

Wavelength Sensitivity of Enhanced Photodegradable Polyethylenes, ECO, and LDPE/MX

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SYNOPSIS

The wavelength sensitivity for decrease in percent elongation at break of ethylene carbon monoxide copolymer (ECO) and a low density polyethylene containing a metal compound prooxidant (LDPE/MX) on exposure to a borosilicate-filtered xenon-arc source was determined using a set of sharp cut-on filters. The spectral region primarily responsible for the degradation at 60°C is 323–328 nm for ECO and 323–338 nm for LDPE/MX. At 77°C, the sensitivity shifts about 10 nm to longer wavelengths. Based on the wavelength sensitivity of these materials to solar simulated radiation and the transmission properties of window glass, these materials can be expected to lose desirable mechanical properties when exposed to window-glass-filtered sunlight. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Photodegradation of polyethylene and its copolymers has been widely studied. These studies have included the elucidation of mechanisms of photoprocesses^{1,2} based on analyses of reaction products by either infrared^{3,4} or UV-visible⁵ spectroscopy and studies on kinetics of photooxidation.^{2,6–8} The effect of temperature on photooxidation of polyolefins has also been reported.^{9,10} The wavelength sensitivity of the photodegradation of polyethylene has not been extensively studied, but using a spectrographic technique, Searle¹¹ determined that the maximum concentration of carbonyl moieties in polyethylene films (4 mil) exposed to a borosilicate-filtered xenon arc source was caused by a spectral band centered at about 340 nm. We have also studied the wavelength sensitivity of the light-induced loss of extensibility of injection-molded polyethylene samples exposed to filtered xenon radiation using the cut-on filter technique with film samples.¹² The most effective wavelength range for loss of elongation was 308–329 nm.

The present study was undertaken to establish the wavelength sensitivity of changes in tensile

properties of enhanced photodegradable ethylene-carbon monoxide copolymer films (designated ECO) and low-density polyethylene films containing a metal compound prooxidant (designated LDPE/MX). The carbonyl moiety in ECO has a broad absorption band extending beyond 340 nm.¹³ It is similar to that obtained with long-chain symmetrical ketones such as 12-tricosonone. The presence of several types of ketones in the copolymer might be responsible for the broadness of the absorption band.¹⁴ Addition of metal compound prooxidants (particularly iron and magnesium compounds) to polyethylene will catalyze both the photooxidative and thermooxidative degradation processes. In both instances, the principal role of the metal is believed to be the catalysis of hydroperoxide decomposition via the well-known redox reactions.¹⁵

Because of the urban litter problems caused by disposable plastics packaging products, there is renewed interest in plastics designed to rapidly disintegrate outdoors when exposed to sunlight. It is important to insure maintenance of useful mechanical properties during or prior to use when these materials are exposed to indoor illumination including window-glass-filtered sunlight. Therefore, it is of interest to determine the wavelengths of solar radiation responsible for the photodegradation. The borosilicate-filtered xenon-arc source was used for

the present study because it has a spectral irradiance distribution similar to that of terrestrial sunlight. Tensile elongation at break was used as the criterion of degradation because of its practical relevance in plastic film applications and because it is a particularly sensitive measure of degradation.¹⁶

EXPERIMENTAL

Materials

Two types of enhanced photodegradable polyethylenes were used in the study: a 0.42 mm thick sheet of ethylene-carbon monoxide copolymer with 1% of the CO comonomer, designated ECO (supplied by HiCone Division, Illinois Tool Works, Co. Chicago, IL); and a 0.030 mm extrusion-blown low-density polyethylene film (supplied by Plastigone Company, Miami, FL) containing iron and manganese compound prooxidants, designated LDPE/MX. The polymer film samples used in the present study were typical of those available commercially for enhanced degradable plastics applications. The ECO copolymer in the thickness studied here is used to fabricate photodegradable six-pack carrier rings, and the LDPE/MX material is used as an agricultural mulch film. Both samples were wrapped in black paper and stored under dry conditions in a refrigerator until exposure.

