The Effect Of The Ratio Of Jerbung Shrimp Waste Flour (Fenneropenaeus Merguiensis De Man) And Purple Yam Starch On The Characterics Of Bioplastics

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Abstract

This research aims to determine the effect of the ratio of jerbung shrimp waste flour and purple yam starch on the physical, mechanical and barrier properties of bioplastics. This research used a Completely Randomized Design (CRD) with treatment ratios of jerbung shrimp waste flour and purple yam starch consisting of 5 ratio treatments (0:5g, 0.5:4.5 g, 1:4 g, 1.5:3.5g and 2:3g) each treatment was repeated 3 times so that 15 experimental units were obtained. The test parameters included tensile strength, elongation, thickness, water resistance, *water vapor transmission rate* and biodegradation. The research results showed that the treatment ratio of jerbung shrimp waste flour and purple yam starch had a significant effect on tensile strength and thicknes, water resistance and *water vapor transmission rate*. However, it does not have a significant effect on elongation. The best bioplastic characteristics are found in the ratio of shrimp waste flour and starch (1:4 g) producing a tensile strength of 9.67 MPa, elongation of 132.38%, thickness 0.38 mm, water resistance 82.90%, *water vapor transmission rate* 20.65 g/m2.hour and this bioplastic degrades more easily than synthetic plastic.

Keywords: *Bioplastics; ratio; jerbung shrimp waste flour; purple yam starch*

1. Introduction

One of the factors that causes environmental damage is plastic waste which is widely used in everyday life. caused by several factors, including economical price, not easily damaged, durable, light and easy to obtain.

Bioplastic is an environmentally friendly plastic compared to plastic in general because it can be degraded naturally. One source of raw material for making bioplastics is starch from uwi tubers [1]. Purple yam has great potential to be developed as a film-making material, because of its high starch content of 86.12% [2]. However, starch is generally hydrophilic which can affect stability, is not heat resistant and has low bioplastic mechanical properties from the resulting starch and is unable to retain water and microorganisms. To correct the weaknesses of this starch-based bioplastic, it can be combined using materials that are strong and resistant to water and microorganisms.

One of the materials that can be added to improve the physical, mechanical and barrier properties of bioplastics is flour from shrimp waste. This is because shrimp waste flour contains 42.23% crude protein; crude fiber 19.87%; fat 2.89%; calcium 13.23%; phosphorus 2.08%; chitin content 9.56% [3]. Chitin and its derivative products can be used as raw materials for bioplastics [4]. Chitin is a compound that is stable against chemical reactions, non-toxic and biodegradable. Chitin is not soluble in water (it is hydrophobic) [5]. Chitosan is a protein modification of chitin found in shrimp shells and is good for forming into films and has antimicrobacterial properties [6] ; [7].

So that shrimp shell flour can be used as a bioplastic material, it is necessary to carry out a processing process that converts shrimp waste consisting of shrimp heads and shells into chitin and chitosan while retaining some of the proteins and minerals that can be useful in making bioplastics. This process includes treatment using a weak acid such as acetic acid and a strong base such as NaOH [8];[9]. The application of shrimp shell waste flour resulting from processing using acids and bases as stated above has never been done in the manufacture of bioplastic.

Based on this background, researchers will conduct research on "The Effect of the Ratio of Waste Flour of Jerbung Shrimp (Fenneropenaeus merguiensis de Man) and Purple yam starch on the Characteristics of Bioplastics". Where in this research variations were carried out in the ratio of the addition of jerbung shrimp waste flour and purple yam starch to the characteristics of bioplastics.

2. Research Methods

2.1 Material

The materials used in this research were jerbung shrimp waste, purple yam, NaCl, CaCl2, NaOH, Mg(NO3)2), CH3COOH, glycerol, distilled water, tissue and soil. The tools used in this research were an oven, analytical balance, screw micrometer, caliper, texture analyser and desiccator.

