Degradation Behaviors of Linear Low-Density Polyethylene and Poly(L-lactic acid) Blends

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ABSTRACT: In this study, the degradability of linear low-density polyethylene (LLDPE) and poly(L-lactic acid) (PLLA) blend films under controlled composting conditions was investigated according to modified ASTM D 5338 (2003). Differential scanning calorimetry, X-ray diffraction, and Fourier transform infrared spectroscopy were used to determine the thermal and morphological properties of the plastic films. LLDPE 80 (80 wt % LLDPE and 20 wt % PLLA) degraded faster than grafted low-density polyethylene–maleic anhydride (M-g-L) 80/4 (80 wt % LLDPE, 20 wt % PLLA, and 4 phr compatibilizer) and pure LLDPE (LLDPE 100). The mechanical properties and weight changes were determined after composting. The tensile strength of LLDPE 100, LLDPE 80, and M-g-L 80/4 decreased by 20, 54, and 35%, respectively. The films, as a result of degradation, exhibited a decrease in their mass. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1993–1998, 2012

Key words: degradation; differential scanning calorimetry (DSC); polymer blends

INTRODUCTION

The large use of synthetic nondegradable polymers and plastic materials produced from petrochemicals has led to serious environmental pollution.[1,2] Synthetic plastics accumulate at a rate of 25 million tons per year in the terrestrial and marine coastal environments. Polyethylene represents 64% of the synthetic plastics produced, and it is mainly used for the manufacture of plastic bags, bottles, and disposable containers, which are discarded within a short time.[3,4] The degradation of polymers involves several physical and chemical processes accompanied by small structural changes, which lead, nevertheless, to significant deterioration of the quality of the material.[5] Degradation is an irreversible change, resembling the phenomenon of metal corrosion. Polymeric materials are not easily biodegraded. Efforts have been directed to the development of mild physicochemical procedures, which include thermal and radiation pretreatments,[6,7] to enhance the biodegradation process.

One answer to this problem is the use of biodegradable polymers, and it is necessary to know their biodegradability in natural environments to extend their use. In the determination of the biodegradation of a polymer, composting has been accepted world wide as one of the most promising technologies for the management of plastic waste. Because of the high microbial diversity of compost, it shows good potential degradation capacity for polymer materials.[8,9]

The degradation of plastics in nature is a very slow process, which is first initiated by environmental factors and followed by indigenous microorganisms. The environmental factors include temperature, humidity, pH, and UV radiation. Biodegradation is the ability of microorganisms to influence abiotic degradation through physical, chemical, or enzymatic action.[3,6,10,11] Interplay between biodegradation and different factors in the biotic and abiotic environments is very important. The microorganisms reported for the biodegradation of polyethylene include fungi (*Aspergillus niger, Aspergillus flavus, Aspergillus oryzae, Chaetomium globusum, Penicillium funiculosum*, and *Pullularia pullulan*), bacteria (*Pseudomonas aeruginosa, Bacillus cereus, Coryneformes bacterium, Bacillus sp., Mycobacterium, Nocardia, Coryne bacterium*, and *Pseudomonas*), and actinomycetes (*Streptomycetaceae*). Their activity on the polymer have been studied by growth tests on solid agar medium for a definite period of time. Changes in the molecular weight, structure, crystallinity, density, weight loss, and mechanical, optical, and dielectric properties have also been measured.[12–18]

The rate of biodegradation of polyethylene, even after prolonged exposure (10–32 years) to a microbial consortia of soil, was found to be very low; this, thus, accounts for the carbon mineralization of less

