where $S_q^{(p)}$'s are Stirling numbers of the first kind.[11] For most applications, only the first few coefficients are needed and these are given by the matrix

$$\{a_{ki}\} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 3 & 1 & 0 \\ 0 & -11 & 7 & 6 & 1 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \ddots \end{bmatrix} \tag{IV.9}$$

The moments for $Q_{n,m}$ and $M_{n,m}$ are given by similar expressions. Thus all the live polymer moments can be obtained by performing the indicated differentiation on (II.5) and (II.6).

The dead polymer moments must be found by making use of eq 29 to give the rate of production of $\textcircled{\scriptsize H}(s, u)$

$$r_{\textcircled{\tiny H}} = \sum_n \sum_m s^{n+m} u^{nw_a+mw_b} r_{\mathrm{M}n,m} \tag{IV.10}$$

Then by performing the differentiation with respect to s and u on eq IV.10 we get rates of formation of all the moments. For example

$$r_{\lambda_k{}^{\mathrm{M}}} = \sum_{i=0}^{k} a_{ki} \left[\frac{\partial^i r_{\textcircled{\tiny H}}}{\partial s^i}\right]_{s=u=1} \qquad k = 0, 1, 2, \ldots \tag{IV.11}$$

and the other moments are obtained by similar expressions.

---

(11) G. A. Korn and T. M. Korn, "Mathematical Handbook for Scientists and Engineers," McGraw-Hill, New York, N. Y., 1968.

Photooxidation of Polypropylene Films. IV. Surface Changes Studied by Attenuated Total Reflection Spectroscopy[1,2]

D. J. Carlsson* and D. M. Wiles

Division of Chemistry, National Research Council of Canada,
Ottawa, Canada. *Received December 16, 1970*

ABSTRACT: The photooxidation of unstabilized polypropylene films was found to occur primarily in thin surface layers of the samples. The formation of -OH and >C=O oxidation products was monitored by transmission and attenuated total reflection (ATR) spectroscopy in the infrared. By selecting appropriate reflection conditions, the ATR spectra of surface layers corresponding to four different depths of penetration of the ir beam were recorded with each sample. The phenomenon of surface oxidation was found to occur with all of the commercial film samples and uv sources employed, and is believed to result in the brittle failure of the degraded films at very low overall degrees of oxidation. Surface product concentrations and concentration–depth distributions are derived from the spectroscopic data at various irradiation times.

The photooxidative deterioration of polypropylene films and fibers at relatively long ultraviolet (uv) wavelengths (>3000 Å) has been found to involve several competing or consecutive radical and molecular reactions.[3] These reactions result in a buildup in oxidation products, together with various associated physical changes, such as a drop in molecular weight and an increase in the brittleness of the polymer sample. Polymer photodeterioration has frequently been studied by such techniques as chemical analysis, transmission spectroscopy (in the infrared (ir) or uv regions), solution viscometry, and stress–strain analysis. For many purposes, these methods can provide adequate experimental information. However, all of these techniques usually give results which sum or average changes which have occurred across the total thickness of the sample, and give no information on the exact location of the onset of deterioration. This shortcoming can be expected to be of great importance in the study of polymer–gas reactions, owing to the possibilities of nonuniform product distributions in such systems. For example, during the photooxidation of polyolefins diffusion effects[4] and variations in polymer reactivity may cause preferential reaction in certain regions.

Attenuated total reflection (ATR) ir spectroscopy provides a means of observing surface changes in a given sample, and hence, when used in conjunction with transmission ir spectroscopy, provides a means of studying reaction uniformity in solids. The technique of ATR spectroscopy involves the measurement of the ir spectrum of the surface of a sample which has been placed in intimate contact with a suitable reflection element.[5] With the correct choice of reflection element and angle of incidence, it is possible to record the ir spectra corresponding to various depths of penetration (usually from 0.1 to 4.0 μ) of the ir beam into the surface of a given sample. By the use of this technique, one can build up a partial "concentration profile" across the thickness of the sample. The scope of this ATR procedure and the normalization procedure which is required in order to make meaningful quantitative comparisons between ATR spectra have been discussed previously.[6] In this paper, we discuss the use of the ATR technique to study the extent of photooxidation of polypropylene films as a function of distance into the sample from the film surface.

Experimental Section

Polypropylene Films.[7] Six films (designated A–F) were obtained

---

(1) Issued as NRCC Report No. 11864.

(2) Previous paper in this series: D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 597 (1969).

(3) (a) Y. Kato, D. J. Carlsson, and D. M. Wiles, *J. Appl. Polym. Sci.*, **13**, 1447 (1969); (b) J. H. Adams, *J. Polym. Sci., Part A-1*, **8**, 1269, 1279 (1970).

(4) J. E. Wilson, *J. Chem. Phys.*, **22**, 334 (1954).

