

Accelerated Weathering-Induced Degradation of Unprotected Multilayer Polyethylene Slabs. II

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SYNOPSIS

The effect of photodegradation on the properties of multilayer polyethylene slabs was evaluated. It was found that photodegradation causes an increase in the degree of crystallinity accompanied by an increase in the elastic modulus and a decrease in elongation and oxygen permeability. It was shown that oxygen and not UV light is the controlling factor in the photodegradation process. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In a previous publication,¹ it was shown that in multilayer polyethylene (PE) slabs obtained by compression of several polyethylene (PE) films the outer layers degraded most and the inner layer least when exposed to UV radiation in a QUV apparatus. It was shown that the carbonyl concentration was the highest and the mechanical properties the poorest at both exterior sides with insignificant differences between the front side which was directly irradiated and the back side to which the UV light reached after passing through the PE slab. The variation in carbonyl content, elongation at break, toughness, and ultimate tensile strength followed a symmetrical parabolic pattern around the most inner layer of the nine film layers constructing the slab. It was therefore concluded that oxygen and not UV radiation was the controlling parameter in the degradation of PE.

The present article describes additional results on the properties of the UV-irradiated components of the PE slabs. These results together with the results of the previous article (Part I) enlighten the role of oxygen in the photodegradation of PE and the resultant change in properties.

EXPERIMENTAL

Materials

The following resins were used for manufacturing the commercial blown films: an LDPE resin with MFI = 0.3 g/10 min and a density of 923 kg/m³; an ethylene-vinyl acetate copolymer (EVA) resin with 17% vinyl acetate content; and a nylon-6-resin suitable for blown-film coextrusion. Three different types of commercial blown films were used in the multilayer samples:

Type A, 100 micron thickness, 100% LDPE.

Type B, 110 micron thickness, 99% LDPE + 1% EVA.

Type C, five-layer coextruded barrier film: 37 μ m LDPE/3 μ m tie/20 μ m nylon-6/3 μ m tie/37 μ m LDPE.

The oxygen permeability of film Types A and C was found to be 231 and 4.4 cm³ mm/(m² day atm), respectively, according to ASTM-D3985.

Samples

For the sake of clarity, the structure of all samples reported in Part I of this study are described below, although the results in the present part refer to two samples only:

Sample I: Nine layers of Type B film.

Sample II: Nine layers of Type A film.

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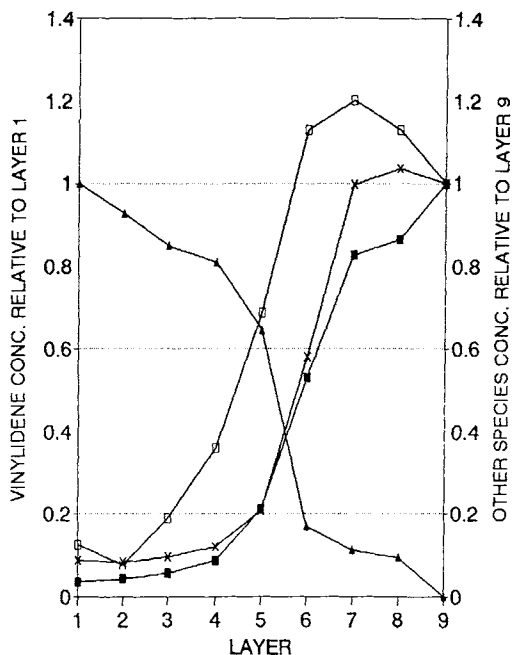


Figure 1 Concentration of various byproducts in different layers of Sample IV, after 284 h exposure in the QUV: (■) carbonyl, (◻) *trans*-vinyl, (×) vinyl, and (▲) vinylidene.

Sample III: Nine layers of Type A film + one layer of Type C film on top (facing the dark side of the QUV).

Sample IV: Nine layers of Type A film + one layer of Type C film on top (facing the radiation source in the QUV).

