

## Photochemical Degradation of Poly(ethylene Terephthalate). II. Effect of Wavelength and Environment on the Decomposition Process

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### Synopsis

Poly(ethylene terephthalate) has been irradiated with UV light of different wavelengths and in various atmospheres. The extent of degradation was monitored by measuring the tensile strength, molecular weight, carboxylic acid endgroups, and fluorescence emission of the polymer. The importance of wavelengths <315 nm in causing deterioration was demonstrated to be mainly due to strong surface absorption which results in surface crazing and ultimate fracture under stress. Irradiation in nitrogen and under vacuum were found to give similar results, but with oxygen present in the system several significant differences were observed. In nonoxidative irradiations, crosslinking and discoloration of the polymer occurred. Under oxidative conditions, chain scissions and fluorescent material build-up resulted, whereas no crosslinking and only slight discoloration was observed. The possibility of a photo-oxidation reaction has thus been suggested, involving hydroperoxide formation, to explain the discrepancy in results obtained for the two types of environments.

### INTRODUCTION

Poly(ethylene terephthalene) (PET) articles on exposure to terrestrial sunlight, gradually lose their chemical and physical properties to give a brittle, fragile material. Such deterioration in properties is attributed to photochemical reactions initiated by the absorption of near-ultraviolet radiation.

The degradation of PET under a variety of artificial light sources has been reported,<sup>1-14</sup> but few detailed studies have been made concerning the effect and importance of the wavelength and of the environment. In the majority of cases the photochemical decompositions were studied under normal atmospheric conditions when it must be assumed that photo-oxidation played an important role in the decomposition process. The exceptions are the studies of Stephenson et al., who compared the effects of a nitrogen and vacuum environment on some physical properties,<sup>4</sup> crosslinking and fragmentation processes,<sup>5</sup> and the decomposition products obtained<sup>6</sup> as a result of irradiation. This group later considered the effects of oxygen on the physical property changes as a result of exposure to UV light. Mar-

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cotte<sup>9</sup> has also reported a detailed study of the photolysis of PET under vacuum conditions in which the degradation products were determined and assessments were made of the fracture and crosslinking processes.

A detailed examination of the effect of wavelength on the decomposition of PET has not been reported, although in several cases at least two irradiation light sources were employed<sup>3,9</sup> and the results compared.

We have already reported irradiation experiments with the xenon and carbon arc in which several techniques were used to monitor the degradation of the polymer.<sup>1</sup> In this present study, the effect of filtered radiation in the 200–400 nm region has been examined using these techniques. The effect of environment on the decomposition of PET was investigated by performing the irradiations in a variety of atmospheres and once again observing the measured physical and chemical properties.

### EXPERIMENTAL

The poly(ethylene terephthalate) film employed in this investigation was supplied by du Pont and was reported to contain no UV stabilizers. The film was  $21 \mu$  thick, with a density of 1.398, corresponding to a crystallinity content of approximately 50%.<sup>15</sup> The apparent absorption spectrum of the

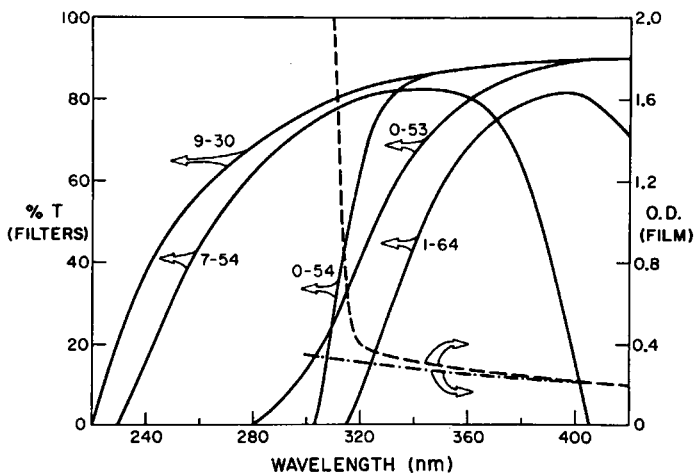


Fig. 1. Transmission characteristics of the filter systems employed and the apparent O.D. (—) and scattered-light O.D. (---) of the PET film.

