

Studies on the photo-oxidative degradation of LDPE films in the presence of oxidised polyethylene

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Abstract

This paper reports the results of photo-oxidative degradation studies of LDPE in the presence of varying amounts of oxidised polyethylene (OPE), which was prepared by heating LDPE films containing 0.1% cobalt stearate in oxygen atmosphere at 100 °C. OPE, with a CI of 12 was used as an additive for LDPE. Varying amounts of OPE (0.5–5%) were blended with polyethylene in an extruder and films of 70 µm thickness were prepared by film blowing process. The physico-chemical properties of the films were evaluated and these were found to be proportional to the amount of OPE. The films thus obtained were subjected to UV-B exposure at 30 °C for extended time periods. The chemical and physical changes induced by UV exposure were followed by monitoring the changes in mechanical properties (tensile strength and elongation at break), carbonyl index (CI), morphology, molecular weight, MFI and DSC crystallinity. Incorporation of OPE was found to be effective in initiating the photo-degradation of LDPE in relatively short span of time and the degradation was found to be proportional to the amount of OPE in the formulation.

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Keywords: Low-density polyethylene; Prooxidant; Cobalt stearate; Mechanical properties

1. Introduction

Solid waste disposal and litter are among the many problems that arise from the relationship between man and his environment [1]. The present generation commodity plastics, especially the packaging materials, contribute significantly to the solid waste disposal problem. The use of plastic materials that can re-enter the biological life cycle, appear to be one of the most promising solution to this problem [2]. One of the most common techniques used to render a polyolefin degradable is to add prooxidants at the processing stage. The additives normally used for the initiation of degradation are organosoluble transition metal ions, aromatic ketones,

dithiocarbamates, acetyl acetonates, etc. which act as thermal and/or photo-oxidant for the polymer [3–7].

Attempts have also been made to develop degradable polymers based on partially degraded polymers [8]. Studies on the blends of photo-oxidised polypropylene with virgin polypropylene have been reported [9,10]. Considering the large number of carbonyl groups in these blends, a higher rate of degradation is expected. However, ageing studies on such blends have not been performed so far. This paper deals with the development of a photo-degradable low-density polyethylene (LDPE) composition containing small amount of partially degraded oxidised polyethylene (OPE) as a degradation promoter. Films containing varying amounts of oxidised polyethylene were prepared and then exposed to UV-B for accelerated ageing studies. The degradation behaviour was monitored by measuring the changes in structure (by FTIR), mechanical properties, molecular weight (by viscometry) and crystallinity.

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The study was performed on LDPE keeping in mind its prime importance in the packaging field and its inherent resistance towards degradation. This paper describes the preparation of polymer films having varying amounts of oxidised polyethylene and evaluation of its degradation behaviour as a function of irradiation time.

2. Experimental

2.1. Materials

Commercial grade LDPE (Indothene, 24FS 040) was used for the preparation of films. The MFI for the polymer was 3.7 g/10 min, with crystalline melting point of 110 °C and density of 0.92 g/cm³. Cobalt acetate, sodium hydroxide and stearic acid (analytical grade) procured from M/s E-Merck were used without any purification.

2.2. Preparation of oxidised polyethylene (OPE)

Films containing 0.1% cobalt stearate were prepared by conventional extrusion followed by sheeting process according to the procedure described elsewhere [11,12]. The films were heated in an air oven at 100 °C for 12 h to prepare oxidised polyethylene (OPE). The degradation of polyethylene was monitored by noting the changes in the carbonyl index and mechanical properties. After 12 h of heat treatment in an air oven at 100 °C, powdery films were obtained with a carbonyl index of 12. The MFI of OPE could not be determined as it flowed freely under the test conditions.

2.3. Preparation of LDPE films containing OPE

Thin films (70 µm) were prepared by mixing varying amounts (0.5–5%) of OPE with LDPE in a film blowing machine using an extruder (Dayal make) with a 19 mm screw of L:D::22:1 attached to a film blowing die. An annular die with a diameter of 2" and a die gap of 1 mm was employed for this purpose. Films of uniform thickness were prepared by maintaining a constant nip roller, take up speed of 35 rpm under constant blowing. The temperature in the barrel zones were maintained at 120 °C, 130 °C and that of the die section was 135 °C.

Neat LDPE films have been designated as PE and films containing OPE have been designated as OPE followed by a numerical suffix indicating the amount of OPE multiplied by 10. For example LDPE films containing 0.5% and 5% OPE have been designated as OPE5 and OPE50 respectively. The details of formulation and sample designation are given in Table 1. The blow up ratio (BUR) and draw down ratio (DDR) values were calculated according to the following formula. $BUR = d/D$, $DDR = H/H_0$ where d is the diameter of the bubble, D is the diameter of die, H is die gap and H_0 is the thickness of films.

Both BUR and DDR give a measure of the extensibility of material towards transverse and machine direction, respectively. BUR, DDR and film thickness are also listed in Table 1.

Table 1
Physico-chemical characteristics of blown films

Sample code	Film thickness (µ)	OPE (%)	PE (%)	DDR	BUR	[η] (g/mL)	MFI
PE	70	—	100	14.2	5.5	87	3.7
OPE5	70	0.5	99.5	14.2	5.5	86	4.0
OPE10	70	1	99	14.2	5.5	84	4.2
OPE20	80	2	98	12.5	5.3	78	6.3
OPE30	85	3	97	11.7	4.9	75	7.4
OPE50	90	5	95	11.1	4.8	72	8.0
OPE	—	100	—	—	—	19	—

It was observed that with increasing OPE content, the BUR and DDR decreased as a result of which relatively thicker films were obtained. A stable bubble was difficult to obtain when the concentration of OPE was increased beyond 5% due to the relatively low melt strength of OPE as compared to polyethylene.

