PROGRESS IN APPLIED SCIENCE AND TECHNOLOGY
Faculty of Science and Technology
Rajamangala University of Technology Thanyaburi
Vol.11 No.2 (2021): 26–36
ISSN (Print): 2730-3012
ISSN (Online): 2730-3020
https://ph02.tci-thaijo.org/index.php/past

Received 07th February 2021,
Revised 06th April 2021,
Accepted 20th April 2021

DOI: 10.14456/past.2021.10

Effect of Filler Starches on Mechanical, Thermal and Degradation Properties of Low-Density Polyethylene Composites

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Abstract

In this study, five types of starches (sago, corn, tapioca, potato, and wheat starches) were blended with low-density polyethylene (LDPE) via melt blending technique followed by injection molding to manufacture LDPE/starch composites. Each starch content varied from 5-30 wt% of LDPE. Starch inclusion in LDPE reduced tensile strength, elongation at break, and impact strength, while tensile modulus increased significantly with increasing starch content. To provide fine starch dispersion, glycerol (30 wt% based on the starch content) was used as a plasticizer and compatibilizer. The effect of thermoplastic starch content on the properties of LDPE composites was investigated. The presence of a plasticizer or compatibilizer in the LDPE/starch composite produced better properties for sago starch-filled composite than other starches-filled composites, indicating better dispersion and homogeneity of starch in the matrix. Morphological studies of fractured surfaces using scanning electron microscopy (SEM) have revealed that the miscibility of such a blend depends on the type of starch used. The thermal testing results show that the addition of thermoplastic starch in the LDPE can increase the degradation temperature as well as the decomposition temperature and melting temperature of these composites did not change but the degree of crystallinity of the LDPE phase was slightly decreased. The water uptake of composite increased with soaking time and the application of thermoplastic sago starch samples was found to be the lowest water absorption compared to other starches. However, outdoor weather tests can show that the biodegradability of thermoplastic starch composites has increased with increasing degradation time.

Keywords: Composites, low-density polyethylene, thermoplastic starch blends, morphology, mechanical and thermal properties

1. Introduction

Plastic has long-lasting and striking properties and is an essential component of many applications including low cost, outstanding strength, lightweight, easy to manufacture, easy processing, and durable. Thermoplastic materials such as polyethylene (PE) and polypropylene (PP) are progressively being used as their packaging ingredients due to their low cost and abundant good tensile and tear strength, good barrier properties of oxygen and perfume compounds, and thermal sealing ability (1). On the other hand, this feature makes them highly preventive to microorganisms and other natural decay forces, so they stay in the environment even after disposal. It was operated in addition to environmental hitches and property deficit hitches for solid wreck management (2). Almost everywhere, the cost plastics on the collection and disposal of solid municipal waste. Recyclable plastics can deliver the opportunity to reduce municipal solid waste and substitute conventional non-recyclable synthetic plastic products through biological recycling from plastic ecosystems. Also, these biodegradable polymers are recommended to come from agronomy or other renewable sources for durable conditions.

The decomposable polymer that can be spontaneously decayed in its natural state is arousing municipal interest (3). Degradable polymers like starch, cellulose, or proteins have very attractive ingredients for potential wrapping ingredients. Starch is especially fascinating as it is comparatively low-cost and accessible in large quantities. Starch is one of the maximal plentiful naturally happening polymers in natural products. It can be blended with another polymer to lower the cost and to confer partial environmental degradability to the blends (4). The maximal notable sources of starch are sago, corn, tapioca, potato, wheat, and rice. Starch is a carbohydrate natural polymer derived from green plants in the form of granules, which is composed of amylose and amylopectin. Amylose is a linear molecule with insufficient branches, while amylopectin is a broad branched molecule made up of about 95% (α, 1- 4) and 5% (α, 1- 6) linkages. Amylopectin unit chains are slightly shorter than amylose molecules with wide delivery outlines. They are usually 18–25 units in length (5).

Over the last few years, the mixing of plastic components with organic fillers such as starch has gained significant manufacturing and academic interest in developing new materials with the desired properties (6). PE is a hydrophobic polymer that takes one hundred years like high molecular weight degradation (7). The potential application of this strategy in the disposal of plastic waste mixed with starch with LDPE has received considerable attention. PE mixed with starch has already been identified as a potential candidate for replacing non-degradable thermoplastics. A possible alternative to microbial attack on LDPE with a guarantee of at least partial biodegradation such as starch adding natural polymers. The use of granular starch as a disinfectant filler in LDPE was first reported by Datta (8). Corn, wheat, and tapioca starch are dried to prevent any formation of bubbles by reducing the moisture by less than 1%. The dried starch is then melted in hot plastic. Although starch is a cheap, renewable, and completely sterile raw material, polar starch promotes poor adhesion of non-polar PE to polymer/starch composites. Plastifying agents primarily improve the compatibility of the LDPE/starch-based blending system, and the addition of glycerin usually enables bacterial invasion (9). The physical embrittlement of the polymer leads to a pore and mechanically weakens the polymer. Plasticizers reduce film brittleness by increasing molecular volume due to increasing molecular volume by binding hydrogen bonds between lipids and HCL atoms (10). In most previous studies, composites were made by mixing LDPE with one or two types of starch (11, 12). Our previous study found that LDPE composites filled with five types of thermoplastic starches (sago, corn, tapioca, potato, and wheat) from botanical sources significantly affected mechanical and morphological properties (13). The present study focuses on the exploration of the mechanical, morphological, thermal, and biodegradation properties of this composite. Despite this work, no one has focused on these five types of thermoplastic starch-field-LDPE composites in the mechanical, morphological, thermal, and biodegradability of these partially biodegradable systems. However, the biodegradation behavior of those composites is not well known. As such, the properties have been determined through different parameters: different types of thermoplastic starches, starch loading, and processing factors.