(5) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, New York, N. Y., 1967.

(6) D. J. Carlsson and D. M. Wiles, *Can. J. Chem.*, **48**, 2397 (1970).

(7) The results obtained with the commercial films used in this work should not be considered to endorse or discredit the products of any manufacturer. Many of the samples were experimental grades, or subjected to unusual treatments.

from various resin manufacturers. The details of film thickness, density, and extrusion method for each of these samples are tabulated in a following paper.[8] All of the films were predominantly isotactic polypropylene homopolymer, and had good clarity. Several other films from various manufacturers, including films of Japanese origin, were also obtained and showed the same general photooxidation behavior as the well-characterized films. None of the samples was appreciably oriented except for film F (the ICI sample).

Most of the films were free of uv stabilizers or contained acetone-soluble stabilizers. Prior to use, all samples were acetone extracted (48 hr) to remove additives, then vacuum dried and stored. No crystallites were detectable by optical microscopy in any of the films. The film surfaces were frequently marred by fine parallel marks, which caused some loss of quality in the recorded ATR spectra.

Ir Spectra. Transmission spectra of a double thickness of each photooxidized film were recorded on a Beckman IR8 spectrometer. Surface spectra were recorded on this spectrometer fitted with a Wilks No. 9 ATR attachment. Germanium or KRS-5 reflection elements (2 × 20 × 52.5 mm) with 45° facets were used at 30 or 45° (Ge) and 45 or 60° (KRS-5) and were held in a modified Wilks MIR-29 sample holder. The holder modification, holder assembly procedure, and selection of optimum experimental conditions have all been described previously.[6]

The optical densities (OD) of bands of interest were normalized to unit depth of penetration by dividing the OD in question by the OD of the polypropylene $-CH_2-$ stretching band at 2840 cm^{-1}. Both bands were always recorded during the same scan. This procedure also automatically corrects for variations in sample area, in sample–reflection element contact, and in the number of interfacial reflections. The normalization procedure and methods used to estimate peak heights have been described previously.[6]

Photooxidation. All films were stored in air for 20 hr or longer prior to uv irradiation. Most polypropylene films were photooxidized under a Hanovia high-pressure mercury-vapor lamp (450 W, L-679A burner). The sample–source distance was 17 cm. The film samples were mounted in a sealed cell, which had opposite parallel faces (~2 mm apart) made from a Corning CS 1-64 filter (the cell face toward the source) and a quartz plate. The irradiation wavelength was >3200 Å. A slow air stream was drawn through the cell during irradiation, and care was taken to prevent any O_3 produced by the lamp reaching the samples. The cell assembly was air cooled throughout the irradiation. Since both sample temperature and wavelength of irradiation were found to have a marked effect on rate of photooxidation and product distribution, care must be exercised in the comparison of results obtained under differing irradiation conditions.

Some irradiations were performed in an Atlas carbon-arc Fade-Ometer (ambient air temperature 35°) and in an Atlas xenon-arc Weather-Ometer (ambient air temperature 37°). Film samples were backed with white cards on Atlas SL-LSR holders.

The hydroperoxide contents of photooxidized films were determined by the chemical method described previously.[2]

Tensile Measurements. Stress–strain curves were recorded for 2.0 × 50 mm film strips with an Instron tensile tester at a crossheads speed of 5.2 cm min^{-1} with load cell C (500 g full-scale deflection). The experimental procedure was similar to ASTM No. D882-67. The strips were all cut at right angles to the surface marks on the film. The initial separation of the grips was 1.3 cm. A minimum of five good breaks was made on strips cut from each film sample. Tensile strengths at break usually agreed to within ±5%; percentage elongations at break of a given highly photodegraded sample frequently varied by ±30%.

Density. Film densities were determined by floatation in a methanol–water mixture at 25°. Care was taken to remove clinging air bubbles from the films. Reproducibility was usually better than ±0.0002 g $ml.^{-1}$.

Results and Discussion

Transmission ir spectroscopy of unstabilized isotactic polypropylene films shows two major changes during photooxidation in the near-uv.[3a] These changes are represented by the buildup of a broad absorption centered at 3400 cm^{-1} and the concurrent buildup of a multicomponent absorption with its maximum at ~1715 cm^{-1}, which is caused by several types of carbonyl oxidation products.[9] During irradiation, these ir changes are accompanied by increases in both brittleness and film density. Examples of changes in transmission ir, density, and percentage elongation at break (inversely proportional to brittleness) during irradiation in air are shown in Figure 1. The 3400-cm^{-1} band is attributable to hydrogen-bonded –OH groups such as hydroperoxides and alcohols. Chemical analysis of films photooxidized with either the filtered mercury lamp or in the carbon- or xenon-arc Weather-Ometers indicated that hydroperoxide accounts for over 70% of the observed 3400-cm^{-1} absorption, even at degrees of degradation corresponding to brittle failure. (The hydroperoxide 3400-cm^{-1} extinction coefficient was taken to be 70 M^{-1} cm^{-1}.)[2] In addition, heating photooxidized films under vacuum (55 hr, 80°) resulted in the loss of most (>60%) of the 3400-cm^{-1} absorption of the films, and an associated increase in carbonyl absorption, in disagreement with the results of Adams.[3b] Hence, under our experimental conditions, assignment of the 3400-cm^{-1} absorption to hydroperoxides appears justified.

