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Structure and mechanical property variation of low density and high density polyethylene films on soil burial

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ABSTRACT

Most of the packaging applications need easy and cheap availability of material, inertness towards outside factors like heat, chemicals, radiation and microorganisms. Polyolefins are the right choice and have attracted much attention of environmentalists in recent years mainly due to their extensive use in the packaging industry. Even though several methods are adopted to reduce the usage and recycle the used material the final fate of these materials is to get incinerated or dumped in land or sea. With the view to understand the structural changes that are taking place during soil burial or composting of polyolefin films, in the present investigation, both low density and high density polyethylene films were buried in clay soil, typical for Virudhunagar, Tamil Nadu State, India. The samples were retrieved at different intervals of time and were analyzed for the structural variation using FTIR and the mechanical property loss was followed by studying the tensile properties using an Universal Testing machine. The results clearly indicate that after an induction period of 200 days, both LDPE and HDPE film samples show the formation of carbonyl groups and then the amount of carbonyl group gradually increases. The elongation at break value decreases at a much faster rate for LDPE when compared to HDPE.

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KEYWORDS

Polyethylene;
Composting;
Oxidation products;
Carbonyl Index;
Tensile property.

INTRODUCTION

Polymers have been replacing papers, metals, glasses and ceramics in packaging, transportation, construction, electrical and electronic equipments, appliances, furniture, pipes and heavy industrial equipments^[1]. In a nutshell, from agriculture to transport and from aerospace to food packaging, the use of plastics has be-

come an integral part of our daily living.

Polyethylene is ideally suited for film application because of its toughness, puncture resistance and clarity which are important properties for most of the final forms of film products. Low density polyethylene (LDPE) films dominate the applications needing clarity and flexibility. The typical low density polyethylene film products include food packaging, retail grocery bags,

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garment bags, heavy duty shopping sacs, industrial liners and shrink and stretch shopping wraps.

High density polyethylene (HDPE) film is chosen for products requiring high strength, stiffness and low permeability. Merchandise bags, grocery bags and multi wall sack liners are typical products using HDPE films. It should be noted from the proceeding that some product applications can use either LDPE or HDPE. Polyethylene contributes nearly 70 weight % of commodity plastic waste^[2-4].

Plastic film packaging and carrier bags are fairly resistance to degradation, are often brightly coloured and have a high surface-to-volume ratio. This has led to such a widespread visual pollution problem. Governments of different countries are exploring various ways of solving this problem^[5]. Increasing film thickness to encourage reuse and recycling is one strategy being considered^[6]. Despite these efforts, it is anticipated that the littering problem will continue for some time to come.

The huge volume of plastic products used by consumers and industry become part of the municipal solid waste and has raised concern among environmentalist about disposal^[7]. Environmentalists are concerned that the chemical inertness and stability of thermoplastic resins may contribute to solid wastes disposal problems because the conventional polymers do not degrade naturally within a reasonable period of time.

Waste plastics are mainly composed of polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET)^[8-10]. The presence of halogenated polymers places particular challenges upon disposal. This variability creates a challenge in recovering value from plastics waste. So also is the need to depolymerize plastics in order to make new products, as depolymerizing the polymers to the monomers is difficult and expensive and recovery of monomers from mixed polymers is impractical.

Waste management has a number of different concepts, which vary in their usage between countries or regions. The waste hierarchy classifies waste management strategies according to their desirability. The term 3 R's or "Reduce – Reuse - Recycle" has also been used for the same purpose. The waste hierarchy has taken many forms over the past decade, but the basic

concept has remained the corner stone of the most waste minimization strategies. Some waste management experts have recently incorporated a "Fourth R": "Re-think", with the implied meaning that the present system may have fundamental flaws and that a thoroughly effective system of waste management may need an entirely new way of looking at waste. The aim of the waste hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste. Incineration and disposal are the lost choices preferred in effective waste management. The utilization of waste polymers by incineration has ecological limitations^[11].

Waste disposal can be either in ocean or in earth. Although Ocean dumping is not a preferred route in terms of severe water pollution, around 25000 metric tones of waste materials are being dumped into the ocean. Open dumping and land filling are the two major routes of waste disposal in earth.

