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Synthesis of biodegradable plastic from tapioca with N-Isopropylacrylamid and chitosan using glycerol as plasticizer

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Abstract. One of natural polymers that can be used as raw material in the manufacture of biodegradable plastic is tapioca and chitosan. The addition of other compounds such as glycerol as plasticizer is to improve the characteristics of the plastic that already produced. N-Isopropylacrylamid (NIPAm) is an organic compound that can be synthesized into a polymer or polymer grafting which also biodegradable too. This research aims to study the synthesis of biodegradable plastics from tapioca with the addition of chitosan, NIPAm, poly(NIPAm) and analyze the characteristics of biodegradable plastics that already produced. This research was done in three stages, there are (1) polymerization NIPAm, (2) the grafting of chitosan-poly NIPAm and (3) the synthesis of biodegradable plastics from starch mixture with variation of addition chitosan, NIPAm, poly(NIPAm), chitosan-graft-poly(NIPAm) and also variations of glycerol as plasticizer. The results of this research is a thin sheet of plastic which is will get analyzed for the characteristics of functional groups, mechanical, morphological and its biodegradability. FTIR spectra showed the grafting process with the new group formation of CO single-bond at 850 cm^{-1} . Plastic with the addition of NIPAm and 1 ml glycerol has the highest tensile strength value about 31.1 MPa. Plastic with poly(NIPAm) and 4 ml glycerol produces the highest elongation value about 153.72%. Plastic with Chitosan-graft-poly(NIPAm) with 1 ml glycerol has the longest biodegradation because of the small mass-loss for six weeks which is about 6.6%.

1. Introduction

The using of plastics as food packaging has increased along with the increase of population and human needs. This is because plastic has many advantages. Some plastic advantages are include having good mechanical properties, a good barrier against water and air, cheaper price, light weight material compared to the other materials, sheet-formed so that it can be made into bags, and the ease of the process and its application. However, plastic also has a disadvantage because it is hard to degradable in a long term, so it will cause environmental pollution and environmental damage. Therefore, it needs a package that can be degradable naturally by microorganism or biodegradable. Some natural biopolymer which could be synthesized into a plastic sheet are starch, protein, cellulose, chitosan, etc.

Tapioca is a cassava starch which has been widely used as raw material of biodegradable plastic and showed a promising result [1]. To improve the characteristic of biodegradable plastic needed some other materials such as plasticizers. Plasticizers is an organic material which has a low molecular weight which



is added to weaken the inflexible character of the polymer, increased the flexible and extensibility of the polymer. Plasticizer is dissolved in each polymer chains so it will facilitate the polymer molecule movements and makes the glass transition temperature lower, crystallized temperature or melting temperature from polymer. The purposed of the addition of plasticizer is to produce a film that is more flexible and not brittle [2].

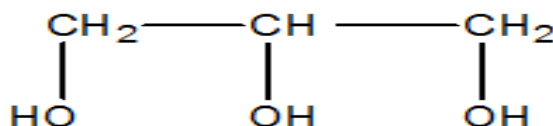


Figure 1. Structure of the glycerol molecule.

N-Isopropylacrylamid (NIPAm) is one of acrylamide's monomer which is white, odorless, crystalline solid that is highly soluble in water and easily to react through amide reaction or double bond. These compounds can form long polymer chains are called poly(N-isopropylacrylamid) or poly(NIPAm). Poly(NIPAm) is a thermosensitive material that can form a hydrogel. Applications poly(NIPAm) has been widely applied in various fields, such as in wastewater treatment, thickeners, papermaking, iron ore processing or to form other compounds. The main weakness of hydrogel homopolymerpoly (NIPAm) is having a relatively low mechanical properties and fragile, so the development of applications is limited [3]. Considering that the last few years of intensive research is being done to modify poly(NIPAm) [4]. McDowall et al. (1984) suggested that chemical modification through graft copolymerization (grafting) with various synthetic monomers are known to improve the properties such as the ability to absorb water, elasticity, ion exchange capability, thermal resistance, and resistance to microbial attack.

