JOURNAL OF INNOVATION AND TECHNOLOGY
eISSN:2805-5179 Vol. 2023, No.16

Morphology and Crystallinity Study of Sago Starch-Based Degradable Plastic with Chitosan and Calcium Carbonate as Additives

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Received: *8 August 2023;* ***Accepted:*** *6 December 2023;* ***Published:*** *11 December 2023*

Abstract: To reduce the consumption of synthetic polymers, researchers have studied the use of carbohydrates, lipids, proteins and composites to generate biodegradable plastic. In this study, degradable plastic from sago starch modified with prepolymer polyurethane synthesized from diphenylmethylene diisocyanates and polyol with the addition of chitosan as additive and polypropylene or polyethylene as matrix was produced. The research method conducted were consisting of several stages, preparation of thermoplastic starch, blending thermoplastic starch with polypropylene or polyethylene, synthesis of degradable plastic and irradiation process. Thermoplastic starch was characterized using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) and X-Ray Diffraction (XRD). SEM-EDX to study surface morphology, meanwhile XRD to determine the crystallinity of thermoplastic starch. The SEM analysis of 5000x magnification showed the presence of many material elements in the thermoplastic starch matrix that are visible on the entire surface of the plastic. The results of EDX analysis revealed the presence of chemical elements such as carbon, oxygen, magnesium, calcium, titanium, palladium, gold, and carbon dioxide. These elements came from the thermoplastic starch made from sago which contains magnesium (iron), calcium and the main additive $CaCO_3$. From the XRD analysis results, it can be shown that thermoplastic starch was amorphous and crystalline. XRD analysis of thermoplastic starch has a low crystallinity value at 26.8514^0.

Keywords: degradable plastic; sago starch; irradiation; morphology; crystallinity

1. Introduction

Thermoplastic requires heat to make it can be formed and after cooling will change back to its original shape. 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. There are several sources of thermoplastic from nature such as starch and cellulose. Starch can be generated from all source of carbohydrate such as sago, potatoes, cassava etc, meanwhile cellulose are available abundantly in the agricultural waste such as rice husk, corncob, sugarcane bagasse, etc.

Generally, plastics synthesized from starch containing small amounts of water are often brittle. To reduce this brittleness, starch is plasticized with a hydrophilic plastic such as glycerol and melted to make thermoplastic starch (TPS). Among the modifiers currently available, the isocyanate group has a high activity to react with the hydroxyl group of starch. Polyurethane prepolymers (PUP) containing isocyanates are often used to fortify starches.

Additives such as plasticizers (for brittleness reduction and increased flexibility and toughness), antimicrobial materials (for increasing the product's shelf-life), flavour, and colour agents (for increased sensory properties and overall acceptability) can be used in the production of plastic (Samira B et al., 2020). Characterization of polyurethane tissue derived from plant-based polyols comparing it to synthesis-based polyurethane tissue. The results obtained by polyurethane based on plant polyols have a lower tensile strength in accordance with the increase in the molecular weight of polyurethane (Carme et al., 2008). Transparent film mixture of castor oil-based PU (castor oil) and p-phenylene diamine soy protein (PDSP) (Liu Dagang et al., 2008). The morphology and properties of the mixed films were tested by FTIR, DSC, DMA, SEM, moisture adsorption, thermal degradation and tensile tests. Both components are suitable for a large number of ratios as a result of hydrogen bonding or chemical cross-links between PU and PDSP. The elongation, thermal stability, and water resistance of PU/PDSP films are increased by the addition of PU. Lu et al., (2015) developed PU from rapeseed oil-based polyols, and used it to modify glycerol plasticized starch (PS) to overcome the disadvantages of starch materials, such as poor mechanical properties and sensitivity to water. The results showed plasticized glycerol starch can be mixed with rapeseed oil-based PU at PU content below 20% and phase separation occurs when the PU content increases. The addition of PU into the starch matrix also increases the resistance of the film to water (Lu et al., 2015). Modified TPS uses corn starch with PUP made from Diphenylmethane diisocyanato and Polyols derived from castor oil. This modification produces a filler material that forms microparticles to obtain sago starch micro-composite material.