Open dumping of waste materials causes severe air, water and land pollution. Disposing of waste in a landfill is the most traditional method of waste disposal and it remains a common practice in most countries. A well systematic landfill can be hygienic and relatively inexpensive method of disposing of waste materials. Nature and type of the soil at the site along with the geographical location of landfill play a significant role in waste management method.

When a polymeric material is subjected to harsh and aggressive environments, many agents can initiate or develop physical or chemical processes that change the material properties. In general the degradation rate of plastics seem to be a function of the prevailing weathering conditions including sunlight, temperature, rain, humidity, pollutants, thermal cycles and oxygen content^[12]. Taking these factors into consideration, in the present investigation both LDPE and HDPE films were buried in the clay soil located in Virudhunagar (Tamil Nadu State, India) area. Samples were retrieved at various time intervals and the properties were investigated. The results are presented and discussed.

EXPERIMENTAL

Materials

The low density polyethylene (Grade: 24FS040 – Indian Petrochemicals Corporation Limited, India) and

high density polyethylene (Grade: F46003 - Reliance Industries Limited, India) were used in the present investigation. The materials were blown into films using standard extrusion technique. The thicknesses of the materials were 40 and 89 microns for LDPE and HDPE respectively. The materials were cut into 18 cm (Length) x 4 cm (Breadth) dimensions and were used for further investigations.

Location of composting

The location selected for composting of packaging films was Kamaraj College of Engineering and Technology premises which is situated at S. P. G. C. Nagar, K. Vellakulam Post - 625 701, India, by the National Highway - 7 which connects Kanyakumari and Varanasi. The location is 8 Km North of Virudhunagar and 36 Km South of Madurai in the state of Tamil Nadu, India. Virudhunagar is located at the latitude of $9^{\circ}36'$ and longitude of $77^{\circ}57'$ E.

Dimension of composting pit

The top view of the composting pit and its dimensions is shown in Figure 1.

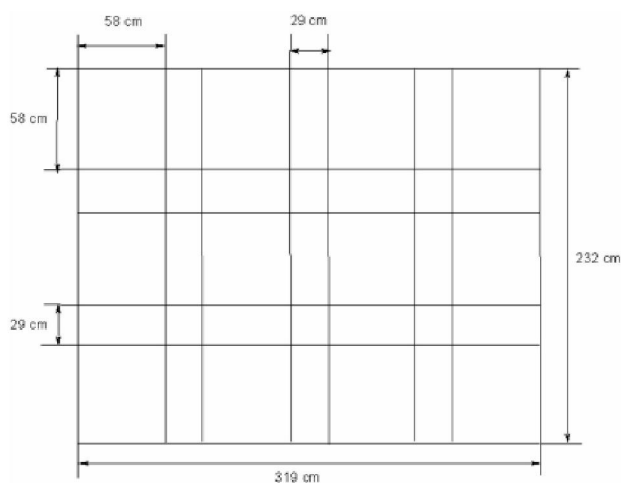


Figure 1 : Dimensions of the composting pit in centimeters

The overall dimension of the pit used for composting the film samples was 319 (length) x 232 (breadth) x 58 (depth) cm. The pit was divided into 12 equal parts having 4 columns and 3 rows (Figure 1), each having the dimension of 58 (length) x 58 (breadth) cm.

Soil analysis

The nature of the soil in which the samples were buried was found to be black soil. A complete identification of the type and property of the soil was done at

the Mobile Soil Testing Centre, Tamil Nadu State Agricultural Department, Aruppukottai - 626 101, Tamil Nadu State, India. The character of the soil and its variation with respect to the depth of the soil is presented in TABLE 1.

TABLE 1 : Properties of Black Soil Found at the Location of Composting

Depth (cm)	Character
0-14	Very dark brown, clay - strong coarse angular blocky dry very hard sticky, moist firm, plastic, slow permeability, abrupt smooth boundary.
14-33	Very dark brown, clay - strong coarse sub angular blocky to medium sub angular, very slow permeability.
33-63	Very dark grey, clay - moderate sub angular, very sticky, plastic, very slow permeability.

The salt content of the soil was also estimated and is found to be 0.3 - 0.6 % desicesim/m (ds/m) and the pH of the clay soil found at the composting location is 8.0 - 8.1. The nutrients (organic compounds, nitrogen, phosphorus and potassium) in the soil were tested layer by layer and are given in TABLE 2.

