Effects of photo-oxidative degradation on low-density polyethylene (LDPE)

Asia Pacific Journal of Multidisciplinary Research
Vol. 8 No.1, 56-62
February 2020
P-ISSN 2350-7756
E-ISSN 2350-8442
www.apjmr.com
ASEAN Citation Index

Shailja Singh[1], Shiv Shankar[2], Shikha*[3]
[1, *3]Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, India; [2]School of Vocational Studies and Applied Sciences, Gautam Buddha University, Yamuna Expressway, India
Shailjasingh578@gmail.com, dr_shikha2003@yahoo.co.in
shiv.nature@gmail.com

Date Received: December 8, 2019; Date Revised: February 6, 2020

Abstract – *Exposure to solar rays can cause significant degradation in several substances. Photo-oxidative degradation due to the effect of UV radiation results in splitting of the polymeric chains, producing free radical and reducing the molecular weight of polymer, causing deterioration of its mechanical properties and converting it into useless materials, after a certain period of time. The photo-oxidative nature of polyethylene has been investigated by FTIR, TGA, DSC, SEM, EDX, XRD and weight loss measurement. In the study performed an increase in carbonyl index, vinyl bond index, internal double bond index and percent crystallinity was observed after sunlight exposure. SEM micrographs revealed cracks and erosioned surface over the LDPE films after the treatment. Weight reduction and decreased carbon content was also observed in treated LDPE films. The results obtained clearly signify that LDPE undergoes a major degree of oxidation and an increase in crystalline fraction. If the LDPE is pretreated by an appropriate radiation they can become suitable for biodegradation without necessity of adding organic agents or photosensitizers. The photo-oxidative degradation of LDPE can be cost incentive and ecofriendly technique to deal with the plastic pollution in the future as the other methods available to deal with plastic waste such as incineration, ozonolysis and dumping of waste at landfill sites impose major threat to the environment.*

Keywords – *Carbonyl index, Vinyl bond index, Internal double bond index, Crystallinity, Enthalpy change.*

INTRODUCTION

The wide spread application of plastic polymers in various sectors causes environmental as well as ecological problems. Polyethylene is a thermoplastic synthetic polymer and its consumption and demand is due to its durability, low cost and easy availability. Plastic utilization has eventually led to increase in amount of plastic waste. Post-consumer plastics are the subject of growing environmental concern and have attracted much criticism due to their potential recalcitrance. High stability of polyethylene under environment and/or photochemical conditions makes their degradation a challenging task. Polyethylene (PE) approximately represents 64% of the synthetic polymer [1]. India itself generates 16 million tons of plastic waste whereas, China and UK produces 4.5 million tons and 1 million tons of plastic waste respectively [2]. Economic growth and development has increased the demand of such plastics that causes its accumulation in environment imposing a great risk on health of human and animals. Plastic pollution also creates environmental problems like contamination of ground water, aquatic pollution, sanitary problem related issues, etc. The increased demand of polyethylenes can increase the plastic solid waste (PSW) that represents a large fraction of the municipal solid waste (MSW) sector. Polyethylene is one of the most common forms of plastic as compared to others such as polyvinyl chloride, polypropylene, etc. Hence, a sustainable and effective plastic waste treatment methods are required to avoid such issues. Although biodegradation of polyethylene has been studied widely, however, the high molecular weight and hydrophobic nature of the polymer has made the task difficult. Under sunlight polymeric material is known to undergo photolytic, thermo-oxidative, photo-oxidative series of reactions which renders chemical changes in the polymer eventually leading to change in color, opacity, brittleness and formation of cracks on the surface of the polymer. The consequences get reflected in terms of reduction in molecular weight, and formation of chemical groups viz., carbonyl, carboxylic acid and hydroperoxides. The photo-oxidative process is an appropriate method and it can be applied in case of a sensitive environment. Photo-oxidative reactions can proceed only in presence of suitable light [3]. So the photo catalytic degradation can be used as one of the eco-friendly and sustainable way of dealing with the plastic waste under solid waste management. In the aforesaid context the aim of the present study entitled "Effect of photo-catalytic degradation on low-density polyethylene (LDPE)" is an attempt to investigate the changes induced in the polymeric structure of the LDPE (Low density polyethylene) due to photo-oxidation effects of solar radiation.

