PROGRESS IN APPLIED SCIENCE AND TECHNOLOGY
Faculty of Science and Technology
Rajamangala University of Technology Thanyaburi
Vol.11 No.1 (2021): xx–xx
ISSN (Print): 2730-3012
ISSN (Online): 2730-3020
https://ph02.tci-thaijo.org/index.php/past

Received 31st January 2021,
Revised 27th February 2021,
Accepted 02nd March 2021

DOI: 10.14456/x0xx00000x

Study on Binary Low-Density Polyethylene (LDPE)/ Thermoplastic Sago Starch (TPS) Blend Composites

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Abstract

Composites with LDPE/TPS have been prepared using different filler loading (TPS), two separate compatibilizers, and additionally maleic anhydride (MA) and dibutyl maleate (DM) using a melt extrusion and an injection molding. Composites are tested for melting flow behavior, static mechanical features (tensile, bending, and Izod impact test), phase morphology, thermal behaviors (DSC and TGA/DTG), and biodegradability of LDPE/TPS (LPTS). As a result, the inclusion of compatibilizers in LPTS has led to significant improvements in melt flow index (MFI) and mechanical properties. Besides, DM to the LPTS (LPTSDM) composite gives rise to excellent dispersion of starch in the matrix and improved features compared to other composites that indicate homogeneity. Moreover, phase morphology, DSC, thermal stability, and biodegradability were performed for various LPTS samples. Also, the water absorption of the LPTS samples was reduced by the inclusion of compatibilizers.

Keywords: Sago starch, LDPE, compatibilizers, mechanical testing, morphology, thermal properties

1. Introduction

In recent decades, the use of plastic has steadily increased, and it has become a new component in many applications, such as newspaper, aluminum, and steel, replacing the little traditional textures. Modern packaging industries depend on plastics, a product derived from petrochemical industries such as polypropylene and polyethylene, as polymeric materials currently in use. Plastic materials have gained wide use in many applications due to their strength, lightweight, easy process, good barrier properties to oxygen, and energy-efficient (1, 2). However, these plastics have vary low water vapor transmission rates and are non-biodegradable and therefore eviromental pollution, which can lead to serious environmental problems. One of the least guaranteed alternatives to these plastics is blending with natural biodegradable polymers. The rationale behind this is that the inclusion of a sufficient amount of biodegradable material metabolized by microorganisms leads to degradation of the matrix, which will accelerate the breakdown of plastics (3).

Ecofriendly plastics such as PLA, PCL, PVA, and PEG are not broadly used, as these polymers are extra costly than PE or PP, which are usually used for wrapping appeals (4, 5). New mechanisns for the production and processing of synthetic plymers and nature polymers should be attractive alternatives to reduce the cost of biodegradable polymers in the market. LDPE blends with cheap natural biopolymers such as starch (6, 7) or natural fibers (8, 9) to make them eco-friendly and degradable. Starch will quicken the invasion of microorganisms in LDPE. Biodegradation happens at what time microorganisms like bacteria and fungi rotten into polymers under gaseous and anaerobic conditions. Natural products such as carbon dioxide and methane are obtained from the deterioration procedure. Thus, biological improvement can be described as the change of polymer components by microorganisms into CO^2/CH^4, bacterial cellular elements, and various by-products (10).

Starch is a cheap, renewable, fully biodegradable natural ingredient (11), and agricultural resources are found in abundance in rich countries like Malaysia. It consists of a natural polymer comprised of 1-4-α-D glucopyranosyl (12) units and a blend of linear and pronged elements. The linear element amylose, a tiny element that usually comprises 20% to 30%, has hundreds of thousands of molecular weights and is a linear polymer due to its helix-like shape (13). The pronged element, amylopectin, is the key ingredient, with millions of molecular weight. The average chain length of amylopectin is 20–30 glucose units, and the branching in amylopectin occurs at C-6 of the glucopyranosyl units (14). In Malaysia, there is

an abundance of sago starch, which is cultivated from the pith sago. Sago starch, made in a few white, brown or pink granules from various genera dates, is elementary used in foodstuffs, pharmaceuticals, paper, textiles, and plywood stabilizers for small white, pink or brown granular foods (15). This starch marks the location of a new use thermoplastics biodegradable filler sago. However, incompatibility and poor interfacial adhesion lead to poor mechanical properties due to polarity and differences in the hydrophilicity of these two phases, synthetic polymers and starch. However, these difficulties can be developed using a compatibilizer that can react with the hydroxyl group of starch and form hydrogen bonds or covalent bonds with man-made polymers. Polyolefin-based polymers with functional groups such as carboxylic acids, anhydrides, epoxies have been shown to react with the hydroxyl group of starch to form miscible polymers (7, 16). Maleic anhydride (MA) is one of the most broadly used vinyl monomers for poly-olefin graft modification (17) because the high polar MA working group is major suitable for starch. Dibutyl maleate (DM) has been chosen because of its low volatility and low toxicity compared to MA. To date, many studies have been done to improve the compatibility of starch changes such as starch and the combination of polyethylene (18-20). However, there is some evidence in studies about the use and compatibility of MA and DM in low-density polyethylene filled with starch. The present effort's key purpose is to examine the influence of filler concentrations and compatibilizers on the physicomechanical properties, morphological structure, thermal and biodegradable features of LPTS composites.

2. Experiment

2.1 Raw materials

LDPE was used as a matrix driven from Petlin Polyethylene (Malaysia) Sdn. Bhd. The manufacturers calculated its MFI and density as 3.29 g/10 min (190°C/2.16 kg) and 0.923 g/cm^3, correspondingly. In this experiment, the sago starch used as a filler was an edible biopolymer. It was provided by a local dealer, G-Far Sago Keropok Enterprise, Johor, Malaysia. Percent moisture was 11 – 13%, and its starch value is above 85%. Maleic anhydride (Polybond 3200) compatibilizer was purchased from MTBE (Malaysia) Sdn. Bhd. and dibutyl maleate compatibilizer was laboratory reagent grade. Dicumyl peroxide (DCP) is achieved from Malaysia's Sigma Aldrich chemical Inc., which is dissolved in absolute ethanol and recrystallized twice, sieving the solution when heated and cooled in water. Reagent grade glycerol ($C_3H_8O_3$) was found from Sigma Aldrich Chemical Inc., Malaysia.

