

Study on the Degradation of Low-Density Polyethylene in the Presence of Cobalt Stearate and Benzil

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ABSTRACT: Degradable polymers are in great demand for a variety of applications such as packaging, agriculture, and medicine. Polyolefins blended with photodegradants/biodegradants are potential candidates for replacing the nondegradable thermoplastics in areas where litter abatement poses problems. In the present article, the effect of metallic photoinitiators like cobalt stearate and a combination of metallic/nonmetallic photoinitiators, i.e., a mixture of cobalt stearate and benzil, on the photooxidative degradation of low-density polyethylene (LDPE) films have been investigated. Attempts have been made to correlate the results as a function of mixed additives. Films of LDPE containing varying amounts of cobalt stearate and a combina-

tion of benzil and cobalt stearate were prepared. The photodegradation of these films has been monitored by various techniques like FTIR spectroscopy, differential thermal analysis, and density and viscosity measurements. Cobalt stearate was highly effective in accelerating the photodegradation of LDPE films at low concentrations. The addition of benzil to cobalt stearate decreased the rate of photodegradation compared to cobalt stearate alone. A retarding effect was observed when benzil alone was added to LDPE. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 236–243, 2006

Key words: degradation; polyethylene; FTIR; viscosity

INTRODUCTION

The synthetic polymer industry has brought great benefits to modern society. Plastics have gained a unique position in the packaging industry for a number of different reasons including high tensile strength, elongation at break, good barrier properties against water-borne organisms, lower cost, higher energy effectiveness, light weight, and good water resistance.¹ However, in the past few years, plastics have been a target of much criticism due to their lack of degradability. The growing environmental concern has led research workers to design degradable polymers for products that have a short life cycle or are impractical to recycle such as household waste, agricultural waste, and other disposables.² A way to obtain plastics with enhanced degradability is to incorporate into common synthetic polymers different additives that accelerate the oxidative process, thereby decreasing the molecular weight of the polymer to a level where biodegradation becomes possible. Photodegradable polymers are produced by introducing chromophoric groups intentionally into the polymer structure by copolymerization or by mixing a photoinitiating additive with the polymer. The additives

normally used for the initiation of photooxidation are organosoluble transition metal ions, aromatic ketones, dithiocarbamates, acetyl acetonates, etc., which act as thermal and/or photooxidants for the polymer.^{3–5} The role of metals/metallic compounds on the photodegradation of polyethylene have been extensively studied by several authors.^{6–9} Aromatic ketones also act as effective photoinitiators for polyolefins.^{10,11} However, the effect of cobalt stearate with or without aromatic diketone photoinitiator on the rates of photooxidative degradation has not been studied systematically. Therefore, it was of interest to investigate systematically the effect of concentration of cobalt stearate, benzil, and a combination of cobalt stearate and benzil on the photodegradation of low-density polyethylene (LDPE).

EXPERIMENTAL

Materials

Benzil, cobalt acetate, sodium hydroxide, stearic acid, and isopropanol (analytical grade, E Merck) were used without further purification. Commercial film grade LDPE, Indothene 24FS 040, was used for preparation of films. The MFI for the polymer was 4 g/10 min, with a crystalline melting point of 110°C and density of 0.92 g/cc. It contained a conventional thermal stabilizer of undisclosed composition. Cobalt

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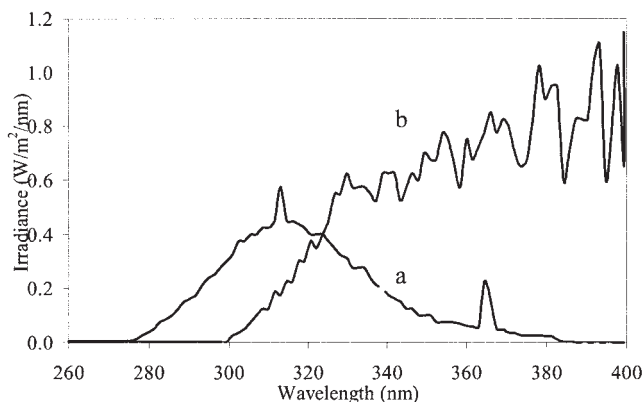


Figure 1 Representative spectral power distribution: (a) UV B; (b) sunlight.

stearate was prepared by the double decomposition technique of sodium stearate with cobalt acetate according to the procedure reported in the literature.¹² Cobalt stearate synthesized in the laboratory was characterized using a GBC atomic absorption spectrophotometer (Model No. 932AA). The content of metal in cobalt stearate was determined by digesting the sample in conc. HCl followed by FAAS and was found to be 6.24%. Elemental analysis was carried out using an Elementar CHNS analyzer (Vario III). The content of C and H was 68.79 and 11.68%, respectively. These results indicate that the molecular structural formula of cobalt stearate is similar to $(C_{17}H_{35}COO)_3 Co \cdot 2H_2O$, whose theoretical C and H content is 68.64 and 11.12%, respectively.

