

Study of Ultraviolet Photooxidative Degradation of LDPE Film Containing Cerium Carboxylate Photosensitizer

YICHAO LIN

Fujian Institute of Testing Technology, Fuzhou, Fujian 350003, China

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ABSTRACT: The carbonyl indices (CI) of photooxidation of low-density polyethylene (LDPE) films containing cerium carboxylate (CeCar₃) with/without aromatic ketones (AK) were determined by infrared (IR) spectroscopy. The effects of these photosensitizers on the rates of ultraviolet (UV) photooxidation of LDPE films and their mechanism in sensitizing photooxidative degradation are studied. Results show that CeCar₃ can cause the accelerated photooxidative degradation of LDPE films, but CeCar₃ in combination with AK may bring about the accelerated or retarded photooxidative degradation of LDPE films to varying degrees. After UV irradiation, followed by long duration storage, LDPE films containing these photosensitizers continued storage oxidative degradation at the storage oxidative rates similar to the past, except for the Michler ketone. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 811–818, 1997

Key words: cerium carboxylate; photosensitizer; photooxidative degradation; low-density polyethylene; photodegradable LDPE

INTRODUCTION

Scott^{1–3} previously proposed that cerium stearate (CeSt₃) may cause the accelerated photodegradation of high-density polyethylene films, Potts^{4–5} also considered that cerium octoate (CeOct₃) or CeSt₃ can lead to the acceleration of photooxidative degradation of LDPE and polypropylene. Tailler⁶ reported that rutile titanium dioxide can retard the rates of ultraviolet (UV) photooxidative degradation of low-density polyethylene (LDPE) films containing CeSt₃. In recent years, Hardene⁷ and Michaels,⁸ respectively, have developed photodegradable food packaging made of LDPE containing CeSt₃ and beverage containers of polypropylene or poly(vinyl chloride) containing CeSt₃. The Rhone-Poulenc Co.⁹ has made photodegradable articles of polypropylene and polystyrene containing CeSt₃.

These studies have pointed out that the changes of elongations at break, carbonyl indices (CI), and molecular weights of LDPE films con-

taining CeCar₃ occurred under UV irradiation. However, the effects of CeCar₃ with/without aromatic ketones (AK) compound photosensitizers on the rates of UV photooxidation of LDPE films have not been investigated systematically. Therefore, in this work, the changes of photooxidative CI of LDPE films containing these photosensitizers were investigated by infrared (IR) spectroscopy and the rates of UV photooxidation of these films and the action mechanism of photosensitizers are discussed using CI as the index.

EXPERIMENTAL

Materials

Cerium dioxide, hydrochloric acid, sodium octoate, sodium laurate, sodium stearate, diphenyl ketone (DPK), Michler ketone (tetramethyl-4,4'-diaminodiphenyl ketone; MK), etc., were all of reagent grade used without purification. Commercial 2F7B type LDPE and the GSRN 7042 type linear LDPE (LLDPE) were used.

Preparation

Cerium octoate, cerium laurate, and cerium stearate were obtained from the reaction of cerium chloride, which was formed by the reaction of cerium dioxide with hydrochloric acid, with sodium octoate, sodium laurate, and sodium stearate, respectively.

Various LDPE mother granules containing photosensitizers were prepared by adding six CeCar₃ with/without AK to the molten LDPE containing dispersing agent, employing a GH50 high-speed mixer and SJ65 single-screw extruder.

Various LDPE films of 50–60 μm thickness were made by adding the mother granules individually to the molten LDPE and LLDPE, employing φ65 film blowing machine.

UV Exposure

All LDPE film samples were irradiated in a high-pressure mercury-arc lamp cabinet with four 450 W lamps. The distance between the samples and the light sources was 40 cm, and the temperature in the cabinet was maintained at 55 ± 1°C.

Characterization

The contents of Ce in cerium octoate, cerium laurate, and cerium stearate were determined by a Shimadzu ICPQ-100 plasma emission spectrophotometer and were 23.10, 18.08, and 13.63%, respectively. The contents of C and H in them were determined by a PE 240c elemental analyzer and were 47.54, 55.90, and 63.21%, and 8.21, 9.65, and 10.78%, respectively. Results show that the molecular structural formulae of these cerium carboxylates are very similar to Ce(OOCC₇H₁₅)₃·2H₂O (CeOct₃·2H₂O), Ce(OOCC₁₁H₂₃)₃·2H₂O (CeLau₃·2H₂O), and Ce(OOCC₁₇H₃₅)₃·2H₂O (CeSt₃·2H₂O). IR absorption spectra of these LDPE films in the region of 4000–400 cm⁻¹ were recorded on a PE 983G IR spectrophotometer. Their CI (A₁₇₁₀/A₂₀₂₀) were calculated by the baseline method.¹⁰

