

# Surface Oxidation of Low-Density Polyethylene Films to Improve Their Susceptibility Toward Environmental Degradation

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**ABSTRACT:** Polyethylene wastes, particularly as films, have accumulated over the last several decades resulting in a major visual litter problem. The aim of this study was to investigate the ability of chemical reagents to oxidize the low-density polyethylene (LDPE) film surface to increase their susceptibility toward photodegradation and thermal degradation. Three chemical agents, namely, potassium permanganate, potassium persulfate, and benzoyl peroxide, were used to oxidize the film surface to generate chromophoric groups, such as carbonyl groups, which are the main reason for the enhanced environmental degradation of photolytic polymers, such as ethylene-carbon monoxide and ethylene-vinyl ketone copolymers. For the chemical treatment, LDPE films of  $70 \pm 5 \mu\text{m}$  thickness were prepared by a film-blowing technique and subsequently reacted with the aforementioned oxidizing agents. To aid the oxidation process, the reaction with potassium persulfate and potassium permanganate was performed under microwave irradiation heating. In the case of ben-

zoyl peroxide aided oxidation, the films were subjected to repeated coating-heating treatments up to a maximum of 10 cycles. The treated films were subjected to accelerated aging, that is, xenon-arc weathering and air-oven aging (at  $70^\circ\text{C}$ ), for extended time periods. The chemical and physical changes induced as a result of aging were followed by the monitoring of changes in the mechanical, structural, and thermal properties. The results indicate that the surface-oxidized LDPE films exhibited enhanced susceptibility toward degradation; however, the extent was reduced as compared to photolytic or other degradable compositions. The ability of the chemicals to initiate degradation followed the order potassium persulfate < potassium permanganate < benzoyl peroxide. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2765–2773, 2011

**Key words:** degradation; functionalization of polymers; polyethylene (PE)

## INTRODUCTION

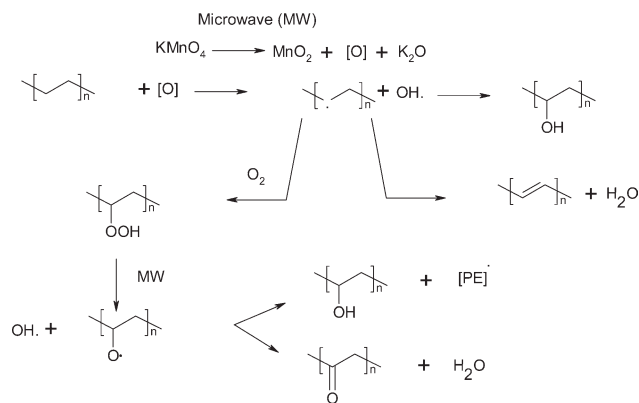
Negligent disposal over the last few decades has led to the accumulation of huge quantities of plastic wastes and has led to a major visual polyethylene (PE) litter problem,<sup>1,2</sup> particularly in areas where waste collection is difficult and/or waste management is not given due importance. Polyolefins, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), and polypropylene, are the main materials used for packaging applications, particularly as carry bags. After serving their useful lifetime, these polymers find themselves in the municipal solid waste streams, where they do not readily degrade because of their inert carbon-carbon chains of extremely high molecular weight. According to Guillet,<sup>3</sup> the most effective way to deal with the litter problem is to

reduce or program the lifetime of objects that have the possibility of ending up as litter.

Polyolefins can be rendered degradable by a variety of routes, the most common being the intentional introduction of chromophoric carbonyl groups to the polymer structure by either copolymerization with carbon monoxide (ethylene-carbon monoxide copolymer)<sup>4–6</sup> or with vinyl ketone monomers (Guillet process).<sup>7</sup> The other approach involves the usage of polyolefins blended with transition-metal-based prooxidants.<sup>8–10</sup> A biodegradable component such as starch is at times blended along with the prooxidant (Griffin process).<sup>11</sup> The former gets consumed by microorganisms leaving behind a matrix with higher surface area thereby accelerating the process.

However, it is imperative to mention here that all of the mentioned strategies deal with the production of new polymer-based packaging that would eventually degrade when disposed in landfills. Efforts toward addressing the current situation, that is, dealing with the disposal of already littered PE waste are relatively limited. The idea behind this study was to generate functionalities on the surface