Preparation of films

A Brabender plasticorder Labstation with a 19-mm-diameter screw of L : D :: 25 : 1, extruder speed of 20

L/min, associated with a roller having a draw speed of 3 m/min, was used to prepare films. Several samples were prepared by blending varying amounts of cobalt stearate (0.05–0.25% w/w) with polyethylene to form films of 70 μm thickness. The LDPE chips were initially dry blended with varying amounts of cobalt stearate ranging from 0.05 to 0.25% w/w in a tumbler and were then fed to the Brabender. The films were obtained by maintaining the following temperatures in the different zones of the extruder, i.e., feed zone, 150°C; compression zone, 165°C; metering zone, 175°C; and die zone, 190°C. Similarly, LDPE films containing benzil (0.1–0.5% w/w) alone and a mixture of cobalt stearate: benzil in the % w/w ratio of 0.1 : 0.05, 0.1 : 0.1, and 0.1 : 0.15 were used to prepare films of 70 μm thickness.

Photodegradation studies

Accelerated photodegradation studies were carried out using four 40-W sunlamps (Philips make) emitting UV-B light in the wavelength range of 280 and 370 nm with maxima at 313 nm. Figure 1 shows the representative spectral power distribution (SPD) of the UV-B lamps compared to the SPD of noontime, summer sunlight.¹³ These lamps were chosen as they include the shortest wavelengths found in the sunlight at the earth's surface and are responsible for most polymer damage. Samples were mounted on racks positioned at a distance of 5 cm from the lamps and the temperature in the cabinet was maintained at $30 \pm 1^\circ\text{C}$. Samples after irradiation were collected at regular intervals of 50, 100, 200, 400, and 600 h, respectively, to evaluate the effect of irradiation time on degradation.

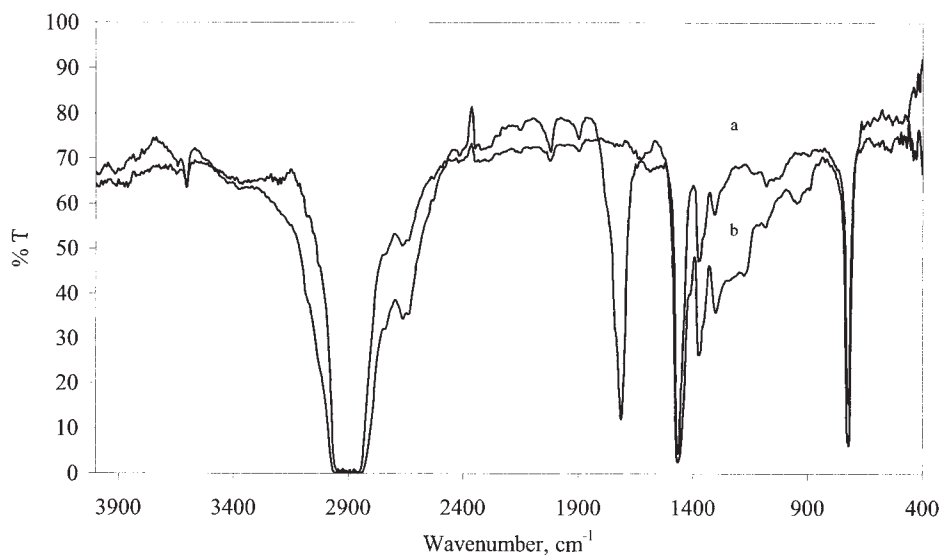


Figure 2 FTIR of LDPE films after UV exposure of: (a) 0 h, (b) 600 h.

