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Evaluation of LDPE Degradation Under Controlled Composting

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ABSTRACT

The compost burial test was performed to determine the degradation of commercially available low-density polyethylene in natural compost for a period of six months. Biodegradability of polyethylene films in compost was monitored using scanning electron microscopy (SEM), Energy dispersive X-Ray, Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and weight reduction analysis. After six months of compost exposure, a major change over the surface of LDPE was observed. SEM images clearly showed the exfoliation and cracks on the film leading to degradation. The other analysis also showed a change in the thermal properties and crystallinity of the LDPE films. The composting method could prove to be the reliable and ecological method of degrading plastic waste without hindering the natural ecosystem.

INTRODUCTION

Composting is basically a natural process by which organic material gets decomposed into humus, which is a soil-like material. The major groups of microorganisms that are involved in composting are bacteria and fungi. These microorganisms decompose the organic substances as their source of food. This process of degradation requires carbon, nitrogen, oxygen, water, and heat. Organisms decompose the organic substance to use carbon and nitrogen as the source of energy and for building their cell structure (Mierzwa-Hersztek et al. 2019). Degradation of the polymers in the compost environment occurs primarily through mechanical, chemical, and thermal degradation (Calabia & Tokiwa 2004). Of all the mechanisms of degradation, chemical degradation is considered the most important for polymers. In the compost method, the specific weight of the plastic is buried under the mixture of a definite amount of mature compost and soil and then kept under natural weathering conditions with maintained moisture content. Biodegradation of polymer is measured based on the amount of carbon present in the polymer converted to gaseous carbon dioxide. The nature and type of compost affect the extent and degree of degradation of polymer (Das & Kumar 2015). This is the natural way of decomposing plastic in an eco-friendly manner. The increased accumulation of plastics in the environment has forced researchers across the world to develop several degradation methods to deal with plastic waste which does not create further stress on the natural environment (Vázquez-Morillas et al. 2016). The study presented here is one such attempt at dealing with plastic waste. To evaluate biodegradability in realistic disposal conditions, a compost burial test of LDPE films was performed for six months. In the experiment, different concentrations of compost were used and kept in pots to degrade the low-density polyethylene (LDPE) films. The investigations on the chemical and morphological changes in LDPE films revealed the extent of degradation.

MATERIALS AND METHODS

Compost Setup

For composting method, different concentration of compost 20%, 40%, 60%, 80% and 100% (w/w) was made. For this, approximately 1 kg of the compost and soil was maintained in different concentration in different pots. The experiment was done in triplets. The LDPE films of area 5cm^2 were buried under the compost in pots for a period of six months.

Characterization of Degraded LDPE Samples

After six months LDPE samples were taken out, washed, and characterized using weight reduction, SEM, EDX, FTIR, TGA, XRD, and DSC analysis.

Scanning Electron Microscopy and Energy Dispersive X-ray Analysis

The LDPE films were subjected to SEM and EDX analysis for determining the changes induced in their morphological structure and elemental composition. The analysis was done using the Scanning Electron Microscope of JEOL (JSM 6490 LV) present at University Scientific Instrument Center (USIC), Babasaheb Bhimrao Ambedkar University, Lucknow (Ambika et al. 2015).

Fourier Transform Infra-red Spectroscopy (FTIR)

The FTIR analysis serves the purpose of detecting the functional group in the substance, which is subjected to the analysis. FTIR scan was taken at a spectrum ranging from 400 cm^{-1} to 4000 cm^{-1} at room temperature. The relative absorbance intensities of the keto carbonyl bond (1740 cm^{-1}) and a double bond (908 cm^{-1}) to that of the methylene bond (1465 cm^{-1}) were calculated using the following equation (Albertsson et al. 1998): keto carbonyl bond index (KCBI) = I_{1715}/I_{1465}; and internal double bond index (IDBI) = I_{908}/I_{1465}. The crystallinity percentage of the polyethylene films was calculated by using following equation: % crystallinity = $100 - [\{1 - (Ia/1.233Ib) / 1 + (Ia/Ib)\} \times 100]$: where *Ia* is absorbance at 1473 and *Ib* is the absorbance at 1463 (Averous & Pollet 2012).

X-Ray Diffraction Analysis (XRD)

XRD analysis was done by the fifth generation Rigaku (Modal no Mini Flex 600) X-ray diffractometer. XRD analysis gives detail about the crystalline nature of the substance subjected to the analysis. In the case of LDPE, the analysis is very important as it shows whether the polymer material has undergone a change or not after its treatment with the compost. For this purpose, LDPE films were cut into pieces and inserted inside the diffractometer.

Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

For TGA analysis, Shimadzu's TGA50 series thermogravimetric analyzer was used while for DSC analysis, Shimadzu Modal no. DSC-60Plus was used. TGA and DSC analysis are performed for determining the thermal properties of the LDPE films. For the analysis, the LDPE films were cut into very small pieces and then kept in the crucible, which was then loaded in the instrument for analysis.

RESULTS AND DISCUSSION

The LDPE films were subjected to the compost treatment of varying concentrations from 20% to 100%. After a period of six months, LDPE films were recovered from the compost and various analysis such as SEM, EDX, FTIR, TGA, DSC, XRD and weight reduction analysis was performed for determining the extent of degradability. The physicochemical parameter of the compost sample was also estimated to observe the post-treatment changes in the compost parameters. The results obtained for various analyses are given as follows.

Scanning Electron Microscopy

In SEM analysis the untreated LDPE film appeared as a smooth, uniform, and homogeneous sheet, whereas, other LDPE films that were kept under the treatment with different concentrations of compost showed significant changes in the morphology (Fig 1). After six months of treatment, the most prominent change was observed in LDPE film that was treated with 80% compost followed by 100%, 60%, 40%, and 20% compost. In LDPE film treated with 100% compost, the deterioration was observed over the surface but it was less prominent than 80% compost treated LDPE. In 60% and 40% compost treated LDPE, some changes such as exfoliation of surface and peeling were observed. The least change was observed in 20% compost treated LDPE due to less amount of compost and more amount of dry soil sample. The LDPE film appeared as a continuous, uninterrupted sheet. SEM micrographs in this study revealed that upon exposure to compost, surface erosion took place and the matrix became perforated. This ultimately resulted in a thinning of the matrix with inconsistent properties which corresponds to the deterioration of the mechanical properties of the LDPE sheets (Kale et al. 2015). Exfoliation was clearly demonstrated in the LDPE. This peeling of a thin layer (exfoliation) can happen only if there is a major erosion of the more accessible amorphous regions in the polyethylene, leaving a crystalline region that degrades very slowly. The SEM analysis clearly reveals the change in the surface structure of the LDPE and moreover, the degradation was observed to be more prominent in 80% compost treated LDPE sample (Bhardwaj et al. 2012).

X-Ray Diffraction Analysis

The crystallinity of the polymer is directly proportional to the diffraction peak intensity. The peaks at 21° and 23.5° are the characteristic peaks of the semi-crystalline polyethylene molecule. The intensities of the different compost treated samples were compared for the intensities at these two significant peaks. The change in crystallinity of treated and untreated samples was compared according to the change in X-Ray intensities at different 2 theta angles. The two obvious diffractive peaks of about 21° and 23.5° correspond to a typical crystalline plane (110), and (200) of the orthorhombic

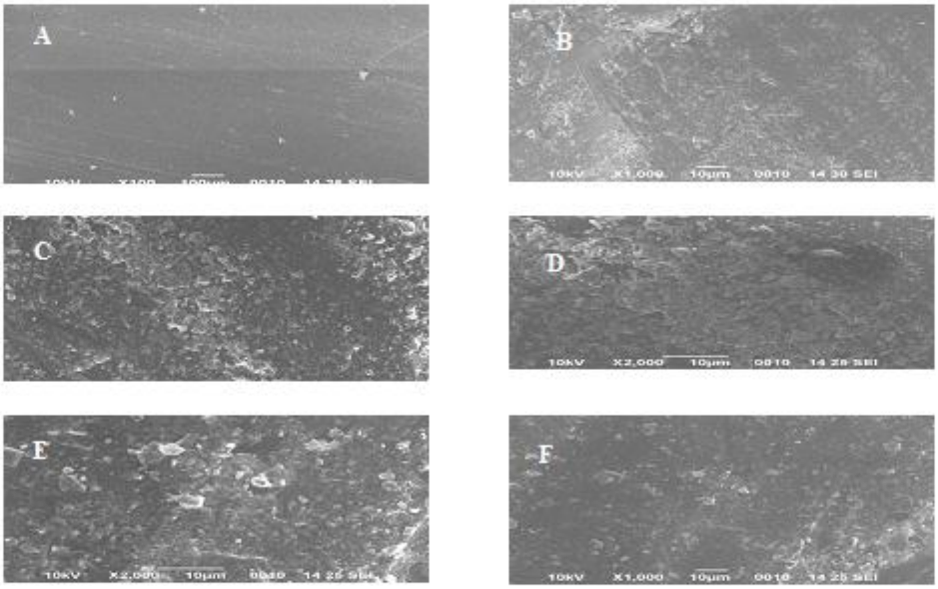

Fig. 1: SEM micrographs: (A) Untreated LDPE (B) 20% compost (C) 40% compost (D) 60% compost (E) 80% compost (F) 100% compost treated LDPE samples.