The process carried out by Wu et al., (2008) strengthens corn starch thermoplastics by using PUP which binds to the starch matrix through urethane bonding. Exploration of the role of particle size on biodegradability as, polybutylene sebacate plastic pellets using four different particle sizes, the surface area was assessed through direct measurement (pellets) or theoretical estimation followed by Image Analysis. Different samples were tested for biodegradation ground for 138 days. The biodegradability rate calculated by linear regression in the first part of the biodegradation process refers to the total surface area of each available (Chinaglia S et al., 2008). Recycling polypropylene with the addition of biodegradable polymers such as polylactic acid (PLA), polyhydroxybutyrate (PHB) and thermoplastic starch. The material obtained is evaluated by studying changes in thermal and mechanical. The results showed that 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 wt. % of biodegradable polymer added (Samper María D et al., 2018). Characterization done were tensile strength, thermal stability through DSC-TGA analysis, qualitative functional group structural through FTIR analysis, and crystallinity through XRD analysis (Samper María D et al., 2018).

Thermal property and thermal stability was analyzed through DSC-TGA analysis. Meanwhile, qualitative functional group structural through FTIR analysis, and crystallinity through XRD analysis (Silviana and Subagiao, 2019). R. Dewi et al., 2018 found, biodegradability of thermoplastic starch with polypropylene matrix was below 2 years by soil burier, however it is depending on soil condition and rain intensity (R. Dewi et al, 2018).

To improve the biodegradability rate, new technology should be applied, one proposed was radiation processing technology. Polymer modification by using highly energetic radiations such as gamma rays and the electron beam is a relatively well-established area of research and development (Ajaya et al, 2022). Using radiation technology, plastic wastes can be converted into a variety of useful purposes presenting powerful opportunities for environmental sustainability and material innovations. Plastics are strong, durable, waterproof, lightweight, easy to mold, and recyclable (Hyeonwook et al, 2021). Irradiation of various kinds, such as electron beam, beta and gamma rays, has been studied in the past as a way of revamping end-of-life polymer properties (Carlos, 2023). The gamma and electron beam radiation are the most frequent radiation techniques used for crosslinking, compatibilizing, and grafting of various polymer blends and composites systems (Amol et al, 2022). This procedure is low cost and versatile, with high reproducibility and free of wastes. The radiation alternative applied for the modification of polymers and their hybrids is the best choice for the preparation of high purity products, the achievement of successful modifications and the guarantee of the efficiency for the foreseen improvement of material properties (Train, 2022).

In this paper, we would like to discuss the effect of irradiation on characteristics of degradable plastic from sago starch modified with prepolymer polyurethane synthesized from diphenyl methylene diisocyanates and polyol with the addition of chitosan as additive and polypropylene or polyethylene as matrix. The research method consists of several stages : extraction of starch from sago, preparation of degradable plastics, irradiation process and testing of degradable plastics produced. Irradiation was done to improve mechanical and biodegradability properties of degradable plastic. The effect of irradiation process will be discussed somewhere else. Plastic was characterized using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) measurement for surface morphology and for chemical elemental analysis of materials, and X-Ray Diffraction (XRD) to determine the crystallinity of materials. Rozanna et al., 2017 found the biodegradability of thermoplastic starch with polypropylene matrix was below 2 years.

2. Methodology

The material used in this research were sago starch produced locally, polypropylene, polyethylene, glycerol, chitosan, Methylene Diphenyl Diisocyanate (MDI), polyol, calcium carbonate as compatibilizer. The materials were used without further purification. The research method conducted were consisting of several stages, preparation of thermoplastic starch, blending thermoplastic starch with polypropylene or polyethylene and irradiation process.

Preparation of Thermoplastic Starch

Sago powder and water were weighed according to the set-up composition and mixed together. The mixture then heated and stirred until become gelatine at a temperature of 70^oC 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 and stirred rigorously until homogeneous. The homogeneous mixture was dried using an oven at 80^oC for 24 hours. The dried mixture will form like a crust and cut into smaller sizes using crusher.