OBJECTIVES OF THE STUDY

The objectives of the study were to analyze the effects of photo-oxidation on the low-density polyethylene. Low-density polyethylene is inert in nature, so its degradation is not an easy process. The increasing burden of plastic pollution has been a matter of global concern. Researchers are finding various methods to deal with the plastic pollution. There are various treatment methods for reducing plastic pollution such as chemical, physical, thermal and biological, among which physical and biological method can be cost effective. Photo-oxidation of LDPE in the presence of solar radiation comes under the physical treatment method. When the polymers are subjected to solar radiation then due to its photo-oxidation phenomena some of the changes are induced in the polymer structure. The study conducted could contribute in the area of plastic degradation.

MATERIALS AND METHODS

Sunlight exposure

In order to examine the degradation of polyethylene due to solar radiation and the environmental factors, fresh untreated samples were obtained and exposed to natural conditions at Babasaheb Bhimrao Ambedkar University, Lucknow for a period of 90 days between May to July 2018. The LDPE samples were then clipped on rigid cardboards. The samples were elevated from the ground facing upward towards the sun that is, it was inclined at an angle of 0° with respect to the horizontal plane. The rigid cardboards were the cut to make a rectangular frame. The samples were clipped at the hollow center position of the frames in order to ensure that the large portion of the sample did not come in direct contact with the cardboard.

FTIR analysis

Infrared spectra were obtained using FTIR spectrometer Thermo Scientific Nicolet present at University Scientific Instrument Center (USIC), Babasaheb Bhimrao Ambedkar University, Lucknow for functional group analysis. Other parameters such as carbonyl bond index were obtained using FTIR data and the relative absorbance intensities of the keto carbonyl bond (1715 cm^{-1}), vinyl bond (1650 cm^{-1}), and internal double bond (908 cm^{-1}) to that of the methylene bond (1465 cm^{-1}) were evaluated. The crystallinity percent was calculated according to [4].

Scanning Electron Microscopy (SEM) analysis

To examine the changes in the surface morphology of the polyethylene samples Scanning Electron Microscopy technique was performed using Scanning Electron Microscope of JEOL (JSM 6490 LV) present at USIC, BBAU. The SEM analysis gives information regarding external morphology, orientation of the substance and its crystalline nature [5].

Energy Dispersive X-ray (EDX)

EDX was done to examine the changes induced in the elemental composition of the sample before and after exposure to the solar radiation. The analysis was performed at USIC, BBAU.

X-Ray Diffraction

X-Ray Diffraction (XRD) was done using PAN alytical X-Ray Diffraction instrument present at Advanced centre for material science (ACMS), IIT Kanpur. Spectra were obtained at room temperature with 2Ө range between 5° to 50°. XRD spectra reveal information about crystalline phase, miller indices and Crystallinity [6]

Thermal Gravimetric analysis

Thermal gravimetric analysis (TGA) was performed using Perkin Elmer Simultaneous Thermal Analyzer STA 8000 present at ACMS, IIT Kanpur. TGA was done in order to determine the temperature of decomposition of polymer. TGA experiment was performed using thermogravimetric analyzer under nitrogen atmosphere at 20ml/min flow rate and at a heating rate of 10°C/min. Heating was done in the temperature range of 30°C to 250°C. Weight loss with respect to temperature was recorded during TGA analysis [7].

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was performed using Perkin Elmer Simultaneous Thermal Analyzer STA 8000 present at ACMS, IIT Kanpur. This technique was used to determine the melting temperature of the sample in the temperature range of 30°C to 250°C at heating rate of 10°C/min. The melting temperature was determined from endothermic peaks [8].

Weight loss determination of polyethylene

The LDPE samples were removed from the sunlight and washed with absolute alcohol for removing dust. The samples were then weighed for determining the weight loss percentage. The weight percentage was calculated using following formula:

