

Photochemical Degradation of Poly(ethylene Terephthalate). I. Irradiation Experiments with the Xenon and Carbon Arc

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Synopsis

Poly(ethylene terephthalate) films were irradiated in a carbon-arc Fade-Ometer and in a xenon-arc Weather-Ometer. The changes in tensile properties, intrinsic viscosities, infrared absorption, and fluorescence emission spectra resulting from these irradiations were measured. Quantitative comparisons between changes in surface (ATR) and transmission infrared spectra, in conjunction with the other results obtained, have established the importance of surface reactions in the photodeterioration of poly(ethylene terephthalate).

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer widely used in the form of fibers and films, and, like many polymers, it is susceptible to actinic degradation. On exposure to near-ultraviolet (UV) light, fibers tend to lose their elasticity and break easily; films of the polymer become discolored, brittle and develop crazed surfaces. Degradation outdoors is due to the absorption of light in the 290-400 nm wavelength range of terrestrial sunlight. The light is absorbed primarily by the ester carbonyl chromophoric groups present in the polymer, and this eventually leads to significant lowering of the molecular weight and serious deterioration of physical properties.

A number of reports of various aspects of the degradation of PET by UV light have been published in which such properties as tensile strength,¹⁻⁷ intrinsic viscosities,^{1,3,5,8,9,10} gel formation,^{3,10,11} acid equivalents,^{1,5} and chromatographic analysis for decomposition products^{5,11,12,13} have been measured. Measurements have also been made of changes in UV,^{5,11} infrared (IR),^{4,5,11} fluorescence,^{13,14,15} and ESR^{11,16} spectra as a result of irradiations. Unfortunately, despite the published data, not enough information is available yet to lead to the acceptance of a mechanism of photodegradation that can account for all the facts. Improvements in current UV stabilization practices require that such a mechanism be established.

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The work described in this paper is connected with the investigation of some of the effects on PET of photochemical damage. In addition to the conventional studies of loss in tensile strength and decrease in molecular weight, measurements are reported here of the build-up of carboxylic acid endgroups and fluorescent products within the polymer. These data will be used in a subsequent publication to support a more comprehensive mechanism for photochemical degradation of PET than it has previously been possible to suggest.

EXPERIMENTAL

Materials

The types of commercial PET films investigated are given in Table I along with some of their properties. The films designated as 3 and 4 were

TABLE I
Characteristics of the PET Films Investigated

Film designation	Manufacturer	Trade name	Type	Thickness, μ	\bar{M}_n	Density, g/m
1	I.C.I.	Melinex	S	23	17,500	1.395
2	du Pont	Mylar	C	12	18,800	1.396
3	du Pont	Mylar	unknown	21	19,700	1.398
4	du Pont	Mylar	unknown	120	—	—

of unknown type but were reported to contain a minimum of additives; films 1 and 2 were typical commercial films. The densities, number-average molecular weights, and thicknesses reported were all determined in this laboratory by standard, accepted techniques. The absorption spectra of films 1 to 3 were obtained with a Cary 15 UV spectrophotometer and are similar (Fig. 1).

Irradiations

Irradiations were carried out using either (i) the Atlas carbon-arc Fade-Ometer (type FDA-R) with a Corex D globe, at an operating temperature of 35°C with no control of the relative humidity; or (ii) an Atlas xenon-arc Weather-Ometer (Model 600-WR) with a Pyrex inner and a clear-glass outer filter system, at a black-panel temperature of 60°C and 30% relative humidity. The spectral distribution of these two light sources were calculated, using the data available,^{6,17,18} to give the emission spectra shown in Figure 1.

Tensile Property Measurements

The physical properties of the films were measured at 20°C and 65% R.H. with an Instron tensile tester (type TT-C). Film strips 5 × 50 mm

