

Degradation Behavior of Linear Low-Density Polyethylene Films Containing Prooxidants Under Accelerated Test Conditions

P. K. Roy,¹ P. Surekha,¹ C. Rajagopal,¹ V. Choudhary²

¹Centre for Fire, Explosive, and Environment Safety, Defence Research and Development Organization, Timarpur, Delhi 110054, India

²Centre for Polymer Science and Engineering, Indian Institute of Technology, Delhi, Hauz khas, Delhi 110016, India

Received 9 July 2007; accepted 20 December 2007

DOI 10.1002/app.27889

Published online 21 February 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article reports the results of studies on the photooxidative and thermooxidative degradation of linear low-density polyethylene (LLDPE) in the presence of cobalt stearate. Various amounts of cobalt stearate (0.1–0.9% w/w) blended with LLDPE and films of $70 \pm 5 \mu$ thickness were prepared by a film-blowing technique. The films were subjected to xenon arc weathering and air-oven aging tests (at 70°C) for extended time periods. We followed the chemical and physical changes induced as a result of aging by monitoring changes in the mechanical properties (tensile strength and elongation at break), carbonyl index, morphology (scanning electron microscopy), melt flow index, and

differential scanning calorimetry crystallinity. Cobalt stearate was highly effective in accelerating the photodegradation of LLDPE films at concentrations greater than 0.2% w/w. The kinetic parameters of degradation, as determined by nonisothermal thermogravimetric analysis, were estimated with the Flynn–Wall–Ozawa isoconversion technique, which was subsequently used to determine the effect of cobalt stearate on the theoretical lifetime of LLDPE. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2726–2733, 2008

Key words: activation energy; degradation; films; polyethylene (PE)

INTRODUCTION

In recent years, the use of polymeric materials for packaging applications has increased tremendously. In the present global scenario of the production of synthetic polymers, about 90% share is held by polymers with a carbon backbone, and the rest (10%) are held by condensation polymers.¹ About 35–45% of vinyl and vinylidene polymers go into the production of single-use disposable items, mainly for packaging applications. Polyolefins, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and polypropylene, are the main materials for packaging purposes, and these have received much criticism due to their lack of degradability. These polymers are relatively inert due to their hydrophobic nature and high molecular weight. It has been estimated that polyethylene biodegrades less than 0.5% in 100 years and about 1% if pre-exposed to sunlight for 2 years.²

A common strategy for obtaining plastics with enhanced degradability is to incorporate into them

certain additives that can accelerate the oxidative degradation process and thereby decrease the molecular weight of these polymers to a level where biodegradation can take over; hence, these type of polymers are often referred as *oxo-biodegradable*. Different approaches for developing these types of polyolefins have been adopted, including the incorporation of carbonyl functionalities during copolymerization and/or the addition of photoinitiating metal complexes,³ particularly transition metals such as Co, Mn, and Fe in the form of carboxylates. As a continuing part of our activity in the preparation of oxo-biodegradable polyolefins,^{4–7} we investigated the effect of cobalt stearate on the thermooxidative and photooxidative degradation of LLDPE films. LLDPE is expected to exhibit a higher rate of degradation than its linear analogue HDPE because of the presence of short-chain butene branches, which are introduced during the copolymerization process in the manufacturing stage.

The relative oxidizability of any polymer has been reported to depend on the number of tertiary carbon atoms in the main chain, and in general, the order of oxidizability is: Polypropylene > LDPE > LLDPE > HDPE.⁸ The effect of cobalt stearate on the degradation behavior of LDPE has been reported in our previous articles; however, such studies on LLDPE have

Correspondence to: P. K. Roy (pk_roy2000@yahoo.com).

not been performed, and hence, they were investigated in this study.

The kinetics of the degradation behavior of the formulations were also investigated with nonisothermal thermogravimetric analysis (TGA) in two different atmospheres, nitrogen and air, and were subsequently used to determine the theoretical lifetimes as a function of service temperature.

EXPERIMENTAL

Materials

Cobalt acetate, sodium hydroxide, stearic acid (analytical reagent grade E. Merck, KGa A, Darmstadt, Germany) were used without further purification. Commercial LLDPE (G-Lene F20S009, Uttar Pradesh, India) was used for the preparation of films. The melt flow index (MFI) of the polymer was 0.9 g/10 min under a load of 2.16 kg at 190°C, with a crystalline melting point of 120°C and a density of 0.95 g/cm³. The procedure for the synthesis of cobalt stearate, along with its detailed characterization, was reported previously.³

Preparation of the master batch

A master batch based on LLDPE and containing 3% w/w cobalt stearate was prepared with an extruder (Dayal make, Delhi, India) with a 19-mm screw with a length/diameter ratio of 22 : 1. The temperatures of the barrel and die sections of extruder were maintained at 130 and 140°C, respectively, and the extruder speed was maintained at 40 rpm.