2. Experimental

2.1 Materials

The use of low-density polyethylene (LDPE) at a density of 0.922 g/cm^3 with MFI of 3.3 g/10 min (190°C/2.16 kg) is provided by Petlin Polyethylene (Malaysia) Sdn. Bhd. This resin could be in the form of extruded pellets. Thermoplastic starch was prepared from sago, corn, tapioca, potato, and wheat starch, respectively. Different types of starches in chemical compositions are listed in Table 1 (14). The sago starch as the filler used in this study was a food-grade biopolymer. It has distributed G-Far Sago Keropok Enterprise in Johor, Malaysia from local suppliers. Another starch was used in this work in all cases of Sigma Aldrich, Malaysia. Reagent grade glycerol (glycerin, $C_3H_8O_3$) as a plastifying agent belongs to Sigma Aldrich, Malaysia. Here benzoyl peroxide (BPO) has been used as a radical initiator. To accelerate the oxidation of LDPE, autoxidizing agents like manganese stearate should be used. Manganese stearate was provided by H.L. Blanchford Limited (Ontario Canada). Reagent grade BPO was bought by Sigma Aldrich Chemical Inc., Malaysia

Table 1 Different types of starch are used in chemical compositions (14).

Component	Sago starch	Corn starch	Potato starch	Tapioca starch	Wheat starch
Ash (%)	0.06-0.43	0.06	0.22	0.044	0.17
Fat (%)	0.10-0.13	0.29	0.28	0.64	0.27
Protein (%)	0.19-0.25	0.27	0.11	0.11	0.20
Carbohydrates (%)	99.29	99.38	99.39	99.21	99.56
Amylose (%)	30	28	27	17	18.10
Amylopectin (%)	77	75	74	75	72
Gelatinization temp. (°C)	69.4-70.1	65.79	62.79	67.34	72.83
Granule diameter (μm)	6.90	5.20	7.14	6.97	12.37

2.2 Methods

2.2.1 Blend preparation

First, a variety of starches was dried at 80°C to remove storage moisture in an oven for 24 h before premixing. In previous studies, different types of starch loads (5 to 30 wt%) were mixed separately with glycerin and added to LDPE at room temperature (15). In this research, five types of starches were selected for the preparation of LDPE/thermoplastic starch composites, and the detailed compositions of the prepared samples are listed in Table 2. LDPE/thermoplastic starch includes LDPE/thermoplastic sago starch (LPTS), LDPE/thermoplastic cornstarch (LPTC), LDPE/thermoplastic tapioca starch (LPTT), LDPE/thermoplastic potato starch (LPTP), and LDPE/thermoplastic wheat starch (LPTW). Glycerol was used as a plasticizer and added to mixtures to increase the compatibility of starch and LDPE, which reduced the brittleness of the samples. The mixtures were stored in airtight conditions for 24 h until the starch swelled. The thermoplastic starches were mixed with LDPE with a pro-degradant additive (0.1% manganese stearate) from the Brabender twin-screw extruder (model: TSE20, GmbH and Co. KG, Germany). The amount of initiator (BPO) was determined to be 0.1 wt% based on LDPE weight. Allegations were first made against the LDPE for starting the meltdown. The thermoplastic starch was added after 2 min of thermal application with pro-degradant additives. The mixture was continued for another 8 minutes. The mixture was made at a rotor speed of 60 rpm and the temperature was set at 150°C/150°C/140°C/140°C to die from the feeder (11). Extruded strands were air-cooled and then palletized by a pelletizer. After 24 hours of oven drying at 80°C, the granules were injected into a standard mechanical test sample using an injection-molding machine (Toyo, model: Si180iii-E200, Japan). The barrel temperature and clamping force for each mixture and their composite were determined to be 160°C and 180N respectively.

Table 2 Compositions of different types of thermoplastic starches filled LDPE composites prepared.

Ingredients	Sample code	LDPE (wt%)	Starch (wt%)
Native LDPE	LDPE	100	0
LDPE/TS	LPTS5	95	5
	LPTS10	90	10
	LPTS20	80	20
	LPTS30	70	30
LDPE/TC	LPTC5	95	5
	LPTC10	90	10
	LPTC20	80	20
	LPTC30	70	30
LDPE/TT	LPTT5	95	5
	LPTT10	90	10
	LPTT20	80	20
	LPTT30	70	30
LDPE/TP	LPTP5	95	5
	LPTP10	90	10
	LPTP20	80	20
	LPTP30	70	30
LDPE/TW	LPTW5	95	5
	LPTW10	90	10
	PTW20	80	20
	PTW30	70	30

TS: Thermoplastic sago starch; TC: Thermoplastic corn starch; TT: Thermoplastic tapioca starch; TP: Thermoplastic potato starch; TW: Thermoplastic wheat starch

2.2.2 Mechanical properties

Dumbbell-shaped specimens (125×3 mm^2) have been used to measure the tensile properties of composites. Tensile properties like tensile strength (TS), tensile modulus (TM), and elongation at break (Eb) were measured using Shimadzu Universal Testing Machine (Model AG-1, Japan) with an electronic load cell of 5 kN by the ASTM-D 638-03 standard (16). A crosshead speed of 10 mm/min and a gauge length of 50 mm was used to run the tensile test. The tensile was tested until failure. Notched Izod impact strength was measured using Izod Impact Machine (Toyo Seiki Co., Japan) according to ASTM-D 256 standard. The dimensions of the sample were $63.5 \times 12.7 \times 3$ mm^3. Shortly before the test, the test specimen was controlled at 25 ± 2°C and 50 ± 5% relative humidity, and all tests were performed under the same conditions. All outcomes were taken as the mean values of the five specimens.

