Tapioca Waste-Methyl Methacrylate Irradiation for Biodegradable Plastic Raw Materials

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ARTICLE INFO	Abstract
<p>Article history:</p> <p><i>Received date : 14 November 2019</i></p> <p><i>Revised date : 25 February 2020</i></p> <p><i>Accepted date: 13 April 2020</i></p> <p><i>Available online at :</i> https://doi.org/10.14203/jkti.v21i2.430</p>	<p>Nuclear technology can be applied not only as energy (electricity) but also in industry as an initiator on polymer reaction. The polymer reaction can combine two monomers, as an example, tapioca waste and methyl methacrylate, to make biodegradable plastics. Tapioca waste is used due to its biodegradability properties. Tapioca waste gel is formed by adding an equal aqua dest ratio to waste weight. After gel formed, several concentrations of methyl methacrylate (w/w) is added to the gel then packed into ampules. Using the Co-60 gamma irradiation source, the gel is irradiated at 5 kGy absorbed dose. Glycerol as a plasticizer is added to the gel to increase polymer flexibility. To analyze its mechanical properties, firstly, we need to mold the samples using a pressurized-hot press machine. Then added methyl methacrylate at varying doses. The specimen is tested by analyzing tensile strength characteristics (ASTM D638-14). Fabrication of biodegradable plastic-based packaging by using starch has an increase in the mechanical and thermal properties.</p>
<p>Keywords:</p> <p><i>Irradiation, polymer, tapioca waste, methyl methacrylate, biodegradable plastic</i></p>	<p>© 2020 Indonesian Journal of Applied Chemistry. This is an open access article under the CC BY-NC-SA license (https://creativecommons.org/licenses/by-nc-sa/4.0/).</p>

1. INTRODUCTION

Plastic is always present in every human need. The use of plastics is increasing rapidly because plastics have many applications such as

packaging, and use for several automotive parts. The use of plastic is vital to the life of the community because of its "long-last" character [1]. The plastic raw material is generally still

derived from petroleum that is not naturally degraded. After the useful life is over, the waste heap becomes an environmental problem [2]. Conventional plastic derived from petroleum is very difficult to degrade, and the whole process to run out takes up to 50 years [3]. One alternative to overcome these problems is to make plastics from natural materials so that they are easily degraded (biodegradable) or environmentally friendly [4]. Environmentally friendly plastics are currently needed to overcome environmental problems because of its easily degraded character. The making of environmentally friendly plastics has been investigated by combining natural polymers with synthetic polymers [5]. Biodegradable plastic can be made from materials that contain starch, such as cassava. The Center for Agricultural Data and Information Systems at the Ministry of Agriculture stated that the surplus of cassava production in Indonesia until 2018 was 923.85 thousand tons [6].

Cassava is a raw material for tapioca production. In the tapioca production process, 1 ton of cassava is produced 250 kg of cassava flour and 114 kg of cassava solid waste commonly referred to as tapioca waste. Tapioca waste still contains 45-65 % starch, and some have even examined 67.8 % [7]. The utilization of tapioca waste is currently only limited to animal feed or disposed of as waste. Even though with high carbohydrate content, around 65-90 % with 16 % amylose and 84 % amylopectin content, tapioca waste can be used as an ingredient in making biodegradable plastics. Biodegradable plastics are made from agro polymers [8] such as starch, lignin, pectin, chitin, and natural rubber. The research used tapioca waste and chitosan as trunk polymers and glycerol as the plasticizer. The result showed there is no effect from chitosan addition to tapioca waste mechanical properties but could increase its biodegradability.

There are also biodegradable plastics made from microorganisms such as polyhydroxyalkanoate [9], polyhydroxybutyrate [10], and polyhydroxy butyrate-hydroxy valerate copolymers [11]. Biodegradable plastic can also be synthesized from its monomer derivatives, such as polylactate. Biodegradable plastics derived from by-products of petrochemical processes such as polycaprolactone, aromatic and aliphatic polyester copolymers, and their homopolymers [12].

MMA is used as a reinforcing agent, thus making MMA-g-starch more easily formed/printed. The aim of this research is to develop environmentally friendly plastic based on tapioca waste and methyl methacrylate 5, 10, 15, 20, 25 and 30 grams (w/w) using a gamma-ray irradiation so that it has optimum mechanical properties. The gamma-ray can accelerate the polymerization reaction between tapioca waste and MMA without add any crosslinker/grafting agent to the solution.

2. EXPERIMENTAL

2.1. Materials

Tapioca waste was collected from the tapioca factory in Ciluar, Bogor City, Indonesia. This research utilizes a technical methyl methacrylate monomer (hot curing). Glycerol is used generally to biodegradable plastic films to modify properties such as water sorption, mechanical properties, and glass transition temperature.