Although elongation at break decreases dramatically during uv irradiation, other major features of the stress–strain curves for the photooxidized films (such as yield strength) were not significantly affected by the extent of photooxidation. From Figure 1 is it apparent that the transmission ir changes and density increase only become significant at relatively long photooxidation times, whereas extensive physical deterioration of the polymer has already occurred after about 20 hr of Fade-Ometer irradiation. However, the ATR ir spectra of photooxidized polypropylene films were found to provide considerable information both on the chemical changes which occur during the very early stages of photooxidation and on the physical location of these changes.

Unstabilized polypropylene film (sample A) was exposed to

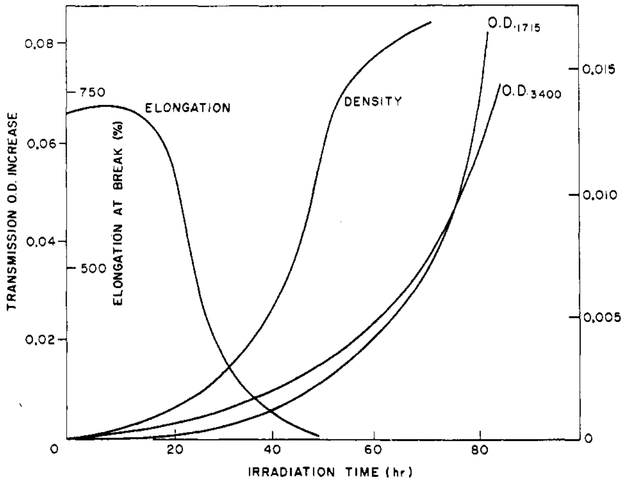

Figure 1. Chemical and physical changes during polypropylene irradiation: carbon-arc Fade-Ometer irradiation at 35°, film sample A (22-μ thickness), density before degradation 0.8858 g ml^{-1}.

---

(8) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **4**, 179 (1971).

(9) D. J. Carlsson and D. M. Wiles, *ibid.*, **2**, 587 (1969).

TABLE I
ATR CONDITIONS AND DEPTHS OF PENETRATION

Reflection element[a]	n_{21}[b]	Nominal incidence angle, deg	θ,[c] deg	N[d]	d_p[e]$/\lambda_0$
Ge	0.375	45	45	25	0.066
Ge	0.375	30	41	29	0.074
KRS-5	0.625	60	51	20	0.143
KRS-5	0.625	45	45	25	0.201

[a] Facet angle 45° in all cases. [b] Ratio of refractive indices of polypropylene (medium 2) to reflection element (medium 1). [c] True angle of incidence, corrected for refraction at the face. [d] Number of reflections from the full length of the reflection element. [e] Depth of penetration, calculated from expressions given by Harrick.[10]

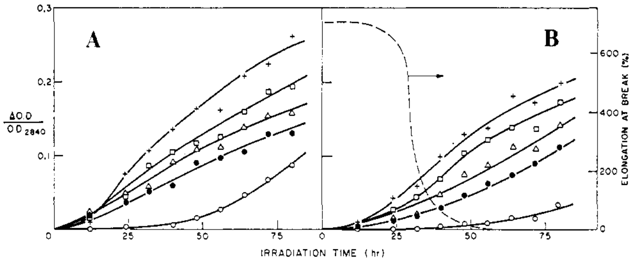

Figure 3. Photooxidation of polypropylene film; sample and irradiation conditions as in Figure 2: (A) 3400-cm^{-1} absorption (-OH), λ_0 2.94 μ, normalized OD values times 3; (B) ~1715-cm^{-1} absorption (>C=O), λ_0 5.84 μ. Transmission spectra, ○; d_p/λ_0 = 0.201, ●; 0.143, △; 0.074, □; 0.066, +.