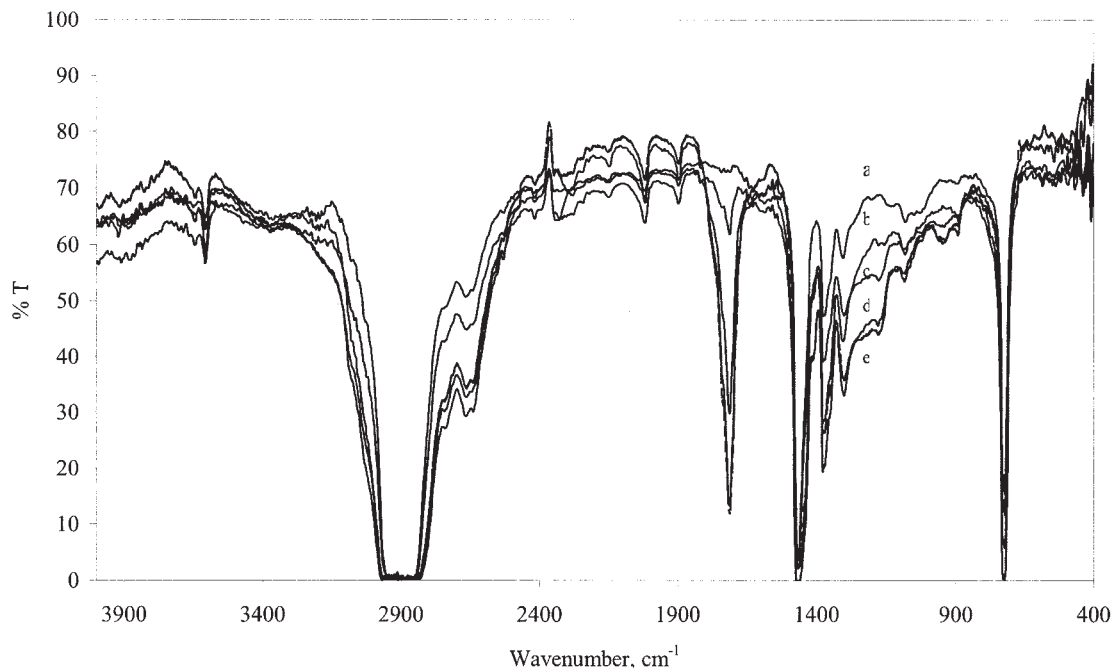


Figure 3 FTIR spectra of films containing 0.1% cobalt stearate due to UV exposure of: (a) 0 h, (b) 50 h, (c) 200 h, (d) 400 h, (e) 600 h.

Analytical characterization

Photodegradation of the films was evaluated by FTIR, differential thermal analysis (DTA), density and viscosity measurements.

Structural changes during degradation were evaluated by recording the FTIR spectra of films using a Bio-Rad (FTS-40) spectrophotometer in the wavelength range 400–4000 cm^{-1} .

The thermal behavior was investigated using Setaram Setsys TG-DTA 16 for recording DTA traces in nitrogen atmosphere.

The apparent density was measured using a Sartorius analytical balance (Model No. ME215S) equipped with density measurement accessory (Model No. YDK01). Isopropanol with a purity of 99.5% (density 0.78 g/cm^3) was used as the liquid medium. LDPE films were dissolved in xylene and the intrinsic viscosity $[\eta]$ was measured using a 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 equation¹⁴

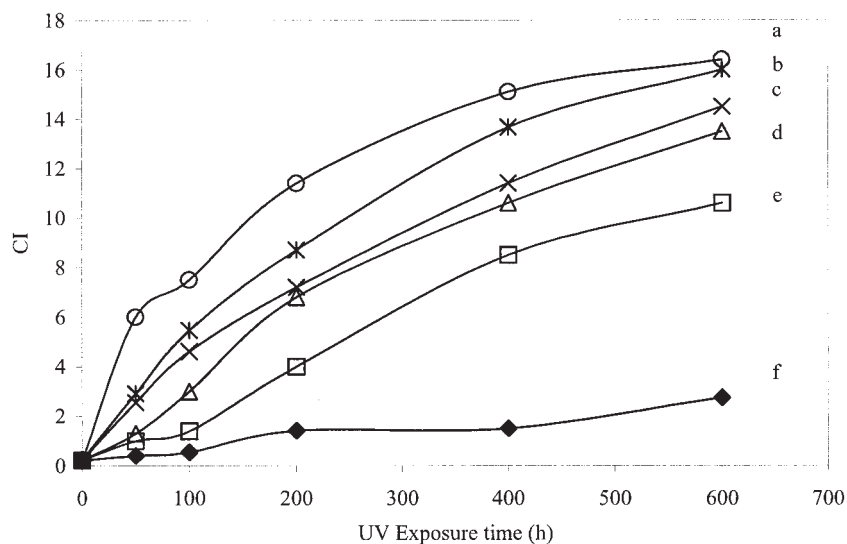


Figure 4 Effect of cobalt stearate concentration on the photooxidation of LDPE films: (a) 0.25% cobalt stearate, (b) 0.2% cobalt stearate, (c) 0.15% cobalt stearate, (d) 0.1% cobalt stearate, (e) 0.05% cobalt stearate, (f) neat LDPE.