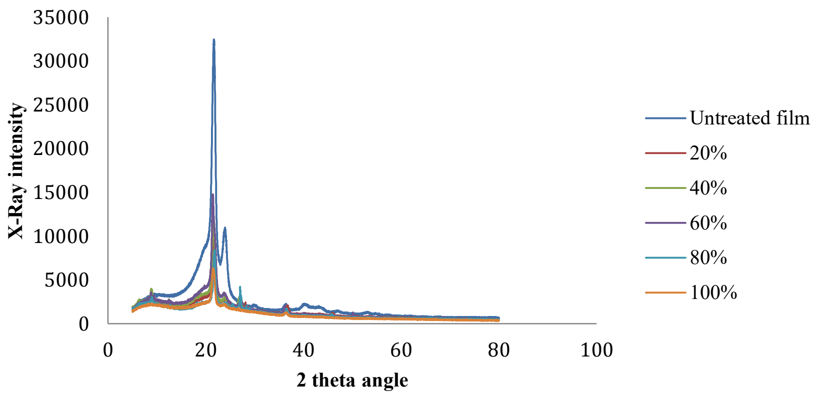

Fig. 2: XRD graph of different compost treated and untreated samples.

phase respectively (Caruso 2015). The graph shown in Fig. 2, clearly shows that the lowest intensity at 21° and 23.5° was observed on 80% compost treated LDPE sample. Maximum intensity was found in untreated LDPE sample followed by 20%, 40%, 60%, and 100% compost treated sample

Energy Dispersive X-Ray (EDX) Analysis

The weight percent of carbon and oxygen of LDPE treated with different concentrations of compost is given in Table 1 below. The EDX analysis revealed that the lowest carbon content was observed in 80% compost treated sample and higher oxygen content was also found in the LDPE treated with 80% compost treated sample. This signifies that the microbial attack began at the surface of the polymer resulting in higher oxygen content on the surface. This step can be described as a development of oxidation skin and as a result, the polymer's surface is damaged with fine cracks indicat-

Table 1: Weight percent of carbon and oxygen.

Sample	Carbon	Oxygen
Untreated LDPE	77.29%	22.71%
20% Compost treated	73.01%	26.42%
40% Compost treated	67.75%	32.25%
60% Compost treated	53.11%	44.20%
80% Compost treated	46.29%	50.26%
100% Compost treated	50.22%	46.32%

ing morphological transformations after which degradation proceeds towards the inner part of the polymer depending on the diffusion rate (Gu 2003).

Thermal Gravimetric Analysis

After six months of incubation in compost, a significant drop in thermal stability of LDPE films was recorded with respect to the untreated LDPE sample. The thermal gravimetric analysis graph shown in Fig. 3 reveals that the maximum reduction in thermal stability was observed in 80% compost treated LDPE. The onset temperature was found to be 403°C and the final decomposition temperature was 486°C with no residue left. Both the temperature for 80% compost treated LDPE obtained were found to be least among all the compost treated samples and untreated samples. TGA results showed the presence of endothermic effects in the compost treated sample. The endothermic effect was due to three processes, which are intermolecular dehydration, vaporization, and solid-state decomposition. The total burning and degradation of the residual polymer backbone took place at a temperature interval of 200°C to 500°C (Sen & Raut 2015).

Differential Scanning Calorimetric (DSC) Analysis

From the curve of DSC analysis shown in Fig. 4, some of the parameters such as glass transition temperature (T_g), onset melting temperature (T_o), melting point temperature (T_m) and end melting point temperature (T_f) were recorded.

The glass transition temperature, onset melting temperature, melting point temperature and end melting point temperature for 80% compost treated sample are 120°C, 395°C, 472°C, 507°C respectively. These values recorded for 80% compost treated sample are highest among all the compost treated and untreated samples. This signifies the increase in crystallinity of the sample. This might be due to the fact that biotic degradation by microbial communities on the LDPE sample attacked the amorphous region, due to which crystalline region remained intact which increased the crystallinity of the polymer. DSC results clearly reveal the increased crystallinity, increased chain scissoring, oxidation, and a minor decrease in tensile strength (Bhatia et al. 2014).