2.4. Photo-degradation procedure

LDPE films were irradiated with four 40 W UV-B lamps generating energy between 280 and 350 nm with a maxima at 313 nm. The spectral irradiance of the lamps has been depicted elsewhere [12]. Samples were mounted on racks positioned at 5 cm from the lamps. Sampling was carried out at regular intervals and the degradation was monitored by techniques described earlier.

2.5. Characterisation techniques

The X-ray diffraction patterns were recorded on an X-ray diffractometer (PW3020, Philips Netherlands) (Cu K α radiation, voltage: 40 kV and current 20 mA). The range of diffraction angles (2θ) was 20°–40° and the scanning speed was 0.05° 2 θ /s. The X-ray crystallinity was determined by ratio of the area bounded by the crystalline peaks to that of the entire region in the plot of s^2I_c against s , where s is $2\sin\theta/\lambda$ and I_c is the intensity of absorption.

The tensile tests were performed on LDPE films according to ASTM 882-85 using a materials testing machine (Model JRI-TT25). Films of 100 mm length and 10 mm width were cut out from the exposed films and subjected to a crosshead speed of 100 mm/min. The tests were undertaken in an air-conditioned environment at 20 °C and a relative humidity of 65%. Five samples were tested for each experiment and the average value has been reported. The thermal behaviour of samples was investigated using a SETARAM SETSYS TG–DTA 16 thermal analyzer under nitrogen atmosphere. The percentage crystallinity was calculated from DSC results using the following relation:

$$\% \text{crystallinity} = \frac{\Delta H_{f(\text{observed})}}{\Delta H_{f(100\% \text{crystalline})}} \times 100$$

where ΔH_f is the enthalpy of the material and $\Delta H_{f(100\% \text{crystalline})}$ is the enthalpy of 100% crystalline material taken from the

literature as 285 J/g [13]. The structural changes occurring in LDPE films upon exposure were investigated using FTIR spectroscopy. The FTIR spectra were recorded using a BIO-RAD (FTS-40) spectrophotometer. Carbonyl index (CI), was used as a parameter to monitor the degree of photo-oxidation of polyethylene and has been calculated according to the baseline method [14].

$$\text{Carbonyl index (CI)} = \frac{\text{Absorption at } 1740 \text{ cm}^{-1} \text{ (the maximum of carbonyl peak)}}{\text{Absorption at } 2020 \text{ cm}^{-1} \text{ (internal thickness band)}}$$

Morphological changes upon degradation were investigated using a scanning electron microscopy. Sample surfaces were sputtered with gold using usual techniques and then analysed using JEOL (JSM-840) electron microscope at a voltage of 10 kV. Photo-micrographs were taken at uniform magnification of 2000 \times . The MFI of polymer was determined according to ASTM D 1238 at 190 °C with 2.16 kg load using a melt flow index testing equipment (International Equipments).

The molecular weight of LDPE samples was determined by viscometry. Films were dissolved in xylene and the intrinsic viscosity $[\eta]$ was measured using Ubbelohde suspension level viscometer at 105 °C in a thermostatted oil bath with silicone oil as the medium. The viscosity average molecular weight was calculated using the following equation [15]:

$$[\eta] = 16.5 \times 10^{-3} M_v^{0.83}$$

3. Results and discussion

3.1. Monitoring the preparation of OPE

The degree of degradation upon exposure to heat in an air oven at 100 °C was monitored by change in the structure

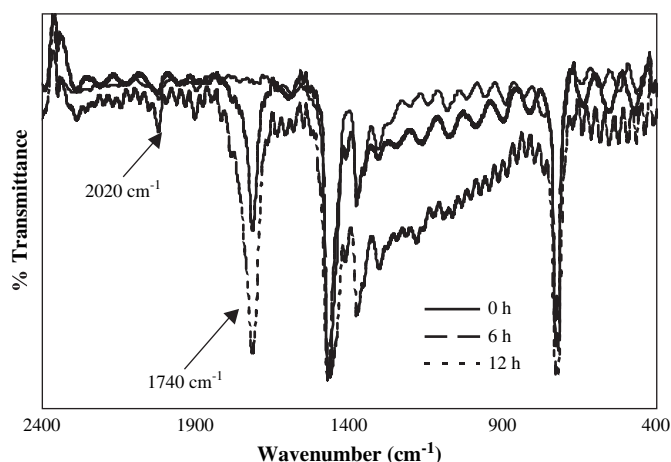


Fig. 1. Structural changes due to thermo-oxidation (FTIR).

(FTIR) and mechanical properties. Thermo-oxidation led to generation of carbonyl groups on the polymer surface. Fig. 1 show the change in FTIR spectra of polymer containing 0.1% CS due to thermo-oxidative treatment at 100 °C. Carbonyl index (CI) was calculated by taking the ratio of absorption bands at 1710 and 2020 cm^{-1} . Fig. 2 show the change in the CI as a function of thermo-oxidation time. It was observed

that for films containing 0.1% cobalt stearate, CI increased exponentially, after an initial short induction period of 2 h. The CI reaches a value of 12 after exposure for 10 h and showed marginal change after further increase in oxidation. The films became brittle and powdery after thermo-oxidative degradation. Neat LDPE on the other hand did not show any increase in the CI during the investigation period.