2.2 Procedures

2.2.1 Procedure of thermoplastic sago starch (TPS)

First, the sago starch was dried in an oven at 60°C for 24 hours to remove storage moisture. TPS was prepared by premixing sago starch in granular form with 30 wt% liquid glycerol and stirring until homogeneous (21). The suspension order was then released overnight to permit the swelling function. The mixture was considered when the starch was completely covered with liquid glycerol after mixing. After the process, the mixture was mixed for five minutes at a rotor speed of 70 rpm, at a barrel temperature of 130°C-130°C-140°C-140°C using a co-rotating twin-screw extruder (Model: TSE 20, GmbH & Co. KG, Germany). The extruder samples were reduced in size using a blender/grinder.

2.2.2 Preparation of LDPE/TPS (LPTS) composites

TPS was melt-blended with LDPE in a twin-screw extruder (Model: TSE 20, GmbH & Co. KG, Germany). Blending was done from the mixing feeder at 160°C-160°C-150°C-150°C and 80 rpm for 10 min (22). LDPE was first added to the mixing chamber, and then TPS was applied 3 minutes after mixing. Thermoplastic sago starch loadings ranged from 5, 10, 15, 20 to 30 wt%. For composites, a solution of MA or DM compatibilizer and DCP (0.2 wt%) was added to LPTS, the amount of MA or DM was fixed by the weight of LDPE at 3 wt%. The composites were prepared with five different weight percentages of thermoplastic sago starch and the amount of LDPE without or with compatibilizers. The formulas for the arranged composites are registered in Table 1. The extruded components were cooled and then palletized by a pelletizer. The resulting mixture was then injected molded using injection molding (Toyo, model: Si180iii-E200, Japan). Barrel temperatures and clamps for each blend and their combination were similarly fixed at 170°C and 180T.

Table 1 Compositions of LDPE/TPS (LPTS) composites prepared.

Samples	LDPE (wt.%)	Starch (wt.%)	MA (wt.%)	DM (wt.%)	DCP (wt.%)
Native LDPE	100	0	-	-	-
Uncompatibilized					
LPTS5	95	5	-	-	-
LPTS10	90	10	-	-	-
LPTS15	85	15	-	-	-
LPTS20	80	20	-	-	-
LPTS30	70	30	-	-	-
Compatibilized					
LPTS5M	95	5	3	-	0.2
LPTS10M	90	10	3	-	0.2
LPTS15M	85	15	3	-	0.2
LPTS20M	80	20	3	-	0.2
LPTS30M	70	30	3	-	0.2
LPTS5D	95	5	-	3	0.2
LPTS10D	90	10	-	3	0.2
LPTS15D	85	15	-	3	0.2
LPTS20D	80	20	-	3	0.2
LPTS30D	70	30	-	3	0.2

2.2.3 Measurement of MFI

MFI assessments were achieved in agreement with the ASTM-D 1238-01 specification. The test was done using the Dynisco Melt Indexer at 180°C and weighing 2.16 kg.

2.2.4 Mechanical tests

The mechanical properties of the composite were performed using Shimadzu UTM (Model AG-1, Japan) with electrical weight cells of 5 kN and 1 kN following the ASTM-D 638-03 and ASTM-D 790 standards (23). Dumbbell-sized samples of (125 × 3 mm^2) were used to perform a composite of the tensile strength (TS) and tensile modulus (TM). The tensile test was performed at a cross-head speed of 10 mm/min and a gauge length of 50 mm. In contrast, samples with dimensions of 125 × 12 × 3 mm^3 were used to measure the flexural strength (FS) and flexural modulus (FM) of the composite. The experiment was piloted at cross-head speeds of 1.3 mm/min and a span length of 50 mm. According to ASTM-D 256 standards, the notched Izod impact strength (IS) was measured using an impact machine (model, Toyo Seiki Co., Japan). The dimensions of the sample were 63.5 × 12.7 × 3 mm^3. All experiments were measured at room temperature (25 ± 2°C) and relative moisture of 55 ± 5%. Five replicated specimens of each composition were individually examined for the property. The resulting data, as well as their standard deviations, were reported.

2.2.5 Morphological observation

The SEM micrographs of the LPTS composites were analyzed by a Zeiss, Evo 50 scanning electron microscope. Microphotographs were taken from the dumbbell samples examined after the tensile test. The fracture edges of the samples were fitted to aluminum spit and covered with a tinny level of gold to elude electric charge throughout the trial.

2.2.6 Thermal analysis

The thermal characteristic of LDPE and the composites were determined by differential scanning calorimeters (Perkin-Elmer DSC-7, Norwalk, Conn., USA). The 8 mg sample was weighed for scanning. It was first agitated to 10°C/min in the nitrogen atmosphere at 25°C to 190°C and kept there for 5 minutes to clear the thermal history, cooled to 25°C and then re-agitated to 190°C at 10°C/min to detect melting behavior. The heat of fusion (ΔH_f) was calculated by integrating the areas under the peak using Dupont General 2.2 software. The degree of crystallinity (X_c%) was found from the ratio between the melting enthalpy (ΔH_m) of the semicrystalline LDPE and the heat fusion (ΔH_f) for crystalline LDPE and was calculated using the following equation (2.1):

$$x_c(\%) = \frac{\Delta H_m}{\Delta H_f} \times 100 \qquad (2.1)$$

To examine the thermal analysis of composites, thermogravimetric analysis (TGA) is carried out on a TA apparatus (New Castle, DE), type TGA Q500 thermal analyzer. The specimen is heated from 30°C to 600°C at a heating rate of 10°C/min and a nitrogen gas flow rate of 40 ml/min.

