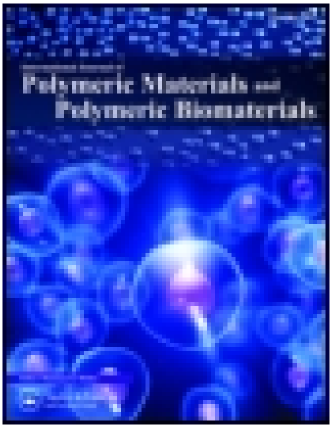

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Biodegradability Studies on LDPE-Starch Blends using Amylase-Producing Vibrios

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Low-density polyethylene, (LDPE) was mixed with two grades of tapioca starch–low-grade and high-grade. Various compositions were prepared and mechanical and thermal studies performed. The biodegradability of these samples was checked using a culture medium containing Vibrios *(an amylase-producing bacteria), which was isolated from a marine benthic environment. The soil burial test and reprocessability of these samples were checked. The studies on biodegradability show that these blends are partially biodegradable. These low-density polyethylene-starch blends are reprocessable without sacrificing much of their mechanical properties.*

Keywords: biodegradability, low-density polyethylene, reprocessability, tapioca starch

INTRODUCTION

Research on degradable synthetic polymers began in the early 1980s. As a consequence of extensive discussions on better waste management strategies, biodegradable polymers have recently attracted a great deal of public and industrial interest [1]. Low-density polyethylene, which is hard to degrade in landfills, is currently one of the most commonly used thermoplastics for packaging applications [2]. The resistance of polyethylene to biological attack is related to its hydrophobicity, high

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molecular weight, and lack of functional groups recognizable by microbial enzymatic systems. These properties limit its applications in which biodegradability is a desirable attribute [3].

Because of its low cost and biodegradability, starch has been extensively used with other polymers to improve the biodegradability of resulting blends [4–6]. The blending of biodegradable polymers, such as starch, with inert polymers, such as polyethylene, has received considerable attention because of the possible application of this technique in the waste disposal of plastics. The logic behind this approach is that if the biodegradable component is present in sufficient amount, and if it is removed by microorganisms in the waste disposal environment, then the base inert plastic should slowly disintegrate and disappear [7].

Low-density polyethylene is defined by a density range of 0.910–0.940 g/cm^3. The high degree of short- and long-chain branches characteristic of the low-density polyethylene molecule inhibits their ability to crystallize. This results in a flexible product with a low molecular weight, and increased ductility [8]. The high degree of branching with long chains gives molten LDPE unique and desirable properties.

Starch is a polymer of glucose. Glucose units are linked together by α-1, 4 and α-1, 6 linkages. Starch occurs in two forms:amylase and amylopectin. Amylopectin is a branched chain of α-1, 4 linkages with α-1, 6 linkages at the branch point, whereas amylase is a straight chain of α-1, 4 linkages [9].

In this study, LDPE was mixed with two grades of tapioca starch, namely low-grade starch (LS) and high-grade starch (HS). Various compositions (5, 10 and 15 wt% of starch) were prepared and their mechanical and thermal properties and biodegradation were studied and reprocessability was evaluated.

EXPERIMENTAL

Materials

The film grade LDPE (24FS040) used in this study was provided by Reliance Industries Limited, Mumbai, India. Low-grade starch and high-grade starch were supplied by Jemsons Starch & Derivatives, Aroor, Alapuzha, Kerala. These fillers were oven dried at 120°C for 1 h prior to mixing.

Mixing

The compounds were prepared in a Thermo HAAKE Polylab System equipped with roller type rotors. The mixing was done at a rotor speed of 30 rpm and at a temperature of 150°C. Initially the LDPE was allowed to melt for 2 min, and then the filler was added. Mixing was continued for another 4 min. The neat polymer was also masticated under the same conditions. Three compositions with each filler and polymer were prepared.

Preparation of Test Specimens

The test specimens were prepared from the compounds by molding in an electrically heated hydraulic press for 5 min at 150°C under a pressure of 20 MPa. After molding the samples were cooled under pressure.