2.2.3 Morphological observations

The SEM micrographs of the LDPE/thermoplastic starch composites were analyzed by a Zeiss, Evo 50 scanning electron microscope. The surfaces of the specimens were coated with a thin layer of gold on aluminum stubs and sputter to avoid electrostatic charging and poor resolution during the test. The image results have been analyzed to investigate the thermoplastic starch distribution between the polymer matrix and their interaction.

2.2.4 TGA-DTG analysis

Measurement of thermal properties is performed under a thermogravimetric instrument (TA instrument, TGA Q500) under nitrogen atmosphere in a temperature range from 25°C to 600°C at a heating rate of 10°C/minutes. TGA was directed to avoid undesirable oxidation with a sample (8 ± 2 mg) placed in a platinum crucible in a nitrogen atmosphere at a flow rate of 40 mL/min. The onset of degradation temperature, at which the weight loss was maximized, and the weight of the residual in percentage was assessed.

2.2.5 DSC measurements

The melting and crystalline behavior of native LDPE and specimens were determined by DSC Q1000 V9.6 Build 290 with a TA instrument. The native LDPE and the specimens were first heated from 25 to 200°C for 10 min to eliminate all thermal history of the specimens before refining the liquid nitrogen. Subsequently, the specimens were cooled to 25°C at a cooling rate of 10°C/min to obtain crystalline properties. Finally, the specimens were heated to 200°C at a heating rate of 10°C/min to obtain their melting properties. All assessments were performed under a nitrogen atmosphere. The weight of the specimen was between 8 ± 10 mg. For the above specimen, the degree of crystallinity can be determined by using Equation 2.1.

$$X_c = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100 \tag{2.1}$$

Where X_c = degree of crystallinity

ΔH_f^* = heat of fusion of LDPE blends, ΔH_f^0 = heat of fusion for 100% crystalline LDPE, (ΔH_f^0 for LDPE = 276 J g^{-1}) (16).

2.2.6 Biodegradation under natural weathering

The dumbbell-shaped specimen has been exposed to naturally actinic radiation on the climbing surface for 6 months at UMP in Malaysia. The rack was fixed to face the equator at an angle of 45° and the rack is located in an open space so it is free from the shadow by other objects. Samples were exposed to all ecological effects such as rain, sunshine, and air (17). The mean temperature was 25.9±1°C with a relative humidity of 55%. Similarly, control tests on prepared specimens are performed indoors rather than from external exposure, which indicates their shelf life. Tests were performed at 1, 3, and 6 months of age to measure the degree of deterioration of weight loss, loss of tensile strength, and loss of percentage elongation.

2.2.7 Water absorption property

Each specimen was cut in a dimension of 7.5 × 2.5 cm^2, and weighed instantly, then insert into the oven, and dried at 80°C for 24 h. The controlled specimens rested on their edges and were completely immersed in a container of distilled water (ASTM-D 570) for 30 days. After this period of immersion, the specimens are removed from the water at regular intervals to be removed with a dry cloth to remove surface water. These specimens were weighed as soon as they were taken out. Water absorption rate (K) is based on the following equation (2.2):

$$K = \frac{w_2 - w_1}{w_1} \times 100 \qquad (2.2)$$

Where, w_2 and w_1 were the final weight and the dried weight of the specimen, respectively.

3. Results and Discussion

3.1 Tensile features

Tensile strength, which is a measure of direct tensile resistance, is important in machinability and packaging applications. Table 3 and Figure 1-2 display the effects of filler loading on TS and TM for unplasticized and plasticized-filled LDPE composites, respectively. The results presented that TS for all types of unplasticized composites was continuously reduced with increasing filler loading (Table 3). It was thus clear that the mechanical inconsistency of the two phases was great with the increase in filler content. TS may be reduced due to the weakening of the interfacial bond of hydrophilic starch with the hydrophobic LDPE matrix.

Table 3 TS and TM of LDPE/starch composites.

Sample code	Starch content (wt%)	Tensile strength (MPa)	Tensile modulus (MPa)
LPS	5	4.24 ± 0.12	94.62 ± 12.3
	10	3.81 ± 0.09	104.12 ± 15.2
	20	3.50 ± 0.07	134.79 ± 11.3
	30	3.22 ± 0.05	146.57 ± 18.1
LPC	5	4.12 ± 0.08	83.17 ± 10.9
	10	3.52 ± 0.09	87.54 ± 12.1
	20	3.33 ± 0.11	92.32 ± 16.3
	30	2.81 ± 0.13	110.78 ± 18.7
LPP	5	3.89 ± 0.12	86.31 ± 10.3
	10	3.45 ± 0.09	92.35 ± 8.7
	20	2.99 ± 0.05	87.41 ± 12.2
	30	2.57 ± 0.07	93.25 ± 11.5
LPT	5	3.87 ± 0.07	76.54 ± 9.1
	10	3.55 ± 0.11	82.62 ± 10.3
	20	3.02 ± 0.07	91.33 ± 13.1
	30	2.43 ± 0.08	96.78 ± 11.4
LPW	5	3.83 ± 0.11	73.44 ± 8.8
	10	3.46 ± 0.08	81.23 ± 10.1
	20	2.99 ± 0.05	87.41 ± 12.2
	30	2.57 ± 0.07	93.25 ± 11.5

LPS: LDPE/sago starch; LPC: LDPE/corn starch; LPP: LDPE/potato starch; LPT: LDPE/tapioca starch; LPW: LDPE/wheat starch

