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### Mechanical, Chemical and Morphological Investigations on the Degradation of Low-Density Polyethylene Films Under Soil-Burial Conditions

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# Mechanical, Chemical and Morphological Investigations on the Degradation of Low-Density Polyethylene Films Under Soil-Burial Conditions

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Commercial formulations of low-density polyethylene (LDPE) films were subjected to an outdoor soil burial test to investigate the environmental degradation under natural conditions. Samples periodically retrieved from soil were examined for changes in physical character, tensile properties, dielectric behavior, X-ray diffraction pattern and FTIR spectra. Irrespective of thickness and color, load-extension curves of all samples reflect complete or partial destruction of plastic and elastic regions after 15 to 17 months of soil exposure. IR spectra after 17 months revealed major absorption

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of the region from 1400–1800  $\text{cm}^{-1}$ , characteristic of carbonyl peak in polyethylene. Upon exposure, the power factor increased remarkably and fairly intense transition peaks were found in dielectric loss curves. XRD graphs reflected possible damage in the amorphous region of the polymer matrix. Disrupted holes under scanning electron microscope further revealed degradation of LDPE films under natural soil conditions.

**Keywords** degradation, LDPE, soil burial

## INTRODUCTION

The stable polymer polyethylene (PE) has already posed a problem of global concern, particularly in developing countries like Bangladesh. Due to its availability, low cost, beauty, manageability and nonporous nature, polyethylene became very popular and within a short time made its way into almost every household, shop and nursery, even to the remotest villages of the countryside. After a time it became a hot environmental issue and the government had to ban the production and marketing of polyethylene shopping bags within the Dhaka metropolis effective from 01 January 2002 (<http://www.sdnbd.org>). In fact, the lack of a proper disposal system has made polyethylene a nuisance in modern life.

The present work was undertaken to study the possible course of degradation of waste polyethylenes under the humid tropical conditions and extensive microbial activity in Bangladesh. When preliminary studies (Khan et al. [1]) showed changes in the appearance and texture of waste polyethylenes, we planned an in-depth view of the polyethylene materials undergoing degradation when buried under soil. Kathiresan [2] found that microbes degrade PE in the soil of Sunderban, situated in the southern part of Bangladesh. The microbial species identified from degrading polythene bags were *Bacillus* sp., *Staphylococcus* sp., *Streptococcus* sp., *Diplococcus* sp., *Micrococcus* sp., *Moraxella* sp., *Pseudomonas* sp., and eight strains of *Aspergillus*. The present workplan included the study of the physical, mechanical and chemical properties of low-density polyethylene films during soil burial.

## MATERIALS AND METHODS

A rectangular plot (76 cm  $\times$  254 cm) was selected in the botanical garden of Dhaka University, Bangladesh. It was weeded and conditioned for two weeks. The texture, pH and moisture-holding capacity of the experimental soil were determined in the Department of Soil, Water and Environment, Dhaka University. The plot was watered occasionally to maintain optimum moisture content.

## Sample Preparation

Four types of commercially available LDPE shopping bags were purchased from local markets. Samples were coded as to the polymer name with additional letters in subscripts referring to its appearance. Thus, white polyethylene film (thickness 0.019 mm, M.P. 124°C) was coded as PE<sub>w</sub>. PE<sub>B</sub> referred to black LDPE film (opaque, thickness 0.010 mm, M.P. 126°C). PE<sub>Tr-HW</sub> stands for thick transparent film (0.05 mm thickness, M.P. 118°C) while PE<sub>Tr-LW</sub> was the code for transparent thin LDPE (thickness 0.015 mm, M.P. 120°C) film.

Samples were manually cut into ca. 20 × 5.0 cm strips, weighed and then buried vertically downward and covered with a layer of soil (about 7.5 cm). The weight of each specimen was tagged at the edge of the samples. The experimental soil bed was maintained and studied for a period of 22 months.

## Film Harvest

Samples were retrieved after exposure periods of 01, 03, 05, 07, 09, 11, 13, 15, 17, 19 and 22 months. After removal, the samples were placed on a tray and washed under slow running tap water before drying and equilibrating to reach a constant weight.

## Mechanical Testing

Tensile properties were studied by a computer-controlled constant rate of extension type (speed accuracy better than 0.2%) LRX Materials Testing Machine (Lloyd Instruments Ltd.) which meets the ASTM E4 accuracy (0.5%) in the measurement of force and less than 5 μm resolution in the measurement of extension. The data were analyzed in accordance with ASTM D882-91. The DAPMAT program calculated the best straight line by the least squares methods for the selected linear portion of the load-extension curve. It also calculated the area under the load-extension curve. The average values of tensile strength, strain percent and Young's modulus were calculated by the software from 3–5 observations for each sample. 50 mm × 5 mm polyethylene strips were used for these studies.