Exposures

Laboratory exposures were carried out in an Atlas Ci 65 series Weather-Ometer, using continuous illumination (no dark cycle or water spray). The equipment uses a 6500-watt borosilicate-filtered xenon arc source.

A convenient experimental approach to studying wavelength sensitivity is the exposure of replicate samples of polymer films to xenon-arc radiation behind a series of cut-on filters. Each shorter wavelength cut-on filter allows exposure to progressively more of the shorter wavelengths and an increasing amount of total UV. Each filter allows only radiation of wavelengths longer than its cut-on wavelength to be transmitted. The latter is the 5% transmission of the filters that are listed in Tables I and II. Transmission spectra for several cut-on filters are shown in Figure 1.

Typically, strips of polymer film samples 0.5×7.0 in. were cut, and four strips were mounted in each of the standard exposure frames. A cut-on filter (2×2 in.) was mounted over the open mid section of

the exposure frame. During exposure, the segment of strips covered by the cut-on filter is irradiated by the source. The experimental sample temperatures reported are those measured by the black panel.

Measurements

Tensile property determinations were carried out according to ASTM D882, Tensile Properties of Thin Plastic Sheeting, using an Instron Model 1122 Universal Testing machine. A crosshead speed of 500 mm/min and a gauge length of 50 mm were used for the measurements.

RESULTS AND DISCUSSION

Ethylene-carbon monoxide copolymer (ECO) readily breaks down on exposure to solar radiation with the rate of degradation, as measured by changes in tensile properties, depending on the ambient temperature and light levels.¹⁶ At ambient and lower temperatures, the chain scission process responsible for deterioration of the film is attributed primarily to Norrish type II process.¹³ Of the various tensile properties, elongation at break is known¹⁷ to be particularly sensitive to degradation in the case of polyethylene and the copolymer ECO. Table I shows the wavelengths in solar simulated radiation responsible for changes in tensile properties. Test data is given of average elongation at break for ECO samples exposed to a borosilicate filtered xenon-arc source, behind cut-on filters. The exposures were carried out at two different temperatures, 60 and 77°C with exposure times of 219 and 117 h, respectively. Figure 2 shows the tensile elongation at break plotted versus the 5% transmission wavelength of the filter for samples exposed at 60°C. Each datapoint in the figure shows the average tensile elongation at break for the sample exposed to all wavelengths of the xenon source spectrum longer than the cut-on wavelength of the filter used with that sample.

The data shows a marked wavelength dependence of the photodegradation process. In the 60°C exposure, decreasing the cut-on wavelength of the filter from 360.5 to 328.1 nm has no effect on the elongation at break of the copolymer. However, a very sharp drop in ultimate elongation is caused by exposure to wavelengths between 322.5 and 328.1 nm. In the 77°C exposure, the largest decrease in elongation at break is caused by wavelengths between 328.1 and 337.9 nm. At the latter temperature, thermal effects appear to be responsible for a significant loss in elongation; but at 60°C, the change in elon-

Table I Average Tensile Elongation at Break of ECO Samples Before and After Exposure to a Borosilicate-filtered Xenon Arc Source, Behind Cut-on Filters

Filter No.	Cut-on Wavelength (nm) (5% Trans.)	Exposure at 77°C/117 h		Exposure at 60°C/219 h	
		Average Percent Elongation	Standard Deviation	Average Percent Elongation	Standard Deviation
Unexposed		922	21	922	21
00	238.2	132	28	—	—
2	262.5	165	15	7	1
3	280.2	57	9	6	2
4	295.0	100	31	40	48
5	303.5	55	52	78	35
6A	313.2	113	31	92	7
6B	318.0	166	56	148	8
7	322.5	107	10	170	16
8	328.1	175	70	932	16
9	337.9	612	70	900	36
10	339.7	460	202	—	—
11	352.4	640	72	992	42
12	359.1	493	234	919	56
13	360.5	525	31	950	50
14	367.5	504	131	—	—
15	373.0	738	80	—	—
16	406.8	369	210	—	—