the radiation from the Hanovia lamp and transmission ir spectra were recorded at various irradiation times. After each irradiation, ATR spectra were also recorded with the four sets of reflection conditions shown in Table I. At a given wavelength, each set of reflection conditions is characterized by a certain depth of penetration (d_p) of the ir beam into the sample surface. The d_p value is defined as the distance measured into the sample, normal to the interface, required for the electric field amplitude to fall to a value of $1/e$ of its value at the interface. The d_p values depend on the incident wavelength in vacuum (λ_0), and d_p/λ_0 values calculated from the expression given by Harrick[10] are shown in Table I for each of the reflection conditions employed. The ATR absorbance bands observed at 3400 cm^{-1} (-OOH) and ~1715 cm^{-1} (>C=O) all showed the same general shapes as the corresponding transmission-absorption envelopes. This is illustrated by Figure 2 in which ATR (curve A) and transmission spectra (curve B) of a photooxidized film are compared. In this example, the oxidation product absorptions are much more intense in the ATR spectrum than in the transmission spectrum. After prolonged irradiation (60 hr or more), a broad absorption develops between ~1500 and 1000 cm^{-1} and is probably attributable to C-C and C-O-C cross-link formation. For the purpose of quantitative comparison, the experimentally observed ATR optical density (OD_X) values of a chromophore X are expressed as the normalized ratio of OD_X/OD_{2840}.[5] The variation in normalized OD values with irradiation time for the -OOH and >C=O absorptions are shown in Figure 3 for the four different reflection conditions, together with the decrease in percentage elongation at break observed with these films.

A uniform distribution of absorbers across the thickness of a film will lead to a set of normalized ΔOD values which are independent of the depth of penetration of the ir beam,[6] whereas certain nonuniform absorber distributions can yield values that are dependent on d_p. The normalized absorption curves shown in Figure 3 indicate that there is extensive photooxidation very close to the film surface (when d_p is very small), but very little oxidation product in the bulk of the sample (as shown by the transmission ir values). For a given irradiation time, the corresponding ATR spectra of both the front (*i.e.*, the surface facing the source) and the rear of the film sample were found to be identical. Consequently, photooxidation appeared to be proceeding in from each film surface at equal rates. This effect is illustrated by Figure 4, which shows the variation in normalized ΔOD_{1715} with d_p for film samples which had been subjected to 40 and 70 hr of irradiation. Obviously a similar profile can be constructed for the distribution of hydroperoxide product across the film at 40 and 70 hr, and profiles can also be constructed for different irradiation times. From Figure 3 it is apparent that extensive surface oxidation has already occurred prior to the dramatic increase in brittleness of the film sample.

The commercial film samples studies showed a wide variation in uv resistance as measured by the onset of brittle failure. However, similar trends to those shown in Figure 3 were observed in the ATR and transmission spectra of all of the commercial film samples examined. For example, although the blown film D was roughly twice as stable as the

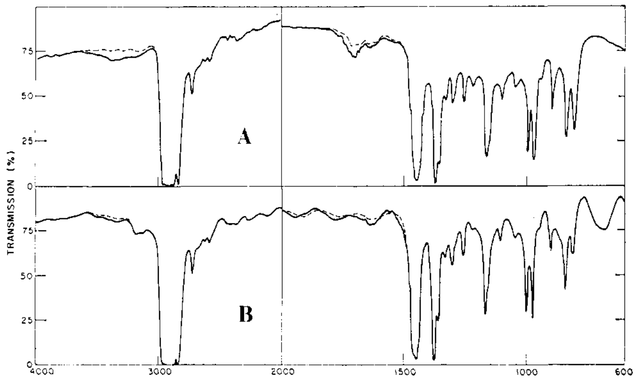

Figure 2. Comparison of ATR and transmission ir spectra after photooxidation; irradiation with the filtered Hanovia lamp at 40 ± 2°, film sample A: (A) ATR spectrum on KRS-5 at 45°; (B) transmission spectrum, 44-μ total thickness; irradiation time — — —, 0 hr; ———, 32 hr.

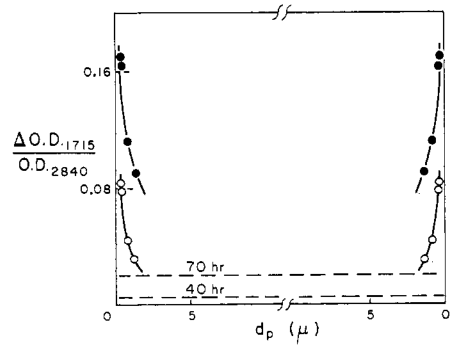

Figure 4. Variation in ir absorption with depth of penetration; sample and irradiation conditions as in Figure 2; d_p values measured in from each surface of the 22-μ film. Transmission values, ———; irradiation times ○, 40 hr; ●, 70 hr.

---

(10) N. J. Harrick and F. K. du Pré, *Appl. Opt.*, **5**, 1739 (1966).

cast film A (the least stable film studied) under the same irradiation conditions, the variations in hydroperoxide and carbonyl absorptions of film D with irradiation time shown in Figure 5 are analogous to those shown in Figure 3. Profiles similar to those shown in Figure 4 can obviously be constructed from the data shown in Figure 5. Thus the phenomenon of preferential surface oxidation during uv irradiation seems to be quite general for commercial film samples and is not peculiar to only one particular film sample. The variation in uv stability among the unstabilized commercial polypropylene films is discussed in greater detail in a following paper.[8]

Various film samples were also irradiated with the carbon-arc Fade-Ometer or the xenon-arc Weather-Ometer, to allow comparison with the data from the Hanovia irradiation. Although the uv lifetime[11] of a given film sample was different for each light source used, the ATR and transmission ir data in all cases followed the same general patterns as shown in Figures 3, 4, and 5.

