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Biodegradable Composites Manufactured from Low-Density Polyethylene and Thermoplastic Sago Starch: Preparation and Characterization

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Abstract

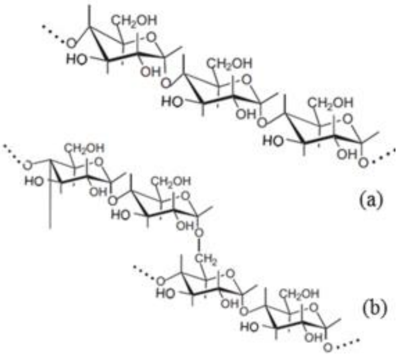
Plastic shopping bags, which are usually manufactured from low-density polyethylene (LDPE), are plastic products with significant environmental nuisance factors. A substance that must be in deteriorate, developing for any reason i.e. hydrolysis, Pseudomonas aeruginosa as well as being exposed by natural weather is interesting enough. In this experiment, sago starch (SS) was treated with sodium trimetaphosphate. SS was mixed with LDPE in different ratios of 0, 10, 20, and 30 wt% and was blended with LDPE using the additives (glycerol/urea, 1% benzophenone, and epolene wax) in the same amount of starch. They were compounded via melt mixing technique tracked by injection molded to form sheets. The outcomes showed that the loss of the tensile features of the untreated composite increased steadily with increasing starch content. At 30 wt% of starch loading, the loss of tensile strength (TS) and elongation at break (Eb) was approximately 23.3% and 87.5%, respectively, compared to virgin LDPE. However, for the treatment composite at 30 wt% starch loading compared to virgin LDPE, the loss of TS and Eb was about 17.3% and 98.8%, respectively. The reduced tensile strength percentage of the treated composite indicates that the good distribution and uniformity of SS in the LDPE was low but more elongated at break than in the untreated composite. The biodegradability of this composite was tested by determining a decrease in weight, morphology, and tensile features during exposure to hydrolysis, Pseudomonas aeruginosa as well as natural weather.

Keywords: Sago starch, Low-density polyethylene, Mechanical properties, Biodegradability

1. Introduction

Contamination by ruined polymeric ingredients poses a major problem as a significant percentage of the municipality's ruined parts contain polymeric materials. It is a challenging task to fight the contamination caused by the degradation of these polymeric wastes into harmful and useful compounds. Solid waste from synthetic polymer materials is identified as a key reason for ecological contamination, which can take up to a thousand years to land (1). It is important to develop some components that can be biodegradable to reduce pollution. These materials not only provide benefits for daily life but also reduce the environmental impact after being used. Renewable natural polymer such as sago starch, fiber, and chitosan were tested alone and include the same with potential advances in plastic properties and product biodegradation. In the last three decades, plastic components have been progressively used in food, textile, housing, transportation, construction, pharmaceutical, and entertainment productions. Thermoplastic polyethylene such as low-density polyethylene (LDPE) materials are tough, light, and durable so it is currently used in plastic films for waste bags, distribution bottles, assemblies, farm bags, compost bags, and various molded laboratory components. Polyethylene is a hydrophobic polymer. It establishes a carbon-carbon connection that microbes cannot land easily. Plastic biodegradability is provided as a solution to the problem of misuse. Starch-based plastics have not harmed the environment and have reduced the greenhouse effect (2). Focus on ecological plastics for food packaging, medical, fishery, and agricultural applications have improved in recent years (3).

Starch is cheap, renewable, fully biodegradable natural ingredients (4), and abundant in agricultural resource-rich countries like Malaysia. It is a natural polymer that repeats 1-4-α-D glucopyranosyl units and is usually composed of a combination of linear component (amylose, secondary) and branched component (amylopectin, main) components. The structure of amylose and amylopectin is shown in Scheme 1.



Scheme 1 The chemical composition of (a) amylose and (b) amylopectin.

The most abundant starch in Malaysia is sago starch (SS), which is extracted from the pith of various tropical palm stems (sago palm). This starch also points to potential biodegradable fillers in thermoplastics as a new use of sago. The blending of SS with LDPE has received considerable attention due to the potential application of this strategy in the removal of plastic waste. Starch-filled polythene composites have shown poor mechanical properties due to imperfections. When different materials are mixed with starch, the hydrophilicity of the starch results in their activities during and after the process (5). Glycerin and starch cross-linked sodium trimethophosphate (STMP) with plasticizing agents will improve the compatibility of LDPE/thermoplastic starch-based mixing methods. STMP has the most important food additives and a low toxic concentration. Although biodegradation of polythene has been extensively studied (6-8), the outcomes were based on polyethylene mixed with starch. The key invading agent of biodegradation is microorganisms (fungi and bacteria), which spread in soil and water. Goheen et al. (9) observed the decay of PE/starch film in the soil using FTIR spectroscopy to evaluate the release of starch and chemical changes in the PE. Despite this work, none relies on evaluating the correlation between morphology, tensile property, and biodegradability of microbial methods. In this case, the effects of starch concentration and the addition of additives to modified SS/LDPE composites and their effectiveness before and after their mechanical properties and biodegradability have been considered.