Table II Average Tensile Elongation at Break of LDPE/MX Samples Before and After Exposure to a Borosilicate-filtered Xenon Arc Source, Behind Cut-on Filters

Filter No.	Cut-on Wavelength (nm) (5% Trans.)	Exposure at 77°C/95 h		Exposure at 60°C/295 h	
		Average Percent Elongation	Standard Deviation	Average Percent Elongation	Standard Deviation
Unexposed	—	398	112	398	112
00	238.2	52	19	51	11
2	262.5	41	12	50	11
3	280.2	8	2	60	13
4	295.0	92	29	59	23
5	303.5	92	37	59	20
6A	313.2	61	11	96	6
6B	318.0	81	8	131	5
7	322.5	162	66	109	18
8	328.1	124	19	181	28
9	337.9	138	21	273	44
10	339.7	150	48	347	—
11	352.4	314	88	287	217
12	359.1	393	93	491	—
13	360.5	176	60	310	146
14	367.5	412	54	—	—
15	373.0	374	—	—	—
16	—	—	—	—	—

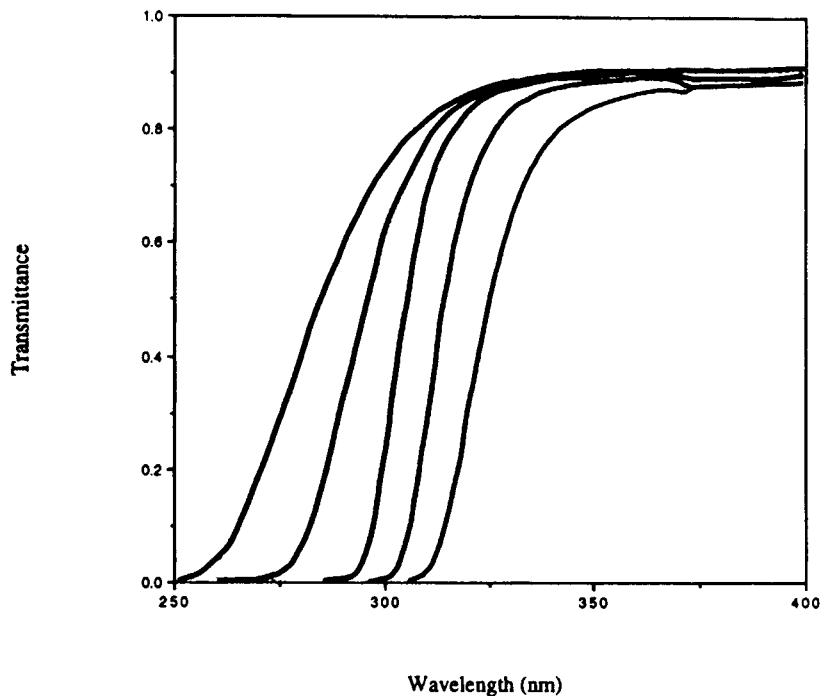


Figure 1 Transmittance of several representative cut-on filters used in the exposure experiment.