Preparation of the LLDPE films

Films of 70 ± 5 μ thickness were prepared by the mixture of various concentrations of the master batch with LLDPE in an extruder attached to a film-blowing unit. The temperatures in the barrel sections of the extruder were maintained at 130 and 140°C, respectively, and that of the die head section was 150°C.

The sample codes of all of the formulations prepared along with their MFI values are reported in Table I. The blow-up ratio (BUR) and draw-down ratio (DDR) values were calculated according to the formulas $BUR = d/D$ and $DDR = H/H_0$, where d is the diameter of the bubble, D is the diameter of the die (2.75 cm), H is the die gap (2 mm), and H_0 is the thickness of the films.

Both BUR and DDR are representative of the extensibility of the material in the transverse and machine direction, respectively. Cobalt stearate did not affect the extensibility of LLDPE, and we pre-

TABLE I
Details of the Formulations and Their Sample Designations

Sample designation	Amount (g)		MFI (g/10 min at 190°C with a 2.16-kg load)
	LLDPE	Cobalt stearate	
F1	100	—	0.9
FCS10	100	0.1	1.0
FCS20	100	0.2	1.0
FCS50	100	0.50	1.0
FCS70	100	0.70	1.0
FCS90	100	0.90	1.1

pared all films by maintaining a BUR of 5.5 : 1 and a DDR of 14.2 : 1.

Degradation studies

Photooxidative degradation

Accelerated photodegradation studies were performed on a Xenon arc apparatus set (Atlas, Gelnhausen, Germany) at 550 W/m² as per ISO standard (ISO 4892-2:1994).⁹ The black panel temperature was set at 63°C for the entire exposure period.

Thermooxidative degradation

Thermooxidative testing was carried out by placement of the blown films in an air oven maintained at 70 ± 1°C for extended time periods^{10,11} and removal of the samples at regular time intervals for monitoring of the degradation.

Evaluation of degradation

Changes in the mechanical properties, that is, tensile strength and elongation at break, were monitored with a materials testing machine (JRagru Instruments, Delhi, India, JRI-TT25). Samples with a gauge length of 500 mm and a width of 10 mm were cut from the films for the measurement of the mechanical properties as per ASTM 882–85. The testing speed was maintained at 500 mm/min as the films did not break at lower strain rates. About five samples were tested for each experiment, and the average value is reported as the mean plus or minus the standard error.

Structural changes upon exposure were investigated with Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the films were recorded with a Biorad (FTS-40) (Hercules, CA) spectrophotometer. The carbonyl index (CI) was used to characterize the degree of degradation of polyethylene. It has been defined as the ratio of absorbance of carbonyl band around 1740 cm⁻¹ and internal thickness band at 2020 cm⁻¹.¹²

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

The thermal properties were investigated with a PerkinElmer Diamond Simultaneous TGA–differential thermal analysis–differential scanning calorimetry (DSC) instrument (Shelton, CT) under a nitrogen atmosphere. The percentage crystallinity was calculated from DSC traces with the following relation:

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

where ΔH_f is the melting enthalpy of sample and $\Delta H_{f(100\% \text{ crystalline})}$ is the melting enthalpy of 100% crystalline polyethylene, which was reported in the literature as 285 J/g.¹³ Elemental analysis was performed by determination of the C, H, and O content with an elemental analyzer (Thermo Finnigan, Flash EA, Milan, Italy) to quantify the content of oxygen in the degraded samples. The MFIs of all resins were measured on a MFI tester (International Equipments, Mumbai, India) at 190°C as per ASTM D 1238. The extrudates were cut at regular intervals of 60 s after the application of 2.16 kg of dead weight. Ten extrudates were cut, and the average value is reported.

Kinetic evaluations

The kinetics of degradation were evaluated by nonisothermal TGA under a flowing atmosphere of nitrogen and air at a purge rate of 200 mL/min. The sample was equilibrated to 200°C before it was heated to 550°C at different heating rates (3–10°C/min). The actual heating rate was calculated from temperature measurements made during the period of polymer decomposition.