## FTIR Analysis

FTIR spectroscopy was used to study the chemical integrity of the test materials before and after soil burial. 21 × 10 mm film strips were used for analysis. The spectrum ranged from 600 to 4000 wave numbers (cm<sup>-1</sup>). The instrument used was a Shimadzu FTIR 8300 model.

## Dielectric Properties

KDK model KC-535B LCR meter was used to measure capacitance ( $C_x$ ) and loss tangent ( $\tan \delta$ ). Type SE-70 electrode (for solids) and type TO-19 thermostatic oven made by Ando Electric Co. Ltd. were used in this experiment. The dielectric properties were measured at the constant frequency of 1 kHz at an approximate heating rate of 4°C from 30°C to 130°C. 18 mm diameter polyethylene discs were cut with a punch-hole borer machine. The average thickness of the discs was measured with a screw gauge. The value of dielectric constant was calculated by the following equation:

$$\text{Dielectric constant } (\epsilon') = \frac{14.39}{D} \cdot C_x t_x$$

where  $C_x$  = electrostatic capacity (pF);  $t_x$  = thickness (cm);  $D$  = effective electrode diameter (cm) = 1.8 cm (for SE-70 electrode). Loss tangents were given directly by LCR meter.

## X-Ray Diffraction (XRD) Analysis

X-ray equatorial diffraction profiles were studied by a JEOL diffractometer (JDX-8P) using  $\text{Cu}_{K\alpha}$  radiation at the operating voltage and current of 30 kV and 20 mA, respectively, from 5 to 50° of the  $2\theta$  range at a scanning speed of 1°/min. Polyethylene films of 2.5 × 2.5 cm in size were used for XRD analysis.

## Scanning Electron Microscopy

Scanning electron microscopy (SEM) analysis was performed in the Department of Instrumentation Services, Jadavpur University, Kolkata, India. The surface morphology of the untreated and 17–22 months-treated samples were examined under a JEOL scanning electron microscope (Model JSM 5200).

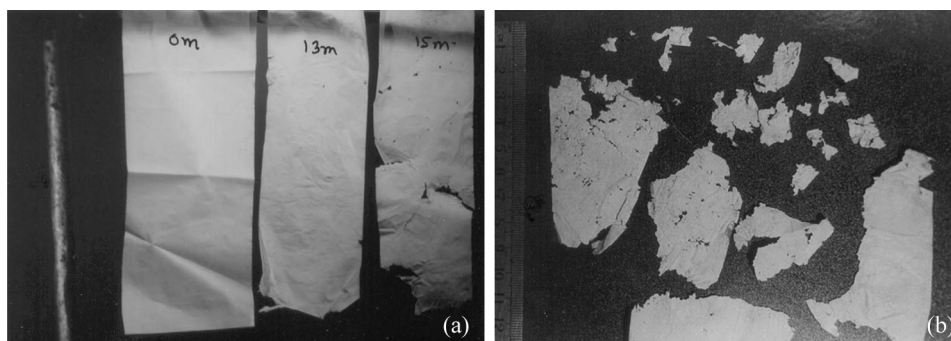
## RESULTS

### Soil Properties

The experimental soil was a silty loam having 19.92% sand, 22.58% silt and 57.5% clay. The pH of the soil was found to be 6.83. The moisture content of the soil in field capacity was 12.46%.

### Changes in Visual Appearance

The weight loss of the test samples after burial was not evident until 12 months of soil exposure. However, changes in physical characteristics were

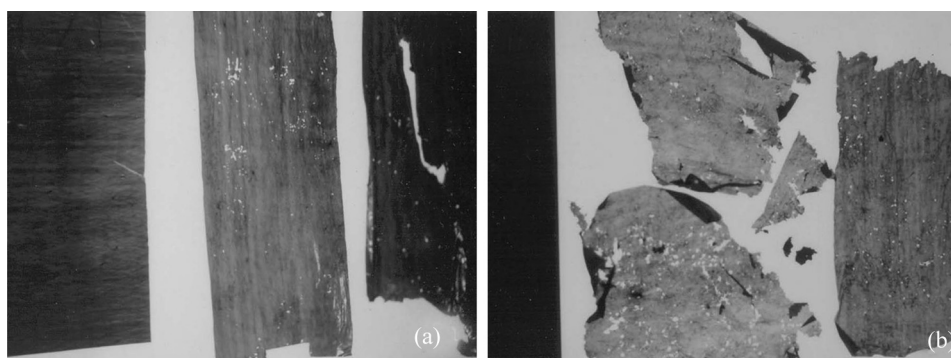


**Figure 1:** Photographs showing changes in physical characteristics of PE<sub>W</sub> during soil burial. (a) After 0, 13 and 15 months (from left to right) and (b) disintegration of sample after 22 months.

