



The Performance and Characterization of Biodegradable Plastic From Tapioca Starch: Effect of Modified Chitosan

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Abstract

The performance and characterization of biodegradable plastic from tapioca starch were studied. This study is aimed at preparation and characterization of the biodegradable plastic by analyzing the effect of modified chitosan in a mixture of poly (NIPAM) and lemongrass oil. Biodegradable plastic was produced from tapioca starch as a new main replacement forming material under influence a mixture of chitosan-poly N-isopropyl acrylamide (NIPAM)-lemongrass oil and glycerol as plasticizer. The produced biodegradable plastics were thin sheet plastic, elastic and transparent. The biodegradable plastic performance had tensile strength between 2,26-3.73 MPa, elongation ranges from 17.24 to 76.76%, and water absorption ranges from 30.81-268.9%. In the organoleptic test, apples were wrapped in plastic and had significant mechanical properties change on the 8th day. Morphology scanning result showed that within the chitosan-poly(NIPAM) there were no cavities may be caused high hydrophilicity in the biodegradable plastic.

Keywords: biodegradable plastic, tapioca starch, poly(NIPAM), chitosan.

1. Introduction

Plastic is the biggest waste in the world. It is due to the nature of the plastic which is strong, not easily broken, heat-resistant, light, inexpensive and stable so that it is widely used daily (Coniwanti et al., 2014). Every year the use of plastic as a packaging material more increasing. Unfortunately, the public awareness of managing plastic waste is still very low so may cause very serious problems (Kumoro et al., 2014). The complex structure of plastic molecules makes it very difficult to degrade so that it will accumulate and directly cause problems and damage to the environment. A solution to overcome the problem is to make plastics that can decompose naturally (biodegradable plastics) can match the quality and properties of commercial plastics. The decomposition of biodegradable plastic will produce carbon dioxide, methane, water, biomass, humic material and various other natural substances that are easily removed (Gill, 2014).

In general, biodegradable plastic can be interpreted as plastic that can be recycled and degraded naturally. Conventional plastic is formed from petroleum, coal and gas. While biodegradable plastic is made up of natural polymers like cellulose (starch), collagen, casein, protein or lipids (Leejarkpai

et al., 2011). Biodegradable plastic is a material under certain conditions, changes in their chemical structure within a particular time, which affects the properties it has by the influence of microorganisms such as bacteria, fungi, algae (Fachry et al., 2012).

Starch is the main ingredient for producing biodegradable plastics. Starch has biodegradable properties, a simple process, and cheap. Starch is produced from materials such as cassava, bananas, corn, and potatoes which has abundant availability in Indonesia (Lazuardi et al., 2013). Starch doesn't dissolve in cold water, alcohol in esters, but can expand and form a paste in hot water. The temperature of tapioca starch gelatinization was 59 °C-69 °C (Safwani, 2015). The principle of the formation of biodegradable plastics is the interaction of polymer chains to supply larger and stable polymer aggregates (Safitri, 2016). Biodegradable plastics from only starch will produce hydrophobic plastics where the resistance to water is extremely low. Therefore we need other materials to improve the durability and flexibility of plastics such as plasticizers and other additives (Kaisangsri et al., 2012).

The plasticizer is defined as a nonvolatile material with low molecular weight, and has a high boiling point so that if added to other

materials can change the material's properties (Jaramillo et al, 2016). The addition of plasticizer can reduce intermolecular strength and increase film flexibility and decrease film barrier properties. The plasticizer can increase elasticity by reducing the degree of hydrogen bonding and increasing the distance between molecules of the polymer. The more use of plasticizer will increase its solubility (Makhtar et al., 2013).