2. Experimental

2.1 Materials

LDPE pellets obtained from Petlin PE (Malaysia) Sdn Bhd division have been used as a matrix. The density and the melt flow indexes of LDPE were 0.928 g/cm^3 and 3.2 g/10 min, respectively. Percent moisture was 11–13% and its starch value was above 85%. Biodegradable agents are a mixture of glycerol, SS, and urea. To accelerate the photodegradation of LDPE, benzophenone should be used as a photosensitizer agent. Benzophenone was provided by H.L. Blanchford Limited (Ontario Canada). Reagent grades glycerol (glycerin, $C_3H_8O_3$) as the plasticizing agents, STMP as a starch cross-linker in SS blends, and urea and epolene wax were purchased from Malaysia.'s Sigma Aldrich Chemical Company Inc.

2.2 Methods

2.2.1 Refined Sago starch

SS was modified by the Shin et al. method (10, 11) due to its poor processing and incompatibility with LDPE. SS (50 g) was modified with cross-linked STMP (5.40 g) at 45°C for 2 h. Grounded cross-linked SS was then used to dry and prepare the composite in an oven at 50°C for 2 h.

2.2.2 Sample preparation

All components were dried in a vacuum oven at 80°C for 20 h to reduce humidity before use. Granular SS was mixed with LDPE in different ratios of 0-30 wt%, and treated SS were mixed with LDPE by adding the same amount of starch additives (glycerol/urea and 1% benzophenone) initially in a Mini Blender (Most Machine Builder Fairfield, New Jersey, USA) contains 2% dissolving mediator (Epolene wax E-43p, white group, USA). Chemical compositions are presented in Table 1. The above mixer was made by melt blended with a co-rotating twin-screw extruder (model: TSE 20, GmbH & Co. KG, Germany) and then a composite sheet was formed with injection molding. The compounding process was conducted at a rotor speed of 90 rpm and the temperature die (150°C/150°C) was carried out from the feeder (160°C/160°C). The extruded components were then palletized by a pelletizer. Dumbbell-shaped specimens were made from these platelets using the injection-molded machine (Toyo, model: Si180iii-E200, Japan). The preparation of the biodegradable film is presented schematically in Figure 1.

Table 1 Prepared sample composition.

Sample code	LDPE (wt%)	Starch (wt%)	A	B	C
Virgin LDPE	100	0	–	–	–
L90S10 (LUS10)	90	10	–	–	–
L80S20 (LUS20)	80	20	–	–	–
L70S30 (LUS30)	70	30	–	–	–
L90S10GU15 (LMS10 A)	90	10	15	1	2
L80S20GU15 (LMS20 A)	80	20	15	1	2
L70S30GU15 (LMS30A)	70	30	15	1	2

L: LDPE; U: unmodified sago starch; M: SS treated with STMP; The number after the letter S indicates the percentage of starch; A; additives; glycerol:urea=2:1 (wt%); B: benzophenone; C: Epolene wax (wt%).

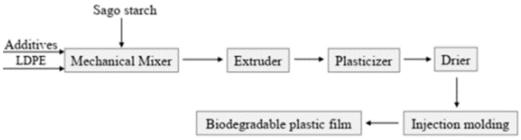


Figure 1 Schematic diagram for biodegradable film preparation.

2.2.3 Mechanical test

Dumbbell-shaped specimens (125 × 3 mm^2) have been used to measure the tensile features of composites. Tensile features of the composite were evaluated using Shimadzu UTM (Model AG-1, Japan) by the ASTM-D 638-14 standard (12). The tensile test was achieved at a crosshead speed of 10 mm/min and a gauge length of 50 mm. All experiments were measured at 25 ± 2°C and relative humidity of 55 ± 4%. All outcomes were examined as the mean value of five specimens.

2.2.4 Morphological observation

Before and after biodegradation, the tensile fractured surfaces of untreated and treated SS plastic composites were analyzed by a Zeiss, Evo 50 SEM at a voltage of 20 kV. The samples were fractured in liquid nitrogen and the fracture edges of the samples were embedded in aluminum sputum and covered with a thin layer of gold to disperse the electric charge during the test.

2.2.5 Degradation tests

The biodegradation behavior of the composite in virgin LDPE, LUS30, and LMS30A was revealed by percent weight loss during hydrolysis, tensile properties (tensile strength (TS) and elongation at break (Eb), and morphology, exposure to *Pseudomonas aeruginosa*, natural weather, and buried in the ground.

2.2.5.1 Hydrolysis studies

2.2.5.1.1 Simple hydrolysis

The technique of use was proposed by Arvanitoyannis et al. (13). For general hydrolysis, dumbbell-shaped specimens were immersed in 30 ml of distilled water at 80°C. Weight variations were calculated every 3 hours to record weight loss over the period.