LDPE films were dissolved in decalin, and the intrinsic viscosities [η] at 135°C were measured with a Ubbelohde viscometer. The viscosity average molecular weights M_{η} of LDPE films were calculated with the following equation¹¹:

$$[\eta] = 46 \times 10^{-3} \times M_{\eta}^{0.73}$$

RESULTS AND DISCUSSION

UV Photooxidation of LDPE Films Containing CeCar₃

Figure 1 shows that polymeric chains of LDPE film containing CeSt₃ formed various functional groups during UV photooxidative degradation. The most significant changes of IR absorption spectra were in the carbonyl (1785–1700 cm⁻¹), amorphous (~ 1300 cm⁻¹), unsaturated (909 or 887 cm⁻¹), and hydroxyl (~ 3400 cm⁻¹) regions. The functional groups present were ketone RCOR' (1720 cm⁻¹), carboxylic acid —COOH (1710 and 1185 cm⁻¹), aldehyde —CHO (1735 cm⁻¹), ester —COOR (1748 cm⁻¹), peroxy-carboxylic acid (ester)—COOOH (R) (1785 cm⁻¹), vinylene RR'C=CH₂ (887 cm⁻¹), vinyl RCH=CH₂ (909 cm⁻¹), internal double bond RCH=CHR' (1645 cm⁻¹), and hydroxyl group —OH (~ 3400 cm⁻¹), etc.¹⁰ Thus, photooxidative degradation of these LDPE films during UV irradiation may be evaluated by CI. It is generally believed that LDPE films enter into the decay stage at CI greater than 6,¹² and enter into the embrittlement stage at CI greater than 45.

Figure 2 shows that after 7.5 days of UV irradiation, the CI of LDPE film containing no CeCar₃ was greater than 6 and entered into the decay stage. After 14 days of UV irradiation, it was still in the decay stage with CI of 12. On the other hand, the CI of LDPE films containing 0.3 wt % CeSt₃, CeLau₃, or CeOct₃ were greater than 6 after 2, 3, or 4.5 days of UV irradiation, respectively, and got into the decay stage. After 8, 9.5, or 11.5 days of UV irradiation, these LDPE films individually had CI greater than 47 and got into the embrittlement stage. It can be seen that the rates of UV photooxidation of these LDPE films increased with UV irradiation duration and alkyl carbon chain length of ligand. The photosensitizing activities of 0.3 wt % CeCar₃ on UV photooxidative degradation of LDPE films decreased in the order of CeSt₃ > CeLau₃ > CeOct₃.

Figure 3 shows that, after UV irradiation (see Fig. 2) followed by 575 days of storage, LDPE film without CeCar₃ stopped photooxidative degradation [see Figs. 2(a) and 3(a)], but LDPE films containing 0.3 wt % CeCar₃ continued oxidative degradation at the rates similar to the past. This fact illustrates that, after long storage their oxidative rates were still controlled by the initial UV photooxidation. After the initial six-day UV irradiation, LDPE films containing 0.3 wt % CeSt₃, CeLau₃, or CeOct₃ had CI of 31, 22, or 14 [see

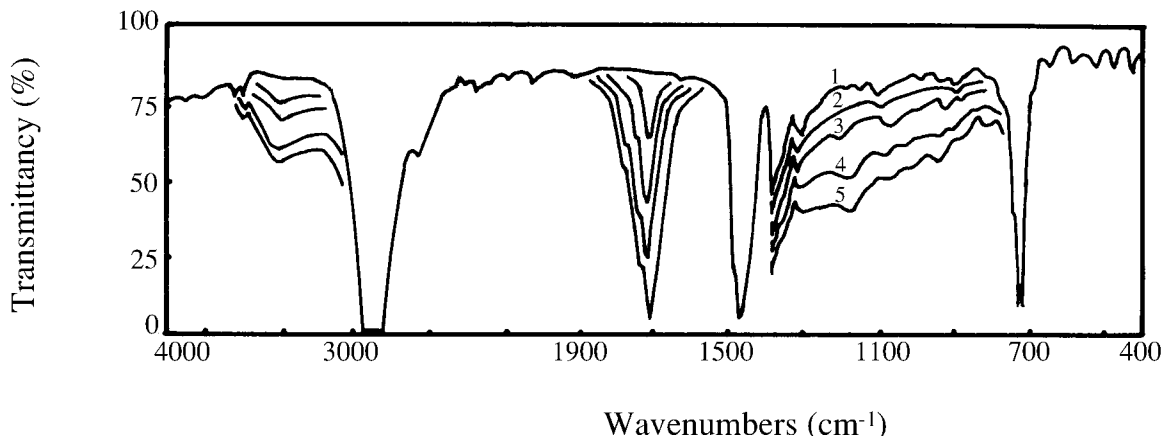


Figure 1 Changes of IR spectra of LDPE films containing 0.3 wt % CeSt₃ during UV photooxidative degradation. Numbers on curves indicate UV irradiation time (days): (1) 0, (2) 2, (3) 4.75, (4) 6.75, and (5) 10.45. For Cl, (1) 0, (2) 6.0, (3) 17.0, (4) 35.1, and (5) 59.2.

