

Comparative Effects of Cobalt Carboxylates on the Thermo-Oxidative Degradation of LDPE Films

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ABSTRACT: This article reports the effect of three cobalt carboxylates—cobalt stearate (CoSt₃), cobalt palmitate (CoPal₃), and cobalt laurate (CoLau₃)—on the thermo-oxidative degradation of low-density polyethylene (LDPE) films prepared by sheeting process. The carboxylates were blended with LDPE in the concentration range of 0.05–0.2% (w/w). The degradation was monitored by techniques such as FTIR spectroscopy, change in the mechanical properties (tensile strength and elongation at break), viscometry, surface electron microscopy, melt flow index measurements, and apparent density measurements. Studies indicate that films containing these additives are highly susceptible to thermo-

oxidative degradation. Oxygen containing functionalities such as carbonyl and vinyl species are generated on the surface of polyethylene because of thermo-oxidation, as indicated by FTIR studies. This oxidative process is accelerated in the presence of cobalt carboxylates. The degradation of LDPE was found to increase proportionally with concentration as well as with increasing chain length of the cobalt carboxylate, and follow the order CoSt₃ > CoPal₃ > CoLau₃. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3758–3765, 2007

Key words: cobalt carboxylate; LDPE; pro-oxidant; thermo-oxidation

INTRODUCTION

In the past few years, packaging polymers, particularly polyethylene, have received much criticism because of their lack of degradability.¹ Besides packaging, low-density polyethylene (LDPE) is extensively used for a variety of applications, such as medicine and agriculture, thereby resulting in its increased production. Polyethylene has a relatively low specific gravity (0.91–0.99 g/cm³), as a result of which it forms huge amounts of visible waste because of littering. This has led to the partial ban on the use of this versatile polymer, especially in the packaging sector. Polyethylene blended with photodegradants/biodegradants are potential candidates for replacing nondegradable thermoplastics in areas where litter management poses challenges.

The most frequently adopted approach to design degradable polymers has been to incorporate different pro-oxidative additives into synthetic polymers, that accelerate the oxidative process, thereby decreasing the molecular weight of the polymer to a level at which biodegradation becomes feasible. Previous studies reveal that in most cases biodegradation has to be preceded by abiotic attack on the polymer chain.² The additives normally used for enhancing abiotic degradation include organic photosensitizers such as aro-

matic ketones and their derivatives or organosoluble transition metal ions in the form of carboxylates which act both as thermal and/or photo-oxidant^{3–6} for the polymer.

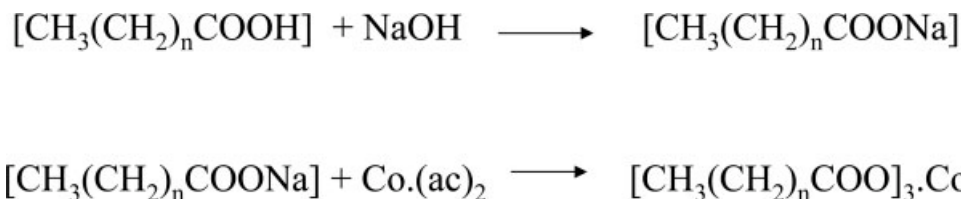
Cobalt carboxylates have been widely employed as an additive for the development of photodegradable polymers. The effect of cobalt carboxylates on the photo-oxidative degradation of LDPE has been investigated and reported in our previous paper.⁷ However, there have been no studies on the thermo-oxidative degradation of LDPE containing cobalt carboxylates. It is well known that most of the municipal waste, including its plastic fraction, finds its way to the landfill sites and gets buried in the soil, where UV light is unable to penetrate. It has been reported previously that temperature soars to 70°C during composting conditions in such landfill sites.⁸ Therefore it was considered of interest to investigate the effect of cobalt carboxylates on the thermo-oxidative degradation of LDPE. The present work deals with such studies with an aim to investigate the effect of chain length and concentration of these additives on the degradation of LDPE.

EXPERIMENTAL

Materials

Cobalt acetate, sodium hydroxide, stearic acid, lauric acid, palmitic acid (AR grade, E. Merck, KGaA, Darmstadt, Germany) were used without further purifica-

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Scheme 1 Double decomposition technique for synthesis of cobalt carboxylate.

tion. Film-grade low density polyethylene (LDPE) (Indothene, 24FS040, Reliance Industries, Vadodara, India) was used for the preparation of the films. The experimentally determined characteristics of the polymer are as follows: melt flow index (MFI), 4 g/10 min; melting point, 110°C; and density, 0.920 g/cm³. Milli Q ultrapure water was used throughout the course of this work.

