Rice Bran-Filled Biodegradable Low-Density Polyethylene Films: Development and Characterization for Packaging Applications

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ABSTRACT: Rice bran was incorporated into low-density polyethylene (LDPE) at different concentrations by compounding in a twin-screw extruder and blown into films of uniform thickness. The rice bran incorporation influenced physical, mechanical, barrier, optical, thermal properties, and biodegradation of LDPE. The mechanical and optical properties decreased as the percentage of rice bran increased. The effect of rice bran on the morphology of LDPE blends was examined using scanning electron microscopy. Oxygen transmission rate and water vapor transmission rate increased with the increased content of rice bran. Addition of rice bran did not alter the melting temperature (T_m) of the blends; however the thermal stability decreased, while glass transition temperature (T_g) increased. Kinetics of thermal degradation was also investigated and the activation energy for thermal degradation indicated that for up to 10% filler addition, the dispersion and interfacial adhesion of rice bran particles in LDPE was good. Aerobic biodegradation tests using municipal sewage sludge and biodegradation studies using specific microorganism (Streptomyces species) revealed that the films are biodegradable. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4514–4522, 2006

Key words: rice bran; blown film; mechanical properties; low-density polyethylene; biodegradation

INTRODUCTION

Biodegradable plastics are attaining more importance in packaging applications as they considerably reduce the negative impact of solid wastes on environment.[1] Low-density polyethylene (LDPE) is one of the most commonly used polymeric materials in numerous applications including food packaging. Biodegradability of these materials is quite limited and only minimal degradation has been observed even after long-term exposure to environmental conditions. Several studies have been conducted to enhance the biodegradability of LDPE by incorporating different additives like starch.[2,3] Rice bran, the outer layer of rice is a low cost, under utilized coproduct of rice milling, having 65–70% starch along with other constituents like protein, fat, sugar, etc.,[4] which can be incorporated into LDPE for enhancing the biodegradability. India is a major rice producing country in the world and a large quantity of rice bran is going as waste. Our study is an attempt to make low cost biodegradable films for packaging applications by incorporating rice bran into LDPE. Use of rice bran as such will help reduce cost considerably by avoiding the tedious process, involved in the extraction of starch, without compromising biodegradability. Blending and extrusion blowing of rice bran with LDPE produces films with uniform thickness. The structure at the molecular level of such blends may be complex and to optimize the polymer materials for suitable packaging applications, the structure–property relationship between these blends needs thorough investigation. Therefore an effort has been made to characterize the properties of such systems, which may be useful in processing these materials as well as predicting their applications in food packaging.

The investigations under report involve the incorporation of different concentrations (5–10%) of rice bran into LDPE using a twin-screw extruder and blowing into films of uniform thickness using single screw extruder blowing equipment. Some physicomechanical properties like tensile strength, percentage elongation, tear strength, burst strength, and heat seal strength were determined. The morphology of the films was examined by scanning electron microscopy (SEM). The barrier and optical properties like oxygen transmission rate (OTR), water vapor transmission rate (WVTR), and gloss, which are important in case of food packaging, were also analyzed. Global migration from these packaging materials, important to ensure quality and safety of packed materials, were determined using different food simulant systems. Thermal properties of these films were evaluated

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using differential scanning calorimeter (DSC) and themogravimetric analyzer (TGA). DSC provided information regarding the physical transitions that can take place within the material, while TGA gave an idea about their thermal stability. Biodegradation of these newly developed films was investigated by determining the aerobic biodegradability in presence of municipal sewage sludge as well as some specific microorganism, which are capable of degrading starch.

EXPERIMENTAL

Materials and film blowing

Low-density polyethylene (Indothene 24 FS 040, having density of 0.922 g/cm^3, melt flow index of 4.0 g/10 min, and melting range of 105–109°C) was purchased from M/s IPCL, Baroda, India. Rice bran was procured from local rice mills and predried at 60°C for 24 h in a hot air drier before using. It was then physically blended with LDPE at different concentrations (5–10%) for a period of 20 min. This blend was then compounded in a Haake twin-screw extruder (Model CTW 100) in the temperature range of 110–165°C. The screw speed was adjusted to 38 rpm, while the torque was maintained between 5 and 11.6 N/m. The compounded polymer strands were cooled in a cool air stream and pelletized. These pellets were then blown into films (75 μm thickness) using a single screw extruder (L/D ratio 22:1) with film blowing unit in the temperature range of 110–165°C.

Apparatus and procedures

Mechanical properties like tensile strength, percentage elongation at break, and heat seal strength of the newly developed films were measured using an Instron Universal testing machine (Model 4302) with a crosshead speed of 500 mm/min at room temperature. The samples were prepared in both machine and cross direction as per ASTM D 882. For determining heat seal strength, two strips of same plastic films (6.25 cm × 2.5 cm) were sealed together using a heat-sealing machine (Model No 24 lab, M/s Vertrod, USA) at 120–150°C for 5 s. Heat seal strength was determined using Instron, UTM as per ASTM D 1876. Elmendorf tearing tester (Model No 6323, H.E. Messmer, London) was used to determine the tear strength of the material (ASTM D 1004), while burst strength was measured using burst tester (M/s Goodbrand and Co, England) as per ASTM D 774.

The morphology of rice bran-filled LDPE films were evaluated using a SEM (Model 100 CX II, ASID 4D, JEOL) at 20 kV. The film samples were mounted on to copper stubs using double sided sticky tapes. The mounted stubs were gold-coated (20 nm thickness) in a sputter coater (EMS 550). The micrographs of the samples were taken at higher magnifications to identify the changes on sample surfaces due to the incorporation of rice bran.