2.2.7 Biodegradability test

Biological improvement of the specimens was measured using weight loss over time in a soil ambiance. Blend specimens with 20 × 20 × 3.0 mm^3 dimensions were dried and weighed to obtain a dry weight. These samples were then buried 15 cm below the surface of alluvial soil placed in perforated boxes which were regularly moistened with water. After several time intervals, the specimens are carefully removed from the soil and refined quietly with pure water to comply with the coil circumference. Specimens were dried at 70°C under a vacuum oven until a certain weight was achieved. The weight loss percentage is counted using the resulting equation (2.2):

$$\text{Weight loss}(\%) = \frac{W_2 - W_3}{W_2} \times 100 \qquad (2.2)$$

Where W_2 is the initial weight (i.e., weight before degradation) and W_3 is the final weight (i.e., weight after degradation).

2.2.8 Water absorption test

Water absorption of the native LDPE and LPTS composites was measured using a dimension of 7.5 × 2.5 cm. Before testing, the specimens were dried in a vacuum oven at 80°C for 6 h to remove the amounts of water. After that, the specimens were completely dipped in pure water for 30 days. After this time of dipping, the specimens were separated at regular intermissions, wiping the surface water with tissue paper and weighed using analytical balances with a resolution of 0.1 mg.

3. Results and Discussion

3.1 Melt flow index measurement

Fundamentally, these key purpose ingredients have evidence extrusion rates. MFI values for virgin LDPE, non-compatibilized, and compatibilized composites are presented in Table 2. It was found that the MFI of virgin LDPE was higher than that of non-compatibilized composites. It can be perceived that the MFI of the LDPE/TPS composites reduced as the starch content increased. Decreasing the MFI value indicates an increase in the viscosity of the composite. MFI is also reduced because starch particles are denser than LDPE. However, the decline of MFIs was becoming more balanced by including maleic anhydride (MA) or dibutyl maleate (DM). MA or DM reduces the intermolecular force between the polymer coils and increases the molecular space (24), and increases the MFI as a result of the mobility of the

polymers. Its composites melt and normal flow will be disturbed in fillers that prevent the dynamism of the flow chain section. At larger filler concentrations, the composite melt flow was disrupted, and the amount of composite flow resistance was further increased, which donated to the minor MFI of the composite. In similar filler concentrations, LPTS composites with MA or DM showed higher MFI than composites without MA or DM. MA or DM inclusions reduce the viscosity of composites in LPTS and develop their fluidity. Generally, increasing the value of MFI shows a superior molecular pace within the polymer chain. Weak interfacial bonding between hydrophobic polymer matrix and hydrophilic starch. Compatibilizers, MA or DM, have improved interfacial interaction between matrix and filler, which have higher flow characteristics to melt composites. MA or DM treated composites have shown low viscosity that would suggest processing action.

Table 2 MFI with and without compatibilizer with native LDPE and LPTS composites

Sample code	LDPE (wt%)	Starch (wt%)	MA (wt%)	DM (wt%)	DCP (wt%)	MFI (g/10 min)
Native LDPE	100	0	-	-	-	2.85 ± 0.62
Uncompatibilized						
LPTS5	95	5	-	-	-	2.53 ± 0.09
LPTS10	90	10	-	-	-	2.32 ± 0.15
LPTS15	85	15	-	-	-	2.24 ± 0.11
LPTS20	80	20	-	-	-	2.12 ± 0.14
LPTS30	70	30	-	-	-	1.98 ± 0.03
Compatibilized						
LPTS5M	95	5	3	-	0.2	2.71 ± 0.25
LPTS10M	90	10	3	-	0.2	2.63 ± 0.02
LPTS15M	85	15	3	-	0.2	2.51 ± 0.14
LPTS20M	80	20	3	-	0.2	2.40 ± 0.24
LPTS30M	70	30	3	-	0.2	2.34 ± 0.33
LPTS5D	95	5	-	3	0.2	2.82 ± 0.19
LPTS10D	90	10	-	3	0.2	2.73 ± 0.21
LPTS15D	85	15	-	3	0.2	2.62 ± 0.32
LPTS20D	80	20	-	3	0.2	2.54 ± 0.25
LPTS30D	70	30	-	3	0.2	2.42 ± 0.18

3.2 Evaluation of mechanical characteristics

3.2.1 Tensile properties

The inclusion of sago starch in the LDPE matrix is primarily aimed at improving its mechanical properties. Generally, the mechanical properties of immiscible mixtures except compatibility are weakened owing to poor interfacial bonds among the ingredients. Figures 1 and 2 represent the outcomes of TS and TM of the LDPE and LPTS composite with or without MA or DM. It is also true that tensile assets are enormously reliant on the concentration of starch. Experimental outcomes exhibit that adding sago starch without MA or DM reduced the tensile strength of LPTS composite than LDPE. For virgin LDPE, TS was observed at 7.2 MPa. At 5% starch concentration, TS decreased 7.6%, whereas 10% starch concentration decreased it to 13.8%. For 20% and 30% starch content, it decreased by 26.6% and 30.3%, respectively. As the content of starch increases, the tensile strength decreases. Because of this, during larger starch content, the filler-filler contact transform more clearly than the filler-matrix interaction. Due to the reduction of the composite's efficient cross-sectional area, the driven force is not moved from the polymer matrix to the filler elements. These reports were consistent with the outcomes presented by others (25, 26). As will be seen later in the SEM micrographs, the starch particles are uneven in size and have an affinity for forming aggregates, specifically at 30% starch concentration. The composite indeed had no compatibilizer as a result of few adhesions between the matrix and the filler. Poor interfacial areas indicate that stress transfer from the polymer matrix to the filler will not be operative.