Product Concentration Profiles. The curves shown in Figure 4 indicate that extensive oxidation has occurred close to the sample surface, whereas the bulk of the film is little degraded. However, these curves are not simply related to the true concentration–depth profiles which exist across each sample. It is obviously of interest to try to establish actual surface concentrations, and also the true profiles which exist at a given irradiation time.

At a given ir wavelength, the absorbance which results from a single attenuated reflection[12] from the interface between an absorbing film and a reflection element is related to the concentration of the absorber $[\mathrm{C}]_z$ and electric field amplitude E_z at penetration z into the film by the expression[14]

$$\mathrm{OD} = \frac{\epsilon n_{21}}{\cos\theta}\int_0^\infty E_z^2[\mathrm{C}]_z \mathrm{d}z \qquad (1)$$

where θ is the angle of incidence, ϵ the molar extinction coefficient of the absorption band, and n_{21} the ratio of the refractive indices of the film (2) and the element (1). For the limiting cases of (a) an infinite uniformly absorbing substrate, *i.e.*, when $[\mathrm{C}]_z$ is a constant, and (b) a very thin layer of an absorber on the surface of a transparent substrate, *i.e.*, when both $[\mathrm{C}]_z$ and E_z are constant across the thickness of the absorber, expression 1 has been solved[10,14] to give the relationships

infinite substrate

$$\mathrm{OD} = \frac{n_{21}\epsilon[\mathrm{C}]_0 E_0^2}{2\gamma\cos\theta} \qquad (2)$$

thin layer

$$\mathrm{OD} = \frac{n_{21}\epsilon[\mathrm{C}]_0 E_0^2 d}{\cos\theta} \qquad (3)$$

E_0 is the electric field amplitude at the interface, γ is an experimental constant ($\gamma = \pi n_1(\sin^2\theta - n_{21}^2)^{1/2}/\lambda_0$), and $[\mathrm{C}]_0$ is the absorber concentration at the interface. In expression 3, d is the thickness of the absorbing surface layer. (The refractive indices of the surface layer and the supporting substrate have been assumed equal in the derivation of eq 3.) For a thin ir absorbing surface layer on the (infinite) polypropylene, the experimental parameter (the normalized ΔOD value for a band X) is then given by[6]

$$\frac{\Delta\mathrm{OD_X}}{\mathrm{OD_{CH}}} = Kd[\mathrm{C}]_\mathrm{X} n_1(\sin^2\theta - n_{21}^2)^{1/2} \qquad (4)$$

where $K = 4\pi\,\epsilon_\mathrm{X}/(\lambda_0\epsilon[\mathrm{C}])_\mathrm{CH}$, and can be readily evaluated from known constants.[15] Expression 4 has been shown to hold for film samples which have been surface modified by corona treatments.[6]

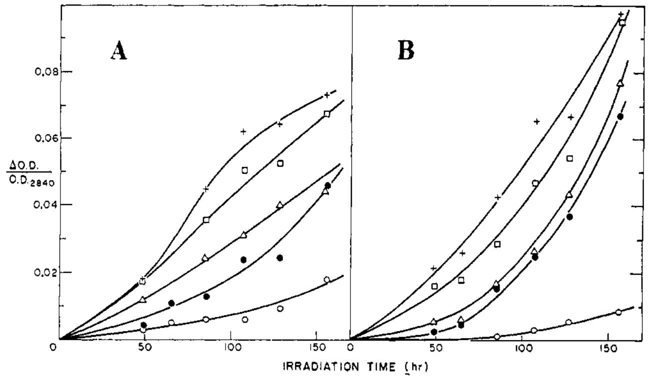

Figure 5. Photooxidation of polypropylene film; irradiation with the filtered Hanovia lamp at 35 ± 2°, film sample D (manufactured by tubular extrusion). ATR spectra were recorded on the inner surface of the blown tube: (A) 3400-cm^{-1} absorption (-OH), λ_0 2.94 μ; (B) ~1715-cm^{-1} absorption (>C=O), λ_0 5.84 μ. Transmission spectra, ○; d_p/λ_0 = 0.201, ●; 0.143, Δ; 0.074, □; 0.066, +.