An automatic manometric gas permeability tester (LYSSY AG, Switzerland) was used to measure the oxygen transmission rate through the films as per ASTM D1434. Samples of the size 100 mm × 110 mm with known thickness were mounted between the test cells having a test area of 50 cm^2, for determining the oxygen permeability at 23 °C. Circular film samples of 8.7 cm diameter were used to determine the WVTR using desiccant method (ASTM D 96). In this method the test specimen is sealed to the open mouth of a test dish containing a desiccant and the assembly is placed at 38°C and 90% relative humidity (RH). By periodic weighing, the rate of water vapor permeation was measured. Five samples were used for each test, and the mean and standard deviation were calculated. Specular gloss values of the films were measured with a reflectance meter (M/s Rhopoint Instrumentation, England) as per DIN 67350. Reflectance measured at an angle of 45° from the normal has been reported as gloss unit (G.U.) based on the mean of five measurements for each samples

Global migration analysis was performed gravimetrically on the films having uniform thickness to ensure the uniformity of results. Samples (10 cm × 10 cm) were cut with a stainless steel template and weighed on an analytical balance (Model AE 200, Mettler). Global migration was determined in four different food simulants—water, 3% acetic acid, 50% ethanol, and *n*-heptane. The water used was double distilled and all the chemicals were obtained from M/s S d fine chemicals, India. For each combination, five samples were immersed in 200 mL of food simulant and kept at room temperature. After 24 h, the film samples were removed and volatile simulant were evaporated. Global migration was calculated from the dry residue weight in case of each simulant.

Differential scanning calorimeter model DSC 2910, Dupont, with a thermal analyst 2100 system (TA instruments, USA) was used to determine the glass transition (T_g) and melting (T_m) temperatures. The temperature and heat flow calibration of the equipment was done with Indium under similar conditions as for the samples. All the experiments were carried out with a sealed empty pan as the reference, with N_2 gas flushing. The sealed pans with samples (5–10 mg) were first cooled to −50°C, held isothermally for 1 min, and then ramped (5°C/min) to 400°C to obtain the heat flow curves. Themogravimetric analyzer (TGA, Q50, TA Instruments, USA), a thermal weight change analysis instrument, was used in conjunction with a thermal analysis controller. The TG analyzer was employed to measure the amount and rate of change in weight of the material, either as a function of increasing temperature or time, in a controlled atmosphere. The initial

weight of each sample was ~10 mg. The samples were kept in a platinum crucible and heated in the furnace, flushed with N_2 gas at the rate of 40 mL/min, from 30 to 600°C, at the rate of 20°C/min. The percentage weight loss and derivative weight loss were plotted against temperature for all samples.

For determining the kinetic parameters of thermal degradation, the samples were heated at different heating rates like 2, 5, 10, and 20°C/min. Flynn and Wall[5] derived a method for determining the kinetic parameters of thermal degradation, like activation energy, based on the equation

$$\text{Log } \beta \equiv 0.457\ (-E_a/RT) + [\text{Log } (AE_a/R) - \text{Log } F\ (\alpha) - 2.315]$$

where β is the heating rate, T is the absolute temperature, R is the gas constant, α is the conversion, and A is the pre-exponential factor. For same conversion values, the activation energy was obtained from the slope of the plot of Log β versus $10^3/T$.

The aerobic biodegradation of LDPE rice bran blends were evaluated on exposure to activated municipal sewage sludge inoculum under laboratory conditions as per ASTM D 5209-92. Sewage sludge having diverse composition of inoculum, collected from municipal sewage, is aerated for 4 h and homogenized in a high speed mixer. The supernatant solution is used for preparing 1% inoculum. Known weight of LDPE, 5 and 10% rice bran-filled LDPE films along with pure rice bran as standard were exposed to aerated inoculum and biodegradability is evaluated by measuring the carbon dioxide (CO_2) evolved as a function of time. The CO_2 evolved as a result of biodegradation is trapped in 0.025N barium hydroxide ($BaOH_2$) solutions and amount of CO_2 evolved is calculated by titrating against 0.05N HCl. The amount of CO_2 evolved is plotted against time. The test is continued until a plateau level of CO_2 evolution achieved.

The biodegradability of rice bran-filled LDPE films was also determined using Streptomyces sp. as a specific microorganism. The biodegradation tests were conducted as per ASTM D 5247-92. The test organism used, Streptomyces sp. QMB841 (NCIM 2214), was obtained from National Collection of Industrial Microorganism, Chandigarh, India. The plastic film samples were cut into strips as per ASTM D 882 for mechanical testing and disinfected by universal disinfectant, followed by conditioning at room temperature for 60 min. After equilibration, each of the samples were placed in a sterile preweighed petridish aseptically to determine the initial weight. These samples were then kept in 200 mL bacterial culture broths in 250 mL flasks fitted with cotton plugs and allowed to shake continuously for 14 days in an orbital shaker (M/s Scigenics Biotech, India) at 125 rpm and 37°C. Similarly, samples were placed in uninoculated control culture flasks and kept under the similar conditions for comparison. After incubation, residual films were washed, dried, and used for determining weight loss and percentage elongation.