The changes in the mechanical properties are displayed in Fig. 3. The results have been represented as mean \pm S.E. The tensile strength did not show much change after the thermal ageing for either of the samples. LDPE films containing cobalt stearate lost \sim 50% of the elongation after 6 h of thermal ageing and became very brittle after \sim 10 h. The films broke down on touching which were subsequently pulverized to prepare a fine powder. This powder was used as an additive to prepare blends. On the other hand neat LDPE did not show much decrease in the elongation at break either. The TG/DTG traces of PE and OPE in nitrogen atmosphere are shown in Fig. 4. It is apparent that OPE starts degrading at much lower temperatures than LDPE. In the DSC scans of LDPE and OPE,

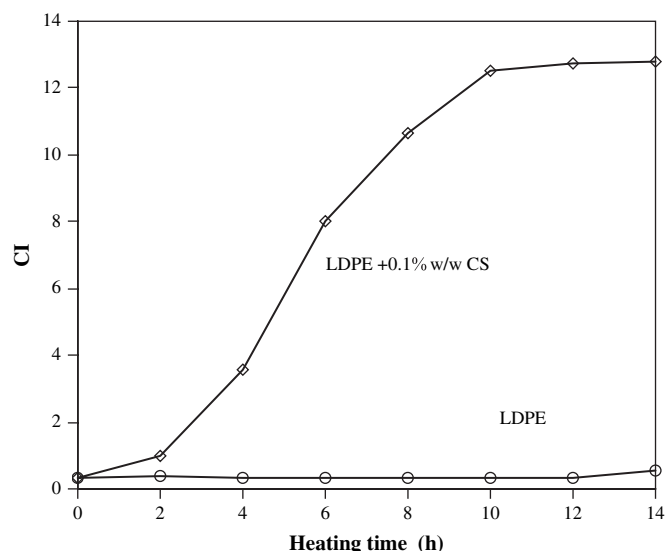


Fig. 2. Change in the CI due to thermo-oxidation at 100 °C.

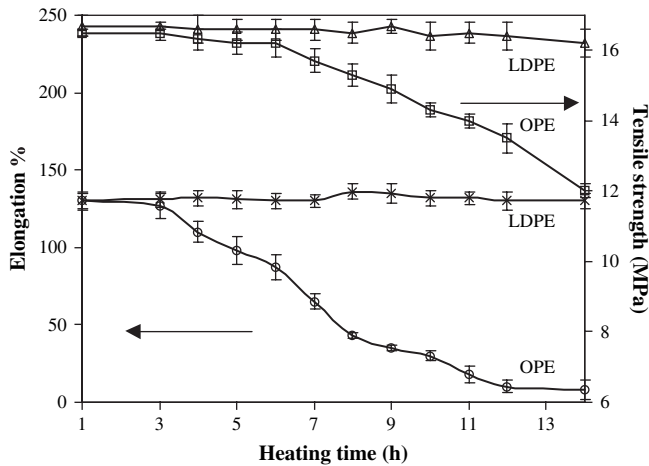


Fig. 3. Effect of thermal aging on the mechanical properties.

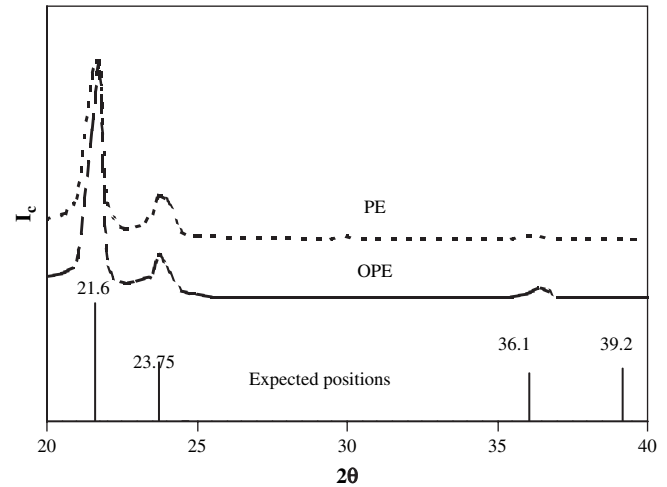


Fig. 5. X-Ray diffraction patterns of LDPE and oxidised LDPE (OPE).

an endothermic transition due to melting was observed at 110 °C. This implies that there is no change in the melting point due to oxidation. The crystallinity however is expected to increase due to gradual erosion of the amorphous regions. The percent crystallinity was found to be 59.3% (OPE) and 44.8% (LDPE). The increase in crystallinity was confirmed by X-ray diffraction studies. The X-ray diffraction patterns (XRD) of LDPE and OPE are shown in Fig. 5. The vertical lines at the bottom of the figure are the expected positions for polyethylene (PCPDF No. 11-0834). The XRD of LDPE films show peaks at 21.5°, 24.7° and 36.07°, which remain unaltered on oxidation. These correspond to inter-lamellar spacing of 4.1, 3.6 and 2.49 Å, respectively. A plot of s^2I_c vs s , which is used for determination of crystallinity is displayed in Fig. 6, where s is $2\sin\theta/\lambda$ and I_c is the intensity of absorption. The percentage crystallinity, as determined by the area under the curve was found to increase from 39.4% in PE to 43% in OPE.

The intrinsic viscosity of OPE as determined by viscometry is 19.3 ml/g which corresponds to a M_v of 4.87×10^3 g/mol. The MFI of OPE could not be determined as it flowed freely under load of 2.16 kg at 190 °C. LDPE in the absence of prooxidant cobalt stearate did not show any change in the MFI and remained unaltered at 3.6 due to thermo-oxidation for 12 h. The intrinsic viscosity of LDPE containing 0.1% cobalt stearate decreased from 84 to 19 ml/g after 10 h of heat treatment while neat LDPE did not show any change in the intrinsic viscosity.