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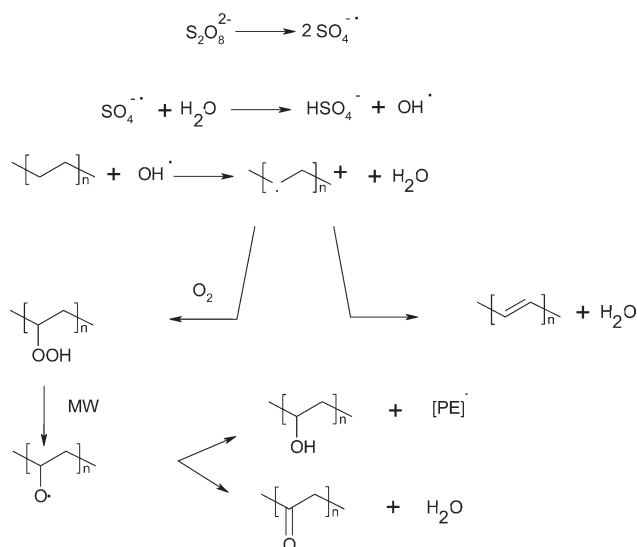
**Scheme 1** Scheme for the oxidation of PE in the presence of potassium permanganate.<sup>14</sup>

of littered PE to enhance its susceptibility to degradation. Previous studies have revealed that the treatment of LDPE with nitric acid for extended periods (6 days at 80°C) has led to increased growth of microorganisms on its surface when it is exposed to a biotic environment.<sup>12,13</sup> This leads us to believe that if the PE surface could be sufficiently oxidized, this could enhance the degradability of the polymer.

In this study, we aimed to generate carbonyl functionalities on the surface of PE using different chemical agents<sup>14,15</sup> to increase the susceptibility of the polymer to photodegradation and thermal degradation. These surface-oxidized polymers could be expected to undergo photolysis by Norrish-type reactions, as reported in the case of ethylene-carbon monoxide (E/CO)<sup>16</sup> and ethylene-vinyl ketone copolymers.<sup>10</sup> In this regard, we attempted to oxidize the LDPE film surface by treatment with different chemicals: potassium permanganate, potassium persulfate, and benzoyl peroxide.

#### Oxidation with potassium permanganate: Microwave treatment

It has been reported that microwave-assisted degradation is associated with attractive features, such as lower activation energies and higher degradation rates, which automatically result in a reduced reaction time.<sup>15</sup> It is the existence of this so-called microwave effect that enhances the rate of degradation compared to thermal degradation. The use of potassium permanganate as an oxidizing agent for PE in conjunction with microwave irradiation was reported by Mallakpour et al.<sup>14</sup> The reaction scheme for the same is presented in Scheme 1. In the presence of microwave irradiation, potassium permanganate decomposes to generate nascent oxygen, which abstracts hydrogen from PE to form free radicals of both hydroxide and PE. The latter can subsequently react with oxygen to form PE hydroperoxides, which subsequently decompose to generate hydroxide or carbonyl functionalities on the polymeric chain.



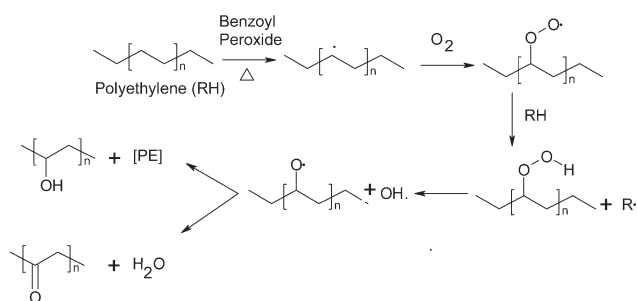
**Scheme 2** Scheme for the oxidation of PE in the presence of potassium persulfate.<sup>15</sup>

#### Oxidation with potassium persulfate: Microwave treatment

Potassium persulfate has been employed to initiate degradation in poly(ethylene oxide) when it is exposed to microwave irradiation.<sup>15</sup> In the presence of microwave irradiation, potassium persulfate dissociates to form sulfate radical anions; this leads to the formation of hydroxide radicals on reaction with water (Scheme 2). This OH• abstracts hydrogen from PE to form PE free radicals, which meet the same fate as already presented in the previous scheme.

#### Benzoyl peroxide treatment

Keeping in view the widespread use of benzoyl peroxide as a free-radical generator, one can expect to generate carbonyl functionalities on the surface of PE, as per Scheme 3, if enough time is available for the PE macroradicals to react with atmospheric oxygen. Benzoyl peroxide, on heating, leads to the generation of free radicals, which can subsequently react with oxygen to generate hydroperoxides, which can



**Scheme 3** Proposed oxidation of the PE chain in the presence of benzoyl peroxide.

further decompose to generate carbonyl groups. There have been several attempts in which free-radical initiators such as benzoyl peroxide have been used to generate free radicals on the surface of PE films, which have been subsequently grafted with acrylonitrile<sup>17</sup> and methyl methacrylic acid.<sup>18</sup> Benzoyl peroxide has also been reported to cause the crosslinking of PE.<sup>19</sup> However, to the best of our knowledge, the ability of benzoyl peroxide to oxidize the PE surface has not been reported to date.

LDPE was chosen as the model polymer for this study because it has been reported to degrade to a much larger extent compared to its other analogues, such as LLDPE and HDPE, because of the presence of a larger number of tertiary hydrogens in the former, which is a result of its branched structure. The technique could be applied to the latter polymers after its potential applicability is proven.