RESULTS AND DISCUSSION

Mechanical properties

Yoo et al.[6] have reported the reduction in physical and mechanical properties in starch-incorporated polyethylene films. Neilsen and Landel[7] reported that the incorporation of fillers like zein/corn gluten meal decreased the tensile strength of such films by changing the morphology of the films and the nature of the interface between the two phases. Various research workers like Obuz et al.[8] and Herald et al.[9] have reported the reduction in percent elongation at break of LDPE with the incorporation of starch, wheat gluten, corn zein, etc., and a similar trend was observed in this study also. As the rice bran content was increased to 10% the tensile strength and percent elongation decreased by 56 and 43%, respectively in machine direction, while the reduction in cross direction was 54 and 41%, respectively (Table I). This may probably be due to rice bran, which would have caused discontinuity in LDPE matrix and thus reduced tensile strength as well as percent elongation. Further, because of the

TABLE I
Mechanical Properties of Various LDPE Films

Sample	Direction	Tensile strength (MPa)*	% Elongation*	Tear strength* (g)	Burst strength* (MPa)	Heat seal strength* (kg/10 mm)
LDPE	M/C	13.61 ± 0.31	248.29 ± 10.1	361.6 ± 15.6	0.223 ± 0.04	1.25 ± 0.12
	Cross	8.77 ± 0.29	97.63 ± 8.6	246 ± 14.2		
LDPE + 5% rice bran	M/C	8.18 ± 0.42	173.71 ± 10.8	89.6 ± 8.3	0.108 ± 0.02	0.986 ± 0.11
	Cross	5.59 ± 0.21	79.68 ± 8.1	244.8 ± 13.8		
LDPE +10% rice bran	M/C	5.94 ± 0.38	141.99 ± 9.8	81.6 ± 8.1	0.094 ± 0.09	0.912 ± 0.04
	Cross	4.04 ± 0.30	57.19 ± 7.9	246.4 ± 12.6		

* Mean ± S.E.; n = 5.

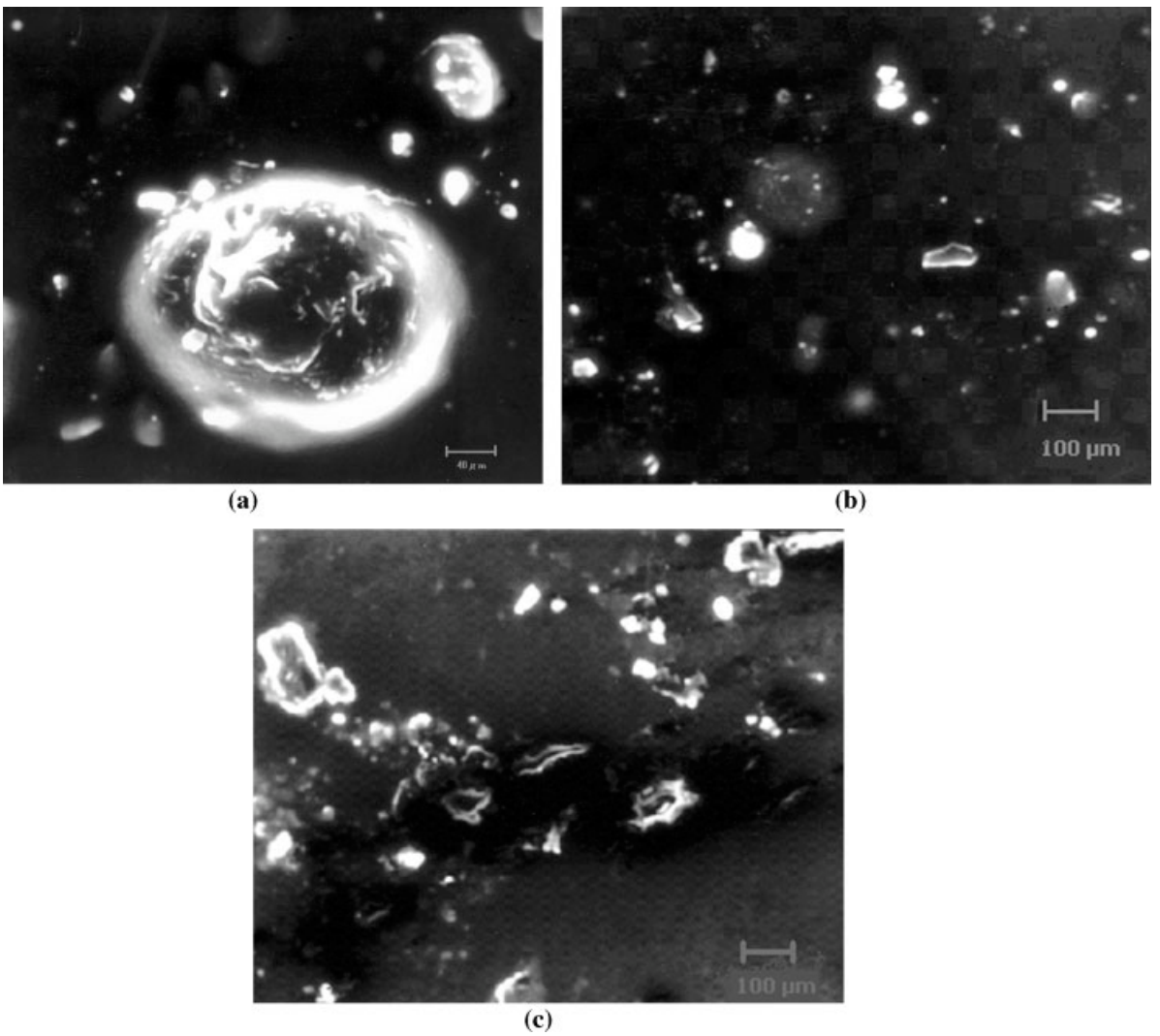

Figure 1 SEM micrographs of LDPE/rice bran blends: (a) Rice bran (×800); (b) 5% rice bran-filled LDPE (×500); (c) 10% rice bran-filled LDPE films (×500).