As the concentration of starch increases, the effective cross-sectional area of spherical starch reduces. From the TS reduction of the mixture, it was suggested that the fillers do not reinforce LDPE. The hydroxyl group on the surface due to starch exhibits hydrophilic properties and strong molecular association through hydrogen bonding. This filler is low compatible with hydrophobic polyolefin due to its hydrophilic nature and strong intermolecular hydrogen bonding (18). Although lower TS has been observed for LPT composites compared to native LDPE, it has declined compared to LPS composites. The ultimate value of TS for all LPS composites was greater than that of LPT composites. The stronger hydrogen bonding between LDPE/starch and plasticizer molecules could favor the desired LDPE/starch interactions instead of the intermolecular and intramolecular within the LDPE or starch molecules, thus improving the compatibility between LDPE and starch, which resulted in higher tensile properties. Addition plasticizers increase TS and reduce the interaction between LDPE and starch and increase the mobility of LDPE/starch chain segments. As shown in Figure 1, the composite of LDPE/thermoplastic sago starch (LPTS) had a higher TS (6.65 MPa) than other types of starches. The great TS of LPTS composites is because sago starch has the highest amylose content than other types of starches.

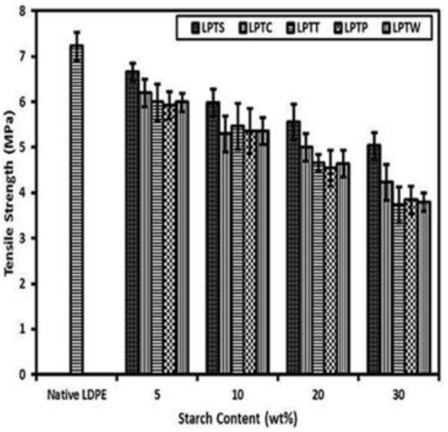

Figure 1 Tensile strength versus starch content for LDPE/thermoplastic starch composites.

TM was often used as a marker to evaluate the rigidity of polymeric materials and it was used here. The results obtained from the tensile modulus determination indicate that the increase in filler loading showed a tendency to increase the composite stiffness for the composite of LPS and LPT (Figure 2 & Table 3). As the increase in modulus has been observed, the filler-filler interaction becomes more pronounced than the filler-matrix interaction as the number of starch increases. Again, where a requesting agent exhibits high stiffness than the polymer material its inherent properties are more filler to the modulus of filler growth. This result was acknowledged by Ardhyananta et al. (19).

Composite specimens become more rigid and stiffer than composites without starch. The starch granules were stiffer than the LDPE matrix where they were dispersed. In most cases, the modulus was closely related to the hard domain. Starch content increases, hard domain increases as well as the blending modulus. Since starch was crystalline, the crystalline characterized by modulus was likely to increase. Crystallinity modulus brings about growth. Adding crystalline starch to the binary PE-starch blend shows an increase in modulus with increasing content of starch (20). Thermoplastic sago starch in the LPTS composite showed the highest TM showed blends with sago starch that were very tough. This was because during processing, the starch granules did not melt and their granule shape was maintained. These granules were hardened and acted as rigid fillers. Furthermore, since the starch was harder than the LDPE, the modulus was increased due to the stiffening effect of the starch granules. Since starch has both amorphous and crystalline regions, the calculated starch module averages have reflected the contribution of comfort level. Consequently, sago starch was stiffer and more rigid than other types of starch. Filler addition reduces the elongation at break. Table 4 displays the effect of filler load on elongation at breaks of composites. As we noticed, the increase in elongation at breaks for composites decreased the filler loading. The decrease in elongation at break with increased starch content may be attributed to the fact that the starch particles didn't work coherently with LDPE. Thus, less strain was required for the sample to fail. Also, weak interactions between starch and LDPE result in weak interfacial bonds that allow easy crack propagation. Thus, composites fail at low values of elongation at breaks with increasing starch load. It can be seen that the elongation at break for the LPTT composite was lower than that of the LPTS composite.

Table 4 Elongation at break and impact strength of LDPE/thermoplastic starch composites.

Starch content (wt%)	**Elongation at break (%)**		**Impact strength (J/mm^2)**	
0 (LDPE)	127.04 ± 11.34		1.64 ± 0.41	
	LPS	LPTS	LPS	LPTS
5	81.2±12	74.9±14	0.95±0.2	1.06±0.3
10	65.5±13	53.1± 7	0.91±0.2	1.01±0.2
20	56.8±10	33.6±11	0.76±0.1	0.82±0.1
30	30.7±8	21.9±9	0.72±0.1	0.78±0.1
	LPC	LPTC	LPC	LPTC
5	85.4±13	78.11±17	0.91 ±0.1	1.2±0.2
10	71.1±10	48.7±12	0.85±0.2	0.94±0.4
20	63.2± 9	24.3±11	0.72±0.3	0.79±0.2
30	42.13±6	15.5±9	0.59±0.1	0.64±0.1
	LPT	LPTT	LPT	LPTT
5	83.3±14	75.4±12	0.92±0.1	1.1±0.1
10	65.5±11	37.8±17	0.87±0.2	0.90±0.4
20	58.2±9	27.8±14	0.81±0.1	0.86± 0.1
30	37.3±4	15.3±5.0	0.77±0.1	0.81±0.2
	LPP	LPTP	LPP	LPTP
5	85.13±12	76.4±16	0.95±0.1	1.5±0.1
10	71.2±9	48.9±10	0.92±0.1	1.3±0.1
20	60.6±7	32.13±3	0.74±0.1	0.80±0.3
30	45.3±5	22.03±6	0.59±0.1	0.71± 0.2
	LPW	LPTW	LPW	LPTW
5	87.12± 7	78.7±8	0.97±0.1	1.4±0.3
10	76.7±9	54.9±12	0.88±0.3	0.93±0.5
20	63.23±10	32.3±2	0.82±0.2	0.91±0.5
30	52.3±6	20.7±1.5	0.67±0.1	0.73±0.2