Synthesis and characterization of cobalt carboxylate

Cobalt laurate, cobalt palmitate, and cobalt stearate were synthesized by the reaction of cobalt acetate with sodium laurate, sodium palmitate, and sodium stearate respectively, according to the procedure reported in the literature⁹ (Scheme 1).

The concentration of cobalt in the carboxylate was determined using a GBC atomic absorption spectrophotometer (GBC model 932AA, Victoria, Australia). Other characteristics of the additive, namely ash content, apparent density, surface area, nonvolatile content, WATER content, and free fatty acid content, have been reported previously.⁷

Film preparation

Varying amounts of cobalt carboxylate (0.05–0.2% w/w) were blended with LDPE by conventional extrusion, followed by sheeting process using the procedure described in our previous papers.^{4–5,7} The

details of samples, along with their designation, are given in Table I.

Thermo-oxidative tests

The thermo-oxidative tests were carried out by placing the extruded films in an air oven at 70°C for 600 h.^{10,11}

Evaluation of degradation

The changes due to thermo-oxidation were monitored by recording changes in FTIR, tensile properties, M_w , MFI, surface morphology, and density. The mechanical properties, i.e., tensile strength and elongation at break, were monitored using a Materials testing machine (Jragrau, model JRI-TT25, Delhi, India). Film samples with a gauge length of 100 mm and width of 10 mm were cut for tensile strength measurements as per ASTM 882-85.¹² The speed of testing was 100 mm/min. The tests were undertaken in an air-conditioned environment at 20°C and a relative humidity of 65%. Five replicates for each sample (for each type of additive and concentration) were tested and the average value has been reported.

Structural changes upon exposure were investigated using FTIR spectroscopy. FTIR spectra were recorded at regular intervals using an FTIR SPECTROPHOTOMETER (BIORAD model FTS-40, Hercules, CA). Carbonyl index (CI), as calculated by baseline method,¹³ was used to characterize the degree of degradation of polyethylene.

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

The apparent density of films was measured using an analytical balance (Sartorius model ME215S, Goettingen, Germany) equipped with density measurement accessory (MODEL YDK01) as per the standard procedure.¹⁴ Isopropanol with a purity of 99.5% (density, 0.78 g/cm³) was used as the liquid medium.

Scanning electron microscopy was performed to investigate the change in the morphology due to thermo-oxidative degradation. Sample surfaces were sputtered with gold using usual techniques and then

analyzed under surface electron microscope (JEOL model JSM-840, Tokyo, Japan) using a voltage of 10 kV. Photomicrographs were taken at uniform magnification of 2000×.

The MFI of the polymer was determined according to ASTM D 1238¹⁵ at 190°C with 2.16 kg load using MFI testing equipment (International Equipments, Mumbai, India).

LDPE films were dissolved in xylene and the intrinsic viscosity $[\eta]$ was measured using Ubbelohde

TABLE I
Details of Formulations and Their Sample Designation

Sample designation	Amount (g)			
	LDPE	Cobalt stearate	Cobalt palmitate	Cobalt laurate
F1	100	–	–	–
FCS5	100	0.05	–	–
FCS10	100	0.10	–	–
FCS15	100	0.15	–	–
FCS20	100	0.20	–	–
FCP5	100	–	0.05	–
FCP10	100	–	0.10	–
FCP15	100	–	0.15	–
FCP20	100	–	0.20	–
FCL5	100	–	–	0.05
FCL10	100	–	–	0.10
FCL15	100	–	–	0.15
FCL20	100	–	–	0.20

lohde suspension level viscometer at 105°C in a thermostatted oil bath (Photonix Instruments, India), with silicone oil as the medium. The viscosity average molecular weight was calculated using Mark Houwink equation

$$[\eta] = KM_{\eta}^a$$

where $[\eta]$ is the intrinsic viscosity and K and a are Mark Houwink constants. The K and a values for LDPE in xylene solvent are 16.5×10^{-3} and 0.83 respectively.¹⁶