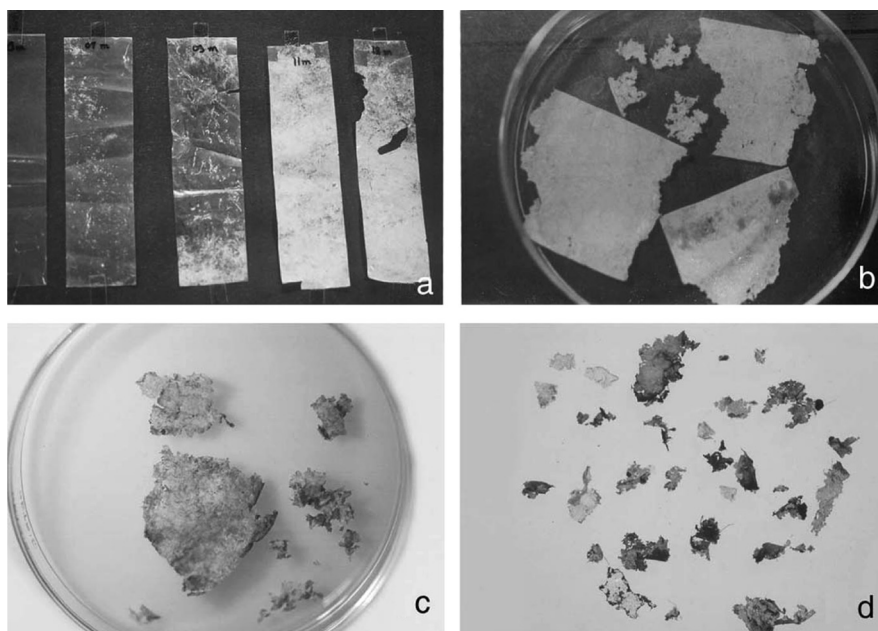
apparent at earlier exposure periods (Figures 1–4). The white and black opaque films lost their gloss; the surface became matted, and perforations of different sizes were developed on the film surface. The transparent films (PE<sub>Tr HW</sub> and PE<sub>Tr LW</sub>) lost their transparency, became totally opaque, papery and brittle, and finally disintegrated into pieces. White spots on the film appeared gradually, increased in number and finally covered the whole film of PE<sub>Tr HW</sub> within 11 months. Fragmentation of the film was noticed from 17 months onwards. Very tiny pieces of the sample were recovered after 22 months after screening through a sieve of 1 mm pore size.

## Mechanical Testing

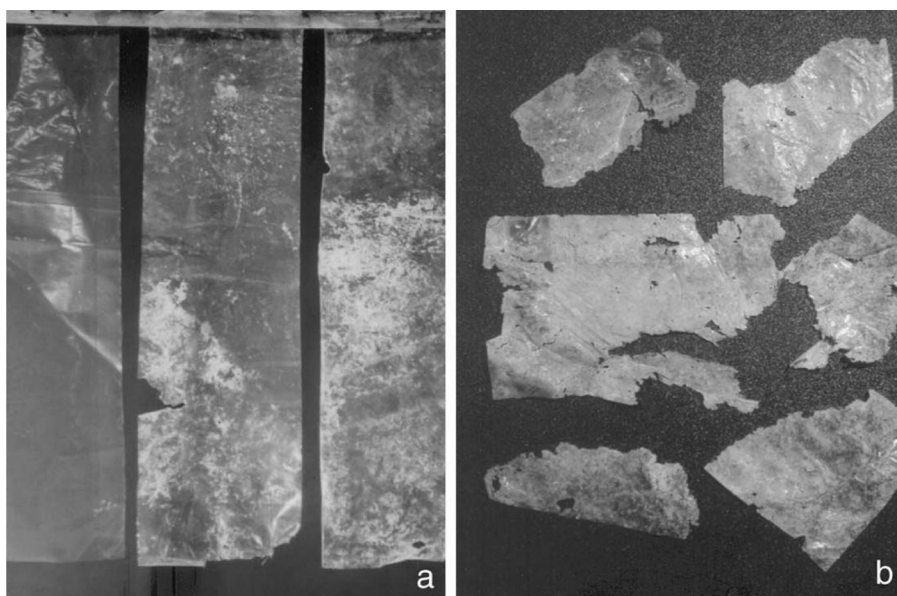
Load-extension curve, maximum stress, and strain at maximum load (%) were measured following ASTM specification D 882-91 by Lloyd Instruments LRX Materials Testing Machine.



**Figure 2:** Photographs showing visual appearance of PE<sub>B</sub> after (a) 0, 13, 15 (from left to right) and (b) 22 months.