Production of Degradable Plastic and Irradiation Process

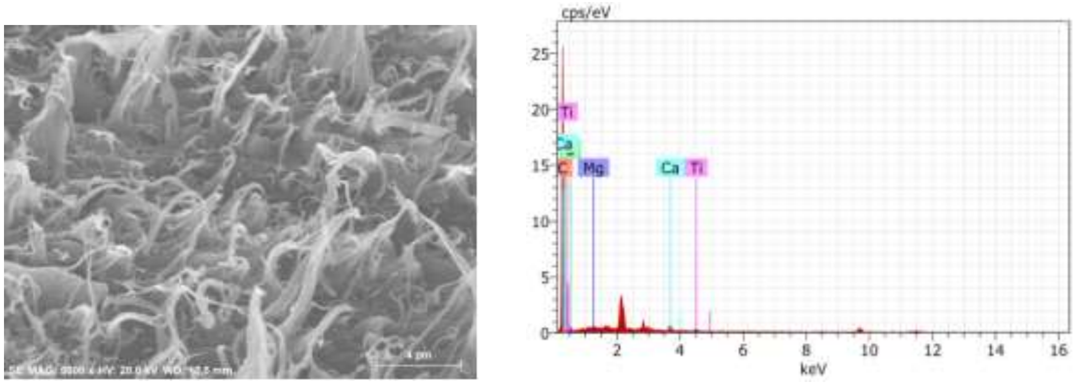
Thermoplastic starch that has become crusted was blended into a finer size to facilitate mixing. Polypropylene (PP) and Polyethylene (PE) was heated at 110^oC until melted and mix with thermoplastic starch until homogeny using Raw mill. The mixture was then chopped into smaller size in the crusher and then process to become plastic pellet using extruder. Plastic pellet was molded to become product for household purpose such as plate, bowl and vas using injection molding machine. Morphological and chemical analysis using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX) to surface morphology and for chemical elemental, meanwhile X-Ray Diffraction (XRD) to determine the crystallinity of thermoplastic starch. Irradiation was conducted at 5 kGy dose. Irradiation was done to improve mechanical and biodegradability of plastic which will be discussed elsewhere.

3. Results and Discussion

The thermoplastic starch was characterized by a combination of SEM-EDX. Scanning Electron Microscopy (SEM) is a type of electron microscope that produces images of samples by scanning the surface with a focused electron beam with magnification up to a certain scale. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. Energy Dispersive X-Ray (EDX) is used for chemical elemental analysis of materials. The characterization capability is largely due to the basic principle that each element has a unique atomic structure that enables a unique set of peaks on its electromagnetic emission spectrum (which is the principle of spectroscopy). X-Ray diffraction patterns of thermoplastic starch were analyzed using X-Ray Diffraction (XRD). X-Ray Diffraction (XRD) was performed to identify the crystallinity structure and determine what phases are present in the material as well as the concentration of constituent materials in degradable plastic.

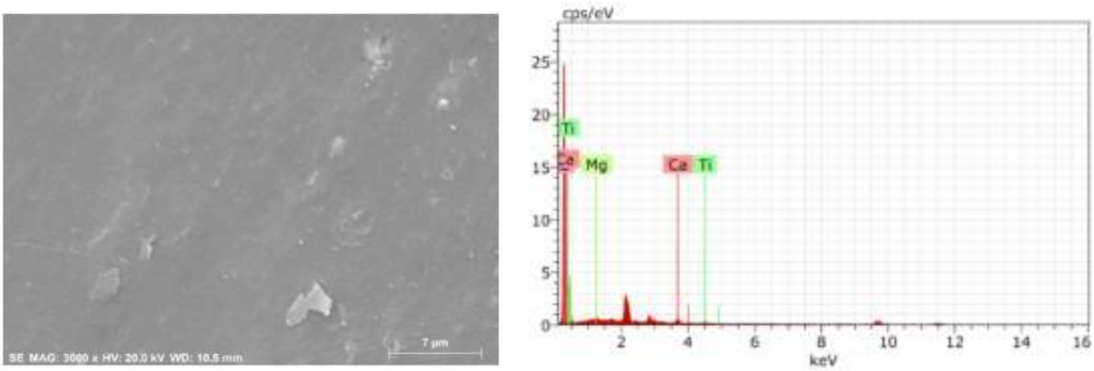
SEM-EDX Characterization Analysis

Degradable Plastic testing used the SEM-EDX test to analyze the shape and surface morphology, as well as the constituent composition of a material