RESULTS AND DISCUSSION

Mechanical properties

Figures 1 and 2 represent the changes in the mechanical properties of the formulations due to thermo-oxidation, which are considered as direct indicators of degradation.^{17,18} The standard deviations have not been included in the figures for clarity; however, they are in the range of $\pm 5\%$. The initial tensile strength and elongation at break of all the formulations were similar, implying that one time processing in the presence of these additives does not cause significant degradation. Thermal exposure at 70°C led to a rapid decrease in these properties and was also found to be proportional to the amount and nature of the cobalt carboxylate. This is more clear from the results on tensile testing of films containing cobalt carboxylate at low concentration ($<0.1\%$ w/w).

As is apparent from Figure 2, all films containing cobalt carboxylates show a rapid elongation loss of $>70\%$ within 100 h of exposure at lower concentrations ($<0.1\%$ w/w). At higher concentrations, i.e., $>0.1\%$ (w/w) of the additive, this elongational loss increases to $\sim 99\%$ within 100 h of exposure and the films could not be tested further. The decrease in the elongation

of LDPE at low concentration of cobalt carboxylate confirms that chain length has a pronounced effect on the rate of degradation. At higher concentrations, the degradation was very rapid, resulting in degradation in very short time and hence the effect of chain length is not apparent. Neat LDPE films however lost $\sim 25\%$ of their elongation within 100 h of exposure and retained 40% of their elongation even after 600 h of thermo-oxidation.

FTIR study

The degradation was also assessed by monitoring the changes in the FTIR spectra. Figures 3 and 4 show the change in the FTIR spectra of LDPE films as well as films containing cobalt stearate after thermo-oxidation. Carbonyl Index has been used as a parameter to monitor the degradation. The FTIR spectra show evolution of various functional groups, especially absorption in the carbonyl region ($1785\text{--}1700\text{ cm}^{-1}$), hydroxyl region (3400 cm^{-1}), and amorphous regions (1300 cm^{-1}). The absorption band around 1714 cm^{-1} , which can be assigned to the C=O stretching ketonic functionality, grows in intensity and exhibits band broadening, which indicates the presence of more than one oxidation product. Thermo-oxidation leads to the generation of several oxygen containing functionalities, such as aldehydes and/or esters (1733 cm^{-1}), carboxylic acid groups (1700 cm^{-1}), and γ lactones (1780 cm^{-1}),^{19–22} which absorb in the same region, leading to the observed band broadening. All films containing cobalt carboxylate showed similar changes in the spectra and the change was more pronounced at higher concentrations of the additive or after longer exposure period. LDPE films in the absence of cobalt carboxylates, however, show very little change in these regions. The increase in CI with exposure has been presented in Table II. The absorption due to other groups generated, e.g., hydroxyl, vinyl, acetaldehyde, and vinylidene, has been reported to follow the same trend as that of carbonyl.²³ Polyethylene reportedly enters the decay stage when the CI increases to 6.³ As can be seen, the CI of F1 does not increase to 6 even after 600 h of thermo-oxidation, while all the films containing cobalt carboxylates start decaying within 100 h of exposure, depending on the nature and concentration of the additive.

Apparent density measurements

The apparent density of LDPE increases marginally from 0.92 to 0.93 g/cm^3 after 600 h of thermal exposure (Table III), while the density of the films containing cobalt carboxylates increases to $\sim 0.95\text{ g/cm}^3$ after 100 h of exposure. The increase in density can be attributed to the increase in crystallinity as the material becomes denser because of closer packing and

