

Characterization of Biodegradable Composites from Polypropylene, Polypropylene Grafted Maleic Anhydride, and Durian Seed Starch

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Abstract. The characterization of biodegradable composite from durian seed starch that is mixed polypropylene, and polypropylene grafted maleic anhydride has been done. The stages of this preparation were, the first had prepared durian seed starch, the second had the process of grafting maleic anhydride into polypropylene and the third had made of composite with the composition of PP:PP-g-MA: DSS (7:0.5:0.2); (7:0.5:0.3); (7:0.5:0.4); (7:0.5:0.5); (7:0.5:0.6) (w/w). The biodegradable composites obtained were characterized by tensile strength, surface morphology analysis by SEM, differential thermal analysis (DTA), analysis in nature with the ability to decompose biodegradable test, and functional groups analysis by FTIR spectroscopy. The results showed that the biodegradable composites have the best properties in the ratio of PP:PP-g-MA: DSS was (7:0.5:0.5) (w/w) with the test results of tensile stress is 12.556 N/m², and the elongation is 8.600%, the images on a few flat surfaces and improved homogeneity, temperature change, and strong group interactions as well as having good biodegradable properties.

Keywords: Durian Seed Starch; PP-g-MA; Grafted; Biodegradable Composite

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1 Introduction

Currently, there are many types of materials used to package food including various types of plastic, paper, glass, fibreboard, and aluminum (Syamsir, 2008). Broadly speaking, plastics can be classified into two major groups, namely thermoplastic and thermoset plastics. Thermoplastics can be easily reshaped and processed into other shapes. In contrast, the thermoset has hardened, it cannot be re-softened. The most commonly used plastic in everyday life is thermoplastic, along with technological developments, the demand for plastic continues to increase (Amin, S, 2011).

Durian (*Durio zibethinus Murr*) is an annual tree, leaf drop does not depend on the season but there is a certain time to grow new leaves that occurs after the fruiting period is complete.

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Durian seeds have a fairly high carbohydrate content of around 42.1% so they have the potential as an alternative to food ingredients, as fillers or binders.

Various studies have been carried out that aim to produce a composite material that is biodegradable as was done by (Clemons, 2003) who made a composite material by combining polypropylene plastic material with cellulose mixed and then produced in two ways, namely press molding with a matrix material injection system polypropylene (PP) to produce a biodegradable composite.

Cellulose was chosen as filler because of its good heat stability and high purity. The results of the compression molding and injection method showed a decrease in elasticity properties with an increase in the percentage of cellulose. In the results of the matrix injection method, better results were obtained on the surface test, because the arrangement of cellulose was more orderly than in the compression molding method.

This research is expected to provide information on the characteristics of the biodegradable composite of Durian Seed Starch (DSS), Polypropylene (PP), and polypropylene grafted (PP-g-MA) Maleic Anhydride and find ways to reduce durian seed waste and increase the added value of durian seeds and also as an alternative material that can be used for the manufacture of biodegradable composites.

2 Materials and Methods

2.1 Equipments

In this study, the equipments used were the Liebig Cooler, hot plate stirrer, magnetic stirrer, volumetric flask, thermometer, blender, sieve, beaker glass, analytical balance, measuring cup, oven, spatula, hot press, internal mixer, filter paper, vacuum pump, a set of the scanning electron microscope (SEM), Universal Testing Machine (UTM), differential thermal analysis (DTA), and fourier transform infrared (FTIR) spectroscopy.

2.2 Materials

The materials used were durian seeds, isotactic polypropylene, 97% of maleic anhydride, 98% of dikumil peroxide, 99% of methanol, 99.8% of xylene, and 99.8% of acetone.

2.3 Preparation of Durian Seed Starch

The durian seeds that have been separated from the flesh were washed thoroughly, dried in the sun to remove the water, then peeled the epidermis, sliced thinly, and then dried, blended until smooth and dried in the sun to reduce the moisture content in the starch.

2.4 Manufacturing of Polypropylene Grafted Maleic Anhydride

As much as 95%: 3%: 2% of polypropylene, dicumyl peroxide, and maleic anhydride (w/w) were weighed and mixed using an internal mixer at 165° C and will produce polypropylene that has been grafted with maleic anhydride (PP-g-MA).

2.5 PP-g-MA Purification Process

As much as 30 g of PP-g-MA was weighed and then put into a bottom flask. Added 200 mL of xylene and refluxed until dissolved. Then precipitated with 150 ml of acetone and filtered with filter paper connected to a vacuum pump. The precipitate was washed with methanol repeatedly. The precipitate was dried in an oven at $\pm 120^{\circ}\text{C}$ for 6 hours.