Chitosan acts as a preservative for biodegradable plastics. Its properties are waterproof, very non-toxic and anti-bacterial so that it can function as a preservative and antimicrobial. Chitosan is a natural substance used as an amplifier. It can also reduce plastic moisture because it is not soluble in water. This material is a macromolecule that can be found in crab shells, shrimp, and insects. Chitosan is chosen as an alternative to making plastic environmentally friendly plastics as have good biodegradation properties (Ginting , 2016). The addition of chitosan to the starch mixture enhances mechanical properties because the addition can form hydrogen bonds between chains with amylose and amylopectin in starch. Chitosan has amine groups, primary and secondary hydroxyl groups. The presence of these groups results in chitosan having a high chemical reactivity because it can form hydrogen bonds which make chitosan the ideal choice for mixing (Safitri, 2016)

N-isopropylacrylamide (NIPAM) is an organic compound that can be synthesized into a biodegradable polymer or crosslinking polymer. NIPAM is one of the acrylamide monomers which has white colour, odorless, solid crystals shaped so that easily soluble in water and react in amide reactions or their double bonds (Syaubari , 2018) . These compounds can produce long polymer chains which called poly (N-isopropylacrylamide) or poly(NIPAM). NIPAM monomers are synthesized into poly(NIPAM) by utilizing reactive groups directly for grafting with other polymers or conjugating with ligands. The selection of polymers for grafting is influenced by two factors namely specific material and reversible affinity parts for purified parts and polymers having chemical groups that can be modified to move the matrix without damaging the binding affinity (Safitri, 2016).

The applications of Poly(NIPAM) have been widely carried out in various fields, for example as electrophoretic membranes,

biomedical membranes, flocculants for the separation of solids and liquids in the treatment of liquid waste, microspheres synthesis as drug conductors, thickeners, or to form other compounds. However, the use of poly(NIPAM) still has characteristics that are still not good, so many studies conduct to improve it, one of which is by crosslinking with other monomers (Safitri , 2016).

Many research that has been studied to produce the biodegradable plastic packaging but still very limited. It is due to the limited research technology. This research was conducted to study the effect of chitosan modification with other ingredients in the performance and characterization of the resulted biodegradable plastic.

2. Materials and Methods

2.1. Materials

Materials used for this study were tapioca starch (Liauw Liaong Pit Tapioca Flour No.1 Tjap Orang Tani, Bogor-Indonesia), glycerol (Merck), chitosan (Chemical Industry Co. Ltd), lemongrass oil pure were purchased from distributor in Bandung, acetic acid glacial (Merck), ethanol (Merck-Ethanol absolute for analysis, EMSURE), NIPAM monomers, aquades, azobisisobutyronitril (AIBN) initiator and mercaptopropionic acid (MPA) initiator were purchased from Aldrich-Chemie Germany. All other reagents used were of analytical grade

2.2. NIPAM synthesis

NIPAM polymerization was carried out by dissolving 10 grams of NIPAM into 20 ml of ethanol in an erlenmeyer. Then AIBN and MPA was added as much as 1 ml and 0,6 ml, respectively then stirred until dissolved. The mixture was incubated at 60 °C for 20 hours. Precipitate products can be taken by entering diethyl ether solution. The precipitate obtained was dried in the oven for 12 hours at 80 °C.

2.3. Biodegradable Plastic Producing

Ten grams of tapioca starch was dissolved with 50 ml of distilled water in a beaker and stirred for 25 minutes. After homogeneous, the starch solution was placed in a hot plate. Stirring were used to prevent lumps forming on the starch during heating and to help heat distribution. The starch was heated to temperature at 70 °C for 20 minutes. Furthermore, glycerol plasticizer was added, a mixture of chitosan-poly(NIPAM) and

lemongrass oil into a starch solution. At the time of the addition of glycerol, a mixture of poly (NIPAM)-chitosan and lemongrass oil, the starch solution must continue to be stirred for 15 minutes to avoid lumps and accelerate the homogenization of the mixing between starch and glycerol, chitosan and lemongrass oil. After the mixture thickens, the beaker was removed from the hot plate. The solution must be stirred until the normal temperature around 25-30 °C for 30 minutes so that the thickness was maintained.

After the temperature of the starch solution was normal, casting on a glass plate with a thickness of 1 mm that has been given adhesive on the edge was done. The purpose of the adhesive is to keep the solution from spilling over the edge of the plate. The pouring of starch solution must be done slowly. The thin layer formed on a glass plate is put into an oven at 80 °C and allowed to stand for 4 hours to harden and dry. Thin sheet is removed from the glass plate, then stored in a desiccator for 1 day in a place that was not in direct sunlight.