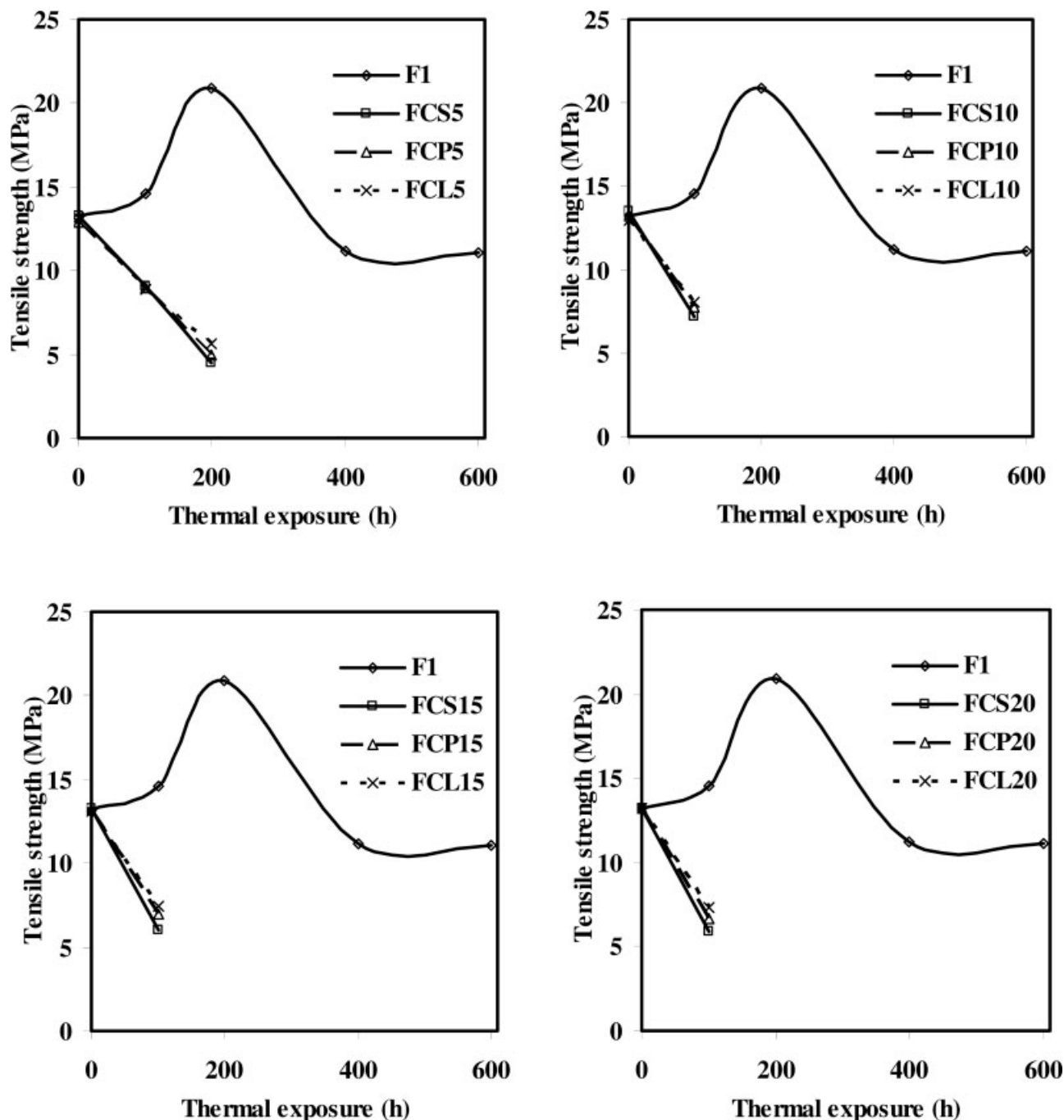


Figure 1 Effect of thermal exposure on the tensile strength of formulations.

also because of incorporation of oxygen into the polymeric matrix.¹⁹

Molecular weight measurements

It has been reported that LDPE films containing prooxidants enter the embrittlement stage after the M_n decreases to ~ 5000 g/mol.³ Table IV shows that the viscosity-average molecular weight (M_v) of LDPE films containing cobalt carboxylate decreases dramatically upon thermal exposure and reaches ~ 5000 after

100 h of exposure from an initial value of $\sim 28,000$. Similar decrease in M_v was observed in all samples containing cobalt carboxylates, and the extent of decrease was found to be proportional to the amount of additive.