## EXPERIMENTAL

### Materials

Benzoyl peroxide [analytical reagent (AR), Central Drug House, Mumbai, India] was purified by dissolution in chloroform followed by methanol recrystallization. *N,N*-Dimethyl aniline (AR, Central Drug House, Mumbai, India), potassium permanganate (AR, Loba Chemie, Mumbai, India), and potassium persulfate (AR, Loba Chemie, Mumbai, India) were used without further purification. Commercial LDPE (24FS040) was used for the preparation of the films. The melt flow index (MFI) of the polymer was determined at 190°C under a load of 2.16 kg as per ASTM 1238. Ten extrudates were cut at regular intervals of 60 s, and the average value was found to be 3.7 g/10 min. The polymer exhibited a melting point of 110°C and a density of 0.92 g/cm<sup>3</sup>. Solvents such as toluene and chloroform were used as received. Distilled water was used throughout the entire course of study. A domestic microwave oven (LG, MC-808WAR, Korea) with a magnetron source for microwave generation was used for the micro-

wave treatment of the films. The oven had a maximum power of 900 W with a frequency of 2.45 GHz.

### Preparation of the films

Neat LDPE films of  $70 \pm 10 \mu$  thickness were prepared with an extruder (Dayal make, Delhi, India) attached to a film blowing unit. The temperatures in the barrel sections of the extruder were maintained at 110 and 120°C, independently, and that of the die head section was 130°C. 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 directions, respectively. Films were prepared by maintaining a BUR of 5.5 : 1 and a DDR of 14.2 : 1.

### Chemical treatment

Oxidation with potassium permanganate:  
Microwave treatment

Oxidation of LDPE by potassium permanganate was carried out as per the procedure reported in the literature with minor modifications.<sup>14</sup> Briefly, 2 g of LDPE film was dipped in 50 mL of a 0.5M aqueous KMnO<sub>4</sub> solution to arrive at a composition corresponding to a molar ratio of 3:1 (repeating units of PE to KMnO<sub>4</sub>); this has been reported to be the most effective composition for the said oxidation purpose.<sup>14</sup> This was placed in wide-mouthed glass tubes and subjected to microwave treatment for extended time periods at 180 W of power. Films were removed at regular intervals and washed with an aqueous solution of 20% sulfuric acid before being finally washed with distilled water until the pH reached 7.

The description of the treatments along with the sample designations of the films, which were subsequently investigated for their degradation behavior, are presented in Table I.

TABLE I  
Sample Designations and Description of Chemical Treatments

Description of treatment	Sample designation
Film-blown LDPE, no chemical treatment	LDPE
Ten minutes of 180-W microwave irradiation of LDPE film in distilled water	MLD-10
Ten minutes of 180-W microwave irradiation of LDPE film in an aqueous potassium permanganate solution (0.5M)	MPM-10
Ten minutes of 180-W microwave irradiation of LDPE film in an aqueous potassium persulfate solution (1 g/L)	MPS-10
Eight repeated coating–heating cycles with benzoyl peroxide, each cycle composed of the dipping of the LDPE film in a 2% w/v xylene solution for 60 min followed by heating at 90°C for 30 min	BC-8
Ten repeated dipping–heating cycles in the absence of benzoyl peroxide, each cycle composed of the dipping of LDPE film in xylene for 60 min followed by heating at 90°C for 30 min	C-10

#### Oxidation with potassium persulfate: Microwave treatment

An LDPE film weighing 2 g was dipped in an aqueous potassium persulfate solution (1 g/L) and subjected to microwave treatment for extended time periods at 180 W of power. Films were removed at regular intervals and washed with distilled water. The films were designated with MPS followed by the irradiation time (in minutes).

#### Cyclic treatment with benzoyl peroxide

We reacted the neat LDPE films with benzoyl peroxide by dipping them in a solution of 2% (w/v) benzoyl peroxide in xylene for 60 min.<sup>17,18</sup> The film was then removed, dried, and subsequently heated to 90°C in an air oven for 30 min for the peroxide to decompose. This cyclic process of coating the LDPE films with benzoyl peroxide and subsequent heating was repeated several times, up to a maximum of 10 coating cycles. The sample designation of the films along with the description of treatment is presented in Table I.

### Degradation studies

#### Photooxidative degradation

Accelerated photodegradation studies were performed on a xenon-arc apparatus set at 550 W/m<sup>2</sup> as per ISO standard (ISO 4892-2 : 1994). The black panel temperature was set at 63°C for the entire exposure period.

#### Thermooxidative degradation

Compost piles have been reported to reach temperatures as high as 70°C; therefore, the thermooxidative testing was performed by placement of the treated films in an air oven maintained at 70 ± 1°C for extended time periods<sup>20</sup> and removal of the samples at regular time intervals to monitor the degradation.

