

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

G. YANAI,¹ A. RAM,¹ and J. MILTZ^{2,*}

Departments of ¹Chemical Engineering and ²Food Engineering and Biotechnology, Technion-Israel Institute of Technology, Haifa, 32000, Israel

SYNOPSIS

The in-depth degradation of unprotected low density polyethylene (LDPE) induced by photooxidation was studied by following the carbonyl content and other by-product groups as well as the retention of mechanical properties as a function of time and distance from the surface. The multilayer slabs were prepared by hot pressing of nine LDPE film layers. Weathering of the samples was performed in a Q.U.V. apparatus running dry at 55°C for different time periods. The carbonyl content, as measured by FTIR spectra, showed a parabolic symmetry around the center layer which was least affected. Oxygen barriers placed on one or both surfaces of the slabs significantly reduced the photooxidation. The retention of mechanical properties followed a similar profile as that of the carbonyl. However, the outermost layers, especially those that were close to the UV-radiation source were slightly more affected. The results of this study lead to the conclusion that photooxidation is autocatalytic and is affected primarily by diffusion of oxygen. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Synthetic polymers are susceptible to oxidative reactions due to their organic nature. These reactions are promoted by UV radiation and lead to significant loss of the mechanical properties and service life. The rate of photooxidative degradation at a given depth from the polymer's surface depends on both the concentration of oxygen and the intensity of UV radiation at that point.

Accelerated weathering of multilayer slabs was reported in earlier studies.^{1,2} By separating the different layers after exposure, this technique allows spectroscopic and mechanical analysis of the material at various depths of the polymer slab and thus determines the degradation as a function of the distance from surface.

Studies with multilayer low density polyethylene (LDPE) slabs exposed to accelerated weathering conditions (UV radiation, air, and heat) are de-

scribed. The aim was to learn the mechanism in which diffusing oxygen and UV radiation interact in causing degradation of samples up to 1 mm in thickness.

The isolated effect of UV radiation on polymer degradation was evaluated by using samples with a transparent oxygen barrier film on one or both of their sides. The transparent barrier film allowed penetration of UV radiation while limiting oxygen flux into the sample.

THEORY AND DEFINITIONS

To establish a model that predicts the overall rate of degradation of a thick polymer sample, it is necessary to study the rate and characteristics of oxygen diffusion through the polymer²⁻⁴ as well as the polymer's UV-radiation transmission properties (transparency and screening effects). It is also necessary to postulate an equation that describes the local rate of reaction in terms of local oxygen by-products concentration as well as of UV-radiation intensity.

* To whom correspondence should be addressed.

Cunliffe and Davis³ proposed the use of an equation based on Fick's Law for diffusion combined with an expression for reaction between the solid slab (polymer) and a gas (oxygen) diffusing in it as the basis for such a model:

$$\frac{dC(x, t)}{dt} = \frac{Dd^2C(x, t)}{dx^2} + R[C(x, t)] \quad (1)$$

where C is concentration, t exposure time, D diffusivity, R rate of reaction, and x distance from surface.

The degree of photooxidation may be experimentally evaluated from the concentration of carbonyl groups produced in the polymer as a consequence of this reaction.^{1,2} Other degradation mechanisms (crosslinking, chain scission, etc.) may occur together with photooxidation. "Global" degradation (the combined effects of all degradation mechanisms) can be roughly evaluated from loss of mechanical properties.⁵

From the degradation data, after different exposure times and at different depths in the slabs, the parameters in eq. (1) may be found for a given set of weathering conditions.^{3,4}

EXPERIMENTAL

Materials

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

Three different types of commercial blown films were used in the multilayer samples.

1. type A, 100- μ m thickness, 100% LDPE;
2. type B, 110- μ m thickness, 99% LDPE + 1% EVA;
3. 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, where "tie" stands for the tie layer.

The oxygen permeability of film types A and C was found to be 231 and 4.4 cm³mm/(m² day atm), respectively according to ASTM-D3985.

Samples

1. I: nine layers of type B film
2. II: nine layers of type A film
3. III: nine layers of type A film + one layer of type C film on top (facing the dark side of the Q.U.V.)
4. IV: nine layers of type A film + one layer of type C film on top (facing the radiation source in the Q.U.V.)
5. 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 \times 0.15 m temperature-controlled plates and a water cooling system was used for the preparation of the slab samples. Accelerated weathering was performed in the Q.U.V. accelerated weathering tester (Q-Panel Co., Cleveland, OH) apparatus as described in ASTM-G53.

