

Photooxidative Effects on Properties and Structure of High-Density Polyethylene

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SYNOPSIS

The environmental degradation of high-density polyethylene (HDPE) has been studied, in addition to that of HDPE blends, containing various concentrations of ethylene carbon monoxide copolymer. Extruded sheets of each material were exposed to natural Arizona sunlight for times up to 6 months. Exposed samples were then analyzed with respect to molecular weight, density, thermal behavior, mechanical properties, and infrared absorption. Additional samples were exposed to laboratory weathering conditions, evaluated in terms of property changes, melted, reformed, and then reevaluated without further weathering exposure. Results indicate that sunlight exposure causes decreased elongation to break, increased embrittlement, decreased molecular weight, and increased crystallinity. Environmental oxidative degradation is elucidated by the measurement of specific infrared bands, sensitive to the formation of carbonyl and vinyl end groups. As environmental degradation causes reductions of molecular weight, polymer chain mobility increases, leading to a higher degree of crystallinity. This increased crystallinity, along with the decreased molecular weight, accounts for the loss of ductility, indicated by a sharp decrease in ultimate elongation. The presence of carbon monoxide copolymer in the blended samples accelerates the process of environmental degradation, however, the degradation mechanisms appear to be similar to those observed for nonblended HDPE. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

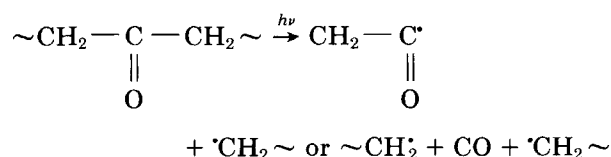
Polyolefins are commercial plastics of great economic importance. They are also materials with potential for significant outdoor exposure. For this reason, many studies have been conducted over the years to investigate various aspects of their weathering behavior.¹⁻¹⁶ Baum¹ investigated changes in carbonyl concentration, percent elongation, and oxygen uptake, in relationship to various weathering, sample treatment, and additive conditions. Melchore² compared degradation results, obtained after exposing polypropylene to assorted laboratory and outdoor weathering conditions, at several different light wavelengths. Properties were compared in terms of elongation, tensile strength, brittleness, and carbonyl formation. Winslow^{3,4} described radical and nonradical mechanisms proposed as routes

of polyolefin degradation, as well as various stabilization mechanisms. The natural weathering of low-density polyethylene (LDPE) was investigated by Akay, Tincer, and Ergöz.⁵ They found that, although vinyl and carbonyl index increased with exposure time, these changes could not easily be correlated with mechanical property reductions. LaMantia⁶ also investigated natural weathering of LDPE and provided some structure and property correlations through analyses of density, viscometry, tensile, and dynamic mechanical results.

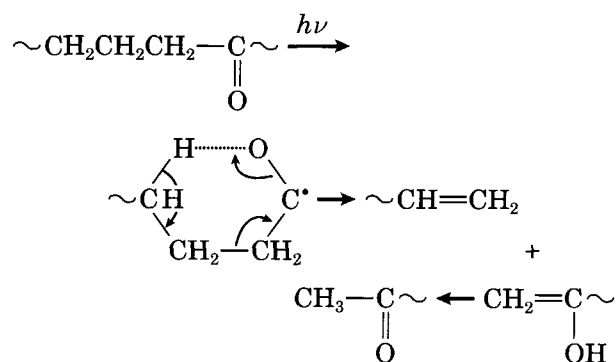
Photooxidative stability of polyolefins was found by Scott and co-workers,⁷⁻¹⁰ to be strongly dependent upon the degree of oxidation, which occurred while the polymer was processed in the melted state. During the early stages of subsequent ultraviolet (UV) exposure, vinylidene and hydroperoxide concentrations were found to be among the most important initiators of photooxidative degradation. During later stages of photooxidative degradation, carbonyl initiation was found to be an important autoaccelerating photoactivator. A review article, by

Heaps and Austin,¹¹ shows that exposure of polyethylene to UV light, increases its rate of oxidative degradation. They concluded that polyethylene's sensitivity to UV radiation was "caused by carbonyl groups derived from the initiator or otherwise generated during polymerization."

Allen and McKellar¹² published an extensive review concerning the sensitized degradation and stabilization of low- and high-density polyethylene. In their view, carbonyl groups were the main light-absorbing species, responsible for the photochemical initiation reactions of sunlight-exposed polymers. Norrish type I reactions were shown to produce free radicals from carbonyl group precursors, as shown below.



The six-membered cyclic intermediate of the type II Norrish process was then shown to produce an olefinic group as well as an enolic group, which could then rearrange into a carbonyl structure as follows.



While most investigators have been concerned primarily with maintaining the photooxidative stability of polyethylene, several studies have focused on obtaining increased rates of photodegradation.¹³⁻¹⁶ Copolymers of ethylene and carbon monoxide have proven to be suitable for use in studies of the photochemical degradation of polyethylene.¹³ In most of these studies¹³⁻¹⁶ copolymers irradiated in the presence of oxygen were shown to experience molecular weight degradation, evolution of carbon monoxide, and formation of terminal vinyl and hydroperoxide groups.

A variety of mechanisms have been proposed to elucidate the photooxidative degradation processes of polyethylene. In many cases, these processes have

been described in terms of hydroperoxide, carbonyl, and vinyl end-group concentrations. Very few studies, however, are available relating the effects of specimen crystallinity to polymer degradation and embrittlement. The current investigation is directed toward clarifying the interactive relationships among various property changes resulting from this degradation. High-density polyethylene has been weathered under natural sunlight for up to 6 months, with properties measured after various exposure times. To provide additional degradation models, polyethylene blends containing 5 and 10% ethylene carbon monoxide copolymer (ECO) have been included. Changes in mechanical properties, infrared absorption characteristics, molecular weight, and crystallinity have been followed throughout exposure. Additional unblended samples have been exposed to accelerated laboratory weathering, in order to further demonstrate the relationships between molecular weight and crystallinity, which occur during sample embrittlement.

EXPERIMENTAL

Materials and Exposure Conditions

Commercial processing conditions, with zone temperatures ranging from 190 to 210°C, were used to prepare extruded strips of high-density polyethylene (HDPE), as well as polyethylene blends containing 5 and 10% ECO. An initial concentration of 1% carbon monoxide was present in the unblended ECO copolymer. The extruded strips, with thicknesses of about 0.6 mm, were exposed to natural Arizona sunlight for up to 6 months. Additional extruded strips of unblended, Allied 60003, HDPE were compression molded at 190°C, with an applied load of 15,000 lb, using a Carver press. After being cooled to room temperature between metal plates, the molded sheets were die cut as tensile specimens and subjected to accelerated laboratory weathering. Accelerated weathering was accomplished at 23°C with samples about 0.3 mm thick, located 4 in. below two Voltare 40-W fluorescent UV lamps. Physical property evaluations were performed on samples after various weathering times and conditions. Selected samples that had been stored under accelerated laboratory weathering conditions were recompression molded after property evaluations had been completed. Without additional UV exposure, the remolded samples were then evaluated in terms of previously measured physical properties.