Fig. 2(b-d)] and were in the decay stage; but after continuous 575-day storage, their CI increased to 55, 52, or 47 [see Fig. 3(b-d)], and all entered into the embrittlement stage. Thus, the sensitizing activities of CeCar₃ on the storage-oxidative degradation still decreased progressively as follows: CeSt₃ > CeLau₃ > CeOct₃.

UV Photooxidation of LDPE Films Containing CeCar₃ and DPK

Figure 4 shows the effects of adding 0.1 wt % DPK to LDPE films containing 0.3 wt % CeCar₃ on pho-

tooxidation of these films. DPK almost had no effect on the rate of photooxidation for the films containing CeOct₃ [see Figs. 2(b) and 4(b)]. However, it increased the rate of photooxidation of the films containing CeLau₃ [see Figs. 2(c) and 4(c)], while it decreased the rate of films containing CeSt₃ [see Figs. 2(d) and 4(d)]. It is evident that the photosensitizing activities of a combination of DPK and CeCar₃ on UV photooxidative degradation of LDPE films decreased successively, as follows: CeLau₃ + DPK > CeSt₃ + DPK > CeOct₃ + DPK.

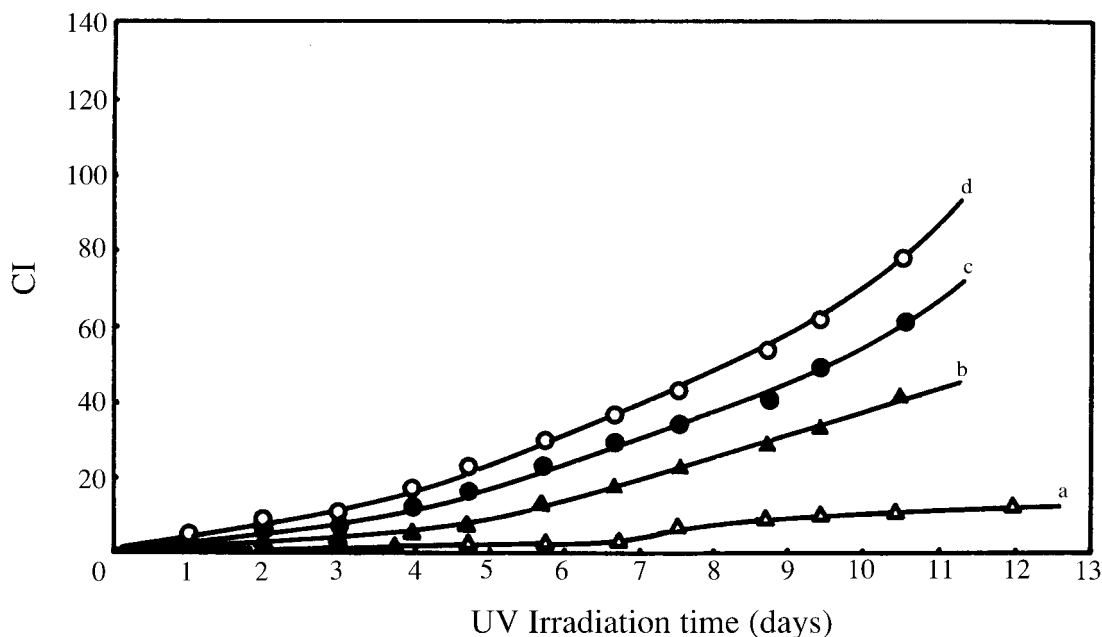


Figure 2 Effects of 0.3 wt % CeCar₃ on the rates of UV photooxidation of LDPE films: (a) no CeCar₃; (b) CeOct₃; (c) CeLau₃; (d) CeSt₃.

