Comparative Degradation of LDPE, HDPE and HMHDPE under Different Soil Conditions

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Abstract: The Present work includes, degradation of polyethylene under different environmental conditions to know the effect of physical, chemical and biological factors prevailing in those conditions on degradation of polyethylene. Plastic films viz., Low density polyethylene (LDPE), High density polyethylene (HDPE) and High molecular weight high density polyethylene (HMHDPE) each were incubated in three different conditions viz., black soil, sandy soil and red soil for a period of 3 months. The changes in the properties of plastic films after incubation was studied by change in the weight of the plastic film and mechanical parameters like tensile strength, breaking load and percentage of elongation. Among all the plastic films HDPE was found to be highly susceptible with 33% weight loss and 40% reduction in percentage of elongation compared to LDPE with 26% weight loss and 34 % reduction in percentage of elongation in black soil. Whereas HMHDPE found to be highly resistant in all the soils with no significant weight loss and percentage of elongation (15%). None of the plastic films had shown degradation in sandy soil even after incubation for 3 months. FTIR spectroscopy results showed that HDPE film incubated in black soil had undergone extensive degradation when compared with un incubated HDPE film.

Keywords: Polyethylene, Environment, Polymer, Black soil, Degradation.

INTRODUCTION

Polyethylene plastic films, which are used as carry bags are the most widely and commonly used plastics. The widespread use of these carry bags led to increase in environmental pollution, because of disposal problems and also due to its non-degradable nature [1]. This resistant nature of plastics comes from its properties and structure [2]. These plastics replaced paper bags because of their properties like resistance to high temperature, durability, resistance to water and microorganisms [3]. Mainly because of their durability, these plastics can be seen in litter and causing more environmental pollution than any other material [4]. For a plastic bag to get degraded in the environment, it takes around 100 years. In 1990's the consumption of plastics was over 107 million tonnes and was estimated to increase up to 300 million tonnes by 2020 [5]. Plastics are too large to handle by microorganisms present in nature and thus they have to be degraded into monomers, later can be consumed by them. Various chemical, physical and biological forces like prooxidants, photo degradation and action of certain fungi can cause degradation of polymer into monomeric constituents [6]. The physical and chemical forces breakdown the polymer surfaces and expose the chemical constituents of polymer to react with biochemical agents, an important step in degradation of plastics [7].

Naturally, microorganisms like fungi present in soils can initiate degradation of plastics by secreting a specific enzyme and H_2O_2. These two can act together and cause degradation of plastics slowly [8, 9]. In addition to these, certain exudates secreted by microorganisms can create an environment, which makes the polymers chemically unstable. For example sulphuric acid produced by sulphur reducing bacteria like *Desulfovibrio vulgaris* [10], organic acids produced by fermentative fungi with the utilization of plant materials [11, 12]. These acids or bases produced can create an unstable environment for the plastics present in the vicinity and further, improves the rate of degradation of plastic.

Commercial plastics like polyethylene, polyolefin, and polystyrenes are very much resistant to microbial attack and thus has to be degraded abiotically into low molecular mass fragments that can be consumed by microorganisms [13]. Thus, abiotic degradation of plastic mustprecede before biodegradation that produce carboxylic acids, carbonyl groups, alcohols and other derivatives, which can be utilized as nutrients by microorganisms [14]. Previously, it was showed that polyethylene of molecular weight below 500 Daltons was utilized by microorganisms as a carbon source [15]. In another study, polyethylene pretreated by UV irradiation showed maximum biodegradation [16].

Abiotic degradation, initially brings down the molecularweight of polyethylene to the point, where microorganisms can utilise the polymer [17]. The

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degradation of plastics begins with photo oxidation *via* sunlight by oxidising the polymer [18]. In a previous study, air pollutants such as ozone, nitric oxides and sulphuric oxides were found to promote abiotic oxidation of polyethylene [19]. These clearly states that different synthetic polymers will undergo degradation by different mechanisms. Further, the rate of degradation also depends on surrounding environmental conditions. In a study, optimum temperature required for abiotic degradation of poly lactic acid was found to be 55-60 °C [20].

In the present study are investigated the degradation of polyethylene samples under different soil conditions. The changes in weight, mechanical properties were studied to quantify the extent of degradation in different soils. Structural changes in polyethylene samples were determined by using FTIR.