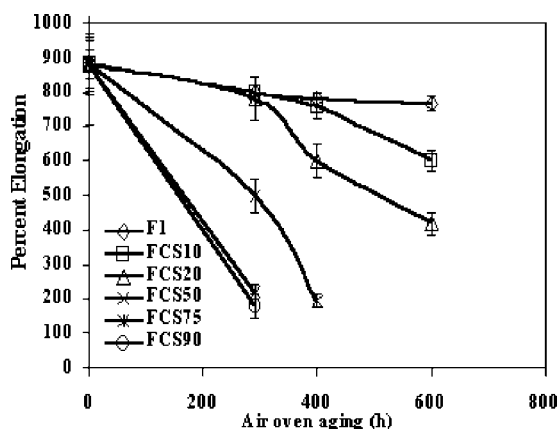


Figure 1 Effect of air-oven aging on the elongation at break of the formulations.

RESULTS AND DISCUSSION

Mechanical properties of the films

Figures 1 and 2 present the effect of air-oven aging and xenon arc weathering on the longitudinal percentage elongation at break (%EB) of the LLDPE films and other formulations. Mechanical properties, such as tensile yield strength (TS) and %EB, have been reported to be direct indicators of degradation.^{14,15} However, because the effect of the degrading environment is more pronounced on %EB; therefore, only the variation in %EB has been presented here. The initial mechanical properties of the films were not affected by processing in the presence of cobalt stearate. Neat LLDPE films retained high levels of TS and %EB for the entire exposure time. On the other hand, LLDPE films containing cobalt stearate exhibited a significant decrease in both properties. Films containing 0.5% w/w cobalt stearate after 400 h and those containing > 0.5% w/w after 270 h of air-oven aging could not be tested as they turned brittle and broke during handling. Xenon arc weathering was found to cause much more rapid degradation than air-oven aging, and films containing 0.5% w/w cobalt stearate turned brittle within 100 h of xenon exposure, as compared to 400 h of air-oven aging.

Structural characterization

Figures 3 and 4 show the changes in the FTIR spectra of F1 and FCS90 due to thermooxidation and xenon arc weathering. As shown, degradation resulted in the formation of several functional groups, particularly in FCS90. The most significant changes

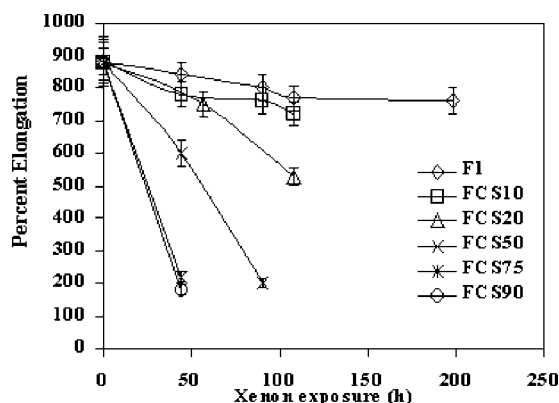


Figure 2 Effect of xenon arc weathering on the elongation at break of the formulations.

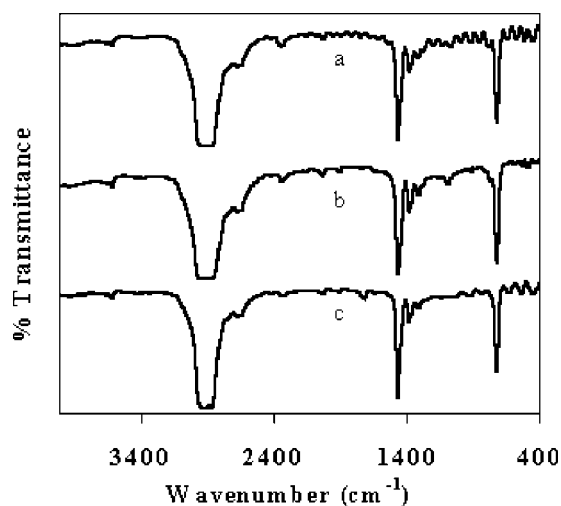


Figure 3 FTIR of F1: (a) 0 h, (b) 200 h of xenon arc weathering, and (c) 600 h of thermooxidation.

were in the carbonyl ($1785\text{--}1700\text{ cm}^{-1}$), amorphous (1300 cm^{-1}), and hydroxyl (3400 cm^{-1}) regions. The absorption bands increased in intensity, and at the same time, a band broadening was also observed, which indicated the presence of multiple oxidation products overlapping in the same region. However, the change in the FTIR spectra of F1 was insignificant. CI, which characterizes the degree of degradation of polyethylene,¹² was calculated by the baseline method, and the results are displayed in Figures 5 and 6.