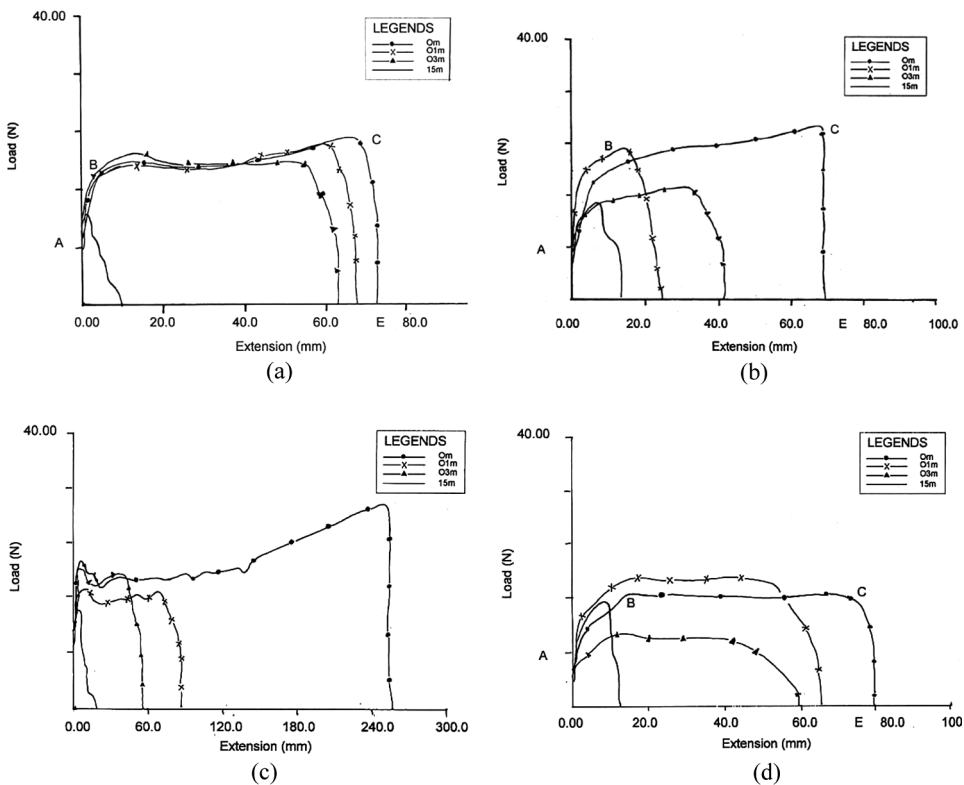
**Figure 3:** Photographs showing changes in the optical and physical characteristics of PE<sub>T<sub>r</sub>-H<sub>w</sub></sub> during soil burial. (a) films after 0, 07, 09, 11 and 13 months (from left to right). Disintegration of the film after (b) 17 months (c) 19 months and (d) 22 months of soil exposure.



**Figure 4:** Sequentially arranged photographs showing the degradation of PE<sub>T<sub>r</sub>-L<sub>w</sub></sub> after (a) 0, 11, 13 (from left to right) and (b) 22 months of soil burial.

It is seen from the load-extension curves of four samples (Figures 5a–5d) that break occurs earlier as soil burial time increases. In the case of PE<sub>W</sub> and PE<sub>Tr-HW</sub>, complete destruction of the elastic and plastic region was observed after 15 months. Samples gradually deteriorated by the reduction of elastic and plastic regions with the progress of exposure period. For PE<sub>B</sub> and PE<sub>Tr-LW</sub>, on the other hand, graphs after 15 months of soil burial showed almost a total destruction of elastic and plastic regions.

The stress-strain curve (data not shown) of polyethylene sample no. PE<sub>B</sub> attained minimal values after 17 months. For PE<sub>W</sub>, % strain at maximum load gained minimum values after 15 months of soil burial whereas maximum stress value plateaued near about 13 months. Sharp drop in the values of % strain at maximum load and maximum stress (N/mm<sup>2</sup>) for PE<sub>Tr-HW</sub> occurs within 3 months. Strain tends to zero by 15 months of soil burial. PE<sub>Tr-LW</sub> behaved in the same way as PE<sub>W</sub>, as minimum values are observed for both specimens after 15 months of soil burial.



**Figure 5:** (a) Load-extension curve of PE<sub>W</sub> after 0 (—●—), 01 (—×—), 03 (—▲—) and 15 (—) months of soil burial. (b) Load-extension curve of PE<sub>B</sub> after 0 (—●—), 01 (—×—), 03 (—▲—) and 15 (—) months of soil burial. (c) Load-extension curve of PE<sub>Tr-HW</sub> after 0 (—●—), 01 (—×—), 03 (—▲—) and 15 (—) months of soil burial. (d) Load-extension curve of LDPE PE<sub>Tr-LW</sub> after 0 (—●—), 01 (—×—), 03 (—▲—) and 15 (—) months of soil burial.



## FTIR Analysis

Compared to the control sample, all samples retrieved after 17 months of burial showed decrease of transmittance and also changes in the C-H deformation band and reduction of the absorption band due to CH<sub>2</sub> rocking vibration (Figures 6a–6d). The bands corresponding to carbonyl absorption were also suppressed. Albertsson et al. [6,7] postulated that carbonyl peak rose in polyethylene samples due to both abiotic and biotic degradation. With prolonged incubation time, the carbonyl index (ratio of absorption peak at 1715 and 1465 cm<sup>-1</sup>) decreased gradually. FTIR spectra after 17 months of soil burial showed major absorption of bands between 1400–1800 cm<sup>-1</sup>. This may reflect the latter stage of degradation.