Weight loss (%) = {(Initial Weight − Final Weight)/Initial Weight} ∗ 100

RESULTS

FTIR analysis

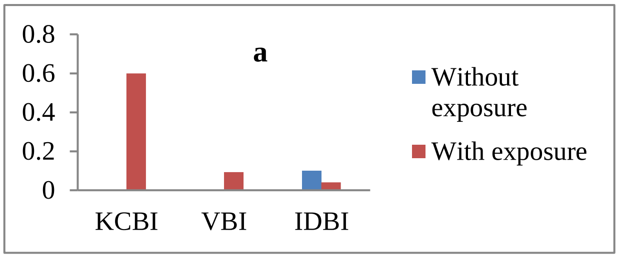
Fourier Transform Infrared Spectroscopy, also known as FTIR Spectroscopy, is an analytical method to identify organic, polymeric and inorganic materials. The structural changes resulting from photo-oxidation were investigated by recording the FTIR spectra of the LDPE samples with and without exposure to sunlight (Fig. 2). Significant changes were observed in sunlight exposed LDPE sample. The most important change in IR spectra was observed in carbonyl (1785-1700 cm^{-1}) peak. After specific period of photo-oxidation an increase in the intensity of absorption band at 1720 cm^{-1} was observed, which denotes C=O stretch of the saturated aliphatic keto-carbonyl group [9]. Suresh et al. [10] reported similar change, as they also described an increase in the intensity of carbonyl peak due to photo-oxidation of LDPE sample. FTIR analysis of LDPE samples revealed disappearance of number of peaks along with appearance of new peaks due to addition or removal of some of the functional group and chemical bonds in the LDPE samples exposed to sunlight.

Table 1. Various FTIR derived parameters of LDPE sample

Samples	KCBI[a]	VBI[b]	IDBI[c]	Crystallinity(%)
Without exposure	0	0	0.1	35
With exposure	0.6	0.093	0.04	37

KCBI[a] = Keto carbonyl bond index
VBI[b] =Vinyl bond index
IDBI[c] = Internal double bond index

Various parameters were derived from the FTIR spectra obtained. The polymers in presence of solar radiation were rapidly oxidized, as indicated by the increase in carbonyl bond index and vinyl bond index (Table 1). The higher carbonyl bond index in the exposed polymer indicated the photooxidation of polymer matrix. The carbonyl group is of ketone group because no signature peaks of aldehydes and acid were detected [6]. In the weathered sample the KCBI, VBI and IDBI had increased (Fig.1(a)). This proves that some sort of degradation changes had occurred due to weathering effect and solar radiation on the structure of polymer. The Crystallinity percent of the sample exposed to sunlight was found to be more than that of unexposed sample (Fig. 1(b)). The increase in the Crystallinity of the polymer in the solar irradiated sample can be attributed due to the introduction of carbonyl group [11]. This increase in Crystallinity made the polymer hard and brittle but lowered its impact resistance which means further it could be subjected biodegradation for enhanced degradation process of polymers in nature. The peaks that were found common in both the LDPE samples with and without exposure are: CH_2 asymmetric stretching (2919 cm^{-1}); CH_2 symmetric stretching (2851 cm^{-1}); CH_2 bending deformation at 1463 cm^{-1}; wagging deformation (1351 cm^{-1}) and rocking deformation (720 cm^{-1}) [12]. The spectral band that generated after the photo-oxidation of the LDPE samples were at 1738 cm^{-1} corresponding to carbonyl group (R-CO-OR’) [9]; at 1068 $cm^{-1}$to (RCH_2-CHOH-CH_2R’); at 1375 cm^{-1} CH_3 symmetric deformation [13]. The band that was found absent in the sunlight-exposed sample was at 1306 cm^{-1}, which corresponded to twisting deformation.



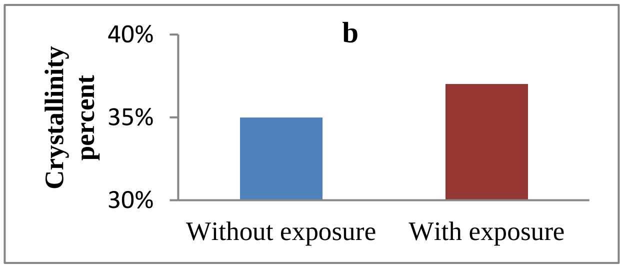


Fig. 1. FTIR parameters of LDPE samples with and without exposure to solar radiation obtained after natural weathering (a) keto carbonyl bond index (KCBI), vinyl Bond Index (VBI), internal double bond index (IDBI) of PE samples (b) Crystallinity percent of the LDPE samples.

