosidik
	>400-900	TiO_2

FTIR characteristics of biodegradable plastic films from cassava waste based on the Table, several wave number peaks are produced in each region range. In range I there is a peak with a wave number without titanium oxides 3294.17 (cm^{-1}) and 2937.2 (cm^{-1}) and after adding titanium oxide increased with wave numbers 3294.30 (cm^{-1}) and 2936.89 (cm^{-1}). This is caused by the increase of -OH carboxyl group on starch. The number of -OH carboxyl groups is very likely to bind with water. The peak corresponds to the absorption caused by O-H and C-H bonds. C- H groups are the main groups that make up bioplastics. In the range of region III there is a peak with a wave number without titanium oxide 1643.79 (cm^{-1}) and after adding titanium oxide has increased with a wave number of 1644.70 cm^{-1}. The peak corresponds to the absorption caused by the C = O bond. In the range of region IV there are peaks with wave numbers without titanium oxide 1335.18 and 1018.92 cm^{-1} and after adding titanium oxide increased with wave numbers 1335.28 and 1078.69 cm^{-1}. These peaks correspond to the absorption caused by C-O ester and β -1,4 Glycosidic bonds. Glycosidic shows the properties of typical of starch. The presence of carboxyl O-H groups, C-O ester, β - 1,4 Glycosidic cause bioplastics can be degraded by nature. (Darni and Herti, 2006).

CONCLUSION AND SUGGESTION

Based on the results of bioplastic research from tapioca waste with titanium oxide filler (TiO_2), the following conclusions are obtained:

1. Titanium oxide as a filler in bioplastics from tapioca waste can improve the characteristics of bioplastics.
2. Titanium dioxide used as a biodegradable plastic material will reduce the moisture level of biodegradable plastics, because titanium dioxide is insoluble in water. In this study, the highest water resistance value of biodegradable plastic is DS4TI0(2) (47.73%).
3. Titanium oxide (TiO 2) as a filler affects the tensile strength of bioplastics from tapioca waste. The highest tensile stress was obtained at a percentage of 0.8307 MPa, and had a better tensile stress than without the addition of titanium oxide. The highest strain in this study was obtained at a percentage of 0.0951%. In the addition of filler (10: 4), the highest modulus of elasticity was obtained at 11.4411 MPa.
4. In the biodegradability test, sample UB4TI02 with a value of 47.77% with the addition of titanium oxide filler is qualified to be used as a biodegradable plastic base material because it can be decomposed well with EM4 bacterial decomposers.

For further research related to the manufacture of bioplastics from tapioca waste with titanium oxide filler (TiO 2), the authors suggest the following:

1. We should pay attention to the mixing process between titanium oxide fillers and bioplastics from tapioca waste so that it is more evenly distributed, resulting in a good interface bond.
2. We should pay attention to the type of compound used as filler in future research.

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