CI of neat LLDPE increased from 0.8 to 1.3 after 200 h of xenon arc aging. However, the incorporation of cobalt stearate into the polymer led to a significant increase in CI in a relatively shorter time span. It is generally believed that polyethylene films enter into the decay stage at CI values greater than 6. This implies that LLDPEs containing a higher con-

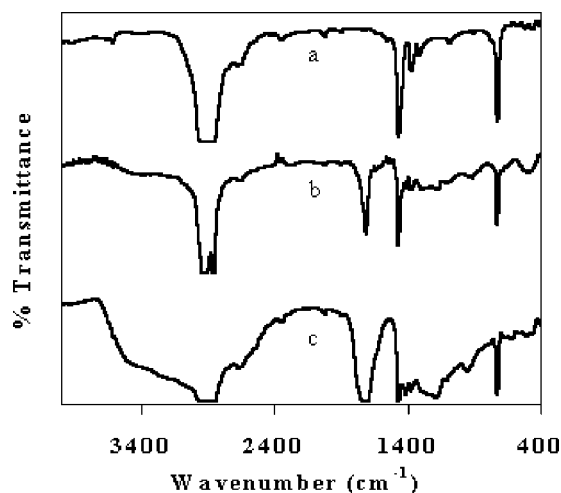


Figure 4 FTIR of FCS90: (a) 0 h, (b) 50 h of xenon arc weathering, and (c) 200 h of thermooxidation.

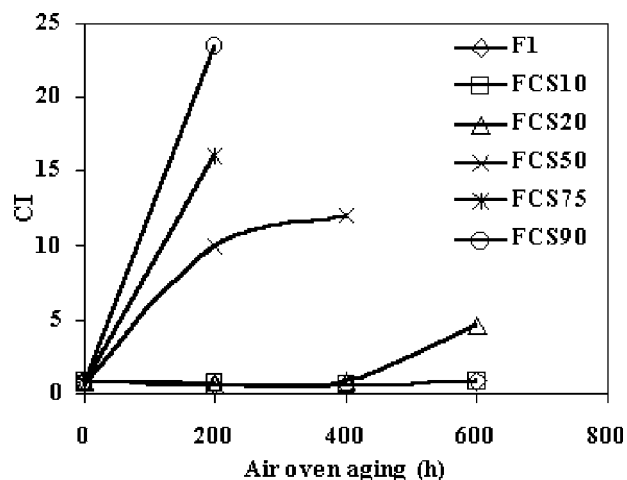


Figure 5 Dependence of CI on the cobalt stearate concentration and thermooxidation time.

centration ($>0.2\%$ w/w) of cobalt stearate would start decaying within 50 h of xenon lamp exposure, whereas those containing lesser quantities would require longer time periods. From the results, we concluded that the concentration of cobalt stearate could be varied to obtain films with specific and controllable lifetimes. In HDPE, the concentration of cobalt stearate has been reported to show no appreciable effect on the degradation behavior;¹⁶ however, in LLDPE, it showed a significant effect. Actually, LLDPE contains butene branches, which are capable of acting as weak linkages. The degradation leads to a generation of stable tertiary radicals on the surface of LLDPE, which are absent in the case of HDPE.

Elemental analysis of the samples was also performed to confirm the assimilation of oxygen into the polymer matrix due to aging. Initially, the carbon and hydrogen contents in all of the samples were 85.7 ± 0.2 and $14.3 \pm 0.1\%$, respectively, with the

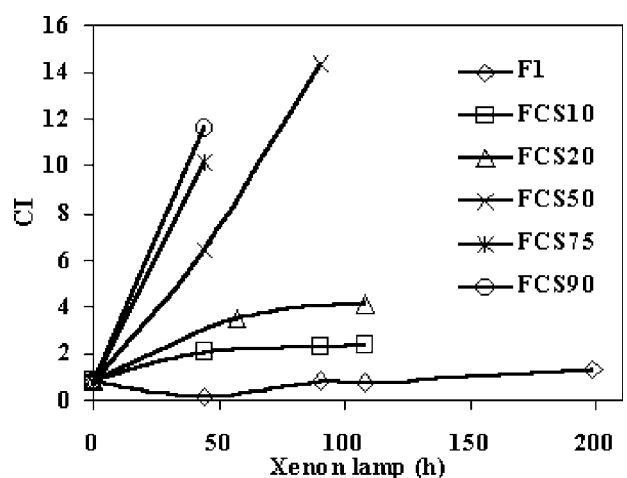


Figure 6 Dependence of CI on the cobalt stearate concentration and xenon arc weathering duration.