MFI measurements

The decrease in molecular weight was confirmed by determining the increase in the MFI of samples with heat aging. Initial MFI of all the formulations was

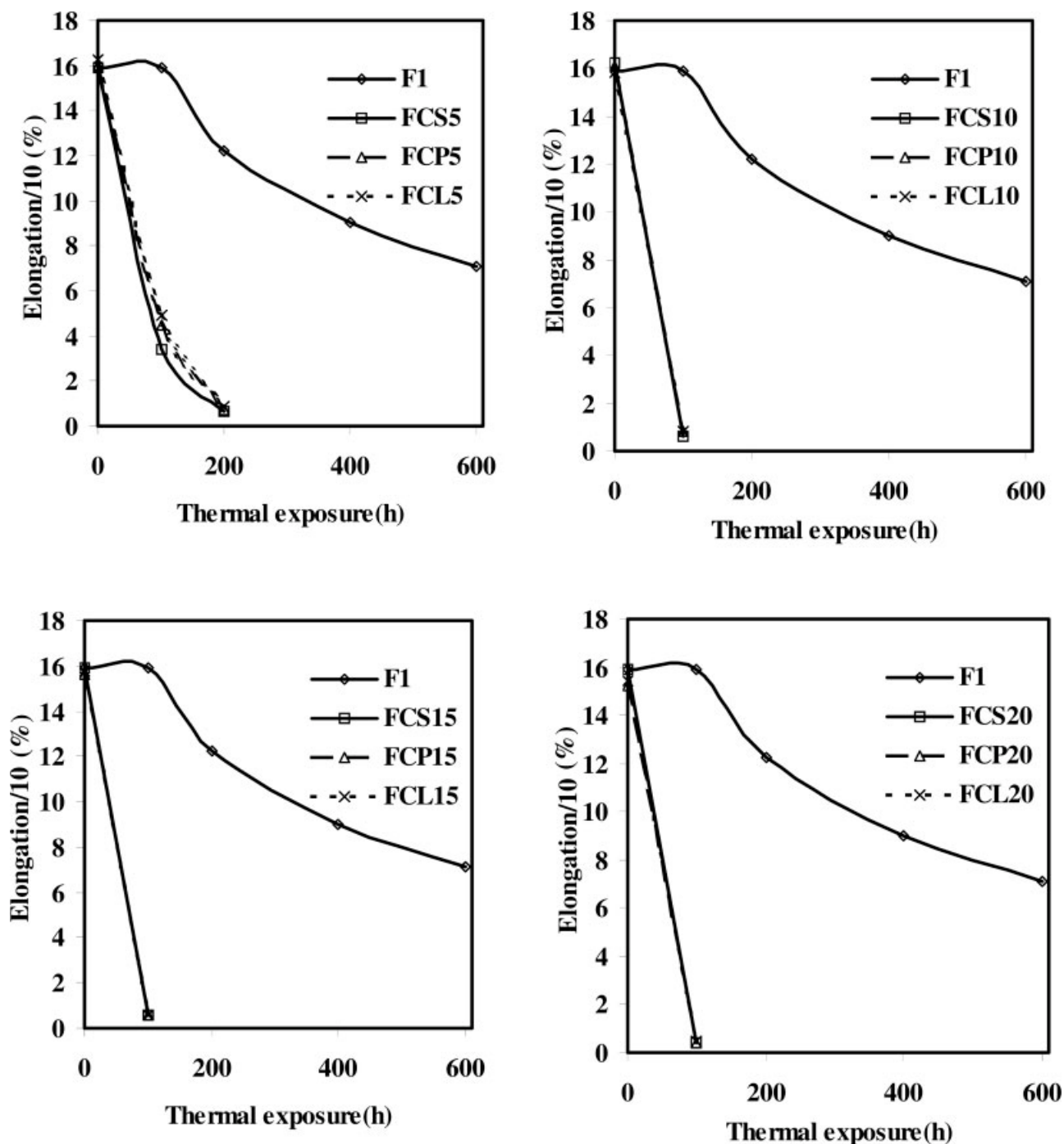


Figure 2 Effect of thermal exposure on percentage elongation of formulations.

~ 3.7, indicating that the polymer does not undergo degradation due to single time processing. The MFI of F1 increases from 3.7 to 6.5 after 600 h of thermal exposure, while it was not possible to determine the MFI of samples containing cobalt carboxylates, as the formulations flowed freely under the operating temperature (190°C) of MFI testing, indicating very high MFI values (>300 g/10 min).