formation of clumps, which is evident in SEM photographs, proper stress transfer across the LDPE-rice bran interphase is affected, and the stress on the continuous phase increased with the increase in percentage of rice bran, which in turn lowered the tensile strength. The increased filler content can affect the dispersion of rice bran within the polymer matrix and reduce the mobility of polymer chains by accumulating in adjacent chains resulting in reduced elongation properties. The tear strength of these films (Table I) decreased considerably in machine direction but was not affected in the cross direction. Heat seal strength and bursting strength data have been summarized in Table I. The incorporation of rice bran was found not to seriously affect the burst strength and sealing properties of LDPE films. Furthermore, seals were intact, confirming good heat-sealing properties. Although the incorporation of rice bran leads to decrease in mechanical properties, these films were still useful for packaging applications.

Phase morphology

The morphology of rice bran-filled LDPE films were examined by SEM and the photographs are shown in Figure 1(a–c). Figure 1(a) shows the morphology of rice bran particles at higher magnification (800×) and appears to be spherical in shape, having some irregularities in the surface. Figure 1(b,c) depicts the images of 5 and 10% rice bran domains dispersed in LDPE matrix. At lower concentration (5%), the dispersion and distribution of rice bran seems to be uniform, but when it reaches to 10% concentration, the granules are grouped together leading to the formation of clumps, possibly due to the hygroscopic nature of

TABLE II
OTR, WVTR, Gloss, and Global Migration of Additives for Various LDPE Films

Samples	OTR* (mL/m^2/day at 23°C)	WVTR* (g/m^2/day at 38°C and 90% RH)	Specular gloss* (GU)	Global migration*			
				Distilled water (mg/kg)	3% Acetic acid (mg/kg)	50% Ethanol (mg/kg)	*n*-Heptane (mg/kg)
LDPE	298.99 ± 10.6	15.71 ± 0.12	42.33 ± 0.096	35.6 ± 1.140	31.6 ± 1.141	30.4 ± 1.303	32 ± 1.142
LDPE + 5% rice bran	312.44 ± 12.2	28.51 ± 0.23	26.28 ± 0.091	41.6 ± 1.302	41.0 ± 1.581	30.8 ± 1.302	35 ± 1.303
LDPE +10% rice bran	495.83 ± 14.5	38.87 ± 0.47	16.98 ± 0.096	60 ± 1.152	75 ± 2.236	52 ± 1.583	63.4 ± 2.408

* Mean ± S.E.; n = 5.

rice bran. It is evident from the micrographs that the increased rice bran content decreases the homogeneity of the films, which in turn contributes to the decreased mechanical properties.

Barrier and optical properties

The barrier properties like WVTR and OTR of rice bran-filled LDPE films have been summarized in Table II. The incorporation of rice bran resulted in an increased oxygen transmission (495 mL/m^2/24 h at 23°C) and water vapor transmission (38.87 g/m^2/24 h at 38°C and 90% RH) rates. Rice bran incorporation may have led to changes in amorphous and crystalline phases of LDPE and subsequent weakening of intermolecular forces between the polymer chains. Rice bran as a starchy material has a tendency to absorb moisture and thus probably affected the water vapor transmission and oxygen permeabilities. The optical properties like specular gloss are important for food packaging films as they have a direct bearing on the consumer appeal. The addition of rice bran was found to reduce gloss by 60%, mainly because of its existence as filler in the LDPE matrix.

Global migration

Any packaging material used for food contact applications shall not transfer any additives into the food in unacceptable quantities and hence must be evaluated for its migration characteristics into food simulants.[10] Migration values for LDPE and LDPE-rice bran blends have been given in Table II. The results indicated that as the rice bran content increased global migration also increased. This may be due to the leaching of the remnant concentration of starch in the film surface. Since rice bran is a starchy biomaterial, it may not impart any adverse effect to the products, when used for food contact applications.

Thermal properties

Differential scanning calorimetry

DSC is a common technique used for studying the thermal properties of polymers and detects the heat flow changes associated with both first order and second order transitions. Figure 2 shows the heat flow curves of LDPE, rice bran, 5% rice bran-filled LDPE and 10% rice bran-filled LDPE. For LDPE a melting peak was observed at 113.22°C. The addition of rice bran up to 10% did not affect the T_m of these blends significantly (Table III). The DSC trace of native rice bran showed a broad endothermic peak starting from 80 to 230°C. The enthalpy of the melting process was found to be 150.32 J/g. In rice bran-filled LDPE, as the rice bran content increased, the enthalpy for melting also increased (Table III). Control LDPE showed a lower enthalpy (40.58 J/g). This clearly indicated that the energy required for the melting of rice bran fractions was more as compared to that for LDPE. In case of rice bran, an additional crystalline melting endotherm was observed at lower temperature, which may be due to the crystalline melting of rice starch present in it. Baik et al.[11] have also reported a similar behavior for a rice starch gel system. The heat flow curves for 5 and 10% rice bran-filled LDPE films also showed a similar endotherm, which confirmed the presence of rice starch in the film. Jenkins[12] reported that the glass transition temperature of LDPE was 60°C, while in this investigation an onset of change in heat flow curve was also observed at 57.86°C, which can be considered as T_g. However, as the percentage