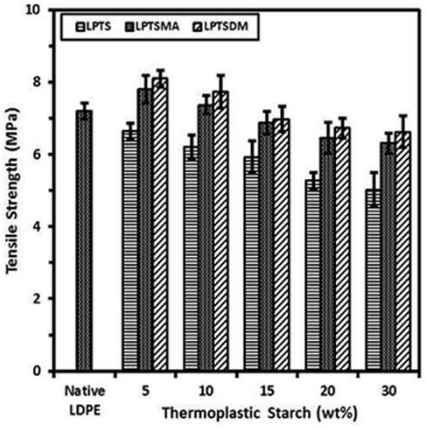


Figure 1 Compatibilizing effect on the tensile strength of LPTS composites.

Figure 2 shows the influence of starch loading on tensile modulus (TM) for native LDPE and LPTS composites with or without MA or DM. The results obtained from the TM determination indicated that increasing starch loading shows a tendency to increase the composite stiffness for LPTS composites. The tensile modulus of the composites increased by increasing from 5 to 30 wt%. As the amount of filler loading with LPTS composite reaches 30 wt%, tensile modulus increased nearly 50% compared to that of the native LDPE. The modulus of the composites is because the starch particles are more rigid than the distributors in LDPE (27). Stiff fillers are usually recognized in situations where reinforcement or even modulus growth will not occur. Another reason for the larger modulus was that the starch particles did not melt enough and keep their size as a stiff filler throughout processing. As the concentration of starch increases, the particles become denser, and the particle-matrix bond decreases. Typically, the modulus component is closely linked to the strict domain. Starch content increases the hard domain as well as the composite modulus. Since starch is partially crystalline, the crystalline characterized by modulus was more likely to grow. Crystallinity modulus brings about growth. The addition of crystalline starch to the PE/starch mixture shows an increase in modulus as the content of starch increases (23). The tensile modulus for LPTS composites with the addition of compatibilizer showed a higher modulus than the non-compatibilized LPTS composites. This result may be due to the compatibility effect of DM on the composites, which enhances the higher interfacial bonding between the fillers and the matrix where the fillers strengthen the composite materials.

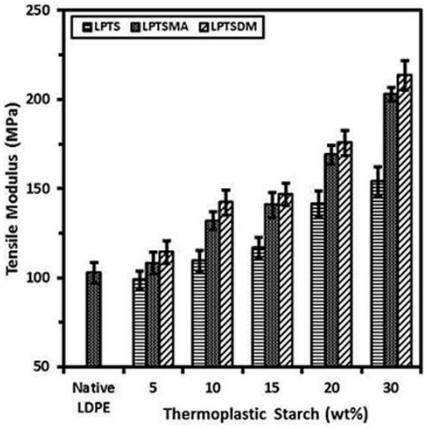
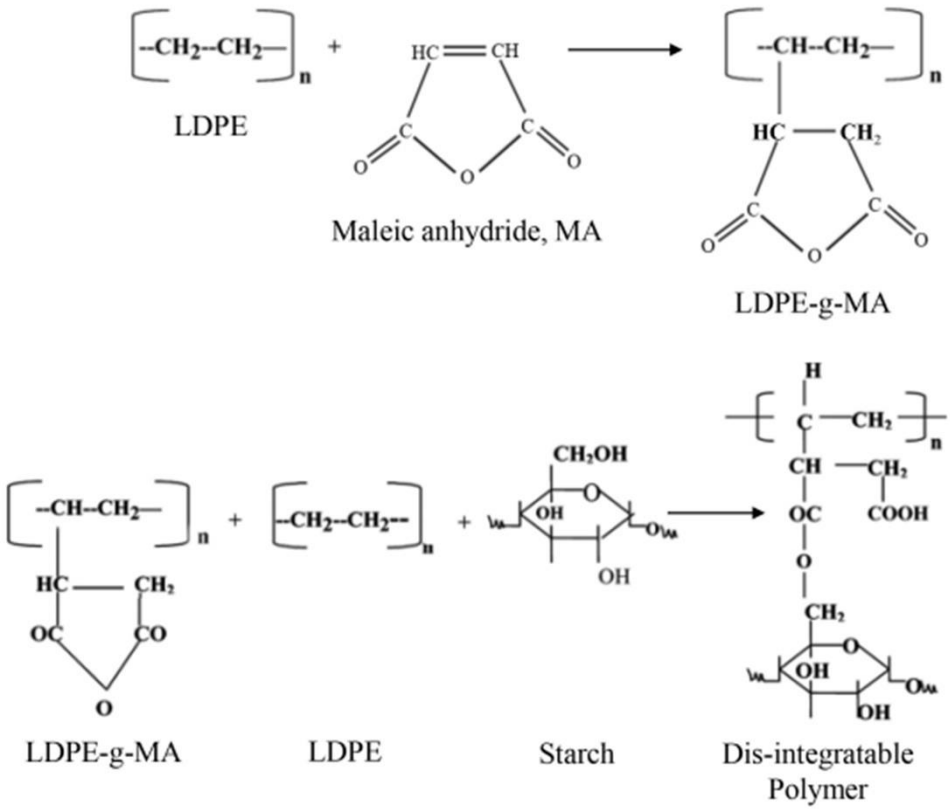
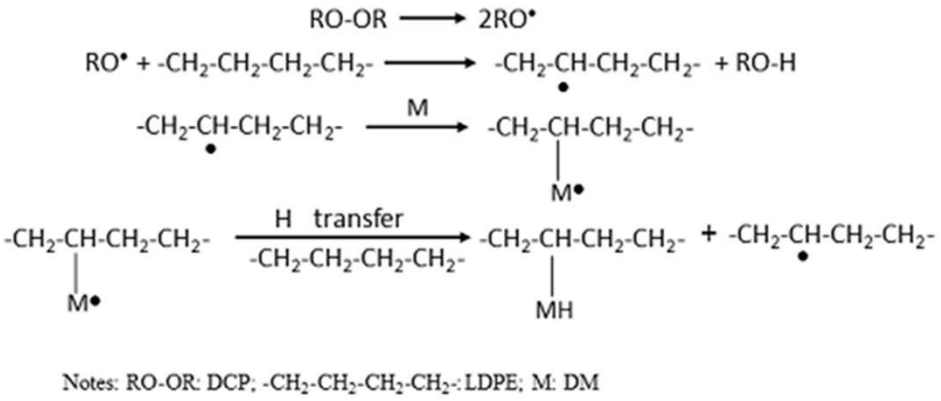


Figure 2 Compatibilizing effect on the tensile modulus of LPTS composites.