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than 1%.[19,20] More recently, it has been demonstrated in soil burial tests that the use of suitable additives in polyethylene films induced substantial oxidation with consequent fragmentation, a drop in molecular weight, and an increase in wettability, ultimately followed by high mineralization (60–70%) and a fixation of about 8–10% of carbon into cell biomass.[21,22] The low rate of biodegradation in plastics is usually due to a lack of water solubility and the size of the polymer molecules, which prevent them from getting transported directly into cells.[23,24] The two major problems with polyethylene are its high hydrophobicity (due to the presence of only $-CH_2$ groups) and its high molecular weight (more than 30 kDa). The biotic mechanism reported for the degradation of high-molecular-weight polymers include extracellular enzymes produced by microorganisms, which degrade the main polymeric chain and result in intermediates of lower molecular weight with modified mechanical properties; this makes the materials more accessible for microbial assimilation.[25] Thermal or radiation treatments of polyethylene reduce the polymeric chain size and form oxidized groups, such as carboxyl, carbonyl, and hydroxyl groups. These treatments modify the properties (crystallinity level and morphological properties) of the original polymer and facilitate polymer biodegradation.[3]

The degradation of a polymer may be achieved by two major paths, namely, (1) the design of a polymer from monomers that are vulnerable to microorganisms and (2) the incorporation of biodegradable additives or groups in the polymer. This, in turn, can be done by two methods. The first one involves the copolymerization of biodegradable monomers with a nondegradable monomer, and the second method involves the blending of a biodegradable additive/polymer with a nondegradable polymer. A blend of poly(L-lactic acid) (PLLA) and linear low-density polyethylene (LLDPE) was the subject of a report,[26] but there was no discussion of the degradation behavior. We reported the melt blending of LLDPE and polylactide, which was performed in an extrusion mixer with a postextrusion blow-film attachment.[27]

In this study, LLDPE, PLLA, and blend films were incubated with mature compost (municipal solid waste) as per modified ASTM D 5338. The degradation was monitored through the physicochemical changes that took place in the plastic films.

EXPERIMENTAL

Materials

Commercial-grade LLDPE [trade name Halene-L, melt flow index (MFI) = 1.41 g/10 min with a 2.16-kg standard die at 190°C, grade 71601S] was obtained from Haldia Petrochemicals, Ltd. (Haldia, India). Commercial-grade PLLA (trade name Biomer L 9000, weight-average molecular weight = 20 kDa, number-average molecular weight = 10.1 kDa, MFI = 3.0 g/10 min with a 2.16-kg standard die at 190°C) was supplied by Biomer Forst-Kasten-Str Kailling (Krailling, Germany). The commercial-grade compatibilizer, grafted low-density polyethylene maleic anhydride [M-g-L; trade name OPTIM E142, MFI = 4.0 g/10 min with a 2.16-kg standard die at 190°C, density = 0.925 g/mL, melting temperature = 103°C], was obtained from Pluss Polymers Pvt., Ltd. (New Delhi, India). The compatibilizer was M-g-L resin, and it contained 0.9–1.3% maleic anhydride.

In this investigation, pure linear low-density polyethylene (LLDPE 100), LLDPE 80 (80 wt % LLDPE and 20 wt % PLLA), M-g-L 80/4 [80 wt % LLDPE, 20 wt % PLLA, and 4 phr compatibilizer (M-g-L)] films of size 80 × 25 mm^2 with a thickness of 0.125 mm were made by the melt blending of LLDPE and PLLA in an extrusion mixer with a postextrusion blown-film attachment, as reported in our earlier work. Market-available biodegradable polymer films [controlled sample films (CSFs)] of size 80 × 25 mm^2 with a thickness of 0.11 mm were kindly provided by M/s Balson Industries (Pune, Maharashtra, India, http://www.balsonindustries.com).

The mature compost (municipal solid waste) was obtained from a compost plant (New Delhi Municipal Council, Okhla, New Delhi, India). The compost inoculum was well-aerated from the organic fraction of municipal solid waste and sieved on a screen of less than 10 mm. The compost inoculum was as free from larger inert materials (glass, stones, metals, etc.) as possible. These items were removed manually as well as possible to produce a homogeneous compost inoculum. The compost properties were evaluated as per the American Public Health Association:[28] the total solid content at 100–105°C was 81%, and the volatile solid content at 550°C was 18% (pH 7.2, C/N ratio = 15.3).