The purpose of this research is to study the synthesis of biodegradable plastics from the main raw material starch and chitosan were added to the treatment variations of NIPAm, poly(NIPAm) and grafting of chitosan-poly(NIPAm) using glycerol as a plasticizer and see its effect on the functional groups are formed, mechanical properties, morphology, and biodegradability of plastic produced.

2. Materials and methods

The materials that is needed in this study are tapioca, chitosan, 2% acetic acid, glycerol, ethanol, monomer NIPAm, NaOH, azobisisobutyronitrile initiator (AIBN), mercaptopropionic acid initiator (MPA), N activator, N-Dicyclohexylcarbomide (DCC) and distilled water.

2.1 Nipam polymerization into poly (Nipam)

Polymerization NIPAm made by dissolving 10 grams NIPAm in 20 ml of water. Then added 0.1 grams of AIBN and 10 ml of MPA and stir until dissolved. The mixture precipitated in ethanol at 60 °C for 20 hours. The precipitate obtained was dried in an oven for 12 hours at a temperature of 80 °C.

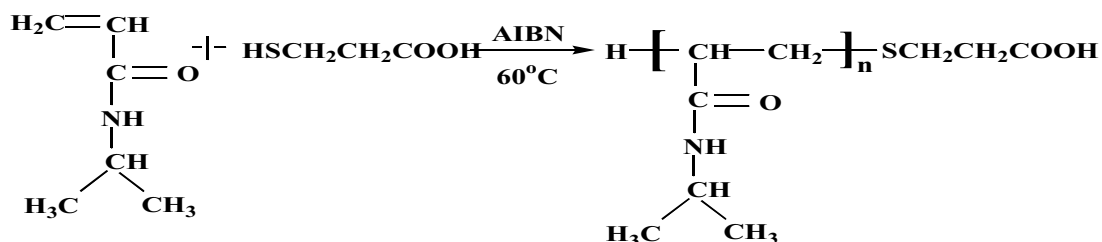


Figure 2. The polymerization reactions NIPAm into poly(NIPAm).

2.2 Grafting Chitosan and Poly (NIPAm)

Synthesis grafting of poly(NIPAm) with chitosan to form khitosan- graft- poly(NIPAm) by mixing a solution of chitosan and poly solution (NIPAm) was then added NaOH to pH 6.5. After that DCC was added step by step for 24 hours. Then the solution is precipitated in ethanol for 24 hours, then filtered the sediment. The precipitate that formed was washed with Tris HCl and distilled water and then dried at 80 °C for 5 hours.

2.3 Synthesis of biodegradable plastic

Synthesis of biodegradable plastics made by blending method that is mean to mix the material with variation 1) tapioca and chitosan, 2) tapioca, chitosan and NIPAm, 3) tapioca, chitosan and poly (NIPAm) and 4) tapioca and chitosan- graft- poly(NIPAm). The mixture was heated with stirring using hot plate and magnetic stirrer until form a paste (gelatinization) on temperature 70 ° C. Then each solution of starch paste is added at a concentration of glycerol as plasticizer 1ml;2 ml;3 ml and 4 ml. After that, the casting procedure in hot conditions with pouring material on the surface of polyethylene evenly and dried at room temperature for 24 hours.