Mechanical Properties

Tensile mechanical properties were determined according to ASTM D 882, using a table model Instron 1101 Tensile Tester. Sample strips 1.27 cm (0.5 in.) wide; with gauge lengths of 10.2 cm (4 in.) and thicknesses of about 0.6 mm (23 mils) or gauge lengths of 5.1 cm (2 in.) and thicknesses of about 0.3 mm (13 mils), were pulled at Instron crosshead speeds of 5.1 cm/min (2 in./min.).

Molecular Weight

Molecular weight values were determined at 135°C using a Waters 150 C high-temperature gel permeation chromatograph (GPC), equipped with Zorbax PSM columns. Finely chopped samples (0.1% w/v) were dissolved overnight at 135°C in 1,2,4-trichlorobenzene, to which Irganox 1076 (0.01% w/v) and orthodichlorobenzene had been added to act, respectively, as antioxidant and internal standard. All solutions were passed through 0.5- μ m filters at 135°C before analyses. Reported values were based on a calibration curve prepared using NBS linear polyethylene broad molecular weight standard 1475 and calculated using Nelson Analytical 2900 GPC software.

Density

Density values were determined at 25°C according to ASTM D 1505-85. The density gradient column was prepared from aqueous isopropyl alcohol solutions and calibrated with glass beads of known densities.

Thermal Properties

Thermal properties were monitored at heating rates of 10°C per minute, using a Perkin-Elmer differential scanning calorimeter (DSC-2). Analyses were performed under a nitrogen purge to prevent oxidative degradation. Melting endotherms, recorded during the initial heating of each sample, were utilized to calculate heats of fusion with Perkin-Elmer TADS 3600 computer software, and reported as ΔH , kJ/kg.

Infrared Absorption

Variations in absorbance peak heights were monitored with transmitted infrared energy at selected bands, using a Perkin-Elmer FT-IR, Model 1600 spectrophotometer. Peak heights, measured using

standard Perkin-Elmer software, were divided by sample thickness. Bands for terminal vinyl, carbonyl, and crystallinity were taken, respectively, at approximately 908, 1720, and 1896 cm^{-1} .

RESULTS AND DISCUSSION

As commercial grades of HDPE are exposed to environmental weathering conditions, various photooxidative reactions occur. The following work describes material and property changes produced in HDPE sheets as a result of natural and laboratory weathering conditions. Blends of HDPE with 5 and 10% ECO have been included in this study in order to provide additional degradation information.

One of the most widely recognized physical changes, known to result from outdoor weathering of HDPE, is loss of elasticity, which leads to embrittlement. Figure 1 illustrates changes in elonga-

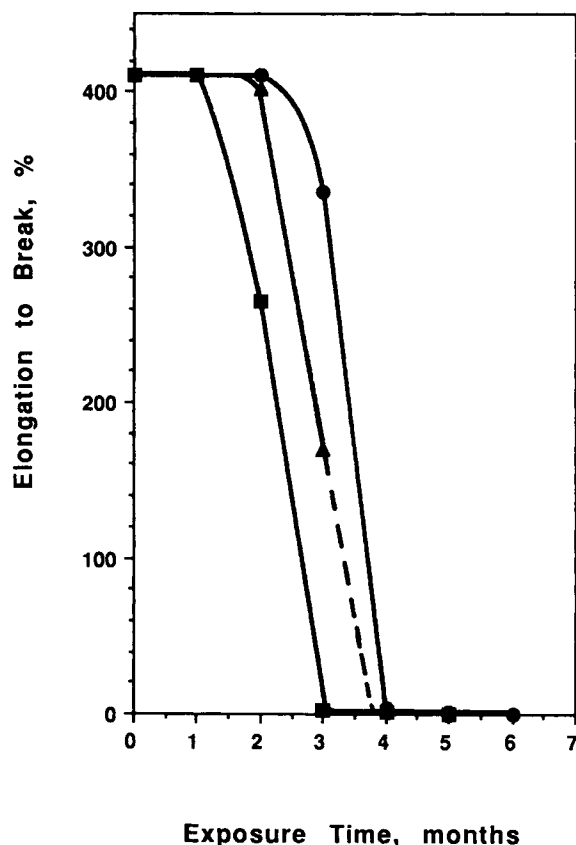


Figure 1 Elongation to break values in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

tion to break properties as functions of outdoor exposure times. These samples were weathered under natural Arizona sunlight, for up to 6 months. It can be seen that increased concentrations of ECO cause embrittlement to occur after shorter exposure times than recorded for unblended HDPE. The 10% ECO sample exhibits significant loss of elasticity, after only 2 months of outdoor exposure, while the unblended HDPE does not behave in a brittle manner, until exposure approaches 4 months.

The nature of embrittlement and the chemical reactions involved with its occurrence can be further investigated with the aid of infrared spectroscopy. Many workers¹⁻¹⁶ have followed the photooxidative degradation of polyethylene in terms of carbonyl-containing decomposition products, represented by the 1720 cm^{-1} infrared band. Figure 2 gives examples

of this carbonyl band shape, location, and intensity, after various weathering conditions, for unblended HDPE as well as the 10% ECO blend. The carbonyl band is absent for unexposed HDPE, but it develops, broadens, and shifts after several months of outdoor exposure indicating the presence of a variety of carbonyl-containing degradation products. As expected, the carbonyl band intensity is fairly high for the unexposed 10% blend. Increased outdoor blend exposure results in greater carbonyl absorbance, as well as shifting of the broadened band, consistent with results obtained for unblended HDPE. An overview of relative carbonyl absorbance values, for samples after various exposure conditions, is shown on Table I. These data are represented graphically in Figure 3. It can be seen that carbonyl intensity remains low, for unblended HDPE, throughout the first 3