2.2.5.1.2 Alkali hydrolysis

The technique of use was suggested by Arvanitoyannis et al. (15). The dumbbell-sized specimens were immersed in 30 mL 0.1N NaOH solution at 80°C. Weight variations were calculated every 3 hours to record weight loss over the period. Before testing, the molded samples were weighed correctly. The mold samples were also weighed correctly after being placed in a degraded environment for 18 hours. The weight loss percentage was measured by the following equation (2.1):

$$Weight\ loss\ (\%) = \frac{W_b - W_a}{W_b} \times 100 \qquad (2.1)$$

Where W_b refers to mold weight before degradation, W_a refers to mold weight after degradation.

2.2.5.2 Readiness of bacterial growth

The sample was cut into 5 × 5 cm^2 of flat parts and seated on the surface of the nutritious agar in the Petri dish. *P. aeruginosa* was refined by a nutritious agar medium in an infertile situation. The bacterial suspension was made in saline and spread over the sample. It contained a piece of parafilm with dimensions of 4 × 4 cm^2 and then covered for 90 days at a humidity of more than 90 at 30°C.

2.2.5.3 Natural weather experiment

The dumbbell-shaped specimens were planted in racks and exposed to naturally actinic radiation at UMP Gambang, Pahang, Malaysia for 180 days. The rack is fixed facing the equator at an angle of 45° and the rack is free from any open space where it is covered by other objects. Specimens were exposed to rain, sunlight, wind, etc. (14) and were taken for 1 month, 3 months, and 6 months later to measure degradation. The mean temperature was 28.5±0.35°C with a relative humidity of 58%. A control test was conducted indoors on similarly prepared samples for comparison with outdoor exposure, indicating their shelf life. Percentage loss in features was measured after 1 month, 3 months, 6 months.

The evolution of the carbonyl group was measured by FTIR (Perkin Elmer System 2000). Specimens were scanned in a frequency range of 4000-400cm-1. For each spectrum, 52 consecutive scans with a 4 cm-1 resolution were recorded. The Carbonyl Index (CI) was used to identify the degree of photo-oxidation of PE. It is defined as the ratio of absorbance of carbonyl around1715 cm-1 to an internal thickness band at 1465 cm-1. The CI was measured by the following equation (2.2):

$$CI = A_{1715}/A_{1465} \qquad (2.2)$$

3. Results and Discussion

3.1 Assessment of mechanical features and morphological observations

Figures 2(a) and (b) show the influences of untreated and treated starch content on the percentage loss of TS and Eb for SS plastic composites. We noticed that the percentage loss for untreated composites (LUS_{10}, LUS_{20}, and LUS_{30}) of TS increased steadily compared to virgin LDPE (Figure 2a). The TS of virgin LDPE was about 9.86 MPa. Increasing the starch content has increased the loss of TS. Loss of TS may be due to the weakening of the interfacial bond between starch and LDPE. As the content of starch increases, spherical starch has a less effective cross-sectional area of LDPE. The hydroxyl group on the surface due to starch exhibits hydrophilic features and a strong intermolecular hydrogen bonding. This observation agrees with the results presented by the researchers (15). The percentage decrease in TS of treated SS plastic composites ($LMS_{10}A$, $LMS_{20}A$, and $LMS_{30}A$) compared to virgin

LDPE has been steadily increasing but it is less than the untreated SS plastic composites (LUS_{10}, LUS_{20}, and LUS_{30}). This is probably due to better interfacial bonding that occurred after the addition of LDPE matrix and additives (glycerol: urea = 15%, ferric stearate 0.1%, and epolene wax 2%). The –OH group of cross-linked starch reacted strongly with the phosphate group in STMP, and the functional -OH group reacted less with STMP as the cross-linked starch decreased. As a result, strong hydrogen bonds between LDPE/starch and plasticizer molecules can support the desired starch/LDPE interaction between LDPE or starch molecules instead of intermolecular and intramolecular, thus reducing the loss of compatibility between LDPE and starch, which resulted in a lower loss of TS.

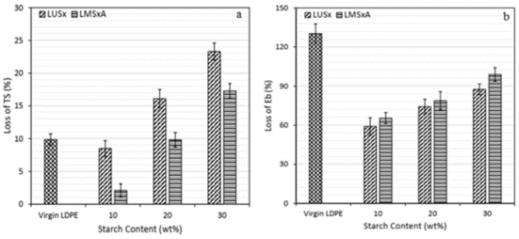


Figure 2 Effect of starch content on the percentage loss in (a) tensile strength (TS) and (b) elongation at break (Eb) of LUS_x and LMS_xA composites. LUS: LDPE/untreated SS; LMSA: LDPE/treated SS with additives. The subscript x after the letter S indicates the percentage of starch.