2.6 Pressing Process by Varying The Weight of Durian Seed Starch

Durian seed starch was weighed with various 0.2 g, 0.3 g, 0.4 g, 0.5 g, and 0.6 g, respectively. Then PP-g-MA was also carried out with the weight variation of PP-g-MA being: 7 g. Sample 1 was mixed into a beaker glass, dried in a blender until smooth then poured into a mold, and pressed on a hot press at 160°C for 30 minutes. The result was cooled to room temperature and removed from the mold. Then the same procedure was carried out for the other samples.

3 RESULT AND DISCUSSION

3.1 Characterization Based on Analysis of Mechanical Properties with Tensile and Elongation Tests

Analysis of tensile strength and elongation of the biodegradable composite of durian seed starch using polypropylene, polypropylene grafted maleic anhydride with various composition and mass variations presented in Table 1 and the graph of tensile and elongation indicated in figures 1 and 2.

Table 1. The calculation results of tensile strength and elongation of biodegradable composites

Ratio (Composition: Starch)	Tensile Strength (N/m ²)	Elongation (%)
Polypropylene	58.618	10.296
PP: PP-g-MA: DSS (7: 0.5: 0.2)	3.885	3.820
PP: PP-g-MA: DSS (7: 0.5: 0.3)	3.846	3.200
PP: PP-g-MA: DSS (7: 0.5: 0.4)	8.878	7.800
PP: PP-g-MA: DSS (7: 0.5: 0.5)	12.556	8.600
PP: PP-g-MA: DSS (7: 0.5: 0.6)	7.377	7.160

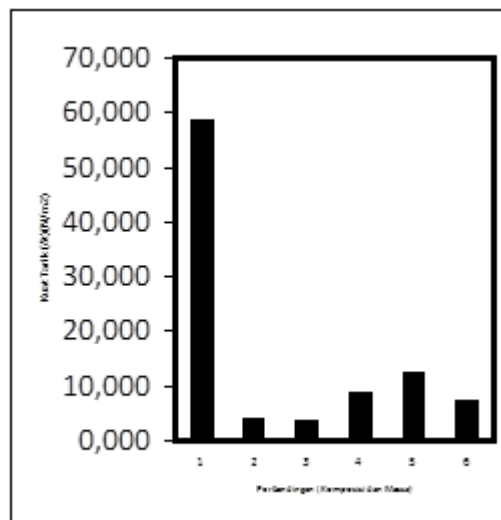


Figure 1. The tensile strength graph of biodegradable composite

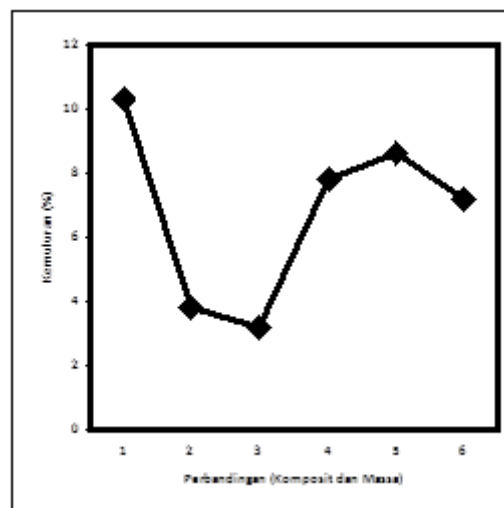


Figure 2. The elongation graph of biodegradable composite

Based on the calculation of the tensile strength and elongation of the biodegradable composite, the variation in the ratio between PP:PP-g-MA: DSS (7:0,5:0,5) g has the maximum mechanical properties of 12.556 N/m². In contrast, the maximum elongation value in the PP:PP-g-MA: DSS (7:0,5:0,5) g was 8.600%. Based on the calculation of tensile strength and elongation above, it can be concluded that the tensile strength does not depend on the increase in the added durian seed filler.

3.2 Differential Thermal Analysis (DTA)

Figure 3. a is the result of the DTA analysis graph of durian seed starch show there are 3 critical temperature peaks, such as the first critical temperature, DSS changed in thermal properties at 80°C, at the second critical temperature, there was also a thermal change at 275°C. , and at the third critical temperature, DSS had been burned at 380°C.