Fourier Transform Infra-red (FTIR) Spectroscopic Analysis

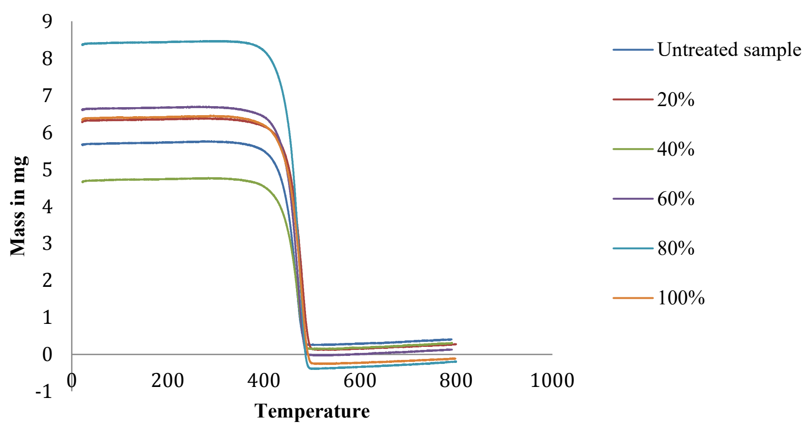

Fig. 3: Thermal gravimetric analysis graph of compost treated LDPE sample.

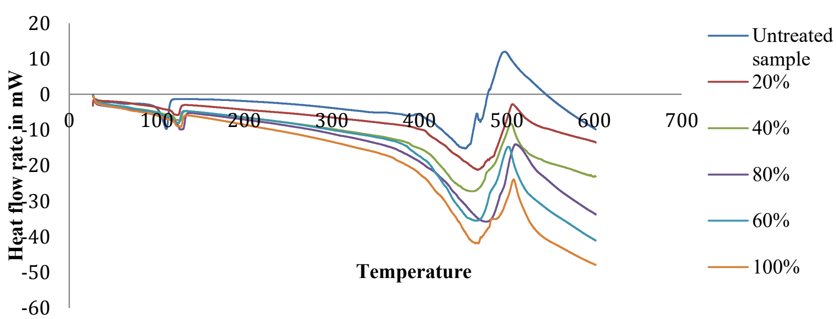

Fig. 4: Differential scanning calorimetry curve of LDPE samples.

FTIR study was conducted to determine the functional groups of the treated and untreated LDPE samples. The spectroscopic graphs are shown below in Fig. 5 & 6 and various functional groups observed in the treated LDPE samples are show in Table 2. The overall trend obtained after aging LDPE by burying it under the different concentrations of compost is that there are higher transmittance values at certain wavenumbers like 2840 cm^{-1}, 2916 cm^{-1}, 1480 cm^{-1}, and 719 cm^{-1}), representing an increase in C-H bond intensity, which can be explained by chain scissoring or increase of CH_3 endings (Sathiskumar & Madras 2011). All the compost treated samples composted formed new spectra at a wavenumber of 1380 cm^{-1}, representing the hydroxyl group. Furthermore, new transmittance peaks were also observed at wavenumbers 997 cm^{-1} and 933 cm^{-1}, indicating the formation of C=C bonds (Giudicianni et al. 2013).

The keto carbonyl bond index and the internal double bond index were found to be maximum in the case of 80% compost treated LDPE. The formation of double bonds in the polymeric chain can be due to the Norrish type II reaction and an increase in the concentration of the carbonyl group could be responsible for a higher carbonyl bond index.

Low-density polyethylene is insoluble in nature due to its crystalline. In this study, there was an observed reduction in the crystallinity of the polyethylene after six months of incubation with the compost. The crystallinity percent for untreated LDPE and 20%, 40%, 60%, 80% and 100% compost treated samples were 86.32%, 81.67%, 79.51%, 74.91%, 65.48% and 71.13% respectively. The lowest crystallinity value was observed in 80% compost treated LDPE. The decrease in crystallinity supports the conversion of crystalline structures of the LDPE films into an amorphous structure as a consequence of degradation.

Weight Reduction Analysis

Polyethylene degradation was monitored by dry weight reduction of polyethylene films treated with the different composts. The present findings revealed that the compost treatment showed some deterioration effect on the LDPE samples. Among all the samples, a maximum weight reduction of approximately 17% was observed in 80% compost treated sample (Fig 7). For rest of the 20%, 40%, 60%, 100% compost treated samples, weight reduction obtained was 6.3%, 8.45%, 11.97% and 14.29%.