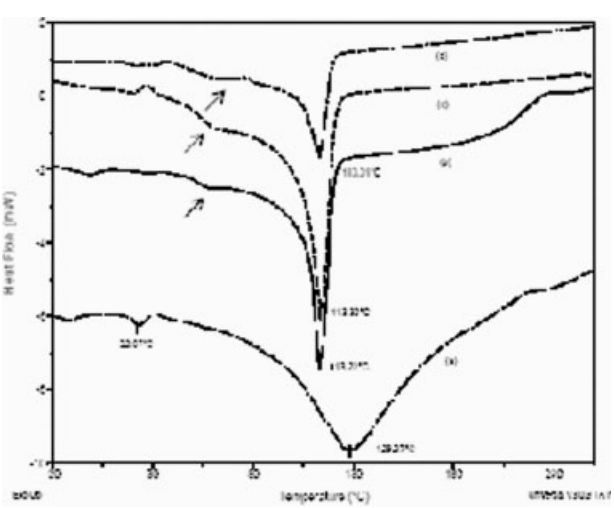

Figure 2 DSC heat flow curves for (a) Rice bran; (b) LDPE; (c) 5% rice bran-filled LDPE; (d) 10% rice bran-filled LDPE films.

TABLE III
Thermal Properties of Various LDPE Films

Sample	T_m* (°C)	T_g* (°C)	ΔH* (J/g)	Temperature for 10% weight loss* (°C)
LDPE	113.22 ± 0.04	57.86 ± 0.14	40.58 ± 0.19	458.6 ± 0.64
LDPE + 5% rice bran	113.33 ± 0.06	60.68 ± 0.20	55.79 ± 0.23	450.96 ± 0.81
LDPE +10% rice bran	113.31 ± 0.06	79.93 ± 0.21	66.2 ± 0.26	434.29 ± 0.75

* Mean ± S.E.; n = 5.

rice bran content increased, the T_g also increased (Table III). Probably the addition of rice bran may have restricted the free polymer chain movement and thus increased the T_g values.

Thermo gravimetric analysis

Thermo gravimetric analysis, a continuous process that measures sample weight against temperature, has been widely used to study the heat-related degradation behavior and kinetics of thermal degradation of polymers. In this investigation the degradation behaviors of rice bran-filled LDPE films as well as control LDPE and rice bran were determined (Fig. 3). The TG curve of rice bran exhibited two mass loss steps. The initial mass loss below 100°C may be due to the evaporation of absorbed moisture. The second mass loss occurring between 175 and 500°C may be due to the degradation of different constituents in the rice bran such as protein, sugar, and fiber present along with starch.[4] DTG curves of rice bran (Fig. 4) showed that the major mass loss steps occurred at 230.5 and 329.03°C. The first peak indicated the degradation of constituents like protein and sugar, while the second peak indicated the degradation of starch. The occurrence of subsequent peaks may be due to the degradation of crude fibers and other constituents present in rice bran. At 600°C, the ash content of rice bran was found to be 20.65%, which may be due to the presence of silica. For LDPE the mass loss occurrence was very slow initially and when temperature reached above 400°C, the degradation process was found to be rapid. The thermal degradation of LDPE was mainly due to the random chain scission mechanism and the major decomposition products were low molecular weight hydrocarbons.[13] The DTG curve showed the mass loss peak at 454.12°C. The addition of rice bran resulted in a decrease in thermal stability of LDPE, while the ash content increased. The temperature for 10% weight loss decreased from 458.60 to 434.29°C, as the rice bran content increased (Table III). This type of decreased thermal stability may be attributed to the low thermal stability of rice bran. From DTG it is clear that two mass loss steps occurred for these blends, one at 294.36°C and another at 454.12°C. The initial mass loss was due to the degradation of constituents of rice bran, while the second one was due to LDPE degradation.

Nonisothermal TGA of LDPE rice bran blends was carried out at four different constant heating rates of 2, 5, 10, and 20°C/min. The TGA and DTG curves for 10% rice bran-filled LDPE films have been shown in Figures 5 and 6. As the heating rate increased, the thermograms shifted toward high temperatures because the sample took less time to reach a given

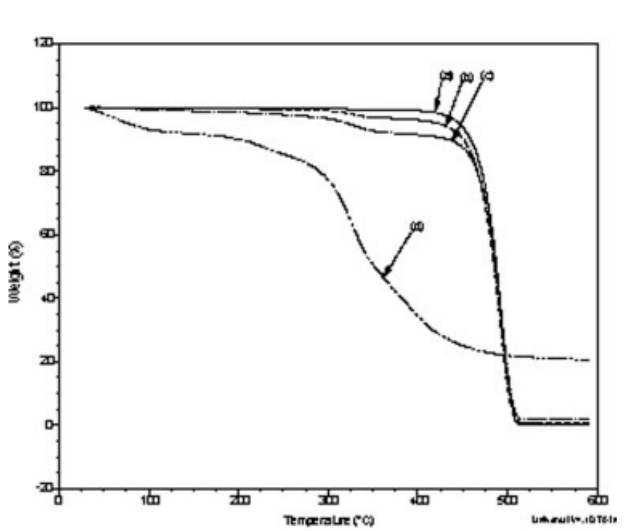

Figure 3 TGA curves of (a) LDPE; (b) 5% rice bran-filled LDPE; (c) 10% rice bran-filled LDPE; (d) rice bran.