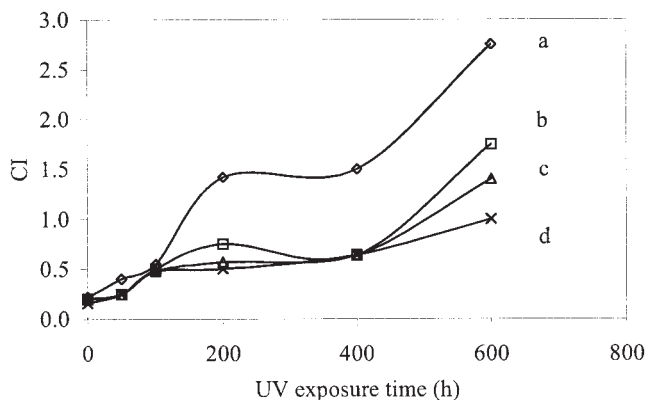


Figure 5 Effect of concentration of benzil on CI: (a) neat LDPE, (b) 0.1% benzil, (c) 0.3% benzil, (d) 0.5% benzil.

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

RESULTS AND DISCUSSION

Structural characterization

Figures 2 and 3 show the FTIR spectra of LDPE films and LDPE + 0.1% (w/w) cobalt stearate, respectively, before and after 600 h of irradiation. The FTIR spectra clearly show that the photooxidative degradation of LDPE resulted in the formation of several functional groups; however, the amount of such functional groups is much more in the presence of cobalt stearate (Fig. 3). Most significant changes in the FTIR spectra were in the carbonyl ($1785\text{--}1700\text{ cm}^{-1}$), amorphous (1300 cm^{-1}), and hydroxyl regions (3400 cm^{-1}). The absorption band around 1740 cm^{-1} , due to the C = O stretching, increases in intensity and at the same time a band broadening is observed, which indicates the presence of more than one oxidation product. The carbonyl band can be assigned to C = O stretching

TABLE I
Intrinsic Viscosity of Films after Exposure to UV Radiation

Concentration of cobalt stearate (%)	Intrinsic viscosity (mL/g) after exposure time (h)					
	0	50	100	200	400	600
0	84	83	83	82	80	80
0.05	84	80	79	75	63	43
0.1	83	79	75	64	48	36
0.15	83	78	70	60	45	33
0.2	83	75	68	57	43	31
0.25	83	73	62	48	33	27

vibrations in aldehydes and/or esters (1733 cm^{-1}), carboxylic acid groups (1700 cm^{-1}), and γ lactones (1780 cm^{-1}).¹⁵⁻¹⁸ The carbonyl index (CI), defined as the ratio of absorbance of carbonyl around 1740 cm^{-1} and internal thickness band at 2020 cm^{-1} , which characterize the degree of photooxidation of polyethylene,¹⁹ was calculated by the baseline method. Figure 4 shows the plot of CI as a function of time in LDPE and LDPE containing varying amounts of cobalt stearate. CI of pure LDPE increased from 0.25 to 2.75 after 600 h of UV exposure. However, incorporation of cobalt stearate into the polymer led to a significant increase in the CI in a relatively short span of time. It is generally believed that polyethylene films enter into the decay stage at CI greater than 6. This implies that LDPE containing higher concentration ($>0.2\%$) of cobalt stearate start decaying within 100 h of UV exposure while those containing up to 0.2% cobalt stearate require about 200 h. The sample containing 0.25% cobalt stearate became fragile and brittle after 400 h, while samples containing lesser quantities of cobalt stearate required a minimum 600 h of UV exposure. From the results, it can be concluded that the concen-

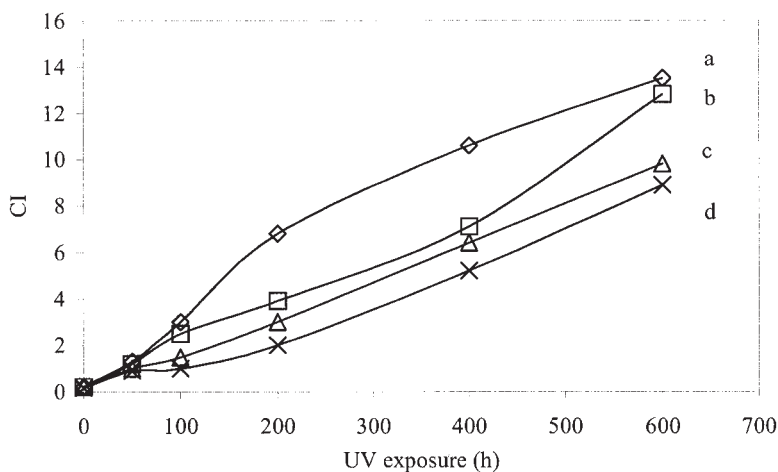


Figure 6 Effect of benzil concentration on photooxidation of LDPE in the presence of 0.1% cobalt stearate: (a) no benzil, (b) 0.05% benzil, (c) 0.1% benzil, (d) 0.15% benzil.