2.4 Biodegradable Plastic Analysis and Characterization

Water absorption analysis was conducted in term of water resistance when the plastic contacted directly with water. A good plastic is plastic that is as little as possible soluble in water. Percent of water absorption was calculated by the equation (Cobb's method):

$$S (\%) = \left(\frac{m_1 - m_2}{m_1} \right) \times 100$$

Where :

S : swelling

m₁ : weight dried plastic

m₂ : weight plastic after soaking

The resistance of plastics to water was tested to determine the level or regularity of bonds in the polymer by adding the weight of the plastic after undergoing the swelling process.

The biodegradable plastic was tested for tensile strength and elongation to find out how strong the plastic can be maintained intact when given a load (Juandi, 2016). The test was done by means of the tip of the sample clamped on a tensile strength testing machine. Tensile strength test is carried out using MesdanLab strength tipe Tensolab 5000 designed and made in Italy. The sample is cut according to ASTM-D638 size

as shown in figure 1. Testing is done by clamping the tip of the sample on tensile testing machine.

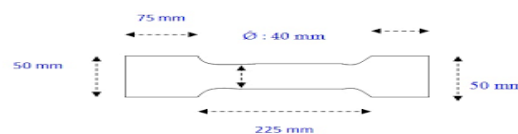


Figure 1. Grip used to test tensile strength

Infrared spectrum analysis (Fourier Transform Infrared spectroscopy, FTIR – Shimadzu, Kyoto, Japan) was performed to determine the mixing mechanism that occurs by identifying functional groups contained in each stage of biodegradable plastic mixing so that new functional groups can be seen or not from the mixture when compared with specific functional groups of each component forming biodegradable plastic. The sample is placed into the holder of the set, then the appropriate spectrum is sought. The result will be obtained diffractogram relationship between wave numbers with intensity. The FTIR spectrum was recorded using a spectrophotometer at room temperature.

The morphology of biodegradable plastic was analyzed with scanning electron microscopy (SEM JSM-6510 A/JSM 6510 LA). Sample is affixed to the set holder with double adhesive, then coated with gold metal under vacuum. Sample is put into SEM, then the topographic image is observed at magnification 1000 times.

Biodegradability test is carried out to find out how long it takes for plastic to decompose in the soil with the help of microorganisms. Plastic with size of 5 cm x 5 cm is planted in a poly bag containing organic soil. Changes in biodegradable plastic that occur are observed using visual observations once every 7 days.

Organoleptic test is a way to measure, assess or test the quality of commodities by using the sensitivity of the human senses (eyes, nose, mouth and tip fingers). Organoleptic tests are also called subjective measurements because they are based on human subjective responses as a measuring tool. The type of organoleptic test used is discriminative test.

3. Results and Discussion

3.1. Scanning Electron Microscopy

Fig. 1 shows the SEM cross-sectional test results on biodegradable plastic with the

addition of chitosan. Based on fig. 1A, the picture showed white spots which are less homogeneous granules with a mixture of other ingredients. One of them was starch which is not completely dissolved or the rest of chitosan that is insoluble when mixing.

Fig. 1B is a cross section biodegradable plastic with the addition of chitosan-NIPAM. There are many cracks on the plastic surface. Cracks formed produce cavities that can absorb water. This causes the hydrophilicity of the plastic to be high.

A cross sectional of plastic with the addition of chitosan -poly(NIPAM) shown in Fig. 1C. It can be seen no cracks in the plastic. Air bubbles were formed which were thought to have been caused by an imperfect emulsion process between lemongrass oil and water.

