

BIODEGRADABLE, MORPHOLOGY, AND THERMAL ANALYSIS ON THERMOPLASTIC SAGO (*Metroxylon Sagu Rottb.*) STARCH/POLYETHYLENE/POLYETHYLENE GRAFTED MALEATE ANHYDRATE

Riyanto¹, S. Hasibuan^{2,✉}, D.A. Tanjung², Z. Noer² and V. Sisca³

¹Department of Biology, Faculty of Saintek, Universitas Medan Area, Medan, Indonesia-20223

²Department of Agrotechnology, Faculty of Agriculture, Universitas Medan Area, Medan, Indonesia-20223

³Department of Biology/ STKIP YPM Bangko, Merangin Jambi, Indonesia-37313

✉Corresponding Author: syahbudin@staff.uma.ac.id

ABSTRACT

The purpose of this study was to examine the effect of adding polyethylene to thermoplastic sago starch in the presence of a coupling agent (polyethylene grafting maleate anhydrate) on the degradation rate, morphology, thermal gravimetry, and differential thermal analysis. The compound of thermoplastic sago starch/polyethylene/polyethylene grafting Maleic Anhydrous was carried out using the mixing method in an internal mixer. Based on the results of the study, there was a shift in the wave number in the O-H, C-H, and CH₂ groups in bioplastic composites. The surface morphology showed that the dispersed phase (Polyethylene) was evenly distributed over the entire surface of the matrix (sago starch). The gravimetric analysis of the thermal curves shows that the thermal degradation occurs in three stages: 201°C, 350°C, and 500°C. The addition of polyethylene can increase the thermal resistance from 350°C to 600°C. It can be seen that there are endothermic and exothermic peaks on the Thermal Differential Analysis curve. The addition of polyethylene resulted in a decrease in the rate of degradation in freshwater, seawater, and soil burial media.

Keywords: Bioplastic, Coupling Agent, Sago, Plasticiser, Polyethylene.

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INTRODUCTION

In 2025, it is estimated that the demand for bioplastics will increase to 1,800 tonnages according to the European Bioplastics, 2020. Related to the increasing market demand for these bioplastics, researchers continue to develop various bioplastic products, especially those made from starch.²⁻³ Starch-based bioplastics have advantages and disadvantages. Some of the advantages of starch are abundant in nature, renewable, and can be decomposed naturally in a short time. While the disadvantages are low tensile strength, stiffness, high water absorption ability, and low thermal resistance. Starch-based bioplastics have advantages and disadvantages. Some of the advantages of starch are abundant in nature, renewable, and can be decomposed naturally in a short time. While the disadvantages are low tensile strength, stiffness, high water absorption ability, and low thermal resistance. The addition of natural polymers (starch) with synthetic polymers is a solution to improve the quality of bioplastics, as in previous studies adding polyethylene, polypropylene, and others to natural polymers. tensile strength, elasticity, and thermal resistance can be increased and reduce water absorption.³⁻⁴ Fillers such as bentonite, chitosan, calcium carbonate, etc. can also be added to improve the mechanical properties of a material as reported in the previous studies.⁵ Modification of starch structure to increase elasticity has been carried out by previous researchers by adding plasticizers, such as Polyol, Ethylene Glycol, Glycerol, and others.⁶⁻⁷ The difference in polarity between the two polymers can be overcome by adding a compatibilizer, as a link between natural polymers (starch) and synthetic polymers (Polyethylene, Polypropylene, etc.).⁸⁻⁹ The purpose of this study was to examine the effect of adding polyethylene to thermoplastic sago starch in the presence of a coupling agent (polyethylene grafting maleate anhydrate) on the degradation rate, thermal gravimetry, and differential thermal analysis.

EXPERIMENTAL

Material and Methods

The material used in this research is sago starch from Indonesia. Polyethylene (LLDPE) produced by PT. Chandra Asri, Indonesia. Glycerol, Maleate Anhydride (MA), Benzoyl Peroxide (BPO), Preparation of bioplastic composites using the blending method in an internal mixer (Haake Polydrive Thermo).