Figure 2(b) shows the filler load effect of Eb percent loss of untreated and treated SS plastic composites. The Eb of virgin LDPE was found to be 130.23%. We noticed that the percentage loss in Eb for composites increases with increasing filler loading. This starch can impose hydrophilic nature and may interfere with the absorption effect by absorbing moisture and reducing the effect of physical bonding between the LDPE/SS interface (16). As mentioned earlier, towards higher filler materials, agglomeration may occur at higher points of stress concentration, which initiate crack propagation in the mixtures. This induces a percentage loss of Eb in the mixture with increasing starch content. Wang et al. (17) observed a similar trend with natural filler-filled LDPE mixtures.

The morphology of SS, virgin LDPE, untreated SS plastic composite (LUS_{30}), and treated SS plastic composite ($LMS_{30}A$) is displayed in Figure 3. Figure 3(a) displays the granular sizes of SS from 10 to 40 μm. The morphologies of the virgin LDPE, LUS_{30}, and $LMS_{30}A$ composites are shown in Figure 3(b)-3(d), respectively. Figure 3(c) shows that the addition of SS to LDPE outcomes in a weaker spread between SS and LDPE. This micrograph proved to be the cause of the deterioration of the mechanical features of the mixture with the starch content. The interfacial bond between LDPE and starch can form in very weak stress concentration regions. Figure 3(d) displays the SEM micrograph of $LMS_{30}A$ composite with a mixture of glycerol/urea plasticizers, benzophenone, and dispersing agent. We noticed that when the treated starch was added to the mixtures, the size or agglomeration of SS decreased than the LUS_{30} composite. The morphology revealed that the sample in $LMS_{30}A$ of Figure 3(d) showed that phase separation between SS and matrix could not be detected. It can be noted that the interfacial morphology has improved a lot due to better interfacial adherence compared to Figure 3(c). The mixture of plasticizers, STMPs, and dispersing agents can build further hydrogen bonds with SS because glycerol/urea weakens the intermolecular and intramolecular hydrogen bonds between LDPE and starch. This clarifies the better mechanical features inspected for the $LMS_{30}A$ composite than the LUS_{30} composite.

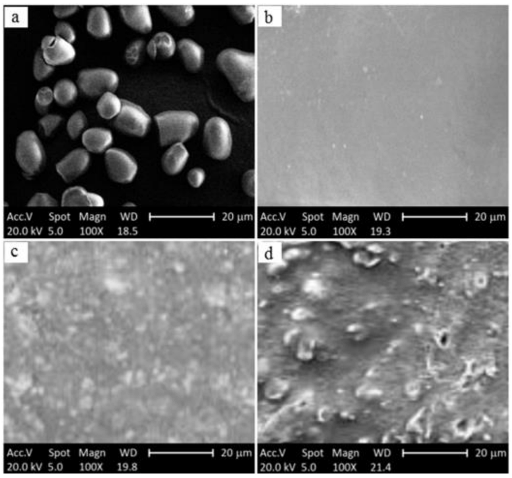


Figure 3 SEM photomicrographs of (a) SS granules, (b) virgin LDPE, (c) LUS_{30} and (d) $LMS_{30}A$ composites.

3.2 Degradation tests

3.2.1 Simple and alkali-accelerated Hydrolysis

Table 2 summarizes the weight loss percentage of the composite of virgin LDPE, LUS_{20}, LUS_{30}, $LMS_{20}A$, and $LMS_{30}A$ during simple hydrolysis and alkali-accelerated hydrolysis. Virgin LDPE has significantly slowed down weight loss than the LDPE/SS composites. LDPE has shown high weight loss with high amounts of starch and exposure time. This may be due to the degradation of SS dissolved in water. As shown in Table 2, alkali hydrolysis may outcome in higher weight loss in comparison to simple hydrolysis. The objective of this method for determining the biodegradability of a composite is to prove that synthetic composites may have different values of pH falling into the water. High pH values can accelerate starch-based mold decay.

Table 2 Weight changes of virgin LDPE, LUS_{20}, LUS_{30}, $LMS_{20}A$, and $LMS_{30}A$ blends after 18 h of hydrolysis.

Samples	Weight loss (%)		
	6 h	**12 h**	**18 h**
Simple hydrolysis			
Virgin LDPE	0.000	0.003	0.012
LUS_{20}	0.541	1.324	2.352
LUS_{30}	0.826	1.834	2.741
$LMS_{20}A$	0.264	0.553	0.923
$LMS_{30}A$	0.392	0.934	1.832
Alkali hydrolysis			
Virgin LDPE	0.006	0.011	0.017
LUS_{20}	1.325	2.321	4.576
LUS_{30}	1.556	2.475	5.231
$LMS_{20}A$	0.621	1.023	2.586
$LMS_{30}A$	0.758	1.127	3.285

Figures 4(a) and 4(b) display the SEM micrographs of the $LMS_{30}A$ composite after 18 hours of exposure to simple and alkali-accelerated hydrolysis. The SEM micrograph confirmed the observed decay of starch particles in the LDPE matrix. From Figure 4 (a), simple hydrolysis is seen in big voids on the smooth surface of LDPE, which causes its collapse, revealing embedded starch granules. As shown in Figure 4(b), alkaline hydrolysis shows many more voids and holes than simple hydrolysis. These pores revealed the rate of biodegradation and confirmed the elimination of SS by hydrolysis. Absorption of SS by hydrolysis outcomes in holes of LDPE and ultimately degradation of LDPE.