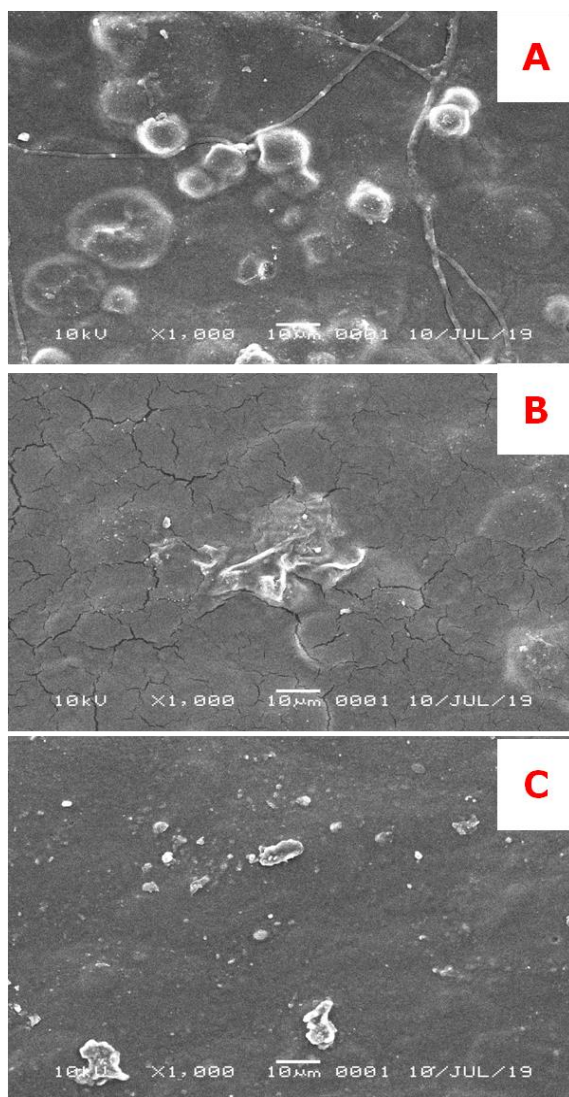


Figure 2. SEM of biodegradable plastic with (A) chitosan, (B) chitosan-NIPAM, (C) chitosan-PolyNIPAM.

3.2. FTIR spectroscopy

The biodegradable plastic FTIR spectrum with various plastic forming components were shown in Figure 2.

From the spectra of all components, there was a very wide stretch of hydroxyl group (-OH) at wave number 3330-3500 cm^{-1} which indicates the characteristics of the organic compounds that make up the biodegradable plastic structure. The emergence of single and double nitrile amine (CN) vibrations at wave numbers 1180-1360 cm^{-1} and 2100-2140 cm^{-1} was seen as a typical spectrum indicating the presence of chitosan as a constituent component of biodegradable plastic.

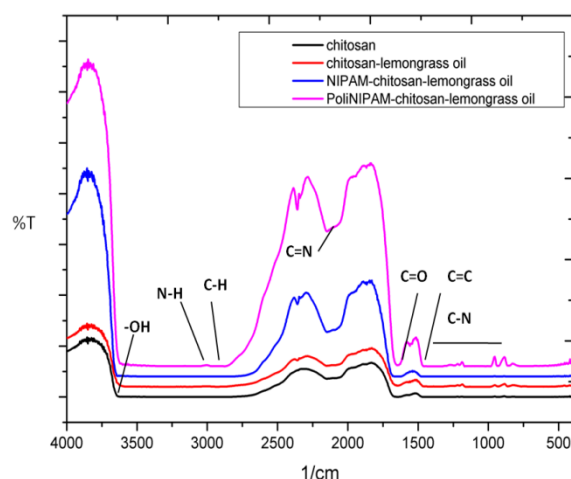


Figure 3. Fourier Transform Infrared Spectra of chitosan, chitosan-lemongrass oil, chitosan-NIPAM -lemongrass oil and chitosan-poly(NIPAM)-lemongrass oil.

The occurrence of stretching of amine / amide (NH) groups overlapping with hydroxyl groups (-OH) at wave number 3310-3500 cm^{-1} occurs in component chitosan-NIPAM-lemongrass oil and chitosan-poly(NIPAM)-lemongrass oil which indicates the entry of a new groups which is typical of the presence of NIPAM. The NIPAM polymerization process is characterized by a slight increase in the intensity of absorption in the alkene group (C=C) i.e at wave number 1554 to 1558 cm^{-1} and the reduction in absorption of the C=O group at about 1650 cm^{-1} . The differences overall between the spectra were not very significant. It showed that the plastic formed was the result of physical mixing so as not to cause the emergence of new groups.