2.2. Methods

Tapioca waste is dissolved with distilled water at 80 °C using a hot plate stirrer to form a paste. MMA is added to the paste in a hot state. Surfactant is added to the solution to make MMA and tapioca waste mixed in distilled water. MMA concentration was varied at 5, 10, 15, 20, 25 and 30 grams (w/w). This variation aims to find out the optimal point of MMA addition can

improve the mechanical properties of MMA-g-starch. The sample is chilled and then packed in bottles of Polyethylene Terephthalate (PET) and irradiated using simultaneous Co-60 γ -ray sources at an absorbed dose of 5 kGy at 1.97 kGy/h dose rate.

After irradiation, the sample was extracted using acetone to remove homopolymers, and the degree of copolymerization (DC) was calculated to determine the optimal concentration of MMA addition. The degree of copolymerization is calculated using the equation:

$$DC = (W_2 - W_1) / W_0 \times 100\% \quad (1)$$

Where

DC = degree of copolymerization (%),

W_2 = the dry weight of the sample after copolymerization (g),

W_1 = the dry weight of the sample before copolymerization (g), and

W_0 = the weight of methyl methacrylate (g).

Then the sample is dried and pressed using hot press hydraulics. Before hot-pressed by hydraulics machine, glycerol 5 mL is added to copolymer as a plasticizer to increase the flexibility of copolymer. The hot-pressed machine is set up at pressure 110 kg/cm² for 5 min. The mechanical properties (tensile strength and elongation at break) of the composites formed were analyzed using the Universal Testing Machine (UTM) using the ASTM D638-14 methods.

3. RESULT AND DISCUSSION

3.1. Optimum Monomer Concentration

Tapioca waste used for this study was 20 grams each. The reaction of copolymerization is 5 kGy absorbed dose. The absorbed dose is a minimal dose that can affect both degraded and

cross-linked polymers. When tapioca waste containing starch is given 5 kGy doses, it will produce free radicals which will modify the structure of starch. Viscosity will decrease when starch is given a higher dose, which will cause the starch to increase in solubility and acidity. The change in viscosity is caused by the degradation of starch structure because influenced by gamma irradiation, which causes oxidative degradation [13]. DC values are obtained after soxhlet extraction using acetone for 24 hours.

Table 1. Degree of copolymerization tapioca waste-methyl methacrylate

W_0 (g)	W_1 (g)	W_2 (g)	DC (%)
0	20	20.0003	-
5	20	20.6878	13.7560
10	20	22.3365	23.3650
15	20	25.3374	35.5827
20	20	29.7741	48.8705
25	20	32.0173	48.0692
30	20	34.5038	48.3460

DC value is the difference between the dry weight after and before the copolymerization process compared to the monomer weight, which added to tapioca waste.

Table 1 shows that the greater the addition of x monomers, the greater the degree of copolymerization obtained. The addition of 20 g monomers indicates the highest DC value. It means that it has a ratio of 100 % to the weight of tapioca waste. The addition of 20 g monomers has an average DC value of 27-73 % higher compared to the others additions. Soxhlet extraction is usually used to separate components that have opposite hydrophobicity properties. In all procedures that are used to isolate the grafted polymer, there will always be a part of the monomer removed in the

copolymerization process. Some grafts contain mostly starch and they are not hydrophobic enough to be combined with synthetic polymers [14].

The addition of monomers above 20 g or more than 100 % by weight of tapioca indicates that there is no significant increase in the degree of copolymerization. Data shows that the maximum limit of the addition of monomers above 100 % will only form MMA homopolymers, as seen from DC the addition of 25 g and 30 g monomers results in DC, which is approximately equal to the addition of 100 % tapioca weight (20 g MMA). Monomer ratio of 1: 1 or 100 % by weight of starch (in this study tapioca waste), the conversion to the copolymer reaches maximum results. If the monomer is added more than 100 %, the DC will go down. The increasing concentration of the monomer also increases the diffusion within the monomer in tapioca waste so that increasing the DC of the copolymer. Also, high monomer concentrations are suitable for forming complexes (receptor-contributor) between tapioca waste and its monomers [15]. Hence, the optimum monomer concentration from this study is 1:1 (100 % monomer addition, 20 g). Even the simultaneous irradiation can be done easier, there is loss of control at high monomer consumption. The maximum addition of methyl methacrylate (100 %) only give less than 50 % of DC. Therefore, we assume that an active backbone site [16] as a result of irradiation can only be polymerized with less than 100 % MMA.

