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Effect of Amylase Producing Vibrios From the Benthic Environment on the Biodegradation of Low Density Polyethylene-Dextrin Blends

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Effect of Amylase Producing Vibrios From the Benthic Environment on the Biodegradation of Low Density Polyethylene-Dextrin Blends

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Low-density polyethylene was mixed with dextrin having different particle sizes (100, 200 and 300 mesh). Various compositions were prepared and their mechanical properties were evaluated and thermal studies have been carried out. Biodegradability of these samples has been checked using liquid culture medium containing Vibrios (an amylase producing bacteria), which were isolated from marine benthic environment. Soil burial test was done and reprocessability of these samples was evaluated. The results indicate that the newly prepared blends are reprocessable without sacrificing much of their mechanical properties. The biodegradability tests on these blends indicate that these are partially biodegradable.

Keywords Biodegradability; Dextrin; Polyethylene; Reprocessability

INTRODUCTION

The need for a completely biodegradable plastic is pressing. Millions of tonnes of plastic waste, including refuse sacks, carry bags and packaging, are buried in landfill sites around the world every year. Though other disposal routes such as recycling are possible, these roots are not always cost-effective for small items such as carry bags as much of the waste plastic is mixed up with other materials in the domestic and industrial waste streams and their separation is expensive.

Research on degradable synthetic polymers began in the early 1980s. The recognized lack of biodegradability of large volume of commercial polymers, particularly commodity plastics used in packaging focused public attention on a potentially huge environmental accumulation of plastic waste and pollution problem that could persist for centuries[1]. Biodegradability of plastics has been proposed as a solution for the plastic waste accumulation problem.

Low-density polyethylene (LDPE) 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 low-density polyethylene molecules inhibit their ability to crystallize. This results in a flexible product with lower tensile strength and increased ductility[2].

Dextrins are obtained by degrading starch in various ways, e.g., acid hydrolysis at low temperatures or at high temperatures. The dextrins formed under different conditions differ in structure[3]. Dextrin and starch have the general formula $[C_x(H_2O)_y]_n$, $y = x - 1$, in which glucose units are joined to one another usually head-to-tail, but dextrin has a smaller and less complex molecule as compared to starch.

Low-density polyethylene, which is hard to degrade in landfills, is currently one of the most commonly used thermoplastics used for packaging applications[4]. The resistance of low-density polyethylene to biological attack is related to its hydrophobicity, high molecular weight, and lack of functional groups recognizable by microbial enzymatic systems. These properties make the low-density polyethylene not suitable for applications in which biodegradability is a desirable attribute[5]. 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[6]. The advantage of biodegradable plastic is that, under suitable conditions (sun-light, moisture, oxygen, etc.), the plastic degrade to the point where organisms are able to digest them. This reduces problems with litter and minimizes harmful effects on wildlife.

In this study, LDPE was mixed with different grades of dextrin (100, 200 and 300 mesh). Three compositions (5, 10 and 15 weight %) with each filler grade were prepared and their mechanical properties, thermal properties, reprocessability and biodegradation studies have been carried out.

EXPERIMENTAL
Materials

The film grade LDPE (24FS040) used in this study (Melt Flow Index (190°C/2.16Kg) 4.0 g/10 min and Density (23°C) 0.922 g/cm^3) was provided by Reliance Industries Limited, Mumbai, India. The dextrins (100, 200 and 300 mesh) were supplied by Jemsons Starch and Derivatives, Aroor, Alapuzha, Kerala. As these fillers were hygroscopic in nature these were oven dried at 120°C for 1 hour 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 minutes, and then the filler was added. Mixing was continued for another 4 minutes. The neat polymer was also masticated under the same conditions.

Preparation of Test Specimens

The test specimens were prepared from the compounds by moulding in an electrically heated hydrolic press for 5 minutes at 150°C under a pressure of 20 MPa. After moulding the samples were cooled down to room temperature under pressure.

Mechanical Testing

The stress-strain properties were evaluated as per ASTM D 882 (2002) in a Shimadzu Autograph AG-I series Universal Testing Machine at a crosshead speed of 50 mm/minute.