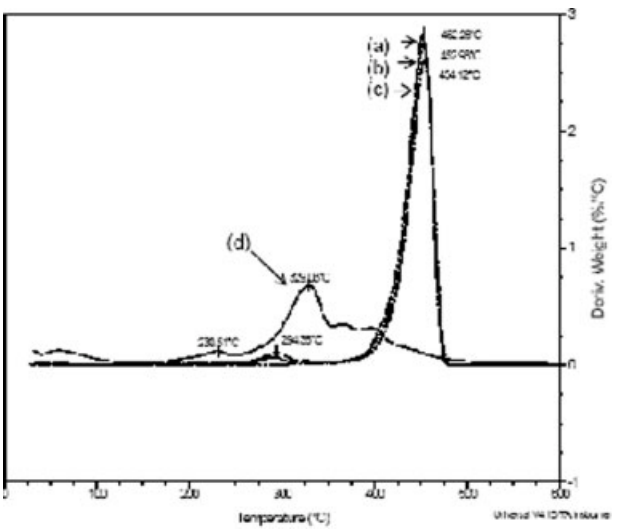

Figure 4 DTG curves of (a) LDPE; (b) 5% rice bran-filled LDPE; (c) 10% rice bran-filled LDPE; (d) rice bran.

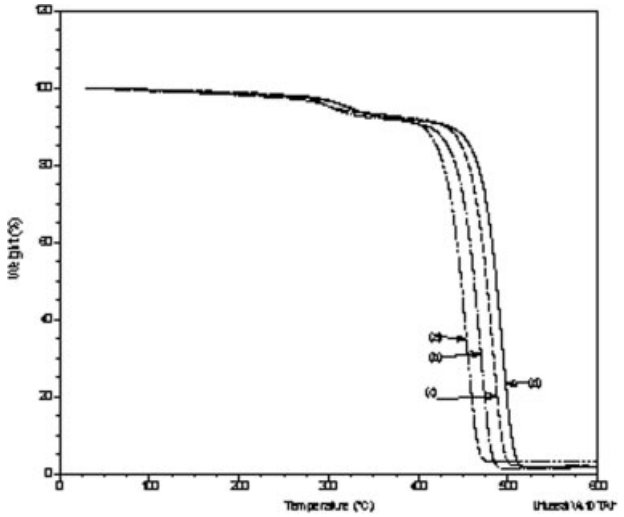

Figure 5 TGA curves of LDPE + 10% rice bran at (a) 2°C/min; (b) 5°C/min; (c) 10°C/min; (d) 20°C/min heating rates.

temperature. Figure 7 shows the Log β versus $10^3/T$ plot for LDPE from 5 to 90% conversion. The straight lines obtained at different conversion values were approximately parallel to each other. From the slope of these plots, activation energy was calculated. Figures 8 and 9 depict the Log β versus $10^3/T$ plots of 5 and 10% rice bran-filled LDPE films. As the percentage of rice bran increased, the straight lines were found to be more broadly distributed, indicating that the rice bran content affected the thermal stability and degradation kinetics of these blends.

The activation energy of the thermal decomposition curves for these blends has been shown in Figure 10. Activation energy depends on the energy barrier preventing polymer chain movement from one location to another, dispersion of the filler, and interfacial adhesion between the filler and the polymer. Kim et al.[14] reported the effect of rice husk on the activation energy of HDPE and PP. In this investigation also a similar trend has been observed on incorporation of rice bran into LDPE. In case of LDPE films, the activation energy gradually increased as the percentage conversion increased, while for 5% rice bran-filled films, the activation energy increased following a pattern similar to LDPE, indicating that at 5% filler level, the dispersion and interaction between filler and polymer matrix was good. In case of 10% rice bran incorporation, the activation energy decreased initially up to 20% conversion level followed by a gradual increase, revealing that up to 20% conversion, the presence of rice bran affected the kinetic process. This also indicates a decrease in the interfacial adhesion between the polymer and filler at higher

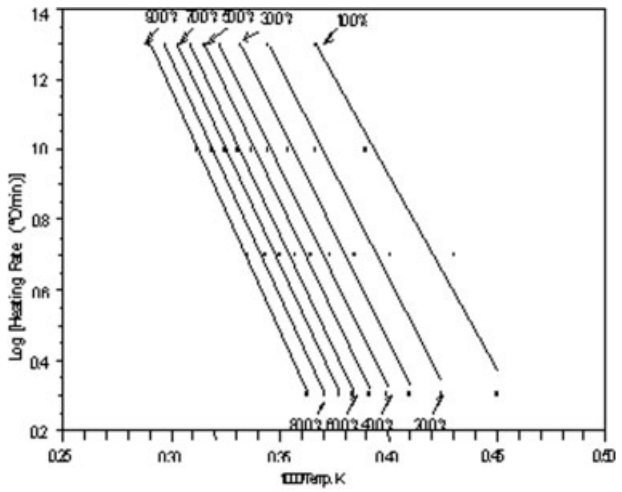

Figure 7 Log β versus $10^3/T$ curves of LDPE at different conversion values.