Experimental normalized ΔOD values for >C=O and ROOH buildup during ~40 hr of irradiation (the data shown in Figure 3) can be shown to obey expression 4 quite accurately, *i.e.*, $\Delta\mathrm{OD_X}/\mathrm{OD_{CH}}$ is linearly dependent on $n_1(\sin^2\theta - n_{21}^2)^{1/2}$ for a given irradiation time. The results for -OH and >C=O buildup are plotted in this manner in Figure 6 for 20, 40, and 70 hr of irradiation of the Eastman film. At 70 hr, marked deviations from linearity are obvious, indicating that significant oxidation has now occurred at depths at least as great as the smaller depths of penetration employed, *i.e.*, of the order of 3000 Å from the surface. For the 20- (-OH and >C=O) and 40-hr (>C=O) plots, the fair linearity indicates that the oxidation products are confined to a layer which is appreciably less than the lowest d_p values in thickness. Although the slopes of the linear plots allow the calculation of the product $d[\mathrm{C}]_\mathrm{X}$, the ATR data cannot give an unambiguous value for each parameter. However, if d is assumed to be ≤1000 Å, the slopes of the linear plots in Figure 6 lead to oxi-

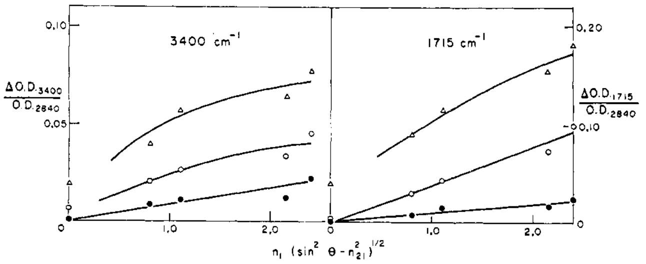

Figure 6. Polypropylene photooxidation, "thin absorber" treatment; sample and irradiation conditions as in Figure 2: irradiation time (hr) ●, 20; ○, 40; Δ, 70.

---

(11) The uv lifetime of a film sample is considered here to be the number of hours of irradiation required to reduce the per cent elongation at the break value to <50%.

(12) The OD resulting from N reflections from an interface has been shown to be N times the OD resulting from a single reflection, provided that the absorptions are small.[13]

(13) W. N. Hansen, *Spectrochim. Acta*, **21**, 815 (1965).

(14) N. J. Harrick, *J. Opt. Soc. Amer.*, **55**, 851 (1965).

(15) Both expressions 2 and 3 are polarization dependent. However, expression 4 is little affected by quite wide changes in the relative polarization ratios of the ir beam at $(\lambda)_\mathrm{X}$ and $(\lambda)_\mathrm{CH}$.

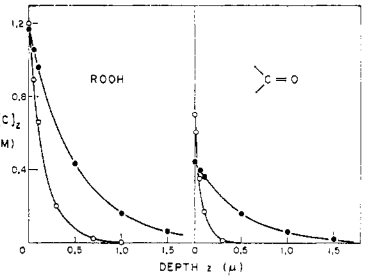

Figure 7. Calculated photooxidation product distributions; sample and irradiation conditions as in Figure 2; depth z measured into film surface: irradiation time (hr) ○, 40; ●, 70.

dation product concentrations of [>C=O] ≫ 0.06 *M* (20 hr) and >0.25 *M* (40 hr) and [-OH] ≫ 0.25 *M* (20 hr) in the surface layers. ($\epsilon_{C=O}$ is assumed to be ~300 M^{-1} cm^{-1} [9] and ϵ_{OOH} ~70 M^{-1} cm^{-1}.[2])

The thin-surface-layer treatment is obviously invalid at higher degrees of degradation, as shown by the curvature of some plots in Figure 6. However, these curved plots allow an estimation of the surface concentration of the products, since the curves can be extrapolated to a constant normalized ΔOD value (*e.g.*, ~0.08 for the 70-hr ROOH curve) as $n_1(\sin^2\theta - n_{21}^2)^{1/2}$ becomes very large, *i.e.*, d_p becomes very small. The extrapolated normalized ΔOD values can be derived from expression 2 when d_p is infinitely small, since the beam is effectively interacting with an infinite substrate. Then

$$\Delta OD_X/OD_{CH} = (\epsilon[C]\lambda_0)_X/(\epsilon[C]\lambda_0)_{CH} \tag{5}$$

Substituting the experimental extrapolated values leads to surface ROOH concentrations of ~0.6 *M* (40 hr) and ~0.9 *M* (70 hr) and a surface carbonyl concentration of ~0.3 *M* (70 hr).

