The Effect of Ultraviolet Radiation on Chemically Crosslinked Low-Density Polyethylene

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Synopsis

Tensile properties of UV-irradiated thermoplastic and crosslinked low-density polyethylene were studied as function of the irradiation time, degree of crosslinking, and the presence of a UV stabilizer. Well-crosslinked samples (about 70% gel) and UV-stabilized are shown to be of superior weathering resistance. Crosslinking by itself results in an insignificant improvement which is much less than the effect of UV stabilization of the noncrosslinked polymer. The combination of crosslinking/UV stabilization produces samples of significant resistance to UV irradiation.

INTRODUCTION

It is well established that ultraviolet (UV) radiation has a deteriorating effect on many plastic materials including low- and high-density polyethylenes. These materials, when exposed to the outdoor environment, undergo significant changes, namely, photodegradation, causing premature failure. Most polymers absorb energy in the 280–350 mμ range, polyethylene (PE) being most sensitive to 300-mμ radiation,[1] and this radiation is responsible for their failure. The main types of failure are discoloration and loss of mechanical and electrical properties. Many factors affect the effective life of outdoor-exposed plastics. Besides the intrinsic properties of the polymer (such as structure, molecular weight, and molecular weight distribution), temperature and its variation, wind, rain, and moisture may affect its stability. However, the greatest damage to polymers is caused by the UV portion of the sunlight even though this portion represents only about 5% to 6% of the total energy reaching the earth from the sun.

To improve the weatherability of plastics, different kinds of additives are usually incorporated into them. These additives may act to retard photodegradation in two ways[2]:

a. The additive itself may absorb most of the UV radiation leaving little to be absorbed by the polymer. These additives are called ultraviolet-radiation absorbers or screening agents.

b. The additive may absorb little of the UV radiation, but it may interact with the photoexcited polymer in a way that the excitation energy is trans-

ferred to it before any other reaction takes place in the polymer. These additives are called excited-state quenchers.

Derivatives of 2-hydroxybenzophenone, 2-(2H-benzotriazol-2-yl)phenol, and phenyl esters belong to class (a) while nickel-containing compounds (nickel chelates) belong to class (b).

Baseman[3] and Savides[4] mention several desirable properties for a UV stabilizer: (1) high absorptivity at low concentrations to compete with the polymer absorption; (2) stability to light so that it will not degrade on exposure to light during the useful life of the polymer; (3) compatibility which will assure that the additive does not exude from the polymer; (4) stability to heat and low volatility since most of the polymers are processed at elevated temperatures; (5) very little color so as not to impart any color to the polymer; (6) chemical inertness and low toxicity; (7) low cost.

One of the best UV stabilizers for polyethylene is carbon black. The black color imparted to the polymer, however, is in many cases undesirable. Other pigments may also improve stability to light especially when incorporated into the polymer together with light stabilizers,[5,6] but this is not a general rule. Among the colorless UV stabilizers recommended for PE are[2] Cyasorb UV 531 (2-hydroxy-4-octoxybenzophenone); Cyasorb UV 1084 {2,2-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol]ato(2−)} (butylamine)nickel; and Tinuvin 327 [2,4-di-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)phenol]. It has been observed[7] that when Cyasorb UV 531 and Cyasorb UV 1084 are used together in the ratio of 1:1, a synergystic effect occurs resulting in much better stabilization than with each of the stabilizers separately. The recommended concentration of the stabilizers is 0.1–2.0% weight.[4]

The research reported herein deals with the effect of UV radiation on crosslinked polyethylene (CLPE). Although many articles concerning the UV stabilization of polyethylene have been published, the only reference found by the authors regarding the UV stabilization of CLPE was a citation of Kadowaki[8] by Benning[9] that CLPE has outstanding weathering and UV stability.

EXPERIMENTAL

Low-density polyethylene (LDPE) powder with a melt flow index (MFI) of 2.0 g/10 min and a density of 0.919 g/cc was dry blended with predetermined amounts of 50% active 2,5-dimethyl-2,5-di(*tert*-butylperoxy)hexane (Varox) as the crosslinking agent and with 1% Tinuvin UV 327 as the UV stabilizer. The mixtures were further milled for short periods on a two-roll mill at temperatures slightly above the crystalline melting point of the polymer. The rough sheets thus obtained were compression molded at 210°C for 25 min to give crosslinked polyethylene sheets 2 to 3 mm in thickness.

ASTM Type IV-shaped specimens were cut from the molded sheets and placed on the turntable of a UV Sunlighter II (The Test-Lab Apparatus Co., Soners, Conn.) for periods ranging from 250 to 1000 hr. After half of the predetermined irradiation time, the specimens were turned over, thus exposing them to the same dose of UV radiation on both sides. The gel content of the specimens before and after irradiation was determined in boiling toluene.[10] Tensile tests were carried out using an Instron Testing Machine. A cross-

head speed of 0.5 cm/min was used for determining the modulus and 50 cm/min for tensile strength and elongation.