2.2 Implementasi of research

This research was carried out using a completely randomized design (CRD) with 5 different ratio treatments of jerbung shrimp waste flour and purple yam starch as listed in Table 1. Where this bioplastic was made into 2 layers. Each treatment was repeated 3 times to obtain 15 experimental units.

Table 1. Composition ratio of bioplastic waste shrimp starch and purple yam starch

Treatment	Jerbung shrimp shell flour (g)	Purple yam starch (g)	Glycerol (g)	CH_3COOH (g)	Aquadest (g)	Total (g)
P1	0	5	2	5	138	150
P2	0,5	4,5	2	5	138	150
P3	1	4	2	5	138	150
P4	1,5	3,5	2	5	138	150
P5	2	3	2	5	138	150

2.2.1 Making Shrimp Waste Flour

The shrimp shells used in this research were jerbung shrimp. The shrimp shells used are in good condition with the characteristics of not having a bad smell, having a hard texture and still fresh, then the shrimp shells are washed using running water with the aim of getting clean shrimp shells (no dirt). The cleaned shrimp shells were then homogenized and dried in the oven at 100°C for 5 hours. After the drying process is complete, the size reduction process is carried out using a blender until smooth and then sieved with a 60 mesh sieve. Next, the shrimp shell flour was weighed and soaked in a 10% acetic acid solution for 1 hour. Then filter and wash with distilled water until the pH is neutral. Next, put the material in an Erlenmeyer. Then 0.5 M NaOH solution was added and soaked while stirring at a temperature of 65°C for 2 hours with a hot plate. After the mixture has cooled, it is filtered and washed with distilled water until the pH is neutral. The soaked shrimp shells are dried in the oven at 100°C for approximately 4 hours. After the drying process is complete, it is then sieved with a 60 mesh sieve. The shrimp shell flour is then packaged in plastic and stored for further analysis.

2.2.2 Production of purple yam starch extraction

Purple yam cleaned, washed until clean, sliced 2 mm to 3 mm thick. The purple yam slices were then soaked in 15% table salt (NaCl) solution for 30 minutes and rinsed with water 3 times. The purple yam slices were ground in a blender with the addition of 1:2 water (uwi : water), then the pulp obtained was filtered using a 200 mesh sieve. The suspension obtained was deposited for 6 hours, then the sediment obtained was rinsed using water until a clear supernatant was obtained. The starch precipitate was dried in an oven at 50°C for 6 hours. The dried starch is sieved using a 60 mesh sieve, packaged in a closed container and stored in the refrigerator.

2.2.3 Making Bioplastics

Put shrimp waste flour that has been soaked using 5% acetic acid for 1 hour and purle yam starch into a beaker containing distilled water. The starch suspension is heated on a hot plate until it reaches a temperature of 80-85°C while continuing to stir. Then 2 g of glycerol was added from a total solution volume of 150 g. The starch solution was continuously heated at 80°C with stirring using a magnetic stirrer for 20 minutes. The homogenized film solution was then poured into a glass mold measuring 20 cm x 20 cm. Next, it is dried using an oven for 24 hours at a temperature of 50°C. Then the bioplastic is glued into 2 layers using a mixture of 1 tablespoon of starch and glycerol which has been heated until it thickens. Next, it is dried using an oven for 24 hours at a temperature of 50°C. Bioplastics were equilibrated in a desiccator with RH 52% using a saturated Mg(NO3)2) solution for 48 hours before analysis. The film sheets are then tested for their characteristics which include tensile strength, elongation, thickness, water absorption capacity, biodegradation and water vapor transmission rate.

