

The Effect of Radiation Technology on Surface Morphology of Sago Based Eco-friendly Plastic

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ABSTRACT

The variety and production continue of plastic has increased and it has brought difficulties in dealing with plastic waste disposed to nature and cannot be decomposed in a long time. Modified thermoplastic starch derived from sago palm crosslinked with polyurethane prepolymer obtained from diphenylmethane diisocyanate and castor oil polyol had better mechanical, thermal and chemical characteristics than bioplastics. In this study, eco-friendly plastics from sago starch modified with prepolymer polyurethane with the addition of chitosan as additive and polypropylene or polyethylene as matrix was produced. The research method conducted consisted of several stages, preparation of thermoplastic starch, blending thermoplastic starch with polypropylene or polyethylene and plastic irradiation technology using gamma rays with dosage of 5, 10 and 20 kilogray (kGy). The effect of radiation technology on surface morphology of sago based eco-friendly plastic was analyzed through Scanning Electron Microscopy (SEM) analysis to observe the effect of gamma rays exposure to the plastic surface. The result showed that the dots appeared on the surface and possibly showed non-uniformity of the plastic surface due to less homogeneity of mixture when stirred. Thermoplastic starch was not blended perfectly into PP and this could be due to the high temperature difference required to melt PP while thermoplastic starch as an organic material cannot stand high temperature and become scorched at high temperature. To overcome this problem, mixing time should be increased to ensure high homogeneity. Overall, SEM analysis showed radiation does not provide effect to plastic surface morphology, which means it did not ruin the polymer structure as well as its binding. Similar appearance observed on the plastic surface morphology before and after radiation, even with the highest radiation dose. From the analysis, it can be stated that radiation technology does not influence plastic surface structure, hence plastic binding remains the same.

Keywords: *Eco-friendly Plastic, Thermoplastic Starch, Radiation Technology, Scanning Electron Microscopy (SEM).*

1. INTRODUCTION

Plastic is often identified as the most abundant physical pollutant on the seafloor. Plastic is a polymer of long chains of atoms that bind to each other. These chains form many repeating molecular units or "monomers". The term plastic includes synthetic or semi-synthetic polymerization products, but there are some natural polymers such as starch [1]. Polymeric materials can be classified into either thermoplastics or thermosetting polymers. Thermoplastic polymers consist of well-packed, non-covalently bound polymer chains that can melt and flow when heated above the polymer's melting point, while thermosetting polymers consist of networks of polymer chains interconnected through covalent bonds. The latter structures do not melt when heated, and cannot be dissolved in a solvent. Because of its crosslinked chemical structure, thermosetting polymers often exhibit superior mechanical properties, making their breaking down more challenging than that of thermoplastics.

The use of plastic in modern life for human needs is unavoidable. The variety and production continue to increase and cause difficulties in dealing with plastic waste that is disposed of in nature and cannot be decomposed in a long time. Therefore, it is necessary to make plastic materials that can be decomposed naturally. These materials are generally derived from nature and can be renewed so as to increase the added value. One of the ingredients that can be used is starch derived from rice, sweet potatoes, corn and sago. Sago is one of the most economical choices because it is cheap and easily grows. Currently, the use of sago as a staple food has begun to shift. Sago stems are a storehouse of starch. Sago starch contains about 27% amylose and 73% amylopectin. Sago starch can be used as a raw material for making biodegradable plastics to increase economic value.

Unlike most conventional synthetic polymers, starch is a biopolymer directly extracted from biomass and has unique chemical structure and processing behavior. Furthermore, the incorporation of appropriately filler into

starch may not only enhance the performance, but it could also provide new functionalities for new applications due to the resulting novel structures and functional groups [2]. Disadvantages caused by plastics from plant materials (bioplastics) are mechanical properties that cannot be compared with commercial plastics, low elongation power so that the plastic becomes stiff, easily broken and brittle, and absorbs water and moisture from the environment, hence limiting its application. Biodegradation rate of polymers is affected by many factors such as chemical nature of the polymer, environmental conditions, activity of the microbial population, etc.