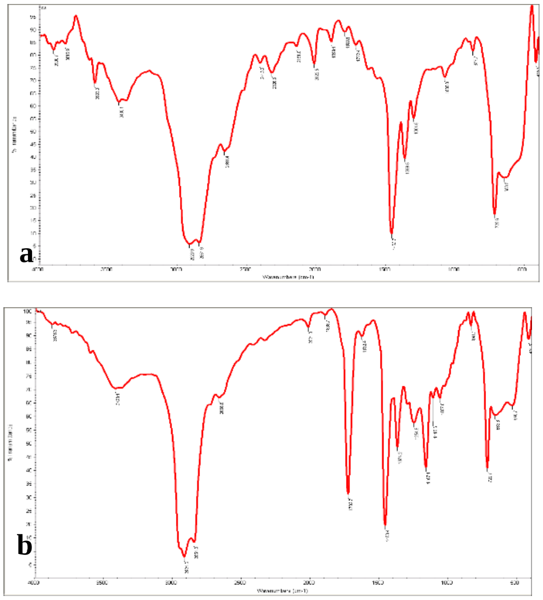


Fig. 2. FTIR Spectra of LDPE samples (a) without exposure (b) with Exposure

SEM analysis

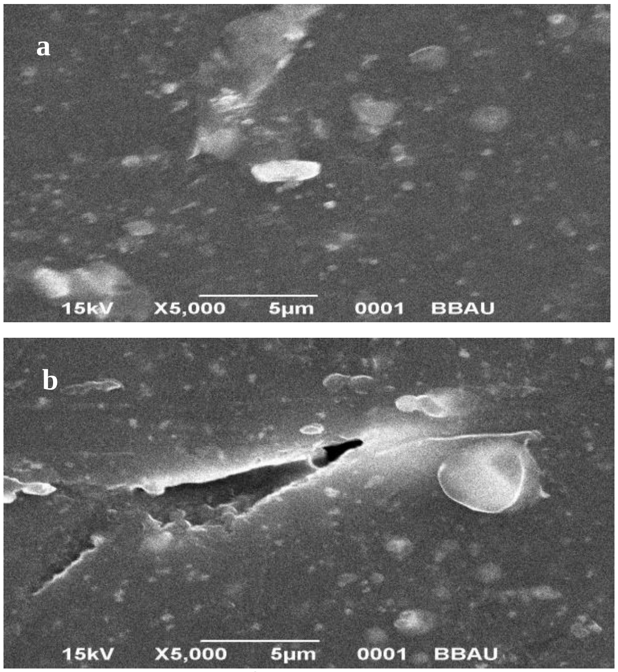


Fig. 3. SEM micrographs of LDPE samples (a) without exposure (b) with exposure to sunlight.

LDPE samples subjected to sunlight exposure and natural weathering conditions were studied through scanning electron microscopy. Significant modifications were found to occur in the surface morphology of LDPE samples without and with exposure to sunlight under natural weathering condition.

The SEM micrographs obtained revealed that the surface morphology of the untreated LDPE sample was smooth (Fig. 3(a)). It did not show any type of defects and cracks. But the LDPE sample exposed to solar radiation revealed cracking and fissures over the surface (Fig. 3(b)). Several researchers have also reported grooves over the surface can also be seen which is absent in the unexposed one [14, 15]. The surface found to be eroded due to solar radiation and other weathering effect. Even the increase in the roughness of the sample has also been noticed in the exposed polymer as compared to unexposed polymer which clearly indicates that the photo oxidation process has influenced the photo-degradation of the polymer causing changes in the surface texture of the polymer, which makes the polymer suitable for further degradation by microorganisms in nature [16].

Energy Dispersive X-Ray analysis

The energy dispersive X-Ray analysis of LDPE samples, with and without exposure to sunlight was done to investigate the composition of various elements in the polymer (Table 2). The results obtained revealed a decrease in the carbon content of LDPE samples exposed to solar radiation as compared to the sample not exposed to sunlight. Oxygen content was also decreased in the exposed polymer (Fig. 4). The decrease in the carbon content in the polymer exposed to sunlight may be due to the main chain scission and side group abstraction during the photo-oxidation process. The decrease in the oxygen content in exposed polymer might be due to the elimination of certain oxygen containing groups.