Methodology

Controlled composting (modified ASTM 5338, 2003)

The plastic films of CSF and LLDPE 100 and its blends (LLDPE 80, M-g-L 80/4) were embedded in the compost and incubated in an incubator (model NSW-152, Narang Scientific Works Pvt., Ltd., New Delhi, India) for a period of 28 days initially and kept at 37°C for a period of 1 day to stimulate a mesophilic startup phase. Subsequently, the temperature was raised to 50°C for a period of 4 days for optimum composting conditions. Then, the

temperature was reduced to 37°C for the remainder of the test period (23 days) to stimulate a mesophilic curing phase, and we maintained the moisture content and aerobic conditions manually as much as possible for controlled composting. Then, the microbial biofilm was removed from the polyethylene surface by incubation of the polyethylene samples in flasks containing a 2% (v/v) aqueous sodium dodecyl sulfate solution for 4 h. The polyethylene samples were then collected on a filter paper, rinsed with distilled water, and dried overnight at 60°C before further testing.

Analytical/testing procedures

Tensile testing. The physical properties, such as tensile strength and elongation at break, were measured according to ASTM D 882-91 on a Zwick universal testing machine (model Z010 Zwick/Roell, Einsingen, Germany) at room temperature (25°C), 50% relative humidity, and a crosshead speed of 50 mm/min. Five replicates were run for each composition, and the average values are reported. The relative elongation and relative tensile strength of the samples treated with compost were compared with those of the untreated control samples.

Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy. FTIR-ATR spectroscopic studies were carried out on the film samples with a PerkinElmer FTIR spectrophotometer (model BX-II, Shelton, USA) in the horizontal ATR mode with a zinc selenide crystal. A total of 16 scans per sample was taken, with a resolution of 4 cm^{-1}. The spectrum was analyzed with spectrum software (LX100627-I, PerkinElmer, Shelton, USA).

Thermal analysis. Thermal analysis was carried out with differential scanning calorimetry (DSC; PerkinElmer DSC-2 Shelton, USA). All measurements were performed under nitrogen. DSC measurements were carried out with heating from room temperature to 300°C at a rate of 10°C/min and were controlled by a compatible computer running the Perkin Elmer (STAR SW900) instrument software. The software-collected data and provided graphical analysis tools were used to determine the transition temperatures and peak areas. DSC studies revealed the significant thermal properties of the samples, such as glass-transition temperature and melting temperature.

Thermogravimetric analysis (TGA) is a helpful tool for characterizing thermal degradation (amount and rate of mass loss), thermal stability, and the lifetime behavior of polymeric materials. Such characterizations provide valuable information for the selection of material, prediction of product performance, and product quality. The thermogravimetric behavior of the polymeric films was determined
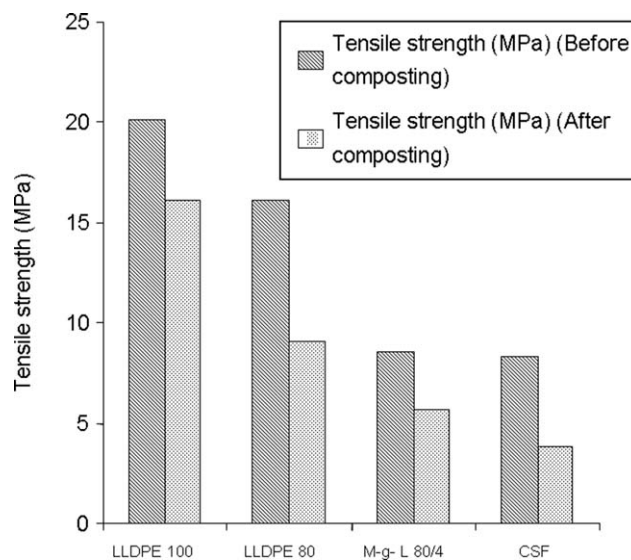
Figure 1 Tensile strength (MPa) of the plastic films before and after treatment.

with TGA (PerkinElmer Pyris, diamond thermogravimeter/differential thermal analysis (DTA)) under a nitrogen flow of 50 mL/min. Samples weighing 3 mg (±1 mg) were heated from 50 to 500°C at a heating rate of 10°C/min.