## Dielectric Properties

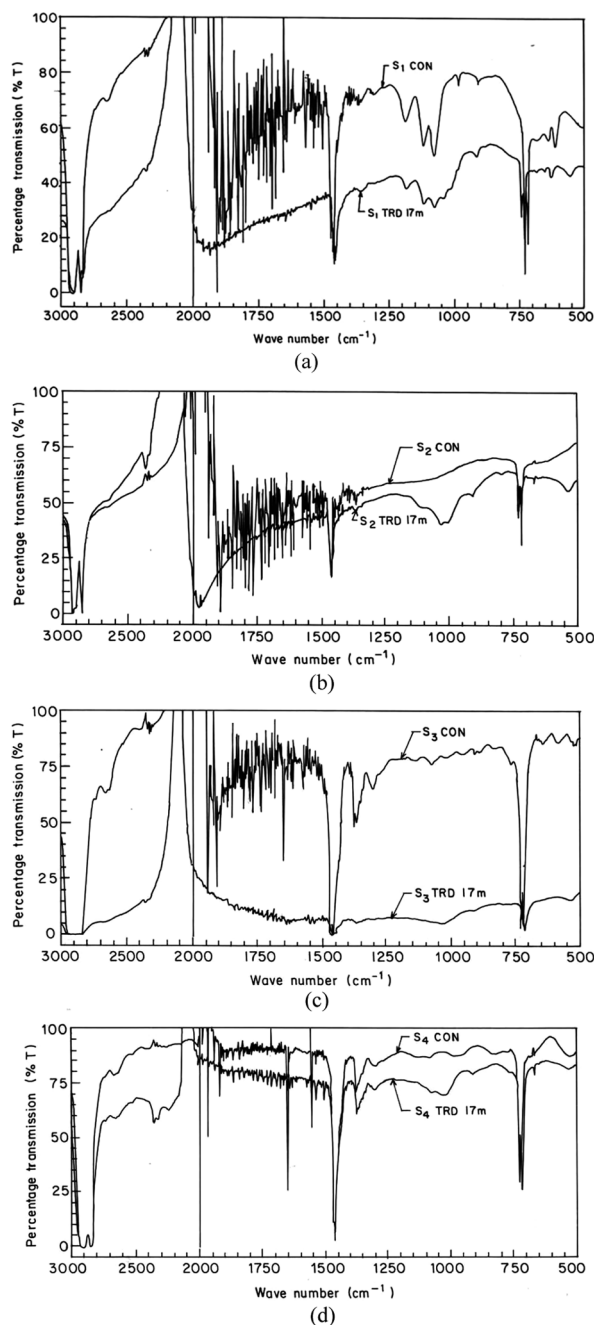
The temperature dependence of the dielectric loss of four individual samples are shown in the graph (Figures 7a–7d). In general, the temperature curve of tan  $\delta$  for nonpolar straight-chain polymers like polyethylene shows two maxima of the loss factor: the  $\alpha$  absorption due to motion of the CH<sub>2</sub> dipoles and the  $\gamma$ -absorption due to relaxation in crystalline regions in PE. Branching in LDPE gives rise to a third absorption region,  $\beta$  absorption, which lies between the  $\alpha$  and  $\gamma$ -absorptions in the tan  $\delta$  curves (Carlowitz [3]).

In Figure 7a, (i) corresponds to the thermal scan of the untreated, control PE<sub>W</sub> and (ii) to the same sample after 17 months of soil burial. It is seen that in the control specimen,  $\alpha_c$ -peak appears between 60–90°C. Upon treatment for 17 months, the loss peak intensifies but is not shifted. Another weak loss peak at 35°C appeared which is supposed to be  $\alpha_a$ - or  $\beta$ -peak. Loss tangents become approximately 100 times greater upon degradation. The  $\beta$ -transition peak for control PE<sub>B</sub> was found to be intensified after degradation (Figure 7b). Again, the loss factor increases 50 times after soil burial.