TABLE 2 : The nutrients present in the clay soil at the composting location

Nutrients in soil	Top Layer	Middle Layer	Bottom Layer
Organic compounds (%)	0.17	0.20	0.23
Nitrogen	62.0	64.0	67.0
Phosphorous	4.0	4.0	4.0
Potassium	172.0	176.0	88.0

Period of composting

The materials chosen were composted from July 2004 to July 2005. The samples were allowed to compost for 73, 128 and 201 days in pits 1 and 2, pits 3 and 4 and pits 5 and 6 respectively. In pits 7 and 8, the samples were allowed to compost for 266 days and in pits 9 and 10 the film samples were buried for 306 and 309 days respectively. The samples were allowed to compost for 365 days in pits 11 and 12. The samples were retrieved very carefully from the pits after the speci-

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fied days and were analyzed.

FT IR studies

SHIMADZU 8400S FT IR spectrophotometer was used in this present investigation to record the FT IR spectrum of all the film samples. The required dimension of the composted sample was cut and the film was scanned in the frequency region from 4000 to 400 cm^{-1} . The maximum absorbance at 1715 cm^{-1} is attributed to carbonyl group.

Tensile property measurement

Elongation at break (%) for the composted samples was determined in a HOUNSFIELD Material Testing Machine (S-Series, H5K-S) having a special grip designed for holding thin film samples. It was operated at a speed of 150 mm/min with a grip distance of 40mm for the film samples.

RESULTS AND DISCUSSION

Weather report

Environmental parameters like temperature, pressure and humidity were measured from July 2004 to July 2005 (13 months), the period at which the LDPE and HDPE samples were buried in clay soil and retrieved periodically. The data were recorded daily and the average values of each parameter for the particular month were calculated and are graphically presented in Figures 2(a), (b) and (c). The total rain fall data for the 13 months (July 2004 to July 2005) were also recorded and are presented in Figure 2(d).

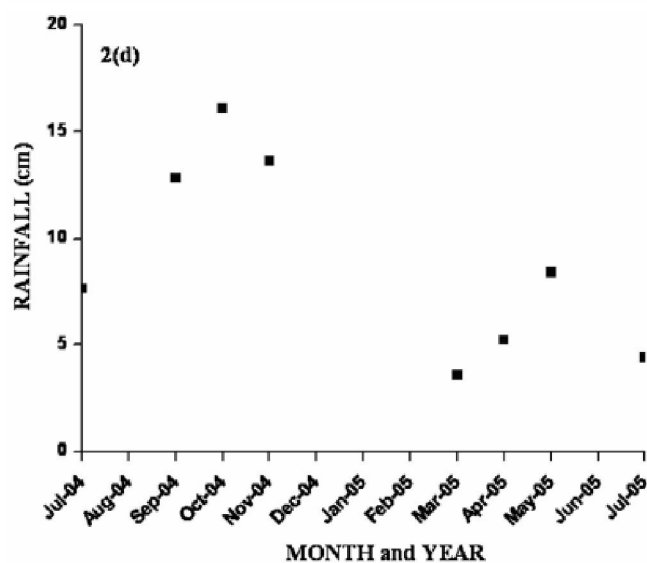
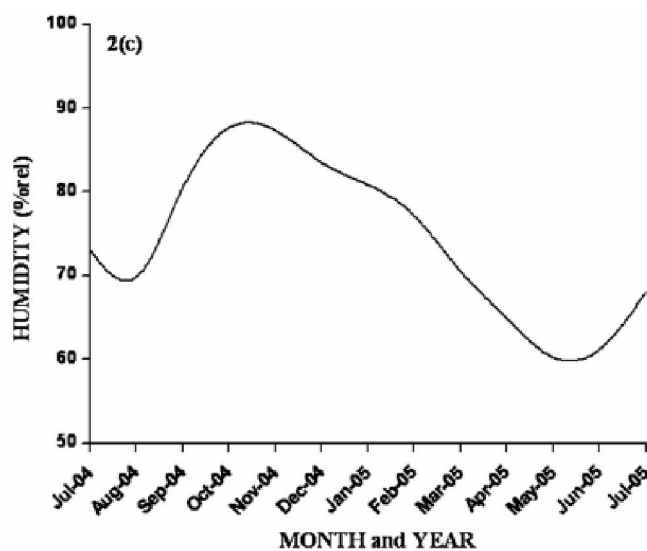
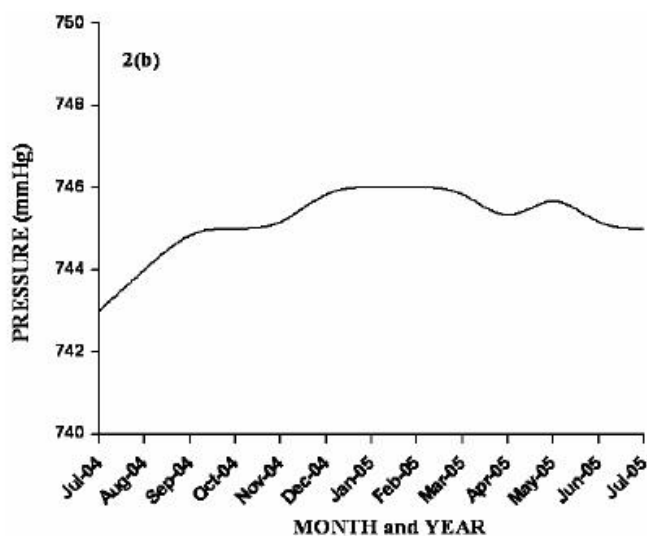
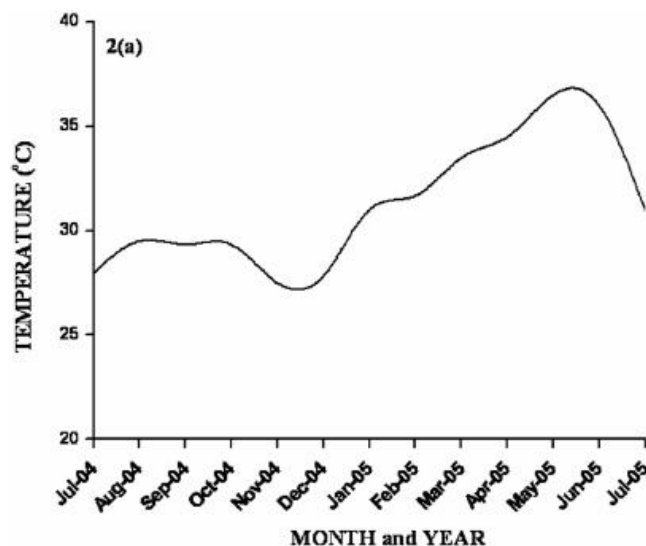