3.2. Degradation studies on LDPE/OPE blends

3.2.1. Mechanical properties of films

Figs. 7–10 represent the effect of UV-exposure time on both longitudinal as well as transverse mechanical properties of the blends. The results are represented as mean \pm standard error. For the sake of brevity, only tensile yield strength and

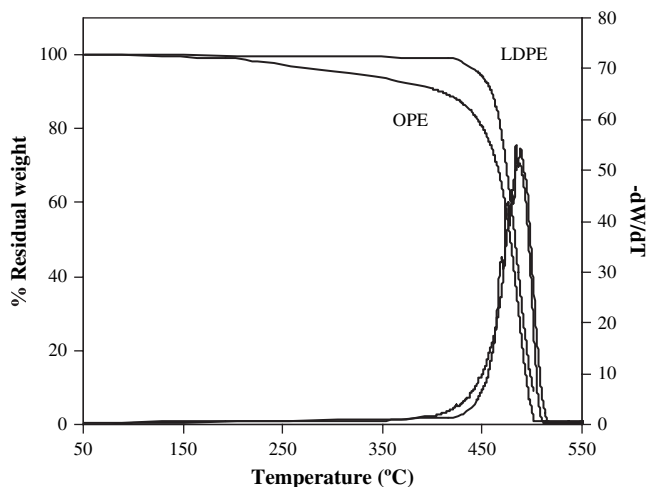


Fig. 4. TG/DTG traces of LDPE and OPE.

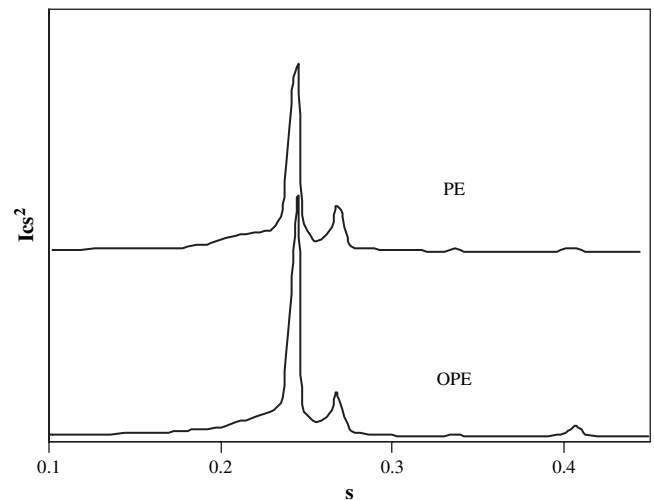


Fig. 6. Plot of $I_c s^2$ vs s for LDPE and oxidised LDPE (OPE).

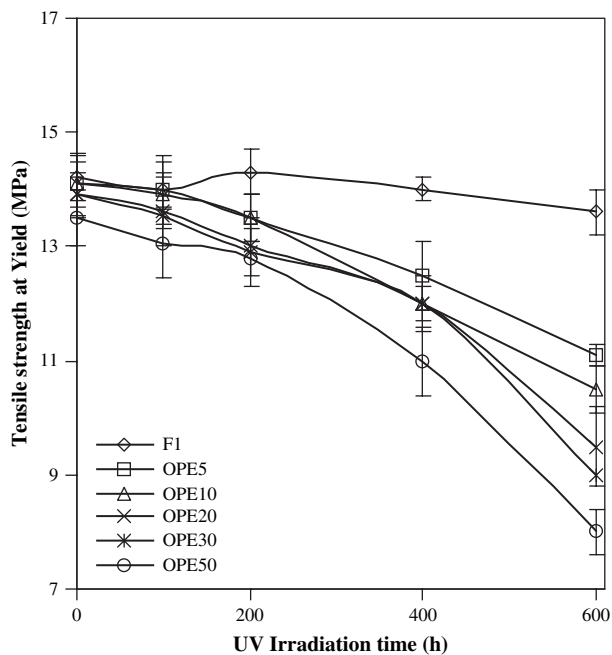


Fig. 7. Effect of UV exposure and OPE content on the tensile strength of LDPE in the machine direction.

elongation at break have been presented here as they are considered to be direct indicators of degradation [16,17]. It should be noted that the initial longitudinal tensile strength is not significantly affected by the incorporation of OPE. LDPE films retained high level of tensile strength for the entire UV exposure period of 600 h, with a slight increase in percentage elongation. On the other hand, LDPE films prepared after blending

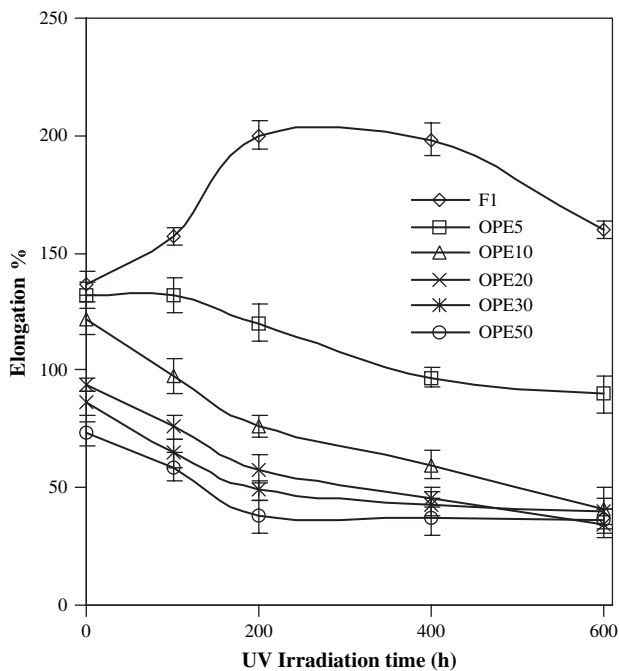


Fig. 8. Effect of UV exposure and OPE content on the %elongation of LDPE films in the machine direction.