#### Evaluation of degradation

Changes in the mechanical properties, that is, the tensile strength and elongation at break, were monitored with a materials testing machine (JRagru Instruments, JRI-TT25, Delhi, India). Samples with a gauge length of 10 cm 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 200 mm/min. About five samples were tested for each experiment, and the average values are reported in the form of mean ± standard error.

The X-ray diffraction patterns were recorded on an X-ray diffractometer (PW3020, Philips, The Netherlands; Cu K $\alpha$  radiation, voltage = 40 kV, and current = 20 mA). The range of diffraction angles (2 $\theta$ 's) was 20–40°, and the scanning speed was 0.05° 2 $\theta$ /s. 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 PE. It was defined as the ratio of absorbance of the carbonyl band around 1740 cm<sup>-1</sup> and the internal thickness band at 2020 cm<sup>-1</sup>.<sup>10</sup>

CI =

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

The thermal properties were investigated with a PerkinElmer Diamond simultaneous thermogravimetric analysis-differential thermal analysis-differential scanning calorimetry (DSC) (Shelton, CT) instrument under a nitrogen atmosphere. The percentage crystallinity was calculated from DSC traces (second heating run) with the following relation:

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

where  $\Delta H_f(\text{observed})$  is the melting enthalpy of the sample and  $\Delta H_f(100\% \text{crystalline})$  is the melting enthalpy of 100% crystalline PE, reported in the literature as 285 J/g.<sup>21</sup> Elemental analysis was performed by determination of the C, H, and O contents with an elemental analyzer (Thermo Finnigan, Flash EA, Milan, Italy) to quantify the content of oxygen in the degraded samples. The MFIs of all of the resins were measured on an MFI tester (International Equipments, Mumbai, India). The apparent density of the films was measured with a Sartorius analytical balance (model ME215S) equipped with a density measurement accessory (model YDK01). Isopropyl alcohol, with a purity of 99.5% (density = 0.78 g/cm<sup>3</sup>), was used as the liquid medium for the density measurements.

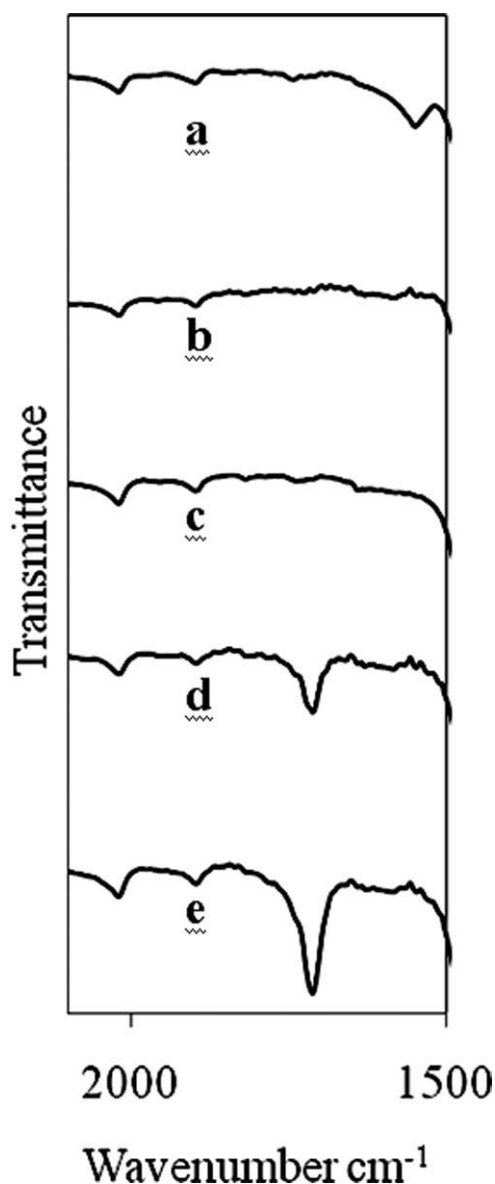
## RESULTS AND DISCUSSION

### Characterization of films after chemical treatment

#### Mechanical properties

Treatment with different chemicals, namely, potassium permanganate, potassium persulfate, and benzoyl peroxide did not lead to any remarkable changes in the mechanical properties of the films. The elongation at break percentages for the films





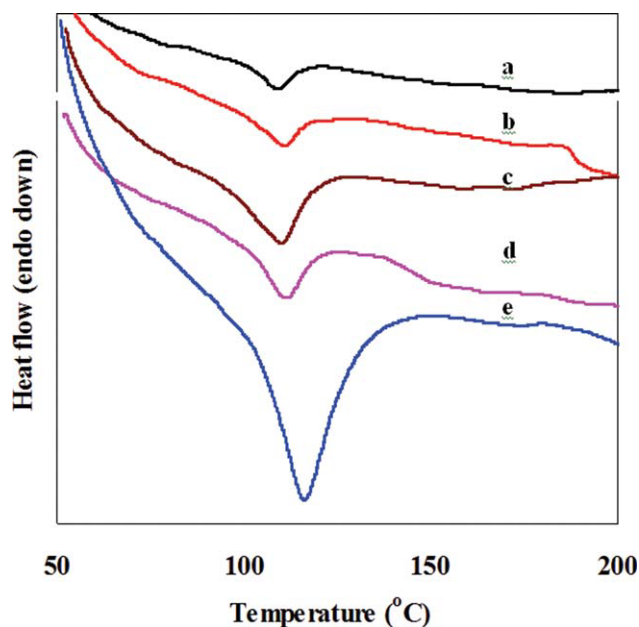
**Figure 1** FTIR spectra of the films: (a) LDPE, (b) MLD-10, (c) MPM-10, (d) MPS-10, and (e) BC-8.