1.1. *Thermoplastic Starch*

Modified thermoplastic starch derived from sago palm crosslinked with polyurethane prepolymer obtained from diphenylmethane diisocyanate and castor oil polyol had better mechanical, thermal and chemical characteristics than bioplastics. The addition of chitosan as a reinforcement as well as antibacterial can improve the performance of the thermoplastic produced. Thermoplastic starch (TPS) is a gelatinized starch-based material. Gelatinization is to destroy the crystalline structure in starch granules, which is an irreversible process. The gelatinization processing involves granular swelling, native crystalline melting and molecular solubilization. These materials can be reheated and form new shapes without significant changes in their properties. This behavior is a result of the absence of chemical crosslinks in these polymers, even after they have been melted [3]. Eco-friendly plastic products synthesized in our previous research were able to decompose in nature within 2 years. Mechanical and thermal properties are still below commercial plastics, so it is necessary to introduce radiation techniques so that the resulting product has better mechanical and thermal properties and can be decomposed in nature in a faster time so that it can contribute to reducing the amount of plastic waste. Among all plastics, polypropylene (PP) is the most demanded for plastic converter industries in Europe. In fact, PP is one of the most used and consumed polymers in the world due to its good processing performance and versatility. PP is used for a wide variety of applications such as commodities, medical applications, automotive, etc. [4].

Chinaglia et al, 2018 have explored the role of particle size on biodegradability, polybutylene sebacate plastic pellets using four different particle sizes, Surface area assessed through direct measurement (pellet) or theoretical estimation followed by image analysis. Different samples were tested for biodegradation in soil for 138 days. The rate of biodegradability was calculated by linear regression in the first part of the biodegradation process referring to the total available surface area. [5]. Samper et al, 2018 analyzed polypropylene recycling with the addition of biodegradable polymers, namely polylactic acid (PLA), polyhydroxybutyrate (PHB) and thermoplastic starch. The material was evaluated by studying changes in thermal and mechanical. The results showed the softening temperature and melt flow index were not affected by the presence of biodegradable polymers in recycled PP. Mechanical properties are affected when more than 5 weight % biodegradable polymer was added. [6].

Sudi et al, 2013 conducted a research on durian seed starch as filler into the synthetic polymer used to form packaging materials and food containers such as polystyrene [7]. Punyamurthy et al, 2005 studied the formation and characterization of untreated benzene diazonium chloride treated (Diazo treated) abaca polypropylene composites with coupling agents [8]. Srithongkham et al, 2012 studied chemical and morphology of nanofibers isolated from rice straw by applying a high shear homogenization technique and its influence on mechanical properties of starch composite foam using thermal compression molding technique [9].

Rozanna et al, 2014 synthesized polyurethane prepolymer from isocyanates and polyols to strengthen starch thermoplastics. Modified thermoplastic starch was cross-linked with polyurethane prepolymer to have better mechanical, thermal and chemical characteristics than bioplastics and could biodegrade naturally [10]. Subsequent research was carried out by adding chitosan as a reinforcement to improve the mechanical performance of the resulting thermoplastic as well as to function as antibacterial [11]. Silviana and Subagio, 2019 utilized cassava bagasse as a matrix of composite reinforced by acetylated micro fibrillated cellulose (MFC) of bamboo and cross-linked with lime to form bio composite. Characterizations done were tensile strength, thermal stability through DSC-TGA analysis, qualitative functional group structural through FTIR analysis, and crystallinity through XRD analysis [12].

1.2. *Influence of Gamma Irradiation on Sago Based Eco-Friendly Plastic*

Gamma rays and X-rays are short-wave radiation of the electromagnetic spectrum which includes radio waves, microwaves, infrared, visible light and ultraviolet. Gamma rays are emitted by radioisotopes such as Cobalt-60 and Cesium-137 while electrons and X-rays are generated by machines using electricity. Radiation sterilization of health products is one of the applications of radiation process technology that is developing very rapidly. When organic matter is irradiated by ionizing radiation, they are divided into two types, degradation (chain cutting) and chain linking (crosslinking). Interest in radiation-degrading chemistry of natural and synthetic

polymers has greatly increased as the potential for using radiation is recognized to improve industrial processes such as pulping, cosmetics and food preservation [13].