Table 1. Study design synthesis of biodegradable plastics from tapioca and variations NIPAm treatment with the addition of glycerol as plasticizer

Treatment variation of NIPAm on plastic material (A)	Gliserol (B)			
	1 ml	2 ml	3 ml	4 ml
1. Tapioca+ chitosan	A1B1	A1B2	A1B3	A1B4
2. Tapioca + chitosan + NIPAm	A2B1	A2B2	A2B3	A2B4
3. Tapioca + chitosan + polyNIPAm	A3B1	A3B2	A3B3	A3B4
4. Tapioca+ chitosan-graft- polyNIPAm	A4B1	A4B2	A4B3	A4B4

2.4 Analysis of materials

The biodegradable plastic that was formed will be to be analyzed to identify the compound that contained in that plastic using a Fourier Transform Infra-Red (FTIR) brand Shimadzu in Instrument Analysis Laboratory, Department of Chemical Engineering Unsyiah and analysis of mechanical properties such as tensile strength and elongation using autograph shimadzu based on ASTM D638 in Instrumentation Laboratory, Department of Physics Unsyiah. Morphological analysis was conducted to study the surface structure of biodegradable plastics using Scanning Electron Microscope (SEM) in the Corrosion Laboratory, Department of Mechanical Engineering Unsyiah. Biodegradability analysis quantitatively by measuring the percentage of plastic weight loss after six weeks.

3. Results and discussion

3.1 Characteristics of functional groups

FTIR spectra at all biodegradable plastics showed an absorption in the range 3500-3300 cm^{-1} with the presence of -NH on chitosan which is reinforced by -OH groups and C-H on tapioca. The addition of NIPAm will presence the absorption of C = O at 1760 cm^{-1} and C = C at 1690 cm^{-1} . The presence of polymerization NIPAm into poly (NIPAm) is shown with the release of the C = C group into clusters C-C on absorption area at 1000-500 cm^{-1} . For the presence of characteristics of grafting is shown by the functional absorption of new single bond of C-O in the region 1000-750 cm^{-1} (Figure 3).

Table 2. Analysis of functional groups for biodegradable plastics from tapioca with treatment variations NIPAm and glycerol as plasticizer

Composition of plastic material	Functional group	Spectrum number (cm^{-1})	Compounds
1. Tapioca+chitosan	N-H C-H O-H	3500 2850 3600	Chitosan Tapioca Tapioca
2. Tapioca+chitosan+NIPAm	N-H C-H O-H C=O C=C	3500 2850 3600 1760 1690	Chitosan Tapioca Tapioca NIPAm NIPAm
3. Tapioca+chitosan+poly(NIPAm)	N-H C-H O-H C=O C-C	3500 2850 3600 1760 1200	Chitosan Tapioca Tapioca NIPAm Poly(NIPAm)
4. Tapioca+chitosan-graft-poly(NIPAm)	N-H C-H O-H C=O C-C C-O	3500 2850 3600 1760 1200 850	Chitosan Tapioca Tapioca NIPAm Poly(NIPAm) Grafting chitosan-NIPAm

The amount of yield that was formed during the grafting process is influenced by a variety of variables including monomer concentration, activator concentration, reaction time and reaction temperature [5]. In this grafting process, the yield of chitosan- graft -poly (NIPAm) was obtained for 12.76%.