X-ray diffraction (XRD) analysis. All of the samples were characterized with an X-ray diffractometer with X'Celerator (X'Pert PRO, PANalytical, Almelo, The Netherlands) with Cu Kα radiation ($\lambda = 1.5418$ Å). During the experiment, the scanning speed and diffraction angle were 5°/min and 5–60° (2θ), respectively, at 45 kV and with a current of 40 mA.

Weight loss. A simple and quick way to measure the biodegradation of polymers is to determine the weight loss. Microorganisms that grow within the polymer lead to an increase in weight due to accumulation, whereas a loss of polymer integrity leads to weight loss. Weight loss is proportional to the surface area because biodegradation usually is initiated at the surface of the polymer. This method cannot be used on polymers that absorb water. Multiple samples were weighed with an accurate four-digit balance, and the average values are reported here.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of the plastic films before and after composting are shown in Figures 1 and 2. After composting, there were decreases in the tensile strength and elongation at break of LLDPE and its blends; this showed that after composting, there was a considerable loss of mechanical properties. A loss of tensile strength of 19.9% was observed with LLDPE 100, a loss of 54.1% was observed with
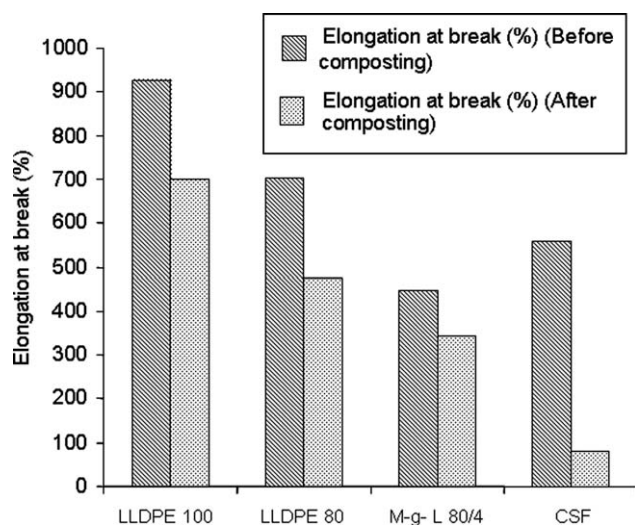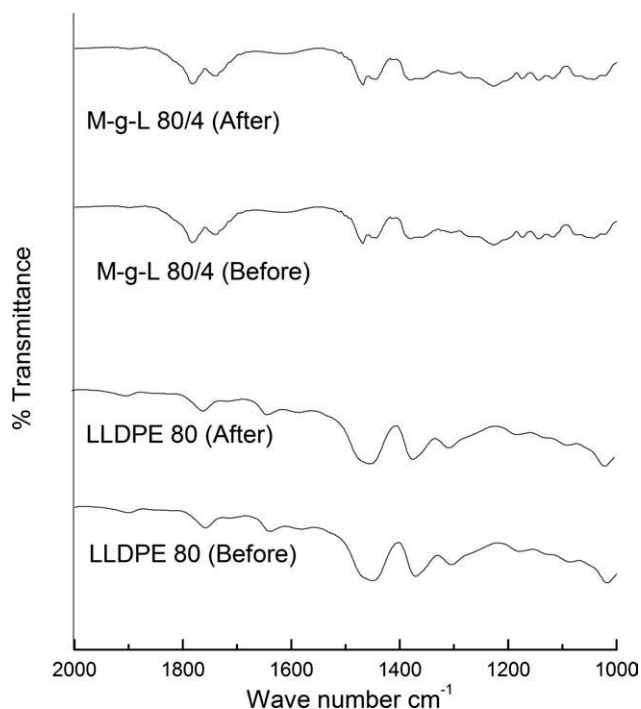
Figure 2 Elongation at break (%) of the plastic films before and after composting.

Figure 3 FTIR spectra of LLDPE 80 and M-*g*-L 80/4 before and after composting.