In this research, Eco-friendly plastic technology was synthesized using sago starch as the basis. After the eco-friendly plastic is formed, the radiation process which is an isotope technology and radiation technology by utilizing ionizing radiation (high energy radiation) is used. Gamma radiation takes about 2-3 hours with varying doses to obtain the optimal dose (kilo Gray/kGy). Optimization of the composition and process of making eco-friendly plastics from sago starch for packaging application has been carried out in our previous work. The results showed that eco-friendly plastics can be synthesized from modified sago starch with chemical, physical, thermal and biodegradability characteristics close to conventional plastics, so the opportunity to develop derivative products is very large. The rate of biodegradability can be increased by using radiation techniques, while improving the mechanical, and thermal properties of eco-friendly plastics. This paper will discuss the effect of irradiation technology on surface morphology of sago based eco-friendly plastic, surface morphology through Scanning Electron Microscopy (SEM) analysis. Meanwhile mechanical properties and thermal characteristics were discussed elsewhere.

2. MATERIALS AND METHODS

The materials used in this research were sago starch that was produced locally. Polypropylene, glycerol, Methylene Diphenyl Diisocyanate (MDI), polyol, water and chitosan were produced by Merck International and was used without further purification. The equipment used during the research were Raw Mill, Crusher, Extruder Machine, Injection Molding, Oven, and other supporting small equipment. The Scanning Electron Microscopy (SEM) test was carried out by looking at the morphology of the plastic. This research method included the stages of preparation of producing thermoplastic starch and eco-friendly plastic and radiation processes. The analysis done was measuring Scanning Electron Microscopy (SEM).

Sago starch and water were weighed according to the set-up composition and mixed together. The mixture is then heated and stirred until it becomes gelatin at a temperature of 70°C for 25 minutes. MDI (Methylene Di-Isocyanate) and polyol was added with a predetermined ratio to modify the thermoplastic starch (TPS) by in-situ mechanism. Glycerol as plasticizer was added 10%, as well as chitosan and calcium carbonate stirred vigorously until homogeneous. The homogeneous mixture was dried using an oven at 80°C for 24 hours. The dried mixture will form like a crust and cut into smaller sizes.

Thermoplastic starch that has become crusted was blended into a finer size to ease mixing. Polypropylene (PP) was heated at 110°C until melted and mixed with crusted thermoplastic starch until homogeneity using a Raw mill. The mixture was then chopped into smaller sizes in the crusher and then processed to become plastic pellets using an extruder machine. After the pellet was ready, it was used to mold products for household purposes such as plates, bowls, flower vases using an injection mold machine. The radiation process which is an isotope technology and radiation technology by utilizing ionizing radiation (high energy radiation) is used. Gamma radiation irradiation takes about 2-3 hours with varying doses to obtain the optimal dose (kilo Gray/kGy). Various radiation doses of 5 kGy, 10 kGy, 20 kGy were applied to improve plastic characteristics. 20 kGy dose is a high enough radiation dose so that it can form many radical sites [14]. The radiation was carried out at the Research and Development Center for Isotope and Radiation Technology of the National Nuclear Energy Agency (P3TIR, Jakarta). Characteristics plastics analyzed were surface morphology by Scanning Electron Microscope (SEM) analysis.

3. RESULTS AND DISCUSSION

Sago starch was synthesized in-situ using Methylene Diisocyanate and Polyol to become polyurethane prepolymer, and sorbitol as plasticizer and chitosan. Furthermore, the thermoplastic copolymer is mixed with Polypropylene/Polyethylene in a ratio according to the desired application. After the eco-friendly plastic is formed, the radiation process which is an isotope technology and radiation technology by utilizing ionizing radiation (high energy radiation) is used. Morphology analysis was done through Scanning Electron Microscopy (SEM). SEM analysis technique allows examining of changes in the morphology of materials at the micro scale. In order to perceive monitoring and the changes in the structure of the samples, images from the SEM were used. The experiment involved images of both the original samples and samples that underwent the radiation process. Each sample was depicted at 100x and 1000x magnification. The illustrations are presented in Figure. 1–4. SEM images analysis makes it possible to verify the considerable quality of the samples.