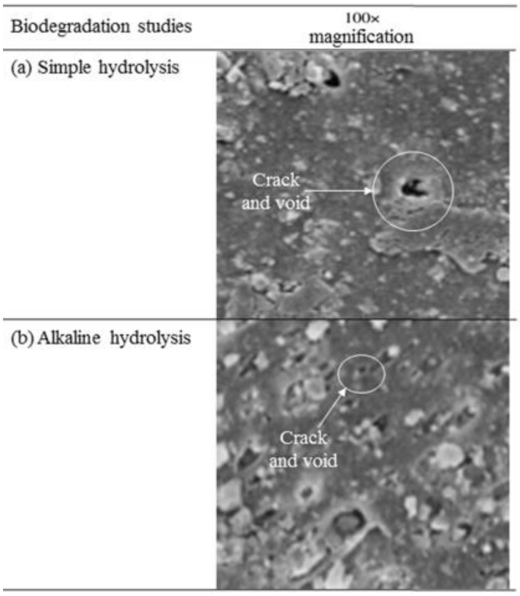


Figure 4 SEM photomicrographs of $LMS_{30}A$ blends after 18 h of (a) simple hydrolysis and (b) alkaline hydrolysis.

3.2.2 Exposure to *Pseudomonas aeruginosa*

The most useful method of weight loss as a function of time is employed to monitor biodegradation (18). Table 3 reveals a reduction percentage of composite features (weight loss, TS, and Eb) in virgin LDPE, LUS_{30}, and $LMS_{30}A$ after 90 days of exposure to *Pseudomonas aeruginosa*. Accordingly, virgin LDPE had a slight weight loss. The reason for weight loss is *P. Aeroginosa* can be blamed for biodegradation, as carbon-free media can reduce LDPE (19). Our studies including biodegradation of $LMS_{30}A$ and LUS_{30} composites show linear growth in weight loss. From Figure 5 portion (B and C), black spots performed on the surface of the sample, indicating bacterial enhancement but virgin LDPE (Figure 5A) showed no visible enhancement. The composites' weight loss increase over 90 days also supported the fact that sago starch in LDPE composites attracted bacteria to attack the composite. The highest rates of biodegradation were found for the LUS_{30}, and $LMS_{30}A$ composites, which were 7.26%, and 5.15%, respectively. Virgin LDPE, however, showed minimal biodegradation, which was only 0.35% after 90 days of exposure to *Pseudomonas aeruginosa.*

Table 3 Weight loss and loss in tensile features (TS, and Eb) of virgin LDPE, LUS_{30}, and $LMS_{30}A$ composites after 90 days of exposure to *Pseudomonas aeruginosa.*

Loss in properties	Time (days)	Samples		
		LDPE	**LUS_{30}**	**$LMS_{30}A$**
Weight loss (%)	30	0.12	3.36	2.86
	60	0.28	5.45	3.65
	90	0.35	7.26	5.15
Loss of TS (%)	30	8.5±0.9	20.2±0.5	13.3±0.7
	60	17.2±0.4	29.4±0.7	18.8±0.5
	90	23.4±0.7	38.6±0.9	26.7±0.8
Loss of Eb (%)	30	15.3±0.5	23.7±0.8	18.4±0.5
	60	26.6±0.7	31.2±0.6	28.2±0.7
	90	37.5±0.8	49.3±1.1	43.4±0.5

Prior to testing, the composite of virgin LDPE, LUS_{30} and $LMS_{30}A$ results in TS and Eb values of 9.86 ± 0.8, 7.56 ± 0.4, 8.15 ± 0.6 MPa and 130.23 ± 15.3%, 16.2 ± 0.9%, 1.47 ± 0.04%, respectively. We noticed that 90 days after being infected with *Pseudomonas aeruginosa* and the percentage loss in TS and Eb increased for all samples, with Eb having the most impact. Eb is a more sensorial measure of the extent of ruin than TS (20). This is why the Eb of LDPE is less flexible as it becomes crystallinity (21); denser so more material is opaque, so its degree depends on the concentration. Losses in the TS of LUS_{30} and $LMS_{30}A$ composites increased steadily as the exposure time increased. The trend was identical to that of Eb. The EB percent loss was drastic in the last phase. While LUS_{30} composites had no interfacial adherence to the LDPE for $LMS_{30}A$

composites, there were more gaps between the LUS_{30} composite and the LDPE. This interval enables the penetration of O_2 and light into the interior of the LDPE. Hence, as the exposure time increased, the LUS_{30} composite was more lost in TS than the $LMS_{30}A$ composite. Ninety days after being infected with *Pseudomonas aeruginosa*, the maximum loss of TS and Eb for composite in $LMS_{30}A$ was 26.7% and 43.4%, respectively.