LLDPE 80, a loss of 34.3% was observed with M-*g*-L 80/4, and a loss of 56.6% was observed with CSF after composting. This showed that after composting, there was a loss in the mechanical properties even in LLDPE 100 and its blends with PLLA. LLDPE 80 showed a great decrease in the mechanical properties, as PLLA is brittle in nature and acts as filler when it is dispersed in LLDPE. In the case of M-*g*-L 80/4, because of the addition of compatibilizer, the drops in the tensile strength and elongation at break were lower, probably because of the high MFI of the compatibilizer and its polymeric nature. The plasticizing effect of compatibilizer could have increased or decreased the elongation at break. It was also observed in M-*g*-L 80/4 after composting that the loss in tensile strength was lower compared to that of LLDPE 80 because the compatibilizer dispersed PLLA in LLDPE, hiding it from direct attack of the composting microorganisms and making it unavailable to the microorganisms during composting.

FTIR spectroscopy

FTIR analysis is a useful tool to determine the formation of new groups or the disappearance of functional groups. So degradation products, chemical moieties incorporated into the polymer molecules, such as branches, comonomers, unsaturation, and the presence of additives such as antioxidants can be determined by this technique. The initial spectra were in agreement with the chemical structures of LLDPE 100 before and after composting; this showed that there was no significant difference after incubation. The absorption band results show that there was no significant change in the bulk, and biodegradation was only superficial. It did not significantly change the chemical structures.[4,29] The FTIR spectrum (Fig. 3) showed a typical carbonyl peak

at 1758 cm^{-1}. The composting of the LLDPE 80 and M-*g*-L80/4 films showed an insignificant reduction in the amount of carbonyl residues, as shown in Table I, which indicated minor degradation during composting. The reduction in carbonyl residues was also estimated in terms of the carbonyl index (CI), which is the ratio between the absorbance peaks of carbonyl to that of CH$_2$ at 1462–1463 cm^{-1}.

Thermal properties

The change in crystallinity after composting was confirmed by DSC measurements. Melting peaks occurred at 125°C because of the melting of crystallites of LLDPE100 and its blends. Figure 4 and Table II show the DSC scans and melting enthalpies, respectively, of the crystalline phase. It was observed that after composting, the change in melting enthalpy (ΔH)

TABLE I
CI Values Obtained from the FTIR Spectra of the Plastic Samples Before and After Composting

Sample	CI ($A_{C=O}/A_{CH2}$)[a]	
	Before composting	After composting
LLDPE 100	Nil	Nil
LLDPE 80	1.10	1.02
M-*g*-L 80/4	1.00	0.99
CSF	Nil	Nil