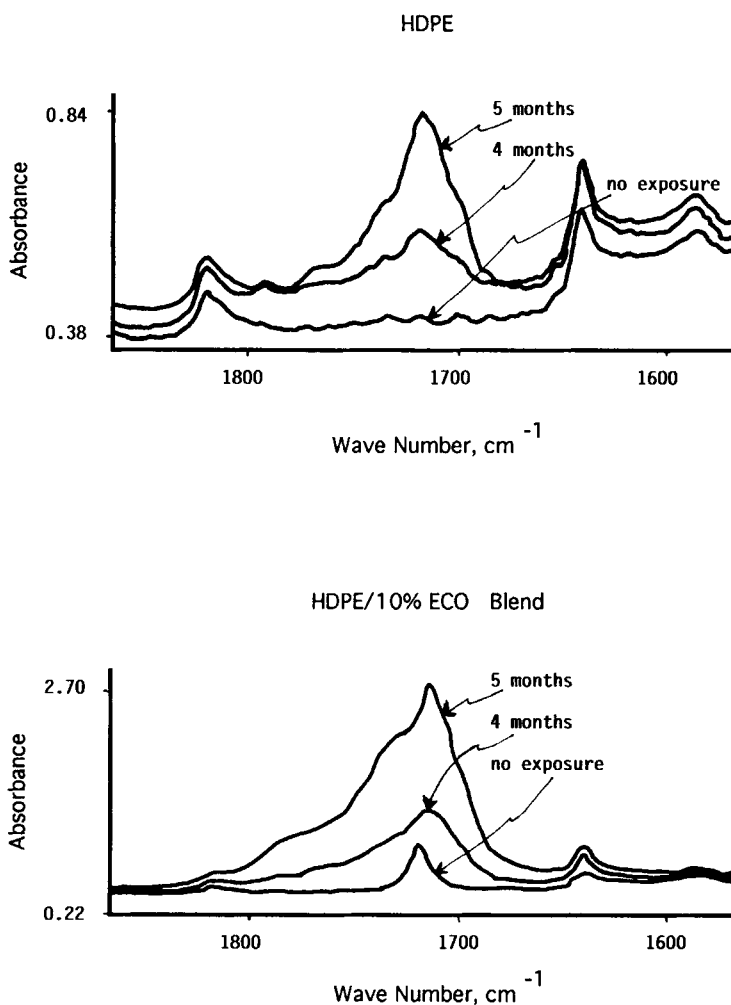


Figure 2 Changes in the shape, location, and intensity of the infrared carbonyl band of unblended polyethylene and its 10% ECO blend, in response to various natural sunlight exposure times.

Table I HDPE Sheets Exposed to Sunlight in Arizona

HDPE Sheets (~ 23 Mils)	Carbonyl	Terminal Vinyl	Sample Condition
	Absorbance 1713-1720 cm ⁻¹ thickness, cm	Absorbance 908 cm ⁻¹ thickness, cm	
No exposure			
0% ECO	0.3	8.1	Good
5% ECO	4.2	7.9	Good
10% ECO	9.1	7.5	Good
1 month			
0% ECO	0.2	7.9	Good
5% ECO	2.3	8.9	Good
10% ECO	6.0	9.6	Good
2 months			
0% ECO	0.2	8.0	Good
5% ECO	1.9	9.4	Good
10% ECO	6.0	11.2	Good
3 months			
0% ECO	0.3	8.0	Good
5% ECO	4.0	10.5	Good
10% ECO	8.5	12.7	Brittle
4 months			
0% ECO	2.0	8.4	Brittle
5% ECO	9.3	12.6	Brittle
10% ECO	13.9	14.4	Brittle
5 months			
0% ECO	6.8	10.2	Brittle
5% ECO	16.3	13.9	Brittle
10% ECO	35.1	14.6	Brittle
6 months			
0% ECO	18.2	12.6	Brittle

months of outdoor exposure. Intensities increase after 4 months and rise even more rapidly with increased exposure. Initial carbonyl intensities are predictably high for ECO blend samples. These values appear to decrease slightly during the initial few months of exposure and then more rapidly increase, as was observed for the unblended samples. Similar results have been reported by Scott et al.⁷⁻¹⁰ They found that extensively oxidized samples have lower hydroperoxide and vinylidene contents than less oxidized samples. The higher initial concentrations of ketonic carbonyl in the more oxidized samples were found to decrease during initial stages of irradiation. They felt this was caused by destruction of the ketonic carbonyl as samples underwent photolysis by the Norrish II process, to give compounds containing vinyl groups as the major initial products, followed by slower growth of secondary carbonyl compounds.

As sample decomposition progresses with increased outdoor exposure, concentrations of terminal vinyl groups also increase, probably through the

Norrish type II reaction.⁷⁻¹⁶ Figure 4 gives examples of changing 908 cm⁻¹ terminal vinyl absorption band intensities, as a result of increased outdoor exposure. In this case, bands for both the HDPE and its blends change only in intensity, not shape or position. Absorption values for each sample composition are shown on Table I and in Figure 5, as functions of outdoor exposure times. The unblended HDPE shows very little change in terminal vinyl concentration during the first 3 months of exposure time. A slight increase is seen after 4 months, followed by a steep increase after longer exposure times. Increased ECO concentrations appear to reduce the delay time before rapid increases in terminal vinyl concentrations are measured. The 10% ECO sample exhibits rapidly increased vinyl concentrations after only 1 month of exposure, and fairly constant changes in concentrations throughout the exposure conditions. It should be noted that after the delay time, rates of increase are similar for the three sample compositions.

Unblended samples of HDPE exhibited no ap-

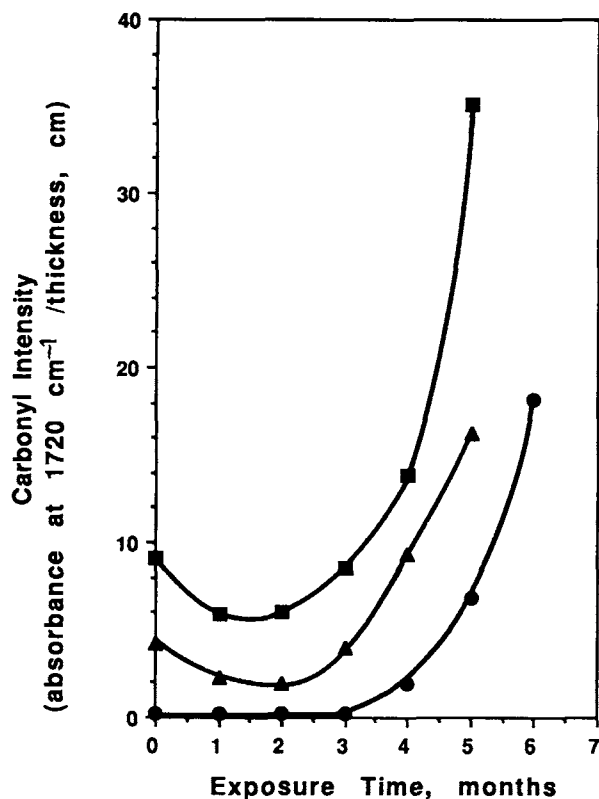


Figure 3 Carbonyl infrared band intensities in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

preciable changes in carbonyl and terminal vinyl concentrations after 3 months of outdoor exposure. After 4 months, slight increases were noted for both degradation products. Samples evaluated in terms of percent elongation were noted to show somewhat decreased elongation after 3 months of exposure. These results clearly indicate that additional factors must contribute to the embrittlement of weathered HDPE.