Procedure

Thermoplastic Sago Starch (TPSS) is made by reacting sago starch and glycerol in a ratio of 65:35% by weight and aqua dest as a solvent as much as 250% by weight of the total mixture of sago starch and plasticizer. Preparation of Polyethylene Grafted Maleate Anhydride (LLDPE-g-MA) by reacting polyethylene, maleic anhydride, and benzoyl peroxide in a ratio of 88: 9: 3 % by weight. The concentration of LLDPE-g-MA used in this study was 10% by weight of TPSS. The TPSS/LLDPE/LLDPE-g-MA mixture was prepared in an internal mixer at a temperature of 130°C with various concentrations of 0, 10, 15, 20, 25, and 30% LLDPE.

RESULTS AND DISCUSSION

Fourier Transform Infra-Red (FTIR) Analysis

FTIR analysis is needed to see whether the resulting product forms a new group or only changes a wavenumber shift. In addition, it can support previous test results. The curve in Fig.-1 shows some changes in wave number due to the reaction between Thermoplastic Sago Flour (TPSS) and LLDPE assisted by LLPDE-g-MA such as detected by a widening peak with medium intensity with a wavenumber of 3265cm⁻¹ on TPSS to 3287 cm⁻¹ on the bioplastic curve were identified as H-Bonded. Furthermore, the peak with stretching vibration of the alkane group (C-H) with a small intensity shifted from 2922 cm⁻¹ in starch to 2914cm⁻¹.¹¹ The wavenumber of 1416 cm⁻¹ in starch which is changed to 1461cm⁻¹ is a CH₂ group by a bending vibration type with a small intensity peak in the bioplastic spectrum. While the functional groups that did not change were C-O groups a strong single bond with stretching vibration was observed at a wavenumber of 998 cm⁻¹. The peak with a small intensity as an aromatic group was at a wavenumber of 1647 cm⁻¹.¹² This wave number shift proves that there has been a reaction between thermoplastic sago starch and polyethylene with the help of a compatibilizer.

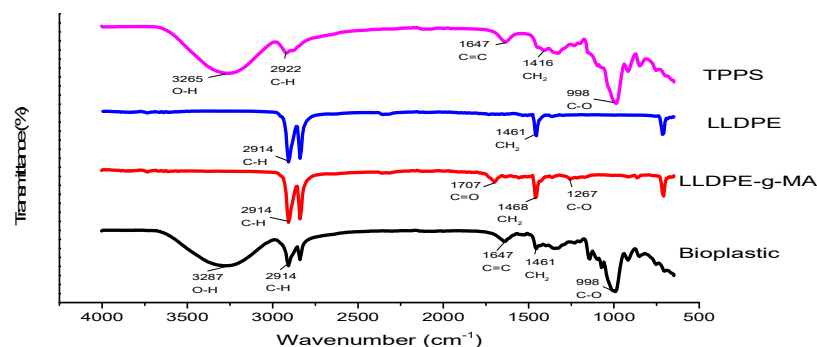


Fig.-1: FTIR Spectrum of TPSS, LLDPE, LLDPE-g-MA, and Bioplastics

Scanning Electron Microscopy (SEM) Analysis

Scanning Electron Microscopy (SEM) analysis was tested to study the surface morphology of thermoplastic sago with certainty before and after the addition of LLDPE. In this study, TPSS was used as the matrix, and LLPDE as the dispersed phase. Figure-2a. Is the surface morphology of TPSS (before the addition of LLDPE) with a magnification of 100x. The sample surface morphology is clean without any dispersed phase (white spots) on the matrix surface. While 2b and 2c are surface morphology of 20% and 30% LLPDE which shows white spots on black circles identified as LLDPE compounds that are evenly distributed throughout the matrix surface. This proves that LLDPE can react with TPSS with the help of a compatibilizer. The addition of LLDPE-g-MA into TPSS/LLDPE has a positive effect on decreasing the interfacial tension and the occurrence of good interfacial adhesion between LLDPE and TPSS. The same picture is also shown in the research before.^{4,12}