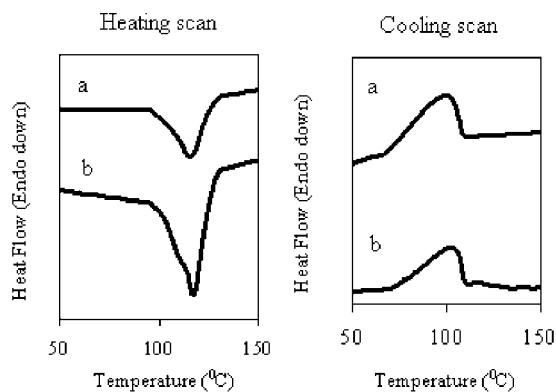


Figure 7 Heating and cooling scans for FCS90: (a) initially and (b) after 50 h of xenon arc exposure.

content of oxygen being negligible. After 200 h of xenon exposure, the oxygen content in neat LLDPE samples increased to 1.18%, whereas that of samples containing cobalt stearate increased to a much higher extent. For FCS75 and FCS90, the oxygen contents increased to 4.01 and 4.22%, respectively, after 50 h of xenon lamp exposure. This further confirmed that degradation led to the formation of functional groups containing oxygen, such as aldehydes, ketones, esters, and lactones.

Thermal characterization

An endothermic transition due to melting at 120°C was observed in all of the formulations, which indicated that blending with cobalt stearate did not affect the melting behavior of the base polymer. Cobalt stearate exhibited a melting point of about 121°C, which was responsible for good mixing during the extrusion process. The heating and cooling scans of FCS90 initially and after 50 h of xenon arc exposure are presented in Figure 7. As shown in Figure 7, degradation did not result in any change in the melting point of the polymer. This could be explained on the basis that the initial degradative

changes occurred primarily in the amorphous regions of the polymer, which left the crystalline regions unaffected, and hence, the melting point remained unchanged. The aging process led to a slight broadening of the polyethylene melting endotherm and crystallization exotherm, which was also reflected in the increased ΔH_f and ΔH_c values and the DSC crystallinity (Table II). LLDPE is a semicrystalline polymer in which the polymeric chains pass through both the crystalline and amorphous regions, and due to the gradual depletion of the amorphous phase, the crystallinity of the samples increased. This increase could also be partially attributed to the changes in the crystalline sizes, molecular weight differences that were brought about by chain breaking and secondary recrystallization.

MFI

MFI, which is indirectly a measure of molecular weight, was also determined for all of the formulations at 190°C under a load of 2.16 kg. All of the samples exhibited an MFI of 0.9 ± 0.1 , which indicated that the processing stage did not induce significant chain scission and/or crosslinking. The increase in MFI as a result of both degradative environments is presented in Table III. The MFI of the samples could not be determined for films containing greater than 0.5% w/w cobalt stearate after exposure, as it flowed freely under the test conditions

Morphological characterization

Changes in the surface morphology were investigated with scanning electron microscopy (SEM). Figure 8 shows the SEM photographs of F1 and FCS90 before and after degradation at a magnification of 2000 \times . As is apparent from the figure, the surface of nondegraded LLDPE was smooth, without cracks and free from defects. However, it developed some cracks and grooves after xenon lamp exposure. The

TABLE II
Results of ΔH_f , ΔH_c , and Crystallinity in LLDPE Before and After 50 h of Xenon Arc Weathering in the Presence and Absence of Cobalt Stearate

Sample designation	ΔH_f (J/g)		Crystallinity (%)		ΔH_c (J/g)	
	0 h	50 h	0 h	50 h	0 h	50 h
F1	128	131	44.9	45.9	140	142
FCS10	132	132	46.3	46.3	141	143
FCS20	131	132	45.9	46.3	140	144
FCS50	130	142	45.6	49.8	142	147
FCS70	128	144	44.9	50.2	143	148
FCS90	130	146	45.6	51.2	143	149

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

TABLE III
Effect of Thermal and Xenon Arc Weathering on MFI

Sample designation	MFI (g/10 min with a 2.16-kg load)		
	Xenon lamp exposure (h)		Thermal exposure (h)
	0	200	600
F1	1.00	2.1	1.5
FCS10	1.00	3.1	2.5
FCS20	1.00	7.1	8.9
FCS50	1.00	— ^a	— ^a
FCS70	1.00	— ^a	— ^a
FCS90	1.00	— ^a	— ^a

^a The MFI could not be determined as it flowed under the test conditions.

extent of the damage was much more pronounced in the samples containing cobalt stearate [Fig. 8(d)] compared to neat LLDPE (8b). It was this progressive deepening of the craters/grooves that resulted

in the formation of defects/or weaker points that finally affected the mechanical properties.