The utmost value of TS and TM for all compatibilized composites was more significant than the non-compatibilized composite. The improvement in tensile properties is due to the entanglement of polyethylene parts between the LDPE and MA molecules in scheme 1. Feedback promotes strong adherence between the filler and the matrix interface, thus improving filler-matrix interactions resulting in higher TS (28). Using the DM compatibilizer, the enhancement of the tensile properties can be accredited where the attachment level between the LDPE and starch increases. The polar carboxyl groups of the lateral chains of grafted PE are well-matched with starch. In contrast, the PE segment of the grafted polymer has good compatibility with LDPEs, thus improving the interaction between LDPE and starch. The reactive process of grafted DM in LDPE is presented in scheme 2. Comparing the LPTS samples added with either MA or DM compatibilizer, the mechanical properties of the LPTS with DM were greater than MA.



Scheme 1 Starch interface with MA and LDPE.



Scheme 2 The reactive mechanism of DM was grafted in LDPE.

3.2.2 Flexural features

Figures 3 and 4 present the effects of starch loading on flexural strength and flexural properties such as flexural modulus for non-compatibilized and compatibilized composites. As observed from Figure 3, the flexural strength increased with increasing starch content for all samples. At the same percentage of starch loading, compatibilized composites exhibited higher flexural strength than those of non-compatibilized composites. The value of FS for native LDPE will be 12.5 MPa when the content of starch is zero. For non-compatibilized composites, the maximum flexural strength was observed at 18.9 MPa and the minimum at 13.8 MPa for 30% and 5% starch content, respectively. However, with the same starch content, LPTS composites with MA or DM compatibilizers show higher flexibility than LPTS composites without MA or DM. This is perhaps owing to the superior interfacial bond between the filler and the matrix after the chemical change. Strong adherence between filler and matrix interfaces can further enhance flexural strength.

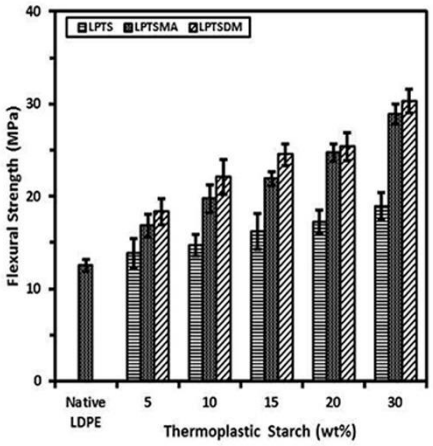


Figure 3 Compatibilizing effect on the flexural strength of LPTS composites.

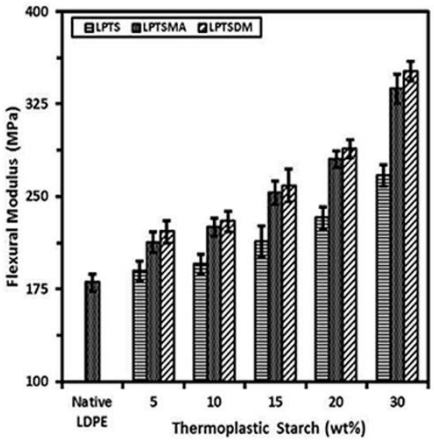


Figure 4 Compatibilizing effect on the flexural modulus of LPTS composites.

Figure 4 shows the flexural modulus of LPTS samples for non-compatibilized and compatibilized composites with different starch contents. The flexural modulus of composites improved from 5 wt% to 30 wt%. As the amount of filler loading with non-compatibilized composite reaches 30 wt%, flexural modulus increased nearly 48% compared to that of the native LDPE. As stated beyond, during more extensive starch content, the filler-filler contact transform more clearly than the filler-matrix interactions, leading to the aggregation of starch particles that are integrally further inflexible or harder than the LDPE matrix (25). Even stiff fillers are usually recognized to raise a composite modulus where the correct force is not applied (29). Thus, the modulus increases with increasing starch content, which is considered for the higher stiffness of starch particles. The flexural modulus for LPTS composites with the addition of compatibilizers showed a higher modulus than the non-compatibilized LPTS composites. This result may be due to the compatibility effect of MA or DM in the composites, which develops high interfacial contact between fillers and PE where fillers strengthen the composite materials.

3.2.3 Impact features

Figure 5 gives a variant of IS with starch content for untreated and treated composites. It was initiated that IS displayed a noteworthy reduction with increasing filler content. Decreased IS has been identified for non-compatibilized composite as the addition of starch content further increases the blend in the bundles and gives low compatibility in the two phases. This reduction is responsible for changing the conduct of elastic to inelastic material. The IS exhibits the same trend as expected for tensile outcomes. The IS of LDPE was 1.6 J/mm^2. For non-compatibilized composites only, the 5% and 10% starch content decreased from 34% to 37% of the IS of 1.06J/mm^2 and 1.01 J/mm^2, respectively. Additional discounts of the composite were perceived for 20% to 30% starch, which decreased to 0.82 J/mm^2 and 0.71 J/mm^2, respectively. Besides, a small enhancement in IS has been observed with the composite of compatibilizers. This enhanced mirror improves the interaction between the two stages. It appears to be sufficient for the growth quality of IS of compatibilized (LPTS with MA or DM) composite as a rise in formless stage, featured by the ability to push impact. At the molecular level, a pendant is a posterior chain related to disinfectant, maleic anhydride, or carboxyl, hence increasing the free volume decreasing due to molecular interaction. In the inclusion of compatibilizer, the maximum impact strength was found to be 1.15J/mm^2 in 5% starch content of LPTS DM, and the minimum impact strength was 0.91 J/mm^2 for 30 % starch content. After proposing a reduction in the IS of starch growth, the filler-filler contact was more closed than the filler matrix contact. The additional possibility of low IS is that the starch melts during expansion and cannot retain its form as a strong filler (30). The particle-matrix interaction decreases with particle aggregate and IS; the starch does not exhibit to harden the composite, but the fracture begins to fail.