were  $170 \pm 10$ ,  $167 \pm 10$ , and  $163 \pm 10\%$  for unexposed films and films exposed to 10 min of microwave radiation in the presence of aqueous solutions of potassium permanganate and potassium persulfate, respectively. However, with the high error associated with this test, these results did not indicate any pronounced effect. However, the decrease was more perceptible in the case of the benzoyl peroxide treated films. Repeated treatment (eight cycles) with benzoyl peroxide led to a decrease in the elongation of films from  $170 \pm 10$  to  $153 \pm 9\%$ . Subsequent cyclic treatment did not lead to any further degradation; hence, the results of studies on the thermooxidative and photooxidative degradation of the BC-8 samples are presented in this article. In the absence

of oxidizing agent, however, microwave irradiation led to marginal increases in both the mechanical properties, with the percentage elongation increasing from  $170 \pm 10$  to  $181 \pm 10\%$  after 10 min of irradiation. The corresponding increase in the tensile strength was from 12.8 to 13.4 MPa. This improvement in the mechanical properties could be attributed to the limited crosslinking that took place between polymer chains upon exposure to microwave radiation.<sup>22</sup>

#### Structural changes

The change in the FTIR spectra of the LDPE films upon chemical exposure is presented in Figure 1. Oxidation by the chemical treatment route led to the introduction of oxygen into the polymeric matrix, which was confirmed by elemental analysis and FTIR. The oxygen contents in the MPS-10, MPM-10, and BC-8 films were estimated to be 0.9, 1.1, and 1.6%, respectively. The introduction of such small amounts of oxygen did not lead to any perceptible increase in the density of the polymer, which remained constant at  $0.921 \pm 0.010 \text{ g/cm}^3$ . On the other hand, the oxygen contents in the LDPE, MLD-10, and C-10 films were negligible, and the films did not exhibit any absorption in the carbonyl region ( $1700 \text{ cm}^{-1}$ ) of the FTIR spectra. However, the oxygen content in these oxidized polymers was not necessarily in the form of ketones but was a mixture of carboxylic acids, aldehydes, and/or esters, some of which are extractable in organic media. The CI of LDPE increased to 0.7, 0.9, and 1.3 for the MPS-10, MPM-10, and BC-8 samples, respectively, from an initial value of 0.33. Microwave irradiation in the absence of an oxidizing agent did not lead to any increase in CI. The X-ray diffraction of the neat LDPE films exhibited peaks at  $21.5$ ,  $24.7$ , and  $36.07^\circ$ , which corresponded to interlamellar spacings of 4.1, 3.6, and  $2.49 \text{ \AA}$ , respectively, and these peaks remained unaltered with any type of chemical or microwave treatment. The DSC traces of the films after chemical treatment are presented in Figure 2. Slight differences in the shape and width of the curve could be observed. This could be attributed to the rearrangement of the crystallites due to higher chain mobility, which the polymer experienced during microwave treatment or repeated thermal exposure. Moreover, during the preparation of BC-8, the samples were exposed to xylene, which could have led to the extraction of an oligomeric fraction and resulted in a different calorimetric trace. However, no significant change in the melting point of LDPE ( $\sim 110^\circ\text{C}$ ) was observed because of oxidation resulting from any type of chemical or microwave treatment. The melt indices remained unaltered at  $3.7 \text{ g/10 min}$ .

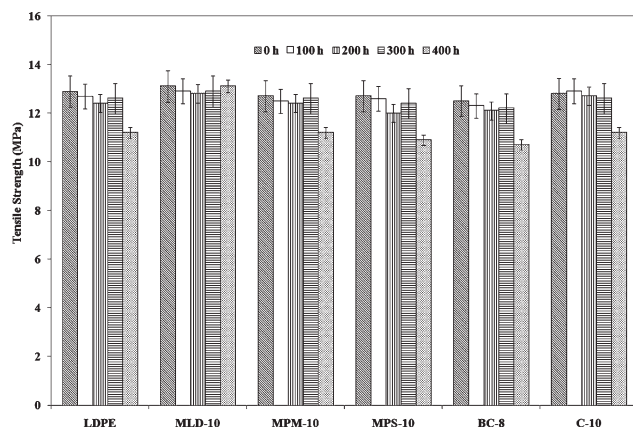


**Figure 2** DSC traces of the films after chemical treatment: (a) LDPE, (b) MLD-10, (c) MPM-10, (d) MPS-10, and (e) BC-8. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