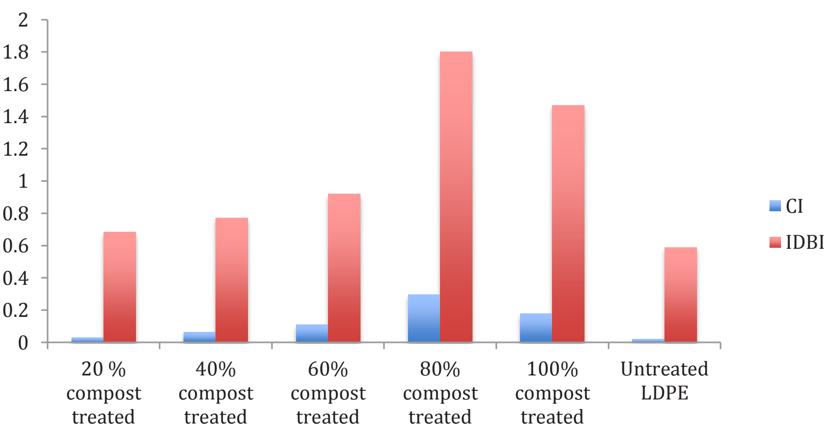

Fig. 5: Graph of carbonyl and internal double bond index of composted LDPE.

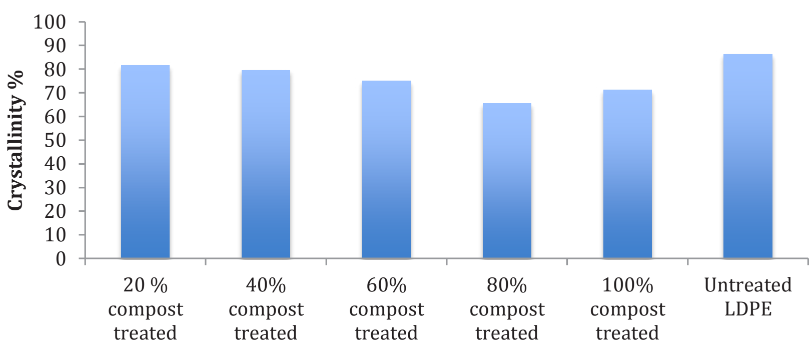

Fig. 6: Graph of crystallinity percent of composted LDPE.

Table 2: Functional groups detected in composted and control LDPE samples.

Origin	Peaks	Functional group	Detected sample
CH_2	2920 cm^{-1}	Alkyl asymmetric stretching	20%, 40%, 60%, 80%, 100% and control LDPE
CH_2	2850 cm^{-1}	Alkyl symmetric stretching	20%, 40%, 60%, 80%, 100% and control LDPE
C=C	1473, 1462, 1437 cm^{-1}	Bending deformation of carbon double bond	60%, 80%, 100% LDPE
C-H	727 and 723 cm^{-1}	Alkane bend mono	20%, 40%, 60%, 80%, 100% and control LDPE
O-H	3200-3450 cm^{-1}	Hydroxyl stretching (intermolecular)	20%, 40%, 60%, 80%, 100% and control LDPE
O-H	1380 cm^{-1}	Hydroxyl bending	80% LDPE
C-O	1160 cm^{-1}	Carbonyl group	20%, 40%, 60%, 80%, 100% LDPE

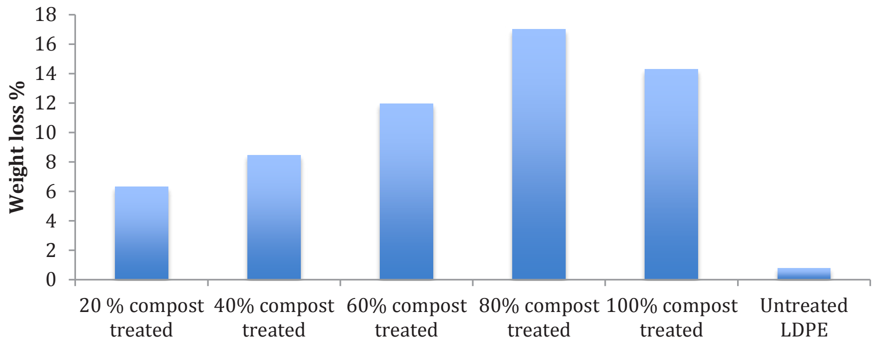

Fig. 7: Graph of weight loss percent of different composted LDPE samples.

CONCLUSION

All the composted LDPE samples showed the changes induced in the polymer. Major changes were observed in LDPE samples treated with 80% compost. A maximum weight reduction of 17% was noted in the 80% compost treated sample. Thermal gravimetric analysis revealed the lowest onset and decomposition temperature with no residue left in the LDPE sample treated with 80% compost treated sample. EDX analysis showed minimum carbon content and maximum oxygen content in 80% compost treated LDPE sample after six months of treatment. In FTIR analysis, a maximum value of carbonyl and double bond index supported the greater extent of degradation in 80% composted LDPE.

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