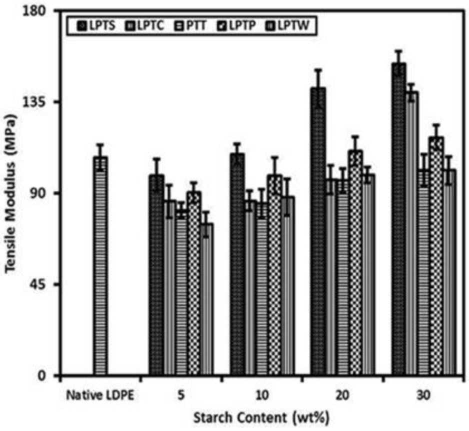

Figure 2 Tensile modulus vs. starch content for LDPE/thermoplastic starch composites.

3.2 Impact properties

An element of impact resistance and the ability of its structure to withstand impact-induced damage. The results of the notched Izod impact test at 25°C are summarized in Table 4.

The results show that increasing the loading level of starch by 5 to 30 wt% has reduced the impact strength of all types of composites compared to native LDPE. Native LDPE has an impact strength of 1.64 J/mm^2. The impact strength showed a similar trend as the tensile strength resulted in a decrease in impact strength as the composition of the starch increased. Although less impact strength was observed for LPT composites than for native LDPE, this reduction was greater than for LPS composites. The ultimate value of impact strength for all LPTT composites was higher than that of the LPTS composite. Impact strength reduction has been identified for LPTS composites because the addition of starch content further increases the composite in the bundles and gives poor compatibility in the two phases. Another likelihood for low impact strength was that starch did not retain its shape as a rigid filler during melting and processing (21). Particle agglomerate and impact strength reduced the particle-matrix interaction with starch reduction but the initiating crack failure does not appear to be stable. The composition of the LPTT composite improvement material reflects the development of interactions between the two phases. The increase in the impact strength of the effect of LPTT composite also seems to be sufficient to characterize the increase in the amorphous phase, which is characterized by the ability to absorb the shock of impact.

3.3 Morphological observation

It is well recognized that the mechanical properties of polymer mixtures are intensely correlated to their morphology. There are also additional features such as miscibility features, uncertainty and unevenness, and some other system imperfections, which can be assessed through morphological study. In this work, these SEM micrographs were performed by direct observation. SEM photomicrographs of the fracture surface of LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT specimens are shown in Figure 3 (a-f), respectively. In these mixtures, the main ingredient (LDPE) forms the matrix and the smaller ingredient (starch) forms the dispersed phase. All starch composites on a flat surface, including some domains, are illustrated, indicating phase separation. A weak bond between LDPE and starch may indicate an interfacial contact of the observed surface cracks and may explain the decrease in mechanical properties after starch is added (22). Nevertheless, different thermoplastic starches are perceived to be completely different from the LDPE in which the cell morphology is filled with LDPE. It has been observed from SEM that each mixture exhibits different structures. This means that the LDPE matrix significantly interferes with cell formation and causes significant changes in the presence of various thermoplastic starches and cell morphology. In other words, the presence of starch breaks down the LDPE matrix and reduces the cell morphology of the mixture. However, thermoplastic sago starch-filled composites have produced excellent structure compared to other thermoplastic starch-filled composites that were homogeneous and had almost no clusters (Figure 3b). The uniform matrix of this composite would be expected to be a good indicator of their structural integrity, and consequently good mechanical properties.

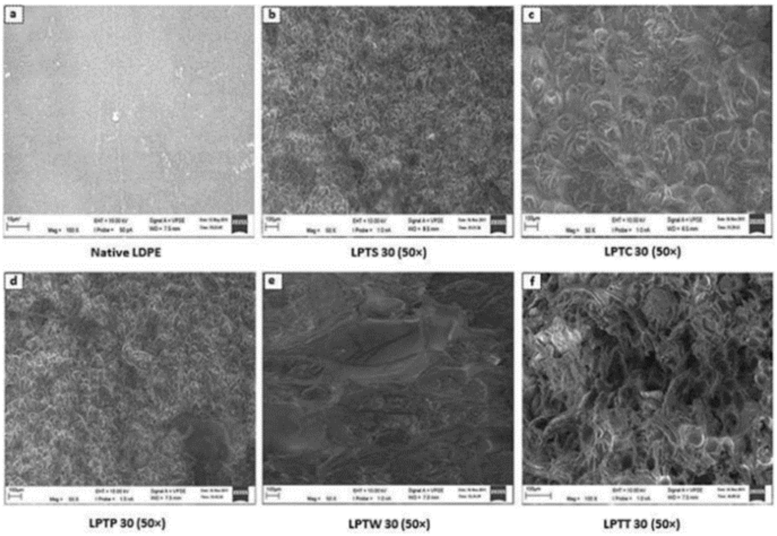

Figure 3 SEM micrographs of the tensile crack surface with 30 wt% starch at 50× magnification of LDPE/thermoplastic starch composite.