MATERIALS

Plastic Samples

All the polyethylene films (LDPE, HDPE and HMHDPE) used in this study were purchased from Shalimar packs Pvt Ltd, Tenali, (India). The densities of LDPE, HDPE and HMHDPE were 0.925, 0.952 and 0.978 g/cm^3 respectively. The chemicals used in the study were obtained from Merck.

On Field Degradation of Polyethylene Films

Polyethylene films used in the study were cut into strips (ca. 10cm x 10cm), preweighed and are placed in three different soils (red soil, sandy soil and black soil) at a depth of 10 cm from the ground level for a maximum period of 3 months. Further, the films were recovered at regular time intervals (15 days, 30 days, 45 days, 60 days and 90 days) and extent of degradation was determined.

Film Harvest

The recovered plastic filmswere washed in distilled water to remove debris, dried at 45°C and equilibrated, and the weights are determined. Each of the films recovered from three different soils at different time intervals are compared with the corresponding untreated polyethylene film (control).

Determination of Weight Loss

Change in weight of plastic films, before and after incubation in soilswas measured by using electronic balance, type AX200, shimadzu corporation, Japan. The percentage weight loss of the incubated plastic samples is given by the following equation 1.

$$\text{Weight loss (wt.\%)} = \frac{\text{(Final weight - Intial weight)}}{\text{Intial weight}} \times 100 \quad (1)$$

Mechanical Tests

The mechanical properties of samples used in the study were examined using universal testing machine, shimadzu, AGS 10KN model. All the films were tested at 25^{o}C with crosshead speed of 10mm/min and gauge length 5cm. All the plastic films recovered from three different soils at different intervals of time were tested and average values of the breaking load, tensile strength and % of elongation were determined.

FTIR Analysis

The FTIR (Fourier Transform Infrared Spectroscopy) analysis was conducted for unincubated and Incubated HDPE plastic samples. Plastic films of 10 x 10 cm size were analysed following incubation in soils by using FTIR, spectrum 400 IR system, PerkinElmer, USA. The entire spectral range between 400 to 4000 cm^{-1} was scanned with a resolution of 2 cm^{-1}. Two types of HDPE plastic films were analysed: (I) Unincubated HDPE (Control), (II) HDPE incubated in black soil.

RESULTS

Degradation of Polyethylene Under Different Soil Conditions

Polyethylene films (LDPE, HDPE and HMHDPE) incubated under different soil conditions were recovered at different time intervals (15 days, 30 days, 45 days, 60 days and 90 days) and change in the weights were determined (Tables **1**, **2**, **3**). All the three films initially found to increase in weight during incubation in all the three soil types. More degradation was achieved in black soil compared to other two soils. All the three films did not exhibited any weight loss in sandy soil even after 3 months. HDPE found to be undergone more degradation (33% weight loss) compared to LDPE (26%), whereas HM HDPE had not shown any significant weight loss. Among the three plastics HM HDPE was found to be highly resistant for degradation.

Determination of Mechanical Changes of LDPE, HDPE and HM HDPE

The elastic nature of films and fibres, was responsible for their broad applications. Thus, changes

Table 1: Change in the Weights of LDPE Films (g) Incubated under Different Soil Conditions at Different Intervals of Time

Time Period→ Soil Type↓	0 Days	15 Days	30 Days	45 Days	60 Days	90 Days
Red soil		0.0625	0.0715	0.0967	0.0614	0.0474
Sandy soil		0.0622	0.0663	0.0842	0.0873	0.0921
Black soil		0.0624	0.0958	0.0776	0.0583	0.0412
Control	0.0623					

Table 2: Change in the Weights of HDPE Films (g) Incubated under Different Soil Conditions at Different Time Intervals

Time Period→ Soil Type↓	0 Days	15 Days	30 Days	45 Days	60 Days	90 Days
Red soil		0.0625	0.0715	0.0967	0.0614	0.0474
Sandy soil		0.0622	0.0663	0.0842	0.0873	0.0921
Black soil		0.0624	0.0958	0.0776	0.0583	0.0412
Control	0.0623					

Table 3: Change in the Weights of HM HDPE Films (g) Incubated under Different Soil Conditions at Different Time Intervals

Time Period→ Soil Type↓	0 Days	15 Days	30 Days	45 Days	60 Days	90 Days
Red soil		0.0644	0.0675	0.0724	0.0888	0.0773
Sandy soil		0.0643	0.0647	0.0686	0.0725	0.0763
Black soil		0.0644	0.0672	0.0748	0.0863	0.0719
Control	0.0646					

in mechanical properties of films is one of the important parameterto determine the nature of plastic films and fibres [21].