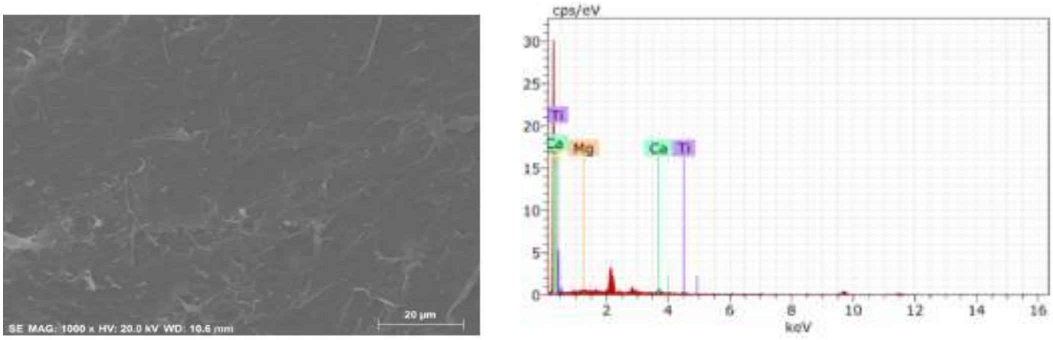
(a) (b)

Figure 1. Degradable Plastic Analysis at 5000x Magnification: a) SEM, b) EDX Spectrum



(a) (b)

Figure 2. Degradable Plastic Analysis at 3000x Magnification: a) SEM, b) EDX Spectrum



(a) (b)

Figure 3. Degradable Plastic Analysis at 1000x Magnification: a) SEM, b) EDX Spectrum

Figure 1 (a) at 5000x magnification clearly shows the presence of many material elements in the thermoplastic starch matrix that are visible throughout the plastic surface. From the spectrum analysis in Figure 1 (b), EDX results can identify the presence of chemical elements such as carbon, oxygen, magnesium, calcium, titanium, palladium, gold. Thus, these elements can be seen due to the thermoplastic starch made from sago which contains magnesium (iron), calcium and the presence of the main additive $CaCO_3$. From the analysis of other spectra, there is a very low content of elements such as palladium, titanium and gold. Meanwhile, the identified elements such as palladium, titanium and gold are likely to be heavy metal migrated from plastics.

In Figure 2 and Figure 3 (a) at 3000x and 1000 x magnification, the morphology of SEM analysis showed spots and inhomogeneous copolymer matrix. From the results of spectrum analysis in Figure 2 and Figure 3 (b), chemical elements such as carbon, magnesium, calcium and titanium were identified which look relatively small. Irradiation process did not influence the morphology of degradable plastic and not affected the constituent compounds; hence it is safe to be used. Eldi et al., (2011) used analyzing the EDX spectra and identified the main additives. Additives which influence the mechanical properties, such as calcium carbonate, talc, potassium chloride, silicon dioxide, magnetite, mica and wollastonite mineral, were easily identified in a qualitative way.

X-Ray Diffraction (XRD) Characterization Analysis

Degradable plastic was analysed by X-Ray diffraction pattern using XRD type Philips X'Pert-Pro X-Ray Diffractometer, operated at 40 Kv voltage and 30 mA current. The diffraction pattern was measured between 2ɵ = 9.970 to 89.970 with a scanning rate of 20^0.