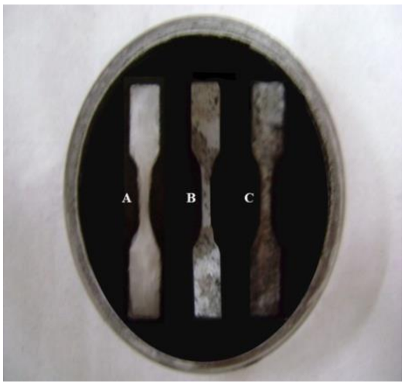


Figure 5 Degradation of samples after exposure to *Pseudomonas aeruginosa* (A) virgin LDPE, (B) $LMS_{30}A$, and (C) LUS_{30} composites.

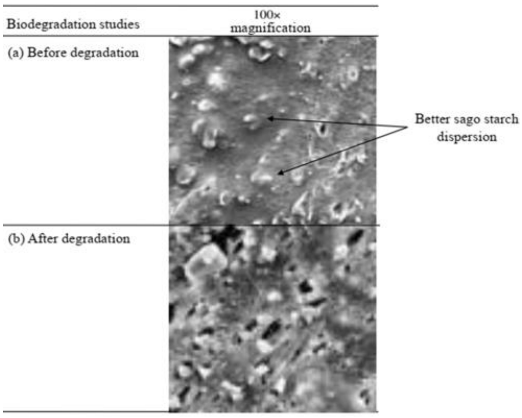


Figure 6 SEM micrographs (magnification 100×) of $LMS_{30}A$ blend composites (a) before exposure to *Pseudomonas aeruginosa*; (b) after exposure to *Pseudomonas aeruginosa* for 90 days.

To confirm bacterial degradation, SEM has been tested. Figure 6 is an SEM micrograph of the composite in $LMS_{30}A$ after 90 days of incubation by *Pseudomonas aeruginosa*. Before being tested, the composite in $LMS_{30}A$ (Figure 6(a)) exhibits a smooth and uniform surface morphology. As shown in Figure 6(b), a few voids and bores in $LMS_{30}A$ are performed on the composite surface. These voids specify the rate of ruin and confirm the removal of SS by the *Pseudomonas aeruginosa*. Show bores regions infected by microorganisms. Consumption of SS by bacteria causes voids in LDPE and ultimately decays LDPE. The process of decomposition is that the consumption of SS by microorganisms leads to the destruction of LDPE chains due to their molecular weight loss. Then, smaller LDPE chains became more hydrophilic and microorganisms more attractive.

3.2.3 Natural weather research

Figure 7 shows composite carbonyl indices and weight loss (%) in virgin LDPE, LUS_{30}, and $LMS_{30}A$ after exposure to natural weather as a function for six months during the exposure period. As can be seen from Figure 7(a), CI increased as its efficacy time for both LUS_{30} and $LMS_{30}A$ composites. The data show that the CI increased further as the exposure time increased. It makes the microstructure of the SS is embedded in LDPE. Therefore, the higher the SS content of the LDPE, which then easily allows the permeation of light and oxygen across the internal parts of the LDPE, resulting in higher CI resulting in increased porosity.

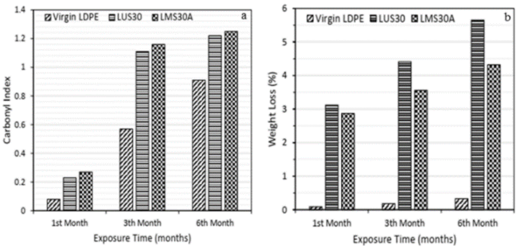
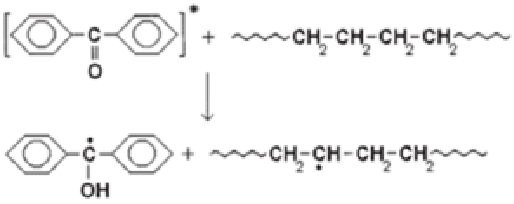


Figure 7 (a) The carbonyl index and (b) weight loss of virgin LDPE, LUS_{30}, and $LMS_{30}A$ blends after six months of natural weather.