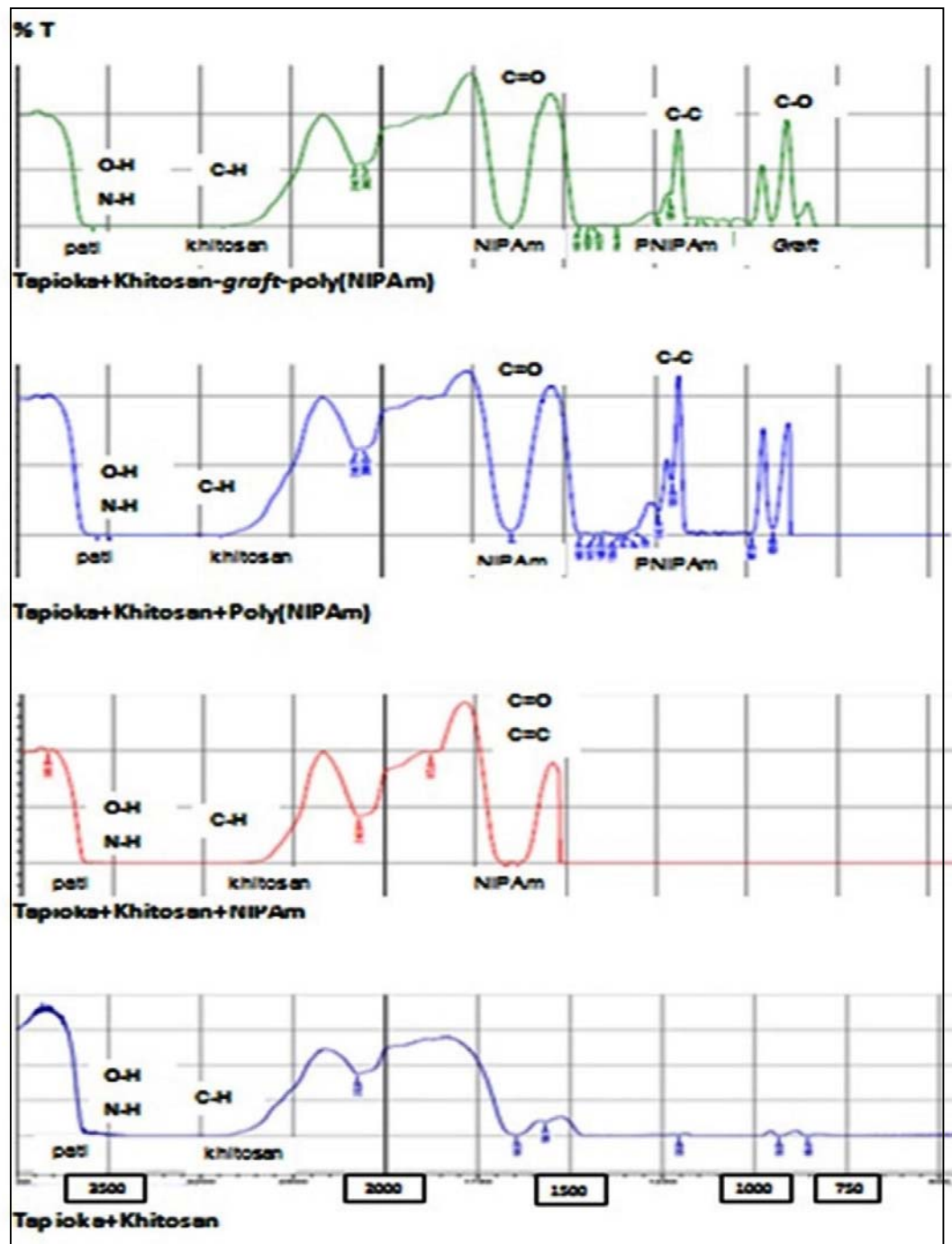


Figure 3. FTIR PB spectra with treatment variations of PNIPAm and the addition of glycerol as plasticizer.

Grafting occurs through the hydroxyl group at C6. Hydroxyl groups at C2 and C3 are hydroxyl groups attached to the secondary carbon atom, for the hydroxyl group at C6 are attached to the primary carbon

atom. Reactivity and acidity of primary and secondary hydroxyl group is different. Besides, the modified polysaccharide can produce macromolecular structured products such as gel or hydrogel, polymer resins, membranes or composite materials that can be applied as a separator material in separation technology [6].

3.2 Mechanical characteristics

Tensile strength is the maximum tensile force that can be held by the film during the measurement takes place. And then the elongation percent is a change in the maximum length of the film before it is broken.