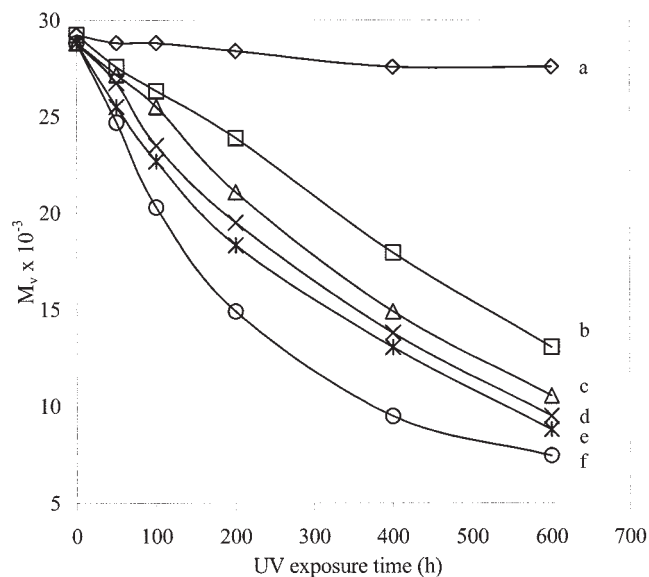


Figure 7 Effect of cobalt stearate concentration on the M_v of LDPE films during photooxidation: (a) neat LDPE, (b) 0.05% cobalt stearate, (c) 0.1% cobalt stearate, (d) 0.15% cobalt stearate, (e) 0.2% cobalt stearate, (f) 0.25% cobalt stearate.

tration of cobalt stearate can be varied according to the expected lifetime. In high-density polyethylene, the concentration of cobalt stearate did not show any appreciable effect on the lifetime of the film;⁶ however, in LDPE it shows a significant effect, i.e., the films became brittle after 100 h if the concentration of cobalt stearate is greater than 0.2%. Since the photooxidation occurs mainly in the amorphous regions of the polymer, which is higher in the case of LDPE than its higher density analog, it can be concluded that LDPE containing cobalt stearate will show a higher rate of

degradation. Also, the tertiary carbon radicals, present more in LDPE, are more stable than secondary and primary radicals, thus requiring less activation energy to be formed. Figures 5 and 6 show the plot of CI as a function of time in the case of LDPE film having varying concentration of benzil (0.1–0.5%) and a combination of benzil and cobalt stearate. In all cases the CI value was lower than that of the LDPE films (without additive). These results clearly show that cobalt stearate accelerates the photooxidative degradation of LDPE whereas benzil, despite having two ketonic groups, retards the degradation. The retarding effect of benzil can be explained on the basis of radical recombination.

The results are indicative of the harmful effect of UV-B radiation on the expected lifetime of the films. The accelerated UV degradation study results, however, cannot be correlated directly to those of natural exposure, as the incident solar energy varies according to the season, presence and absence of clouds, rains, and turbidity of the atmosphere.^{20,21} The lamps used during the course of this study emit radiation much below the normal sunlight cut-on and thereby cause degradation by mechanisms that don't normally occur when materials are exposed to sunlight.

Molecular characterization

It is generally agreed that the LDPE films containing prooxidant enter into the embrittlement stage after the M_n decreases to less than 5000. The results of the $[\eta]$ and M_v obtained using the value of $K = 16.5 \times 10^{-3}$ and $a = 0.83$ are given in Table I. In LDPE a marginal decrease in $[\eta]$ was observed after 600 h of exposure. However, in the presence of 0.05% w/w cobalt stearate $[\eta]$ decreased from 84 to 43 mL/g after 600 h of UV