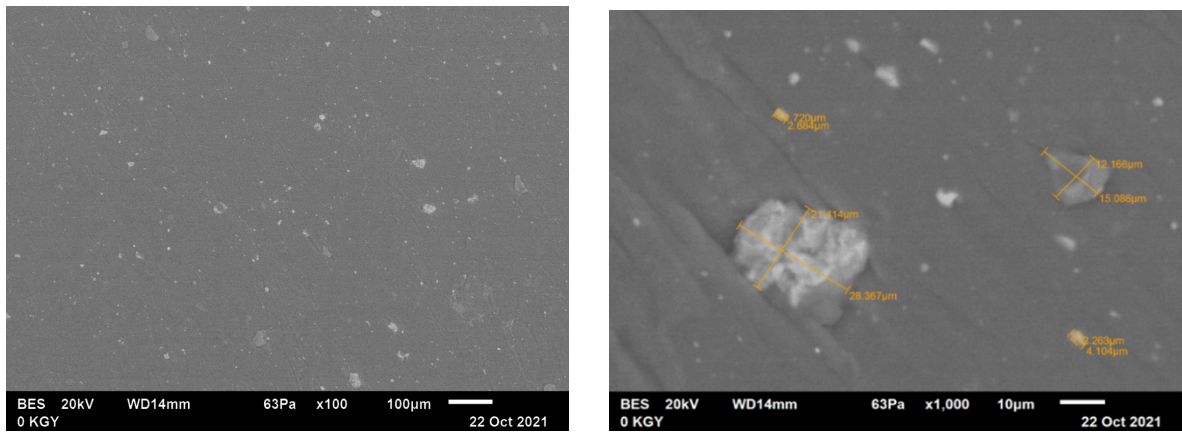


Figure 1 SEM analysis of plastic without radiation at 100x and 1000x magnification

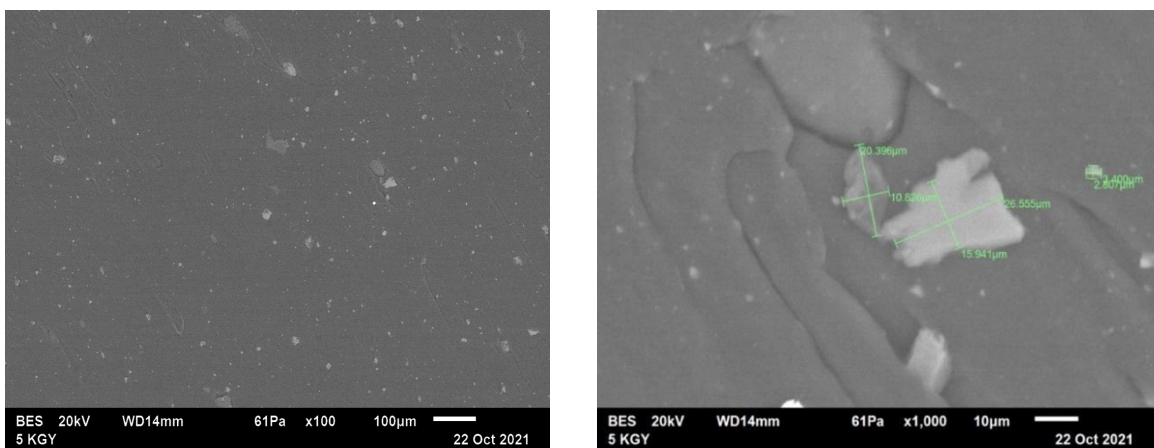


Figure 2 SEM analysis of plastic with 5 kGy radiation dose at 100x and 1000x magnification