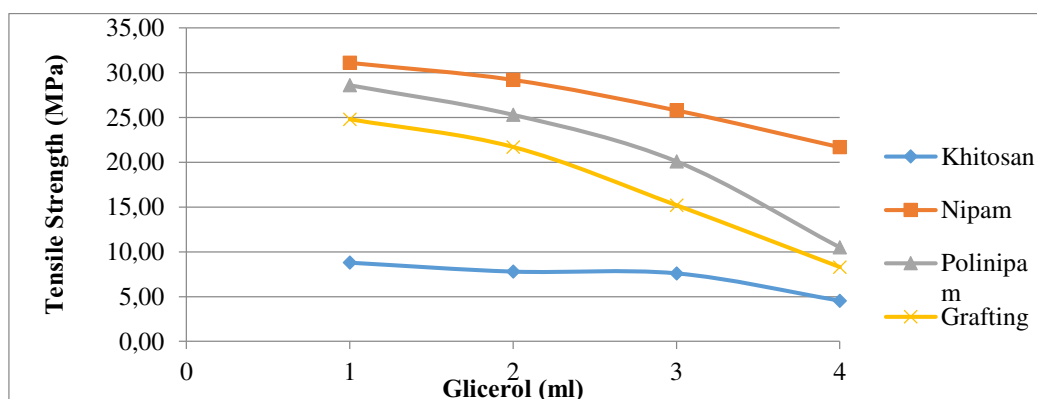


Figure 4. The effect of glycerol concentration and treatment variations NIPAm against tensile strength.

Figure 4 shows the effect of glycerol concentration and the addition of NIPAm treatment variations against the biodegradable plastic tensile strength value. In the picture, we can note that the higher the concentration of glycerol, the value of the tensile strength decreased. However, the higher concentration of glycerol will provide an increasing elongation values as shown in Figure 5.

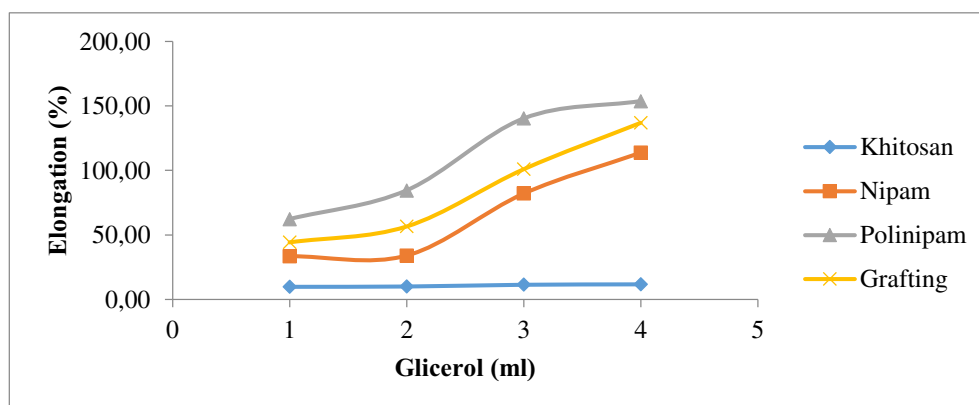


Figure 5. The effect of glycerol concentration and treatment variations NIPAm against elongation.

Research by using chitosan with low molecular weight which is dissolved in 1% acetic acid at a concentration of 3% by weight of chitosan / volume of solution, found that the more the concentration of glycerol were added to the chitosan solution will produce the film with the smaller tensile strength [7].

The addition of plasticizer in the polymer solution will form hydrogen bonds between molecules that cause the interaction between polymer molecules become less so facilitate the movement of polymer molecules. This is case that leads reduced tensile strength of plastic with the addition of plasticizers.

Plastics with the addition NIPAm are hard and stiff because they contain little polymer compound, thus requiring a large force to broke it and less elastic. From the graphic it can be seen that the plastic with the addition of NIPAm has the highest tensile strength value, but has a lower elongation value from plastics with the addition of poly (NIPAm) and plastics with the addition of chitosan-graft-poly (NIPAm).