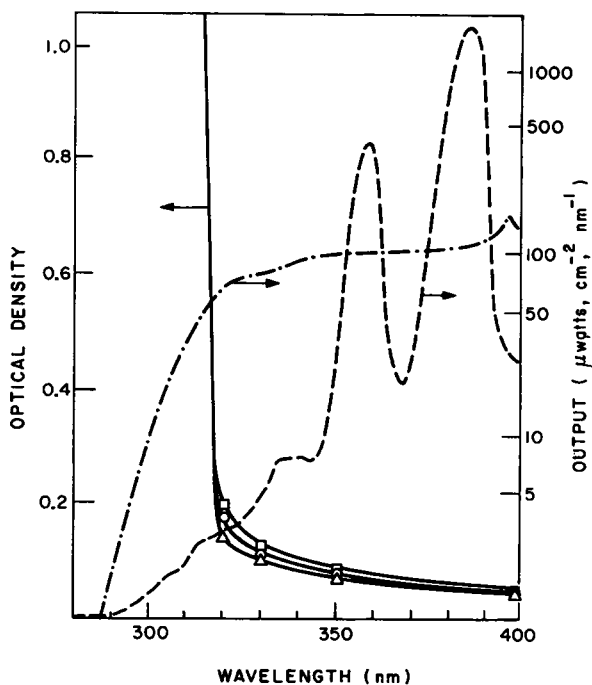


Fig. 1. Emission curves for the light sources: (---) xenon arc with Pyrex/clear glass filters; (—) carbon arc with clean Pyrex globe; and absorbance spectra of PET films: (O) film 1; (Δ) film 2; (\square) film 3.

were employed with a 12.7-mm clamp separation. The cross-head speed was then arranged to give an approximately 20-sec break. The average of ten results was used in each case.

Molecular Weights

Estimates of the change in molecular weight during irradiations were made from intrinsic viscosity values obtained using a Cannon-Ubbelohde dilution viscometer. Measurements were made at 25°C in *o*-chlorophenol. The *o*-chlorophenol used was Eastman Kodak reagent grade, purified by distillation. The number-average molecular weights were then calculated using the relationship of Ravens¹⁹:

$$[\eta] = 1.7 \times 10^{-4} \bar{M}_n^{0.83}$$

Infrared Measurements

The IR spectra were measured using a Beckman IR8 double-beam spectrophotometer. Transmission spectra were recorded between sodium chloride discs to which was added one drop of tetrachloroethylene to prevent the appearance of troublesome interference bands. Surface spectra of the films were measured by means of a Wilks #9 ATR attachment using a KRS-5

crystal at a nominal 45° angle of incidence. Although it has been shown¹¹ that irradiation of PET results in the formation of an absorption band near 770 cm^{-1} , it was not found practical to use this band on a quantitative basis. Instead, measurements were made on the band centered at about 3290 cm^{-1} which was observed to change as a function of irradiation time.

Fluorescence Measurements

The build-up in fluorescent material during irradiation was monitored by the use of a Farrand spectrofluorometer (Mark I). The film strips had to be mounted in a special adapter suitable for reproducible placement diagonally across the 1-cm-square liquid cell holder which is supplied with this instrument. The excitation beam was incident on the front surface of the film at an angle of 45° , and fluorescence measurements were made from the rear surface of the film.

RESULTS

Exposure of PET films to xenon- or carbon-arc radiation resulted in a change in the transmission IR spectrum in the range $4000\text{--}3000\text{ cm}^{-1}$. The IR spectra of film 3 before and after exposure for 1000 hr to the xenon arc is illustrated in Figure 2. Of greatest interest are the absorption bands attributed to O—H stretching vibrations of the aqueous, alcoholic, and carboxylic acid functional groups. One or another of the absorption bands located at 3620 , 3550 , 3420 , and 3290 cm^{-1} may be attributed to these vibrations. Since assignments of the 3550 and 3290 cm^{-1} bands have been made^{20,21} to alcoholic —OH and carboxylic acid —OH, respectively, this has not been reinvestigated, but the assignment of the 3620 and 3420 cm^{-1} bands has been sought.

The relative sharpness of the band at 3420 cm^{-1} and its apparent relative independence to irradiation (assuming overlap interference from the broad bands centered at 3550 and 3290 cm^{-1}) suggest that it is the first overtone of

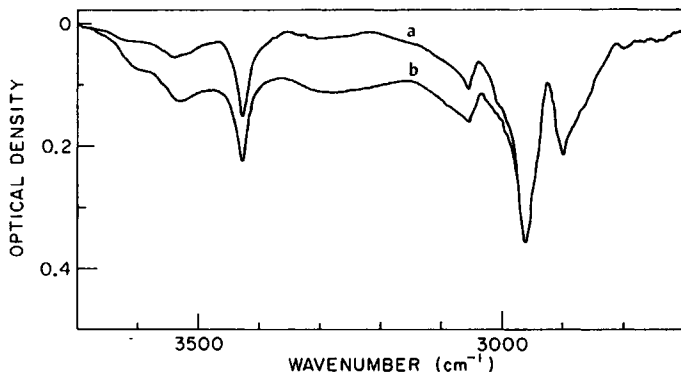


Fig. 2. The transmission IR spectra of film 3 (a) initially and (b) after 1000 hr of irradiation in the xenon arc.