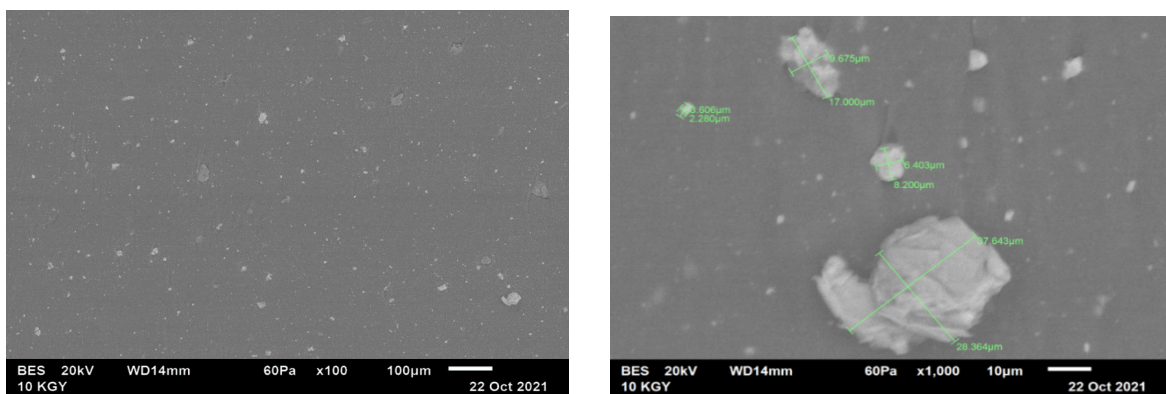


Figure 3 SEM analysis of plastic with 10 kGy radiation dose at 100x and 1000x magnification

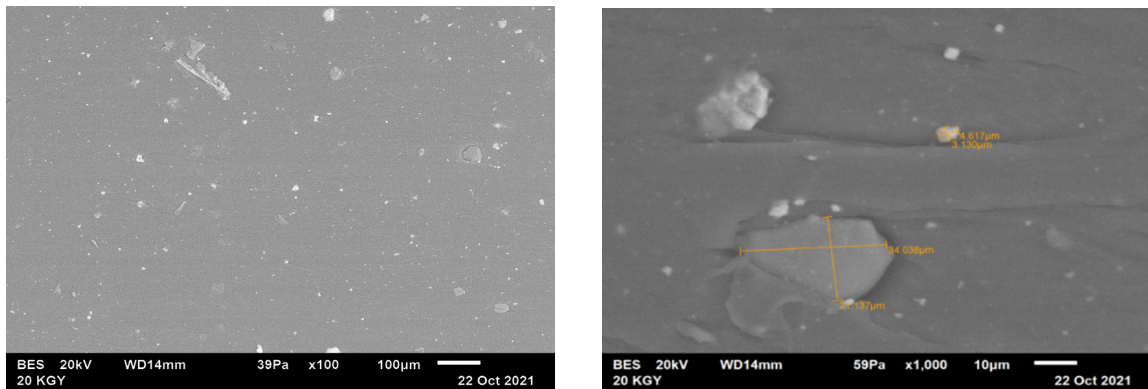


Figure 4 SEM analysis of plastic with 20 kGy radiation dose at 100x and 1000x magnification

SEM analysis was intended to see the comparison between samples with different radiation dose variations of 5 kGy, 10 kGy, and 20 kGy. Plastic without radiation was also analyzed as a benchmark. From Figure 1-4, it can be seen that white dots and indentations on the surface of eco-friendly plastic appeared for all samples. The dots possibly showed non-uniformity of the plastic surface due to less homogeneity of mixture when stirred. Thermoplastic starch was not blended perfectly into PP and this could be due to the high temperature difference required to melt PP while thermoplastic starch as an organic material cannot stand high temperature and become scorched at high temperature. To overcome this problem, mixing time should be increased to ensure high homogeneity. Fig. 1-4 showed radiation does not provide effect to plastic surface morphology, which means it did not ruin the polymer structure as well as its binding. Similar appearance observed on the plastic surface morphology before and after radiation, even with the highest radiation dose. From the analysis, it can be stated that radiation technology does not influence plastic surface structure, hence plastic binding remains the same.

AUTHORS' CONTRIBUTIONS

All authors conducted the contribution to this experiment. Rozanna Dewi conducted the experiments and analyzed the data. Novi Sylvia also contributed to the experiment process and assisting to draw the tables and graphics. Zulnazri was involved in data analysis and writing the paper. All authors contributed to manuscript revisions and all authors agreed to the final version of this manuscript.