3.2. FTIR Characterization

The FTIR spectra of irradiated MMA-g-starch using glycerol as a plasticizer are shown in Figure 1. It reveals that the FTIR spectra of starch (tapioca waste) show a typical spectrum with three major peaks region marked as 1 (3700-2700 cm^{-1}), 2 (2100-1000 cm^{-1}), and 3 (900-450 cm^{-1}). As it can be seen in the spectrum

of tapioca (P1), the presence of O-H group (3285,7 cm^{-1}), confirmed by the presence of band at 1420,7 cm^{-1}) that suggest the existence of the C-C group. The appearance of the absorption band at 2930,9 cm^{-1} is confirmed by the presence of band at 1345,7 cm^{-1} . Bending vibration of C-C at the tapioca spectrum can be observed at 1012,7 cm^{-1} , whereas stretching vibration of C-O appears at 1150,4 cm^{-1} . These band adsorptions was came from glucose unit of tapioca waste [17]. FTIR spectrum of MMA shows C=C group band at 1640,6 cm^{-1} , whereas 1275 cm^{-1} linked with C-O-C from ester. Group of C=C alkene and C=O carbonyl can be seen at 3430 cm^{-1} and 1729,7 cm^{-1} .

Fig. 1. FTIR spectra of tapioca (P1), MMA (P2), and irradiated MMA-g-starch (P3).

FTIR spectrum of irradiated MMA-g-starch (P3) shows a shift at the C=O carbonyl group which found in MMA FTIR spectrum (P2). The C=O group adsorption from MMA is 1729,7 cm^{-1} but in the Fig. 1 (P2) C=O group adsorption shifted to 1712, 8 cm^{-1} . This shift is suggested as addition of the polymerization reaction to the C=C bond at MMA so that the conjugated double bond is defected and causes energy change to C=C stretch [18].

3.3. Mechanical Properties

The pressing process for tapioca waste-MMA copolymer is needed to support the mechanical properties test to have a standard specimen for ASTM D368. Before pressed by a hot press hydraulics machine, glycerol is added to copolymer as a plasticizer to increase the flexibility of copolymer because glycerol has better efficiency than sorbitol to modify the mechanical properties of copolymer [19]. The tensile strength of the plastic containing 20 g of monomer is about 20 times higher than 5-15 g monomer addition. This is due to the higher addition of methyl methacrylate so that the mechanical properties obtained in copolymer tapioca waste-methyl methacrylate is higher. MMA and tapioca waste mixture can be crosslinked by γ irradiation so increase the tensile strength of the graft [20].

Based on the results it can be concluded that the addition of methyl methacrylate can affect the tensile strength of a specimen. The effect of adding methyl methacrylate on tensile strength has increased and decreased under certain conditions. The more the composition of methyl methacrylate and the less tapioca waste used, the higher the tensile strength value is produced. Tensile strength (TS) test results produced with the addition of methyl methacrylate of 10.33-24.78 MPa (10-30 g MMA), this corresponds to the standard criteria of the tensile strength of biodegradable plastics in Indonesia SNI 7188.7:2011 of 5-100 MPa (Requirements for biodegradable packaging materials containing starch and thermoplastic mixtures and containing degradation agents can be used as packaging materials) [21].

Elongation at break (EB) of tapioca waste-MMA was found to be simultaneously improved by the attachment of poly-MMA graft on the tapioca waste surfaces [22]. Because, graft MMA-tapioca waste is added glycerol as a plasticizer which makes graft more flexible. Many polymers pores is filled by glycerol, thus increase the graft elasticity [23]. Also, according to Xiu-Li, tapioca waste can increase the elasticity of the graft too [24]. The attachment of

only 5g MMA caused almost 5 times higher EB. The highest EB is at 20 g MMA addition, the value of its EB is 22-41 % more efficient than any other MMA concentration. Based on the results of the mechanical test, it concluded that 20 g MMA could be considered as an optimum concentration (weight) for the increasing on the mechanical properties of tapioca waste-MMA.

Table 2. Mechanical properties of tapioca waste-co-methyl methacrylate

Conc. MMA	TS (MPa)	EB (%)
0	0.56	1.05
5	1.96	4.86
10	10.33	6.53
15	18.03	10.41
20	24.78	11.81
25	24.23	11.97
30	24.55	11.43

4. CONCLUSION

Biodegradable plastic can be obtained from the copolymerization process between tapioca waste and MMA monomers using gamma-ray irradiation. Biodegradable plastic waste tapioca-MMA has tensile strength that meets the requirements of 24.78 MPa and has an optimum elongation at break for the addition of MMA at 20-25 g.

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- 80 | ”Tapioca Waste-Methyl Methacrylate Irradiation...”: Akhmad Rasyid Syahputra, et.al.