Surface morphological studies

Figures 5 and 6 present a comparative compilation of scanning electron micrographs of two samples (LDPE and FCS10) at a uniform magnification of 2000 \times . As is apparent from Figure 5(a), the surface of non degraded LDPE is smooth, without cracks and free from defects. Figure 5(b,c) are SEMs of LDPE after 100 and 600 h of

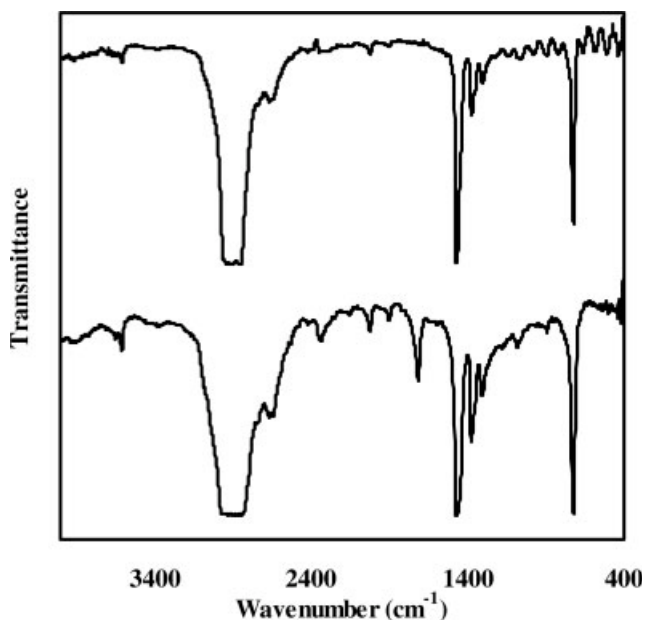


Figure 3 FTIR spectra of F1 films (a) before exposure and (b) after 600 h of thermal aging.

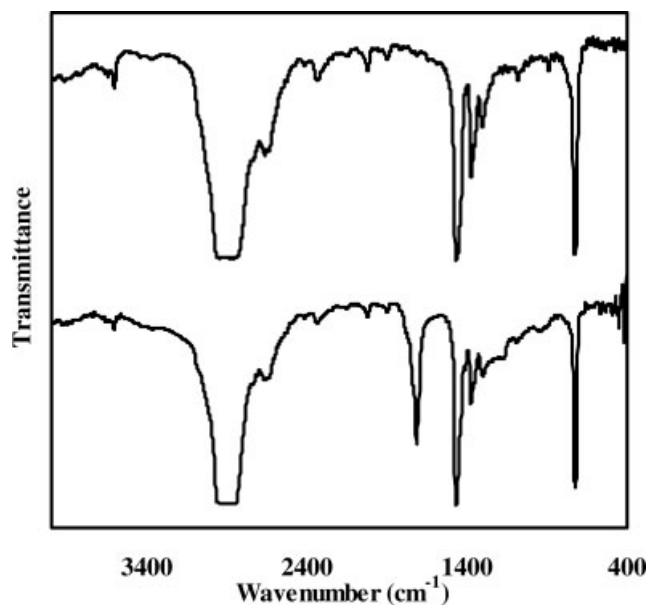


Figure 4 FTIR spectra of FCS10 film (a) before exposure and (b) after 100 h of thermal aging.

thermal degradation. It was observed that the surface developed some cracks and grooves because of thermal exposure. However, the extent of damage was much more pronounced in the samples containing cobalt stearate. Figure 6(a and b) are electron micrographs of FCS10 before and after thermal exposure of 100 h. The damage is more evident in this case, and the

sample after 100 h of exposure showed extensive grooves and pits as a result of thermo oxidation.

Degradation mechanism

Transition metals carboxylates initiate polyethylene degradation by producing free radicals on the poly-

TABLE II
Effect of Thermal Exposure (70°C) on the Carbonyl Index of Formulations

Thermal exposure (h)	F1	FCS5	FCP5	FCL5	FCS10	FCP10	FCL10	FCS15	FCP15	FCL15	FCS20	FCP20	FCL20
0	0.33	0.23	0.23	0.23	0.33	0.23	0.23	0.23	0.23	0.23	0.24	0.24	0.33
100	0.23	7.9	7.0	5.00	15.1	14.9	13.9	15.3	15.4	14.8	15.6	15.6	15.6
200	1.96	-	-	-	-	-	-	-	-	-	-	-	-
400	2.83	-	-	-	-	-	-	-	-	-	-	-	-
600	3.28	-	-	-	-	-	-	-	-	-	-	-	-

FCS, FCP, and FCL samples became brittle and broke off after 200 h of thermal exposure at 70°C; hence, CI could not be determined.