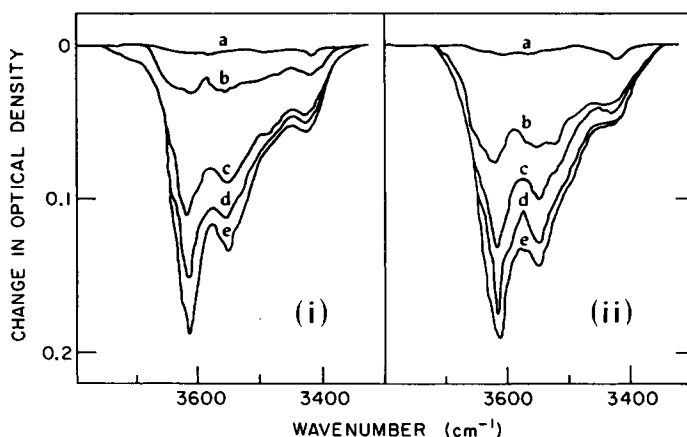


Fig. 3. Optical density changes produced in (i) untreated film; (ii) photo-oxidized film (200 hr xenon arc), by purging with N₂ for (a) 0 hr, (b) 0.3 hr, (c) 1 hr, (d) 2 hr, (e) 24 hr.

the fundamental C=O absorption situated at 1710 cm⁻¹ (not shown in Fig. 2). The position and intensity are in fact consistent with its assignment to this overtone.²²

The observation (Fig. 2) that the other three peaks (3620, 3550, and 3290 cm⁻¹) are relatively broad is indicative of hydrogen-bonded O—H vibrations.²² The peak responsible for the aqueous O—H vibration was determined by removal of the adsorbed and absorbed water by each of two techniques.

The film sample (film 4 in Table I) was placed in a flask at room temperature, and a purging atmosphere of dry nitrogen was passed through the flask at a flow rate of 30 cc/min. The sample was immediately removed

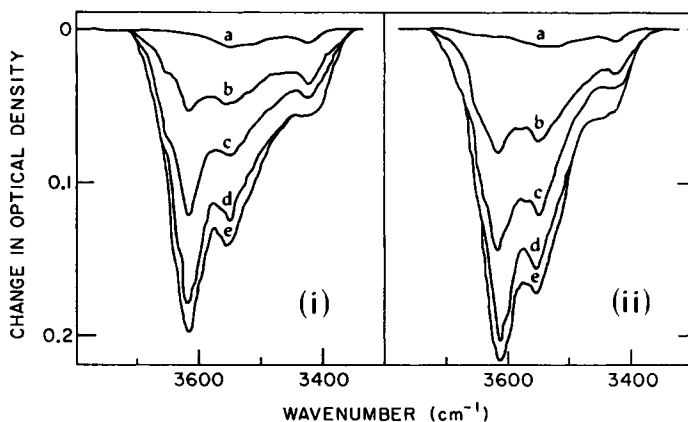


Fig. 4. Optical density changes produced in (i) untreated film; (ii) photo-oxidized film (200 hr xenon arc), by evacuation at room temperature for (a) 0 hr, (b) 0.3 hr, (c) 1 hr, (d) 2 hr, (e) 24 hr.