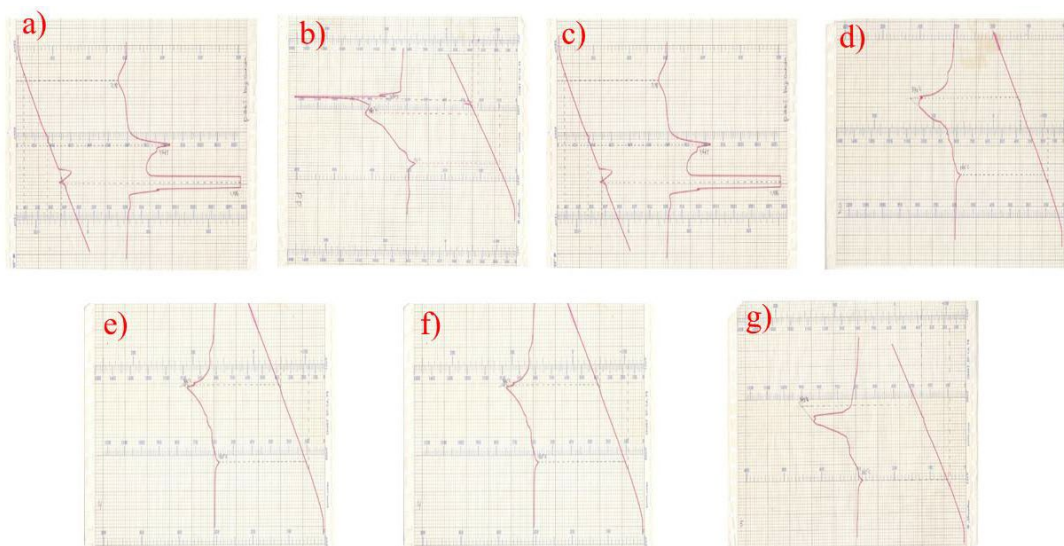


Figure 3. The DTA graphs of (a) DSS, (b) PP, (c) PP-g-MA (7: 0.5: 0.2), (d) PP-g-MA (7: 0.5: 0.3), (e) PP-g-MA (7: 0.5: 0.4), (f) PP-g-MA (7: 0.5: 0.5), and (g) PP-g-MA (7: 0.5: 0.6) (w/w)

Figure 3. b is the result of the DTA PP analysis graph shows that there are 3 critical temperature peaks, namely at the first critical temperature, PP changed in thermal properties at a temperature of 170°C, at the second critical temperature, there was also an increasing thermal at 340°C, at the third critical temperature, PP had been burned at 380°C.

Figure 3. c is the DTA graph of PP: PP-g-MA: DSS (7: 0.5: 0.2) shows that there are only 2 critical temperature peaks, namely at the first critical temperature, PP: PP-g-MA: DSS (7:0.5:0.2) changed in thermal properties 160°C, at the third critical temperature PP:PP-g-MA: DSS (7:0.5:0.2) burned at 375°C. While PP: PP-g-MA: DSS (7:0.5:0.2), at the second critical temperature there was no critical temperature because if PP and DSS were mixed with PP-g-MA, these three ingredients interact, this is evidenced by the appearance of 2 peaks in PP: PP-g-MA: durian seed flour ((7:0.5:0.2) so at 375°C, PP: PP-g-MA: DSS (7:0.5:0.2) immediately burned.

Figure 3.d is the DTA graph of PP: PP-g-MA: DSS (7:0.5:0,3) shows that there are only 2 critical temperature peaks, namely at the first critical temperature, PP:PP-g-MA: DSS (7:0.5:0.3) changed its thermal properties at 160°C, at the third critical temperature PP:PP-g-MA: DSS (7:0.5:0.3) burned at 370°C. While PP: PP-g-MA: DSS (7:0.5:0.3) at the second critical temperature there is no critical temperature appears because if PP and DSS when mixed with PP-g-MA, these three ingredients interact, this is evidenced by the appearance of 2 peaks in PP: PP-g- MA: DSS (7:0.5:0.3) so at 370°C, PP:PP-g-MA: DSS (7:0.5:0.3) immediately burned.

Figure 3. e is the DTA graph of PP: PP-g-MA: DSS (7:0.5:0.4) shows that there are only 2 critical temperature peaks, namely at the first critical temperature, PP: PP-g-MA: DSS (7:0.5:0.4) changed in thermal properties at 160°C, at the third critical temperature PP: PP-g-MA: DSS (7:0.5:0.4) burned at 375°C. While PP: PP-g-MA: DSS (7:0.5:0.4), at the second critical temperature, there is no critical temperature appears because if PP and DSS were mixed and added with PP-g-MA then these three ingredients will interact, this is evidenced by the appearance of 2 peaks in PP: PP-g-MA: DSS (7:0.5:0.4) so at 375°C, PP: PP-g-MA: DSS (7:0.5:0.4) immediately burned.