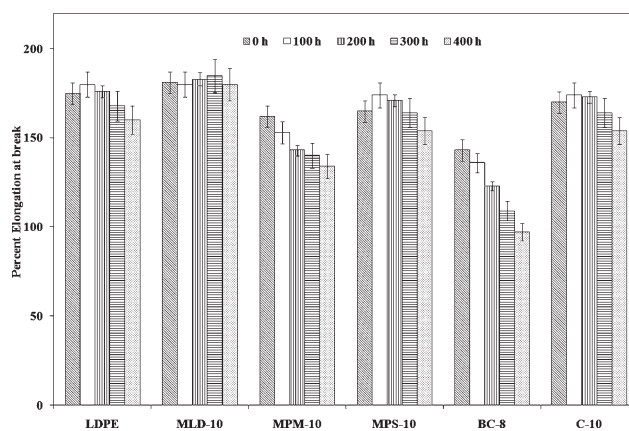
### Degradation studies on the oxidized films

#### Mechanical properties of the films

Figures 3 and 4 present the effect of air-oven aging on the longitudinal mechanical properties of the LDPE films and other formulations. The results are presented as mean  $\pm$  standard error. For the sake of brevity, only tensile yield strength and elongation at break are presented here, as they have been reported to be direct indicators of degradation.<sup>23</sup> Characterization of the treated films indicated that chemical exposure did not affect the mechanical properties substantially. However, it was interesting to note that these films degraded to a greater extent when they were exposed to a thermooxidative aging envi-



**Figure 3** Effect of air-oven aging on the longitudinal tensile strength of the formulations.

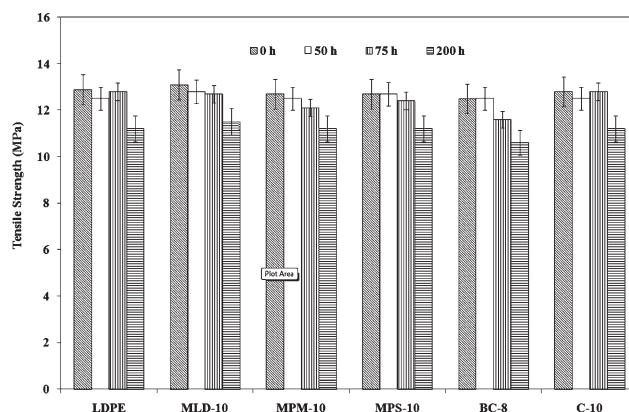


**Figure 4** Effect of air-oven aging on the percentage elongation of the formulations.

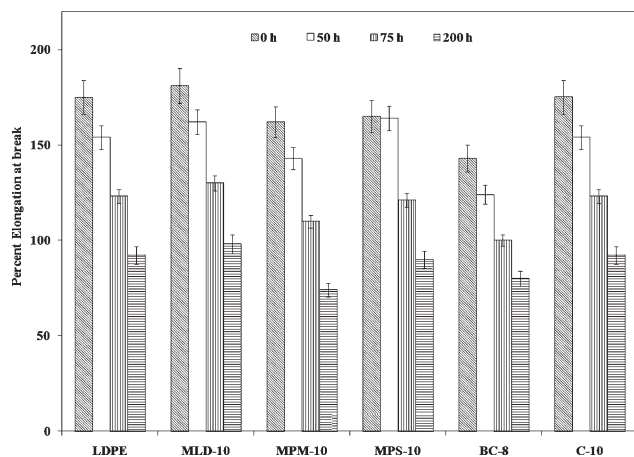
ronment. As is apparent, the degradation in terms of a decrease in the mechanical properties was most significant in the case of the benzoyl peroxide treated films.

The effects of xenon-arc weathering on the tensile strength and elongation at break are presented in Figures 5 and 6, respectively. The effect of the degrading environment on the elongation at break was found to be more pronounced compared to the changes in the tensile strength. As expected, xenon-arc weathering was found to cause more rapid degradation than air-oven aging because this weathering is associated with a combination of both high temperatures (63°C) and high-energy radiation (550 W/m<sup>2</sup>).