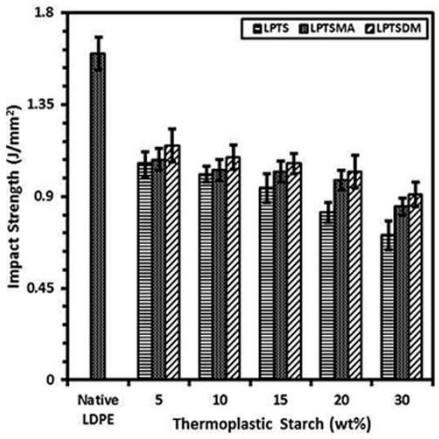


Figure 5 Compatibilizing effect on the impact strength of LPTS composites.

3.3 Morphological properties

The morphology of polymer blends needs to be studied depending on such mechanical features. To distribute the starch tightly in the matrix in general, good interfacial bonding between the two layers is required to successfully wet the starch by the matrix and obtain a composite material with useful mechanical features. Figure 6 displays the SEM tensile fracture surface of LPTS (30 wt%) (designated as LPS30), LPTS30MA, and LPTS30DM composites. Figure 6 (a) displays several starch phases with large irregular shapes and sizes of individual agglomerates. Different cavities are formed due to the separation of the starch agglomerate from the LDPE. Agglomerates and cavity production evidence an increase in the interfacial tension and severance stage between starch and LDPE material. The micrograph shows matrix fibrils, poor interfacial bonding, and voids in the matrix and filler.

Poor distribution of starch in LDPE occurs owing to the creation of hydrogen bonds and the extensive characteristic differences between LDPE and starch. Figure 6 (a) shows that the starch was poorly soaked when LPTS was used. It is owing to the significant difference in surface strength between the starch and the LDPE (31). As shown in Figure 6 (b), the LPTS30MA sample has an improved distribution and uniformity of starch in the matrix. Figure 6 (b) also indicates that a small amount of starch is covered with LDPE to a certain degree. The compatibilized blend shows a dimpled surface marking the contact between the filler and the matrix with the elongated void. Improved interfacial adhesion was attributed to chemical reactions between the anhydride group and the sago starch of the hydroxyl group and under physical interactions between LDPE and MA (32) under high temperature and high shear extrusion conditions. In Figure 6(c), the fracture surface of the LPTS30DM sample shows that the starch particles disperse well in the matrix as no straightforward interface can be observed between the starch and the LDPE. It is due to the adherence of polymers given across the bond between starch and LDPE growth. Extended bonds are based on improving the compatibility of grafted polymers with starch and LDPE. As shown above, there is a good bond between filler and matrix outcomes in composite growth.

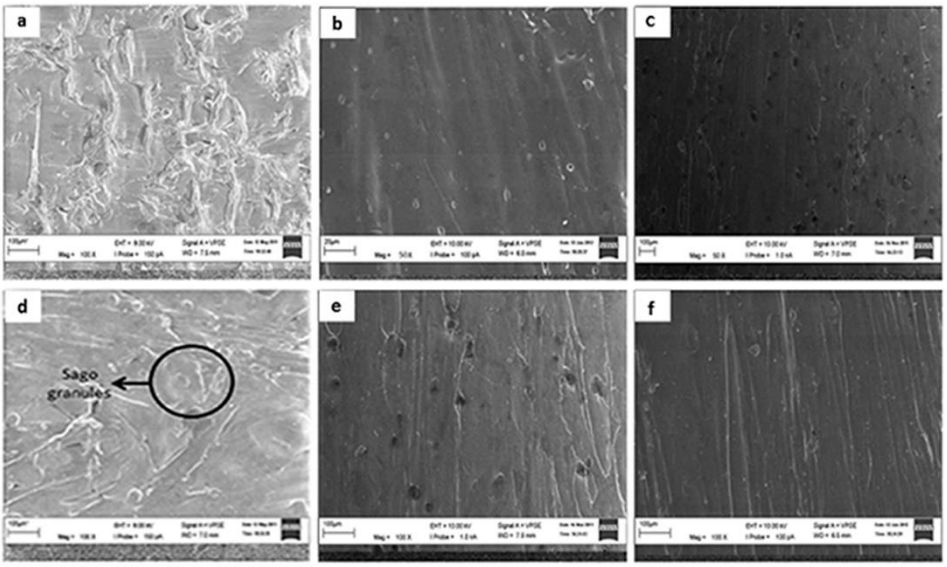


Figure 6 SEM photomicrographs on the fractured surface of (a, d) LPTS30 (at ×100 and ×1 k magnification), (b, e) LPTS30MA, and (c, f) LPTS30DM composite (at ×50 and ×100 magnification).