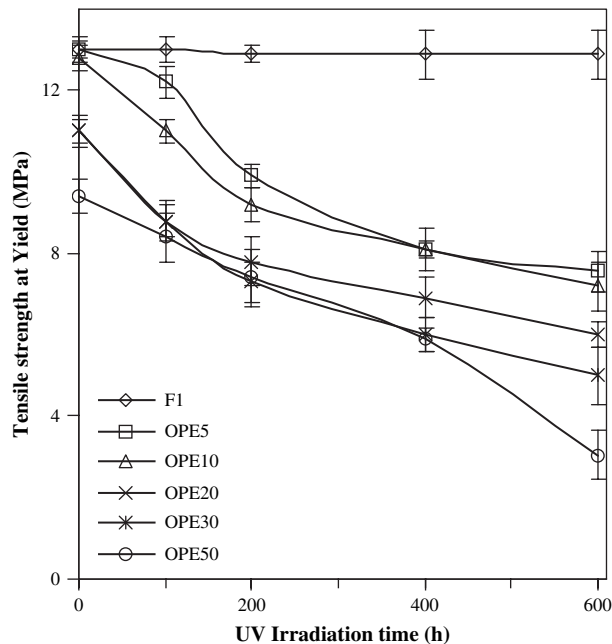


Fig. 9. Effect of UV exposure and OPE content on the tensile strength of LDPE films in the transverse direction.

with varying amounts of OPE, showed a significant decrease in the tensile strength and elongation. Films became powdery after 600 h of exposure. This clearly shows that the presence of OPE accelerates the degradation of LDPE.

The properties in the transverse direction also show a similar trend, however, the extent of damage is more in this direction. This can be explained on the basis that the molecular

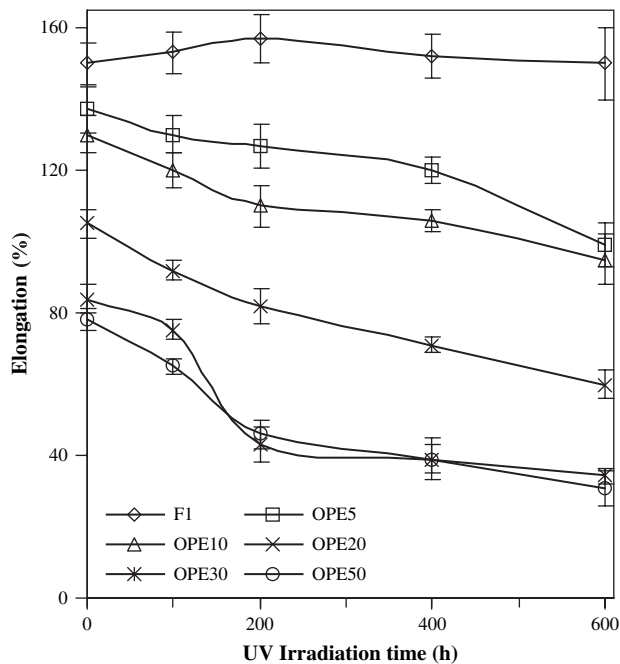


Fig. 10. Effect of UV exposure and OPE content on the %elongation of LDPE films in the transverse direction.

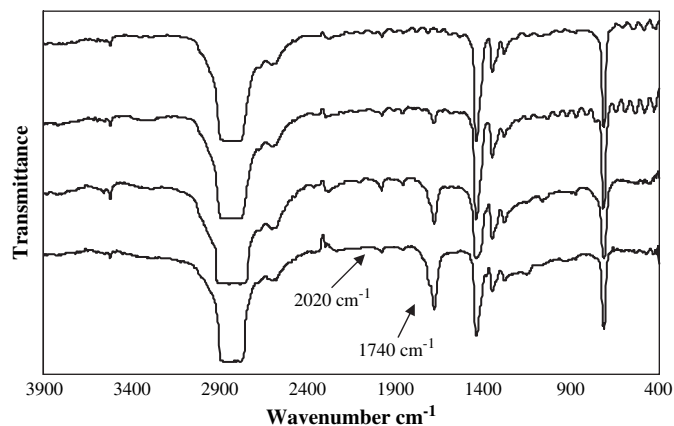


Fig. 11. Effect of irradiation time on the FTIR spectra of OPE50.

chains get oriented in the longitudinal direction during the blowing process, as a result of which the longitudinal properties are better than those in the transverse direction. On exposure, the amorphous regions are more affected as oxygen diffuses into the amorphous phase leading to chain scission thereby weakening the intermolecular forces further and thereby the transverse properties are affected more strongly than those in the longitudinal direction.

3.2.2. FTIR studies

Structural changes upon irradiation were investigated by recording the FTIR spectra of films having varying amounts of OPE before and after irradiation. Fig. 11 shows the FTIR spectra of samples as a function of irradiation time. The most significant changes in IR absorption spectra were in the carbonyl ($1785\text{--}1700\text{ cm}^{-1}$), amorphous (1300 cm^{-1}) and hydroxyl region (3400 cm^{-1}). The absorption band around 1714 cm^{-1} , which can be assigned to the C=O stretch of ketonic groups, increased in intensity and at the same time a broadening of the band was observed which indicates the presence of more than one oxidation product. The carbonyl band is a result of overlap of various stretching vibration bands including those of aldehydes and/or esters (1733 cm^{-1}), carboxylic acid groups (1700 cm^{-1}) and γ lactones (1780 cm^{-1}) [18–21].

Carbonyl index was calculated by taking the ratio of the intensity of signals ($1740/2020\text{ cm}^{-1}$) and the results are tabulated in Table 2. As is evident, there was negligible increase in the CI of neat LDPE whereas significant change was

Table 2
Effect of UV exposure on carbonyl index of LDPE and OPE samples

Sample designation	Carbonyl index (CI) after UV irradiation			
	0 h	200 h	400 h	600 h
F1	0.3	1.4	1.5	2.7
OPE5	1.0	1.0	1.9	3.1
OPE10	1.0	1.4	3.3	4.0
OPE20	1.4	2.1	5.0	6.2
OPE30	1.2	4.0	6.7	8.0
OPE50	1.8	5.0	7.1	9.0