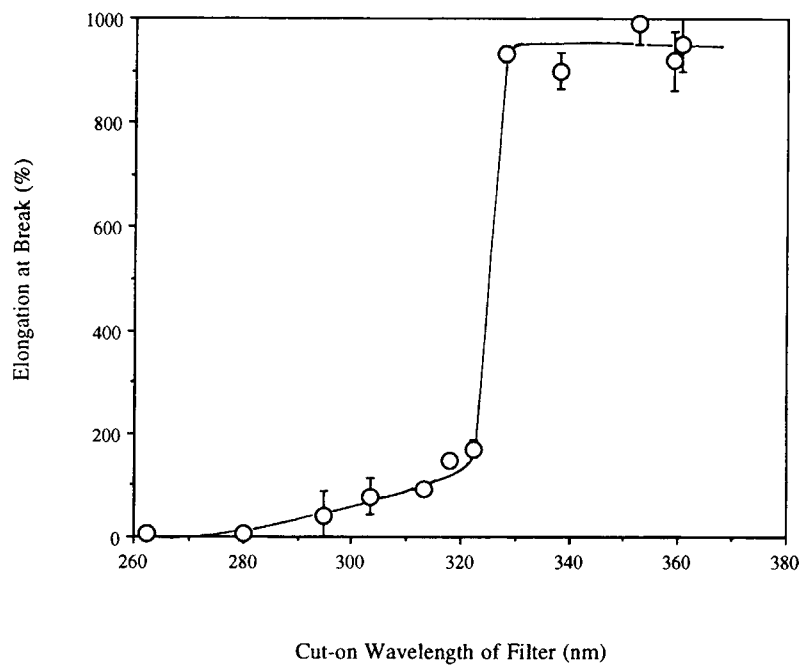


Figure 2 Average tensile elongation at break of ECO samples exposed at 60°C to a borosilicate-filtered xenon-arc source, behind different cut-on filters, identified by the wavelength at 5% transmittance.

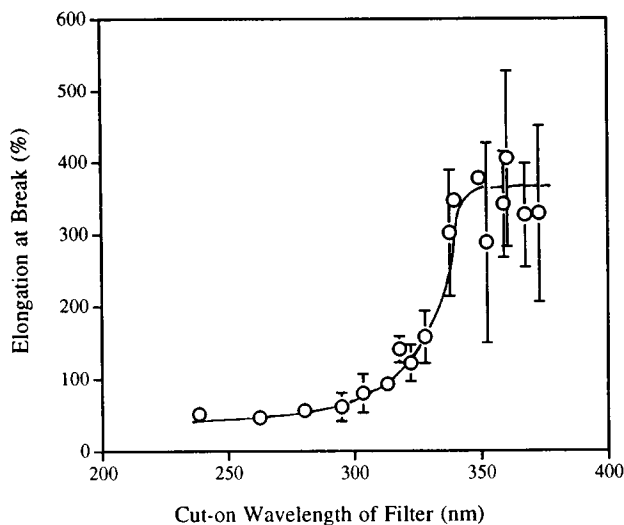


Figure 3 Average tensile elongation at break of LDPE/MX samples exposed at 60°C to a borosilicate-filtered xenon-arc source, behind different cut-on filters, identified by the wavelength at 5% transmittance.

gation is caused only by light. The data shows a fairly high degree of scatter, which is inherent to this type of measurement. Tensile strength of the samples were also determined, although not shown in Table I. When plotted similarly, the average tensile strength of exposed samples also showed a sharp decrease in the same wavelength range. However, the value changes by only about 30%.

Since the ECO copolymer has a broad absorption band that extends to wavelengths longer than 340 nm,¹³ the effectiveness of UV-A radiation in deteriorating the ECO films is not unexpected. Inherent wavelength sensitivity of the copolymer is magnified due to the sharp increase in intensity of the source from 300 to 350 nm. Given the sharp drop in elongation observed, it is difficult to establish from the data if wavelengths less than 322.5 nm are also effective in deteriorating the ECO copolymer. As with most materials, the more energetic shorter wavelength radiation should be more effective in reducing the tensile elongation at break of this material. However, in the solar simulated spectrum, shorter wavelengths decrease in intensity sharply with decrease in wavelength.

Data from wavelength sensitivity experiments on LDPE/MX are summarized in Table II; one was carried out at 60°C for 295 h, and the other at 77°C for 94.5 h. As with the ECO copolymer samples, a relatively sharp change in elongation is observed as the cut-on wavelength of the filter is progressively decreased. In this case, the major decrease occurs between 339.7 and 352.4 nm in the exposure carried

out at 77°C and about 323–338 nm at 60°C. The data obtained at 60°C, is shown in Figure 3. The decrease in extensibility is not as sharp as with ECO samples, possibly because of concurrent thermooxidative chain scission. The metal catalysts employed are well known to autocatalyze the thermooxidative chain scission processes, even at the moderate temperatures (60–77°C) used in the Weather-Ometer exposure. Therefore, the total deterioration suffered by this type of sample exposed in a Weather-Ometer cannot be attributed solely to photochemical processes. Some thermal oxidation can also take place in ECO copolymer, but it is less significant than that in a catalyzed oxidation process as in LDPE/MX samples.