Mechanical Testing

The mechanical properties were measured according to ASTM D 882 (2002) in a Shimadzu Autograph AG-I series at a crosshead speed of 50 mm/min.

Thermal Studies

Thermogravimetric Analysis

Thermogravimetric analyses of the samples were carried out in a TGA Q-50 thermal analyzer (TA Instruments) under a nitrogen atmosphere. The samples were heated from room temperature to 800°C at a heating rate of 20°C/min and a nitrogen gas flow rate of 40–50 cm^3/min. Sample weight varied from 10 to 15 mg. Thermograms were recorded from room temperature to 800°C. The onset of degradation temperature, the temperature at which weight loss is maximum (T_{max}) and residual weight in percentage were evaluated.

Differential Scanning Calorimetry

Crystallinity of the samples was studied using a TA Q-100 thermal analyzer (TA Instruments) at a heating rate of 10°C/min. Samples of 5–10 mg were heated in a nitrogen atmosphere from −50° to 170°C at a heating rate of 10°C/min, and kept at 170°C for 3 min to erase the thermal history. Then a cooling was performed at a rate of 10°C/min from 170 to −50°C, followed by a second heating from −50 to 170°C at the same rate. Polymer crystallinity was calculated from the melting enthalpy obtained by endothermic peak integration, and as reference the melting enthalpy of a perfect LDPE crystal (277.1 J/g) was used.

Biodegradability

Vibrios, with the ability to produce amylase enzyme, was selected for checking the biodegradability of the samples. 15 amylase-producing bacteria were grown until 1 OD (10^8 CFU/ml). These cultures were inoculated into starch minimal medium, followed by the insertion of the plastic test specimens. Appropriate positive and negative controls were also kept. The conical flask containing plastic strips and cultures were kept on shaker at 120 rpm at room temperature. Strips were retrieved at the end of every week. Weight loss and tensile strength were checked to measure the degree of degradation. Biodegradability in soil was also checked by placing the samples in soil for 8 weeks. After 8 weeks the tensile strength and weight loss were measured for determining the degree of degradation.

Reprocessability

The reprocessability of the samples was studied by masticating the molded samples in a Thermo HAAKE Polylab System equipped with roller type rotors for 6 min at a rotor speed of 30 rpm at 150°C. The samples were remolded in an electrically heated hydraulic press for 5 min at 150°C under a pressure of 20 MPa. The process of mastication and molding was repeated up to 3 cycles. The stress-strain properties of the molded specimens after each cycle were measured.

RESULTS AND DISCUSSION

Mechanical Properties

Figures 1a and 1b show the variation of tensile strength and elastic modulus of LDPE-starch blends. The tensile strength and elastic modulus were found to decrease both in case of LDPE-LS and LDPE-HS blends. The decrease in tensile strength and elastic modulus may be due to weakness of interfacial adhesion of the hydrophilic starch with the hydrophobic matrix of LDPE. As the starch concentration increases, there is less effective cross-sectional area of LDPE between the spherical starch. The tensile strength of LDPE-LS blends is lower compared to LDPE-HS blends, whereas the elastic modulus shows an opposite trend. The decrease in tensile strength of the blends suggests that the fillers do not reinforce LDPE.

Starch exhibits hydrophilic properties and strong intermolecular association via hydrogen bonding due to hydroxyl groups on the surface. This hydrophilic nature and strong intermolecular hydrogen bonding make these fillers less compatible with the hydrophobic LDPE [9].