Changes in molecular weight, resulting from outdoor weathering of polyethylene could significantly influence the polymer's elastic characteristics. Molecular weight values, calculated for each sample composition and exposure condition, are shown on Table II. The relationships between weight-average (\bar{M}_w) and number-average (\bar{M}_n) molecular weights are based on the following equations, in which N_i is the number of molecules having molecular weight M_i .¹⁷

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Polydispersity index values indicate distributions of polymer molecular sizes, with larger numbers signifying wider distributions and smaller numbers denoting narrower distributions. Values approaching unity would imply all molecules were of the same size. As can be seen from Table II, highly weathered samples exhibit much narrower distributions of molecular weight than samples with less exposure. It is also apparent that sample molecular weights decrease significantly after long outdoor exposure times.

Figure 6 shows the decreases in weight-average molecular weights as functions of exposure times for the three material compositions. These changes are found to correspond to those previously described for terminal vinyl intensity. This is an expected relationship since photoinitiated chain cleavage can result in simultaneous increases in terminal vinyl concentration and decreases in polymer molecular weight. As with previously described results, molecular weight degradation begins to occur much more quickly with increased ECO blend concentration, while the unblended HDPE sample exhibits a delay of almost 4 months before significant degradation occurs. Similar changes in number-average molecular weight are shown in Figure 7. All molecular weight calculations are based on the assumption that changes in hydrodynamic volume resulting from the addition of ECO are negligible.

In addition to loss of molecular weight, increased polymer crystallization could be an important factor in sample embrittlement. Density values are frequently used to monitor the crystalline versus amorphous contents of polymers. In Figure 8, density of each sample composition is plotted as a function of outdoor exposure time. It can be seen that unblended HDPE exhibits very small, steady density increases during the initial 4 months of exposure. After longer exposure times, density increases occur much more rapidly. The 5 and 10% ECO blends display similar changes in densification rates, however, their more rapid density increases occur after only 2 months of weathering.

Melting endotherms can also be used to record changes in polymer crystallinity. As samples become more highly crystalline, correspondingly greater amounts of energy are required to melt the crystals, thus larger melting endotherms (ΔH values) are generated. Weathered sample endotherms were noted to be larger and also narrower than endotherms recorded for unexposed samples. These recorded differences indicate that outdoor exposure results in higher levels of crystallinity, but decreased distributions of crystalline structures. Figure 9 shows

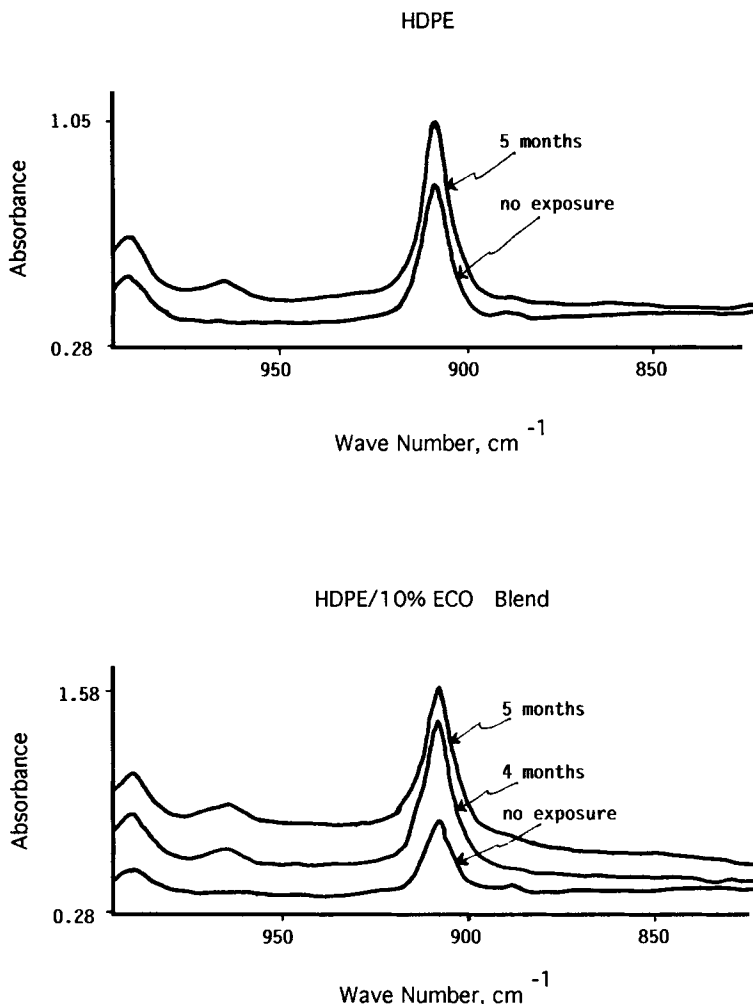


Figure 4 Changes in the intensity of the infrared terminal vinyl band of unblended polyethylene and its 10% ECO blend, in response to various natural sunlight exposure times.

each sample composition's heat of fusion (ΔH value), plotted as a function of exposure time. Results, shown in this figure, are very similar to those previously described for density determinations. Unblended HDPE initially shows only a slight increase in ΔH , followed by greater increases after longer exposure times. The blends again show more uniform changes throughout their exposure times. Unblended HDPE is seen to exhibit higher overall ΔH values than the blended samples. These differences result primarily from the addition of the ECO copolymer, which inherently has a lower heat of fusion than pure HDPE.

Volume fractions of crystallinity (V_f) can be calculated from density values of unblended HDPE samples, using the following equation.¹⁸

$$V_f = (\rho - \rho_a) / (\rho_c - \rho_a)$$

In each case ρ is the sample density, measured after each storage condition. The value for the amorphous (ρ_a) density of HDPE is taken to be 0.854 g/cm³,¹⁸ and that for totally crystalline material (ρ_c) as 0.997 g/cm³.¹⁸ Similar calculations could be made for blend samples, by using appropriate values for totally amorphous and crystalline blend compositions. Relative levels of crystallinity can also be calculated with the use of melting endotherms (ΔH) obtained from calorimetry. In this case, the heat of fusion for 100% crystalline HDPE is assumed to be 293 J/g,¹⁸ and substituted into the following equation:

% crystallinity of sample

$$= (\Delta H \text{ sample} / \Delta H \text{ 100\% crystalline HDPE})$$

$$\times 100$$

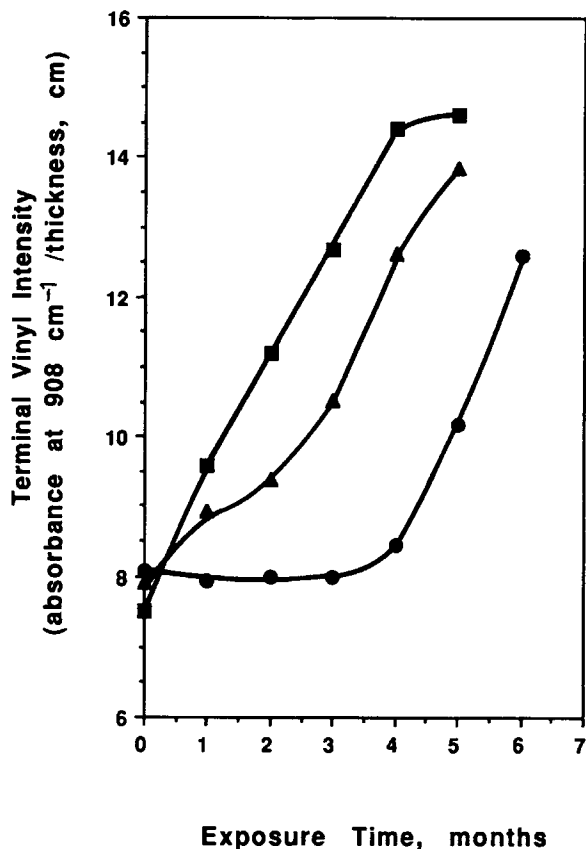


Figure 5 Terminal vinyl infrared band intensities in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

Changes in HDPE crystallinity, found to result from various times of outdoor exposure, are shown in Figure 10. Crystallinity values, calculated from calorimetry scans, are higher than those from density data; however, relative changes are similar for the two techniques. Both methods show very gradual crystalline increases over the first few months of exposure, followed by more rapid increases after longer times.

Infrared absorption spectra have also been used to monitor changes in the crystalline structure of polyethylene.¹⁹ The band near 1896 cm⁻¹, has been the frequent choice for measurement of bands assumed to be in the crystalline trans orientation. Figure 11 shows crystalline intensity changes, as functions of outdoor exposure, for HDPE and the two blend compositions. As can be seen, the blend intensities increase at about the same rates throughout their exposures, while the HDPE intensities increase more slowly during the first 3 months of exposure. After the initial 3 months, data converge and appear

Table II HDPE Sheets Exposed to Sunlight in Arizona^a

Exposure Time	0% ECO			5% ECO			10% ECO		
	Weight Average \bar{M}_w	Number Average \bar{M}_n	Polydispersity Index \bar{M}_w/\bar{M}_n	Weight Average \bar{M}_w	Number Average \bar{M}_n	Polydispersity Index \bar{M}_w/\bar{M}_n	Weight Average \bar{M}_w	Number Average \bar{M}_n	Polydispersity Index \bar{M}_w/\bar{M}_n
No exposure	147,400	22,800	6.5	151,300	23,400	6.5	152,800	20,800	7.3
1 month	138,400	20,600	6.7	146,100	19,500	7.5	113,400	18,200	6.2
2 months	130,400	19,700	6.6	120,200	19,400	6.2	70,200	17,300	4.1
3 months	134,800	21,900	6.2	73,400	16,900	4.3	56,700	15,500	3.7
4 months	119,900	21,000	5.8	48,000	14,800	3.2	41,700	13,000	3.2
5 months	75,100	18,600	3.9	38,700	13,100	3.0	29,300	10,300	2.8
6 months	34,100	12,500	2.7	—	—	—	—	—	—

^a Determined using gel permeation chromatography at 135°C in 1,2,4-trichlorobenzene.

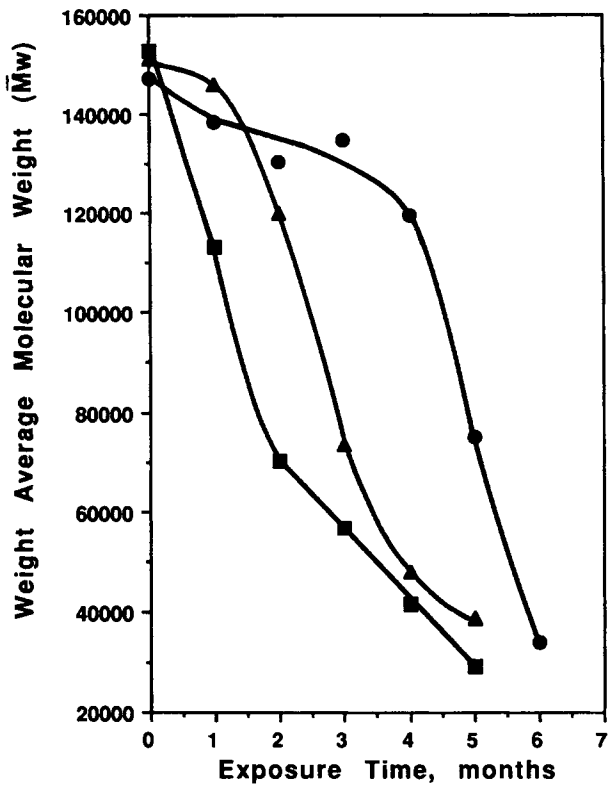


Figure 6 Weight-average molecular weights in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