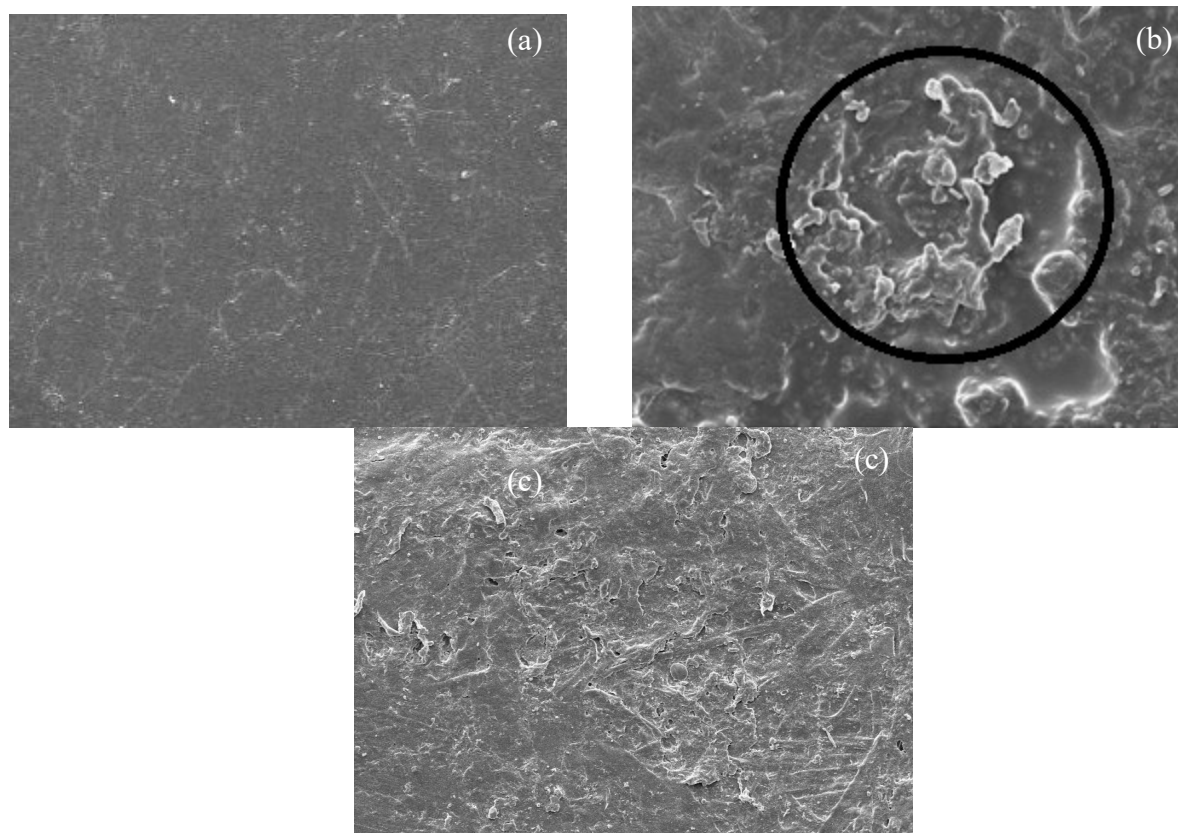


Fig.-2: SEM Image of TPSS/LLDPE/LLDPE-g-MA, (a). 0% LLDPE. (b), 20% LLDPE. (c), 30% LLDPE

Gravimetry Thermal Analysis (TGA)

The thermogravimetry analysis technique was used to determine the thermal decomposition and stability of the TPSS/LLDPE blend films. Samples were tested with concentrations of 70% TPSS, 30% LLDPE, and 10% LLDPE-g-MA (based on the weight of TPSS). The weight of the sample used for this thermal analysis is 7.733mg, with a speed of $10^{\circ}\text{C}/\text{min}$. TGA test results, thermal decomposition occurs in 3 stages (Fig.-3). The initial stage of thermal degradation occurs at a temperature of $0-201.1^{\circ}\text{C}$ with a mass loss of 17.1%. At this stage, there is evaporation or dehydration of water molecules into H_2 and O_2 gases at a temperature of 100°C with a mass loss of 6.36%. This means that the sample contains 6.36% moisture. In addition to water, glycerol also evaporates at this stage. The evaporation temperature of glycerol ranges from $125-290^{\circ}\text{C}$ to produce simpler compounds such as methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide, and hydrogen gas, referring to research before.¹³