From the figures, it is clear that thermooxidation/photooxidation of films after chemical treatment led to degradation in terms of a loss of mechanical properties compared to the neat films. However, this loss appeared to be negligible compared that related to the degradation of photolytic polymers.<sup>24</sup> This difference in degradation behavior could be attributed primarily to two reasons, the first being the presence of chromophoric functionalities in the bulk of

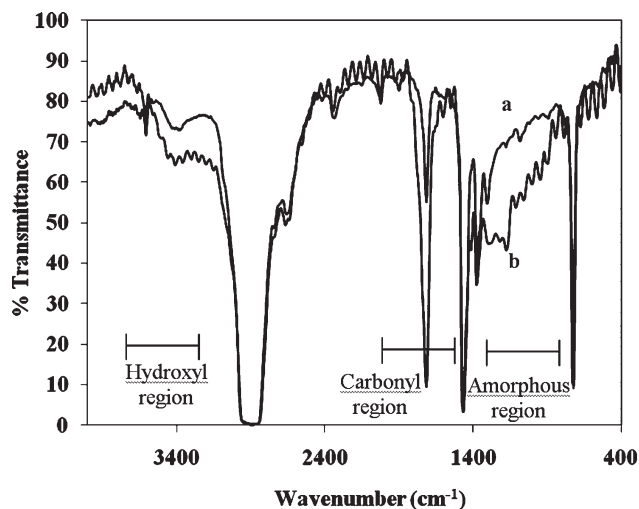


**Figure 5** Effect of xenon-arc weathering on the longitudinal tensile strength of the formulations.

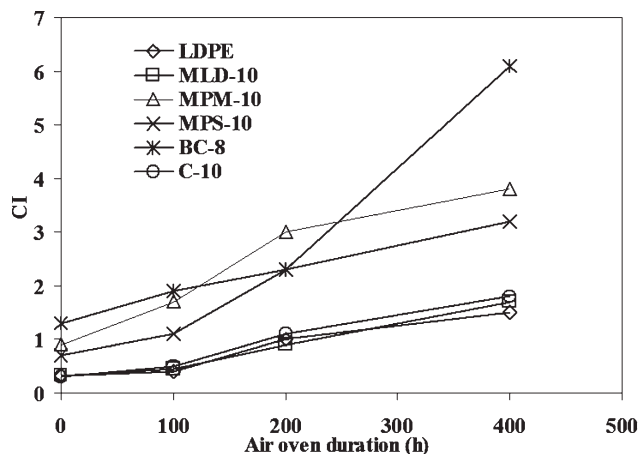


**Figure 6** Effect of xenon-arc weathering on the percent elongation of the formulations.

photolytic polymers. On the other hand, immaterial of the choice of method employed, a two-phase reaction between the solid film and the aqueous/organic oxidant was largely nonhomogeneous and was limited only to the surface of the film. Because of its inherent nonhomogeneous nature, the oxidation/free-radical formation was localized; this resulted in the observed behavior. Second, the carbon monoxide concentration normally present in the E/CO polymer ranged from 1 to 9%, which was much higher than what could be achieved by chemical treatment. In the case of photolytic polymers, the oxygen is present in the form of ketone functionalities only, which can undergo Norrish-type reactions leading to chain scission. On the other hand, as in this investigation, oxidation leads to the incorporation of oxygen not only in the form of ketones but also as hydroxides, as shown in Schemes 1–3, which do not aid in the chain scission process upon exposure to



**Figure 7** FTIR spectra of BC-8 after xenon exposure for (a) 0, (b) 75, and (c) 200 h.



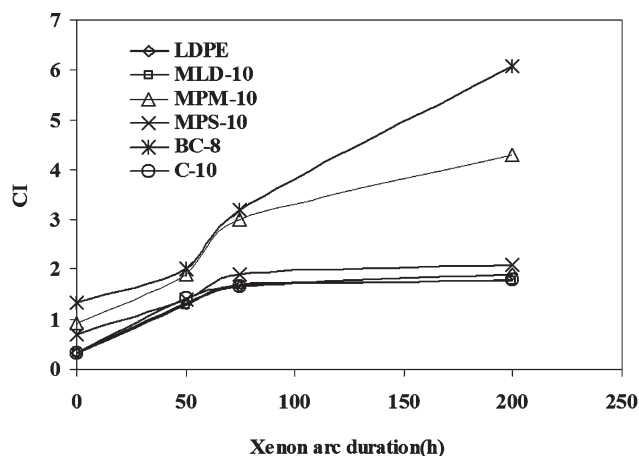
**Figure 8** Increase in CI of the samples due to thermooxidation.

light or heat. Other products formed, particularly carboxylic acids, have also been reported to be completely inert to photolysis and, hence, would not further accelerate the degradation process.

On comparison of the results with the weathering characteristics of prooxidant containing compositions, our previous studies indicated that transition metals, such as manganese, cobalt, and iron, in the form of stearates are effective prooxidants, which cause the rapid degradation of LDPE when added at the processing stage.<sup>25</sup> The difference in the degradation behavior of LDPE after chemical treatment and that of a transition-metal-carboxylate-based prooxidant could be attributed to the catalytic ability of the transition metal to decompose the hydroperoxides. In this investigation, the metal was not available in the bulk of the polymer for the catalytic decomposition process.