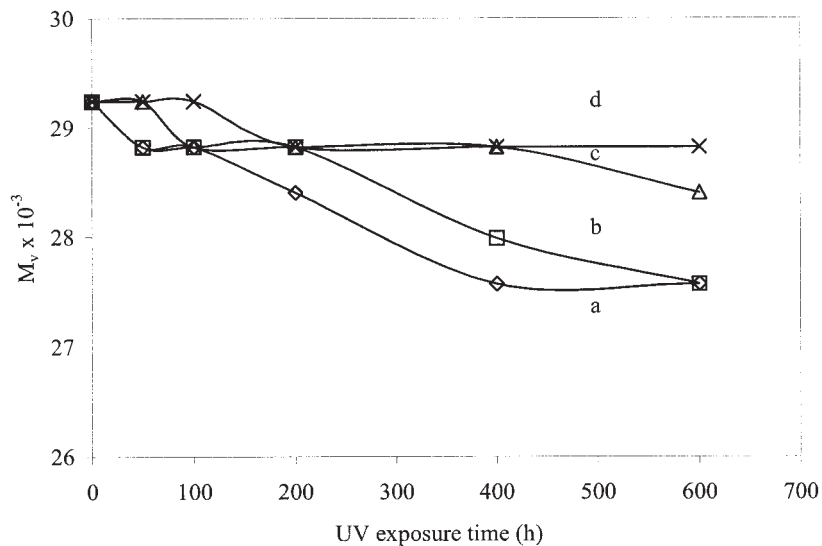


Figure 8 Effect of addition of benzil on M_v of LDPE films: (a) neat LDPE, (b) 0.1 benzil, (c) 0.3% benzil, (d) 0.5% benzil.

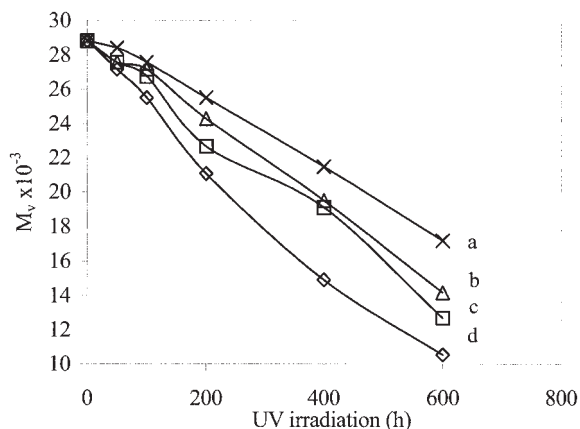


Figure 9 Effect of addition of benzil on M_v of LDPE films containing 0.1% CS: (a) no benzil, (b) 0.05% benzil, (c) 0.1% benzil, (d) 0.15% benzil.

exposure. A decrease in $[\eta]$ as well as molecular weight increased with increasing amounts of cobalt stearate. In the presence of cobalt stearate, brittle films were obtained as the molecular weight after 600 h of exposure was in the range of 7400–13,000 for the samples having varying amounts of cobalt stearate (Fig. 7). LDPE films containing varying amounts of benzil showed no/marginal change in the molecular weight after irradiation (Fig. 8). Samples containing 0.1% w/w cobalt stearate along with varying concentration of benzil showed less change in molecular weight, which further decreased with increasing concentration of benzil (Fig. 9).

Thermal characterization

An endothermic transition due to melting at 113°C was observed in LDPE, which remained unaltered by blending with varying amounts of cobalt stearate and benzil. Figure 10 depicts the slight changes in the calorimetric behavior that take place during photooxidation. New thermal energy absorption peaks (shoulders and a broadening of the endotherm) were observed in the case of LDPE films containing cobalt stearate. LDPE films containing a combination of benzil and cobalt stearate also showed a similar behavior. However, no changes were observed in the case of films containing benzil alone. Surprisingly, no change was observed in the melting point of the polymer after photooxidation in any of the samples, irrespective of the photoinitiator. This can be attributed to the fact that the initial degradative changes take place in the amorphous regions of the polymer, leaving the crystalline regions unaffected. The slight broadening of the endothermic melting peaks can be attributed to the changes in the crystalline sizes, molecular weight differences that are brought about by chain breaking and secondary recrystallization.

Density measurements

As illustrated by Figures 11 and 12, the apparent density increases with time of weathering exposure. The increase in density in samples containing cobalt stearate and a mixture of cobalt stearate and benzil can be attributed to the increase in the crystallinity of the