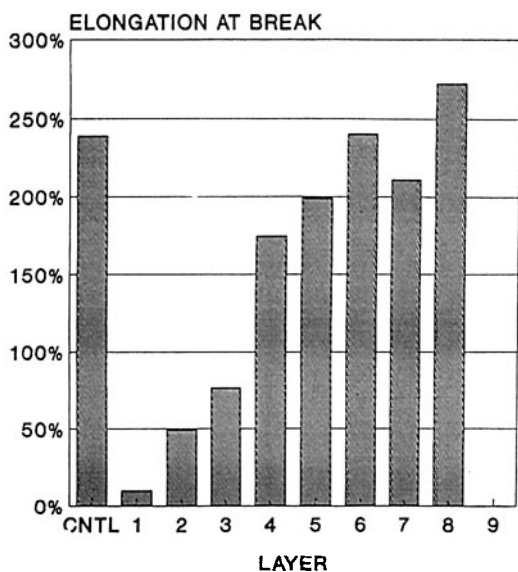


Figure 2 Elongation at break of the different layers of Sample III (back-covered) and of the control after 284 h exposure in the QUV.

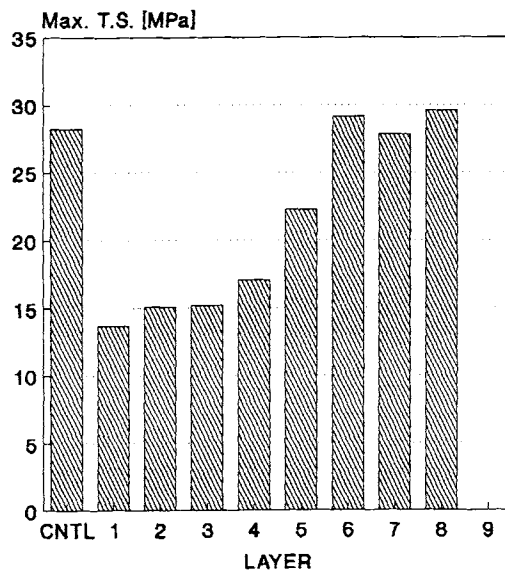


Figure 3 Maximum tensile strength of the different layers of Sample III (back-covered) and the control after 284 h of exposure in the QUV.

Sample V: Nine layers of Type A film + one layer of Type C film on top of each side.

Methods

A 10 metric tonne hydraulic press with 0.15 × 0.15 m temperature-controlled plates and a water-cooling

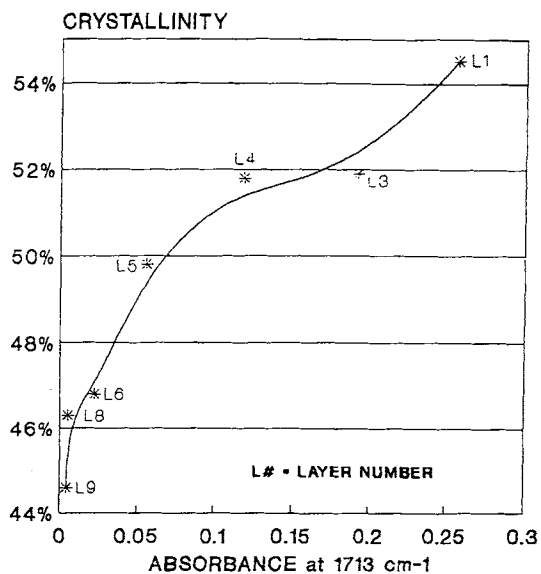


Figure 4 Degree of crystallinity (from first DSC endotherm) vs. absorbance (carbonyl concentration) in Sample III after 284 h of exposure in the QUV.