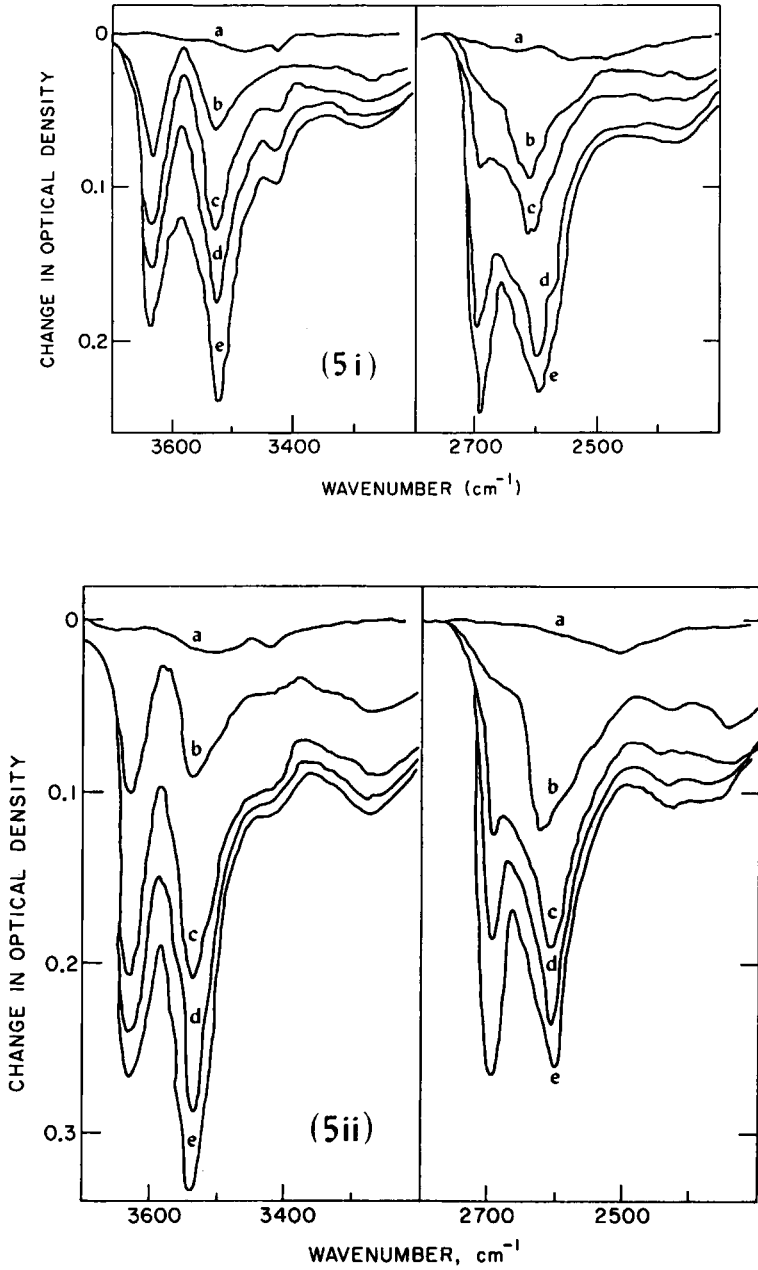


Fig. 5. Optical density changes produced in (i) initial film, (ii) photo-oxidized film (200 hr xenon arc), on exposure to D₂O vapor for (a) 0 hr, (b) 0.3 hr, (c) 1 hr, (d) 2 hr, (e) 24 hr.

and placed in the reference beam of the IR instrument with an untreated film in the sample beam. The differential spectrum was then recorded in order to determine the effect of the treatment on the IR absorptions. The optical density measured under these conditions corresponds to the water retained in the untreated film in the sample beam. The procedure was repeated with samples purged for different times in order to determine the effect of duration of treatment on the changes observed, Figure 3(i). The technique was then repeated with a sample of film 4 that had been exposed to the xenon arc for 200 hr. The differential spectrum was obtained in this case with an untreated photo-oxidized film in the sample beam. Since the purging treatment would be expected to remove only adsorbed water, any major changes in the differential spectra, Figures 3(i) and (ii), should be attributed to changes in the intensity of aqueous O—H stretching vibrations. Thus, since the band centered at 3620 cm^{-1} shows the largest changes as a result of this progressive water removal and appears to be virtually independent of photo-oxidation, it may be assumed to be due to adsorbed H_2O . Confirmation of this assignment was obtained by performing an alternative procedure which would be expected to remove the adsorbed water slightly faster. This involved pumping the film in a vacuum desiccator at room temperature for different periods of time and then recording the differential spectra as previously described. The results obtained with the unirradiated and irradiated film are shown in Figures 4(i) and (ii), respectively. It will be noted that once again it is the 3620 cm^{-1} band which shows the most significant changes and at a slightly faster rate than was observed on nitrogen purging. These results thus confirm the assignment of the band at 3620 cm^{-1} to the stretching vibration of adsorbed H_2O molecules in PET film.

The identification of the absorption bands due to the presence of alcoholic and carboxylic —OH endgroups was determined by a different treatment. This involved placing a film sample in a flask at room temperature and purging the flask with an atmosphere of nitrogen saturated with D_2O at a flow rate of 30 cc/min. Under these conditions, in addition to the replacement of adsorbed H_2O by adsorbed D_2O , hydrogen atoms in accessible OH groups would be expected to be replaced by deuterium. The film sample was removed from the flask after a predetermined time and placed in the reference beam of the IR instrument with an untreated film in the sample beam, and the differential spectrum was recorded between 4000 and 3000 cm^{-1} . The film positions were then reversed (i.e., treated film placed in sample beam and untreated film in reference beam), and the differential spectrum was recorded between 3000 and 2000 cm^{-1} . The results obtained are shown in Figure 5(i). The procedure outlined above was repeated using an irradiated film (identical to the one employed in the H_2O experiment above) to give the results obtained in Figure 5(ii).