Table 2. Elemental compositions of LDPE samples

Elements	Without exposure (Weight %)	With exposure (Weight %)
Carbon	29	21
Oxygen	52	44
Sodium	9.77	12
Phosphorus	6.84	16
Chlorine	0.24	5.92
Potassium	1.38	1.08
Titanium	0.27	0

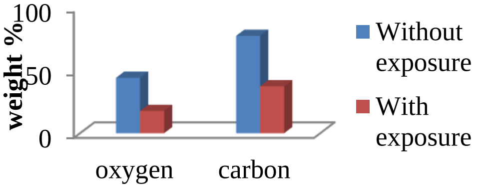


Fig. 4. Carbon and oxygen weight percent of LDPE samples

X- Ray diffraction analysis

XRD analysis was done to determine modifications induced by the solar radiation such as crystallite size and Crystallinity. The XRD pattern obtained clearly showed the presence of amorphous as well as crystalline region (Fig. 5). The peak at 22° denotes the amorphous structure. Three crystalline peaks at 21.5°, 24.3° and 36.5° appeared during the experiment corresponds to the crystalline structure [6]. These peaks were common in both the LDPE sample with and without exposure. But some of the new major peaks at 16° and 15° were found to appear in the LDPE sample exposed to sunlight. Other peaks centered at 26°, 28°, 30° and 35° have shown increase in the intensity as compared to the LDPE not exposed to sunlight. The increased and intense number of peak in the LDPE polymer with exposure marks the increase in the crystalline region of the polymer. This may be due to the fact that amorphous region are more prone to photo-oxidative degradation as compared to the densely packed crystalline part. From FTIR it has been concluded that there has been an introduction of the carbonyl group in the exposed polymer, which indicates an increase in the Crystallinity of polymer. The orthorhombic phase of the peak located at 21.5°, 24.3°, 36.5° are 110, 200 and 210 respectively [17]. These phases depict the orthorhombic crystal plane.

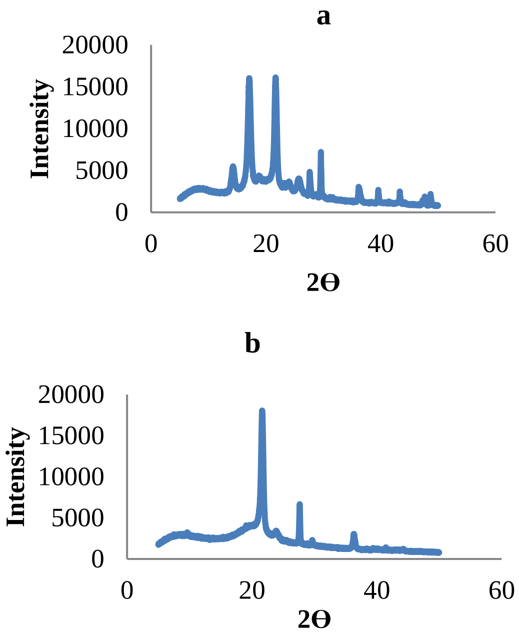


Fig. 5. XRD pattern of LDPE samples (a) without exposure (b) with exposure.

Thermal Gravimetric Analysis (TGA)

Thermal profile of polyethylene samples was checked for determining the influence of sunlight on exposed as well as unexposed polyethylene sample. Thermal analysis of both the samples revealed the decrease in weight % of solar irradiated LDPE by 0.189% whereas an increase in weight % by 0.459% in non-irradiated sample of LDPE. In the exposed sample the final mass decreased whereas in the unexposed LDPE sample mass was increased at the end temperature. The graph of thermal analysis clearly showed the difference (Fig. 6) of mass Vs temperature. The final decomposition temperature (T_f) for sunlight-exposed polyethylene (162°C) was achieved at higher temperature as compared to unexposed polyethylene (138°C). The decrease in weight % of the exposed sample obtained may be due to the decrease in thermal stability of the polymer and weakening of the bond between polymeric chains because of weathering effect. This shows that the polymer becomes brittle when subjected it to solar radiation [18].

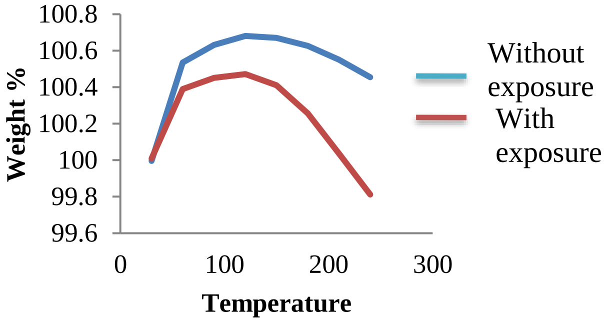


Fig. 6. Thermal Gravimetric Analysis of LDPE samples.