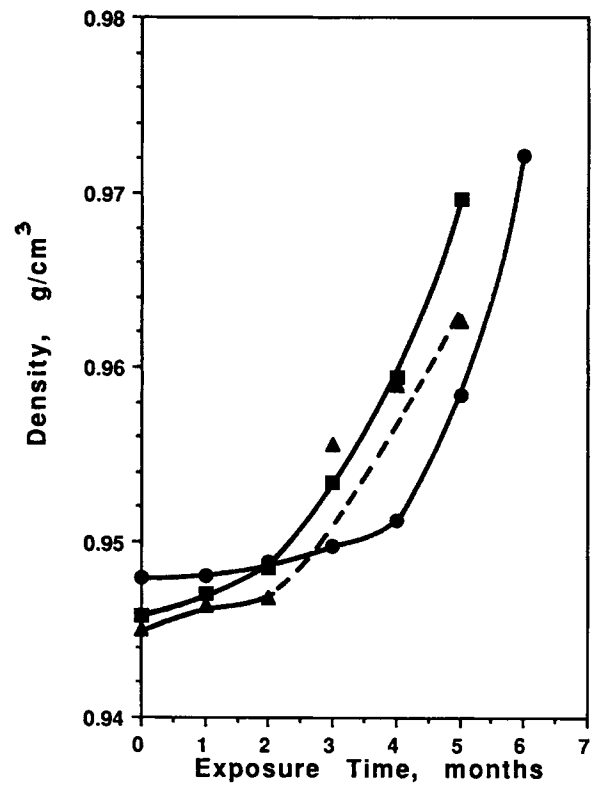


Figure 8 Density values in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

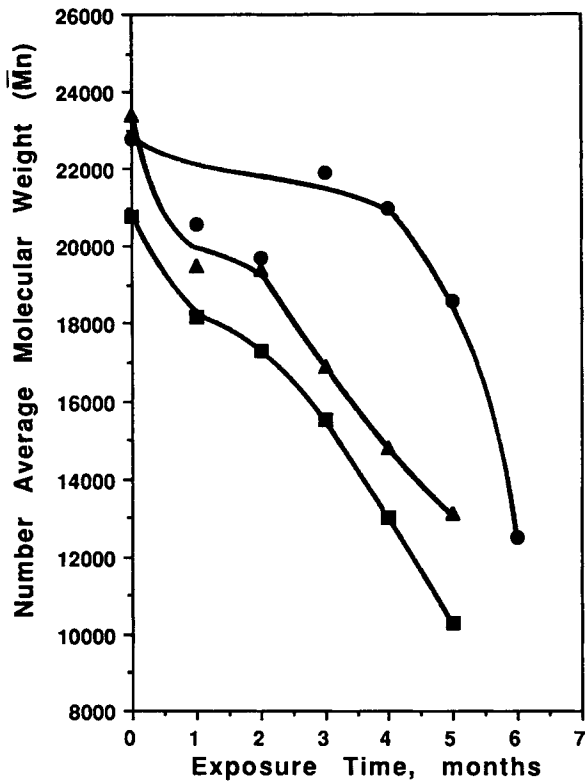


Figure 7 Number-average molecular weights in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

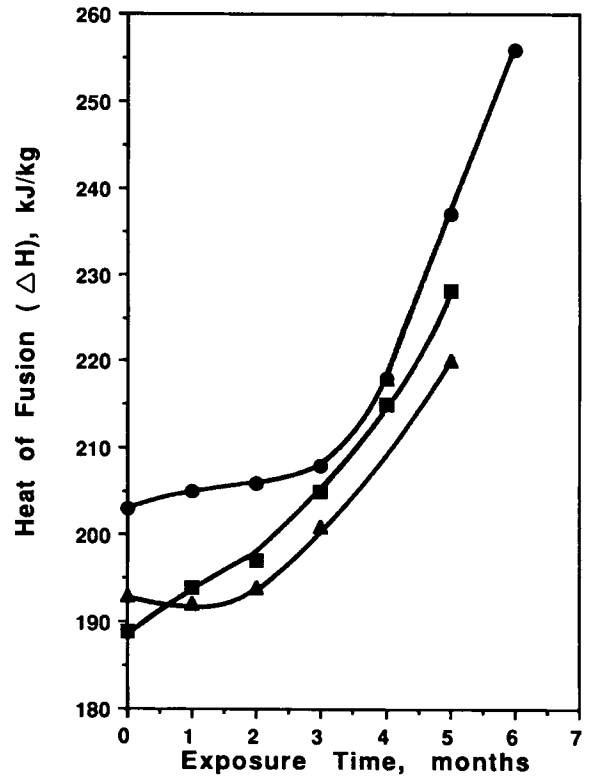


Figure 9 Heats of fusion in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

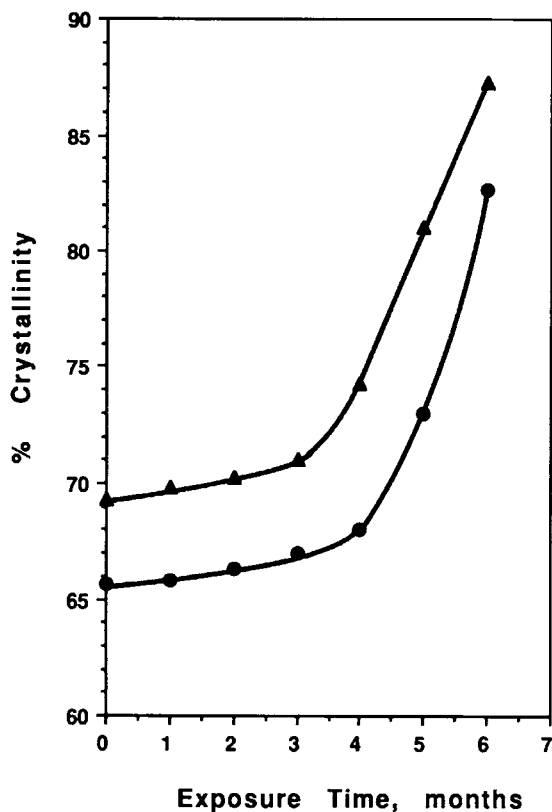


Figure 10 Crystallinity values, calculated from (●) density and (▲) melting endotherm results, in relationship to natural sunlight exposure times for unblended polyethylene samples.

to form a single line representing similar changes among the three materials.

As samples undergo photooxidative degradation they show decreased elongation to break and increased crystallinity. Elongation to break values are plotted versus heats of fusion in Figure 12 and versus crystalline infrared absorption intensity in Figure 13. From these figures, it can be seen that, although a relationship exists between increased sample brittleness and increased crystallinity, other factors such as reduced molecular weight, are also important.

A study by Winslow et al.²⁰ addressed the question of molecular weight versus crystallinity and the relative importance of each during polyethylene oxidation and embrittlement. They concluded that embrittlement of this nature resulted primarily from a "loss in weight average molecular weight rather than a gain in crystallinity." Blais, Carlsson, and Wiles²¹ exposed polypropylene films to UV irradiation in air. Using infrared and electron microscopy techniques, they observed a restructuring of the film surfaces that they "believed to be entirely responsible for the decrease in percentage elongation at

break which results from photodegradation." Paboit and Verdu²² also studied changes in mechanical behavior of linear polymers during photochemical aging. They found that chain scission resulting from oxidative degradation occurred essentially in the amorphous phase of the polymer. This scission was believed to give rise to sufficient chain mobility to produce secondary crystallization that resulted in crack initiation. These structural changes were found to affect mechanical properties primarily during the final rupture phases of analyses, with low strain mechanical properties remaining relatively unaffected.