Kinetics of degradation

Multiple constant heating rates: Flynn–Wall–Ozawa method

The apparent kinetic parameters for degradation were determined by measurement of the weight loss during material decomposition by nonisothermal thermogravimetry at different heating rates, which was then fitted into the Arrhenius equation.

$$\frac{d\alpha}{dt} = Ae^{\frac{-E_a}{RT}}(1 - \alpha)^n$$

where A is the frequency factor, n is the reaction order, E_a is the activation energy for degradation, R is the gas constant, α is the conversion, and T is the

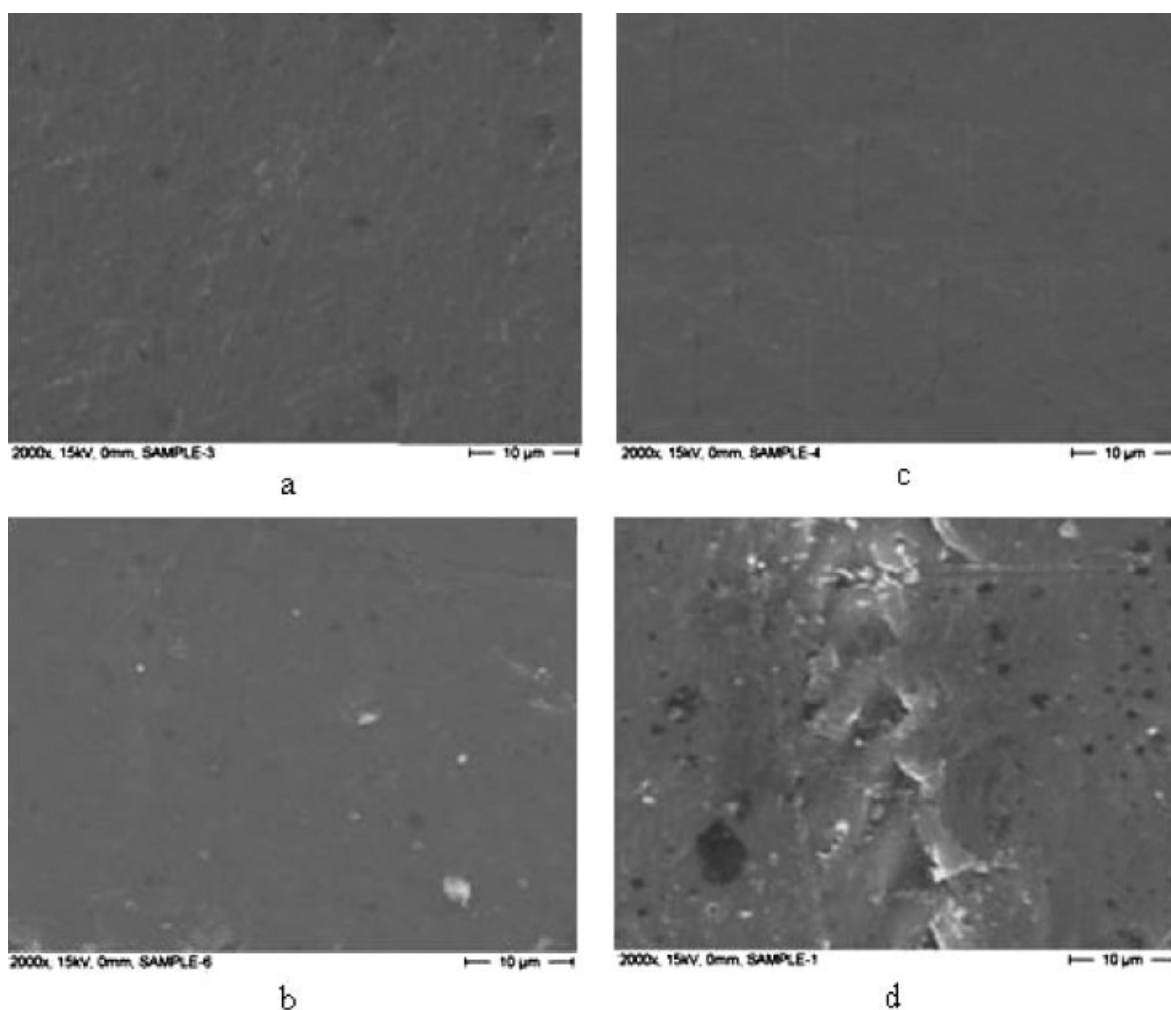


Figure 8 SEM photographs: (a) F1, 0 h; (b) F1, 400 h of air-oven aging; (c) FCS90, 0 h; and (d) FCS90, 50 h of xenon arc weathering.

absolute temperature. E_a was then determined with the Flynn–Ozawa equation:^{17,18}

$$\log \beta \cong 0.457 \left(\frac{-E_a}{RT} \right) + \left[\log \left(\frac{AE_a}{R} \right) - \log F(\alpha) - 2.315 \right]$$

where β is the heating rate. Thus, at the same conversion, E_a was obtained from the plot of $\log \beta$ against $1/T$.