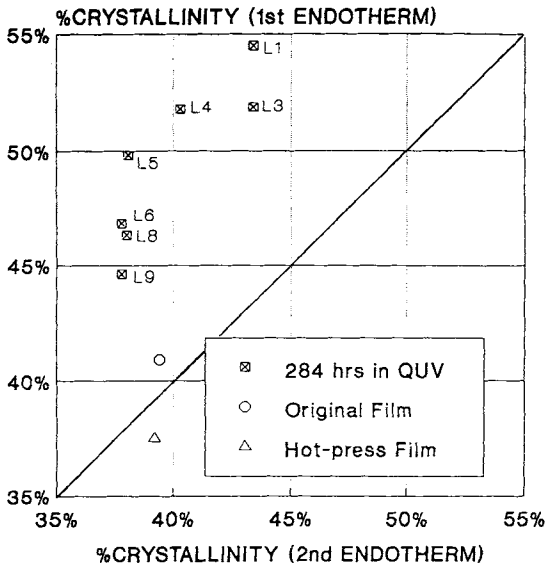


Figure 5 Degree of crystallinity in the different layers of Sample III after 284 h of exposure in the QUV determined from the first and second endotherm.

system was used for the preparation of the slab samples. Accelerated weathering was performed in the QUV-accelerated weathering tester (Q-Panel Co., Cleveland, OH) apparatus as described in ASTM-G53.

A tensile tester (Testometric Model 220M, The Davenport Co., U.K.) interfaced to a computer to facilitate the analysis of data was used to determine the mechanical properties of the single film layers, according to ASTM-D882. Carbonyl and other oxidation groups' concentration in the polymer was determined with the help of an FTIR spectroscope interfaced to a computer.

Each multilayer sample was prepared from a stack of film squares (0.18×0.18 m). The stack was covered with a mold-release film and then placed between two metal plates, 1 cm thick. The whole arrangement was introduced into the hydraulic press preheated to 95°C and rapidly pressed to 10 tonnes for a few seconds. This initial pressing was intended to expel the air between layers. The pressure was then released slowly to 5.5 tonnes and maintained there for 8 min. Then, the pressure was raised again to 10 tonnes and maintained for 4 more min. Finally, the heaters were turned off, the press was water-cooled to room temperature, the pressure slowly released, and the sample removed.

All edges of the multilayer samples were heat-sealed with an impulse sealer and samples were cut to approximately 0.08×0.15 m. Samples of each system were affixed to exposure racks with metal

rings and introduced into the QUV tester. Weathering was performed with only four lamps on one side of the samples. The temperature in the apparatus was set to 55°C , no water was present, and no condensation cycles were performed (the actual temperature of the samples during exposure was directly measured by means of a glass thermometer and was found to be $57\text{--}58^\circ\text{C}$).

Samples of each system were removed from the apparatus at various intervals of time as follows:

- After 147 h, one sample of Sample I.
- After 170 h, one sample of Sample V.
- After 284 h, one sample of Samples II, III, IV, and V.
- After 340 h, one sample of Sample I.

Each sample was separated into its layers. The FTIR spectrum of each layer was plotted and its carbonyl concentration calculated with the following equation²:

$$\% \text{ Carbonyl} = (A_{1715} - A_{1835}) \times F/T \quad (2)$$

where A_x is the absorbance at wavenumber $X \text{ cm}^{-1}$, $F = 125.12$ for T in microns, and T is the thickness (microns).

The average carbonyl concentration in the samples was obtained by calculating the average concentrations of all its individual layers. For Sample

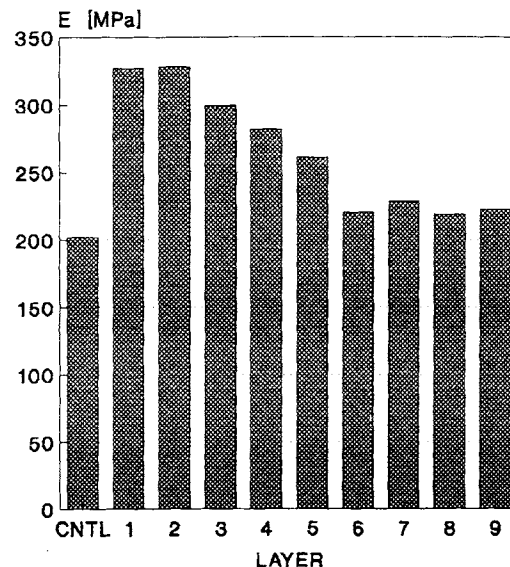


Figure 6 Elastic modulus of the different layers of Sample III after 284 h of exposure in the QUV.