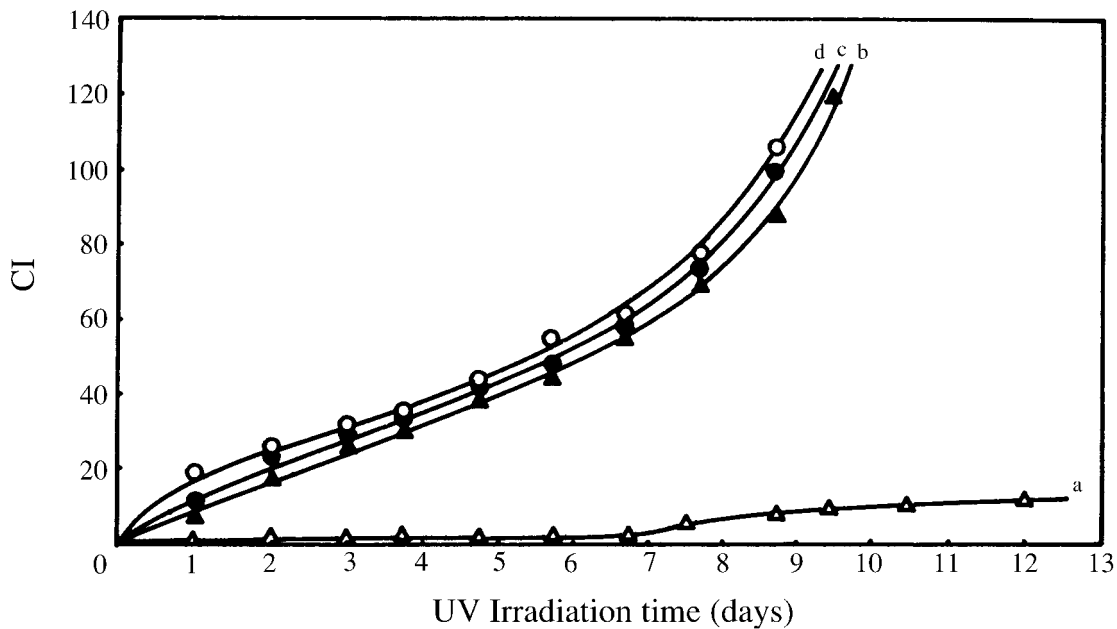


Figure 3 Effects of 575-day storage on the rates of the storage oxidative degradation of LDPE films containing 0.3 wt % CeCar₃ after UV irradiation: (a) no CeCar₃; (b) CeOct₃; (c) CeLau₃; (d) CeSt₃.

Figure 5 shows that after UV irradiation (see Fig. 4), followed by 575-day storage, LDPE films containing 0.3 wt % CeCar₃ and 0.1 wt % DPK still continued oxidative degradation at a similar oxidative rate to that of CeCar₃ alone, as shown in

Figure 3. After the initial six-day UV irradiation, LDPE films containing 0.1 wt % DPK with 0.3 wt % CeSt₃, CeLau₃, and CeOct₃ had CI of 21, or 32 or 14, respectively [see Fig. 4(b-d)], and got into the decay stage. Furthermore, after continuous

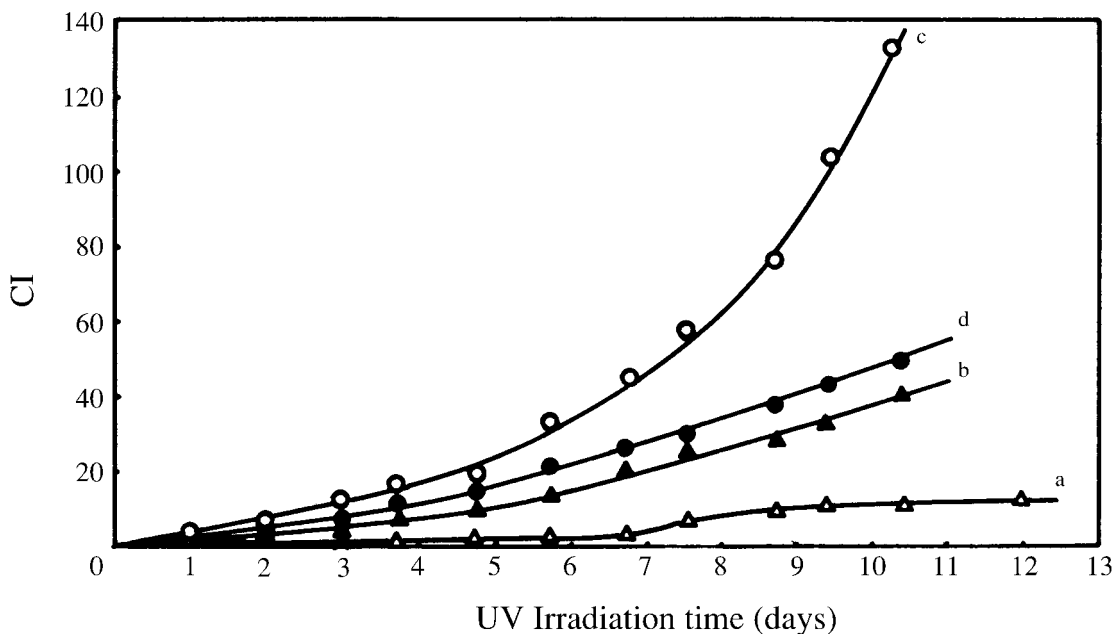


Figure 4 Effects of 0.1 wt % DPK on the rates of UV photooxidation of LDPE films containing 0.3 wt % CeCar₃: (a) no additive; (b) CeOct₃ + DPK; (c) CeLau₃ + DPK; (d) CeSt₃ + DPK.