A tensile tester (Testometric Model 220M, The Davenport Co., England), interfaced to a computer to facilitate analysis of data, was used to determine 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 \times 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 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 \times 0.15 m. Samples of each system were affixed to exposure racks with metal rings and introduced to the Q.U.V. 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 di-

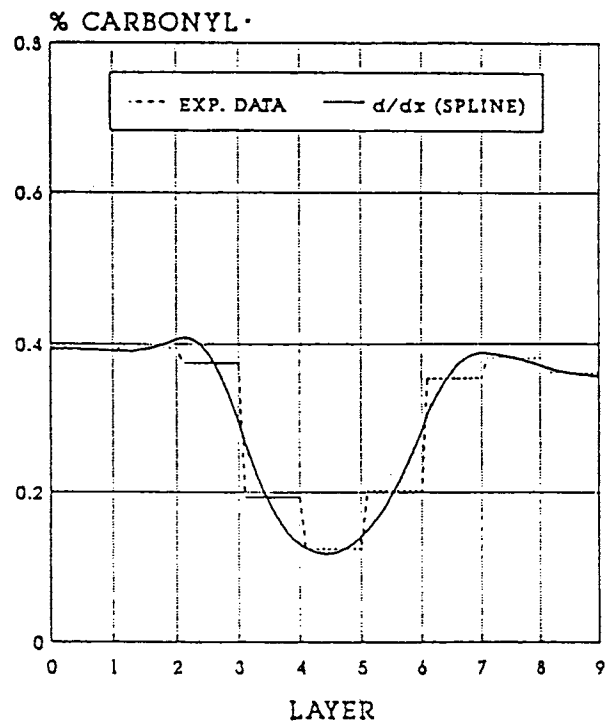


Figure 1 Carbonyl profiles in sample I after 147 h of exposure to UV radiation.

rectly measured by means of a glass thermometer and was found to be 57–58°C).

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

1. after 147 h, one sample of sample I;
2. after 170 h, one sample of sample II;
3. after 284 h, one sample of samples II, III, IV, and V;
4. 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 equation:

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

where A_x is absorbance at wavenumber $X \text{ cm}^{-1}$, $F = 125.1$ for T (thickness in microns).

The average carbonyl concentration in the samples was obtained by calculating the average concentrations of all its individual layers. Dumbbell shaped specimens (ASTM-D638; type IV) of sample I exposed for 147 h 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 extensom-

eter was used. The following tensile properties were determined: tensile strength, yield strength, elongation at yield, elongation at break, toughness (area under the stress-strain curve), and modulus of elasticity (tangent at 2% elongation).

RESULTS AND DISCUSSION

In all figures, layer 1 was the closest to the UV radiation source. Sample I removed from the QUV after 340 h degraded to such an extent that separation of the layers for testing was impossible. Figure 1 shows the carbonyl concentration profiles in sample I exposed for 147 h of UV radiation. This profile consists of a symmetric parabola with respect to the center layer in spite of the fact that the sample was irradiated through only one of its sides. The parabolic profile is followed by a plateau at the three outermost layers on both sides of the sample. A slightly higher carbonyl concentration was noted at the irradiated side of the sample.

In Figure 2, the percent carbonyl in the different layers of sample II is shown after 170 and 284 h of exposure. By comparing Figure 1 with Figure 2 it becomes evident that the autocatalytic degradation starts and the parabolic profile is obtained in sample