As can be seen, these various conclusions are not totally in agreement with each other or with the results of the current investigation. In order to more fully explore and clarify the influences of crystallinity upon sample brittleness, additional samples were prepared. For this portion of the work, extruded strips of HDPE were compression molded into thin sheets. Samples were then cut from the compression-

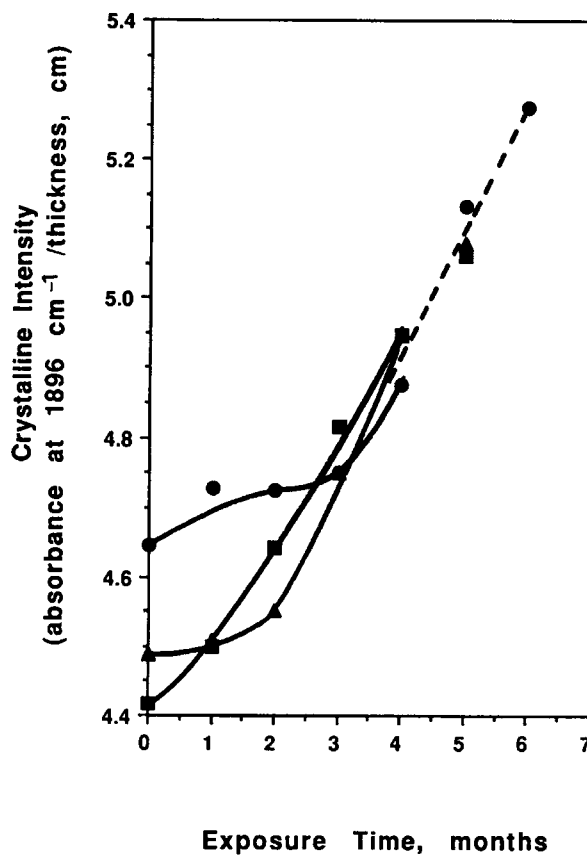


Figure 11 Crystalline infrared band intensities in relationship to natural sunlight exposure times for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

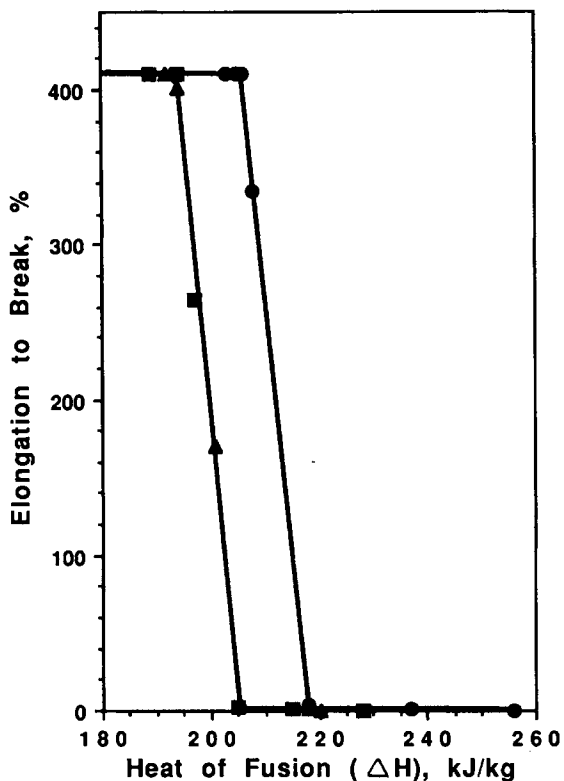


Figure 12 Elongation to break values in relationship to heats of fusion for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

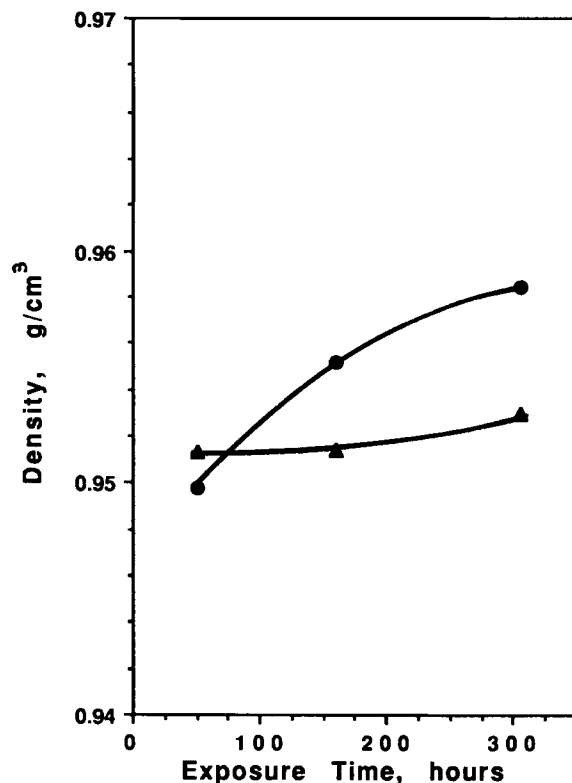


Figure 14 Density values obtained for laboratory-weathered polyethylene samples immediately after various (●) exposure times as well as after being (▲) melted and reformed without additional UV exposure.

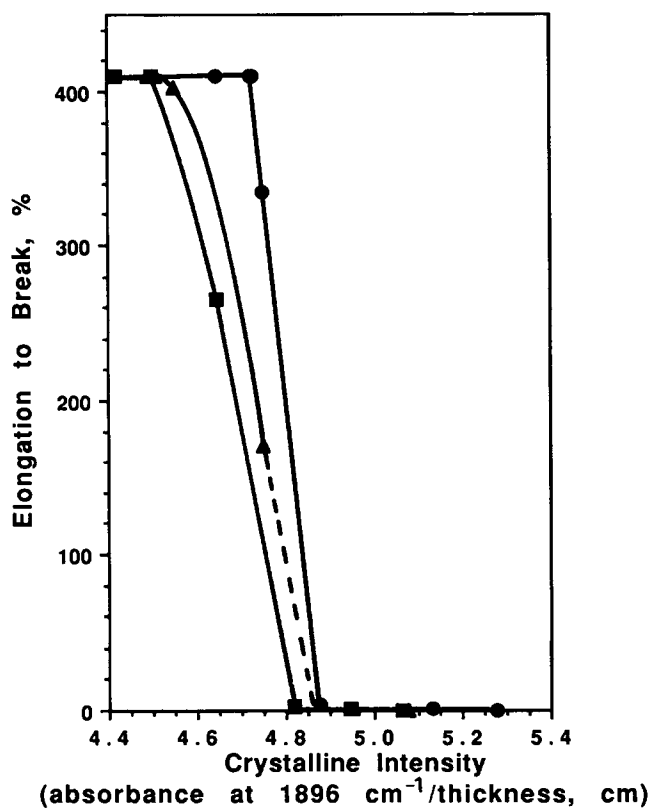


Figure 13 Elongation to break values in relationship to crystalline infrared band intensity values for polyethylene samples (●) unblended and prepared as blends containing (▲) 5 and (■) 10% ECO.