Figure 2 : Weather parameters measured during the period July 2004 – July 2005: (a) Temperature (°C), (b) Pressure (mm Hg), (c) Humidity (% rel) and (d) Rainfall (cm)

From Figure 2(a), it is explicit that Virudhunagar region had the minimum mid day temperature of 27°C from November 2004 to December 2004 and had maximum mid day temperature of about 37°C during the month of May 2005 and June 2005. The pressure (Figure 2 (b)) was fluctuating between 743 mmHg and 746 mmHg. Maximum humidity was about 89 (%rel) in the month of October 2004 and the minimum humidity was 59 (%rel) in the month of May 2005 (Figure 2(c)). Virudhunagar received the bulk of the rainfall (Figure 2(d)) during North East monsoon in the months of September, October and November 2004 (about 16 cm). A reasonable quantity of rain was noted during the South West monsoon (4.4 cm) in the months of May, June and July 2005.

FT IR studies

Fourier Transform Infra Red Spectroscopy is a powerful tool to study the structure of organic compounds. This technique affords a simple, sensitive and nondestructive means of detecting degradation. It is used to identify and follow the quantitative loss or growth of a particular functional group. The growth of carbonyl and hydroxyl region has been successfully followed by FT-IR spectroscopy^[13-15]. The evolution of carbonyl is a well known method to follow thermal oxidation and photo oxidation in many polymers^[16-18]. The FT IR spectra are taken for all soil buried (composted) samples after being retrieved from the pit. The results for LDPE and HDPE are presented in Figures 3 and 4 respectively.