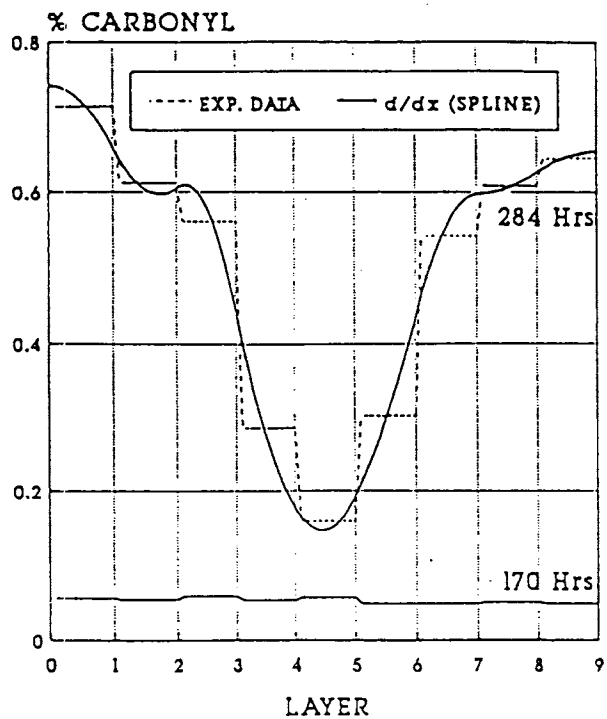


Figure 2 Carbonyl profiles of sample II exposed to 170 and 284 h of UV radiation.

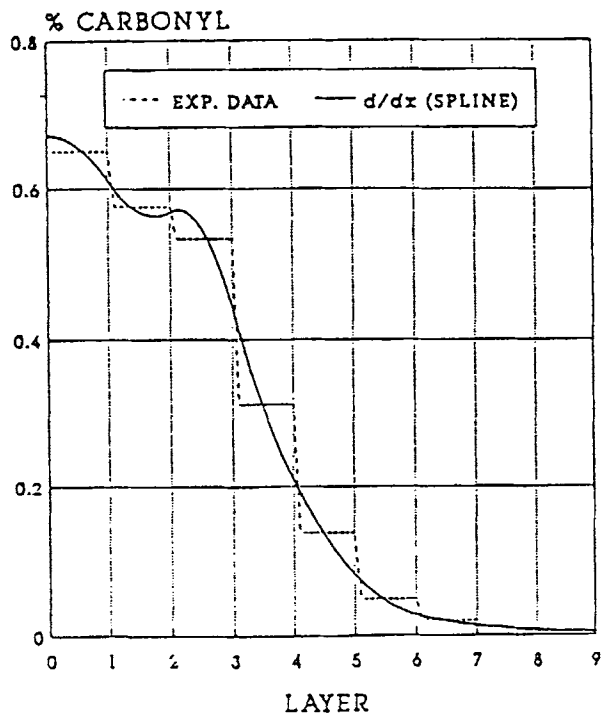


Figure 3 Carbonyl profiles of sample III exposed for 284 h of UV radiation.

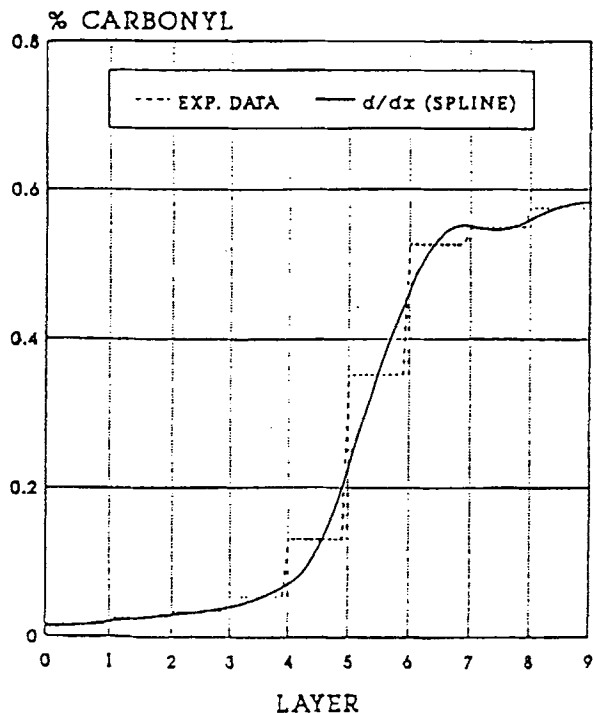


Figure 4 Carbonyl profiles of sample IV exposed for 284 h of UV radiation.