Grafting will produce a branching structure that lowers the crystallinity. Irregularities in the structure of the polymer chain, for example branching, will inhibit the chain to be able to interact with each other, and therefore the crystallinity be limited [8]. Polymer which has a higher crystallinity generally harder, stronger, more turbid, more resistant to solvents, and its density is higher than amorphous polymers [9]. Therefore, plastics with the addition of poly(NIPAm) has a tensile strength greater than the plastic with the addition of chitosan-graft-poly(NIPAm) because plastic with poly(NIPAm) will formed a more crystalline structure. While plastics with the addition of chitosan-graft-poly (NIPAm) will formed a more amorphous structure.

3.3 Biodegradability

The simplest quantitative methods to characterize the occurrence of biodegradation of a polymer is to determine the mass loss of the polymer material [10]. Mass loss is determined by weighing the mass of the polymer before and after biodegradation process for a certain time. The greater the mass loss plastic means the faster degradable plastic.

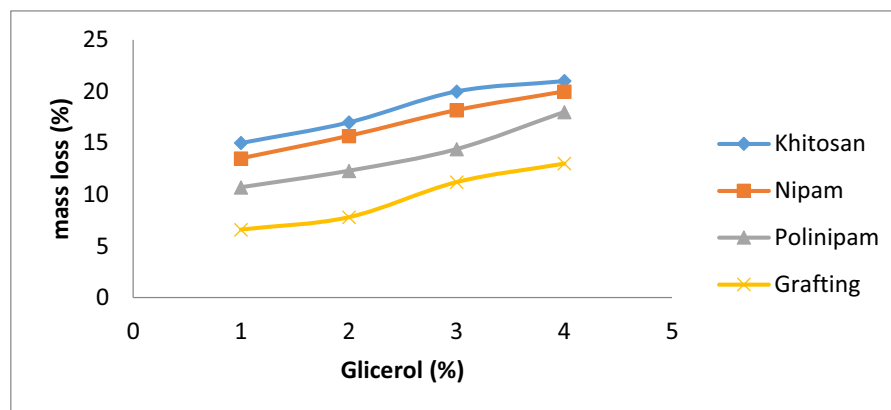


Figure 6. The effect of glycerol concentration and treatment variations of NIPAm against of weight loss from biodegradable plastic from tapioca for 6 weeks.

Biodegradable plastic mass loss increased with increasing concentrations of glycerol. It shows that the high glycerol cause more plastic hydrophilic because of glycerol and starch having an OH group which can initiate the hydrolysis reaction, so that the polymer into small pieces [11] Plastics with the addition of chitosan-graft-poly(NIPAm) has the smallest mass loss. This suggests that the grafting of chitosan and poly(NIPAm) can improve the biodegradability of plastic as a branching structure that forms require more enzymes to decide. [12] also added that polymer degradation is influenced by the composition, polymer properties such as molecular weight, melting temperature, crystallinity and the transition temperature, the more hydrophilic, the faster degradable polymer.

4. Conclusions

From the research results above, it can be concluded that:

1. The process of grafting of chitosan and poly (NIPAm) indicated by the uptake of new functional groups on a single C-O at $1000\text{-}750\text{ cm}^{-1}$ with a yield of 12.27%.
2. The higher the concentration of glycerol, then the value of the tensile strength (tensile strength) plastic lower, but the elongation value will be higher.
3. Within six weeks, plastics with high glycerol content will have a greater mass loss so more quickly degraded.
4. Plastics with the addition NIPAm is hard so it has the highest tensile strength values but it has a low elongation value and rapid degradation.
5. Plastics with the addition of poly (NIPAm) has the highest elongation value and the longer degradation of plastic with the addition NIPAm
6. Plastics with the addition of chitosan-graft-poly (NIPAm) has the lower tensile strength and elongation compared to plastic with the addition of poly (NIPAm) which is the longest to degraded
7. In general, the addition NIPAm, poly (NIPAm) and chitosan-graft-poly (NIPAm) in the synthesis of biodegradable plastics from tapioca can improve the mechanical characteristics and biodegradability of plastic instead of plastic produced by the addition of chitosan itself.

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