This method is a well-known technique for obtaining assignments of IR absorption bands since the substitution of hydrogen by deuterium results in an alteration of the IR frequencies.²² Examination of Figures 5(i) and

(ii) indicates that the initial change appears to be mainly due to the aqueous —OH band centered at 3620 cm^{-1} , which presumably is reduced preferentially owing to isotopic exchange. However, since exchange of terminal hydrogen by deuterium is also occurring, the positions of the band due to —OH and —COOH endgroups should be revealed. This, in fact, was the case as both Figures 5(i) and (ii) reveal the development of bands centered at 3550 and 3290 cm^{-1} . Since irradiation of PET is known to result in an increase in the number of both —OH and —COOH endgroups,⁵ one would expect the changes in these bands centered at 3550 and 3290 cm^{-1} to be larger for the irradiated film than for the unirradiated film if they are attributable to these endgroups. Comparisons of the intensities, Figures 5(i) and (ii), for these two absorption bands thus indicate the assignment of these bands to terminal —OH and —COOH endgroups.

These changes observed in the IR spectra on deuteration of initial and photo-oxidized PET confirms the assignment of the 3620 cm^{-1} absorption band to the aqueous O—H stretching vibration. Based on the information in the literature,^{20,21} the absorption bands at 3550 and 3290 cm^{-1} can be assigned to the alcoholic O—H stretching vibration and the carboxylic O—H stretching vibration, respectively.

In addition to the removal of absorption bands due to O—H vibrations, the treatment of the polymer with D_2O results in the formation of three additional bands which appear in the differential spectra in the $3000\text{--}2000\text{ cm}^{-1}$ range, Figures 5(i) and (ii). Absorption bands were found centered at 2700 , 2610 , and 2430 cm^{-1} and may be attributed to the aqueous, alcoholic, and carboxylic O—D stretching vibrations. These results give a frequency ratio $\nu_{\text{OH}}/\nu_{\text{OD}}$ of 1.36, 1.36, and 1.35 for the aqueous, alcoholic, and carboxylic —OH groups, respectively. These values are in very close agreement with the theoretical value of 1.37 derived from the simple diatomic harmonic oscillator model,²² i.e.,

$$\frac{\nu_{\text{OH}}}{\nu_{\text{OD}}} = \left[\frac{\text{OH}}{\text{OD}} \cdot \frac{\text{D}}{\text{H}} \right]^{1/2} = \left[\frac{17.008}{18.015} \cdot \frac{2.015}{1.008} \right]^{1/2} = 1.37.$$

These data tend to support the assignment of the bands.

Unfortunately the overlap of the 3620 cm^{-1} and the 3550 cm^{-1} bands prevented their successful use as independent measures of the concentration of adsorbed H_2O and terminal alcoholic —OH groups in PET. The absorption band centered at 3290 cm^{-1} , however, was found to be favorably situated to provide a quantitative estimate of the —COOH endgroups. The experimental principles and techniques used in these measurements will now be described.

The changes in the optical density (O.D.) of the —COOH absorption band at 3290 cm^{-1} were periodically determined throughout the irradiation period by ATR and transmission spectroscopy. The values are expressed as normalized O.D. values, by using the O.D. of the C—H vibration at 2970 cm^{-1} as standard, in order to overcome variations in optical densities which result from differences in contact between the polymer film and the

ATR crystal when ATR measurements were made.²³ This method of expressing the results also enables direct comparisons to be made between the transmission data and surface measurements. The results obtained are shown in Figure 6 for film 3. Similar results were obtained with films 1 and 2 in that the characteristics and order of the curves were very similar.

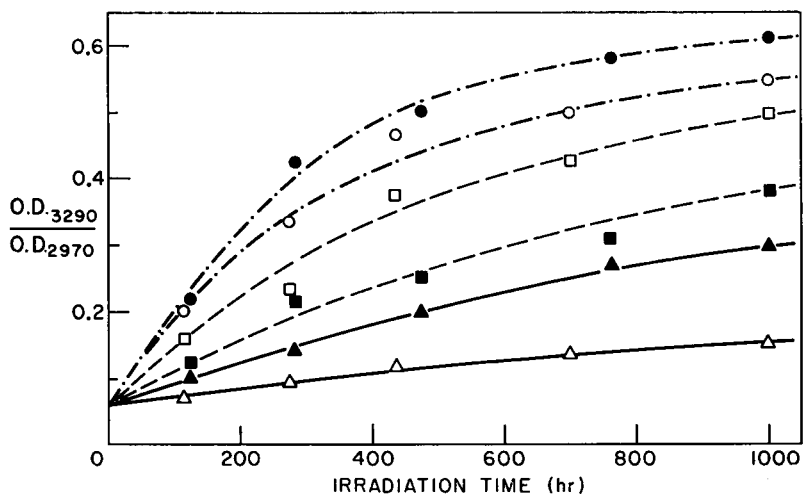


Fig. 6. Effect of irradiation time on $-\text{COOH}$ absorption with (O, □, △) the carbon arc and (●, ■, ▲) xenon arc. (—) Transmission IR; (---) front surface ATR; (---) rear surface ATR.