film is shown in Figure 1 and may be divided into two portions, a true absorption and an "absorption" due to light scattering, both at the surface and in the interior (Rayleigh scattering). Assuming zero true absorption for the film at 400 nm, the apparent absorption curve was corrected for scattering in the 300–400 nm region by extrapolation of the data from the 400–800 nm range. The extrapolated portion of this curve shown in

Figure 1 was derived using a relationship similar to that employed by Partridge<sup>16</sup> for polyethylene. The true absorption curve was then calculated from these data in order that the corrected fractional absorption as a function of wavelength could be obtained.

Irradiations were performed using an Hanovia high-pressure mercury arc (450 W, L-67A burner) as the light source. Variations in the working wavelength range were achieved by the use of appropriate Corning filters. The transmission characteristics of the filter systems employed in this investigation are given in Figure 1 along with the appropriate Corning filter numbers. By using the spectral power distribution of the lamp, the intensity of which was calibrated with an Eppley thermopile, and the transmission characteristics of the filters, the incident light intensities on the films have been computed and are presented in Table I for the 200–400 nm range. The corrected absorption curve for PET was then used to calculate the absorbed incident intensity in the same wavelength range to give the rates of energy absorption shown in Table I. Irradiations in controlled environments were performed in a  $1 \times 1 \times 4.5$ -cm quartz UV cell fitted with a graded seal and standard socket for evacuation and filling on a mercury- and grease-free vacuum line.

TABLE I  
Energies Associated with the Filter Systems

Filter no.	Cut-off $\lambda$ , nm	Incident energy at film, (Einsteins/ sec cm <sup>-2</sup> ) $\times 10^9$	Energy absorption, by PET, (Einsteins/ sec cm <sup>-2</sup> ) $\times 10^9$	$\bar{M}_n$ after 24 hr irradiation
9-30	220	14.8	8.24	11,400
7-54	230	12.8	7.22	11,500
0-53	280	6.80	1.28	13,600
0-54	302	7.38	1.08	14,600
1-64	315	4.60	0.22	18,700

Using the procedures outlined previously,<sup>1</sup> measurements were made of the effect of irradiation on the tensile breaking strength and the percentage elongation at break. Number-average molecular weights ( $\bar{M}_n$ ) were calculated from viscosity measurements, made in *o*-chlorophenol at 25°C, by means of the relation of Ravens.<sup>17</sup> The initial film had a molecular weight of 19,700 when determined by this method.

Optical density measurements were made of the —COOH absorption band, with a Beckman IR8 spectrophotometer, by transmission and ATR infrared spectroscopy. Fluorescence emission spectra were obtained using a Farrand MK. I spectrofluorometer and the UV spectra on a Cary Model 15 spectrophotometer.

## RESULTS

## Effect of Wavelength on Photodegradation in Air

The variation of the per cent elongation at break of the photodegraded films as a function of exposure time are presented in Figure 2, for each wavelength region examined. Since the loss in per cent elongation represents a deterioration of the polymer, which also manifests itself in other measured properties, it is convenient to use this factor as a monitor of the extent of degradation. For the purpose of the discussion which follows, it is assumed arbitrarily that a deterioration of the per cent elongation to a value of 80% can correspond to an extent of degradation which represents mechanical failure.

Evaluation of the intrinsic viscosity of films was made only after the completion of 24 hr of irradiation, and the results obtained are summarized in Table I.