In the second stage, thermal degradation occurs at a temperature of 350.8°C , informing the mass loss of 68.5%. In this second stage, there is the evaporation of the plasticizer compound (glycerol) which is the residue from the first stage, and the initial thermal decomposition of starch which occurs at a temperature of 300°C .¹⁴ At this stage, removal of hydrogen groups, decomposition, and depolymerization of starch carbon chains takes place. The third stage of thermal degradation occurs up to a temperature of 500.5°C with a mass loss of 90.8%. At this stage, the polyethylene begins to degrade at a temperature of 400°C to produce gas and hydrocarbon oil.¹⁵ The three stages of degradation that occurred, the trend showed significant mass loss occurred at a temperature of 320.4°C with a degradation speed of $1.085\text{mg}/\text{min}$ which was the degradation of starch as a matrix (the component with the largest amount). Based on the TGA curve analysis, the addition of LLDPE into thermoplastic sago starch can increase the thermal resistance from 350°C (TPSS thermal degradation temperature) referring to the results of research before¹⁶, to 600°C (Thermal degradation temperature of TPSS/LLDPE/LLDPE-g-MA blends). Thermal resistance properties are closely related to mechanical properties, the higher the thermal resistance of a

material, the higher its mechanical properties. This can be proven by increasing the tensile strength after adding LLDPE.¹⁰

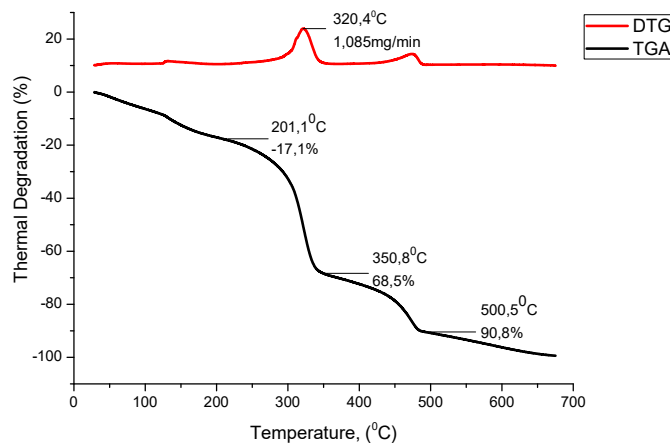


Fig.-3: TGA Curve of 70% TPSS,30% LLDPE, and LLDPE-g-MA

Analisa Differensial Thermal (DTA)

The curve provides information that an endothermic process has occurred, where the sample temperature is lower than the reference temperature with a marked peak pointing downwards at a temperature of 133.0°C (Fig.-4). In this event, the sample absorbs heat for the thermal degradation process of water and glycerol molecules with a DTA value of -18.51 uV. In addition, at the end of the curve, it shows a sharp peak pointing upwards at a temperature of 489.8°C with a DTA value of 11.88 uV. This indicates that the thermal degradation undergoes an exothermic process where the sample releases heat in the decomposition process of Polyethylene.¹⁴⁻¹⁵

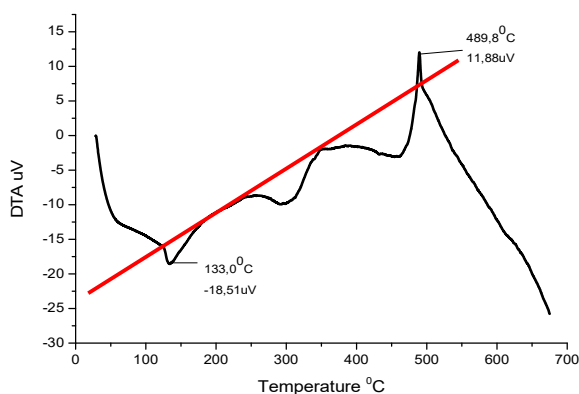


Fig.-4: DTA curve of 70% TPSS,30% LLDPE dan 10% LLDPE-g-MA

Degradation with Freshwater Media

The degradation test was carried out to see the plasticization ability of sago starch with glycerol to form gelatin which has been bound by polyethylene with the help of a degraded compatibilizer on various media. The degradation mechanism in freshwater media is that water molecules enter the pores of the bioplastic composite polymer network and try to break the bond between TPSS and LLDPE. Furthermore, water molecules will degrade the bond between sago starch and glycerol as previously reported.¹⁷ The speed of water's ability to break the bonds between glycerol and plasticized sago starch and polyethylene was calculated as the length of the degradation time. In this degradation test, the authors only focus on the degradation that occurs in TPSS, because LLDPE cannot be degraded within the time specified in this study. Table-1 can be analyzed that TPSS (0% LLDPE) is completely degraded on the 150th day. However, after the addition of various concentrations of LLDPE, the mixture experienced a