[a] CI expresses the ratio between the absorbance peak of the carbonyl (1758 cm^{-1}) and that of the CH$_2$ groups at 1462–1463 cm^{-1}.
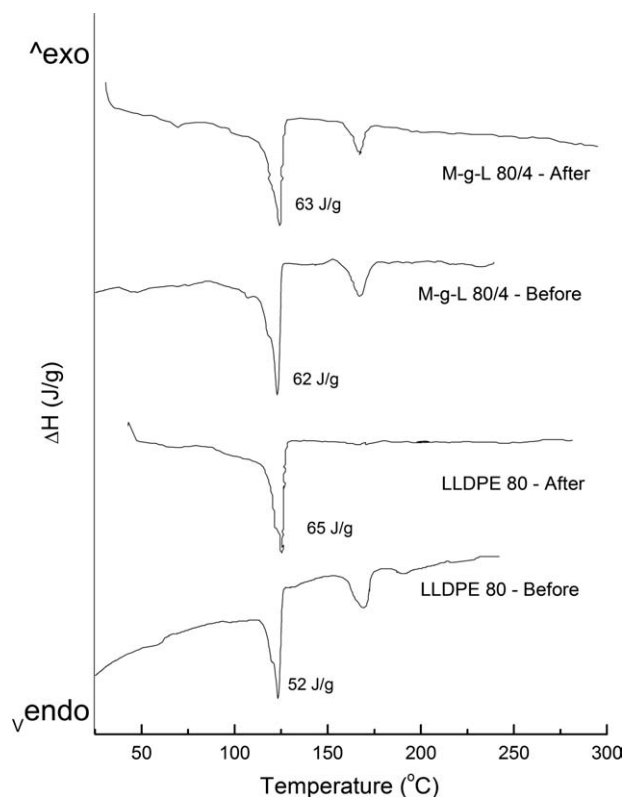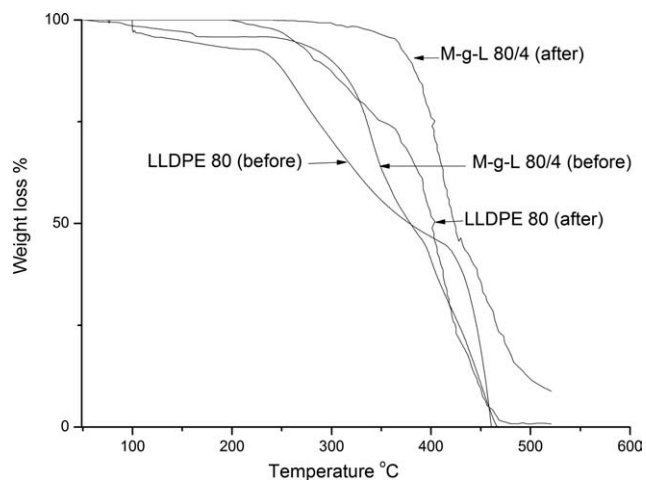
Figure 4 DSC scans of LLDPE 80 and M-g-L 80/4 before and after composting.

was greater in LLDPE 80 as compared to the other films. The increase in crystallinity was confirmed by an increase in the melting enthalpy of the crystalline phase of plastic samples after 28 days of composting, which caused degradation in the amorphous regions of the polymer and left the crystalline region largely unaffected; this resulted in the observed increase in crystallinity.[7]

TGAs of the LLDPE 80 and M-g-L 80/4 films before and after biotic exposure are presented in Figure 5. Increases in the T_{20} (temperature at 20% mass reduction of the sample) values from 266.47 to 328.66°C for LLDPE 80 and from 326.07 to 394.920°C for M-g-L 80/4 were observed. This increase could have been due to the preferential biodegradation of the low-molecular-weight fragments generated during the biotic exposure of the films, as they were recognizable by the microbial enzymes.[15]

TABLE II
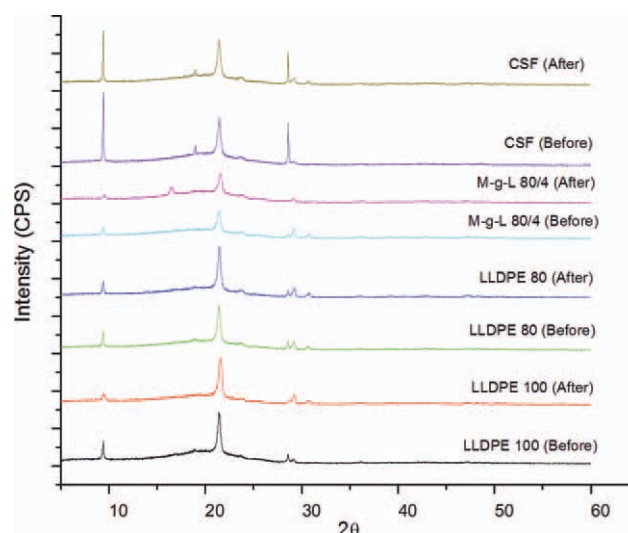**ΔH Values of the Plastic Films Before and After Composting**

Sample	ΔH (J/g)	
	Before composting	After composting
LLDPE 100	61.63	62.30
LLDPE 80	52.07	65.33
M-g-L 80/4	61.78	63.07

Figure 5 TGA of LLDPE 80 and M-g-L 80/4 before and after composting.