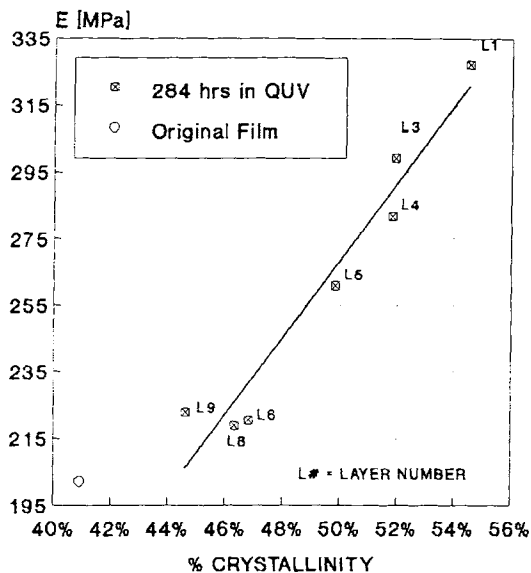


Figure 7 The effect of degree of crystallinity (first endotherm) on the elastic modulus of the layers in Sample III after 284 h of exposure in the QUV.

I exposed for 147 h, dumbbell-shaped specimens[†] were die-cut from each layer and their mechanical properties determined with the tensile tester. Initial grip separation was 50 mm and the rate of extension was 50 mm/min; no extensometer was used. The following tensile properties were determined: maximum tensile strength (Max.T.S.), yield strength, elongation at yield, elongation at break, toughness (area under the stress-strain curve), and modulus of elasticity (tangent at 2% elongation).

The degree of crystallinity was determined by a differential scanning calorimeter (Perkin-Elmer Model PE7) attached to a computer that calculates this value from the area under the endotherm peak, using 293 J/g as the heat of fusion of a single PE crystal. Three scans of the temperature in the range of 35–135°C were made for each sample: (1) heating at a rate of 10°C from 35 to 135°C (first endotherm); (2) cooling from 135 to 35°C at the same rate; and (3) heating the sample again from 35 to 135°C at the same rate (second endotherm).

Oxygen permeability of the films was determined by an Oxtran 100 (Mocon Corp., Minneapolis, MN) instrument. The "hot-press film" in the legend of Figure 5 stands for the film that was compression-molded at 95°C (at the same conditions that the multilayer samples were prepared) before being tested for degree of crystallinity and used as an additional reference.

[†] Described in ASTM-D638 (Fig. 1, Type IV).

RESULTS AND DISCUSSION

In a previous publication,¹ it was shown that when oxygen is limited vinyl and *trans*-vinyl groups are formed as intermediate oxidative groups that later turn into carbonyls. When oxygen is abundant, carbonyl groups are formed preferentially at the expense of vinyl and *trans*-vinyl groups. It was also shown that concentration of the vinylidene group (which exists in the original polymer) diminishes with oxidation. In Figure 1 the concentration profile of the different oxidation groups is shown for the various layers of Sample IV (covered with a barrier film in front of layer 1 facing the radiation source) after 284 h of irradiation relative to layer 9 which was taken as 1.0. The opposite profile of the vinylidene group (compared to other oxidative groups) is clearly demonstrated, in this case, relative to layer 1, which was taken as 1.0. It can also be seen that in layer 1 from which oxygen was blocked the concentration of oxidation groups is practically zero, and in areas where oxygen is limited, more *trans*-vinyl groups are formed. These groups turn into carbonyls when oxygen becomes abundant.