I (containing 1% EVA) much sooner than in sample II (100% LDPE). These findings suggest that the vinyl acetate groups (which are also carbonyls) have the same catalytic effect on the reaction as the carbonyl groups formed as a result of the photooxidation. In sample II, no plateau in the carbonyl concentration of the outer layers was observed after 284 h of irradiation and this concentration continued increasing toward the outermost layers. The carbonyl profiles of samples III and IV are shown in Figures 3 and 4, respectively. These profiles correspond to half of the parabola in sample II. The parabola develops on the side of the sample not covered with the barrier film, while on the covered side of the sample carbonyl concentration remains practically zero. The average carbonyl concentration of the system at different exposure times is given in

Table I. In Sample V, which was covered with barrier films on both sides, the carbonyl concentration is nearly zero after 284 h of irradiation. In samples III and IV, which were covered at opposite sides, the average percent carbonyl was roughly 50% of that in sample II, which was not covered with barrier films (see Table I). This suggests that the average degree of photooxidation is directly proportional to the sample area exposed to UV and air. The average carbonyl concentration in sample II after 170 h of irradiation is about one-tenth of that irradiated for 284 h revealing the autocatalytic nature of the photooxidation, i.e. the rate of reaction increases with increasing by-product concentration. This conclusion is supported by Figure 2 that shows the carbonyl profiles of sample II at two intervals. At the beginning of the photooxidation, the carbonyl concentra-

Table I Average Degree of Photooxidation of Systems I-V

Exposure time (h)	147		170		284		
	I	II	II	III	IV	V	
% Carbonyl	0.309	0.053	0.492	0.252	0.256	0.002	

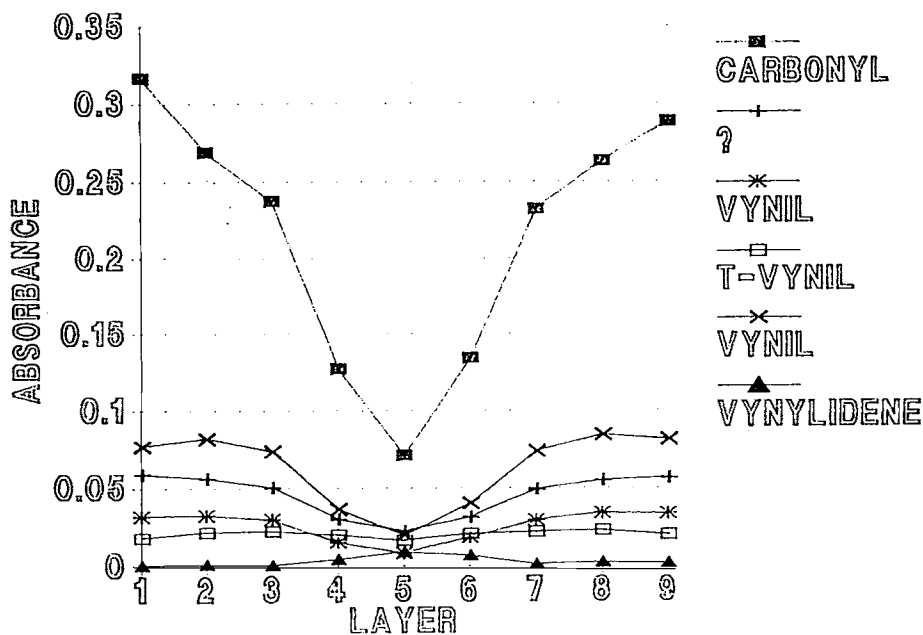


Figure 5 Absorbance profiles of various groups formed during degradation after 284 h of irradiation.

tion is low and so is the rate of reaction. Thus, oxygen is not rapidly consumed and can reach the core layer of the system. At this stage, carbonyl concentration rises uniformly at all depths of the sample. As carbonyl concentration builds up, the rate of reaction increases. This causes the incoming oxygen to be rapidly consumed at the outermost layers, fur-

ther increasing their carbonyl content. At this stage, less oxygen reaches the core layers of the sample and the photooxidation rate in them is lower. The fact that the degree of photooxidation is nearly the same in samples III and IV (Table I) shows that the UV radiation intensity is constant throughout the sample (i.e., neither the PE nor the barrier film