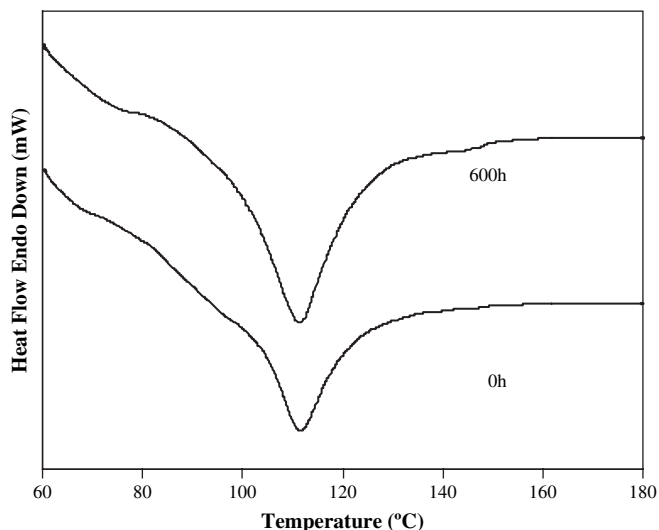


Fig. 12. DSC scan for OPE50 samples before and after UV exposure of 600 h (heating scans).

observed in films containing OPE as a function of time. It is generally believed that polyethylene films enter into the decay stage at CI greater than 6 [3]. This implies that LDPE containing higher concentration of OPE ($>2\%$ OPE) start decaying within 100 h of UV exposure while those containing upto 2% OPE require about 200 h. Films containing 5% OPE became fragile and brittle after 400 h, while samples containing lesser quantities require a minimum of 600 h of UV exposure for embrittlement.

3.2.3. DSC

Figs. 12 and 13 show the DSC scans of OPE50 samples. Both heating and cooling scans were recorded at a programmed heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$. DSC measurements were used to record the changes in the crystallinity of LDPE and OPE samples after irradiation. As is apparent from the DSC

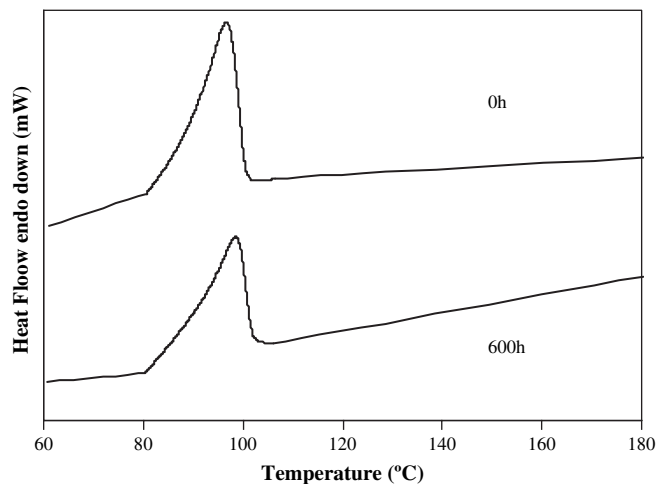


Fig. 13. DSC scans for OPE50 before and after UV exposure of 600 h (cooling scans).

Table 3
Results of ΔH_f , ΔH_c and percent crystallinity in LDPE before and after UV exposure in the presence and absence of OPE

Sample designation	ΔH_f (J/g)		Crystallinity (%)		ΔH_c (J/g)	
	0 h	600 h	0 h	600 h	0 h	600 h
F1	128	141	44.9	49.4	130	146
OPE10	128	150	44.9	52.6	132	150
OPE20	130	150	45.6	52.6	133	154
OPE50	132	154	46.3	54.0	136	160

ΔH_f : heat of fusion; ΔH_c : heat of crystallization.

scans of the samples, an endothermic transition due to melting was observed at ~ 110 °C in the heating scans. This implies that there is no change in the melting peak due to UV exposure, however, the area under the melting endotherm changes upon exposure. During degradation, it is expected that crystalline regions remain unaffected as the degradation occurs mainly in the amorphous regions only.

The thermal characterisation data obtained from DSC traces is listed in Table 3. Such an increase in crystallinity of polyethylene films upon irradiation has been reported in literature [13,22]. The increase in crystallinity is due to scission of the polyethylene molecule in the amorphous region. The chain scission allows the resulting low molecular weight segments to crystallize or act as nucleating agents for enhancing the rate of crystallization. The creation of new intermolecular polar bonds, due to carbonyl may also lead to this effect [23]. The increase in crystallinity also contributes to the embrittlement of the films apart from other factors like reduced molecular weight and/or photo-crosslinking of the polyethylene chains. It is known that chain scission gives rise to sufficient chain mobility to produce secondary crystallization that resulted in crack initiation.

3.2.4. Molecular weight

It is generally agreed that the LDPE films containing OPE (prooxidants) enter into the embrittlement stage when the M_n is <5000 . The results of $[\eta]$ as a function of irradiation time as well as a function of OPE concentration is summarized in Table 4. OPE had $[\eta]$ of 19 ml/g whereas LDPE had $[\eta]$ of 84 ml/g. Incorporation of OPE (0.5–5% w/w) did not affect the $[\eta]$ much and all the samples had $[\eta]$ of 81 ± 3 ml/g. In

Table 4
Effect of UV exposure on the intrinsic viscosity (determined in xylene at 105 °C)

Sample designation	$[\eta]$ (ml/g) after UV exposure (h)				
	0	100	200	400	600
F1	84 [29,243]	83 [28,824]	82 [28,406]	80 [27,573]	80 [27,573]
OPE5	84 [29,243]	80 [27,573]	79 [27,159]	77 [26,332]	74 [25,101]
OPE10	83 [28,406]	79 [27,159]	76 [25,921]	74 [25,101]	70 [23,476]
OPE20	82 [28,406]	76 [25,921]	70 [23,476]	64 [21,073]	60 [19,497]
OPE30	80 [27,573]	73 [24,693]	65 [21,471]	61 [19,889]	52 [16,409]
OPE50	79 [27,159]	70 [23,476]	60 [19,497]	56 [17,942]	43 [13,051]

The numerals within parenthesis represent the M_v calculated using $[\eta] = 16.5 \times 10^{-3} [M_v]^{0.83}$.