decrease in the rate of degradation as the concentration of LLDPE increased. At 10% LLDPE concentration there has been a mass loss of 81% or about 19% which has not been decomposed by water, 9% of which comes from sago starch. While at a concentration of 30% LLDPE has decomposed 63% or there are about 37% that have not been decomposed, of which 7% comes from sago starch. When compared with the degradation rate of TPSS (30% LLDPE), If the mass loss rate is observed from time to time in the table, there is no significant mass loss at any one time, which means that TPSS and LLDPE can react with the help of a compatibilizer to form an evenly distributed polymer network (Homogeneous) on the matrix. The addition of LLDPE to thermoplastic sago starch had a negative effect on the rate of degradation, where the mixture of TPSS/LLDPE/LLDPE-g-MA had not completely decomposed on day 150. This result was in accordance with previous studies.¹⁷

Table-1: The Degradation Test Result with Freshwater Media

LLDPE %	Days to-						
	10	30	60	90	120	150	180
0	49	56	65	78	95	100	100
10	46	64	70	71	74	78	81
15	43	57	60	63	66	70	72
20	40	53	56	59	60	64	67
25	38	48	51	54	58	61	65
30	36	42	44	47	51	58	63

Degradation with Seawater Media

Seawater used as a medium in degrading the TPSS/LLDPE/LLDPE-g-MA mixture comes from the seaside of Belawan Harbor, Medan-Indonesia. Based on Table-2, the ability of the rate of degradation decreased as the concentration of LLDPE increased. The sample can decompose up to 72% on days -180 at a concentration of 10% LLDPE. It is assumed that there is about 28% of the remaining samples have not been decomposed, 18% coming from sago starch. Meanwhile, at a concentration of 30% LLDPE, the sample decomposed up to 68% or about 32% which had not been degraded, of which 2% came from sago starch. When compared with thermoplastic sago starch (0% LLDPE) which can be completely decomposed until the 90th day, the addition of LLDPE into TPSS has a negative effect on the rate of degradation of bioplastic composites.²

Table-2: The Degradation Result from Seawater Media

LLDPE %	Days to-						
	10	30	60	90	120	150	180
0	57	63	79	94	100	100	100
10	47	56	61	66	68	69	72
15	43	49	52	54	55	57	59
20	38	49	51	54	57	59	63
25	33	37	41	45	55	63	67
30	35	39	44	48	53	59	68

Degradation with Soil burial Media

Soil burial media used in degrading bioplastic composites is compost soil. Table-3 shows that the sample's ability to degrade in soil decreased with increasing LLDPE concentration. The sample decomposed up to 87% at a concentration of 10% LLDPE until day 180. There was about 13% undecomposed in the soil, of which 3% came from sago starch. Meanwhile, in a mixture of 30% LLDPE concentration, the sample can be decomposed up to 63%. Where, of the remaining 37% of the sample that has not been decomposed, 7% comes from sago starch. When compared with thermoplastic degradation of sago starch (0% LLDPE), the rate of degradation to complete decomposition in the soil is about 80 days. This means that the addition of LLDPE into thermoplastic sago starch has a negative effect on the rate of degradation of the bioplastic composite mixture.²

Table-3: The Degradation Test Result with Soil Burial Media

LLDPE %	Days to-						
	10	30	60	90	120	150	180
0	46	71	96	100	100	100	100

10	34	50	66	73	75	81	87
15	41	47	55	69	71	78	83
20	43	46	49	54	59	72	73
25	32	36	36	44	50	56	61
30	35	39	42	47	54	57	63

CONCLUSION

The TPSS/LLDPE/LLDPE-g-MA blends can be made through the blending method in the internal mixer. Degradation in 3 environmental conditions such as freshwater, seawater, and soil showed a decrease in the rate of degradation when compared without the addition of LLDPE. Polyethylene can be evenly dispersed onto the surface of the TPSS matrix. The addition of LLDPE in TPSS has a positive effect on increasing the thermal resistance of bioplastic composites, Thermal degradation occurs in 3 stages.

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