Both unincubated and incubated polyethylene films were tested for mechanical changes based on breaking load, tensile strength and elongation break to determine the effect of different soil conditions on degradation of LDPE, HDPE and HMHDPE.

All the plastic films (LDPE, HDPE and HMHDPE) incubated in all the three different soils have shown continuous reduction in their mechanical properties with the increase of incubation time.

Plastic films incubated in black soil showed greater reduction in tensile strength, breaking load and percentage of elongation compared to plastic films incubated in red and sandy soils (Tables **4**, **5** and **6**).

Table 4: Reduction in Tensile Strength, Breaking Load and Percentage of Elongation of LDPE Incubated under Different Soil Conditions

Mechanical Properties→ Soil Type↓	Tensile Strength (Mpa)	Breaking Load (N)	% of Elongation
Red soil	18.66	8.08	328.32
Sandy soil	19.93	8.71	346.56
Black soil	17.38	7.76	300.96
Control	25.56	10.63	456

Table 5: Reduction in Tensile Strength, Breaking Load and Percentage of Elongation of HDPE Incubated under Different Soil Conditions

Mechanical Properties→ Soil Type↓	Tensile Strength (Mpa)	Breaking Load (N)	% of Elongation
Red soil	17.13	7.39	289.4
Sandy soil	17.63	7.78	306.7
Black soil	15.39	6.70	259.2
Control	24.82	9.85	432.0

Table 6: Reduction in Tensile Strength, Breaking Load and Percentage of Elongation of HM HDPE Incubated under Different Soil Conditions

Mechanical Properties→ Soil Type↓	Tensile Strength (Mpa)	Breaking Load (N)	% of Elongation
Red soil	27.72	12.18	572.2
Sandy soil	28.03	12.11	578.7
Black soil	26.82	11.26	546.5
Control	30.14	12.24	643.0

Among the three plastic films, HDPE incubated in black soil showed 38% reduction in tensile strength compared to LDPE (32%) and HMHDPE (11%).

Decrease in breaking load for HDPE incubated in black soil is 32% compared to LDPE (27%) and HMHDPE (8%). Finally reduction in percentage of elongation for HDPE incubated in black soil is 40% compared to LDPE (34%) and HMHDPE (15%).

FTIR Spectroscopy

The results of FTIR analysis was shown in Figure **1**. It was clear that, HDPE incubated in black soil showed significant degradation, when compared to unincubated HDPE sample. The peaks that were present between 1600 and 1440 cm^{-1} in the incubated HDPE sample showed more absorption, compared to unincubated lignin. This shows generation of more carboxylic acids,

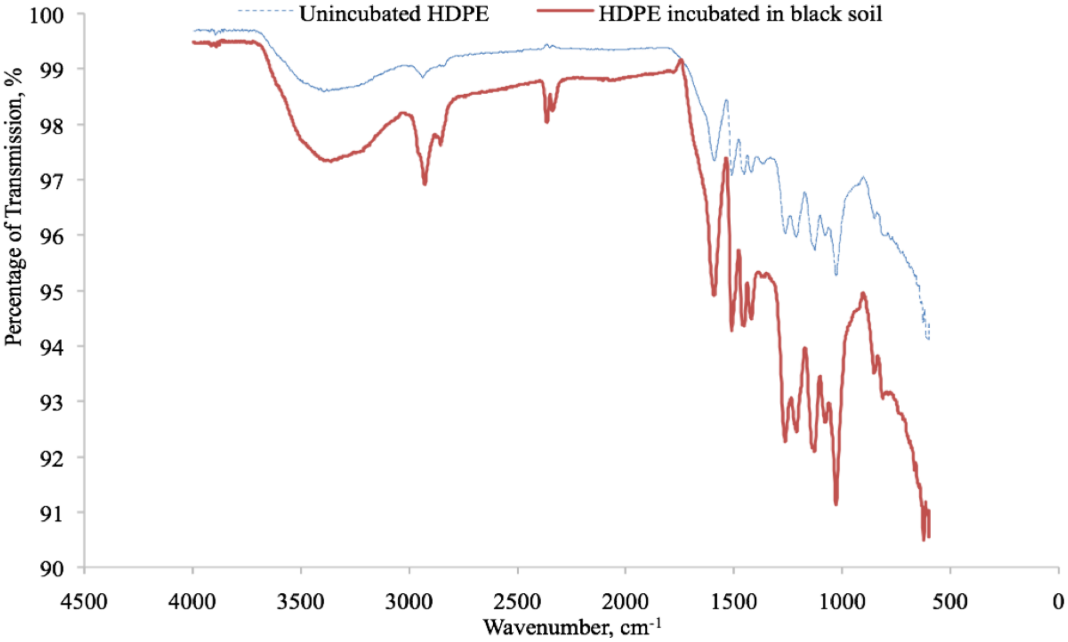

Figure 1: FTIR image of unincubated HDPE and HDPE incubated in black soil.