A decrease in the elongation at break of the sample is indicative of a decrease in the average molecular weight of the polymer. In a recent study, Andrady et al.¹⁶ demonstrated the high degree of correlation between the change in average molecular weight of polyethylene, the elongation at break, and the spectroscopically determined carbonyl concentration for the two types of polymer films used in the present study. This data is particularly useful as the samples were selected from the same batch for both studies. Figure 4 shows a plot of the elongation at break versus the molecular weight for LDPE/MX samples exposed under outdoor conditions at a site in Cedar Knolls, NJ. The reported correlation between the average molecular weights and elongations at break calculated from their reported data can be modelled by the following equations.

For ECO copolymer

$$\text{Mol wt } (M_n) = 52.5 (\text{elongation}) + 1.23 \times 10^4 \quad r^2 = 0.94 \quad (1)$$

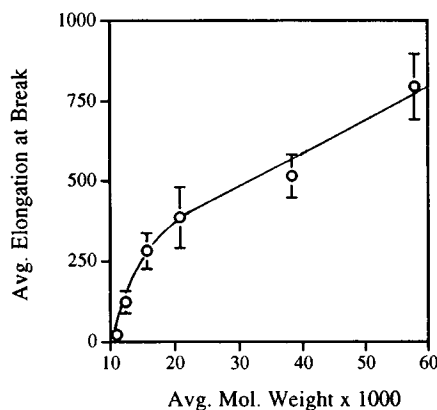


Figure 4 The dependence of the average elongation at break of LDPE/MX films on the number average molecular weight determined by GPC.

For LDPE/MX

Mol wt (M_n)

$$= 9.49 \times 10^3 [10^{0.001(\text{elongation})}] \quad r^2 = 0.96 \quad (2)$$

The correlation coefficients (r^2) indicate the goodness of fit of the data to the linear regression equations. Using these regression equations, the average molecular weights for different samples listed in Tables I and II might be estimated from the measured values of average elongation at break. With the ECO copolymer, the change in average molecular weight that corresponds to the sharp drop in elongation that occurs at filter 7 or 8 (Table I) is moderate. For 77°C data, the estimated average molecular weight for samples exposed behind filters 9 and 8, changes by 52% (from about 44,500 to 21,500). For the 60°C data, the estimated change is about 56% (from 49,000 to 21,300) for samples exposed behind filter 8 and 7.

With LDPE/MX samples at 77°C, samples exposed under filter 10 and 11, undergo a decrease in molecular weight of 32% (from about 19,600 to 13,400). At 60°C, the change in elongation in samples exposed behind filter 9 and 7 is accompanied by an estimated drop in molecular weight by about 31% (from 18,000 to 12,200). Small changes in molecular weights can result in substantial changes in the tensile properties of these films.¹⁶ The molecular weights used for obtaining the above equations were determined using hot-solvent gel permeation chromatography (GPC). The technique is relatively less sensitive to lower molecular weight fractions and therefore tends to overestimate average molecular weights in samples with a significant low molecular weight fraction. This is particularly true of the LDPE/MX material, which is likely to contain significant amounts of low-molecular weight "sol" fragments due to catalysis of scission reaction by metal compounds. The change in average molecular weight for photodegraded LDPE/MX films might, therefore, be somewhat larger than estimated here.