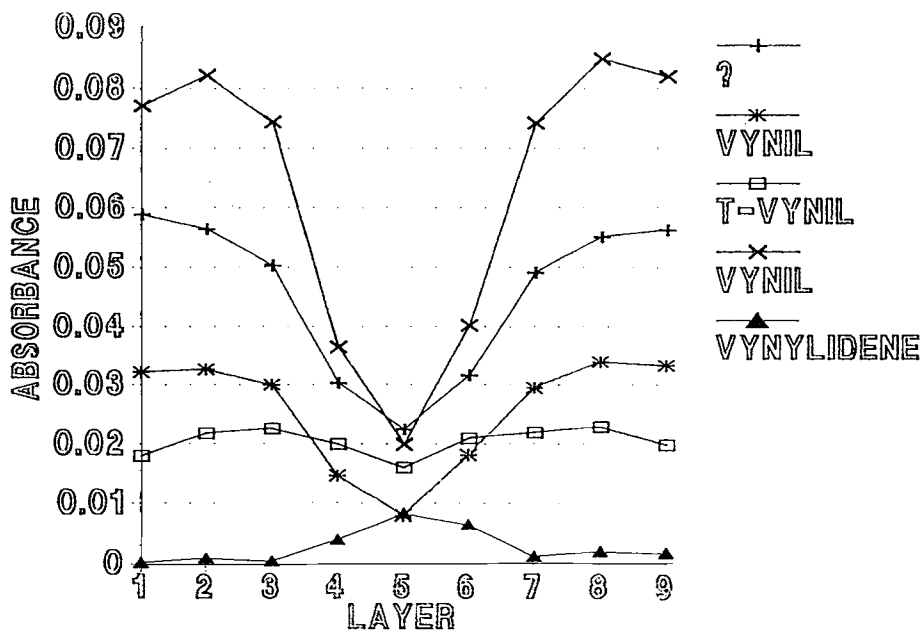


Figure 6 Absorbance of various groups (expansion of Fig. 5).

Table II Mechanical Properties of Layers in System I after 147-h Exposure and Original Type B Film (Control)

Property (in MD)*	Layer									
	Control	L1	L2	L3	L4	L5	L6	L7	L8	L9
Tensile stress (kg/cm ²)	260	139	141	147	187	255	209	141	142	142
Elongation (%)	331	17	100	113	215	320	270	109	85	47
<i>E</i> Modulus (kg/cm ²)	20	27	25	25	24	22	22	26	26	24
Toughness (kg mm/mm ²)	341	9	65	78	172	309	228	72	56	31
Yield stress (kg/cm ²)	—	+	140	144	—	—	—	139	141	141
Yield Elongation (%)	—	+	18	20	—	—	—	19	19	20

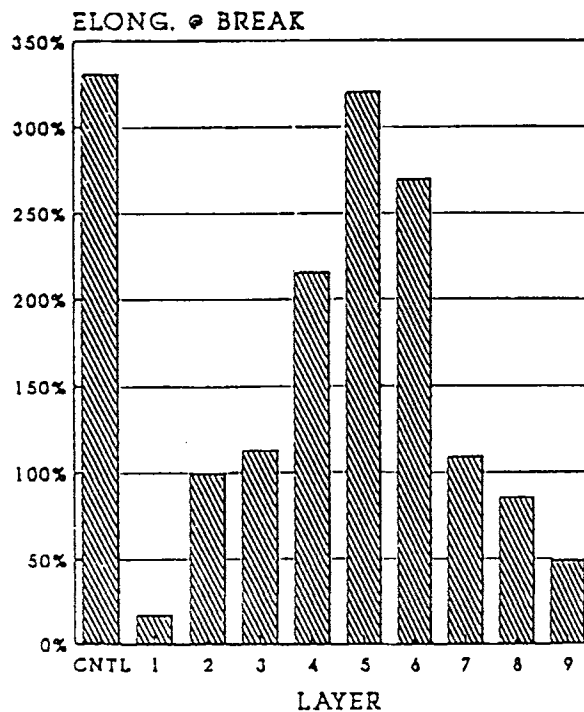
* Machine direction.