3.4 Thermal analysis

3.4.1 Crystallization behaviors

Differential scanning calorimetry (DSC) was used to examine the thermal characteristics of the composites. The compatibility of LDPE/starch can be determined by measuring the thermal properties of mixed components of DSC. The melting temperature (T_m), the heat of fusion (ΔH_f), and percentage crystallinity ($\%X_c$) of the endotherm are commonly used to describe the nonisothermal crystallization of polymers. Figure 7 and Table 3 display the thermal graph and thermal parameters of the composites of native LDPE, LPTS, LPTSMA, and LPTSDM. DSC endotherms showed very little change in the crystalline form of the matrix, meaning that the T_m in this study was dependent on plasticizers and compatibilizers in the temperature range. The T_m of the composites of native LDPE, LPTS, LPTSMA, and LPTSDM was between 133.91-136.23°C. Compared with native LDPE, T_m transferred to higher temperatures of the composite, and maximum T_m is found in LPTSDM composite. The hydroxyl group in glycerin formation can form hydrogen bonds with LDPE and starch. In T_m's, the plasticizer of glycerin can create potential interactions with LDPE and starch. More interaction with more plasticizers and compatibilizers, matching LDPE/starch with higher T_m. It is compatible with the increase in the tensile features of the LPTSMA or LPTSDM composite, as mentioned in the previous section. Table 3 displays that the ΔH_f values of LDPE and LPTS were 103.25 and 105.67, respectively. A comparison between LPTSMA and LPTSDM results showed that the previous ones provided higher values than before, and the increased amount was about ~4 J/g. The increase in ΔH_f is owing to the formation of maleate ester groups. It is derived from the interaction between the –OH group of starch and the maleate ester group of the dibutyl maleate. Table 3 shows that with the inclusion of compatibilizers in the LPTS, the ΔH_f and X_c (%) increased in the prepared specimens as the ΔH_f is proportional to the quantity of LDPE. Incorporating plasticizers and compatibilizers, the percentage crystallinity of the matrix has increased significantly. The degree of crystallinity in LPTS, LPTSMA, and LPTSDM increased by up to 8, 18, and 28%, respectively. The LPTSDM composite exhibited a higher degree of crystallinity than the LPTSMA composite. Therefore the tensile and flexural characteristics of the LPTSMA composite were lower than that of the LPTSDM composite. The crystallization rate of semicrystalline polymers increases with compatibilizer, resulting in higher crystallinity and higher ΔH_f (33).

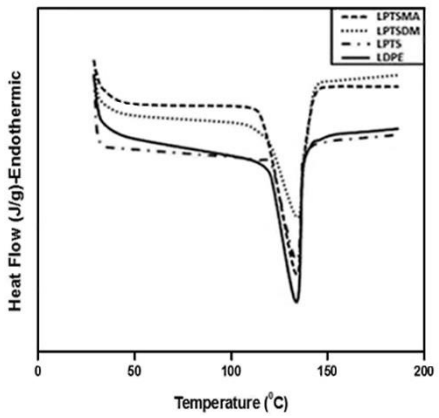


Figure 7 DSC diagrams for native LDPE, LPTS, LPTSMA, and LPTSDM composites.

Table 3 Thermal characteristics of LDPE/sago starch composites.

Samples (wt.%)	T_m (°C)	ΔH_f (J/g)	X_c (%)
Native LDPE	133.91	103.25	35.23
LPTS	134.62	105.67	37.26
LPTSMA	135.34	109.32	41.52
LPTSDM	136.23	113.41	45.14

3.5 TGA analysis

TGA of the composite is performed to evaluate its thermal durability and humiliation temperature. $T_{(onset)}$ and TGA diagrams for LDPE, LPTS, LPTSMA, and LPTSDM composites are shown in Figure 8. It is noteworthy that LPTS showed initial weight loss from about 300°C to 380°C, mainly due to the decomposition of thermoplastic sago starch; the last shift at around 452°C was due to heat decomposition of LDPE. The weight loss of the LPTS composite has been reduced with the inclusion of a compatibilizer. Addition compatibilizers improve the thermal stability of composites. It was found that LDPE, LPTS, LPTSMA, and LPTSDM lost 95.1, 92.3, 91.1, and 89.4% of their weight, respectively. It is believed that weight loss was the result of improved thermal stability (34). The weight loss of LPTSDM composites was less than that of the LPTSMA composites. The good thermal durability of the LPTSDM composite was accredited for better interfacial contact between the -OH group of starch with the maleate ester group of DM, thus improving the interfacial contact between the filler and the matrix.

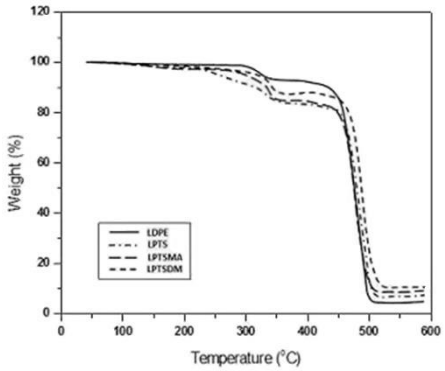


Figure 8 TGA thermogram of native LDPE and its composites.

DTG thermographs of native LDPE and LPTS, LPTSMA, and LPTSDM composites are shown in Figure 9 and Table 4. Matrix weight loss happened in a one-step degradation system ranging from 400 to 500°C. The weight loss of LDPE starts from 287.3°C and is very slow before reaching 400°C. Above 400°C; the degradation system was accelerated as more LDPE was broken down into vaporous products at elevated temperature. Addition of plasticizer to LDPE/starch, starting temperature, maximum temperature, and offset temperature of the composite were higher than native LDPE. The addition of compatibilizers to the LPTS composite further enhances the starting temperature, maximum temperature, and offset temperature.

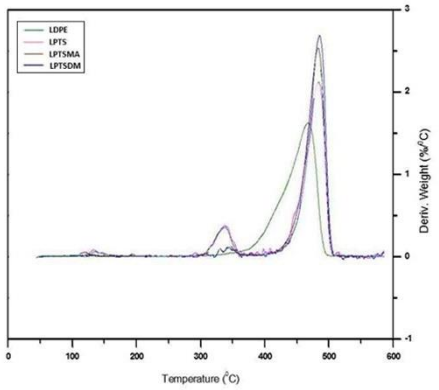


Figure 9 DTG thermogram of native LDPE and its composites.

Table 4 DTG data for native LDPE and its composites.