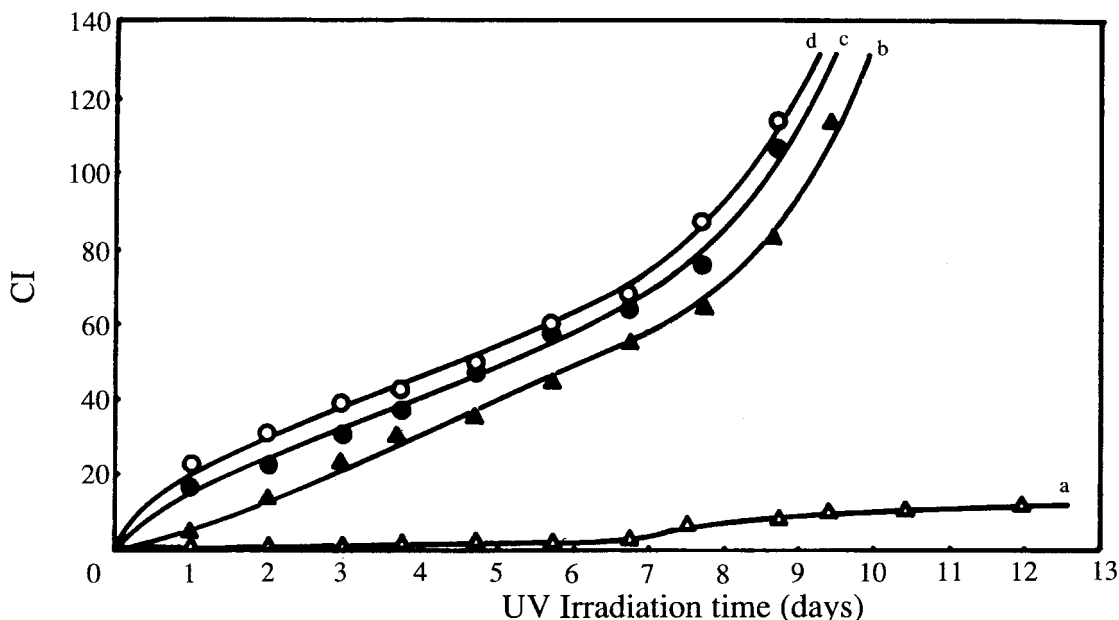


Figure 5 Effects of 575-day storage on the rates of the storage–oxidative degradation of LDPE films containing 0.3 wt % CeCar₃ and 0.1 wt % DPK after UV irradiation: (a) no additive; (b) CeOct₃ + DPK; (c) CeLau₃ + DPK; (d) CeSt₃ + DPK.

575-day storage, these LDPE films had CI of 61, or 57 or 45, accordingly [see Fig. 5(b–d)], and got into the embrittlement stage. It is obvious that the sensitizing activities of CeCar₃ in combination with DPK on the storage–oxidative degradation of LDPE films after UV irradiation decreased progressively, as follows: CeSt₃ + DPK > CeLau₃ + DPK > CeOct₃ + DPK.

UV Photooxidation of LDPE Films Containing CeSt₃ and AK

Figure 6 shows that, after adding 0.1 wt % DPK or MK to LDPE films containing 0.3 wt % CeSt₃, the rates of UV photooxidation of these films obviously decreased [see Fig. 6(b–d)]. It means that DPK and MK retarded the photosensitization of CeSt₃ in LDPE films. After two-day UV irradiation, LDPE films containing 0.3 wt % CeSt₃ had CI greater than 6 and entered into the decay stage. However, LDPE films containing 0.3 wt % CeSt₃ and 0.1 wt % DPK or MK only had CI of 4 or 3 and did not get into the decay stage. Thus, the retardations of AK in LDPE films containing CeSt₃ during photooxidative degradation decreased progressively, as follows: MK > DPK.