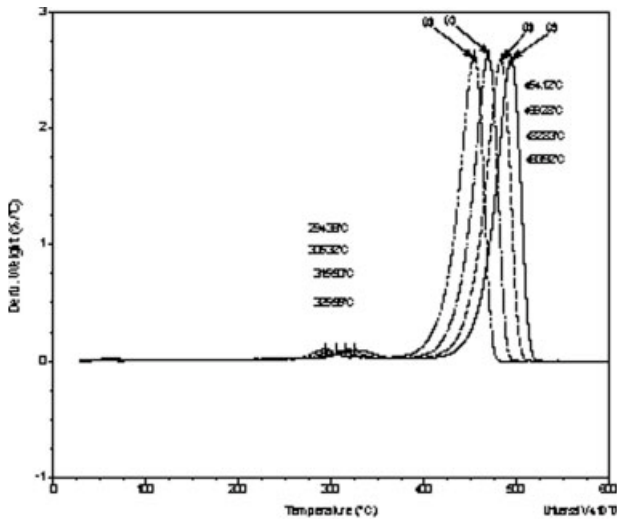

Figure 6 DTG curves of LDPE + 10% rice bran film at (a) 20°C/min; (b) 10°C/min; (c) 5°C/min; (d) 2°C/min heating rates.

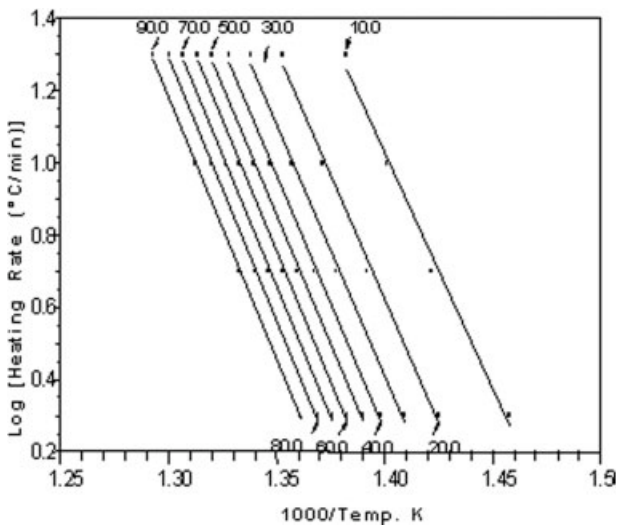

Figure 8 Log β versus $10^3/T$ curves of LDPE + 5% rice bran at different conversion values.

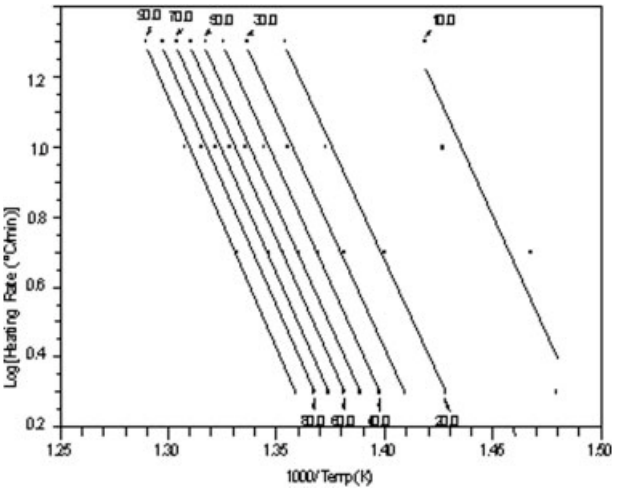

Figure 9 Log β versus $10^3/T$ curves of LDPE + 10% rice bran at different conversion values.

concentrations of rice bran. SEM analysis indicates that the rice bran particles tend to form clumps that in turn reduce the dispersion of filler in polymer matrix. Therefore to improve the interfacial adhesion and dispersion, a compatibilizing as well as coupling agent is required at higher filler loading.

Biodegradation studies

Biodegradable plastics, when subjected to appropriate environment should degrade more rapidly than conventional plastics and to enhance biodegradability, various additives have been incorporated into the polymer matrix. Accelerated laboratory tests have been used for simulating the biodegradation of such plastics, as biodegradation in landfill is time consuming, complex, and attributed to many extrinsic factors.[15] Aerobic biodegradation of rice bran-filled LDPE has been evaluated using activated municipal sewage sludge inoculum as well as specific microorganism like Streptomyces species, which are capable of degrading starch and thus causing loss in weight and plastic integrity.[15] The carbon dioxide evolved during biodegradation in presence of municipal sewage sludge can be determined as a function of time and can be directly correlated with the biodegradability of such materials. Figure 11 indicates the evolution of CO_2 from different rice bran-filled LDPE films, which have been compared to rice bran as such as a control. The weight of rice bran in these three systems was kept constant for easy comparison. LDPE as such is showing negligible CO_2 production because of its limited biodegradability. For 10% rice bran-filled LDPE films, the amount of CO_2 evolved after 30-day evaluation is 299.01 mg, while 5% rice bran-filled LDPE films showed 257.12 mg. The results indicate that around 44% of rice bran is degrading in 10% rice bran-filled films, whereas only 38% is degrading in 5% rice bran-filled films. The weight loss measured after 30-day evaluation reveals that the percentage weight loss for 5 and 10% rice bran-filled LDPE films are 1.87 and 4.34%, respectively, which is in concurrence to the percentage biodegradability calculated by measuring CO_2 evolved during aerobic biodegradation. The incomplete biodegradation of rice bran has been attributed to the physical protection offered by LDPE, as some rice bran particles may be encapsulated within the LDPE matrix, making it unavailable for microbial degradation. Arvanitoyannis et al.[2] also reported similar results in the case of rice starch-filled LDPE films.