Thermal Studies

Thermogravimetric Analyses. Thermo gravimetric analyses of the samples were carried out in a TGA Q-50 thermal analyzer (TA Instruments) under 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 10–15 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 were 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°C to 170°C, and kept at 170°C for 3 min in order to erase thermal history. Cooling was then 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 using the melting enthalpy of a perfect LDPE crystal (277.1 J/g) as reference.

Reprocessability

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

Biodegradability

Biodegradability of the blends was tested using a liquid culture medium containing the selected amylase producing *Vibrios*. *Vibrios* with the ability to produce amylase enzyme were selected for checking the biodegradability of the samples. 15 amylase-producing bacteria were grown until 1OD (10^8 CFU/ml). These cultures were inoculated into starch minimal medium, followed by the insertion of 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 eight weeks. After 8 weeks the tensile strength and weight loss were measured for determining the degree of degradation.

RESULTS AND DISCUSSION
Mechanical Properties

Figures 1a–c show the variation of tensile strength, elastic modulus and elongation at break of LDPE-dextrin blends. As the concentration of dextrin in the blends increased, the tensile strength and elastic modulus showed a decrease while there is only a marginal change in the elongation at break. The decrease in tensile strength and elastic modulus may be due to weakness of interfacial adhesion of hydrophilic dextrin with the hydrophobic LDPE matrix. As the dextrin concentration increases, there is less effective cross-sectional area of LDPE towards the spherical beads of dextrin.

(a)

(b)

(c)
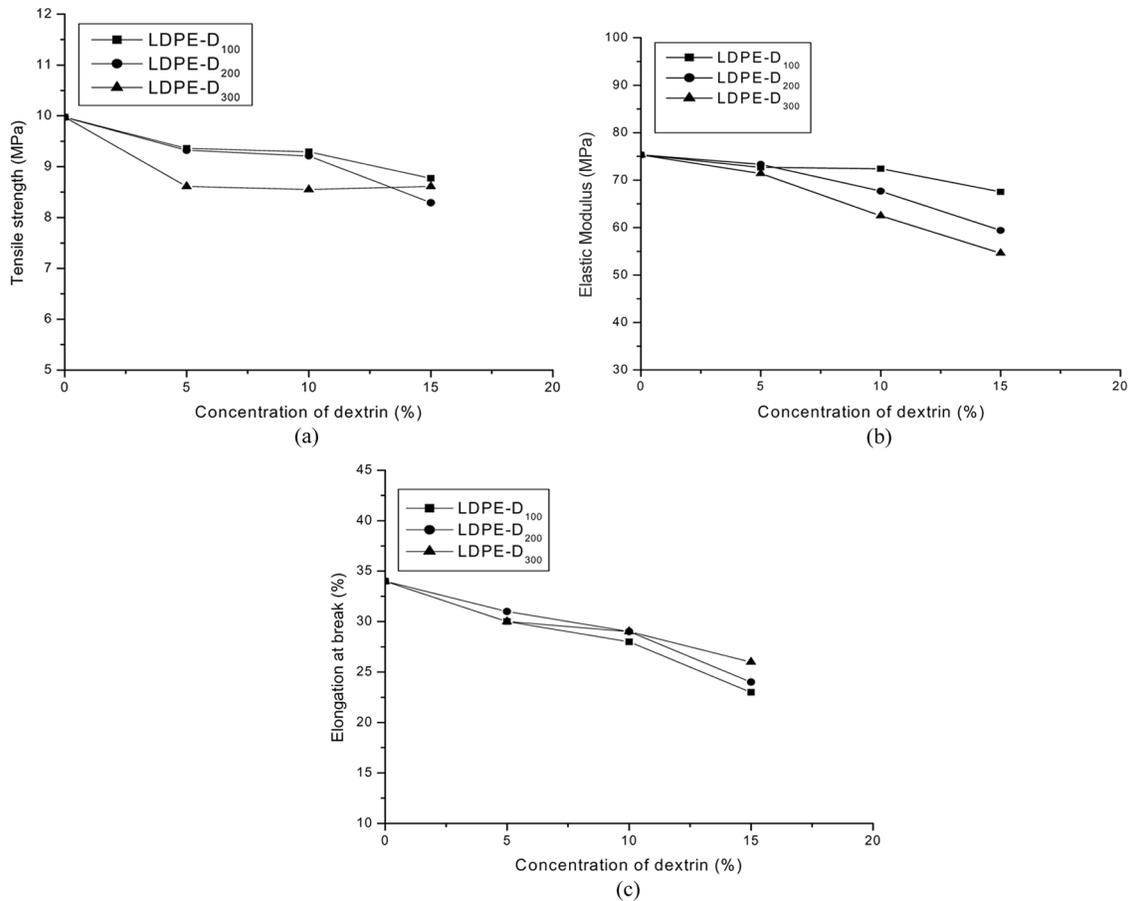
FIG. 1.   (a) Variation of tensile strength with respect to concentration of dextrin in LDPE-dextrin blends (D_{100} – Dextrin 100 mesh, D_{200} – Dextrin 200 mesh and D_{300} – Dextrin 300 mesh); (b) Variation of elastic modulus with respect to concentration of dextrin in LDPE-dextrin blends (D_{100} – Dextrin 100 mesh, D_{200} – Dextrin 200 mesh, and D_{300} – Dextrin 300 mesh); (c) Variation of Elongation at break with respect to concentration of dextrin in LDPE-dextrin blends (D_{100} – Dextrin 100 mesh, D_{200} – Dextrin 200 mesh and D_{300} – Dextrin 300 mesh).