+, Failure occurred prior to yield. (—) No true yielding point observed.

attenuates or screens incoming UV radiation), and that only oxygen concentration varies with depth and time. FTIR was used to determine other groups also (in addition to the carbonyl) formed during the photooxidation. After 170 h of exposure of sample II, there was almost no difference in the concentration of these groups in the different layers. The absorbance of several groups by the various layers of sample II after 284 h of exposure to irradiation is presented in Figure 5. It can be seen that the absorbance of the carbonyl group is by far higher than that of the other groups. This is probably the major reason for the common use, in the literature, of carbonyl concentrations to represent the extent of photooxidation. The absorbance of the different layers follows the parabolic pattern previously discussed. The absorbance of the vinyl and of an unidentified (marked with a question mark) groups (except the vinylidene) follows the same pattern. Figure 6 is an expansion of the lower part of Figure 5 (does not contain the absorbance of the carbonyl) and enables a closer inspection of the other groups. It can be seen that the concentration of the vinyl and *trans*-vinyl groups is somewhat lower at the surfaces than in the next inner layers (on both sides), as opposed to that of the carbonyl groups which is highest at the surface. One possibility could be that the former groups are intermediate by-products of the oxidation reaction and they turn into carbonyl groups as the reaction propagates. As the oxygen required for this transformation is more abundant at the surfaces than in the inner layers, carbonyls are formed faster in the outer layers at the expense of the vinyl and *trans*-vinyl groups. As opposed to other groups, the vinylidene group exists (although at a low concentration) in the original sample and disappears as the photooxidation reac-

tion proceeds. Its abundance after 284 h of UV irradiation is therefore greatest in the inner layer (which was least affected) and lowest at the more degraded outer layers.

The mechanical properties calculated from the stress-strain curves of the nine layers of sample I (LDPE containing 1% EVA) are summarized in Table II. These results show an increase in modulus and a significant decrease in ultimate elongation and toughness with the increase of carbonyl concentration. It was reported in the literature that elongation

**Figure 7** Elongation at break profiles of the various layers in sample I (and control, CNTL) after 147 h of irradiation.

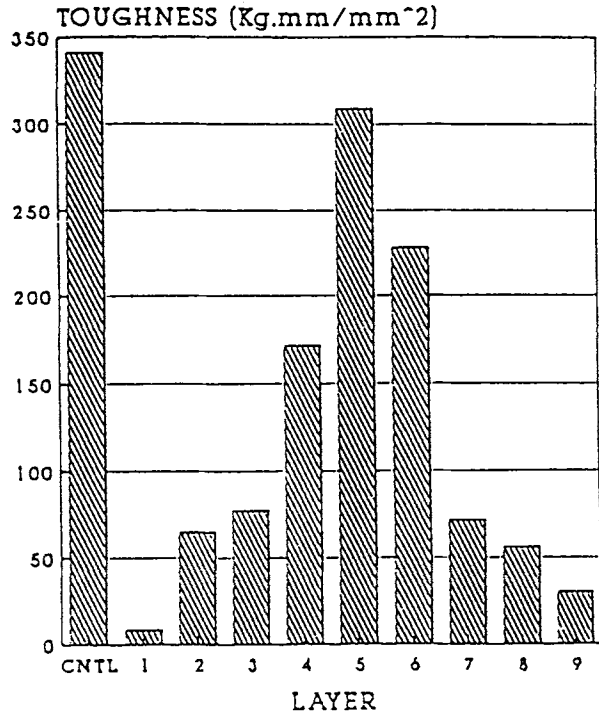


Figure 8 Toughness profiles of the various layers in sample I (and control, CNTL) after 147 h of irradiation.

at break and toughness, which is closely related to it, are the most affected mechanical properties as a result of degradation.^{5,6} A comparison between the elongation at break profile shown in Figure 7 and the similar profile of toughness (Fig. 8) with that of carbonyl concentration (Figs. 1, 2) reinforces these findings. Figure 7 also indicates that the three outermost layers on each side of the sample suffered a higher loss in elongation the closer the layer was to the surface, in spite of the fact that no significant change in carbonyl concentration was noticed in these samples (such a change in carbonyl concentration in the outer layers was found however in sample II after 284 h of irradiation, see Fig. 2). In Figures 9 and 10 the elongation at break and tensile strength, respectively, of the different layers in sample II (100% LDPE) are shown after 284 h of irradiation. The parabolic profile of retention of properties is clearly seen with the highest values retained by the least degraded center layers.

CONCLUSIONS

1. Oxygen diffusion rather than UV-radiation transmission is the limiting parameter in the photooxidation of transparent polyolefins.