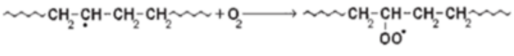
Adding benzophenone may increase CI due to the following method:

1. Benzophenone absorbs UV rays and stimulates the excited state:

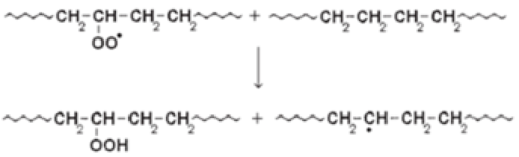
2. Benzophenone in the excited state abstracts the H atom from LDPE and forms an LDPE free radical:



3. This free radical reacts with O_2 and then forms a peroxide radical



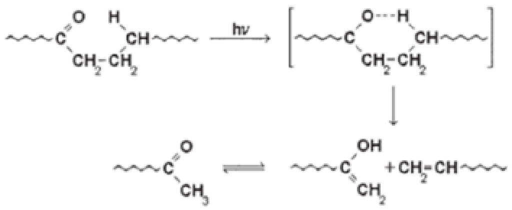
4. ROO. form hydroperoxide (ROOH) by releasing H atom from another polymer molecule:



5. ROOH rots in LDPE molecules with a carbonyl group (CG):

6. The LDPE molecule with CG is then rot by a Norrish type I or type II process.

Norrish type II



Thus, in the above process, the increase in the LDPE chain fragment with the CG results in an increase in the CI in the LDPE chain. This mechanism shortens the polymer chains and at the same time reduces the molecular weight and tensile features of the polymer.

Figure 7(b) displays that the virgin LDPE shows a reversal phase in the first month, followed by a slight weight loss (0.33%), whereas its mixtures with starch exhibit further weight loss. As clearly illustrated in Figure 7(b), weight loss exposure to the LUS$_{30}$ composite can be as high as 5.65% after 6 months. However, the inclusion of benzophenone reduced the weight loss of the LMS$_{30}$A composite by up to 4.32%.

As seen in Table 4, the percentage loss in TS and Eb of virgin LDPE, LUS$_{30}$, and LMS$_{30}$A composite increased with exposure time. These starch particles contain an abundance of hydroxyl groups, due to their water-absorbing nature, which is prone to moisture absorption. Frequent rainfall is related to natural weather tests. The idea is that water molecules will be absorbed by the starch particles, which were located on the outer surface, followed by the penetration of water molecules into the inner layers of exposed SS plastic composites. However, the addition of benzophenone helps to reduce the tensile features of the composites under the outdoor exposure test. The increase in exposure time and the percentage loss in TS with the addition of benzophenone is due to the chain reaction resulting in scission exposure. Benzophenone can produce free radicals and break long polymer chains into short ones. Thus, the highest percentage loss in TS was obtained from a composite with 1% benzophenone. As seen in Table 4, the TS of 1% $C_{13}H_{10}O$ composite decreased by about 38.2% after exposure for 6 months. This means that, after a certain period of exposure, a certain amount of photosensitizer begins to lose its strength and become brittle. As seen in Table 4, Eb is the same trend as TS. The percentage loss in Eb was intense in the 6th month, as the SEM study showed that the SS in the blend had no interfacial bond to the LDPE. This interval is to facilitate the entry of O_2 and light inside the LDPE.

Table 4 Percentage loss in tensile properties (TS and Eb) of virgin LDPE, LUS$_{30}$, and LMS$_{30}$A composites during outdoor exposure.

Loss in properties	**Time (months)**	**Samples**		
		LDPE	**LUS30**	**LMS30A**
Loss of TS (%)	1	11.4±0.6	26.1±0.5	18.2±0.7
	3	20.3±0.5	39.4±0.8	30.3±0.6
	6	29.8±0.8	53.2±0.7	38.2±0.8
Loss of Eb (%)	1	19.2±0.8	31.3±0.8	23.6±0.6
	3	31.6±0.7	45.8±0.9	35.7±0.9
	6	42.4±0.5	71.2±1.2	48.2±1.3

Figure 8 illustrates the surface morphology of LUS30 and LMS30A composites before and after exposure to natural weather. In Figure 8(a), the LUS30 composite had less compatibility between LDPE and starch. As shown in Figure 8(b), after six months of weather, the LUS30 composite was transformed into a rough surface with large cracks, elongated cavities, and droplets. Prolonged cavities may be due to the removal of starch particles due to moisture absorption, which causes the grains to swell, increase in size, and be forced out of the cavity. Figures 8(c) and (d) show the LMS30A composite before and after 6 months of natural weather exposure. The fracture surface of the composite in LMS30A was highly cracked after natural weather was observed. The cavities specify the rate of ruin and confirm the removal of SS by natural weather testing. More and smaller cavities performed in the LDPE lead to a biodegradation rate.

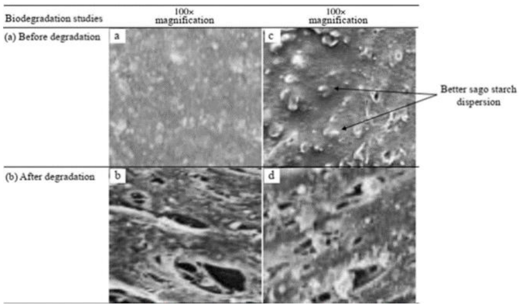


Figure 8 SEM images (magnification 100×) of LDPE/SS blends: (a) LUS$_{30}$ and (c) LMS$_{30}$A composites before exposed to natural weather; (b) LUS$_{30}$ and (d) LMS$_{30}$A composites after exposure to natural weather.