An alternative treatment of the experimental results involves the solution of expression 1 for a realistic expression for $[C]_z$, the absorber concentration at various distances from the interface. The chosen expression for $[C]_z$ must fit the boundary conditions that $[C]_z = [C]_0$ at $z = 0$ and $[C]_z \rightarrow 0$ as $z \rightarrow \infty$, must be as general as possible, and must lead to a soluble integral. Wilson[4] has predicted an exponential dependence of product concentration on depth for polymer–gas reactions. Consequently the expression

$$[C]_z = [C]_0e^{-\alpha z} \tag{6}$$

where α is a constant, represents a reasonable function which satisfies the above conditions. Substitution of this relationship into expression 1 and integration leads to an optical density for the oxidation products given by

$$OD = \frac{\epsilon[C]_0n_{21}E_0{}^2}{\cos\theta(\alpha + 2\gamma)} \tag{7}$$

The optical density attributable to the normalizing C–H band is still given by expression 2. Hence, for a product X

$$\Delta OD_X/OD_{CH} = \left(\frac{2\gamma[C]_0}{2\gamma + \alpha}\right)_X \frac{(\lambda_0\epsilon)_X}{([C]_0\lambda_0\epsilon)_{CH}} \tag{8}$$

where the second part of the product and γ can be readily calculated from known constants. Substitution of the four normalized ΔOD values and the four corresponding γ values for a given degree of degradation of a sample in expression 8 allows $[C_X]_0$ and α to be evaluated.

For example, for the data shown in Figure 3 after 40 hr of irradiation

$$\begin{aligned}[C]_z{}^{ROOH} &= 1.2e^{-6.0z} \\ [C]_z{}^{C=O} &= 0.7e^{-14z}\end{aligned} \tag{9a}$$

and after 70 hr of irradiation

$$\begin{aligned}[C]_z{}^{ROOH} &= 1.2e^{-2.0z} \\ [C]_z{}^{C=O} &= 0.44e^{-2.0z}\end{aligned} \tag{9b}$$

The agreement between the $[C]_0$ values calculated from expressions 9 (when $z = 0$) and the $[C]_0$ values calculated from the curves shown in Figure 6 is excellent, bearing in mind the experimental limitations and theoretical assumptions involved. Plots of the calculated concentration–depth functions (expressions 9) are shown in Figure 7. A comparison of Figures 4 and 7 indicates that in all cases $[C]_z$ falls off much more rapidly with increasing depth than do the corresponding normalized OD–d_p curves.

It is possible to make a partial cross check on the validity of choosing the exponential relationship 6 by comparing the experimentally observed average product concentration (determined from transmission ΔOD values) with the values calculated from the integrations of expressions 9 across the film thickness, taking into account the fact that oxidation has occurred at each face. This leads to the following values: at 40 hr $[>C=O]_{obsd}$ = 0.01 *M*, $[>C=O]_{calcd}$ = 0.005 *M*; $[ROOH]_{obsd}$ = 0.07 *M*, $[ROOH]_{calcd}$ = 0.02 *M*. At 70 hr $[>C=O]_{obsd}$ = 0.04 *M*, $[>C=O]_{calcd}$ = 0.02 *M*; $[ROOH]_{obsd}$ = 0.2 *M*, $[ROOH]_{calcd}$ = 0.05 *M*. A comparison of these values implies that the chosen exponential function decays away more rapidly than the true product distribution function. Nevertheless, the agreement between the calculated and observed average concentrations must be considered to be quite fair, considering the assumptions involved.

The curves shown in Figure 7 indicate that extensive surface oxidation exists after a 40-hr irradiation (~1 *M* in both products) and that prolonged oxidation results in the progressive ingress of oxidation into the polymer. Since density changes can be expected to occur only in the photooxidized surface layers, the observed overall density increases (Figure 1) indicate that very high densities (corresponding to almost 100% crystallinity) must exist in these regions. This conclusion is consistent with the fact that oxidation is normally considered to be confined to amorphous intercrystallite regions (because of limited O_2 permeability into crystallites[16]). Consequently, the concentrations of surface products imply appreciable restructuring of the surface amorphous content because of the chain scission which results from the reactions leading to product formation. Evidence of restructuring has been directly observed by electron microscopy of replicas of irradiated film surfaces[17] which display crack networks after extensive degradation. The presence of surface cracks probably results in the dramatic drop in percentage elongation at break accompanying photooxidation (Figures 1 and 3). The electron microscopy work will be discussed in detail in a future communication.

In conclusion, the preferential surface oxidation can be expected to occur during the irradiation of all commercial polypropylene films with terrestrial sunlight. In addition, the sunlight-induced photodegradation of polypropylene fibers

(16) W. Vieth and W. F. Wuerth, *J. Appl. Polym. Sci.*, **13**, 685 (1969).
(17) P. Blais, D. J. Carlsson, and D. M. Wiles, unpublished results.

can also be expected to originate in their exposed surfaces and to be of great importance because of the high surface-to-volume ratio of fibers. In addition, the observation of polypropylene deterioration by ATR spectroscopy offers a practical accelerated test "for detecting the onset of photooxidation," as suggested by Chan and Hawkins.[18]

The origin of the surface photooxidation effect and its importance in the photodeterioration of polypropylene are discussed in detail in a following paper.[8]

Acknowledgments. The authors wish to thank the companies mentioned in the text for supplying polypropylene film samples and releasing processing data.