Degradation kinetics

The isoconversional graph between the logarithm of heating rate ($\log \beta$) and $1/T$ for different values of percentage conversion for FCS90 and F1 were plotted and were found to be almost parallel straight lines in a nitrogen atmosphere (Fig. 9). The variation of isoconversional E_a with conversion for F1 and FCS90 in air and nitrogen atmospheres is presented in Figure 10. For neat LLDPE, E_a increased moderately from 200 to 280 kJ/mol throughout the degradation processes (nitrogen atmosphere). LLDPE contains olefinic branches, which can act as weak links, and the initial degradation required a relatively low energy (~ 200 kJ/mol). As these weak links were consumed, the limiting step of degradation process shifted toward the degradation initiated by random scission, which required relatively higher E_a values (~ 280 kJ/mol). For FCS90, E_a was much lower (~ 110 – 190 kJ/mol), which indicated that cobalt stearate was capable of catalyzing the degradation process in polyethylene by providing an alternate route for degradation.

The thermal degradation process in air was a complex process and did not exhibit any systematic temperature shifts with heating rate. Similar behavior was observed in the case of LDPE also.¹⁹ Degradation in the presence of air led to the formation of

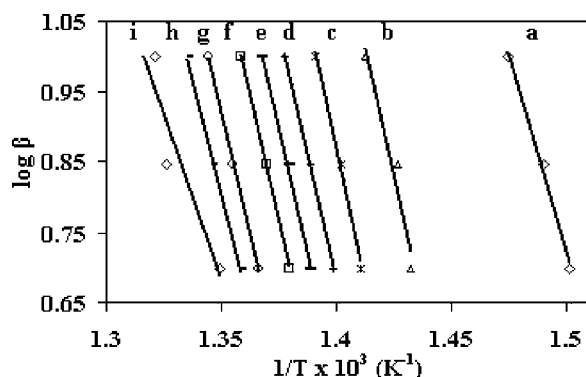


Figure 9 Plot of $\log \beta$ versus $1000/T$ for F1 in a nitrogen atmosphere: (a) 5, (b) 15, (c) 25, (d) 35, (e) 45, (f) 55, (g) 75, (h) 85, and (i) 95% conversion.

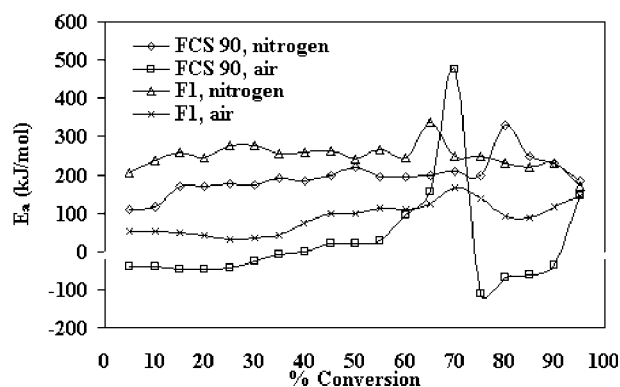


Figure 10 Variation of E_a with the conversion percentage.

several oxidation products, including peroxides, acids, and alcohols. The initial degradation process ($\alpha < 0.2$) led to the formation of peroxides, and the calculated value of E_a in this period (~ 80 – 90 kJ/mol) was consistent with the energy associated with decomposition of peroxides.²⁰ However, after the conversion reached 20%, E_a increased, and the degradation became exothermic at about 400°C . This temperature was consistent with the ignition temperature of many carboxylic acids, which predominate at the later stages of degradation.²⁰ Therefore, the isoconversion plots of $\log \beta$ versus $1/T$ in an air atmosphere were not parallel, as in the nitrogen atmosphere. The variation of isoconversional E_a with conversion in air atmosphere is also presented in Figure 10. It is clear from Figure 10 that E_a was much lower in the air atmosphere than in the nitrogen atmosphere. The erratic changes in E_a indicated that the multistep decomposition in air was a complex mass loss process involving several different reactions with varied mechanisms.