Figure 7 shows that, after UV irradiation (see Fig. 6), followed by 575-day storage, LDPE films containing 0.3 wt % CeSt₃ and 0.1 wt % DPK still continued their oxidative degradation. It is note-

worthy that LDPE films containing 0.3 wt % CeSt₃ with/without 0.1 wt % DPK had very similar oxidative rates [see Fig. 7(c) and (d)], but LDPE films containing 0.3 wt % CeSt₃ and 0.1 wt % MK had very slow oxidative rates [see Fig. 7(b)]. It is evident that in the course of long storage, MK retarded sensitization oxidation of CeSt₃. With 0.1 wt % DPK or MK after initial six-day UV irradiation, the CI of LDPE films containing 0.3 wt % CeSt₃ decreased from 28 [see Fig. 6(d)] to 22 [see Fig. 6(c)] or 13 [see Fig. 6(b)]; after 575-day storage, the CI of these films again decreased from 60 [see Fig. 7(d)] to 54 [see Fig. 7(c)] or 28 [see Fig. 7(b)]. Clearly, after both UV irradiation and long storage, LDPE films containing 0.3 wt % CeSt₃ with/without 0.1 wt % DPK all got into the embrittlement stage, and LDPE films containing 0.3 wt % CeSt₃ and 0.1 wt % MK were still in the decay stage.

M_n of LDPE Films Containing CeCar₃ With/Without AK

It is generally agreed that LDPE films containing photosensitizer enter the embrittlement stage after M_n decreases to less than 5000.¹² Figure 8 shows that M_n of LDPE films containing CeCar₃, with/without AK compound photosensitizers, decreased with increasing CI of UV photooxidation during UV irradiation. Before UV irradiation, the CI of LDPE films was 0.32; thus, M_n was 3.23

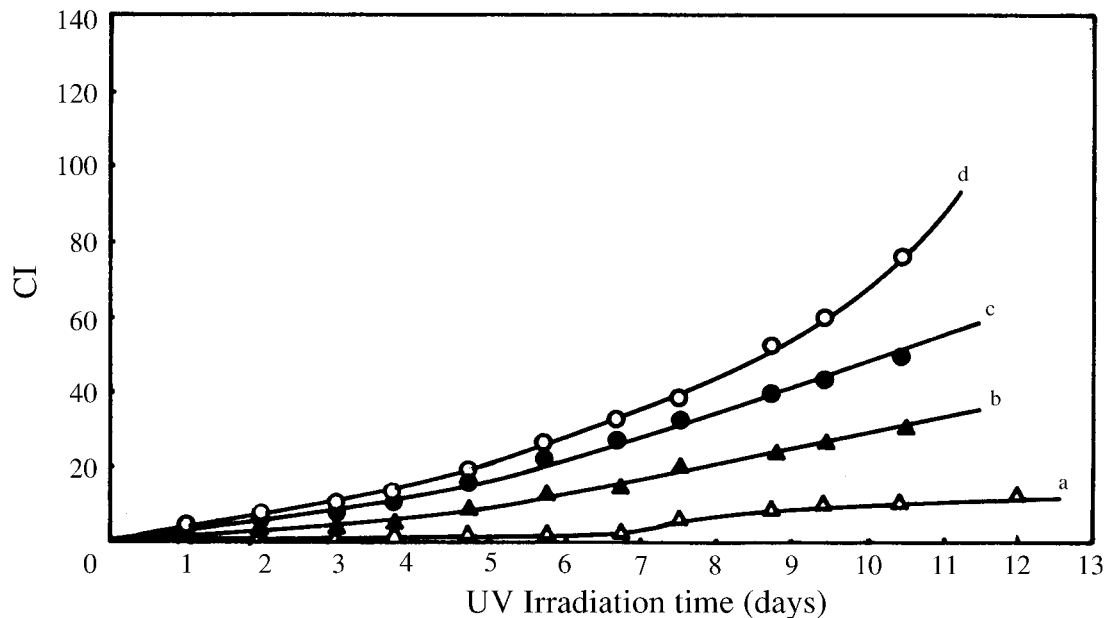


Figure 6 Effects of 0.1 wt % AK on the rates of UV photooxidation of LDPE films containing 0.3 wt % CeSt₃: (a) no additive; (b) CeSt₃ + MK; (c) CeSt₃ + DPK; (d) CeSt₃.

$\times 10^4$. In the course of UV irradiation, when the CI increased to 7.33, M_n was down to 2.28×10^4 , and the films got into the decay stage. When the CI increased to 45 or 70, M_n decreases to 3800 or 2800, and the films got into the embrittlement stage.