Infrared absorption measurements were made at  $3290\text{ cm}^{-1}$ , the absorption maximum assigned to the  $\text{—OH}$  vibration of the carboxylic acid endgroup.<sup>1,18</sup> The changes in  $\text{—OH}$  absorption with exposure time are shown in Figure 3. The normalized ratio of the  $\text{—OH}$  absorption ( $3290\text{ cm}^{-1}$ ) to the  $\text{C—H}$  absorption ( $2970\text{ cm}^{-1}$ ) was employed in all cases<sup>1</sup> in order to obtain meaningful results for the ATR surface measurements which could be compared with the transmission data.<sup>19</sup> Although changes were observed in the transmission and front surface ATR spectra, in no cases were any significant changes observed in the ATR spectra of the rear surfaces during the 24 hr of irradiation.

In a previous paper<sup>1</sup> it was noted that  $\text{—COOH}$  endgroups were formed on the rear surface as well as on the front surface when irradiations were

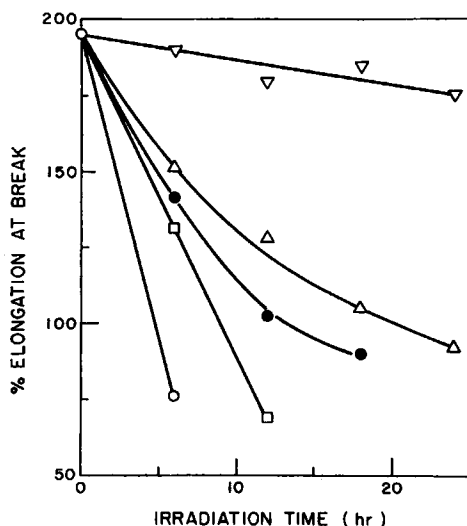


Fig. 2. Variation of ultimate elongation with irradiation time in air, for the following filters: (○) 9-30; (□) 7-54; (●) 0-53; (△) 0-54; (▽) 1-64.

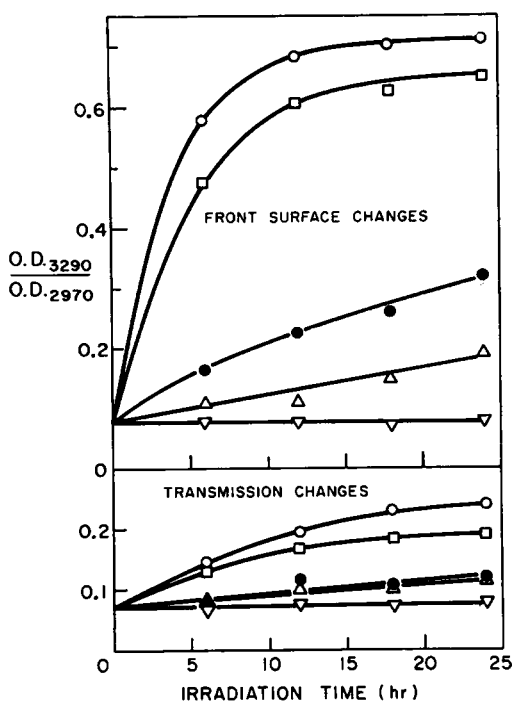


Fig. 3. Effect of irradiation time in air on the —COOH absorption, for the following filters: (O) 9-30; (□) 7-54; (●) 0-53; (Δ) 0-54; (▽) 1-64.

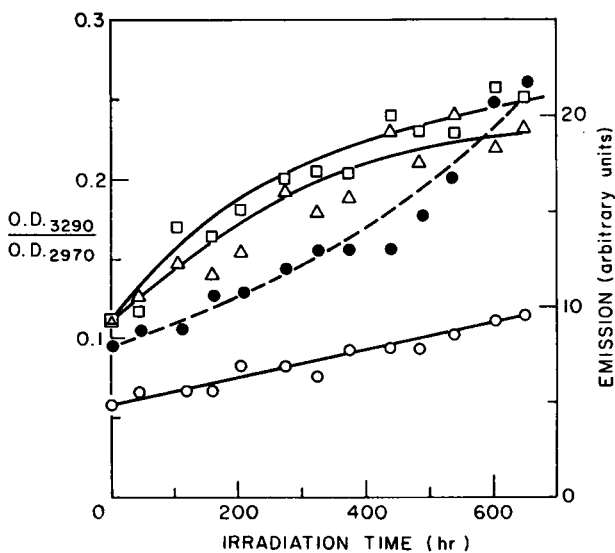


Fig. 4. Variation in —COOH absorption (—) and fluorescence emission (---) with irradiation time in air using 1-64 filter: (O) transmission; (□) front surface; (Δ) rear surface; (●) fluorescence.