Samples	Onset temperature (°C)	Top temperature (°C)			Offset temperature (°C)
		1st peak	2nd peak	3rd peak	
Native LDPE	287.3	468.1	-	-	506.9
LPTS	290.1	295.3	345.4	485.1	522.8
LPTSMA	291.3	297.6	347.2	487.4	524.2
LPTSDM	291.7	307.8	349.6	491.3	525.7

3.6 Soil degradation

Biodegradation studies related to composite behavior are crucial for the environmental application of biocomposites. Figure 10 shows the degradation of native LDPE, LPTS30, LPTS30MA, and LPTS30DM samples in soil. The water present in the soil is expected to be broken down into samples of the blend, resulting in swelling and increased biological expansion. The weight loss of LPTS30, LPTS30MA, and LPTS30DM specimens increased with increasing burial time and continued with increasing burial time. It is recommended that fungi and bacteria present in the soil environment as microorganisms consumed starch and make holes in the polymer matrix. For all composites studied, weight loss after 30 wt% starch content after the first month is 0.94, 0.65, and 0.53% for LPTS30, LPTS30MA, and LPTS30DM, respectively. Weight loss gradually increased with increasing burial time, and after 6 months of study, the weight loss percent was 6.87, 4.63, and accordingly 3.45%. Again, it can be noted that after 6 months of research, the weight loss of the LPTS30 blend was more than 3.45% which corresponded to the overall weight loss percentage of LPTS30DM. Low weight loss of LPTS30DM may be associated with improved interfacial bonding between LDPE and starch and other similar factors that lead to water uptake. Higher biodegradation of LPTS30 may be due to the same factors as its higher water absorption and lower mechanical properties.

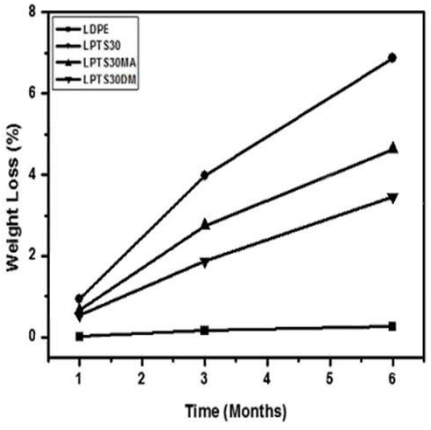


Figure 10 Weight loss versus time of native LDPE, LPTS30, LPTS30MA, and LPTS30DM composites after six months exposure to burial in soil.

3.7 Water absorption analysis

Since one of the significant drawbacks of using starch-based materials is their tendency to absorption water, any improvement in water resistance is crucial (35). The key justification of this drawback is that the -OH group of starch can build hydrogen bonds with water (36). The water helps to provide the elasticity of the starch after it has dried completely and is known to be a suitable plasticizer for the starch (37). The effect of starch content on water absorption of a composite of native LDPE, LPTS30, LPTS30MA, and LPTS30DM after immersion in distilled water for 30 days is shown in Figure 11. It was observed that the water absorption rate of LPTS30, LPTS30MA, and LPTS30DM samples was higher within the initial 7 days, followed by the arrival of regular state saturation. A prompt water uptake has been observed within the first few days of dipping. Nevertheless, it has gradually slowed down with a period. Decreased water absorption rate throughout dipping may be owing to density gradients over the ingredients. It was found that elemental water added to the starch is intensely cramped as in a hydrate. Through this, water enters the samples through the cavities, and the starch particles bind to the -OH group, become swollen and shrink the holes between their molecules, and place in the matrix particle. It was difficult to spread out the water. As a result, the rate of water uptake was reduced. Furthermore, water molecules can easily fill the surfaces of the composite and enter the composite through the cavity, ensuing in more water uptake during the squatter exposure times. Water absorption may decrease slightly as immersion time increases, as some starch particles were removed from the sample (37). It was recommended that after water uptake, the starch particles expand, increase in shape and become compelled (36). LDPE was not uniformly with starch, as was poor water uptake. The figure showed that the lower percentage of water absorption by LPTS30DM compared to LPTS30 composite. Compatibilized LPTS30DM composites have better combinations between matrix and fillers, reducing the structure of agglomerates. Compatibilized LPTS30DM composites with DM reduce the number of free hydroxyl groups on the surface and decrease the percentage of water uptake.

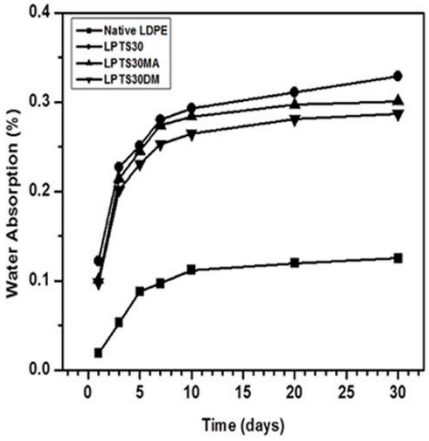


Figure 11 Water uptakes for native LDPE, LPTS, LPTSMA, and LPTSDM composites.

4. Conclusions

In this study, non-compatibilized and compatibilized composites based on LDPE were discussed with the content of sago starch. From the above discussion, we can draw the following conclusions:

1. The MFI values of the LPTS composite with or without compatibilizers have reduced with increasing starch content. LPTSDM composites with DM were shown to be higher MFI than LPTS composites and higher than LPTSMA composites.

2. The TM, FS, and FM composites began to increase as the amount of starch increased, the TS and IS gradually reduced. The addition of compatibilizers further enhances the mechanical properties of the composite.

3. The SEM micrograph provides evidence that a DM compatibilizer can develop a bond between starch and LDPE and that the starch particles are evenly dispersed in the polymer matrix.

4. The DM incorporation has also improved. Since the thermal degradation temperature and the thermal stability of LPTSDM composites, the results of DSC showed the compatibility of the components in the composite system.

5. Water absorption studies have shown that the addition of DM to LPTS30DM composites and water extraction in a soil environment, the compatibilized composite (LPTS30DM) shows a lower biodegradation rate than the non-compatibilized (LPTS30).

Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

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