3.3. Tensile Strength and Elongation

Tensile strength values are obtained from the distribution of maximum stress with cross-sectional area of plastic samples. Elongation is the percentage change in the length of the plastic when it is stretched out

Based on Fig.3, it can be seen that the plastic becomes stronger with increasing chitosan concentration. It was due to the more chitosan composition (Coniwanti et.al., 2014), the higher the number of hydrogen bonds contained in the plastic so that the number of chemical bonds becomes stronger and requires strong energy to break. The highest tensile strength value was 3,73 MPa which occurred in biodegradable plastic composition by Poly(NIPAM) with 0,55 % w/w of chitosan.

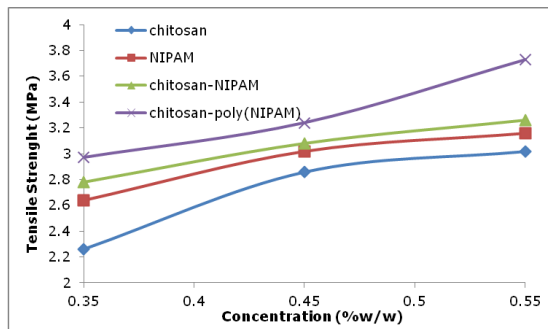


Figure 4. Effect of chitosan concentration (%w/w) to tensile strength of biodegradable plastic in various modified chitosan

It was due the poly(NIPAM) has a straight chain polymer that may binding to the chitosan starch polymer matrix. This bond increasing the tensile strength of biodegradable plastic (Coniwanti et.al., 2014). The lowest tensile strength value was the addition of chitosan as much as 0.35 % w/w which was 2.26 MPa.

The effect of chitosan concentration to elongation was shown in Fig.4. The elongation was getting smaller with increasing concentration of chitosan. According to Sanjaya dan Puspita (2011), it was caused by the smaller bonding distance between molecules so that the plastic becomes stiff and less elastic so that it makes the plastic more easily broken. The greater composition of chitosan caused by the higher number of matrices formed so that the plastic becomes stronger.

The highest plastic elongation value was in the addition of chitosan 0.35% w/w, which was 76.76%. The lowest elongation value was the addition of chitosan as much as

0.55% w/w which was 17.24%. It was because the addition of chitosan decreases intermolecular forces between chains, causing limited chain motion and directly decreases plastic flexibility. The reduced plastic flexibility results in the plastic being rigid and fragile.

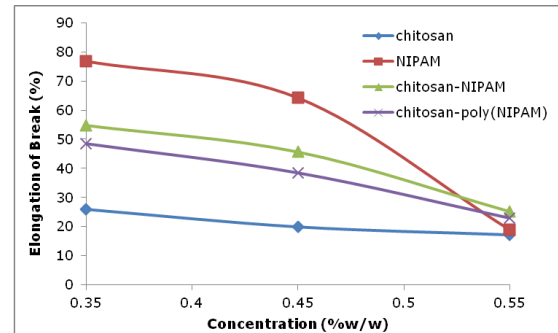


Figure 5. Effect of chitosan concentration (% w/w) to elongation of biodegradable plastic in various modified chitosan

3.4. Water Absorption

The nature of the plastic's resistance to water was done using the water absorption method where the plastic will be left immersed in water so as to reach a constant weight. Water absorption percentage in plastics can be seen in Fig. 5.

Based on Fig. 5, it can be seen that plastic with the addition of chitosan-poly(NIPAM) at 0.55 % w/w had the highest water absorption value of 268.9%. This is due to the large number of hydrophilic groups capable of binding to water in the polymer chain. Safwani et.al., (2014) concluded that the presence of this hydrophilic group causes water to diffuse into the polymer. After reaching equilibrium, the absorbed water will be bound to the carbonyl group and form hydrogen bonds and eventually the water will remain retained so that the plastic expands.