carbonyl groups and their derivatives in the incubated sample. Further, generation of peaks at 2365 cm^{-1} in the incubated HDPE sample corresponds to C-C stretching, was completely absent in unincubated sample. This shows that incubated HDPE sample has undergone extensive degradation, compared to unincubated sample.

DISCUSSION

All the three plastic films, LDPE, HDPE and HMHDPE used in the study were placed in three different soils viz., red soil, black soil and sandy soil for a period of 3 months. Films were recovered at regular intervals of time and extent of degradation was studied using percentage of weight loss and mechanical parameters like tensile strength, breaking load and percentage of elongation. Among all the three films HDPE was found to be more sensitive to degradation and HMHDPE found to be more resistant. The resistant nature of HMHDPE is because of its high molecular weight, melting temperature, crystallinity and complex branching nature. These properties of plastics would affect their biodegradability. Both the chemical and physical properties of plastics influence the mechanism of biodegradation. Physical properties include surface area, crystallinity, elasticity, molecular weight and glass transition temperature. Whereas, chemical properties includeshydrophilic and hydrophobic groups, antioxidants, oxidizable groups and side chains [22].

Generally, polymers with side chains are more resistant than polymers without side chains [23]. The molecular weight of the polymer plays a key role in its degradation, larger the molecular weight, more resistance to degradation.The enzyme, *Rhizopus delemar* lipase degraded low molecular weight PCL at a faster rate compared to high molecular weight PCL [24]. The morphology of polymers also greatly influence their rates of biodegradation. The crystalline property of the polymer is the crucial factor which decides its rate of degradation. This is because most of the enzymes present in nature, were specific towards amorphous regions of the polymer. Thus degree of crystallinity plays a vital role in degradation of polymer. In a study, the degradation of PLA decreases with an increase in crystallinity of the polymer [25, 26].

All the three plastic films showed some sort of degradation in all the three soils. Maximum degradation was achieved in black soil and degradation rate was found to be slow in sandy soil indicating the effect of physical and chemical environment on plastic films. Among all the plastics used in the study HDPE buried in black soil undergone maximum degradation with 40% decrease in percentage of elongation. Previously, it was reported that, polyethylene samples incubated in soil for 10 years showed 3.5 to 8.4% degradation, promoted by UV irradiation [23, 27]. In another report, polyethylene exposed to UV light for 60 hrs showed 39% degradation [25]. Similarly, HDPE incubated for one month under controlled soil conditions exhibiteddecrease in tensile strength loss by 5.3%.

During the degradation of polyethylene, first step involves breakdown of polymer chain by oxidation process, leading to generation of carbonyl groups. These, on further degradationgenerates carboxylic groups, which subsequently consumed by microorganisms *via* β oxidation [28]. This sort of degradation of plastic sample can be monitored by using FTIR and generation of peaks at 1600-1440 cm^{-1} (C=O stretching), 1630-1840 cm^{-1} (C=C stretching)acts as fingerprints to study the mechanism of degradation.

Figure **1** shows the FTIR indices of unincubated and incubated HDPE plastic samples. The increase in absorption of peaks between 1600-1440 cm^{-1} confirms that HDPE incubated in black soil has undergone extensive degradation and further, peaks generated around 2365 cm^{-1}clearly depicts the degradation of HDPE. This indicates that environmental conditions prevailing in black soil results in generation of carbonyl groups, carboxylic acids and its derivatives in HDPE. Previously it was reported that, polyethylene, which was subjected to degradation under abiotic environment, exhibited increase in amount of carbonyl compounds [29].

CONCLUSIONS

The degradation of polyethylene films under different soil conditions was reported here. Among the three plastic films used in the study, HDPE has undergone more degradation compared to LDPE and HM HDPE. Highest degradation of polyethylene films was achieved in black soil compared to red and sandy soils. Further FTIR analysis also confirms the degradation of HDPE in black soil. This encourages in the sense that furthermore studies on chemical properties of the polymers and also studies on various factors effecting the degradation of polymers can be handful in improving the rate of degradation plastics.

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