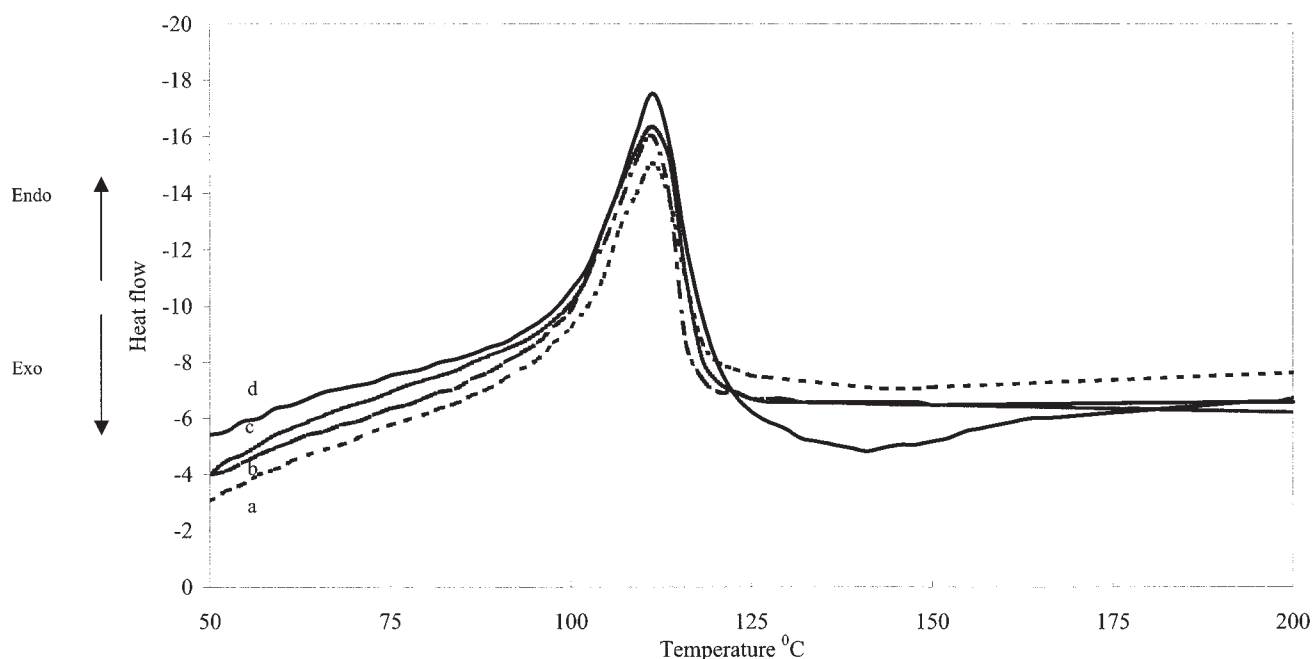


Figure 10 DTA scans of LDPE films containing: (a) no additive before UV exposure, (b) 0.1% cobalt stearate before UV exposure, (c) no additive after 600 h of UV exposure, (d) 0.1% cobalt stearate after 600 h of UV exposure.

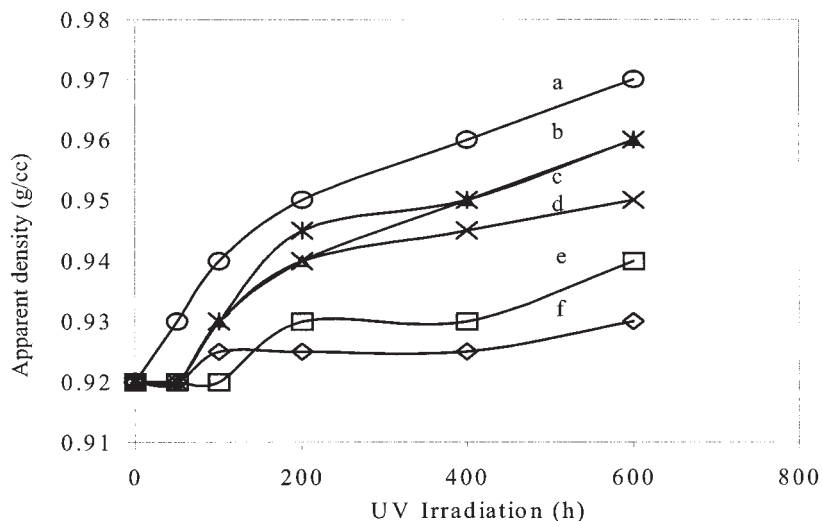


Figure 11 Effect of UV exposure on apparent density on films: (a) 0.25% cobalt stearate, (b) 0.2% cobalt stearate, (c) 0.15% cobalt stearate, (d) 0.1% cobalt stearate, (e) 0.05% cobalt stearate, (f) neat LDPE.

sample. During the aging process the material becomes more and more dense due to tighter packing and incorporation of oxygen into the amorphous regions of the polymer, rendering the polymer heavier. The density of LDPE increased from 0.92 to 0.93g/cc over a period of 600 h of UV exposure. The increase in density was more in the case of films containing cobalt stearate compared to films containing a combination of cobalt stearate and benzil as photoinitiator. The increase in apparent density was 1.08% for LDPE with no additive, 5.43% for LDPE containing 0.25% cobalt stearate, and 2.1% for LDPE containing 0.1% cobalt stearate and 0.15% benzil. No change in density was observed in the case of films containing benzil alone, irrespective of the concentration.