Dextrin exhibits hydrophilic properties and strong intermolecular association via hydrogen bonding due to the presence of hydroxyl groups on the surface. This hydrophilic nature and strong intermolecular hydrogen bonding make these filler less compatible with hydrophobic LDPE. The dextrin and starch have similar structure and behave in the similar way to LDPE matrix. These observations show good agreement with the results presented by other researchers[7,8].

Thermal Studies

Thermogravimetric Analysis. The thermograms of LDPE and LDPE-dextrin (D_{300}, 15 weight %) are shown in Figure 2. In the case of LDPE-dextrin blend, there is considerable decrease in weight in the temperature range 250–350°C. This corresponds to the loss of dextrin, as this is the decomposition temperature of this filler. Above this temperature, a gradual loss in weight occurs. The onset
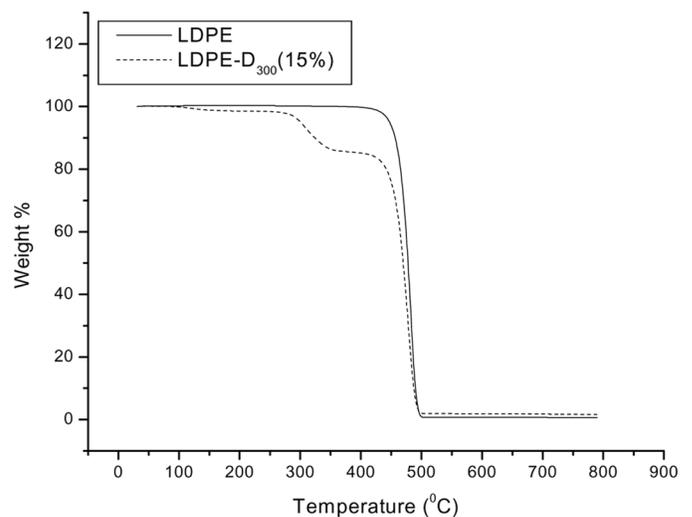
FIG. 2.   TGA thermograms of LDPE and LDPE-dextrin (D_{300}, 15 weight %) blends.

TABLE 1
Thermogravimetric analysis

Sample	Temperature of onset of degradation (°C)	T_{max}[a] (°C)	Residual weight (%)
LDPE	420	482	0.6023
LDPE+D_{100} (15%)	409	478	1.492
LDPE+D_{200} (15%)	411	478	1.535
LDPE+D_{300} (15%)	409	477	1.623

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

of degradation temperature, the temperature at which weight loss is maximum (T_{max}), and residual weight in percentage are given in Table 1. As compared to neat LDPE the LDPE-dextrin blends showed lower T_{max} values indicating decreased thermal stability.