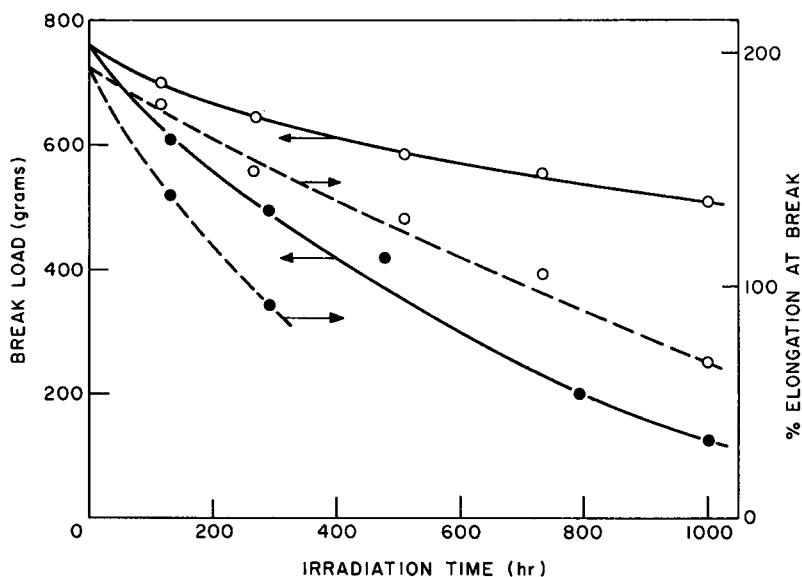


Fig. 7. Variation of break load (—) and ultimate elongation (---) with irradiation time for; (○) carbon arc; (●) xenon arc.

There was, however, a slower overall rate for the —COOH formation with films 1 and 2.

The values of the tensile breaking strength and per cent elongation at break for film 3 as a function of irradiation time are given in Figure 7 for

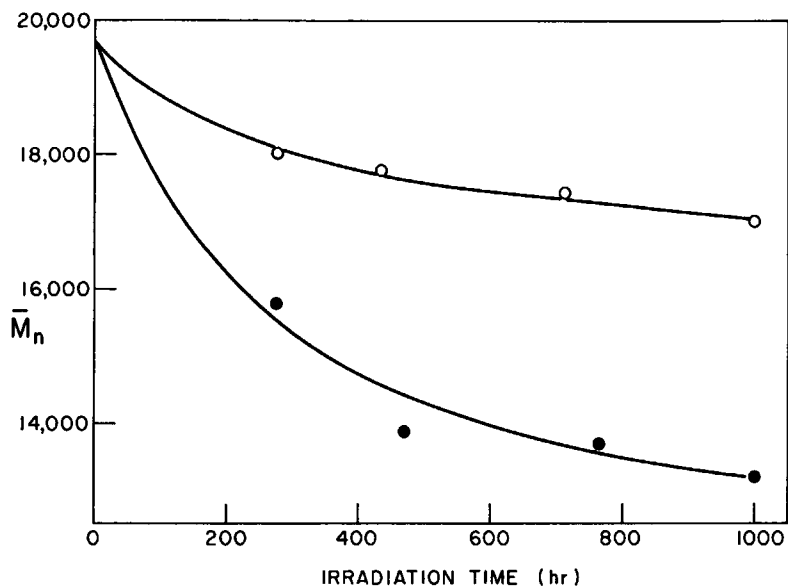


Fig. 8. Variation in number-average molecular weight with irradiation time for: (O) carbon arc; (●) xenon arc.

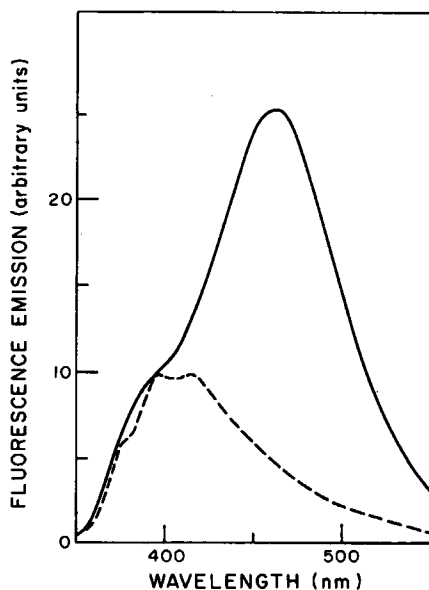


Fig. 9. Fluorescence emission spectra of film 3: (---) initial film; (—) 1000 hr of irradiation in xenon arc. Excitation wavelength 340 nm.