Differential Scanning Calorimetry (DSC)

DSC thermogram of the samples (Fig. 7) revealed the thermal parameters of melting and degradation process. In the calorimetric study several processes associated with melting and thermal decomposition were detected. For both the samples endothermic peaks were obtained.

Table 3. Characteristics of melting and thermal decomposition process of LDPE samples.

Sample	Melting			Decomposition
	T_o(°C)	T_p(°C)	Δh_f(J/g)	T_f(°C)
Without Exposure	62	116	0.2	138
With Exposure	62	118	0.4	162

T_o- Onset temperature; T_p – Melting Peak temperature; Δh_f – Melting enthalpy
T_f – Final decomposition temperature

The onset temperature (T_o) was found to be approx 62°C for both the samples which meant that the sample started decomposing at the same temperature. However, there was no significant change in the melting peak temperature (T_p) but an increase in melting enthalpy and final decomposition temperature (T_f) was observed in LDPE sample exposed to sunlight (Table 3). The area under the melting curve was found to increase in case of LDPE sample with sunlight exposure. The results of DSC obtained in the present study showed similar results obtained by Suresh et al. [10] in which they investigated the thermal oxidation of polyethylene. The increase in the melting enthalpy of the weathered polyethylene may be attributed to the increase in the crystalline fraction of the polymer. The increase in Crystallinity could be the indirect effect of the end chain scission of the LDPE in the amorphous regions of LDPE film. The chain end scission causes the crystallization of resulting low molecular weight segments [9]. The embrittlement of the polymer can be observed due to increase in crystallinity [19].

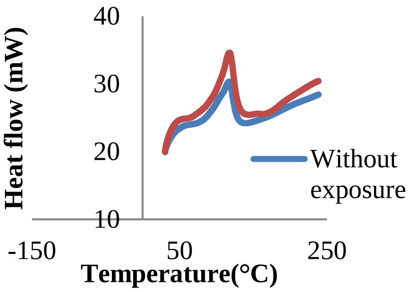


Fig. 7. DSC thermogram of LDPE samples without and with exposure to sunlight.

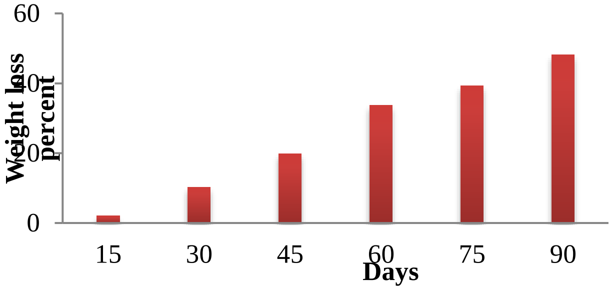


Fig. 8. Weight loss percentage over a period of 90 days

Weight loss determination of polyethylene

Weight reduction analysis of LDPE samples were carried out to study the photo-degradation effects on the samples. (Fig. 8) displays the photo induced weight loss of samples with solar radiation over a period of 90 days. The percent weight reduction increased with increase in exposure time, which is, 2.04%, 10.23%, 19.79%, 33.78%, 39.24%, 48.12% for 15, 30, 45, 60, 75 and 90 days respectively. The increase in weight reduction might be due to the breakage of polymeric chains.

CONCLUSION

In order to deal with the plastic waste we have demonstrated that the conventional polyethylene gets affected when exposed to solar rays. The study was done under the solar radiation in the natural environment without any additives. SEM analysis indicated that solar radiation modified the surface morphology of the polymer. Cracks and grooves were noticed. The increased carbonyl index as examined by FTIR analysis confirmed the photo degradation of polymer on solar treatment while changes in the elemental composition of the polymer confirm breakage in the polymer chain. Various analyses like XRD, TGA and DSC revealed that once the polymer gets brittle their resistance power decreases and microbes can utilize the carbon in the polymer chains for their growth and metabolism. Certain limitations of photo-oxidative degradation of LDPE waste include improper amount of solar radiation that could initiate the chain scission of the polymer. It would be difficult for the regions where sunlight is scarce to deal with photo-oxidative degradation of LDPE. In future this method of degradation can be incorporated with the other methods of biodegradation such as composting, soil-burial method and microbial degradation to completely mineralize the polymers. The study will contribute in the management of plastic waste efficiently and in cost effective manner.

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