2.3 *Research Parameter Analysis*

2.3.1 *Tensile Strength Test (Tensile Strength)*

The tensile strength test was carried out by cutting it to a size of 2 x 10 cm, then attaching it with a 1.5 cm clamp horizontally on both sides. Tensile strength is determined by looking at the maximum load when the bioplastic sheet breaks. To calculate it, use the following formula:

$$Ts = \frac{F_T}{W_T} \times 15 \qquad \text{pers. 1}$$

Description: Ts = *tensile force* (N/15 mm in width)
FT = *maximum force* (N)/gaya
WT = *width of test piece* (mm)

2.3.2 *Percent Elongation (elongation)*

The percent elongation test is carried out on calculating the length of the bioplastic sheet, when the bioplastic sheet breaks. The elongation percentage is calculated using the following equation:

$$\varepsilon = \frac{L-L_0}{L_0} \times 100 \qquad \text{pers. 2}$$

Description: ε = Tensile elongation at break (%)
L = Length after breaking (mm)
L_O = Length before breaking (mm)

2.3.3 *Water Resistance*

The plastic pieces measuring 2 x 2 cm were weighed initially (Wo), then put into a glass containing distilled water at room temperature. This piece of plastic was then taken after 20 minutes and the air on the surface of the plastic was removed with tissue paper after which the weighing was carried out (W). The absorbed air is calculated via the equation:

$$\text{Water absorption (\%)} = \frac{w-wo}{wo} x\ 100\% \qquad \text{pers. 3}$$

Description: W_0 = Initial weight of the sample
W =Weight of the sample after immersion

2.3.4 *Bioplastic Degradation*

Test bioplastic degradation by burying it in neutral pH soil, each sample specimen is cut into 2 x 2 sizes in the soil. The biodegradation rate in the soil was observed until it was completely decomposed

2.3.5 *Thickness*

Edible film thickness measurements were carried out using a screw micrometer with an accuracy of 0.01 mm. The thickness value obtained is the average position of measurements at 5 random points in mm.

2.3.6 *WVTR (Water Vapor Transmission Rate)*

The reaction tube containing 5 g calcium chloride was covered using film. The weight of the tube is then weighed. The tube is placed in a desiccator that is saturated using saturated sodium chloride (RH 75%). The change in tube weight is then recorded and plotted as a function of time. WVTR calculations can use the formula:

$$\text{WVTR} = \frac{\text{Slope}}{A} \qquad \text{pers. 4}$$

Description: WVTR = Water Vapor Transmission Rate Analysis g/m².hour
Slope = Linear function of weight gain and time (g/hour)
A = Film area (m²)

2.4 Data analysis

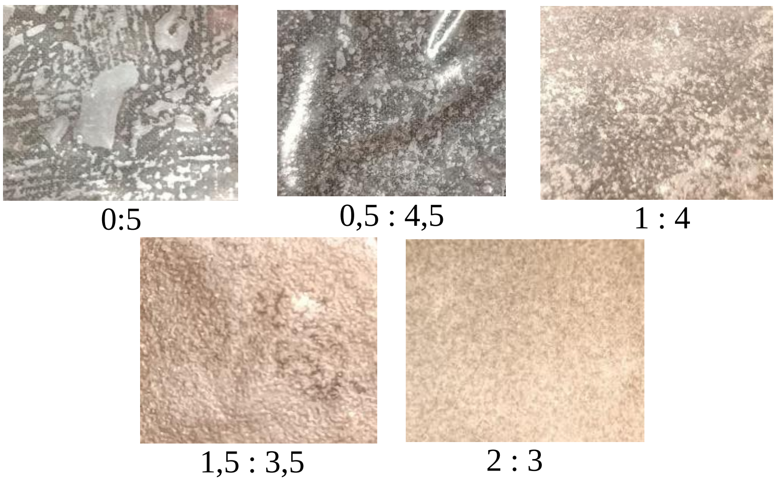
The data obtained were analyzed statistically using analysis of variance at the 1% and 5% levels. If the difference is significant then the Duncan's New Multiple Range Test (DMRT) will be continued at the 5% level. Biodegradation data is analyzed descriptively by displaying research data presented in the form of images.