---

(18) M. G. Chan and W. L. Hawkins, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 9, 1638 (1968).

Photooxidation of Polypropylene Films. V. Origin of Preferential Surface Oxidation[1]

D. J. Carlsson* and D. M. Wiles

Division of Chemistry, National Research Council of Canada,
Ottawa, Canada. *Received December 16, 1970.*

ABSTRACT: The preferential surface photooxidation of many unstabilized commercial polypropylene films in air was found to originate from the presence of surface chromophores, such as -OOH and >C=O, rather than from diffusion control of the degradation, or morphological effects. This was established by the use of attenuated total reflection and transmission ir spectroscopy to determine the photooxidation product distribution within various uv-irradiated film samples. The oxidation of commercial film samples was compared with either uv or γ initiation, and was also studied under controlled O_2 diffusion conditions. After uv irradiation, specially prepared film samples showed either little surface oxidation (films pressed under a N_2 atmosphere) or enhanced surface reaction (films exposed to O_3 or an O_2 corona discharge prior to irradiation). The observed surface photooxidation of commercial films is believed to result from a limited thermal oxidation of the film surfaces during manufacture. The stability of various commercial films is compared and discussed in terms of the extrusion technique used in their manufacture and fluorescent emission spectrum of each sample. The relevance of the results both to the photostabilization and to the accelerated decomposition of polypropylene films is considered.

In the previous paper in this series,[2] unstabilized commercial polypropylene films were reported to undergo rapid photooxidative attack close to the film surfaces, while the bulk of each sample was largely undegraded. This effect was detected by the use of attenuated total reflection (ATR) spectroscopy in the infrared (ir) region, and was demonstrated to occur during the irradiation of many different film samples with various ultraviolet (uv) sources. Since this surface oxidation is sufficient to cause the brittle failure of a stressed film, a study of the origin of the phenomenon is of great importance, both in the development of uv stabilizer systems to extend the useful life of an article, and possibly also in the opposite problem of deliberately introducing "self-destruct" properties into packaging material to reduce environmental pollution.

The concentration of oxidation products (hydroperoxides, ROOH, and carbonyl derivatives, >C=O) close to the surfaces of films as compared with the bulk of each film during air photooxidation might arise from several physical and/or chemical effects. Possible causes may be arbitrarily divided into diffusion effects and kinetic effects. In a situation of uniform polymer reactivity, Wilson[3] has concluded that a steep gas concentration gradient might become established close to the surfaces of a film during a film–gas reaction for certain values of diffusion and reaction constants. Similarly, diffusion effects might also arise from the buildup of a gaseous oxidation product in the film if this product is capable of inhibiting the polymer oxidation. In the absence of diffusion-controlled effects, possible kinetic effects include a high photoinitiation rate or enhanced polymer reactivity close to the surface, or alternatively a lower rate of oxidative chain termination in the surface layer.

In this paper, the origin of the observed rapid surface photooxidation of polypropylene films is investigated by a comparison of the γ- and uv-initiated deterioration, by a study of O_2 diffusion effects, and by an investigation of the importance of various pretreatments on film stability. Product distributions within samples were determined by ATR and transmission ir spectroscopy. The relative photostability of polypropylene films obtained from various commercial sources is also reported, and the observed differences are discussed.[4]

Experimental Section

Polypropylene Films. The manufacturer, extrusion method, thickness, and density of each of the commercial films studied are listed in Table I. None of the films was appreciably oriented, except the ICI sample. The films were initially extracted and dried as described previously.[2] Special films were prepared from an unstabilized polypropylene powder (Moplen, Montecatini Edison) under carefully controlled conditions.[5] The powder was distributed over quartz plates, and these plates were stored under dry N_2 for several days. The powder was then pressed between quartz plates in the N_2 atmosphere at 250° to give 30-μ films, which were immediately quenched in Dry Ice–methanol. The films were carefully stripped from the quartz and vacuum dried.

Ir Spectra. Transmission and ATR spectra of film samples were determined by the previously described methods.[6] ATR spectra

---

(1) Issued as NRCC Report No. 11868.

(2) D. J. Carlsson and D. M. Wiles, *Macromolecules*, 4, 174 (1971).

(3) J. E. Wilson, *J. Chem. Phys.*, 22, 334 (1954).

(4) The results obtained with the commercial films used in this work should not be considered to endorse or discredit the products of any manufacturer. Many of the samples were experimental grades, or subjected to unusual treatments.

(5) Y. Kato, D. J. Carlsson and D. M. Wiles, *J. Appl. Polym. Sci.*, 13, 1447 (1969).

(6) D. J. Carlsson and D. M. Wiles, *Can. J. Chem.*, 48, 2397 (1970).