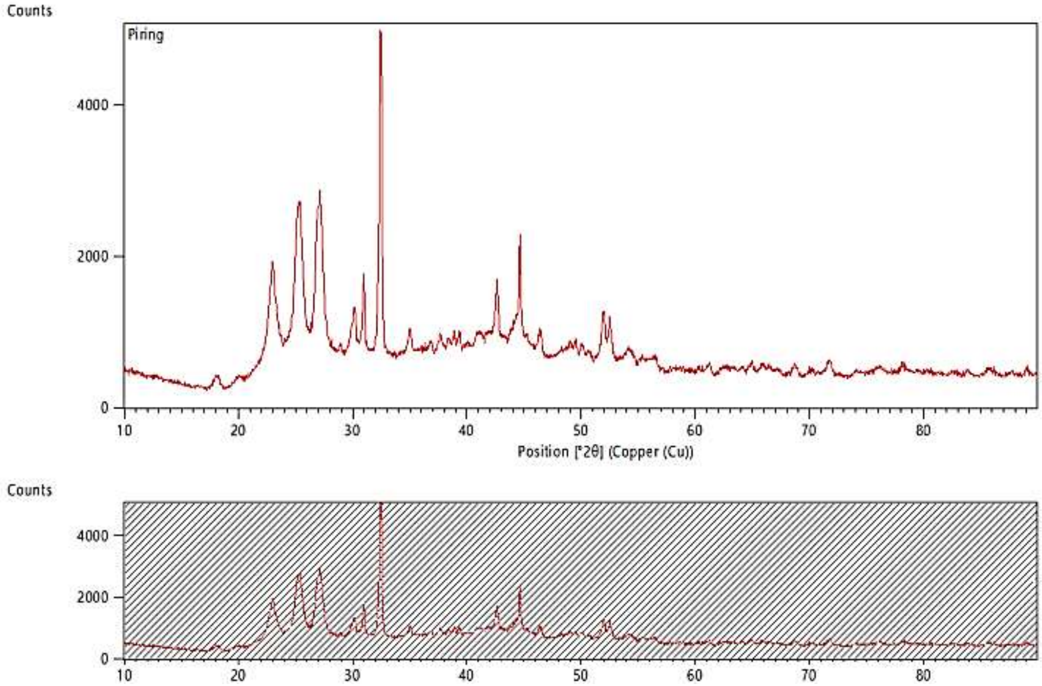


Figure 4. X-Ray Diffraction Analysis Results of Degradable Plastic

Figure 4 shows the resulting XRD pattern of thermoplastic starch. It can be seen that identical characteristics peak around 23.29, 26.20, 27.29, 33.39 and 46.08. The XRD spectra have peaks characterized by sharp curves and different intensities. At each angle. These XRD spectra peaks are referred to as crystalline regions (Engellita Maneking et al., 2020). From the diafactogram image obtained, it can be shown that degradable plastic was amorphous and crystalline. XRD analysis of degradable plastic has a low crystallinity value as seen at 26.8514^0.

4. Conclusions

X-Ray diffraction patterns of degradable plastic were analyzed using X-Ray Diffraction (XRD). X-Ray Diffraction (XRD) was performed to identify the crystallinity structure and determine what phases are present in the material as well as the concentration of constituent materials in thermoplastic starch. The SEM analysis of 5000x magnification showed the presence of many material elements in the thermoplastic starch matrix that are visible on the entire surface of the plastic. From the results of EDX analysis can be identified the presence of chemical elements such as carbon, oxygen, magnesium, calcium, titanium, palladium, gold, and carbon dioxide. Thus, these elements are seen due to the degradable plastic made from sago which contains magnesium (iron), calcium and the presence of the main additive $CaCO_3$. From the XRD analysis results obtained from thermoplastic starch, it can be shown that degradable plastic was amorphous and crystalline. XRD analysis of degaradable plastic has a low crystallinity value at 26.8514^0.

Acknowledgements

This research was conducted at the Chemical Engineering Laboratory, Faculty of Engineering, Malikussaleh University, Aceh. This research was funded by PNBP Malikussaleh University 2023 and DRTPM Ministry of Education, Culture, Research and Technology 2022.

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