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REFERENCES

- [1] Jesse P. Harrison P.J, Boardman C, O'Callaghan K, Delort A and Song J, Biodegradability standards for carrier bags and plastic films in aquatic environments: a critical review, Royal Society Open Science, 2018, The Royal Society Publishing. DOI: <https://doi.org/10.1098/rsos.171792>
- [2] F. Xie, E. Pollet, P. J. Halley, and L. Av erous, Advanced Nano-biocomposites Based on Starch, Polysaccharides, 2014, 37: p. 1552-1596. DOI: 10.1007/978-3-319-03751-66_501
- [3] Jiang T, Duan Q, Zhu Jian, Liu H and Yu L, Starch-based biodegradable materials: Challenges and Opportunities, Advanced Industrial and Engineering Polymer Research 3, 2020, 8-18. DOI: <https://doi.org/10.1016/j.aiepr.2019.11.03>
- [4] Marie Matet, Marie-Claude Heuzey, Eric Pollet, Abdellah Aji and Luc Averous, Innovative Thermoplastic Chitosan Obtained by Thermo-Mechanical Mixing with Polyol Plasticizer, Carbohydrate Polymer, 2013, 95, 241-251. DOI: <https://doi.org/10.106/j.carbpol.2013.02.052>
- [5] Chinaglia S, Tosin M, Degli-Innocenti F, Biodegradation rate of biodegradable plastics at molecular level, Journal of Polymer Degradation and Stability, 2018, Elsevier, 147, pp. 237-244. DOI: <https://doi.org/10.1016/j.polymdegradstab.2017.12.011>

- [6] Samper María D, Bertomeu D, Patricia A., M, Ferri J., M and López-Martínez J, Interference of Biodegradable Plastics in the Polypropylene Recycling Process, *Materials*, 2018, MDPI, 11. 1886. DOI: <https://doi.org/10.3390/ma11101886>
- [7] R. Sudi, The Study of Starch Seeds Durian (*Durio zibethinus*) Effect as the Filler Material on Tensile Strength and Biodegradation of Polymers Polystyrene (PS), *J. Aceh Phys. Soc.*, 2013, 2: pp. 7–8.
- [8] R. Punyamurthy, D. Sampathkumar, R. P. G. Ranganagowda, B. Bennehalli, and C. V. Srinivasa, Mechanical properties of abaca fiber reinforced polypropylene composites: Effect of chemical treatment by benzenediazonium chloride, *J. King Saud Univ. - Eng. Sci.*, 2017, 29: pp. 289–294. DOI: <https://doi.org/10.1016/j.jksues.2015.10.004>
- [9] S. Srithongkham, L. Vivitchanont, and C. Krongtaew, Starch/Cellulose Bio composites Prepared by High-Shear Homogenization/Compression Molding, *J. Mater. Sci. Eng. B*, 2012, 2: pp. 213–222.
- [10] R. Dewi, H. Agusnar, B. Wirjosentono, and M. Riza, Synthesis of modified thermoplastic starch (TPS) using in-situ technique, *Advance Environmental Biology.*, 2014, 8: pp. 26–33.
- [11] R. Dewi, Nasrun, Zulnazi, M. Riza, and H. Agusnar, Improved mechanical and thermal properties of modified thermoplastic starch (TPS) from sago by using chitosan, *Pertanika J. Sci. Technol.*, 2019, 27: pp. 1441–1450.
- [12] Samira B., Marjan G., Nayyer Shahbaz, F. Izadi, Z. Pilevar and Amir M. Mortazavian, The Effects of Novel Thermal and Nonthermal Technologies on the Properties of Edible Food Packaging, *Food Engineering Reviews*, Springer, 2020, 12: pp. 333–345. DOI: <https://doi.org/10.1007/s12393-020-09227-y>
- [13] S. Silviana and A. Subagio, Bio composite characterization of bagasse starch derived from cassava reinforced by acetylated bamboo cellulose and plasticized by epoxidized waste cooking oil, *Rasayan J. Chem.*, 2019, 12: pp. 1470–1477. DOI: 10.31788/RJC.2019.1235240
- [14] Sujayasree O. J and Fasludeen N. S, Application Of Irradiation Technology On Food, *Impact Journal*, 2017, vol. 5, Issue 4, pp. 43-48.