RESULTS AND DISCUSSION

The effect of the presence of Tinuvin UV 327 stabilizer in irradiated thermoplastic LDPE and CLPE was studied as a function of the irradiation time. Table I summarizes the mechanical properties of the irradiated samples. The interference of UV 327 stabilizer with the crosslinking reaction is clearly seen from Table 1. Samples crosslinked with the same amount of Varox contain less gel where UV 327 is being used (compare series 3 with 6, 4 with 7, and 5 with 8 in Table 1). In the absence of UV 327, well-crosslinked samples (more than 50% gel) undergo significant degradation due to irradiation as manifested by the descending values of gel content with irradiation time. On the other hand, well-crosslinked samples (series 8) containing UV 327 are practically unchanged by irradiation (at least up to 1000 hr) as far as the gel content is concerned. Since the gel content is a prominent criterion for CLPE, a higher demand of Varox peroxide is required in compositions containing UV 327 in order to achieve sufficient crosslinking; however, this drawback is compensated by extended service periods of the stabilized CLPE under UV irradiation conditions.

Quackenbos and Samuels[11] state that the ultimate tensile elongation is the most sensitive property to follow irradiation deterioration and the best criterion for failure in weathered samples. The results of the present study support this conclusion, as will be shown later. The effect of irradiation time on the residual elongation (elongation of the irradiated samples divided by the elongation of the nonirradiated ones) is shown in Figure 1.

The lower curves in Figure 1 display one LDPE sample and three CLPE samples without UV stabilizer. This set of curves shows that crosslinking alone results in only a slight improvement in the resistance to UV deterioration. On addition of the UV 327 stabilizer to LDPE or CLPE, a much greater effect is observed. The upper curves in the figure represent the LDPE sample and the three CLPE samples, all stabilized with 1% UV-327. Using the criterion that failure occurs when the elongation has dropped to 10% of its original value,[5] it is found that unstabilized LDPE fails after about 300 hr while unstabilized CLPE (3% Varox) fails after about 600 hr. This improvement, which is the result of crosslinking alone, is small compared to that obtainable with stabilized systems. As can be seen, increasing the degree of crosslinking (Varox concentration or gel content) in the stabilized systems increases significantly the resistance to deterioration. Crosslinked samples (3% Varox) containing UV 327 retain more than 80% of their original elongation after 1000 hr of irradiation, compared to about 40% only for the noncrosslinked samples containing the same amount of UV 327. It is worthwhile to mention that Table I contains absolute as well as residual data while only the latter are shown in Figure 1. Thorough graphic representations have shown that best interpretation is obtained by using the residual rather than the absolute elongation.

The effect of irradiation time on residual tensile strength (tensile strength of the irradiated samples divided by the tensile strength of the nonirradiated