#### Structural characterization

Figure 7 shows the change in the FTIR spectra of the BC-8 sample due to thermooxidation and xenon-arc weathering. As can be seen, degradation resulted in the formation of several oxygenated functional groups, which absorbed mainly in the carbonyl (1785–1700  $\text{cm}^{-1}$ ), amorphous (1300  $\text{cm}^{-1}$ ), and hydroxyl (3400  $\text{cm}^{-1}$ ) regions. The changes in the FTIR spectra of LDPE due to different environments were reported in our previous articles.<sup>25–32</sup> CI, which characterizes the degree of degradation of PE, was calculated by the baseline method, and the results are displayed in Figures 8 and 9. PE has been reported to enter a decay stage when the CI reaches a figure of 6.<sup>33</sup> It was observed that the CI increased for all the samples on exposure; however, only the films treated with benzoyl peroxide reached the decay stage after 400 h of thermooxidation and 200 h of xenon-arc weathering. On comparison, our



**Figure 9** Increase in CI of the samples due to xenon-arc weathering.

previous investigations revealed that LDPE containing a cobalt stearate prooxidant reached the decay stage within 10 h of thermooxidation.<sup>30</sup>

#### Thermal characterization

An endothermic melting transition at about 110°C was observed in all of samples after chemical treatment; this indicated that chemical treatment did not affect the melting behavior of the base polymer (Fig. 2). No change was observed in the melting point of the polymer, even after thermooxidation or xenon-arc weathering in any of the samples. This could be explained on the basis that the initial degradative change occurred primarily in the amorphous regions of the polymer; this left the crystalline regions largely unaffected and, thereby, did not affect the melting point of the polymer. However, as observed previously,<sup>28,30,34</sup> a slight increase in the DSC crystallinity of the samples was observed (Table II). LDPE is a semicrystalline polymer with the polymeric chains passing through both the crystalline and amorphous regions, and because of the gradual depletion of the amorphous phase, the crystallinity of the samples increased, as indicated by the

**TABLE II**  
Results of the Melting Enthalpy ( $\Delta H_f$ ) and Percentage Crystallinity in the Samples before and after 200 h of Xenon-Arc Weathering

Sample designation	$\Delta H_f$ (J/g)		Crystallinity (%)	
	0 h	200 h	0 h	200 h
LDPE	127	145	44.56	50.88
MLD-10	129	135	45.26	47.37
MPM-10	129	150	45.26	52.63
MPS-10	128	147	44.91	51.58
BC-8	132	170	46.32	59.65
C-10	128	144	44.91	50.53

**TABLE III**  
Effect of Air-Oven Aging on MFI of the Samples

Sample designation	MFI	
	0 h	400 h
LDPE	3.7	4.6
MLD-10	3.7	4.7
MPM-10	3.7	4.6
MPS-10	3.7	4.6
BC-8	3.7	6.9
C-10	3.7	4.6

increased area of the endothermic melting peak. 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 indicative of the molecular weight of any uncrosslinked polymer, was determined for a few formulations at 190°C under a load of 2.16 kg, and the results are presented in Table III. Chemical treatment, even under the influence of microwaves, did not lead to any perceptible change in the MFI values, which remained unaltered at  $3.7 \pm 0.1$  g/10 min. However, both thermooxidative and photooxidative aging led to marginal increases in these indices, with the increase being most substantial in the case of benzoyl peroxide coated LDPE samples, of the three oxidants investigated. Four hundred hours of thermooxidative degradation of the BC-8 samples led to an increase in the MFI from 3.7 to 6.9 g/10 min. The ability of benzoyl peroxide to crosslink LDPE was reported previously.<sup>18</sup> It is highly probable that on exposure to the thermooxidative environment, both crosslinking and chain scission took place simultaneously; this resulted in such a small increase in the MFI values. However, the change in the MFI of LDPE oxidized by potassium permanganate and persulfate, was relatively less, that is, from 3.7 to 4.6, and this was very similar to that in the absence of any treatment. It is to be noted here that in the case of prooxidant-initiated degradation, the films turned fragile after 100 h of thermooxidation, and the MFI could not be determined, as the samples flowed under test conditions.<sup>28</sup>

#### CONCLUSIONS

Thermooxidative and photooxidative degradation of LDPE, posttreatment with three chemical agents, namely, potassium persulfate, potassium permanganate, and benzoyl peroxide, was investigated. These studies revealed that chemicals have the ability to oxidize the PE chain to a certain extent, in terms of



oxygen insertion into the polymeric matrix. Of the three chemical treatments, repeated exposure to benzoyl peroxide led to a higher extent of oxidation of the polymer chain as compared to the other two. The ability of the chemicals to initiate the degradation was found to follow the order potassium persulfate < potassium permanganate < benzoyl peroxide. The effect of microwave irradiation on the degradation behavior of the base polymer was also investigated. The studies indicated that microwave irradiation in the absence of an oxidizing agent was incapable of initiating degradation in LDPE. The studies also indicated that the extent of degradation due to xenon-arc weathering was more pronounced compared to that of air-oven aging at 70°C.

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