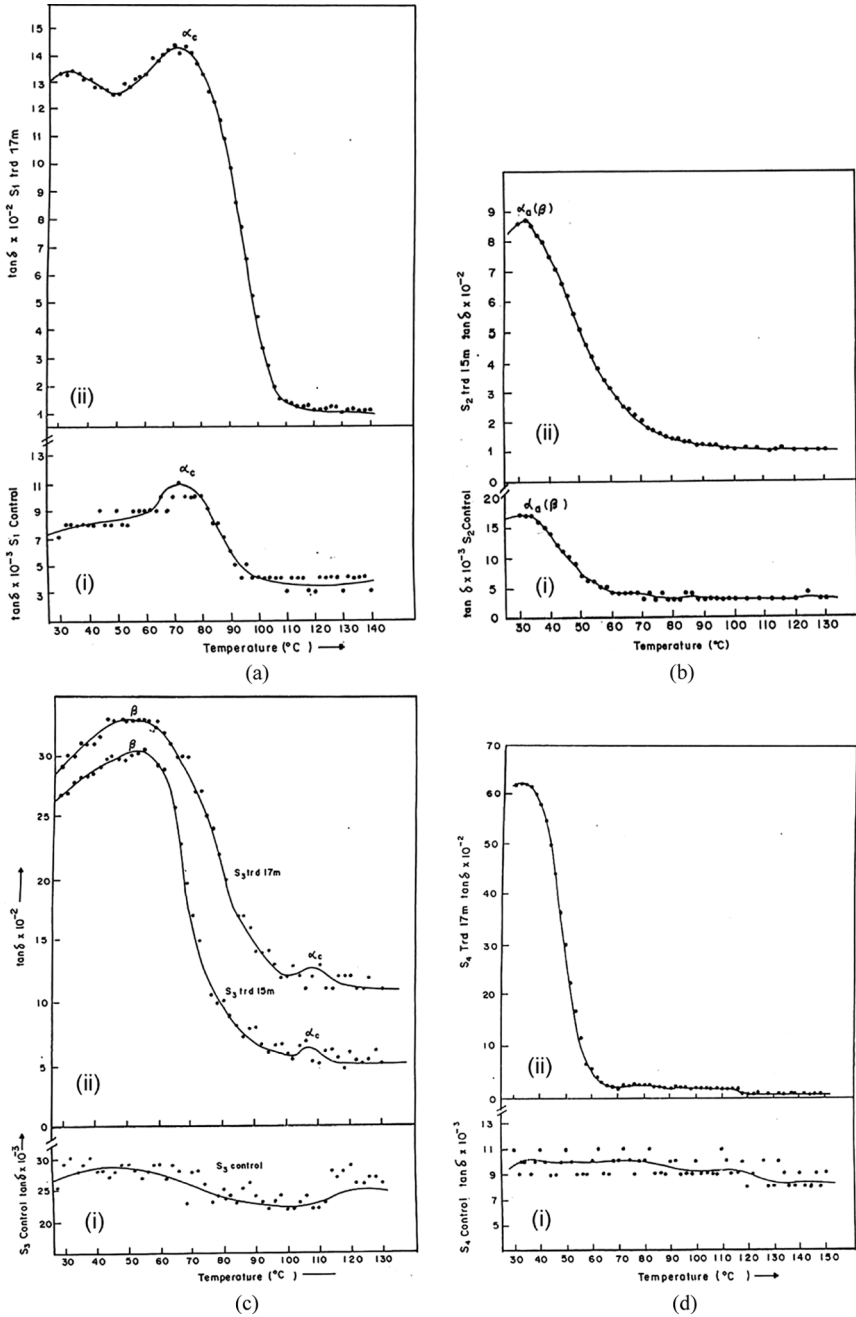
Dielectric relaxation spectra of untreated, thick, transparent LDPE film was found to be very weak (Figure 7c). Upon soil burial for 15 and 17 months the tan  $\delta$  curve at 1 kHz reveals two well-resolved peaks, one at a high temperature between 100–110°C and another broad peak near 40–60°C. As the time progressed, the  $\alpha_a$ -transition peak further intensified. In the case of PE<sub>Tr</sub> LW, the  $\alpha_a$ -transition peak appears and slightly shifts to lower temperature on degradation (Figure 7d).

## X-ray Diffraction (XRD) Analysis

XRD consists of monotonous background scattering due to an amorphous component and peak for crystalline region. Standard polyethylene shows a peak at 2 theta which is due to crystalline content. This peak suggests that there is only short-range ordering and the absence of other peaks establishes



**Figure 6:** (a) FTIR spectra of PE<sub>W</sub> before soil burial (S<sub>1</sub> CON) and after 17 months of soil exposure (S<sub>1</sub> TRD 17 m) and (b) PE<sub>B</sub> before soil burial (S<sub>2</sub> CON) and after 17 months of soil exposure (S<sub>2</sub> TRD 17 m). (c) FTIR spectra of PE<sub>Tr-HW</sub> before soil burial (S<sub>3</sub> CON) and after 11 months of soil exposure (S<sub>3</sub> TRD 17 m) and (d) PE<sub>Tr-LW</sub> before soil burial (S<sub>4</sub> CON) and after 17 months of soil exposure (S<sub>4</sub> TRD 17 m).