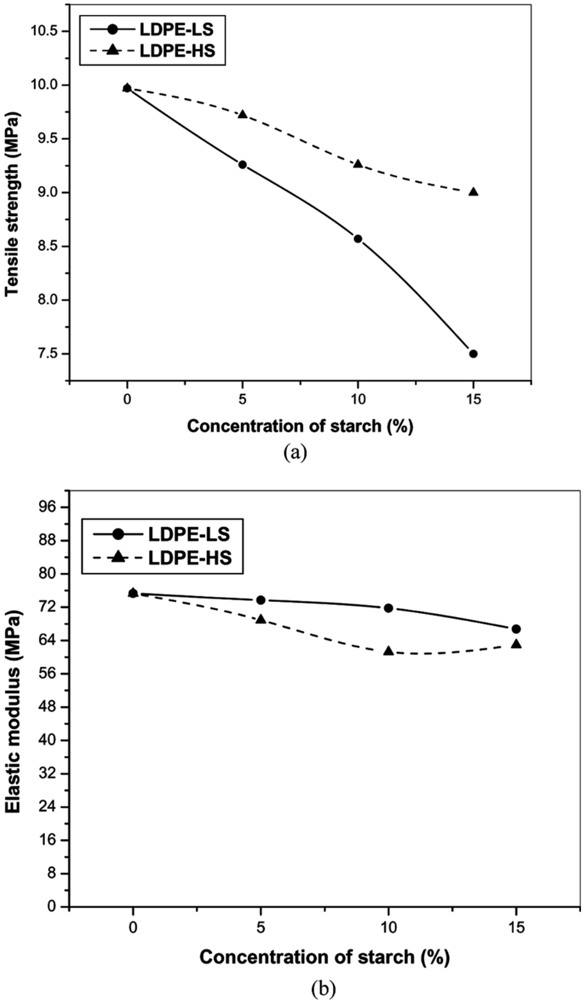


FIGURE 1 (a) Variation of tensile strength with respect to concentration of starch in LDPE-starch blends (LS-low-grade starch, HS-high-grade starch). (b) Variation of elastic modulus with respect to concentration of starch in LDPE-starch blends (LS-low-grade starch, HS-high-grade starch).

Thermal Studies

Thermogravimetric Analysis

Figure 2 shows typical thermograms of LDPE and LDPE-HS (15 wt%) blends. For LDPE-HS, there is a considerable decrease of weight in the temperature range 250–350°C. This corresponds to the

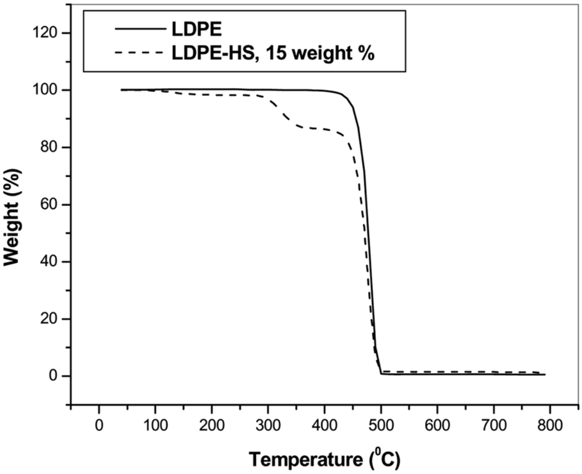


FIGURE 2 TGA thermograms of LDPE and LDPE-starch (HS, 15 wt%) blends.

loss of starch as this is the decomposition temperature for this filler. Above this temperature, a gradual loss of weight occurs. The degradation temperature, onset the temperature at which weight loss is maximum (T_{max}), the maximum rate of degradation and residual weight in percentage are given in Table 1. For LDPE-HS and LDPE-LS T_{max} showed a slight decrease, which indicates a decreased thermal stability of these blends.

Differential Scanning Calorimetry

DSC thermograms of LDPE and LDPE-HS (15 wt%) blends are shown in Figure 3. Table 2 shows the average values for the melting temperature (T_m), crystallization temperature (T_c), enthalpy of fusion (ΔH_f), enthalpy of crystallization (ΔH_c) and % crystallinity for LDPE and LDPE-HS (15%).

TABLE 1 Results of Thermogravimetric Analysis

Sample	Temperature of onset of degradation (°C)	$T_{max}{}^a$ (°C)	Residual weight (%)
LDPE	420	482	0.6023
LDPE-LS (15%)	414	477	1.207
LDPE-HS (15%)	416	477	1.285

[a] The temperature at which the rate of weight loss is maximum.