In Figure 2, the elongation at break of the various layers in Sample III (with a barrier covering the back side, namely, the side opposite to the radiation source) is presented together with the nonirradiated control (CNTL) sample. It can be seen that the side exposed to oxygen was affected most. Similar results are seen in Figure 3 for the maximum tensile

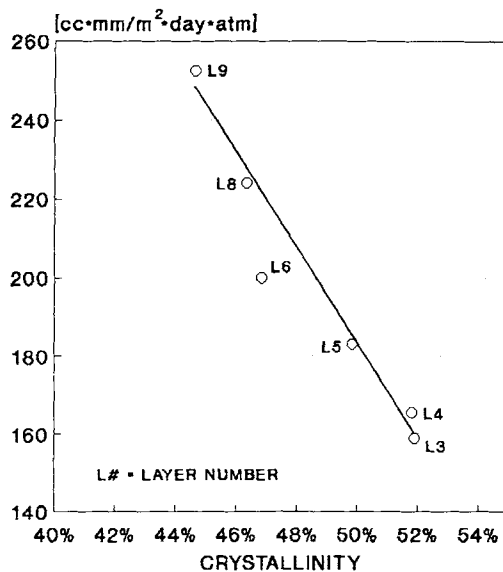


Figure 8 Effect of degree of crystallinity on the permeability coefficient to oxygen of Sample III after 284 h of exposure in the QUV.

strength (Max.T.S.). It was reported³ that cross-linking of PE is accompanied by a reduction in the degree of crystallinity while degradation causes an increase in the degree of crystallinity.^{4,5} The explanation for this behavior is that the shorter chains formed during the degradation can crystallize or recrystallize more easily.

In Figure 4, the degree crystallinity in the films of Sample III (back covered with an oxygen barrier) after 284 h of irradiation is plotted as a function of absorbance (carbonyl). It can be seen that the degree of crystallinity increases with the level of photooxidation. In Figure 5, the degree of crystallinity as determined from the first endotherm is compared with that of the second one in the same back-covered Sample III. It is evident that the further the film was from the oxygen barrier (on top of layer 9) the greater is the deviation from the line of 45° slope, namely, the higher is the level of degradation. The first endotherm represents the structure of the actual film in use, while the second one reflects the properties of the polymer after being melted (during the first heating cycle) and recrystallized. The degree of crystallinity in the film rises rapidly at the initial stage of photooxidation and levels off further on. On the other hand, in the bulk polymer, there is a slight decrease in the degree of crystallinity at the early stages of oxidation (the oxidation products may hinder crystallization). At later stages, however, crystallinity increases, probably as a result of the shorter chains formed during the degradation (as mentioned before).

It was reported⁶⁻⁷ that properties of PE at low strains depend primarily on the degree of crystallinity, while those at high strains, on the average molecular weight. The modulus of elasticity is one of the properties determined at low strains.

In Figure 6, the modulus of elasticity of the various film layers of Sample III is shown after 284 h of exposure in the QUV. It can be seen that the modulus increased as a result of the exposure and that the closer the film was to the unblocked oxygen surface this increase was greater. In Figure 7, the modulus of elasticity is plotted as a function of degree of crystallinity. It is evident that there is a close relationship between these two parameters.

In Figure 8, the oxygen permeability of the individual films of Sample III are plotted as a function of the degree of crystallinity. It is normally assumed that gas transfer takes place in the amorphous phase of semicrystalline polymers⁸ while crystalline regions are gas barriers. Figure 8 demonstrates that oxygen permeability decreases linearly with the increase in degree of crystallinity. These results agree with those published in an earlier paper³ although the relationship is different.

CONCLUSIONS

The results of the present study reinforce earlier findings that degradation of PE causes an increase in degree of crystallinity and a reduction in elongation at break. The increased degree of crystallinity in the photooxidized PE results in a stiffening of the film and a reduction in its oxygen permeability.

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