TABLE I
Summary of Tensile Properties for UV-Irradiated Polyethylene Samples

Composition	Irradiation time, hr	Gel, %	Modulus, psi	Tensile strength, psi	Elonga-tion, %	Residual modulus	Residual tensile strength	Residual elonga-tion
LDPE								
1-1	0	0	10,600	1730	698	1	1	1
1-2	250	1.0	11,300	1420	88	1.06	0.82	0.13
1-3	500	2.9	11,700	1430	61	1.10	0.83	0.09
1-4	700	—	12,300	1300	15	1.16	0.75	0.02
1-5	1000	3.1	12,400	1140	14	1.17	0.66	0.02
LDPE/1% UV								
2-1	0	0	10,400	1850	76	1	1	1
2-2	250	—	10,600	1680	68	1.01	0.91	0.89
2-3	500	0.0	11,100	1640	65	1.06	0.88	0.85
2-4	700	—	11,300	1260	40	1.08	0.79	0.53
2-5	1000	0.6	11,700	1310	20	1.12	0.71	0.38
LDPE/0.2% PO[a]								
3-1	0	1.5	9,900	1930	747	1	1	1
3-2	250	3.1	10,500	1410	81	1.06	0.73	0.11
3-3	500	9.6	11,800	1400	51	1.19	0.73	0.07
3-4	700	19.5	13,200	1160	13	1.34	0.60	0.02
3-5	1000	13.3	13,700	1040	12	1.38	0.59	0.02
LDPE/1.5% PO[a]								
4-1	0	54.5	10,100	2420	75	1	1	1
4-2	250	49.6	10,600	1500	15	1.05	0.62	0.21
4-3	500	49.4	10,600	1500	73	1.05	0.62	0.09
4-4	700	37.6	12,400	1310	22	1.21	0.54	0.03
4-5	1000	35.3	11,000	1130	21	1.16	0.46	0.03
LDPE/3% PO[a]								
5-1	0	80.4	8,900	1680	365	1	1	1
5-2	250	68.6	10,500	1360	98	1.18	0.81	0.27
5-3	500	57.8	11,600	1260	46	1.31	0.75	0.13
5-4	700	57.5	10,800	1140	27	1.22	0.68	0.08
5-5	1000	54.2	10,700	1010	28	1.20	0.61	0.08
LDPE/1% UV/ 0.2% PO[a]								
6-1	0	0.0	11,200	1950	828	1	1	1
6-2	250	1.6	12,000	1930	741	1.020	0.99	0.90
6-3	500	1.6	11,700	1740	642	1.04	0.89	0.78
6-4	700	1.4	12,100	1490	538	1.08	0.77	0.65
6-5	1000	1.4	12,000	1450	515	1.07	0.75	0.62
LDPE/1% UV/ 1.5% PO[a]								
7-1	0	21.2	11,100	2430	881	1	1	1
7-2	250	27.3	11,500	2340	800	1.03	0.96	0.91
7-3	500	30.3	11,400	2190	712	1.03	0.90	0.82
7-4	700	27.3	11,500	1930	673	1.04	0.79	0.73
7-5	1000	34.8	12,200	1900	637	1.10	0.78	0.70
LDPE/1% UV/ 3% PO[a]								
8-1	0	72.3	10,000	2400	717	1	1	1
8-2	250	75.7	9,800	2340	683	0.98	0.98	0.95
8-3	500	76.3	10,100	2190	632	1.00	0.91	0.88
8-4	700	77.1	9,900	1930	570	0.99	0.81	0.80
8-5	1000	77.3	10,500	1900	598	1.04	0.79	0.83

[a] Peroxide.

ones) is shown in Figure 2. The tensile strength data show that the UV stabilized LDPE performs better than the unstabilized one and the stabilized CLPE performs best. Figure 2 shows that the tensile strength of the unstabilized CLPE samples declines faster than that of the noncrosslinked unstabilized ones; thus, contrary to the results of the elongation measurements, crosslinking reduces the tensile strength in the nonstabilized systems. In the UV-stabilized systems, however, crosslinking improves significantly the sta-

bility to UV irradiation. Adoption of Martinovich's second failure criterion,[5] which is the time at which the tensile strength drops to two thirds of its original value, results in failure of all of the unstabilized samples in less than 1000 hr of irradiation while the crosslinked, stabilized samples retained about 80% of their original strength. Comparison of Figures 1 and 2 shows that the deterioration rate with irradiation time as exhibited by residual elongation is faster than that exhibited by residual tensile strength. The residual elongation is thus more sensitive as a failure criterion than the residual tensile strength, in agreement with Quackenbos and Samuels[11] and Stephenson et al.[12]

In view of the elongation-to-break and tensile-strength results of the present study, it has been shown that unstabilized CLPE has almost no advantage over the corresponding noncrosslinked polymer as far as the resistance to UV radiation is concerned. The incorporation of crosslinks into the UV 327 containing polyethylene improves the UV resistance, and thus the "outstanding UV stability of crosslinked polyethylene" mentioned by Benning[9] can only be achieved by the combination of crosslinking and stabilization.

Turi et al.[13] have observed an initial increase in both elongation at break and impact resistance of high-density polyethylene when measured as a function of irradiation time. This initial increase was followed by a sharp drop after about 80 irradiation hr. They explained this behavior by assuming the simultaneous occurrence of chain scission and crosslinking reactions where the latter predominates in the initial stages and chain scission thereafter. Turi et al., however, have not noticed any gel in their samples after varying periods of irradiation while the intrinsic viscosity was found to decrease steadily. They have therefore concluded that during the initial irradiation
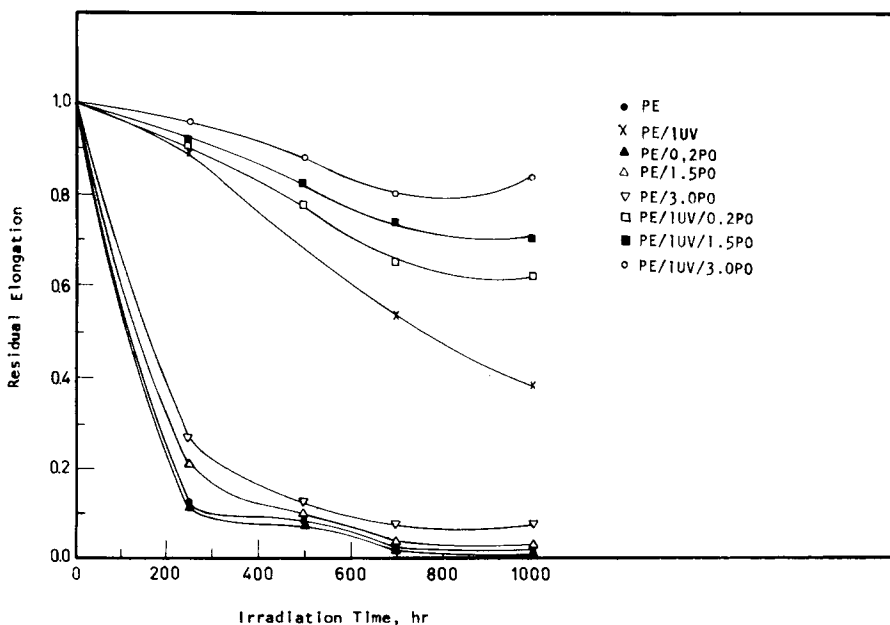