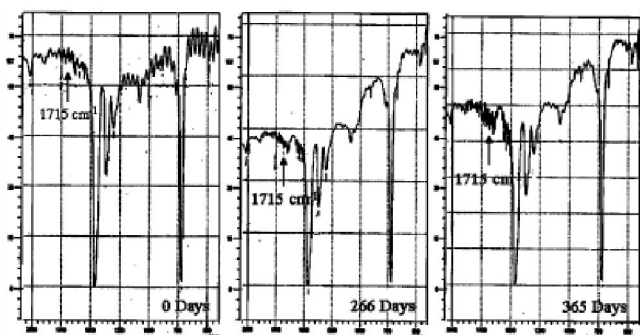


Figure 3 : Comparison of different FTIR spectra of commercial LDPE sample with varying days of composting. (a) 0 days, (b) 266 days, (c) 365 days

The composting of LDPE and HDPE films leads to the production of several oxidation products, most of these are truly characterized by FT IR. The FT IR spectra recorded were very similar in their shape

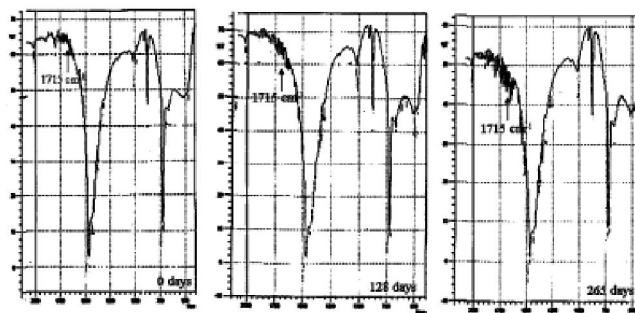


Figure 4 : Comparison of different FTIR spectra of commercial LDPE sample with varying days of composting. (a) 0 days, (b) 128 days, (c) 365 days

whatever the duration of soil burial is. All the samples exhibited carbonyl formation on soil burial environment. The infrared spectra of composted LDPE and HDPE samples showed several structural changes as evidenced by the appearance of a group of sharp peaks in the region 1600 – 1800 cm⁻¹. The peaks were assigned to groups like carboxylic acid (1700 cm⁻¹), ketones (1714 cm⁻¹), aldehydes and esters (1733 cm⁻¹), peresters, peracids and γ - lactones (1780 cm⁻¹)^[19-21].

Carbonyl index measurement

Carbonyl index was defined as the ratio of the intensities of the >C=O band at 1715 cm⁻¹ to the C-H rocking band at 729 cm⁻¹ for polyethylene. The C-H rocking band remains unchanged during the oxidation process while the >C=O peak increased with the extent of composting time^[6].

$$\text{Carbonyl Index} = \frac{\text{Absorbance at } 1715 \text{ cm}^{-1} \text{ (carbonyl peak)}}{\text{Absorbance at } 729 \text{ cm}^{-1} \text{ (C - H rocking band)}}$$

The carbonyl index parameters were calculated for LDPE and HDPE samples (TABLE 3). The calculated TABLE 3 : The variation of elongation at break and carbonyl index values for LDPE and HDPE

Exposure time (DAYS)	LDPE		HDPE	
	Elongation @ Break (mm)	Carbonyl Index	Elongation @ Break (mm)	Carbonyl Index
0	260	0.06	125	0.03
73	242	0.05	64	0.03
128	231	0.06	104	0.03
201	213	0.06	107	0.03
266	198	0.05	68	0.05
306	190	0.06	58	0.05
365	150	0.09	100	0.09

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carbonyl index values for LDPE and HDPE films are plotted against the duration of soil burial and are presented in Figures 5 (a) and (b) respectively. From the figures it is explicit that the carbonyl group formation requires an induction period of 200 days. After that there is a gradual increase in the carbonyl index value. This similar effect of induction period followed by rapid degradation was being observed by many authors^[22-25]. This fact indicates that after 200 days, the films buried in the soil starts to get oxidized.