Differential Scanning Calorimetry. Figure 3 shows the DSC heating curves of LDPE and LDPE-dextrin (D_{300}, 15 weight %) blend respectively. Table 2 shows the average values for the melting temperature (T_m), crystallisation temperature (T_c), enthalpy of fusion (ΔH_f), enthalpy of crystallization (ΔH_c), and % crystallinity for LDPE and LDPE-dextrin (D_{300}, 15 weight %) blend.

ΔH_f and ΔH_c values for the blend were lower compared to virgin LDPE. The melting and crystallization temperatures of LDPE and the blend were almost similar which indicated that LDPE and dextrin are incompatible. i.e., LDPE-dextrin interactions are weak. There is no significant decrease in crystalinity of LDPE in the blend. This also suggests the incompatibility of LDPE and the filler[9,10].
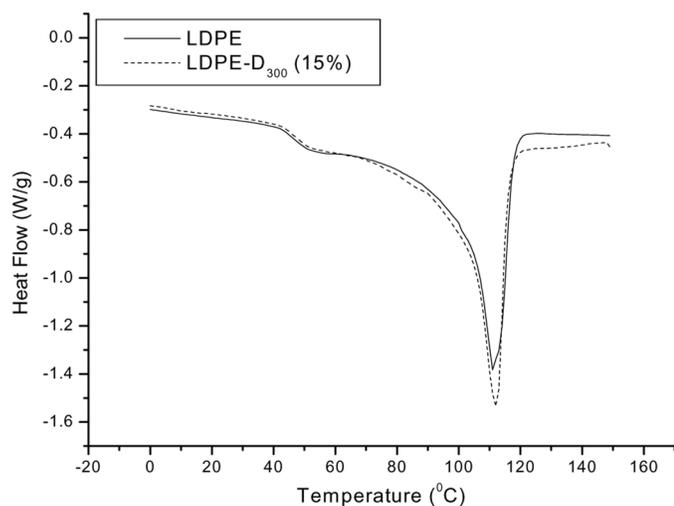
FIG. 3. DSC curves (heating) for LDPE and LDPE-dextrin (D_{300}, 15 weight %) blends.

TABLE 2
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-D_{300} (15%)	112	62	96	75	22

Biodegradability

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

Tables 3 and 4 show the weight loss of LDPE-dextrin blends after biodegradability test in culture medium and soil burial test. There is substantial loss of weight for these blends after immersing these strips in culture medium, which indicates that these blends are partially biodegradable.
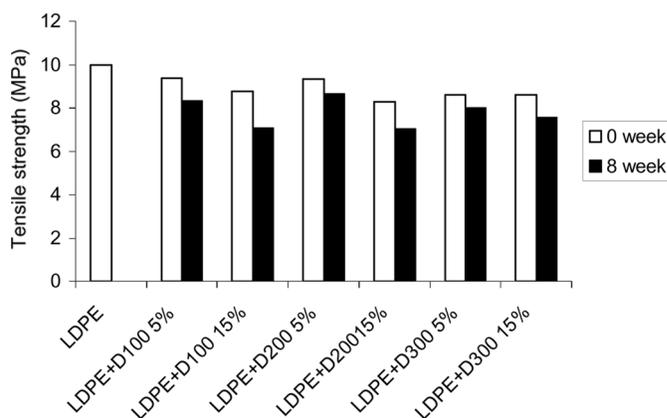
FIG. 4. Biodegradability of LDPE-dextrin blends in culture medium with respect to tensile strength.
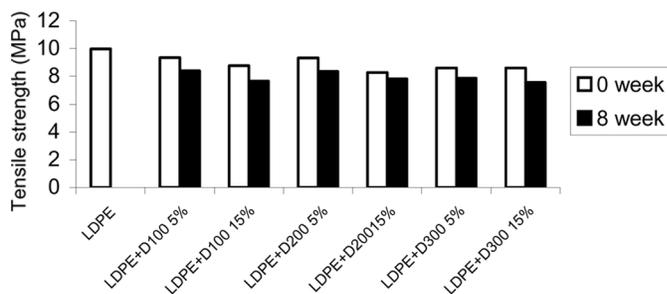
FIG. 5. Biodegradability of LDPE-dextrin blends after soil burial for eight weeks with respect to tensile strength.