Fig. 1. Residual elongation vs. irradiation time for noncrosslinked and crosslinked systems stabilized and unstabilized.

period, the net of the crosslinking and chain scission reactions resulted in a polymer with branched molecules. In the present study, samples were tested after irradiation times of 250 to 1000 hr. Whether an initial increase will show up in the 0- to 250-irradiation hr range is thus unknown. In general (excluding the initial increase), our results on noncrosslinked and unstabilized samples are in agreement with those of Turi et al., although the drop in the mechanical properties was more gradual in the present work.

The effect of UV irradiation on the tensile modulus is shown in Table I. Generally, the modulus increases with irradiation time, a phenomenon referred to in the literature as the "stiffening effect." It appears that in polyolefins this effect is caused mainly by chain scission which results in shorter, more readily crystallizable chains. This results in a polymer of higher density and degree of crystallinity and therefore a higher modulus. Turi et al.[13] and Winslow et al.[14] have found an increase in the density of irradiated high-density polyethylene samples with increasing irradiation time. In addition, Turi et al. have found an increase in degree of crystallinity (from x-ray diffraction measurements), and Winslow et al. have observed an increase in the heat of fusion. Thus, under certain conditions of UV irradiation, the degree of crystallinity of high-density polyethylene may increase due to chain scission. Contrary to chain scission, crosslinking may reduce the degree of crystallinity, as was shown by Narkis and Miltz.[15] These authors found that the degree of crystallinity decreased with an increase in gel content (increasing concentrations of Varox) of chemically crosslinked polyethylene samples. The modulus increase with irradiation as shown in Table I is less pronounced in the UV stabilized CLPE than in the unstabilized CLPE. The unstabilized systems undergo bigger changes than the corresponding stabilized ones,
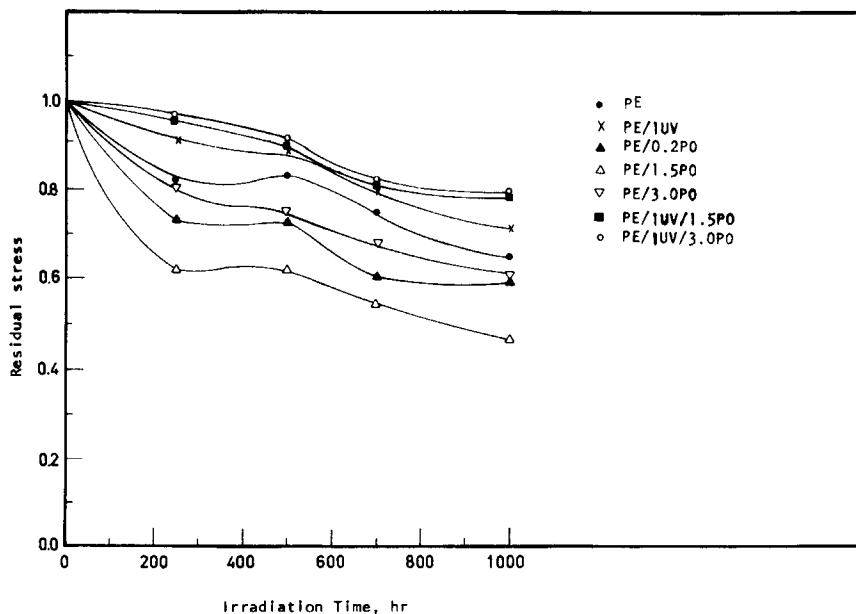

Fig. 2. Residual tensile strength vs. irradiation time for noncrosslinked and crosslinked systems stabilized and unstabilized.

which shows up in the characteristic tensile properties: elongation, ultimate strength, and modulus.

It is important to note that the use of crosslinking agents other than Varox, UV stabilizers other than Tinuvin UV 327, and other polyethylenes and/or irradiation conditions may result in systems whose behavior may differ from those studied in the present work.

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