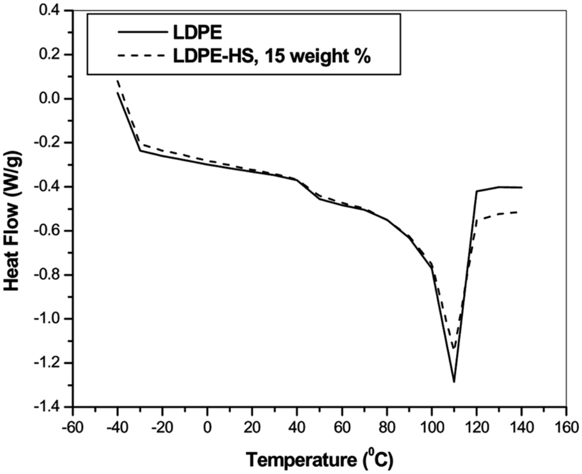


FIGURE 3 DSC curves (heating) for LDPE and LDPE-starch (HS, 15 wt%).

ΔH_f and ΔH_c values for the blends are lower compared to virgin LDPE. There is no significant decrease in crystallinity of LDPE in the mixes, which indicated that LDPE and starch are incompatible, i.e., LDPE-starch interactions are weak. In addition, the melting and crystallization temperature of LDPE and blends were almost similar. This also suggests the incompatibility of LDPE and the fillers [10].

Biodegradability

Figure 4 shows the decrease in tensile strength of LDPE-starch blends after immersing the strips in culture medium for 8 weeks. There is significant variation in the tensile strength of the samples, indicating a higher degree of biodegradation. Figure 5 shows the variation in tensile strength of LDPE-starch blends after the soil burial test. Tensile strength decreases considerably, indicating the increase in the rate of biodegradation.

Tables 3 and 4 show the weight loss of LDPE-starch after the biodegradability test in a culture medium and the soil burial test.

TABLE 2 Results of Differential Scanning Calorimetry

Sample	T_m (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)	% Crystallinity
LDPE	110	67	96	79	24
LDPE-HS (15%)	113	59	96	65	21

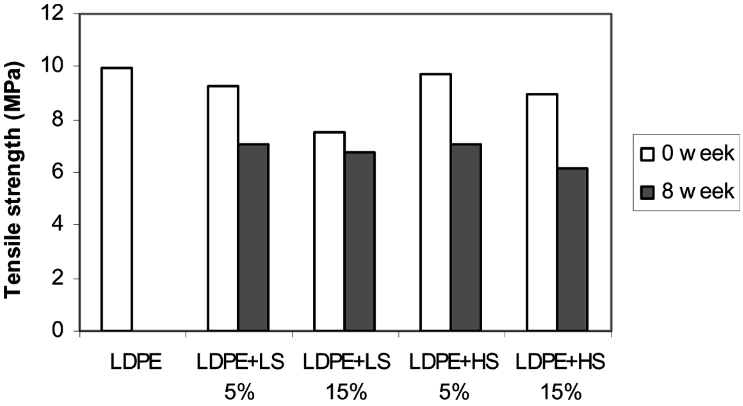


FIGURE 4 Biodegradability of LDPE-starch blends in culture medium with respect to tensile strength.