XRD

XRD showed that there was an increase in the crystallinity of LLDPE 80 by 4.13% and of CSF by 10.16% (Figs. 6 and 7), probably due to the assimilation of the amorphous part of the polymer by the bacteria. Thus, only the crystalline region of the plastic film was left behind; this led to an increase in the crystallinity. However, in the case of M-g-L 80/4, there was no increase in the crystallinity because of the fact that the degradation of the fibers occurred from the outside surface of the fibers. The compatibilizer maleic anhydride had a higher resistance to microorganisms than PLA and LLDPE in the fibers and could wrap PLLA and LLDPE to protect them from degradation. Therefore, LLDPE in the polyblends with a compatibilizer had much less degradation than the pure fibers. No change in the crystallinity of LLDPE 100 was observed, even after 28 days of composting.

Figure 6 XRD patterns of the plastic films before and after composting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
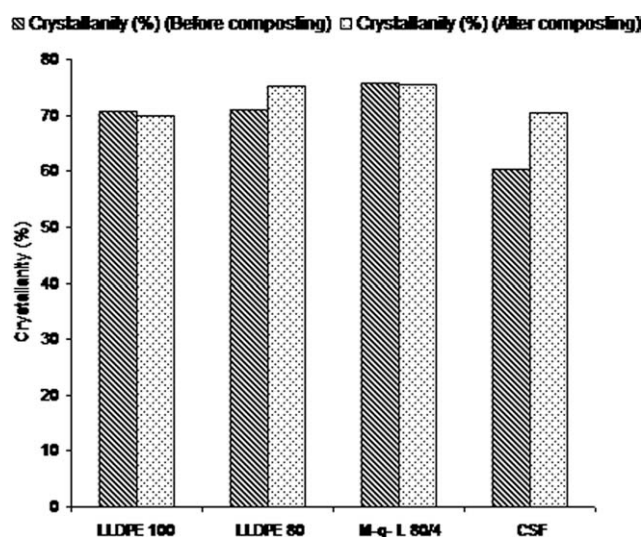
Figure 7 Crystallinity (%) before and after composting.

Weight loss

A maximum weight loss of 17% was observed with CSF under composting within 28 days. Weight losses of 11.6% with LLDPE 80, 1.39% with LLDPE 100, and 0.36% with M-g-L 80/40 under composting were observed (Fig. 8) It was reported that the total weight loss during degradation was 16% for degradable polyethylene (with prooxidant and/or biodegradable additives), and in addition to H_2O and CO_2, shorter hydrocarbons, alcohols, organic acids, ketones, aldehydes, and so on were also formed.[30]

CONCLUSIONS

This investigation revealed that introduction of PLLA into LLDPE led to rapid degradation on composting. LLDPE and PLLA blend films are more susceptible to biodegradation compared to compatibilizer blend films. The films, as a result of degradation, exhibited a decrease in their mass and tensile properties. The spectroscopic investigations revealed that the oxygenated products were preferentially consumed; this led to a decrease in the CI,
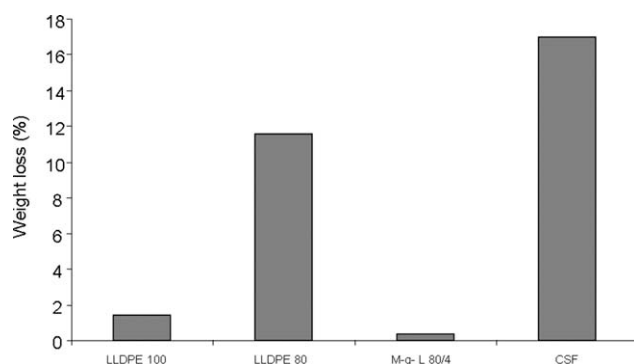

Figure 8 Weight loss after composting of the plastic samples.

which, in turn, led to an increase in the initial decomposition temperature, as observed by TGA. DSC studies of the blend films showed that the burial composting led to the degradation of the amorphous phase and resulted in increased crystallinity; this was also confirmed by XRD analysis.

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