The Action Mechanism of the Photosensitizers

The Photosensitization of CeCar₃

When LDPE film containing CeCar₃ absorbed UV photo energy during UV irradiation, electron transfer occurred in the 4f subshell of the Ce atom of

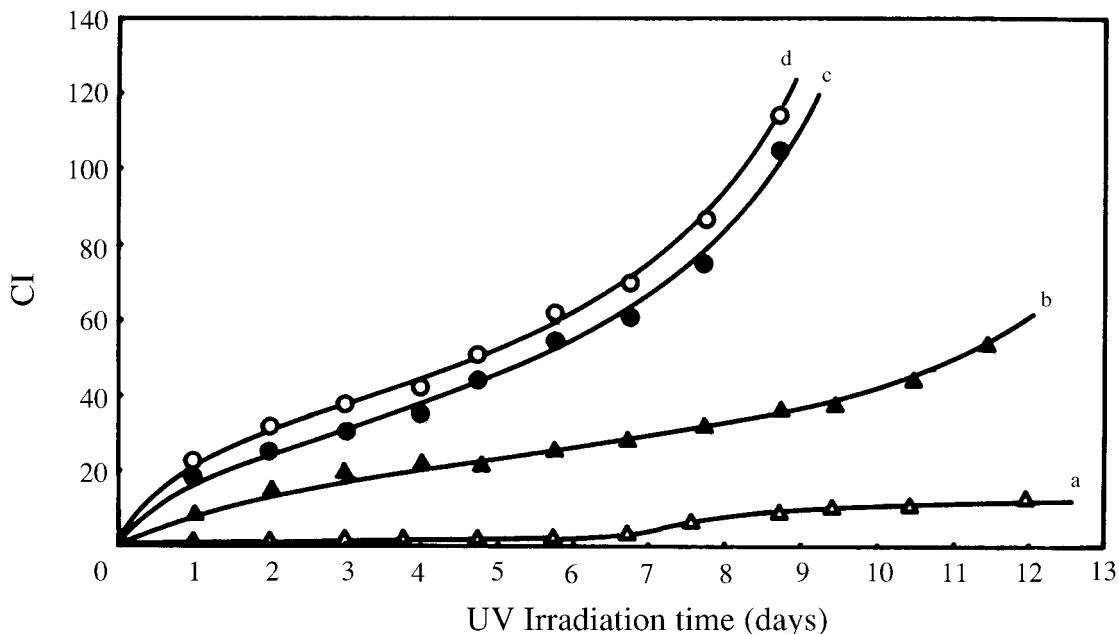


Figure 7 Effects of 575-day storage on the rates of the storage-oxidative degradation of LDPE films containing 0.3 wt % CeSt₃ and 0.1 wt % AK after UV irradiation: (a) no additive; (b) CeSt₃ + MK; (c) CeSt₃ + DPK; (d) CeSt₃.

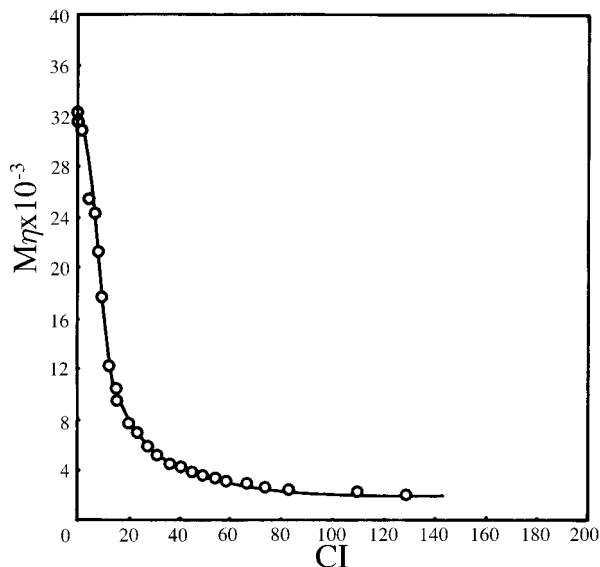
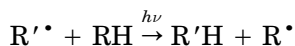
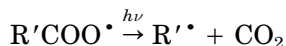
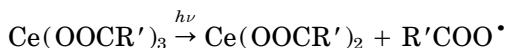


Figure 8 Effects of CeCar₃ with/ without AK on M_n of LDPE films during UV photooxidation.