Both polymers need to be stable under ambient indoor exposure conditions prior to use. With the ECO polymer used in a packaging application, where it is displayed at retail locations, the photostability on exposure to glass-filtered sunlight is particularly important. The transmission spectrum of float-glass used in window glazing begins to show measurable transmittance from 300 nm. The transmittance increases from near zero to over 80%, in the wavelength interval of 300–400 nm and thereafter re-

mains over 80% for UV-visible wavelengths. Depending on type, window glass can transmit as much as 26% at 320 nm, 54% at 330 nm, and 73% at 340 nm.¹⁸ A qualitative consideration of the transmittance data with the wavelength sensitivity data in Figures 2 and 3 suggest that photodegradation of these polyethylenes will readily occur when exposed to sunlight filtered by window glass. The extent of such degradation and its impact on useful properties of the polymer will depend on the duration of exposure.

CONCLUSIONS

The enhanced photodegradable polymers, ECO and LDPE/MX, showed very significant decreases in percent elongation at break when exposed to borosilicate-filtered xenon-arc radiation in the spectral region of 323–328 nm for ECO and 323–338 nm for LDPE/MX for exposures at 60°C. Increasing the sample temperature to 77°C caused the wavelength sensitivity to shift by about 10 nm to longer wavelengths.

Based on the wavelength sensitivity data obtained using solar simulated radiation and the reported spectral transmittance properties of window glass, these polymers can be expected to lose some of their tensile extensibility and strength when exposed to window-glass filtered sunlight. The sensitivity of LDPE/MX extends to longer wavelengths than that of ECO. Since the usefulness of enhanced degradable polymers also depends on their ability to remain undegraded during use under indoor conditions, it is important to protect ECO and LDPE/MX films against indoor illumination by sunlight or other light containing wavelengths shorter than about 350 nm.

REFERENCES

1. F. Gugumus, *Polym. Mat. Sci.*, **58**, 359 (1988).
2. F. Gugumus, *Angew. Makromol. Chem.*, **182**, 111 (1990).
3. J. V. Benham and T. J. Pullukat, *J. Appl. Polym. Sci.*, **20**, 3295 (1976).
4. A. Torikal, A. Takeuchi, S. Nagaya, and K. Fueki, *Polym. Photochem.*, **7**, 199 (1986).
5. R. Geetha, A. Torikai, S. Nagaya, and K. Fueki, *Polym. Deg. Stabil.*, **19**, 279 (1987).
6. G. Scott, ACS Symposium Series 25, 1976, p. 340.
7. C. H. Chew, L. M. Gan, and G. Scott, *Eur. Polym. J.*, **13**, 361 (1977).
8. E. T. Denisov, *Russ. Chem. Rev.*, **47**, 572 (1978).

9. S. W. Bigger and O. Delatycki, *Polymer*, **29**, 1277 (1988).
10. F. H. Winslow, W. Matreyck, and M. Torozzollo, *Soc. Plast. Eng. J.*, **28**, 19 (1972).
11. N. D. Searle, *Preprints of Bewitterung International Symposium on Weathering*, Essen, Germany, Sept. 28–29, 1987.
12. A. L. Andrady and N. D. Searle, unpub. data, 1995.
13. G. H. Hartley and G. E. Guillet, *Macromolecules*, **1**, 165 (1968).
14. S. K. I. Li and J. E. Guillet, *J. Polymer Sci., Polym. Chem. Ed.*, **18**, 2221 (1980).
15. M. U. Amin and G. Scott, *Eur. Polym. J.*, **10**, 1019 (1974).
16. A. L. Andrady, J. E. Pegram, and S. Nakatsuka, *J. Environ. Polym. Deg.*, **1**(1), 31 (1993).
17. A. L. Andrady, J. E. Pegram, and Y. Tropsha, *J. Environ. Polym. Deg.*, **1**(3), 171–179 (1993).
18. W. D. Ketola and J. S. Robins, III, In *Accelerated and Outdoor Durability Testing of Organic Materials; ASTM STP 1202*, W. D. Ketola and D. Grossman, Eds., American Society for Testing and Materials, Philadelphia, p. 133, 1994.

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