TABLE III
Effect of Thermal Exposure (70°C) on the Density (g/cc) of Formulations

Thermal exposure (h)	F1	FCS5	FCP5	FCL5	FCS10	FCP10	FCL10	FCS15	FCP15	FCL15	FCS20	FCP20	FCL20
0	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920	0.920
100	0.922	0.930	0.930	0.929	0.947	0.941	0.938	0.948	0.943	0.939	0.95	0.948	0.942
200	0.923	-	-	-	-	-	-	-	-	-	-	-	-
400	0.925	-	-	-	-	-	-	-	-	-	-	-	-
600	0.930	-	-	-	-	-	-	-	-	-	-	-	-

FCS, FCP, and FCL samples became brittle and broke off after 200 h of thermal exposure at 70°C; hence, density could not be determined.

TABLE IV
Effect of Thermal Exposure (70°C) on the Molecular Weight (Viscosity–Average) of Formulations

Thermal exposure (h)	F1	FCS5	FCP5	FCL5	FCS10	FCP10	FCL10	FCS15	FCP15	FCL15	FCS20	FCP20	FCL20
0	29,242	29,242	29,242	29,242	28,823	28,823	28,823	28,823	28,823	28,823	28,823	28,823	28,823
100	28,823	11,245	11,961	15,651	4,878	5,189	9,834	4,570	4,878	7,118	4,570	4,570	4,878
200	28,405	–	–	–	–	–	–	–	–	–	–	–	–
400	27,573	–	–	–	–	–	–	–	–	–	–	–	–
600	27,573	–	–	–	–	–	–	–	–	–	–	–	–

FCS, FCP, and FCL samples became brittle and broke off after 200 h of thermal exposure at 70°C; hence, molecular weight could not be determined.

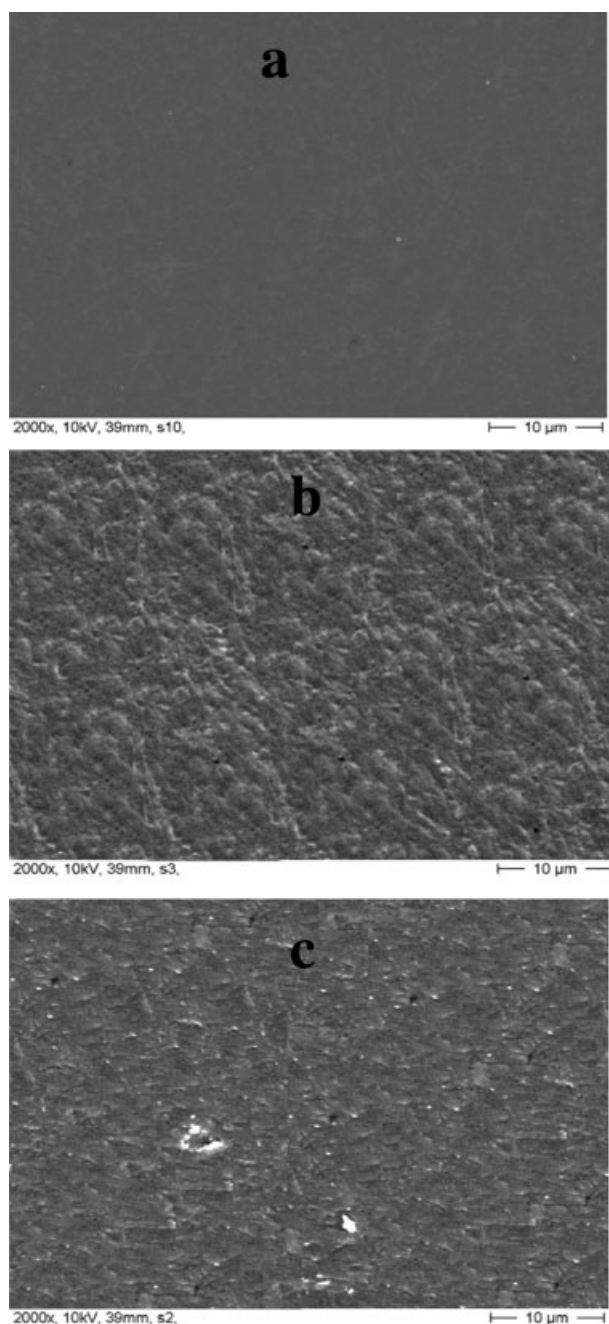


Figure 5 SEMs of (a) LDPE, (b) LDPE after 400 h of thermal exposure, and (c) LDPE after 600 h of thermal exposure.