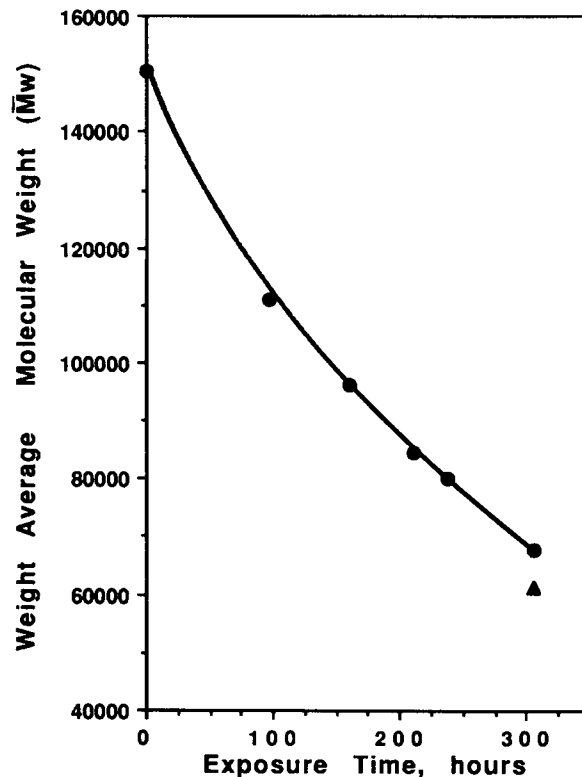


Figure 15 Weight-average molecular weights in relationship to laboratory weathering times, for polyethylene samples immediately after (●) exposure and after being (▲) melted and reformed without additional UV exposure.

molded sheets and exposed to accelerated laboratory weathering conditions for various times.

Accelerated laboratory weathering has often been used to simulate natural outdoor weathering conditions and obtain comparable polymer degradation products. This is possible, since the major degradative effects of natural sunlight are provided by radiation in the wavelength region from 300 to 400 nm.²³ Radiation of this range is customarily provided by UV fluorescent lamps. The lamp type used in the current study emits radiation primarily in the range from 280 to 360 nm, with maximum output at about 315 nm. Samples irradiated for 50 h under these laboratory conditions can be roughly compared to those exposed to outdoor Arizona sunlight for about 1 month.

After accelerated weathering had been completed, specimens were evaluated in terms of density, molecular weight, and tensile properties. Exposed samples were then remelted to destroy all crystallinity and reformed into fresh compression-molded specimens. Without additional weathering exposure, the reformed samples were again evaluated in terms of density, molecular weight, and tensile properties. Figure 14 shows that density values increase as a result of laboratory weathering, indicating increased levels of crystallinity. Densities of melted and reformed exposed samples remained almost constant, however, regardless of previous weathering conditions.

Figure 15 gives weight-average molecular weight values as a function of accelerated laboratory weathering. Molecular weight decreases are seen to be fairly uniform throughout the exposure conditions, with significant degradation occurring after 300 h of exposure. After being melted and re-compression molded, the 300-h sample was remeasured in terms of molecular weight. It can be seen that, unlike density, molecular weight changes resulting from laboratory weathering, have not been reversed as a result of remolding. The molecular weight of the reformed sample (shown as a filled triangle) is in fact slightly lower, as a result of the additional processing history, than that of the freshly weathered sample.

Elongation to break values are found to be extremely sensitive to sample treatment following weathering exposure. Figure 16 shows changes in percent elongation, after various UV exposure times, for samples before and after remelting and compression molding. As with outdoor weathering, increased laboratory UV exposure causes samples to break more readily, after experiencing less elon-

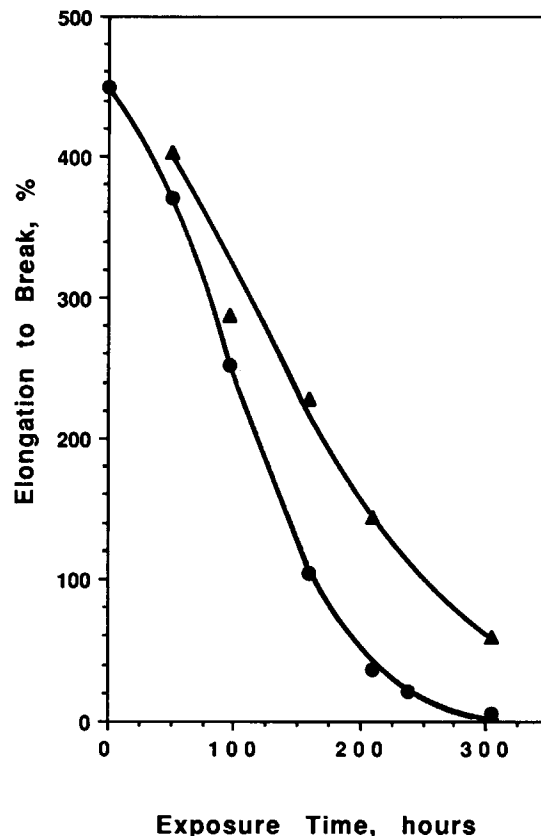


Figure 16 Elongation to break values in relationship to laboratory weathering times, for polyethylene samples immediately after (●) exposure and after being (▲) melted and reformed without additional UV exposure.

gation. The original exposed samples show a much sharper decrease in elongation when tested immediately after exposure and a more gradual decline when stretched after being remolded. This is most apparent at intermediate exposure times. For example, after 200 h of exposure, reformed sample elongation values are around 140%; while those of the original samples, measured before remelting, are less than 40%. These results indicate that HDPE embrittlement is influenced by several important factors that include variations in levels of crystallinity, as well as chain scissions resulting in molecular weight reductions.

SUMMARY AND CONCLUSIONS

High-density polyethylene samples, exposed to various environmental weathering conditions, have

been shown to exhibit reduced elasticity (tensile elongation to break) as a result of photooxidative degradation. As degradation progressed, concentrations of carbonyl and vinyl compounds were found to increase, while molecular weights and molecular weight distributions decreased. Chain scissions, represented as increased concentrations of degradation products and reduced molecular weights, also facilitated increased crystallization of the polymer materials. Shorter polymer chains gain increased mobility and are therefore able to crystallize more readily than longer intact chains. Higher sample crystallinities were measured in terms of increasing densities, melting endotherms, and infrared crystalline absorption bands.

The above results indicate HDPE embrittlement is controlled by a dual relationship between loss of molecular weight through chain scission and increased polymer crystallinity. This conclusion is further demonstrated by increased elongation to break values obtained by melting and reforming photooxidatively degraded samples. Molecular weight values of the reformed samples were equivalent to those measured immediately after exposure, yet the reduced crystallinity, produced by the reforming process, permitted additional elongation before samples fractured. The importance of molecular weight reduction is not disputed, since all samples show reduced elongation after weathering, regardless of their thermal histories.

During the initial stages of environmental exposure, unblended HDPE exhibits a delay period during which most properties remain relatively unchanged. After this delay, property changes resulting from degradation occur at increasingly rapid rates. Since carbonyl concentration is one of the more important factors implicated in the photooxidative degradation process, carbonyl was added to the HDPE in the form of ECO blends. These blends, prepared with higher initial carbonyl concentrations, exhibited property changes indicating material degradation had occurred almost immediately after environmental exposure. Although degradation mechanisms observed for the ECO blends were accelerated, they appeared to be similar to those recorded for unblended HDPE.

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