Soil burial tests

The soil burial tests were performed on the soil, which was sand loam in texture having total organic carbon

(28,880 mg/kg), phosphorus (110mg/kg), and a pH of 7.21. The soil constituents are clay (3%), silt (20%), and sand (77%). Strips of accurately weighed test samples (10 × 2 cm) were buried in soil at a depth of 1 in. in perforated plastic cups to permit the access of microorganisms and moisture. These were subjected to ambient conditions of moisture and temperature. They were watered periodically to replenish any loss of evaporation. After every month the samples were carefully taken out of the wet soil and washed repeatedly with water and finally with 70% ethanol. The films were then dried at 40°C under reduced pressure to constant weight.

Percentage degradation in the samples was calculated using the equation

$$\% \text{ Degradation of blends} = \frac{100(W_0 - W_d)}{W_0}, \quad (1)$$

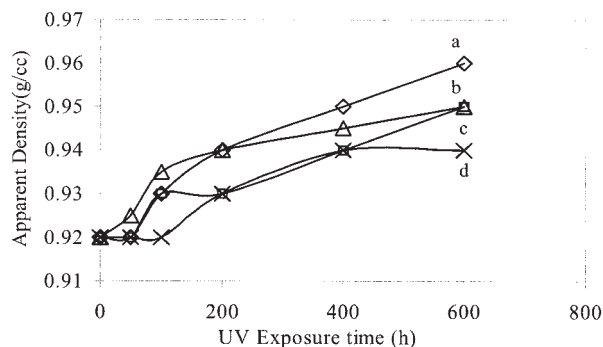


Figure 12 Effect of benzil on apparent density of films containing 0.1% CS: (a) no benzil, (b) 0.05% benzil, (c) 0.1% benzil, (d) 0.15% benzil.

where W_0 is the weight of the film initially and W_d is the weight of the films after degradation. The films were checked for transparency and development of cracks and pits as well as for discolorations or any change in color at various stages of degradation. After 12 months of soil burial, the films containing cobalt stearate and a combination of cobalt stearate and benzil became brittle and broke off, but no physical change was observed in the case of LDPE in the same time period. However, the weight loss in the samples was insignificant (0.33%) in the case of films containing 0.10% cobalt stearate after 12 months as against 0.19% in the case of LDPE (Fig. 13). The results indi-

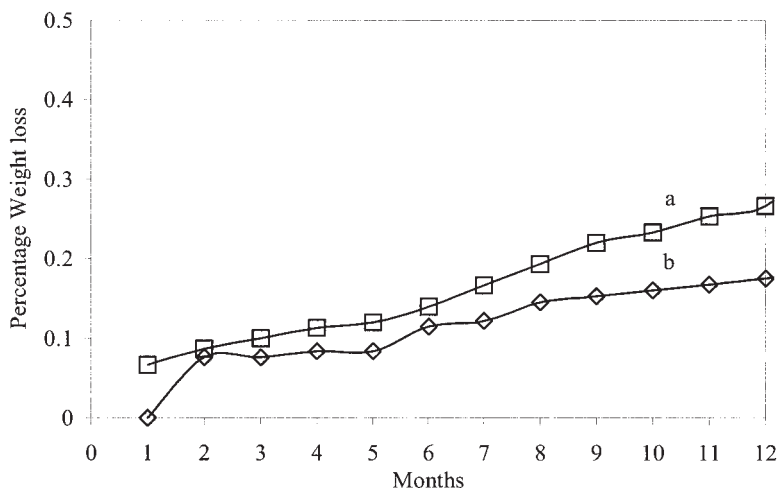


Figure 13 Weight loss of films containing: (a) 0.25% cobalt stearate, (b) neat LDPE.

cate that these films are not amenable to biodegradation.

CONCLUSIONS

The accelerated UV aging of LDPE films containing photoinitiators like cobalt stearate and benzil in varying concentration was systematically studied. The role of photoinitiator on photooxidation of polymer is very complicated and depends on many factors including its ability to transfer its energy to decompose the hydroperoxides to radicals and so on. The results indicate that photoinitiating activity of the cobalt stearate increases progressively with increase in the concentration. However, at higher concentrations (>0.2%), the photooxidation starts off very early, thereby rendering the compositions impractical to be used for packaging applications. Aromatic diketone seems to exhibit a retarding effect on the photooxidizing ability of the cobalt stearate and the effect is proportional to the concentration of the additive, as indicated by lower CI and lower apparent density. The increase in density of the sample with aging indicates an increase in polymer crystallinity.

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