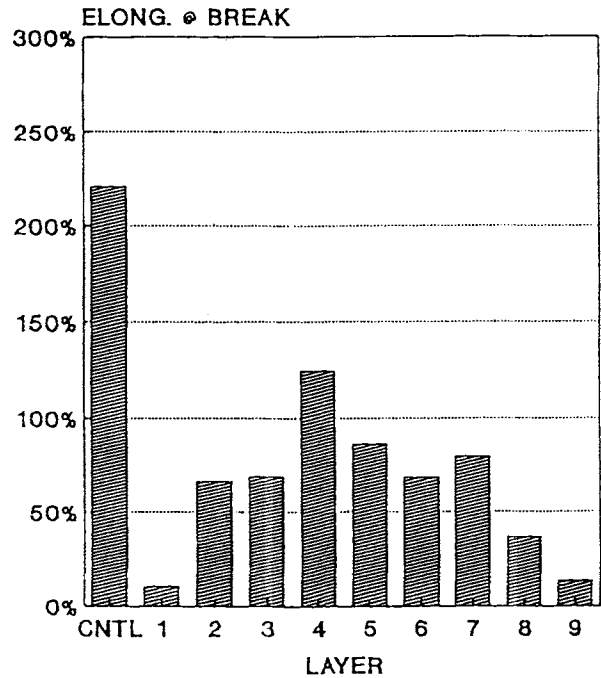


Figure 9 Elongation at break of the various layers of sample II after 284 h of exposure.

2. Mechanical testing together with FTIR spectroscopy can be used to evaluate degradation of polyolefins.

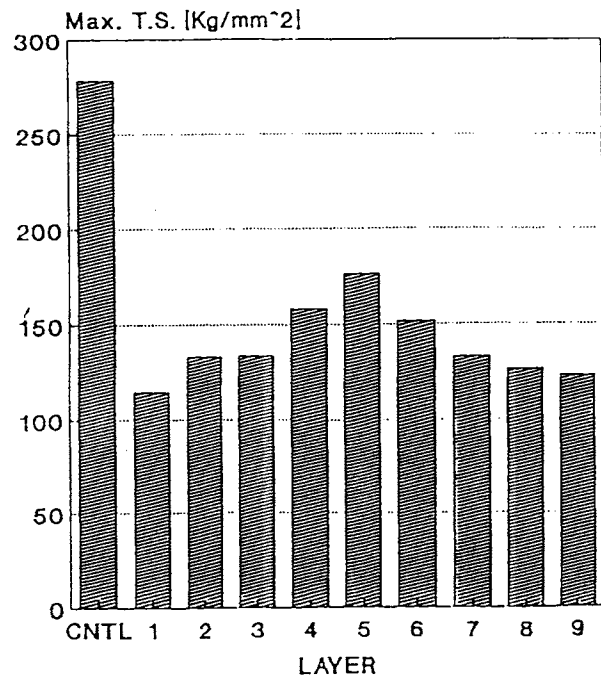


Figure 10 Tensile strength of various layers in sample II after 284 h of exposure.

3. Photooxidation of PE is autocatalytic, i.e., it is enhanced by its by-products.
4. The rate of oxidation of LDPE and EVA blends is faster than of pure LDPE.
5. Thin layers of an oxygen barrier can be applied to the surface of polymer articles to reduce their photodegradation.

REFERENCES

1. E. Fain and M. Wolf, Final project assay submitted to the Dept. of Chem. Eng., Technion-Israel Institute of Technology, Israel, 1985.
2. G. C. Furneaux and K. J. Ledbury, *Polym. Deg. Stab.*, **3**, 431-442 (1980).
3. A. V. Cunliffe and A. Davis, *Polym. Deg. Stab.*, **4**, 17-37 (1982).
4. S. F. Fairgrive and J. R. MacCallum, *Polym. Deg. Stab.*, **11**, 251-265 (1985).
5. A. Ram, T. Meir, and J. Miltz, *Intern. J. Polym. Mater.*, **8**, 323-336 (1980).
6. J. Miltz and M. Narkis, *J. Appl. Polym. Sci.*, **20**, 1627-1633 (1976).

Received July 18, 1994

Accepted December 22, 1994