mer surface, which react with molecular oxygen to generate peroxides and hydroperoxides.^{24,25} The present study indicates that the degradation of LDPE film in the presence of cobalt carboxylate follows the trend $\text{CoSt}_3 > \text{CoPal}_3 > \text{CoLau}_3$. From the cobalt analysis by flame atomic absorption spectroscopy, the cobalt

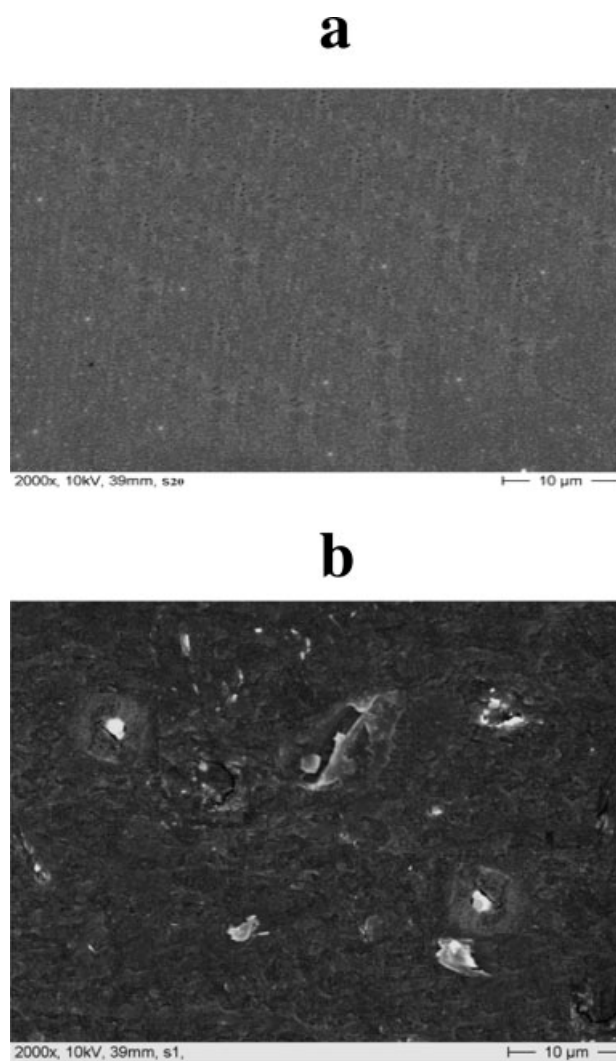


Figure 6 SEMs of (a) FCS10 and (b) FCS10 after 100 h of thermal exposure.

content in CoSt₃, CoPal₃, and CoLau₃ was found to be in the ratio of 1 : 1.08 : 1.37, which indicates that cobalt laurate contains 37% higher cobalt than does cobalt stearate. On the basis of this analysis, cobalt laurate is expected to exhibit the most deleterious effect. On the contrary, cobalt stearate has been experimentally found to exert the most degradative effect. Similar trend has been observed in the case of photo-oxidative degradation also.⁷ There are several factors that contribute to the efficiency of an additive. The increased pro-oxidative ability of cobalt stearate can be attributed to the higher chain length of the same. As the chain length increases, the additive is capable of blending easily with the base polymer LDPE. Also, cobalt stearate melts at a higher temperature (121°C) than do palmitate (115°C) and laurate (80°C), resulting in better mixing; this leads to higher pro-oxidative ability.

CONCLUSIONS

The extent of thermo oxidative degradation of LDPE in the presence of cobalt carboxylates having different lengths of alkyl chain at different concentrations has been compared. The results indicate that all the cobalt carboxylates studied, namely stearate, palmitate, and laurate, promote the thermal degradation of LDPE. The rate of degradation was found to depend strongly on the amount of the additive as well as on the length of alkyl chain in the cobalt salt. The following order of degradation was observed: CoSt₃ > CoPal₃ > CoLau₃, which has been attributed to the increased compatibility of the stearate with LDPE, which overcomes the effect of increased concentration of cobalt in the other carboxylates, namely palmitate and laurate.

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