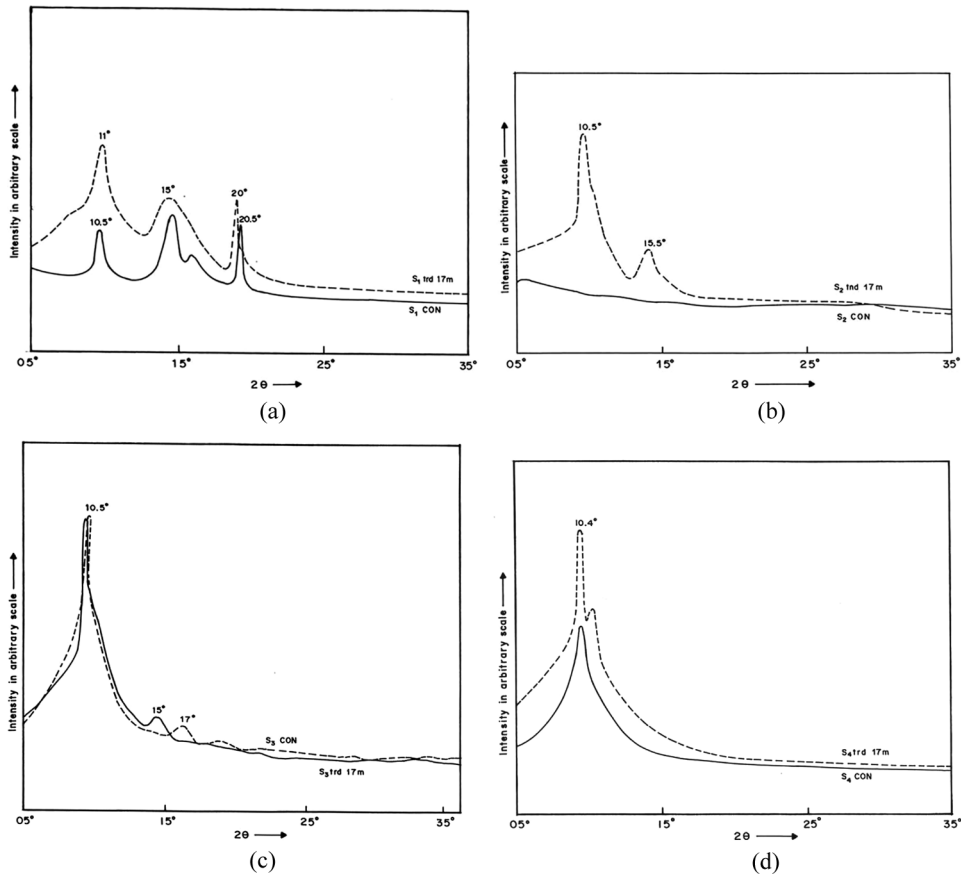


**Figure 7:** Graph showing  $\tan \delta$  versus temperature at 1 kHz for  $\text{PE}_W$  (a) and  $\text{PE}_B$  (b) before exposure (i) and after 17 and 15 months of soil burial (ii), respectively. (c) Graph showing  $\tan \delta$  versus temperature at 1 kHz for  $\text{PE}_{\text{TR-HW}}$  (c) and  $\text{PE}_{\text{TR-LW}}$  (d) before exposure (i) and after 15, 17 and 17 months of soil burial (ii), respectively.

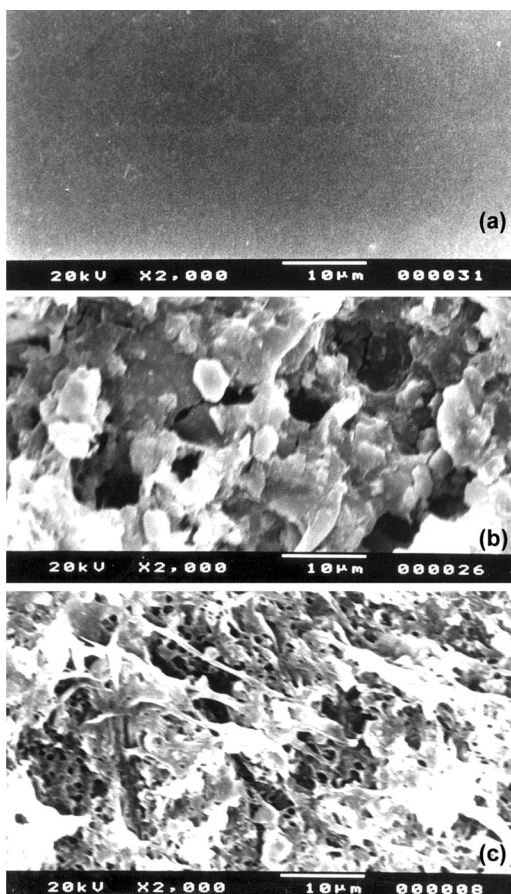
that there is no long-range ordering (Bunn [4]). Wide-angle diffraction patterns of all the control and treated specimens in Figures 8a–8d showed no change in the crystalline portion of the specimens. It may be inferred that the changes take place in the amorphous region. Confirmation is not possible by XRD. Percentage crystallinity was not affected.