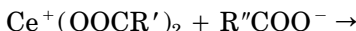
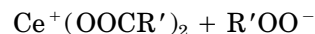
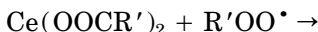
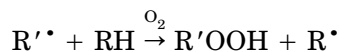
atomic number 57 in the sixth period, resulting in the production of carboxylic acid free-radical R'COO[•]. This species decarboxylated to form an alkyl radical R'[•], which transformed LDPE film from RH into free radical R[•].¹³ These initiation reactions of photooxidation are described as follows:



(R' = C₇H₁₅—, or C₁₁H₂₃—,
or C₁₇H₃₅—, RH = LDPE)

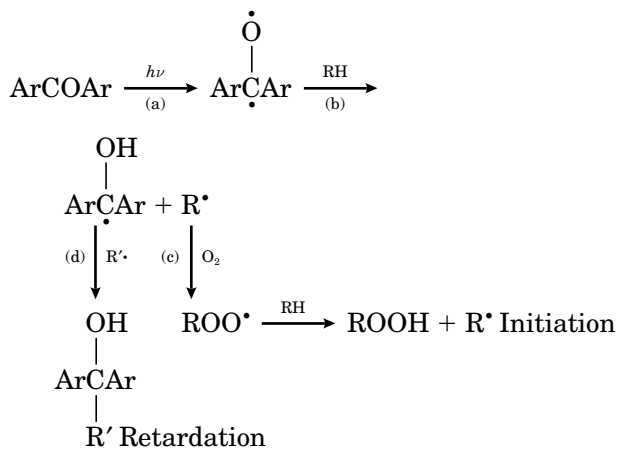
In the presence of both heat and oxygen, LDPE hydroperoxide ROOH was formed by the reaction of LDPE free radical R[•] with O₂. In the presence of both oxygen and UV irradiation, macromolecular aldehyde was produced by the breakdown of main chain of LDPE, or LDPE polymeric ketone was transformed directly. Finally, because of the results of photooxidation and thermooxidation, low molecular weight oxygenated products, such as ketones, carboxylic acids, aldehydes, esters, alcohols, etc., were continuously decomposed by Norrish I or II reactions.¹⁴⁻¹⁵ It seems that after the initial stages, the main catalytic products in sensitized photooxidation of LDPE were again trivalent macromolecular CeCar₃, which were reformed by the reaction of bivalent CeCar₃ and macromolecular carboxylic acids produced. Autoaccelerating photo-

oxidative degradations of LDPE during UV irradiation and long storage were repeated continuously.¹³ Their reactions are as follows:



The Combined Photosensitizations of AK and CeCar₃

The photosensitizations of AK in LDPE films have been studied, and the following reactions were proposed by some authors.¹³



Where Ar is an aromatic group, R'• is R• or a growing polymer chain, and R• is an LDPE free radical. That is, during UV irradiation, AK was decomposed into free radical by the reaction (a). For LDPE, reaction (b) would be slower since the radical R• was more resonance-stabilized. It appears that the relative rates of the reactions (c) and (d) will determine whether initiation or termination of production of AK free radical predominates, and these also depend on the structures of alkyl hydrocarbon of CeCar₃ and LDPE. Mixing of DPK and CeOct₃ may readily lead to the reaction (d) and quenching of LDPE free radical R•, so that, ultimately, only CeOct₃ plays a role in photosensitization [see Fig. 2(b) and Fig. 4(b)]. Mixing of DPK and CeLau₃ may cause reaction (c) to form LDPE hydroperoxide ROOH, which enhances sensitizing of CeLau₃ [see Fig. 2(c) and Fig. 4(c)]. Mixing of DPK or MK and CeSt₃ may partly quench LDPE or CeSt₃ free radicals; as a result, these mixes retard the rates of photooxidation of LDPE [see Fig. 6(b–d)].

After both UV irradiation and long storage duration, DPK in LDPE films containing CeCar₃ may not initiate reactions (a) and (b), so, there, only CeCar₃ worked in sensitizing LDPE, and similar storage oxidative rates appeared [see Fig. 5(b–d) and Fig. 3(b–d)], except for the mixing of MK and CeSt₃ [see Fig. 7(b) and Fig. 6(b)].

CONCLUSIONS

1. The CeSt₃, CeLau₃, and CeOct₃ can be very effective in sensitizing UV photooxidative degradation of LDPE films.
2. The photosensitizing activities of CeCar₃ on UV photooxidative degradation of LDPE films decreased progressively as follows: CeSt₃ > CeLau₃ > CeOct₃.

3. The photosensitizing activities of CeCar₃, in combination with DPK, on UV photooxidative degradation of LDPE films decreased successively as follows: CeLau₃ + DPK > CeSt₃ + DPK > CeOct₃ + DPK.
4. The photosensitive activities of CeSt₃, in combination with MK or DPK, on UV photooxidative degradation of LDPE films decreased by degrees as follows: CeSt₃ > CeSt₃ + DPK > CeSt₃ + MK.
5. After both UV irradiation and long duration storage, LDPE films containing CeCar₃ with/without DPK continued storage–oxidative degradation at the stored oxidative rates similar to the past, except for LDPE films containing MK and CeSt₃.

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