3.4 TGA and DTG studies

TGA of the composite is performed to evaluate its thermal durability and humiliation temperature. The TGA and DTG curves for LDPE and different types of starches-filled-LDPE composites at 30 wt% loadings are shown in Table 5 and Figures 4a and 4b, respectively. Generally, both systems show a two-stage degradation process other than the native LDPE. It can be observed in Table 5 and Figure 4 that the LDPE/thermoplastic starch as the first step showed the onset decomposition temperature of glycerol and the onset decomposition temperature in the range of 312-310°C due to various types of starch. The addition of various types of starch to the LDPE matrix lead increases the onset degradation temperature of the mixture as well as the decomposition temperature. Also, the onset degradation temperature of the LDPE ingredient was achieved at 120°C. This finding seems to agree with Averous et al (22) where the adding of cellulose fillers develops the heat resistance of wheat starch-based mixtures. Also, the onset degradation temperature of thermoplastic starch at about 454-455°C appeared at the second step of the thermogram. Nevertheless, an interesting thing that can also be noticed that the weight loss of the mixture is reduced by the activity of the curves with different types of starch.

As shown, the thermal stability of the mixture decreased with LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT at 30 wt% starch loading, respectively. Among them, LPTS had extremely thermal stability. The reduction in percentage weight loss tends to increase the thermal stability of the LPTS samples due to better adhesion between sago starch and LDPE. The results indicated that adding LDPE improved the thermal stability of thermoplastic sago starch. All types of starches-filled LDPE mixtures are further degraded to 500°C, where the mixture decomposes almost completely. Also, the onset degradation temperature of thermoplastic starch at about 454-455°C appeared at the second step of the thermogram. Nevertheless, fascinating things happening can also be observed in which the weight loss of the mixture is reduced by the operation of the curves with various types of starch. As shown, the thermal stability of the mixture decreased with LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT at 30 wt% starch loading, respectively. Among them, LPTS had the utmost thermal durability. The reduction in percentage weight loss tends to increase the thermal stability of the LPTS samples due to better adhesion between sago starch and LDPE. The results indicated that adding LDPE improved the thermal stability of thermoplastic sago starch. All types of starches-filled LDPE mixtures are further degraded to 500°C, where the mixture decomposes almost completely.

Table 5 The effects of various types of starches filled-LDPE and native LDPE on the onset of degrading temperature and the percentage of weight loss.

Samples	**Onset T_d(°C)**		**Weight loss (%)**		**Residue**
(wt%)	First	Second	at 330°C	at 450°C	at 510°C
Native LDPE	–	419.8	–	39.5	0.58
LPTS30	311.8	454.9	7.25	15.77	1.13
LPTC30	311.6	454.7	8.75	16.83	1.52
LPTT30	310.0	453.6	21.61	29.44	3.26
LPTP30	311.4	454.5	10.45	18.27	1.95
LPTW30	310.5	454.2	11.21	20.35	2.74

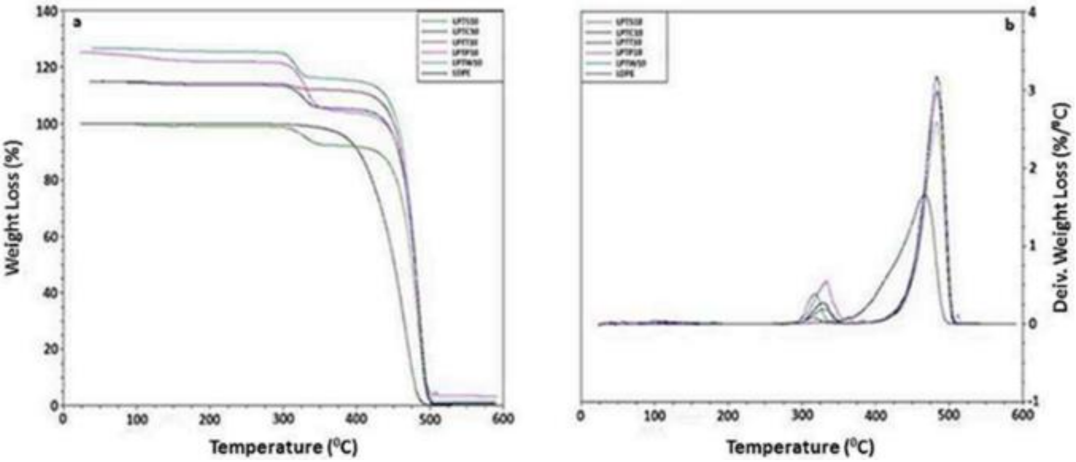

Figure 4 Comparison of (a) TGA and (b) DTG curves of native LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT composites.

3.5 DSC

DSC was used to study the thermal properties of the mixture. The Thermal properties of LDPE and the various types of thermoplastic starch filled-LDPE obtained through DSC are given in Table 6.

Table 6 DSC analysis of thermal parameters various types of starches filled-LDPE mixtures.

Samples (wt%)	T_m (°C)	ΔH_f (J/g)	X_{com} (% crystallinity)	X_{LDPE} (%)
Native LDPE	135.72	103.44	37.47	37.47
LPTS30	135.03	83.02	30.08	33.42
LPTC30	135.24	83.63	30.30	33.66
LPTT30	134.94	82.12	29.75	33.05
LPTP30	134.88	85.01	30.79	34.21
PTW30	135.05	82.98	30.05	33.38

The melting temperature (T_m) and fusion heat (ΔH_f) of LDPE were 135.7°C and 103.4 J/g, respectively. As shown in Figure 5, only the endothermic peaks from DSC curves were present for all types of starch-filled-LDPE mixtures. Likened with the DSC thermogram of LDPE, the endothermic peak for all mixed compounds was approximately the same at the melting temperature of the LDPE phase at about 135.07°C. While there was only one endothermic transition for the LDPE/starch mixture, this does not mean that the mixtures were compatible. Starch has no melting temperature; it does have gelatinization and humiliation temperatures. As a result, the endothermic transitions that happened were uniquely accredited at the LDPE stage. The LDPE phase percentage of the crystallinity can be perceived from the DSC thermogram given in Table 6. The value of ΔH_f^0 (276 J/g) (17) for crystalline PE and the heat of fusion (ΔH_f^*) obtained from the total area of the melted peak, including the initial wide region, was used to calculate the percentage of crystallinity. Comparing the differences between LDPE and LDPE/30 wt% thermoplastic starch composites showed an apparent reduction in fusion heat.