3. Result and Discussion

3.1 Bioplastics

Bioplastics are environmentally friendly plastics compared to plastics in general, also called biodegradable, which can be degraded naturally in the environment. Bioplastics are thin sheets, elastic, transparent and slightly translucent.

Bioplastics of the ratio of jerbung shrimp waste flour and purple yam starch have shiny characteristics, smooth and slightly rough surfaces and there are still many bubbles. The greater the ratio of shrimp waste flour and starch added, the more brownish the color of the plastic and the less transparent it is. Bioplastics with added jerbung shrimp waste flour appear slightly thicker and stiffer. bioplastic characteristics are influenced by the type and color of raw materials in the manufacture of bioplastics. The following is a picture of bioplastic products with the ratio of jerbung shrimp waste flour and starch in Figure 1.



0:5 0,5 : 4,5 1 : 4

1,5 : 3,5 2 : 3

Figure 1. Bioplastics

The parameters resulting from the analysis of mechanical, physical and barrier characteristics of shrimp waste flour and starch bioplastics can be seen in Table 2 below:

Table 2. Results of the bioplastic ratio of jerbung shrimp waste and purpel yam starch

Ratio of jerbung shrimp waste flour: purple yam starch (g)	Tensil strength ($N/15\ mm^2$) ± SD	Elongation (%) ± SD	Thinckness (mm) ± SD	Water resisten (%) ± SD	WVTR (g/m^2.jam) ± SD
0 : 5	8,93 ± 2,55 ^{ab}	69,63 ± 1,64	0,33 ± 0,04 ^{a}	74,90 ± 8,04 ^{a}	38,60 ± 0,97 ^{c}
0,5 : 4,5	13,63 ± 2,60 ^{c}	134,72 ± 56,18	0,35 ± 0,04 ^{a}	75,15 ± 2,18 ^{a}	22,29 ± 1,75 ^{ab}
1 : 4	9,67 ± 0,44 ^{b}	132,38 ± 36,40	0,38 ±0,01 ^{a}	82,90 ±4,26 ^{ab}	20,65 ±0,79 ^{a}
1,5 : 3,5	9,12 ± 1,17 ^{b}	112,00 ± 3,89	0,40 ± 0,05 ^{a}	89,64 ± 9,21 ^{b}	19,98 ± 1,14 ^{a}
2 : 3	5,91 ± 1,38 ^{a}	108,03 ± 4,66	0,57 ± 0,07 ^{b}	87,55 ± 5,25 ^{ab}	24,77 ± 2,97 ^{b}

Notes: The numbers followed by the same lowercase letters are not significantly different at the 5% level according to the DNMRT test.

3.2 Tensile Strength

Tensile strength testing is the maximum force that bioplastics can withstand until it is cut off [10]. Tensile strength is one of the parameters that determine how strong bioplastics are to withstand loads. Tensile strength test to determine the strength of bioplastics in withstanding the load in protecting the product wrapped in bioplastics [11]. Mechanical properties are influenced by the amount of content of the plastic constituent components used in this study using shrimp waste flour and purple yam starch.

Based on the results of the analysis of variance showed that the ratio of shrimp waste flour and purple yam starch had a significant effect of 1% on the tensile strength of bioplastics in each treatment. Increasing the ratio of shrimp waste flour and purple yam starch decreased the tensile strength as shown in Table 2.

Based on Table 2. shows that the highest value of bioplastic tensile strength is found in the ratio of jerbung shrimp waste flour and purple yam starch (0.5: 4.5) which is 13.63 N/15 mm^2, while the lowest value of bioplastic tensile strength is found in the ratio of shrimp waste flour and purple yam starch (0: 5) which is 8.93 N/15 mm2.