Lifetime predictions

The apparent kinetic parameters calculated from this study were used to determine the theoretical lifetimes of the formulations. The estimated lifetime of a polymer to failure has been defined as the time when the mass loss reaches 5 wt %, that is, $\alpha = 0.05$.^{21,22} The lifetime (t_f) has been estimated by

$$t_f = \frac{0.0513}{A} \exp \frac{E_a}{RT} \quad (n = 1)$$

As determined by the kinetic data and the previous equation, the estimated values of lifetime in a nitrogen atmosphere at a mass loss of 5% at various temperatures are presented in Table IV. The theoretically calculated lifetime in nitrogen at 25°C decreased from 1.3×10^{19} to 1.3×10^{10} min as the concentra-

TABLE IV
Dependence of the Lifetime (Nitrogen Atmosphere) on the Service Temperature

Sample	Lifetime (min)					
	25°C	50°C	75°C	100°C	150°C	200°C
F1	1.28×10^{19}	2.13×10^{16}	8.89×10^{13}	7.72×10^{11}	3.14×10^8	6.65×10^{15}
FCS 90	1.36×10^{10}	4.51×10^8	2.43×10^7	1.95×10^6	3.04×10^4	1.15×10^3

tion of cobalt stearate increased to 0.9% w/w. The lifetime was strongly dependent on the service temperature and decreased dramatically as the temperature increased from 25 to 200°C. The kinetics of the degradation process depended strongly on the chain mobility, which further depended on the physical state of the polymer. The chain mobility was much higher in the molten state than in the solid state, which thereby made the predictions relatively inaccurate at temperatures lower than the melting point. Nonetheless, these studies confirmed the prooxidative nature of cobalt stearate on the degradation of LLDPE.

CONCLUSIONS

Accelerated aging studies on LLDPE films containing cobalt stearate as a prooxidant (at various concentrations) were systematically performed. The studies revealed that the photoinitiating and thermoinitiating activities of cobalt stearate increased progressively with increasing prooxidant concentration. However, at higher concentrations (>0.5%), the degradation started off very early and thereby rendered the compositions impractical to be used for packaging applications.

The authors are thankful to Shri A. K. Kapoor, Director of the Centre for Fire, Explosive, and Environment Safety, for taking a keen interest in this work and for providing the laboratory facilities. Thanks are also due to Ashok Kapoor, Solid State Physics Laboratory, for the SEM and to P. K. Rai for the elemental analysis.

References

- Cheillini, E.; Corti, A.; D'Antone, S.; Baci, R. *Polym Degrad Stab* 2006, 91, 2739.
- Khabbaz, F.; Albertsson, A. C. *J Appl Polym Sci* 2001, 79, 2309.
- David, C.; Trojan, M.; Daro, A.; Demarteau, W. *Polym Degrad Stab* 1992, 37, 233.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Raman, R.; Choudhary, V. *J Appl Polym Sci* 2006, 99, 236.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Chatterjee, S. N.; Choudhary, V. *Polym Degrad Stab* 2005, 90, 577.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Chatterjee, S. N.; Choudhary, V. *Polym Degrad Stab* 2006, 91, 1791.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *Polym Degrad Stab* 2006, 91, 1980.
- Rabek, J. F. *Polymer Photodegradation*; Chapman & Hall: London, 1995.
- ISO 4892-2: *Plastics—Methods of Exposure to Laboratory Light Sources: Part 2: Xenon Arc Sources*; International Organization for Standardization: 1994.
- Sharma, N.; Chang, L. P.; Chu, Y. L.; Ismail, H.; Ishiaku, U. S.; Ishak, Z. A. *Polym Degrad Stab* 2001, 71, 381.
- Bikaris, D.; Prinos, J.; Perrier, C.; Panayiotou, C. *Polym Degrad Stab* 1997, 57, 313.
- Amin, M. U.; Scott, G. *Eur Polym J* 1974, 10, 1019.
- Seeba, M.; Servens, C.; Pouyet, J. *J Appl Polym Sci* 1992, 45, 1049.
- Qureshi, F. S.; Amin, M. B.; Maadhah, A. G.; Hamid, S. H. *J Polym Eng* 1990, 9, 67.
- Madfa, H.-A.; Mohammed, Z.; Kassem, M. E. *Polym Degrad Stab* 1998, 62, 105.
- Osawa, Z.; Kurisu, N.; Nagashima, K.; Nankano, K. *J Appl Polym Sci* 1979, 23, 3583.
- Ozawa, T. *Thermochim Acta* 1986, 100, 109.
- Flynn, J. H.; Wall, L. A. *J Polym Sci Part B: Polym Lett* 1966, 4, 323.
- Roy, P. K.; Surekha, P.; Rajagopal, C.; Choudhary, V. *Exp Polym Lett* 2007, 1, 208.
- Peterson, J. D.; Vyazovkin, S.; Wight, C. A. *Macromol Chem Phys* 2001, 202, 775.
- Li, X. G.; Huang, M. R. *Polym Degrad Stab* 1999, 64, 81.
- Huang, M. R.; Li, X. G. *J Appl Polym Sci* 1998, 68, 293.