Nevertheless, when the heat of fusion was modified considering only the LDPE content in the mixtures, it was clear that there was no change in the degree of crystallinity of the LDPE stage. The degree of crystallinity of the LDPE stage in the mixture is slightly reduced with various types of starches. This reduction may be owing to the availability of interaction between LDPE and starch, which prevents close packing of the LDPE chain.

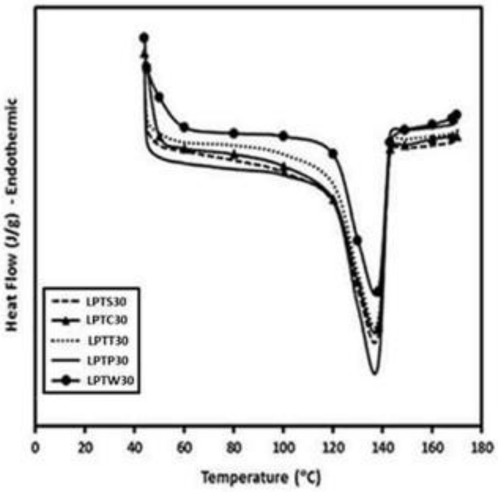

Figure 5 DSC thermogram of different types of starches filled-LDPE composites.

3.6 Biodegradation studies

Biological improvements on composites have a strong significance in the environmentally friendly application of biocomposites. Biodegradation behavior of native LDPE and LDPE/thermoplastic starch composites have been studied to reduce weight and tensile properties during outdoor weather tests.

3.7 Percentage of weight loss

The most useful method for weight loss as a function of time is the biodegradation process (23, 24). LDPE will appear in a lag phase of the first month, after which a small weight loss (0.35%) is observed (Figure 6). Weight loss of LPTS, LPTC, LPTP, LPTW, and LPTT composites increases with increasing degradation time and continues as degradation time progresses.

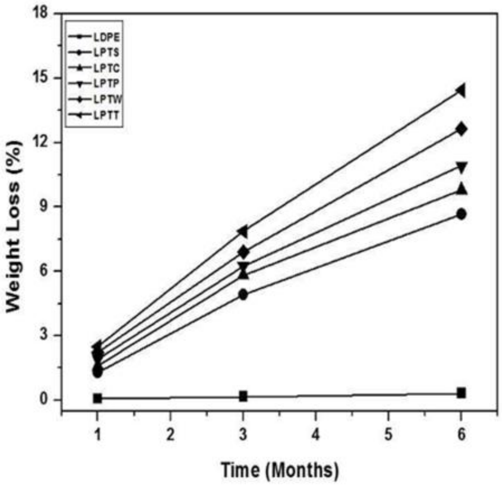

Figure 6 Weight change in the composite of LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT after six months of exposure to natural weather.

This was due to the bleaching, dissolving, or degradation of the starch microorganism attack and increased biodegradation. For all composites, weight loss for the 30 wt% starch content after the first month was 1.3, 1.6, 1.9 2.2, and 2.5% for LPTS, LPTC, LPTP, LPTW, and LPTT, respectively. Weight loss gradually increased during degradation time, and weight loss decreased by 8.7, 9.8, 10.9, 12.7, and 14.4%, respectively, after 6 months of study. Again, it was noted that even after 6 months of the study, LPTS composites had a similar weight loss of 14.4%, which is the percentage of overall weight loss for LPTT. Low weight loss of LPTS may be associated with improved interfacial bonding between the LDPE matrix and starch. Higher biodegradation of LPTT may be due to the same factors leading to lower its mechanical properties.

3.8 Tensile properties and deterioration of composites during outdoor weather testing

Figures 7 and 8 illustrate the outdoor weather performance of tensile strength and elongation at breaks (%) of native LDPE and LPTS, LPTC, LPTP, LPTW, and LPTT composites. The tensile strength for the native LDPE was 7.23 ± 0.5 MPa with an elongation of 127.04 ± 13.2%. The tensile properties of native LDPE and composites vary during the exposure time, which increases the variability of the material insensitive measurements.

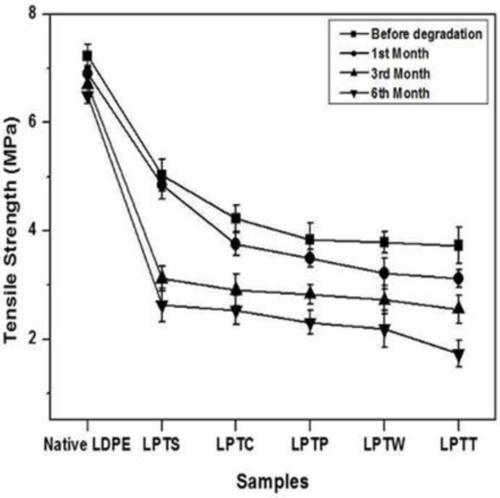

Figure 7 Tensile strength of native LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT composites after six months of exposure to natural weather.