4. Conclusions

Treated SS had better compatibility and interaction with LDPE than untreated SS. Thus, the percentage loss in TS of the treated SS plastic composite was greater than the elongation at break. Alkaline hydrolysis causes highly dramatic changes and manages rapid degradation after 18 hours compared to simple hydrolysis. After exposure to natural weather, the tensile test results indicate that treated SS plastic composites showed a lower loss in tensile features compared to untreated SS plastic composites due to a better interfacial bond between LDPE and starch. The rate of biodegradation of composites has increased with increasing degradation time. Of all the degradation experiments conducted, perhaps the most dramatic change in composites was caused by natural weather. Data show that these new polymer blends can be applied as agricultural plastics in film, flower cases and bags, horticulture, packaging, and related industries where rapid deterioration is recommended.

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Declaration of conflicting interests

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

References

1. Azahari N., Othman N., Ismail H. Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media. J Phys Ther Sci. 2011; 22: 15-31.
2. Bastioli C. Global status of the production of biobased packaging materials. Starch/Stärke. 2001; 53: 351-55.
3. Rujnić-Sokele M., Pilipović A. Challenges and opportunities of biodegradable plastics: A mini review. Waste Manage Res. 2017; 35: 132-40.
4. Ju J., Xie Y., Guo Y., Cheng Y., Qian H., Yao W. Application of starch microcapsules containing essential oil in food preservation. Crit Rev Food Sci. 2020; 60: 2825-36.
5. Qiao D., Li S., Yu L., Zhang B., Simon G., Jiang F. Effect of alkanol surface grafting on the hydrophobicity of starch-based films. Int J Biol Macromol. 2018; 112: 761-66.
6. Beg M.D.H., Kormin S., Bijarimi M., Zaman H.U. Environmentally degradable sago starch filled low-density polyethylene. J polym Eng. 2015; 35: 551-63.
7. Ghatge S., Yang Y., Ahn J.-H., Hur H.-G. Biodegradation of polyethylene: a brief review. Biol Chem. 2020; 63: 1-14.
8. Peres A.M., Oréfice R.L. Effect of incorporation of Halloysite nanotubes on the structure and properties of low-density polyethylene/thermoplastic starch blend. J Polym Res. 2020; 27: 1-10.
9. Goheen S., Wool R. Degradation of polyethylene–starch blends in soil. Journal of applied polymer science. 1991; 42: 2691-701.
10. Shin M., Song J., Seib P.A. In vitro Digestibility of Cross-Linked Starches–RS4. Starch/Stärke. 2004; 56: 478-83.
11. Lee W.-J., Youn Y.-N., Yun Y.-H., Yoon S.-D. Physical properties of chemically modified starch (RS4)/PVA blend films—part 1. J Polym Environ. 2007; 15: 35-42.
12. American Society for Testing and Materials. D638−14 Standard Test Method for Tensile Properties of Plastics. Standard Test Method for Tensile Properties of Plastics. 2014; 17.
13. Arvanitoyannis I., Biliaderis C.G., Ogawa H., Kawasaki N. Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: Part 1. Carbohyd Polym.1998; 36: 89-104.
14. Kiatkamjornwong S., Pabunruang T., Wongvisetsirikul N., Prasassarakich P. Degradation of cassava starch-polyethylene blends. J Sci Soc Thailand. 1997; 23: 135-58.
15. Obasi H. Studies on biodegradability and mechanical properties of high density polyethylene/corncob flour based composites. International Journal of Scientific and Engineering Research. 2012; 3: 259-72.
16. Febrianto F., Setyawati D., Karina M., Bakar E.S., Hadi Y.S. Influence of wood flour and modifier contents on the physical and mechanical properties of wood flour-recycle polypropylene composites. J Biol Sci. 2006; 6: 337-43.
17. Wang Y.J., Liu W., Sun Z. Effects of glycerol and PE-g-MA on morphology, thermal and tensile properties of LDPE and rice starch blends. J Appl Polym Sci. 2004; 92: 344-50.
18. Gattin R., Copinet A., Bertrand C., Couturier Y. Biodegradation study of a coextruded starch and poly (lactic acid) material in various media. J Appl Polym Sci. 2003; 88: 825-31.
19. Agamuthu P., Faizura P.N. Biodegradability of degradable plastic waste. Waste Manage Res. 2005; 23: 95-100.
20. Miltz J., Narkis M. The effect of ultraviolet radiation on chemically crosslinked low-density polyethylene. J Appl Polym Sci. 1976; 20: 1627-33.
21. Danjaji I., Nawang R., Ishiaku U., Ismail H., Ishak Z.M. Degradation studies and moisture uptake of sago-starch-filled linear low-density polyethylene composites. Polym Test. 2002; 21: 75-81.