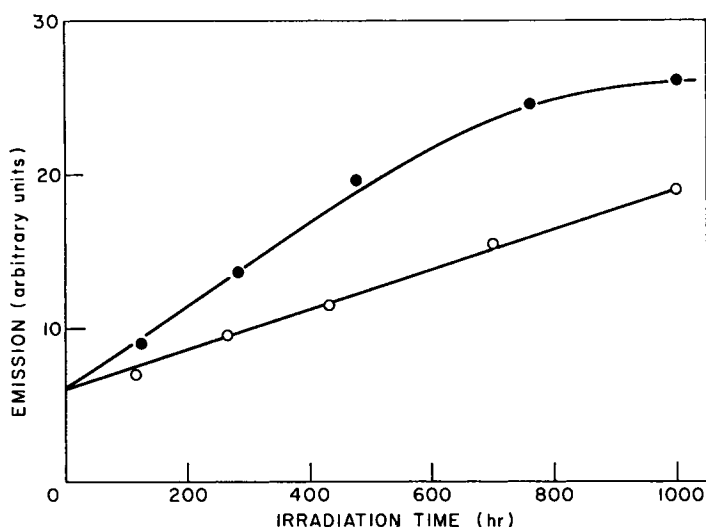


Fig. 10. Increase in fluorescence emission of film 3 as a function of irradiation time for (○) carbon arc; (●) xenon arc exposures.

both carbon- and xenon-arc irradiations. These values were obtained on film strips cut parallel to the film extrusion direction.

The results obtained for film 3 from the molecular weight determinations are shown in Figure 8. Since only the initial and final viscosities were measured in the case of films 1 and 2, these have been presented in Table II. In all cases no insoluble material was observed after 1000 hr of irradiation with either the xenon or the carbon arc.

Irradiation with both light sources was found to result in the formation of a blue-green fluorescing material within the polymer. The intensity of the fluorescence was found to increase with exposure time. The emission spectra obtained from film 3 initially and after 1000 hr of exposure to the xenon arc are given in Figure 9. The excitation wavelength employed in both cases was 340 nm. It was found, in fact, that prolonged irradiation of PET film results in the build-up of a single fluorescent product whose excitation wavelength is 340 nm and emission wavelength is 460 nm. The rate of formation of this fluorescent material is shown in Figure 10 for film 3 using both light sources. In all cases measurements were made at 460 nm with 340 nm excitation light.

TABLE II
The Effect of 1000 hours of Irradiation on Number-Average Molecular Weight

Film no.	Initial \bar{M}_n	Xenon arc final \bar{M}_n	Carbon arc final \bar{M}_n
1	17,500	13,800	16,900
2	18,800	12,300	16,200
3	19,700	13,200	16,500

DISCUSSION

From a comparison of the data available for the three films, it appears that all showed the same basic patterns of degradation and only differed in the degree of decomposition per unit irradiation time.

The rates of loss of tensile properties, decrease in molecular weight, build-up of acid endgroups, and production of fluorescing material all change similarly as a function of irradiation time. This implies that these processes all have similar relations to the primary photochemical processes resulting in chain-breaking steps. Thus, it is convenient to consider these kinetic curves as reflecting equivalently the rate of PET photodegradation.

The rate of degradation of film 3 was observed in all cases to be greater than the rates of films 1 and 2. This agrees with the fact that film 3 was reported to contain only the minimum number of additives, whereas the other two were authentic samples of commercially available films, which presumably contained UV stabilizers. Attention will be concentrated on film 3 in the discussion which follows, unless it is specifically stated otherwise.

Originally the PET film has excellent mechanical properties, but on irradiation with either the xenon or carbon arc it gradually loses these properties until a brittle, fragile film is obtained. The point at which a film is classified as having failed depends to a large extent on the work cycle to which it is subjected. It will be noted (Fig. 7) that the per cent elongations of irradiated samples of film 3 correspond to a value of approximately 80% (a drastic reduction from that of 200% for the original film) after 300 hr and 800 hr of exposure to the xenon and carbon arc, respectively. The resultant brittleness is considered to represent incipient mechanical failure in this work.

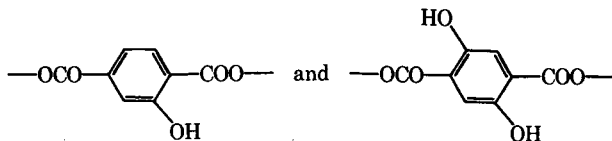
The degradation of the polymer chains in PET is evident from the decreases observed in the number-average molecular weights derived from viscometric data (Fig. 8). Once again, a faster rate of decomposition was observed with the xenon than with the carbon arc, such that a reasonable correlation exists between the molecular weight and tensile strength loss rates. Since gel was not observed during the viscosity measurements, it was concluded that during irradiation, under the conditions employed, crosslinking reactions were insignificant in comparison with chain scission reactions.