For all composites loading 30 wt% starch, the tensile strength and elongation at breaks are abruptly reduced after the first month to 3.6, 7.2, 8.9, 15.3, 16.2%, and 25.1, 15.3, 17.6, 24.1, and 18.4% of its original value for LPTS, LPTC, LPTP, LPTW, and LPTT, respectively. The moisture absorbed into the starch was expelled into the water formation during processing, which creates air bubbles in the matrix plastic. Air bubbles, considered an error, have reduced the tensile properties of the composite. The inclusion of starch and matrix polymers with a dispersing agent is much weaker than that of virgin plastics, which easily causes composite break under heavy loads. Fresnel voids and other phenomena occurred for a specific strain and a certain content of starch probably with a decrease in the tensile properties of a high content starch. The tensile strength and elongation at break gradually decrease with increasing degradation time. After 6 months in the study, tensile strength and elongation at break dropped by 47.7, 51.3, 55.6, 61.6, 65.2%, and 44.7, 39.9, 39.1, 45.8, and 43.3%, respectively. This implies the major role of manganese stearate in promoting weather degradation of composites. The reduction in tensile properties can be attributed to the oxidation-taking place of the material in the air and accelerated by UV. For LPTT composites, higher losses can be observed in the case of decades of tensile strength and elongation in breaks with outdoor exposure. The higher biodegradability of LPTT may be due to the same factors, which result in its lower mechanical properties.

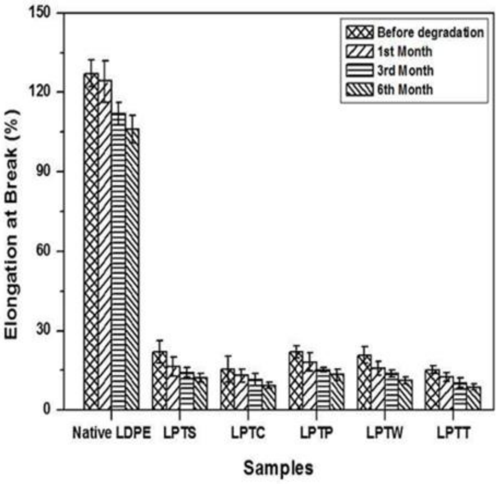

Figure 8 Elongation at break of native LDPE, LPTS, LPTC, LPTP, LPTW, and LPTT composites after six months of exposure to natural weather.

3.9 Water absorption

Water absorption was a significant indicator for estimating the usefulness of composites. Figure 9 represents the water absorption of LDPE and different types of thermoplastic starches filled-LDPE composites at 30 wt% starch loading. It is a rapid water absorption in the first few days of immersion, which gradually decreased over time. This may be due to the density gradient across the two materials. It has been found that the addition of initial water to the starch is strongly bound as a hydrate and when all available hydroxyl groups are used up in this manner then more water is absorbed (25) will be less firmly held composites. The water was spread out thus reducing the rate of water absorption. Furthermore, water molecules can easily replenish the surfaces of synthetic polymer/starch composites and enter into the composites through voids, resulting in higher water absorption in shorter exposure times. The ratio with LDPE and starch does not swell, as it has poor water absorption. Figure 9 reveals that sago starch specimens showed a lower percentage of water absorption than other types of starch, which showed lower water absorption rates.

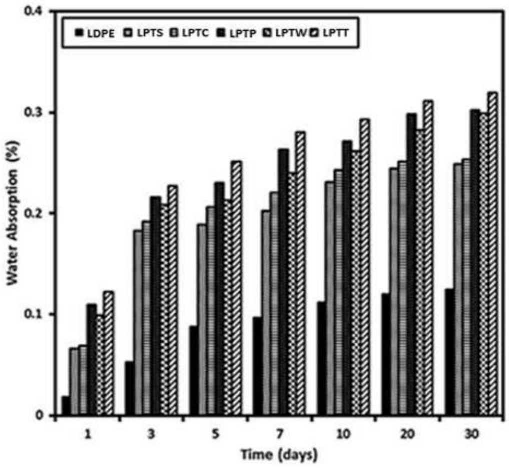

Figure 9 Water absorption of native LDPE, and its composites.

One possible explanation was that water absorption decreased as the amount of amylose in the starch mixture increased. Sago starch contains fewer amylose than other starches. Thus, sago starch shows less water absorption than other types of starch. In all cases, the balance water exploitation and water exploitation rates were lower in mixtures with high amylose contents (77%) than in the case of starch mixtures. This was perhaps owing to the increased gelatinization and degradation of the branch structure of amylopectin in the starch mixtures, which made the mixture more water sensitive.

4. Conclusions

Thermoplastic starches were prepared to order the effects of plasticizers such as glycerin on different types of composites and to evaluate their mechanical, thermal, and biodegradation-related properties. Tensile modulus was increased when mechanical properties such as tensile strength, elongation at break, and impact strength were reduced with filler components. Addition glycerol enhances the mechanical properties of the composite. It has been found that LDPE/thermoplastic sago starch presents greater mechanical properties than other types of starches. Thermoplastic sago starch-filled LDPE composites prepared with 30 wt% starch have a 56.2% increase in tensile strength, a 5% increase in tensile modulus, an 8.7% increase in impact strength, a 28.5% decrease in elongation at breaks than unplasticized composites. From DSC thermograms, no changes are observed in any LDPE melting temperature. The degree of crystallinity of the LDPE phase in mixtures is slightly reduced with the addition of different types of starches. For TGA measurement, the addition of different types of starches to the native LDPE increases the decomposition temperature of the composite compared to the native LDPE. Water absorption results showed that LPTS samples show the lowest percentage of water absorption compared to other starches, and LPTT samples show higher biodegradation than LPTS samples.

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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