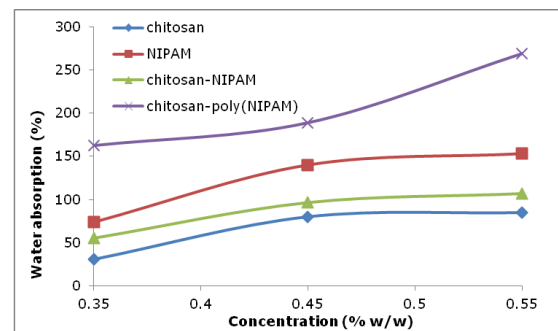


Figure 6. Effect of chitosan concentration to water absorption of biodegradable plastic in various modified chitosan

Plastic with the addition of NIPAM has a higher water absorption percentage value than chitosan. This is caused by NIPAM which contains monomer that's very soluble in water until the water absorption ability is more unlimited where it will absorb as much water before it dissolves into water (Safitri, 2016). In figure 5 can be seen adding as much as 0.35% w/w chitosan produce lowest water absorption value of 30.81%.

3.5. Organoleptic test

Organoleptic tests are called subjective measurements because they are based on human subjective responses as a measurement tool (Juandi et. Al., 2016). Organoleptic testing was done by wrapping apples in plastic. Apples were chosen as testing material because of the nature of apples that are rapidly undergoing changes during storage.

When Organoleptic testing, the browning reaction process for apples is observed every 2 days for 8 days. Organoleptic testing was carried out with each plastic sample and


























compared with commercial plastic and without plastic wrap as control.

Organoleptic test results on the brightness of the apple slices can be seen in Table 1. On the first day, all apple slices show the same brightness. On the 2nd day to the 8th day, the apple slices had a different color change in each sample. Browning process of apple slices is faster in chitosan-NIPAM and chitosan-poly (NIPAM) plastic samples compared to chitosan plastic samples. The higher chitosan content causes apple slices to change color longer because of the antimicrobial properties of chitosan.

3.6. Biodegradability test

The test was carried out to determine and determine when biodegradable plastics break down in the soil (Marfu'ah, 2015). The time needed for plastics will be longer for plastics that contain chitosan-poly(NIPAM) components. It was because the material contains preservative properties that will slow down the activity of bacteria in the soil to break down plastic.

Table 1. Organoleptic test on apple slices

Samples	Observation Time (Day)				
	0	2	4	6	8
Biodegradable plastic with chitosan					
Biodegradable plastic with chitosan - NIPAM					
Biodegradable plastic with chitosan - poly(NIPAM)					
Commercial plastic					
Without plastic					

The biodegradability test is carried out by adding biodegradable plastic into the soil and observed the changes that occur in plastic every 7 days.



Figure 7. Biodegradable plastic decomposes in soil (a) 0 day (b) 28 days (c) 35 days (d) 54 days

Figure 6 was the results of the process of decomposing a sample which requires the longest decomposition time, namely plastic samples in run 2 containing 0,55% w/w chitosan-poly(NIPAM). From the picture it can be seen that plastic begins to break down or begins to break down on 14 days and the plastic begins to tear and was divided into several parts on 28 days. On 35 days the plastic began to tear because of the loss of mass from the plastic and on day 54 the plastic was destroyed.

According to international standards, the duration of degradable plastic for PLA plastics from Japan and PCL plastics from the UK requires about 60 days to decompose as a whole (Coniwanti et al., 2014). In this study, the time for degraded plastic was 54 days and this met the biodegradable plastic degradation criteria.

4. Conclusions

Based on the results of the study it can be concluded that the addition of chitosan-poly(NIPAM) in biodegradable plastic synthesis significantly increases mechanical properties. Plastic with the addition of chitosan-poly(NIPAM) still absorbs more water than plastic with the addition of chitosan. Performance of plastic are best obtained on the addition 0.35 % w/w of

chitosan-Poly(NIPAM) with a tensile strength of 2.97 MPa , elongation at 48.44% and the value of water absorption is 162.3%. biodegradable plastic degradation criteria meet the international standard criteria, which is 54 days in the soil.

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