The higher the ratio of shrimp waste flour, the less the amount of purple yam starch which results in a less compact film solution so that the resulting bioplastics are easily torn, and the resulting bioplastic surface is uneven so that the molecules are quite tenuous. The unfused mixture between the starch solution and shrimp waste flour results in uneven distribution of the molecules of the constituent components of bioplastics, so that the resulting material experiences a decrease in tensile strength [12].

The less fused solution is shown in the rough texture of the bioplastic surface and the uneven thickness of the bioplastic [13]. The main component of shrimp waste residue is chitin along with protein and calcium carbonate [14]. The results of this study are in line with research reported previously by [15] in a study using chitin which stated that increasing tensile strength using the addition of 1-4% chitin decreased the tensile strength from 6.7 to 6.3 MPa. The decrease in tensile strength value is related to the empty space that occurs due to the bond between glycerol polysaccharides. Thus causing the inter-molecular bonds in the plastic film to weaken. Based on Japanese industrial standard JIS Z 7127: 2019, where this bioplastic is included in class 5, which is below 25 N/15 mm^2.

3.3 Elongation

Elongation is the increase in length when the bioplastic film obtains the maximum force influenced by the tensile force until the disconnection occurs and is compared with the initial length [16]. The tensile strength test on bioplastics causes a change in the length increase in the sample called elongation.

Based on the results of the analysis of variance, it shows that the ratio of jerbung shrimp waste flour and purple yam starch has no significant effect of 5% on the elongation of bioplastics. Increasing the ratio of shrimp waste flour and purple yam starch decreased elongation as shown in Table 2.

Based on Table 2. shows that the elongation value is decreasing so statistically it has no significant effect. This is because the increase of shrimp waste resulted in a decrease in the bonding distance between molecules. This is due to the uneven distribution that minimizes the interaction between the matrix and filler. In addition, the presence of bubbles will form holes that result in easy tearing [17].

Elongation or strain is influenced by the amount of plasticizer used. This decrease is related to the empty space that occurs due to the bond between polysaccharides and flour, causing the bond between molecules in the plastic film to weaken, such as hydrophobic properties will gather with hydrophobic. Based on research conducted by [18] explained that the elongation of polymeric materials depends on the mobility of the polymer molecular chain. Glycerol films on various types of starch when added reinforcements the elongation value decreases [12]. Based on the Japanese industry standard JIS Z 7127: 2019, the elongation ratio of bioplastics of jerbung shrimp waste flour and purple yam starch is classified in class 4, namely 20-200 (%).

3.4 Thickness

Film thickness is an important characteristic in determining the quality of edible films produced as packaging for food products [19]. The thickness of the film will affect other film properties such as tensile strength, percent elongation, and gas permeability, the thicker the film will reduce the level of gas permeability and can protect the packaged product well [20]. The thickness value is influenced by the volume of the bioplastic solution and is influenced by the total amount of solids in the solution and mold [21]. Film thickness was measured using a screw micrometer with an accuracy of 0.01 mm and measured at five different and randomly selected places. The average of the five values was then reported as the film thickness result value.

Based on the results of the analysis of variance, the ratio of shrimp waste meal and purple yam starch had a significant effect of 1% on the thickness of bioplastics. Increasing the ratio of shrimp waste meal and purple yam starch increased the thickness as shown in Table 2.

Based on Table 2, it can be seen that the thickness value of bioplastics produced has increased by 0.33 to 0.57 mm. The higher the ratio of jerbung shrimp waste flour and purple yam starch increased the thickness of the film. This is in line with the research on films from starch that the greater the concentration of film constituents added will increase the thickness of the film [21]. Increasing the concentration of film matrix polymer constituents will increase the total soluble solids in the film solution, so that the film obtained will be larger. The addition of 2-3% chitin concentration can increase film thickness [11]. Thick films will be able to provide good protection to food products to be packaged. thick bioplastic films will also reduce the rate of water vapor transmission and elongation will decrease [22].