The increase in carboxyl groups on exposure of PET to irradiation has been measured previously,^{1,5} but in both cases titrimetric methods were employed. In this study the increase in O.D.₃₂₉₀/O.D.₂₉₇₀ ratio, as measured by ATR and transmission spectroscopy, was used as a measure of the formation of new carboxyl endgroups. Since exposure to both xenon- and carbon-arc radiation was observed to produce additional carboxyl groups (Fig. 6), their formation must also be an indirect measure of the extent of damage as a result of certain decomposition reactions. In addition, the rate of build-up of —COOH endgroups relates to the changes with time observed in the other properties measured.

The results of the ATR measurements indicate that there is a greater concentration build-up of —COOH endgroups on the surface of the films as compared to the bulk of the material (Fig. 6). However, this build-up in —COOH endgroups does not appear to be limited to the front surface since it is also observed on the side of the films that were facing away from the light source. While, so far, xenon-arc irradiation has been observed to induce greater changes in the measured properties than the carbon-arc irradiation, there was a larger build-up of —COOH endgroups on the rear surface as a result of irradiation in the carbon arc than as a result of irradiation in the xenon arc. This phenomenon is shown in Figure 6 for film 3 but was also observed for films 1 and 2. This suggests that long-wavelength light, >315 or possibly >350 nm, is responsible for the formation of —COOH endgroups on the rear surface of these films. Wavelengths at least greater than 315 nm must be responsible for this rear surface phenomenon owing to the strong absorption of light by PET of shorter wavelengths (Fig. 1) which would prevent it from reaching the rear surface. The fact that wavelengths >350 nm seem to be partially responsible was concluded from the spectral distribution of the two light sources (Fig. 1), since it is only in this region that the intensity of the carbon arc is greater than that of the xenon arc.

The possibility of these —COOH endgroups being formed from alternative cleavage reactions such as hydrolysis or thermolysis seems unlikely in view of data available for these types of reactions. Extrapolation of McMahon's²⁴ data to a temperature of 45°C and 30% R.H. gave an exceedingly low value for hydrolysis of 1×10^{-6} days $^{-1}$. The fact that the rate of —COOH formation was greater on the rear surface of the carbon arc-irradiated samples than with the xenon arc also seems to rule out hydrolysis, since the R.H. conditions were higher in the latter case than in the former. Thermolysis of the ester linkage to give —COOH endgroups is even more unlikely in view of the kinetic data provided by Goodings²⁵ which indicate a decomposition rate of the order of 1×10^{-10} days $^{-1}$ at 45°C . Acid endgroups thus appear to be photochemical products and not hydrolysis or thermal products under the conditions being employed.

The observance of fluorescent material in PET has been reported previously^{13,14,15} and has been attributed to the formation of mono- and dihydroxy-substituted materials:



The nature of the fluorescence spectrum (Fig. 9) found in this investigation with an emission at 460 nm (excitation 340 nm) agrees with that found by Pacifici¹⁴ at 459 nm for the monohydroxy compound (excitation 340 nm). A suitable mechanism has yet to be proposed to account for the formation of this material.

The rate of formation of this fluorescent material was found (Fig. 10) to follow the same trends as those observed for the other changes measured. The xenon arc once again resulted in a faster rate of formation of the fluorescent material than was observed with the carbon arc.

It has been reported¹⁴ that upon prolonged exposure a second fluorescent compound is formed, as a result of the formation of the dihydroxy compound. However, at no time up to 1000 hr for each film studied in this investigation was such a fluorescent product observed.

From these results it is concluded that several techniques are available for monitoring the extent of degradation of PET under laboratory exposure conditions. Comparison of the effects of the two light sources suggests that the Atlas xenon-arc Weather-Ometer gives an accelerated rate of degradation of PET in comparison to that obtained with the Atlas carbon-arc Fade-Ometer. When the absorption spectrum of PET is considered, these results confirm the importance of the short wavelength radiation, <320 nm.⁶ Since this is the region of strong absorption by the polymer, the results are not unexpected in view of the spectral differences in the energy output from the two arcs.

A more detailed study of the photochemical degradation of PET has been undertaken as a result of this preliminary investigation. With the results obtained it should then be possible to correlate all of the physical and chemical consequences of degradation with specific photochemical processes.

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