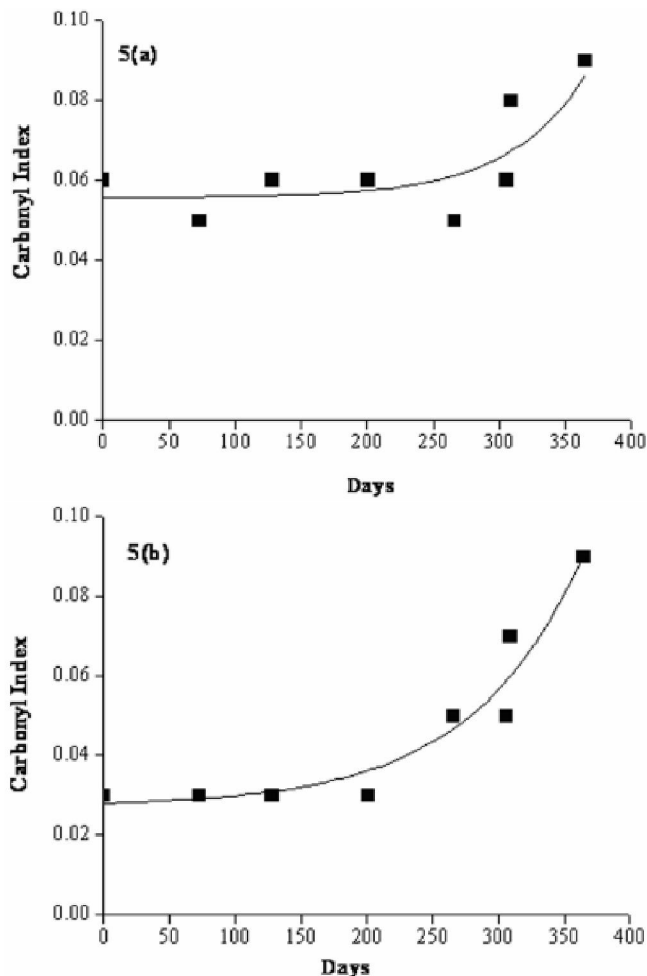


Figure 5 : Carbonyl index value of polyethylene samples versus duration (days) of soil burial. (a) LDPE, (b) HDPE

Soil burial of LDPE and HDPE films has a very complex process of degradation of special practical interest. When a polymer is subjected to harsh and aggressive environments, many agents can initiate or develop physical and/or chemical processes that change the material properties. At least four types of degradation are implied due to the simultaneous action of oxygen, heat, mechanical stress and moisture. Most forms

of environmental attack begin at the polymer surface. An oxidized surface having a high oxygen concentration thus appears; it is brittle, and surface crazing is evident, showing the morphological changes. Sometimes it is obviously colored, leading to aesthetic failure. Then the degradation process advances inside by a diffusion-controlled mechanism. As the duration of soil burial increases after induction period, it shows a sudden change in all macroscopic properties. The general degradation mechanisms of polyolefins are shown in Figure 6.

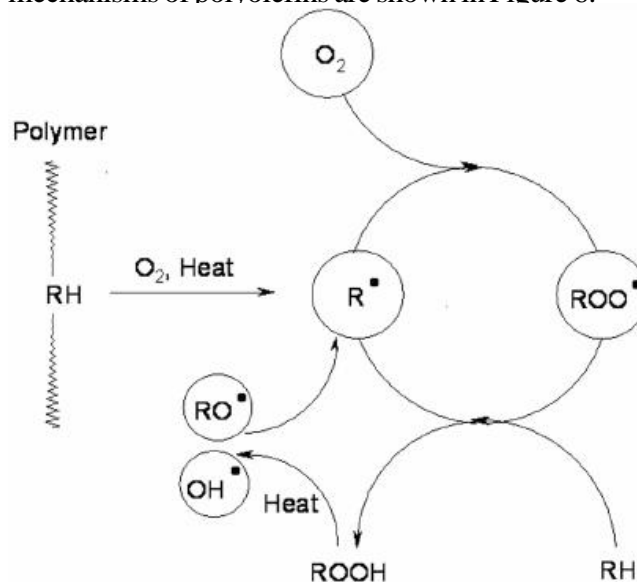


Figure 6 : General degradation mechanism of polyolefins

The mechanisms of oxidative degradation of polymers have been extensively studied and reviewed^[26-30]. It is generally accepted that the key intermediates are hydroperoxide, which are always present because of oxidation during preparation or processing and decompose under the influence of heat, light or transition metal catalysis to produce free radicals. Once radicals are produced they enter into a chain reaction with oxygen and C-H bonds in the polymer, to produce a range of oxidation products. Although the primary products are hydroperoxides, their decomposition yields alkoxy radicals which are responsible for many secondary products. Elimination of alkoxy radicals competes with H abstraction, and leads to chain scission and formation of a variety of carbonyl products^[13].