Table 5
Effect of UV exposure on MFI (g/10 min at 190 °C @ 2.16 kg) of LDPE and OPE samples

Sample designation	MFI (g/10 min at 190 °C @ 2.16 kg)	
	0 h	600 h
F1	3.7	4.7
OPE5	4.0	19.2
OPE10	4.3	26.3
OPE20	6.3	54.1
OPE30	7.4	62.3
OPE50	8.0	69.2

the case of LDPE, the $[\eta]$ was almost unaffected by irradiation whereas it decreased in case of samples containing OPE.

3.2.5. MFI studies

MFI, which is indirectly a measure of molecular weight was also determined for LDPE and samples having OPE as additive (ranging 0.5–5% w/w) at 190 °C under a load of 2.16 kg. Samples containing 5% OPE exhibited 50% more MFI than that of neat LDPE. The MFI was also determined as a function of irradiation time. The results are tabulated in Table 5. Due to relatively larger quantities of sample required for analysis, MFI testing was performed only for two cases i.e. before and after 600 h of exposure.

3.2.6. Morphological characterisation

Changes in the surface morphology was investigated using scanning electron microscopy. Figs. 14 and 15 show the SEM of LDPE and LDPE containing 5% of OPE before and after degradation at a magnification of 2000 \times . The films had a smooth surface before irradiation, however, it developed some cracks and grooves after UV exposure. The extent of damage was much more pronounced in the samples containing OPE (Fig. 15a–c) as compared to neat LDPE. As is evident from SEM, the progressive deepening of the craters/grooves results in the formation of defects/or weaker points which in turn affects the mechanical properties.

3.3. Mechanism of degradation

The initiation of photo-degradation due to OPE can be attributed to the presence of oxidation products which are formed as a result of heat treatment. Hydroperoxides are

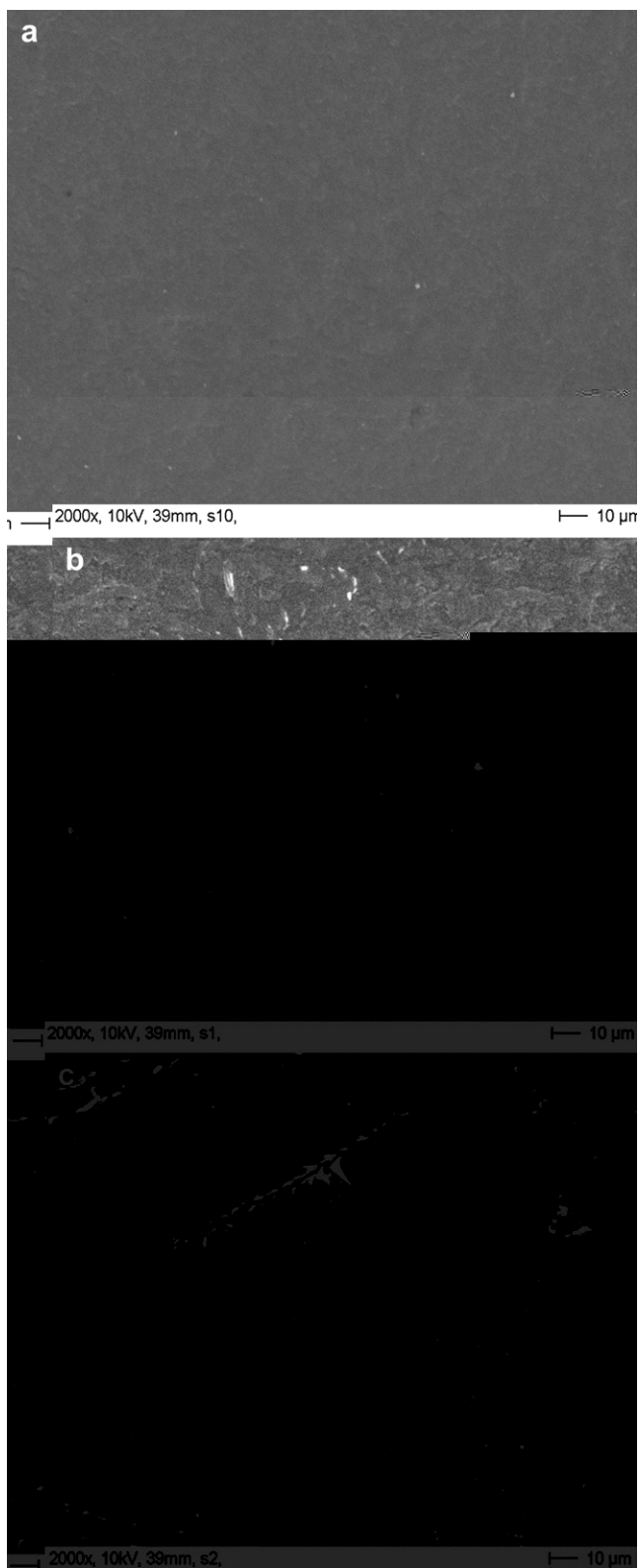


Fig. 14. SEM of (a) LDPE, (b) LDPE after 400 h of UV irradiation and (c) LDPE after 600 h of UV irradiation.