performed with the carbon-arc and xenon-arc light sources. This effect was attributed to prolonged exposure of the films to long-wavelength irradiation. In order to establish that long-wavelength light was responsible for the degradation occurring on the rear surfaces, irradiations were performed using the 1-64 filter (cut-off 315 nm) with prolonged irradiation times. The results obtained are presented in Figure 4, in which it may be seen that the rate of formation of  $\text{—COOH}$  endgroups on the rear surface is only slightly less than the rate of formation on the front surface, while both are greater than the rate in the interior of the film.

The rate of formation of the blue-green fluorescent material with irradiation time is shown in Figure 5 for measurements made at 460 nm (excitation wavelength 340 nm). The emission spectra were in all cases similar to those observed previously.<sup>1</sup>

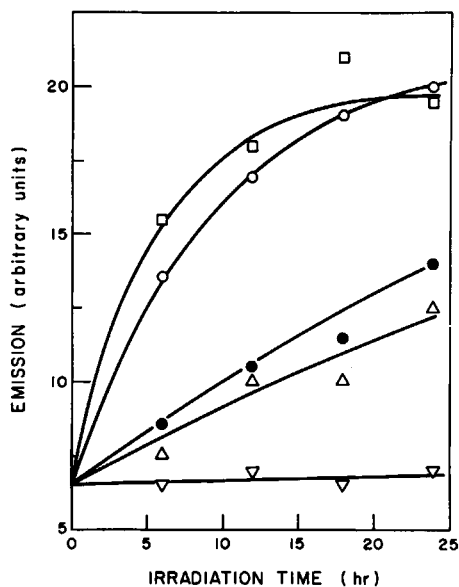


Fig. 5. Variation of fluorescence emission with irradiation time in air for the following filters: (O) 9-30; (□) 7-54; (●) 0-53; (Δ) 0-54; (∇) 1-64.

### Effect of Various Environments on Photodegradation

Only one filter system was employed in the environmental studies, and that was the Corning filter 9-30 (cut-off 220 nm). Once again measurements were made of the number-average molecular weight, infrared  $\text{—COOH}$  absorption, and fluorescence emission of 12-hr-irradiated samples. The environmental conditions employed and the results obtained in these studies are summarized in Table II. In these environmental studies, no attempt was made to measure the tensile strength owing to the small samples being irradiated.

TABLE II  
Effect of Irradiation Using 9-30 Filter on Properties  
Observed in Environmental Studies<sup>a</sup>

Irradiation conditions	$\bar{M}_n$	O.D. <sub>3290</sub> /O.D. <sub>2970</sub>			Fluorescence emission, arbitrary units
		Transmission	Front surface	Rear surface	
Initial material	19,700	0.067	0.075	0.075	6.5
Air at 1 atm	13,100	0.145	0.659	0.088	18.0
Oxygen at 1 atm	15,000	0.158	0.659	0.108	17.0
Air at 5 torr pressure	15,300	0.111	0.432	0.074	6.5
Nitrogen at 1 atm	gel	0.119	0.535	0.071	7.0
Vacuum	gel	0.118	0.425	0.094	6.0

<sup>a</sup> Irradiation time, 12 hr.

No molecular weight data are available for the samples irradiated in nitrogen and under vacuum because the formation of gel prevented complete solubility in *o*-chlorophenol solvent.

In addition to recording the fluorescence emission at 460 nm (excitation wavelength 340 nm), the complete spectrum of each sample listed in Table II was also recorded. The spectra obtained are shown in Figure 6, using 340 nm as the excitation wavelength.