Figure 3. f is the DTA graph of PP: PP-g-MA: DSS (7:0.5: 0.5) shows that there are only 2 critical temperature peaks, namely at the first critical temperature, PP:PP-g-MA: DSS (7:0.5:0.5) changed in thermal properties at 160°C, at the third critical temperature PP: PP-g-MA: DSS (7:0.5:0.5) burned at 370°C. While PP: PP-g-MA: DSS (7:0.5:0.5) at the second critical temperature nothing appears The critical temperature is because PP and DSS were mixed and added with PP-g-MA then these three ingredients will interact, this is evidenced by the appearance of 2 peaks in PP: PP-g-MA: DSS (7:0.5:0.5) so at 370°C, PP: PP-g-MA: DSS (7:0.5:0.5) immediately burned.

Figure 3. g is the DTA graph of PP: PP-g-MA: DSS (7:0.5:0.6) shows that there are only 2 critical temperature peaks, namely at the first critical temperature, PP:PP-g-MA: DSS (7:0.5:0.6) changed in thermal properties at 160°C, at the third critical temperature PP: PP-g-MA: DSS (7:0.5:0.6) burned at 375°C. While PP: PP-g-MA: DSS (7:0.5:0.6) at the second critical temperature nothing appears The critical temperature is because PP and DSS were mixed and added with PP-g-MA then these three ingredients will interact, this is evidenced by the appearance of 2 peaks in PP: PP-g-MA: DSS (7:0.5:0.6) so at 375°C , PP: PP-g-MA: DSS (7:0.5:0.6) immediately burned. The DTA data results of biodegraded composite specimens indicated in Table 2.

Table 2. The DTA data results of biodegraded composite specimens

No	Sample	Critical temperature (°C)		
		I	II	III
1	DSS	80	275	380
2	Polypropylene	170	340	380
3	PP: PP-g-MA: DSS (7: 0.5: 0.2)	160	-	375
4	PP: PP-g-MA: DSS (7: 0.5: 0.3)	160	-	370
5	PP: PP-g-MA: DSS (7: 0.5: 0.4)	160	-	375
6	PP: PP-g-MA: DSS (7: 0.5: 0.5)			370
7	PP: PP-g-MA: DSS (7: 0.5: 0.6)	160	-	375

Table 2 shows that PP and DSS affect each other's thermal properties. This is evidenced by the interaction at the second critical temperature, if PP has been mixed with PP-g-MA and DSS so t at the third critical temperature, PP: PP-g-MA: DSS has been burned. PP and DSS do not react chemically but occur thermally.

3.3 Scanning Electron Microscopy (SEM) Analysis



Figure 4. SEM morphology of biodegraded composites with ratio of PP:PP-g-MA: DSS (7:0.5:0.5) before being buried in garbage soil with 2000x magnification

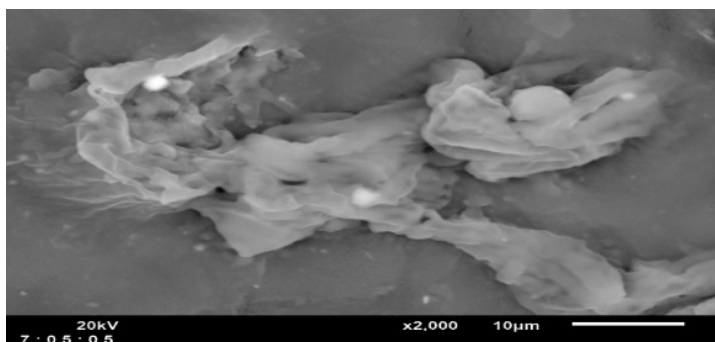


Figure 5. SEM morphology of biodegraded composites with the ratio of PP:PP-g-MA: DSS (7:0.5:0.5) after being buried in waste soil with 2000x magnification

Figure 4 shows that the surface is uneven and the presence of small granule grains indicates that the grain is DSS which can not interact well with polypropylene. In addition, figure 11 shows that the surface is slightly flat and there are few small grains, this is because the composite has been buried in the waste soil and can interact well.

3.4 Analysis of its ability to decompose in nature with biodegradation tests

Specimen planting was carried out in several types of soils, such as garbage soil, garden soil, and sandy soil for 30 days with observations every 10 days. Planting biodegradable composite specimens on various types of soil aims to see the level of biodegradation in nature. The highest decrease of mass (%) in biodegraded composite specimens was in garbage soil.