3.5 Water Resistance

The water resistance test is carried out to find out how much the material absorbs water. In bioplastics, it is expected that very little water is absorbed in the material or in other words, the absorption of the material to water must be low. This property is influenced by the components that make up the plastic film. The greater the water resistance value, the better the material will be used as packaging material [23].

Based on the results of the analysis of variance, it shows that the ratio of shrimp waste flour and purple yam starch has a significant effect of 5% on the water resistance of bioplastics. Increasing the ratio of shrimp waste flour and purple yam starch increased the water resistance as shown in Table 2.

Based on Table 11, it can be seen that the ratio of jerbung shrimp waste flour and purple yam starch has a significant effect on the water resistance of the bioplastics produced. The water resistance value of bioplastics increases with the increase of jerbung shrimp waste flour. Because the higher the component that is less soluble in water and if the amount is large, the more water resistance increases. This is because the shrimp waste flour used has a lower solubility of 3.64% [24].

The increased water resistance of bioplastics is because shrimp waste flour contains chitin which cannot dissolve in water. Chitin is insoluble in water because it is hydrophobic [5]. The results of this study are in line with research reported previously by [25] in research using chitin which states that increasing water resistance using the addition of 1-4% chitin increases water resistance.

This is in line with the research of [11] that the cause of chitin and starch bioplastics is resistant to water because no new crystallization peaks and groups appear on the chitin and cellulose composite, and there is no reaction between chitin and cellulose.

*3.6 Water Vapor Transmission Rate (*WVTR)

Water Vapor Transmission Rate (WVTR) or water vapor transmission rate is the most important parameter in assessing the quality of bioplastic films. Water Vapor Transmission Rate is the movement of water vapor in a certain unit of time through a unit area at humidity temperature. The water vapor transmission rate is strongly influenced by aw, RH, temperature, thickness, type and concentration of plasticizer, and film forming properties. The greater the WVTR value, the greater the rate of water vapor passing through the film.

Based on the results of the analysis of variance, it shows that the ratio of shrimp waste flour and purple yam starch has a very significant effect of 1% on the water vapor transmission rate of bioplastics. Increasing the ratio of shrimp waste flour and purple yam starch increases the WVTR value as shown in Table 2.

Based on Table 2, it can be seen that the value of water vapor transmission rate (WVTR) in bioplastics made from jerbung shrimp waste flour and purple yam starch has a value between 38.60 - 19.98 g/m^2.hour.

The WVTR value decreased due to the hydrophobic nature of shrimp waste meal. When glycerol is added, water molecules interact more strongly with the solid matrix and delay diffusion across the matrix [14]. This is in line with the research [11] which states that chitin bioplastics decrease as the concentration increases. The greater the concentration, the denser the chitin polymer network formed and the smaller the free volume, so the amount of water vapor and oxygen passing through the bioplastic per unit time also decreases [26].

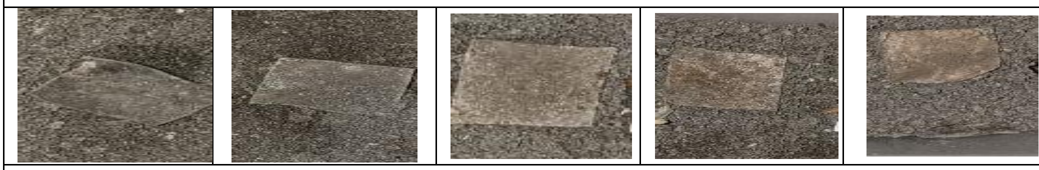
The presence of chitin in starch-based bioplastics will inhibit the attractive force between bioplastics and water so as to prevent the release of water vapor from the bioplastic film. The percentage of water vapor mass shows that the higher the chitin concentration, the lower the mass of water vapor that comes out through bioplastics [25]. In addition, chitin content inhibits hydrogen interactions between starch molecules and water vapor to form hygroscopic interactions [27] in [15]. According to research by [28], this addition shows a more visible impact than chitosan due to the higher number of acetyl groups in the chitin structure.