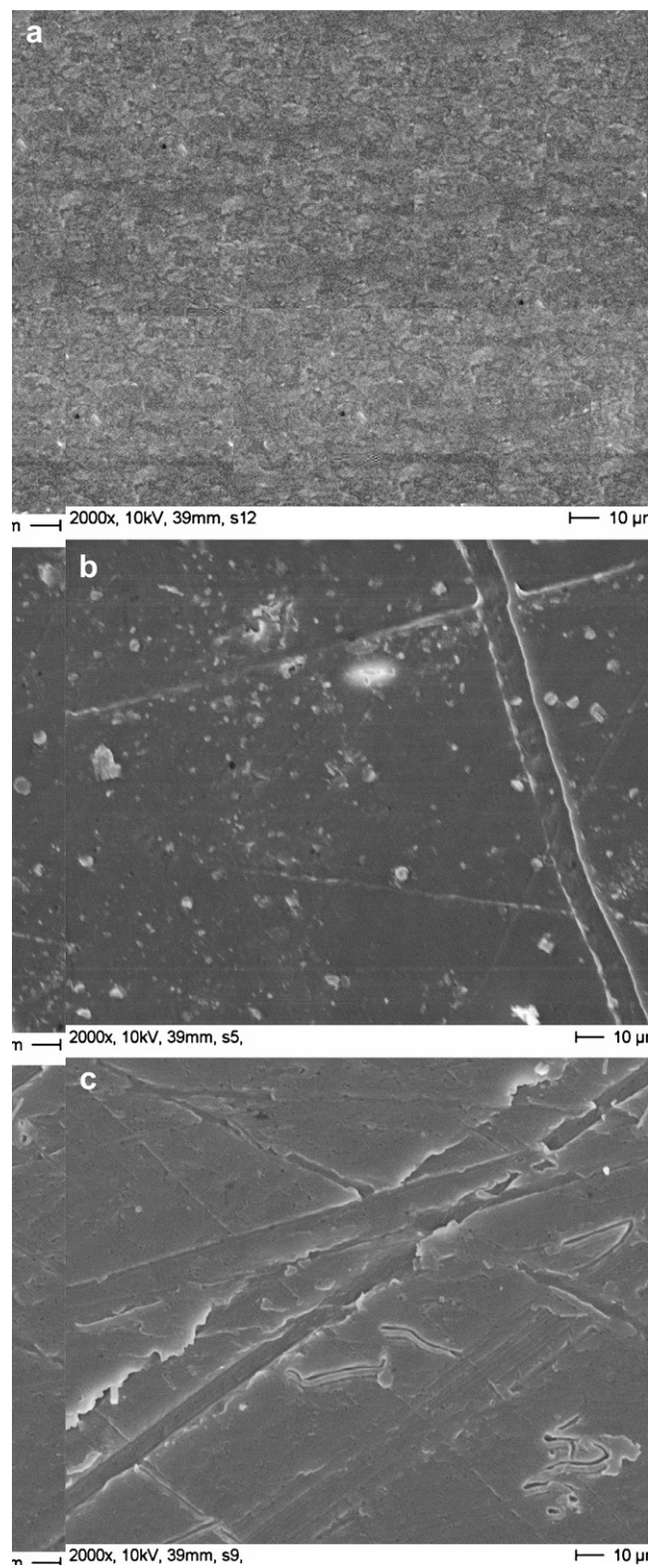
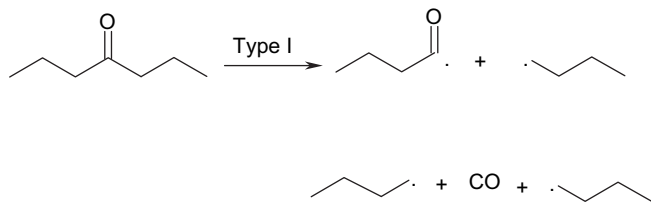


Fig. 15. SEM of (a) OPE5, (b) OPE5 after 400 h of UV irradiation and (c) OPE5 after 600 h of UV irradiation.



Scheme 1. Norrish type I reaction.

commonly the major products of oxidative degradation and are potentially powerful initiators of further degradation. Other functionalities introduced include carbonyl groups, which are basically a result of hydroperoxide decomposition. The carbonyl groups absorb UV radiation readily and get excited to singlet and triplet states which further decompose via Norrish reactions of type I, II and III [24].

Norrish type I reaction (Scheme 1) is a radical cleavage of the bond between the carbonyl group and α C-atom (α -scission), and is followed by formation of CO.

Norrish type II reaction (Scheme 2), a non-radical, intramolecular process occurs via the formation of a six membered cyclic intermediate. Abstraction of hydrogen from the γ carbon results in its subsequent decomposition into an unsaturated polymer chain end, and a polymer chain with an end carbonyl group.

Norrish type III reaction (Scheme 3) is also a non-radical chain scission; however, it involves the transfer of β hydrogen atom and leads to the formation of an olefin and an aldehyde.

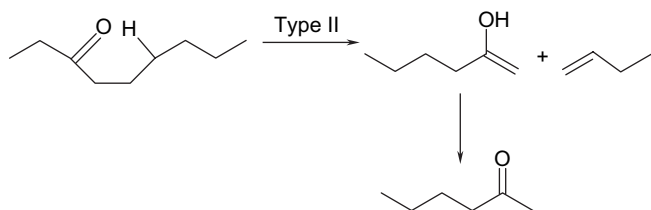
The activation energy of Norrish type reactions are different; the probability of NII ($E_a = 0.85$ kcal/mol) is higher than that of NI ($E_a = 4.8$ kcal/mol); the latter is however more probable at higher temperature.

4. Conclusions

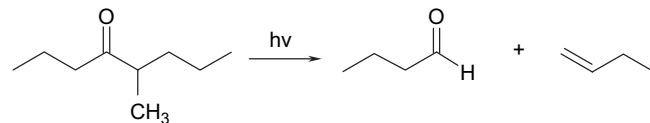
From these studies, it can be concluded that the photo-degradation of polyethylene can be accelerated using thermally degraded polyethylene obtained by using trace amounts of cobalt stearate. The amounts of oxidised polyethylene required to accelerate the degradation do not affect the initial properties of the film.

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Scheme 2. Norrish type II reaction.



Scheme 3. Norrish type III reaction.

interest and for providing the laboratory facilities. We sincerely thank Anshu Goel and Anand Kumar, SSPL, DRDO for X-ray analysis and SEM analysis, respectively.

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