The biodegradation studies were also conducted using specific microorganisms like Streptomyces species. For 5% rice bran-filled films, the weight loss observed in case of inoculated samples was 0.85%,

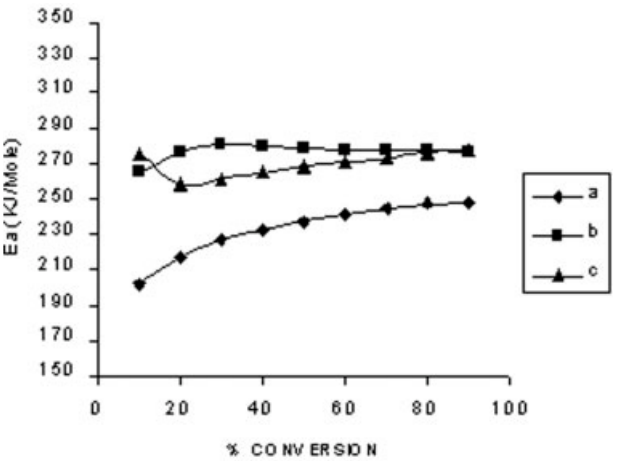

Figure 10 Activation energy of thermal decomposition for (a) LDPE; (b) LDPE + 5% rice bran; (c) LDPE + 10% rice bran films.

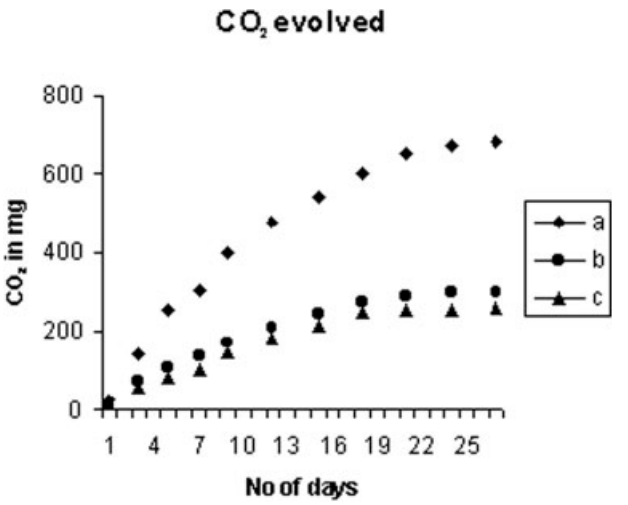

Figure 11 Carbon dioxide evolved during aerobic biodegradation of rice bran LDPE blends using municipal sewage sludge inoculum. (a) Rice Bran; (b) LDPE + 10% rice bran; (c) LDPE + 5% rice bran films.

TABLE IV
Biodegradation Results of Various LDPE Films Using Specific Microorganism

Samples	Percentage weight loss*		Percentage elongation* (machine direction)		Percentage elongation* (cross direction)	
	Inoculated	Uninoculated	Inoculated	Uninoculated	Inoculated	Uninoculated
LDPE	Nil	Nil	248.53 ± 8.12	249.46 ± 11.16	97.12 ± 10.6	98.75 ± 9.18
LDPE + 5% rice bran	0.85 ± 0.01	0.37 ± 0.005	136.69 ± 6.26	187.09 ± 12.83	53.12 ± 10.12	76.04 ± 5.82
LDPE +10% rice bran	1.7 ± 0.011	0.9 ± 0.01	89.47 ± 7.48	149.68 ± 11.41	33.99 ± 9.88	60.24 ± 7.45

* Mean ± S.E.; n = 5.

while uninoculated samples showed lower values (Table IV). The weight loss occurring after biodegradation using this method is comparatively less than what is observed using activated sewage sludge as an inoculum. This may be due to the presence of more diverse microorganisms in the former case, while latter method is having only one microbial species. As the percentage of rice bran increased, the weight loss was also found to increase. A similar trend was observed in case of percentage elongation. The reduction in percentage elongation for inoculated 5% rice bran-filled films in machine direction was 45%, while 10% rice bran films showed a reduction of 64% (Table IV). In cross direction also similar reduction was observed. For uninoculated 5 and 10% rice bran films samples, the reduction in machine direction was 25 and 40%, while in cross direction it was 23 and 39%, respectively. The control LDPE films did not show any change in their properties after these tests. These results indicated that the plastic integrity of rice bran-filled films can be reduced by microbial degradation and pure culture methods are useful to study biological degradation effectively.

CONCLUSIONS

The effect of rice bran incorporation in LDPE films was investigated and the following conclusions were drawn. Although mechanical properties of LDPE were found to decrease by the addition of rice bran, the films were operational for normal packaging applications. Morphological studies using SEM revealed the formation of clumps as the rice bran content increases. The oxygen transmission rate, water vapor transmission rate, and global migration increased with the increase in rice bran content. Optical properties like specular gloss were found to decrease with the increase in rice bran content. DSC analysis indicated a shift in T_g as the filler incorporation increased, but there was no significant change in the T_m of LDPE rice bran blends. Thermal analysis using TGA revealed that thermal stability was affected by the addition of rice bran. Using Flynn–Wall–Ozawa method, activation energy for thermal decomposition was determined and found to be higher for rice bran-filled LDPE films than that for control. From the activation energy profile of 10% rice bran-filled LDPE, it can be concluded that the increase in filler concentration decreased the interfacial adhesion and dispersion of filler in LDPE matrix. At higher loads of rice bran incorporation in LDPE, a compatibilizer as well as a coupling agent is recommended. Aerobic biodegradation study using municipal sewage sludge as well as specific microorganisms revealed that these films tended to loose their properties when subjected to accelerated microbial degradation conditions.

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