At high ratios of prawn waste meal, the amount of available starch is lower which results in a decrease in the viscosity of the starch solution. This affected the dispersion of the shrimp waste meal in the bioplastic film solution. It happens that hydrophobic properties converge with hydrophobic properties.

The decrease in water vapor transmission rate of edible film is inversely proportional to its thickness, where the lower water vapor transmission rate value has a higher thickness value because the thicker the edible film, the more difficult it is for water vapor to penetrate the edible film so that the water vapor transmission rate will be lower. This statement is in line with the research of [29] which states that the thickness of edible film can affect the water vapor transmission rate because it causes the water vapor transmission rate to be lower as the thickness of edible film increases.

3.7 Biodegradation

Biodegradation is the process of decomposing organic matter by microorganisms such as bacteria and fungi that live in the soil. According to [30], the biodegradation test is conducted to determine the time required for bioplastics to be degraded by microorganisms in the environment. Bioplastics are environmentally friendly plastics compared to plastics in general because they can be degraded naturally. In this study, the biodegradation test was carried out by calculating the time it takes for bioplastics to degrade in soil with a neutral pH. Bioplastic biodegradation can be seen in Figure 2

Ratio of jerbung shrimp waste flour: purple yam starch (g)				
0 : 5	**0,5 : 4,5**	**1 : 4**	**1,5 : 3,5**	**2 : 3**
				
Hari ke-7				
				
Hari ke-14				
				
Hari ke-21				
				
Hari ke-28				

Figur 2. Biodegradation Testing

Based on Figure 2. shows that the bioplastic ratio of shrimp waste flour and purple yam starch has not degraded completely for 28 days. The more the ratio of shrimp waste flour and starch decreases, the faster the bioplastics decompose. This is due [31]to the constituent material of bioplastics in the form of starch which has a bond structure of C-O ester and C=O carbonic functional groups which are hydrophilic which causes the binding of water molecules from the surrounding environment which makes it easier for bioplastics to degrade and also because bioplastics are made from natural materials so that they are easily degraded in nature with the help of microorganisms in the soil. This is because the higher the starch bond has hydrophilic properties that can absorb water making it easier for microorganisms to damage the matrix or starch [13].According to [32] in the degradation process of biodegradable plastic polymers includes stages, namely starting from the stage of attachment of microorganisms to the surface of polymers which are hydrophilic, then the growth stage of microorganisms using polymers as a carbon source, then the stage of degradation or enzymatic erosion of polymers with a hydrolysis process that produces carbon and energy, and finally mineralized into H2O and CO2.

Based on Figure 2, the higher the ratio of jerbung shrimp waste flour used, the longer the degradation time, in line with the highest water resistance value which indicates that the bioplastic is more hydrophobic. This is due to the hydrophobic nature of shrimp shell flour, so that the more shrimp shell flour added, the more water-resistant the bioplastic produced [33] This opinion is supported by [34] in their research concluded that the addition of higher chitosan concentration resulted in longer degradation time, because chitosan which is hydrophobic affects moisture and inhibits the rate of water absorption which is a requirement for the growth of bioplastic degrading microorganisms. However, this bioplastic of udan waste flour and starch degrades faster than synthetic plastics.

4. Conclusion

Based on the results of the research that has been carried out, it can be concluded that the ratio of shrimp waste flour and purple yam starch has a significant effect on tensile strength, thickness, water resistance, biodegradation and water vapor transmission rate. However, there is no significant difference in elongation. The best bioplastic characteristics are found in the ratio of shrimp waste flour and starch (1:4 g) which produces a tensile strength of 9.67 MPa, elongation of 132.38%, thickness of 0.38 mm, water resistance of 82.90%, WVTR of 20.65 g /m2.hour and this bioplastic is more easily degraded than synthetic plastic.

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