TABLE 3
Weight loss of LDPE-dextrin blends–biodegradability in culture medium

Sample	Initial weight (g)	Weight after 8 weeks (g)	% Weight loss
LDPE	0.1868	0.1776	4.92
LDPE+D$_{300}$ (5%)	0.1291	0.1206	6.58
LDPE+D$_{300}$ (15%)	0.1833	0.1309	28.58

TABLE 4
Weight loss of LDPE-dextrin blends – Soil burial test

Sample	Initial weight (g)	Weight after 8 weeks (g)	% Weight loss
LDPE	0.8353	0.8346	0.08
LDPE+D$_{300}$ (5%)	1.6112	1.6093	0.11
LDPE+D$_{300}$ (15%)	0.5421	0.5362	1.08
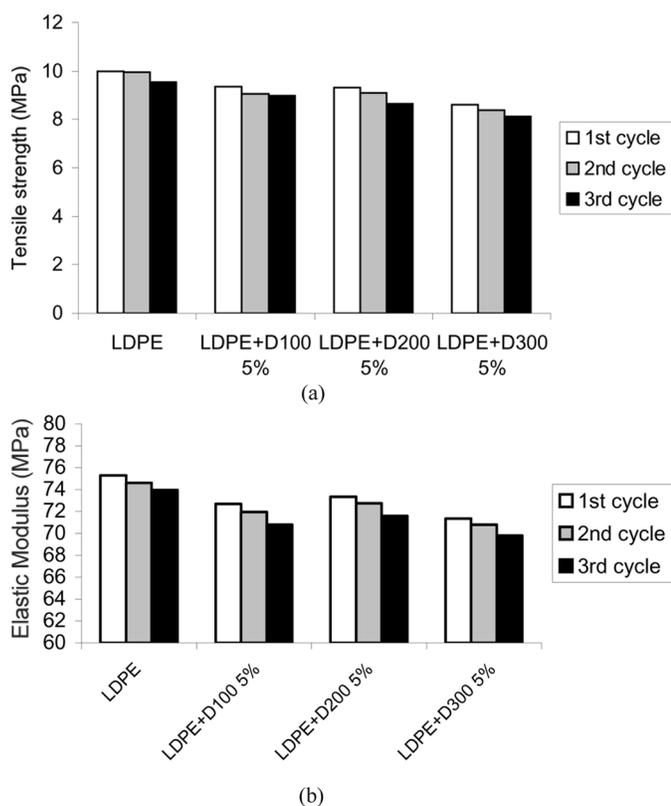
FIG. 6.   (a) Tensile strength of LDPE-dextrin (5 weight %) blends up to three cycles of reprocessing; (b) Elastic modulus of LDPE-dextrin (5 weight %) blends up to three cycles of reprocessing.

Reprocessability

Figures 6a and 6b show the variation of tensile strength and modulus of LDPE-dextrin blends 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 moulding. This shows that the LDPE-dextrin blends could be reprocessed by mechanical recycling without significant deterioration in properties.

CONCLUSIONS

The newly prepared LDPE-dextrin blends showed significant reduction in tensile strength after keeping the samples in the culture medium, containing selected amylase producing *Vibrios* isolated from marine benthic environment, for 8 weeks. Evaluation of biodegradability in soil too showed similar results indicating the possibility for biodegradation. The reduction in the tensile properties of LDPE on incorporation of dextrin suggests that the filler has no reinforcing effect on LDPE. The thermogravimetric analyses indicate that the thermal stability of the blends is lowered by the incorporation of dextrin. There is no significant decrease in crystallinity of LDPE in the blends, which shows that the LDPE and dextrin are incompatible. These blends are reprocessable without sacrificing much of their mechanical properties. The study suggests that the newly prepared LDPE-dextrin blends are partially biodegradable.

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