## Scanning Electron Microscopy

SEM analysis of our selected samples revealed that, upon exposure in soil, surface erosion takes place and the matrix becomes intensively perforated. This ultimately results in a thinning of the matrix with inconsistent properties which corresponds to the deterioration of the mechanical properties of



**Figure 8:** Resolved equatorial X-ray diffraction pattern for PE<sub>W</sub> (a) before exposure (S<sub>1</sub> CON) and after 17 months of soil exposure (S<sub>1</sub> TRD 17 m) and PE<sub>B</sub> (b) before exposure (S<sub>2</sub> CON) and after 17 months of soil exposure (S<sub>2</sub> TRD 17 m). Resolved equatorial X-ray diffraction pattern for PE<sub>TR-HW</sub> (c) before exposure (S<sub>3</sub> CON) and after 17 months of soil exposure (S<sub>3</sub> TRD 17 m) and PE<sub>TR-LW</sub> (d) before exposure (S<sub>4</sub> CON) and after 17 months of soil exposure (S<sub>4</sub> TRD 17 m).



**Figure 9:** Electron micrographs showing morphological changes in  $PE_{Tr-HW}$  (a) smooth surface in control film (b) exfoliation after 17 months and (c) extensive perforation leading to fringe-like appearance after 22 months.

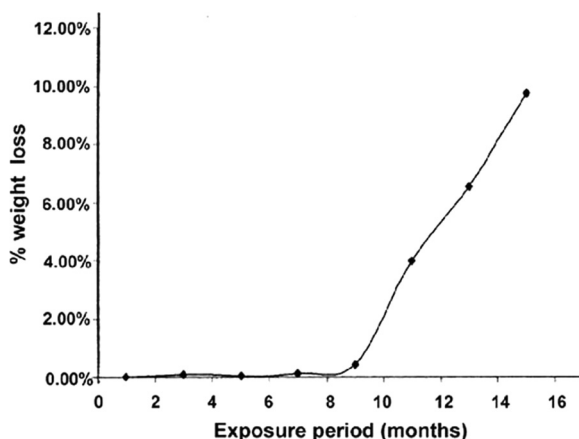
the material. Exfoliation was clearly demonstrated. This peeling off can happen only if there is a major erosion of the more accessible, amorphous regions in the polyethylene. Images taken after 22 months (Figures 9a–c) showed that polyethylene film's integrity was destroyed completely after microbial invasion, probably by the oxidative etching away of the more accessible regions. There is the possibility that bacterial peroxidase enzymes generated free radicals that could catalyze the oxidative attack on LDPE films.

## CONCLUSION

Goheen and Wool [5] conducted degradation experiments with starch-PE blends in soil for a period of over 8 months. The control film (100% LDPE)

was unchanged during the exposure period, whereas in our study partial opacity was noticed after 7 months and complete loss of transparency occurred within 11 months. Starch-blend LDPE films lost 4% of the mass in 8 months. Similar results were obtained for the PE<sub>TR-HW</sub> sample after 11 months of exposure. Average weight was not changed until 9 months and the average weight of the film decreased only afterwards (Figure 10). The load-extension curve for each sample reveals the progressive disappearance of the plastic region with the exposure period. The complete disappearance of the plastic portion occurs after 17 months of soil burial, and the specimens become highly brittle. In the absence of any external load, either mechanical or physico-chemical, the possibility of microbial invasion in the plastic region becomes higher. After 17 months of soil burial, all specimens had a tensile elongation of 5% or less; therefore, these are degraded to the brittle point according to ASTM D3826-91. FTIR spectra after 17 months of soil burial showed major absorption of bands between 1400–1800 cm<sup>-1</sup>. Albertsson et al. [6,7] postulated that carbonyl peak arised in polyethylene samples undergoing both abiotic and biotic degradation. With prolonged incubation time, the carbonyl index (ratio of absorption peak at 1715 and 1465 cm<sup>-1</sup>) decreased gradually.

Polyethylene, being an apolar polymer, does not possess polar groups. This is the reason why dielectric relaxations in untreated control films were not observed. Apolar polymers like polyethylene exhibit dielectric spectra as a result of polar groups formed by oxidation (Hedvig [8]). It is evident from our experiment that, upon soil burial, LDPE films oxidized and thus good dielectric spectra with intense  $\alpha$  or  $\beta$  transition peak appeared after 15 months of exposure. In many cases, the transition peak shifted to lower temperatures, as expected, during the degradation process. On the other hand, as exposure time



**Figure 10:** Graph showing average weight loss of PE<sub>TR-HW</sub> during soil burial.

progressed, transition peaks did intensify showing invasion of the respective regions of the sample.

All the results obtained throughout the study present a revealing picture on the fate of low-density polyethylene films undergoing environmental degradation in soil.

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