Table 3. The degradation of mass (%) biodegraded composite specimens after being buried in the soil.

No	Sample	Garbage Soil			Garden Soil			Sandy Land		
		10	20	30	10	20	30	10	20	30
1	PP: PP-g-MA: DSS (7: 0.5: 0.2)	0.55	0.51	0.47	0.50	0.48	0.46	0.47	0.47	0.47
2	PP: PP-g-MA: DSS (7: 0.5: 0.3)	0.70	0.70	0.70	0.71	0.66	0.65	0.62	0.62	0.62
3	PP: PP-g-MA: DSS (7: 0.5: 0.4)	0.60	0.57	0.55	0.65	0.60	0.61	0.65	0.65	0.65
4	PP: PP-g-MA: DSS (7: 0.5: 0.5)	0.75	0.71	0.69	0.70	0.65	0.65	0.61	0.60	0.60
5	PP: PP-g-MA: DSS (7: 0.5: 0.6)	0.65	0.65	0.63	0.60	0.58	0.55	0.60	0.58	0.57

3.5 Fourier Transform-Infrared (FT-IR) Spectroscopy

The analysis using the infrared spectrum was carried out to determine changes in functional groups that identified chemical interactions between one component and another. The wavenumber of PP: PP-g-MA: DSS (7: 0.5: 0.5) presented in Table 4.

Table 4. The wavenumber of PP: PP-g-MA: DSS (7:0.5:0.5) before being buried in the soil

Sample	Wavenumber (cm ⁻¹)	Functional Group
PP: PP-g-MA: SDS (7: 0.5: 0.5)	3500-3200	O-H
	1840-1810	C=O
	3193.32	Aromatic C-H
	2914.0	Aliphatic C-H
	2722.16	C-H-O
	1711.40	C=O
	1459.0	CH ₃
	1376.0	CH ₂
	1219.33	C-O
	1102.30	C-O
1044.33	C-O	
840.10	Aromatic C-H	

Table 5. The wavenumber of PP: PP-g-MA: DSS (7:0.5:0.5) after being buried in the soil

Sample	Wavenumber (cm ⁻¹)	Functional Group
PP: PP-g-MA: SDS (7: 0.5: 0.5)	3194.46	Aromatic C-H
	2914.0	Aliphatic C-H
	2838.0	Aliphatic C-H
	2722.33	C-H-O
	1713.52	C=O
	1456.0	CH ₂
	1376.0	CH ₃
	1219.45	C-O
	1102.41	C-O
	1044.43	C-O
	Aromatic C-H	840.22

Table 4 shows the FTIR of a mixture of PP: PP-g-MA (7:0.5:0.5) with an absorption peak of 3500 to 3200 cm⁻¹, which indicated the presence of OH band is thought to be derived from starch. The band at 1840 to 1810 cm⁻¹, which assigned the C=O bond. The band at 2722.16 cm⁻¹, which showed the presence of the C-H-O bond, which meant the presence of aldehydes.

Table 5 shows the band at 2838.0 cm⁻¹, which indicated the aliphatic -CH which is thought to be from polypropylene, the band at 1713.52 cm⁻¹, which showed C=O bond from the ester produced even though it is only small. There has been an esterification reaction between maleic anhydride and the OH group of the starch.

4 Conclusion

The biodegradable composite with a ratio of PP:PP-g-MA: DSS (7:0.5:0.5) had the best physical and chemical properties compared to the biodegradable composites with different composition and mass variations. This is evidenced by the mechanical properties obtained a high tensile strength stress value of 12.556 N/m², from the analysis of its ability to decompose in nature with biodegradable tests show the percentage rate of biodegradation of the biodegradable composite was the highest, namely 5% reduction in mass in garbage soil. In addition, the morphological analysis obtained showed a slightly flat mixture shape so that the composite can interact well, the DTA analysis shows that the thermal properties of PP and DSS, influence each other or improve their thermal properties, this is evidenced by the interaction between PP and DSS. Also the FT-IR analysis shows that the band at 2722.33 cm⁻¹, which assigned the C-H-O bond, the band at 1713.52 cm⁻¹, which showed the C=O bond, and the

bands at 1219.45 cm^{-1} ; 1102.41 cm^{-1} , and 1044.43 cm^{-1} , which indicated the C-O bonds, and the durian seed waste can be used for the manufacture of biodegradable composites.

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