In the present investigation the two natural parameters like temperature and the rainfall may have a drastic influence on the degradation of the polyolefin film samples. As already stated, the average temperature increases from 27 to 37°C and similarly enough rainfall

is noted during the summer season. Owing to the heavy dampness in the clayey soil during the rainy season, and the gradual increase in the temperature, the samples undergo both aerobic anaerobic degradation and may also be influenced by microbial attack.

Measurement of tensile properties

Measurement of the mechanical properties of a degraded polymer is a rapid way to determine the degree of degradation. Although this provides little basic information about the ageing process, it is important for practical purposes and is routinely used as a part of an ageing study. The ultimate tensile elongation is more sensitive to degradation than is the ultimate strength. Tensile properties of composted LDPE and HDPE were measured and have been compared with the virgin commercial LDPE and HDPE films (TABLE 3). The results for LDPE and HDPE are graphically represented in Figures 7(a) and (b) respectively.

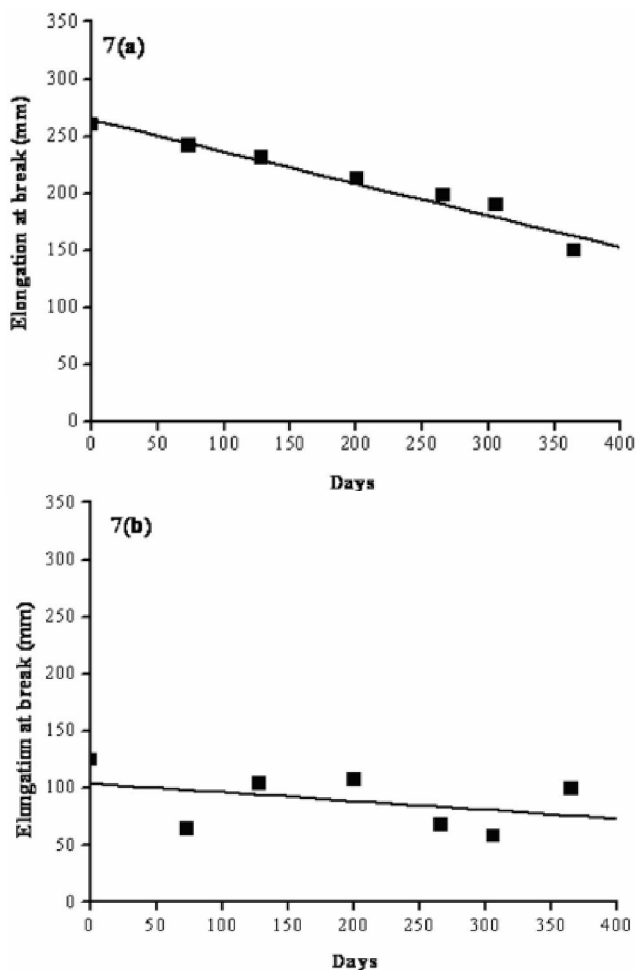


Figure 7 : Variation of elongation at break versus duration (days) of soil burial. (a) LDPE, (b) HDPE

The elongation at break value progressively decreases as the composting period increases. Even though the formation of carbonyl groups needs an induction period, the mechanical property which is focused in the present investigation does not show such behaviour. Further the LDPE samples show much strong mechanical loss, when compared to HDPE. The molecular architecture and other structural parameters also decide the variation of the mechanical properties with respect to increase in composting time. The presence of branching and the probability of easy attack of reagents owing to the amorphous nature may play a role in the loss of mechanical properties in LDPE during composting.

CONCLUSION

The LDPE and HDPE films undergo significant changes in their chemical structure when buried in clay soil, typical for Virudhunagar, Tamil Nadu State, India. Considerable quantities of oxidation products, mainly carbonyl group incorporation and deterioration of mechanical properties are noted. The introduction of carbonyl moiety in both LDPE and HDPE needs an induction period of at least 200 days when these materials are composted in a clay soil. The loss in tensile property (elongation at break) of the samples is progressive for both LDPE and HDPE samples. Commercial LDPE samples deteriorate faster than HDPE samples and can be explained on the basis of their molecular architecture. Further the amount of rainfall and the external temperature may also play a favorable role for the degradation of LDPE and HDPE films. Although composting of LDPE and HDPE were followed for a short period (13 months), the present investigation gives an idea about the initial changes that are occurring in these materials during composting.

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