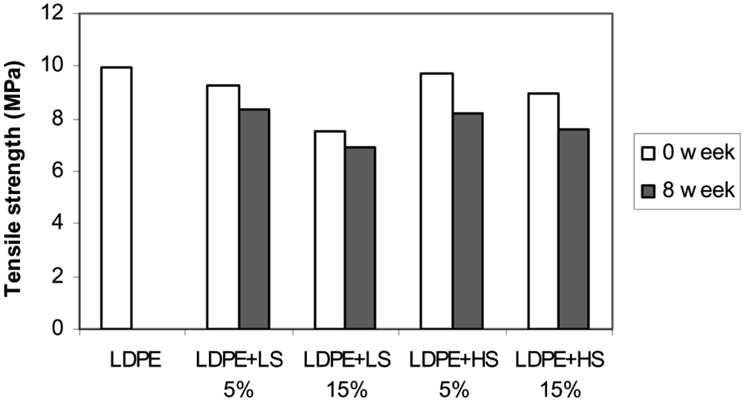


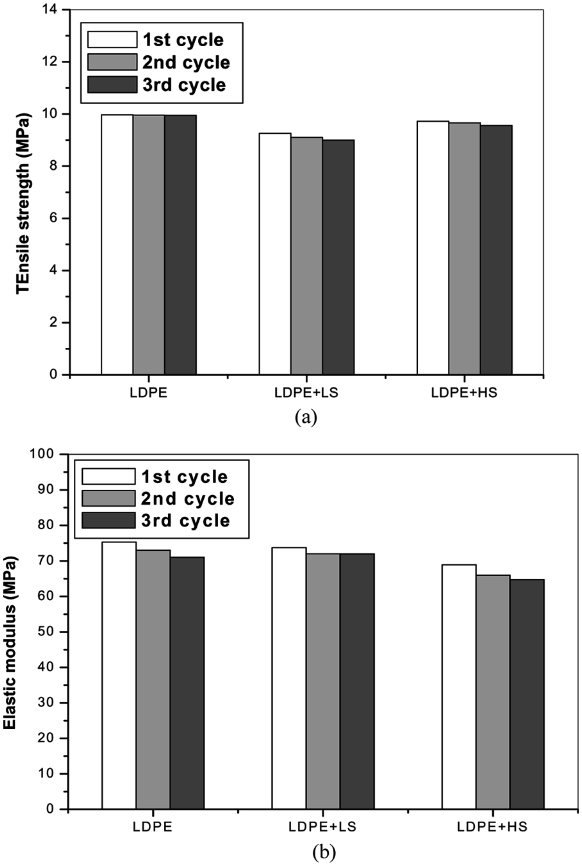
FIGURE 5 Soil burial test: Biodegradability of LDPE-starch blends with respect to tensile strength.

TABLE 3 Weight Loss of LDPE-Starch Blends – Biodegradability in Culture Medium

Sample	Initial weight (g)	Weight after 8 weeks (g)	% Weight loss
LDPE	0.1868	0.1776	4.92
LDPE-LS 15%	0.2137	0.2019	5.52
LDPE-HS 5%	0.2143	0.1784	16.75

TABLE 4 Weight Loss of LDPE-Starch Blends – Soil Burial Test

Sample	Initial weight (g)	Weight after 8 weeks (g)	% Weight loss
LDPE	0.8353	0.8346	0.08
LDPE-LS 5%	0.6603	0.6591	0.18
LDPE-LS 15%	0.2925	0.2871	1.85
LDPE-HS 5%	1.0663	1.0654	0.08
LDPE-HS 15%	0.4113	0.4072	1.00



(a)

(b)

FIGURE 6 (a) Tensile strength of LDPE-starch (5 wt%) blends at different cycles of reprocessing. (b) Elastic modulus of LDPE-starch (5 wt%) blends at different cycles of reprocessing.

There is considerable loss of weight for these blends after immersing the strips in a culture medium and the soil burial test for 8 weeks. This is also in agreement with increased biodegradation.

Reprocessability

Figures 6a and 6b show the variation of tensile strength and modulus of LDPE-starch blends with up to three cycles of processing. It was observed that the tensile strength and modulus remain more or less constant even after three cycles of mastication and molding. This shows that the LDPE-starch blends could be reprocessed by mechanical recycling without significant deterioration in properties.

CONCLUSIONS

The study suggests that the LDPE-starch blends are partially biodegradable. The blends show lower mechanical properties as compared to LDPE, suggesting that the filler has no reinforcing effect on LDPE. The thermogravimetric studies indicated that the thermal stability of LDPE is lowered by the incorporation of starch. There is no significant decrease in crystallinity of LDPE in the mixes, which shows that LDPE and starch are incompatible. These blends are reprocessable without sacrificing many of their mechanical properties.

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