Since a distinct yellowing of the films was observed on irradiation under vacuum and in nitrogen, but not under oxidative conditions, differential UV spectra were recorded in order that some assessment of the coloration could be made. The spectra obtained as a result of the various irradiation

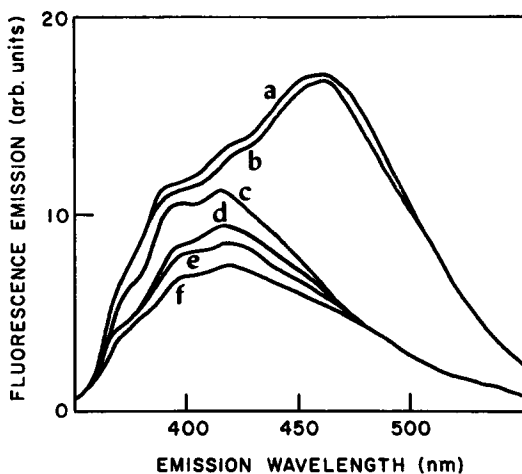


Fig. 6. Fluorescence emission spectra after 12 hr of irradiation with filter 9-30 in: (a) air at 1 atm; (b) O<sub>2</sub> at 1 atm; (c) initial unirradiated film; (d) N<sub>2</sub> at 1 atm; (e) air at 5 torr; (f) under vacuum.

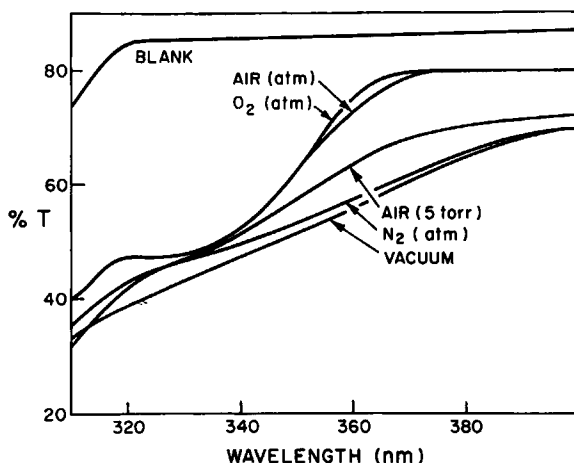


Fig. 7. Effect of environment on the differential UV absorption spectra of films after 12 hr of irradiation with 9-30 filter.

conditions are shown in Figure 7, using double film thickness in both the sample and reference beams.

## DISCUSSION

The effect of irradiation wavelength on the properties measured is summarized in Figures 2, 3, and 5 and in Table I. From these data it is evident that the cut-off wavelength of the filter plays an important part in the rate and the nature of photodegradation of PET. Filter 1-64 (cut-off 315 nm) appears to induce negligible changes in the properties measured in the 24-hr period. This indicates the importance of the wavelengths smaller than 315 nm on the rate of photodegradation of the polymer. The results for the other filter systems verify this finding in comparing the changes observed with the 9-30 and 7-54 filters (cut-off 220 and 230 nm, respectively) with the data for the 0-53 and 0-54 filters (cut-off 280 and 302 nm), since the extent of the changes observed correlate with the absorbed energies of the PET given in Table I.

The results for the 0-53 and 0-54 filters in which there is a crossover at 310 nm (Fig. 1) provide a rather interesting situation in that, while the 0-53 filter allows light down to 280 nm to be absorbed by the polymer, the 0-54 filter transmits light of wavelength  $>302$  nm only. The results (Figs. 2, 3, and 5) indicate that the rate of change in the properties measured (except transmission IR) are all greater for the 0-53 filter than for the 0-54 filter. In the case of the transmission IR measurements (Fig. 3), however, there is little if any significant difference in the results obtained with these two filter systems. These results are to be expected in view of the strong attenuation by the polymer of radiation wavelength  $<310$  nm, whereas that  $>310$  nm is less strongly but more uniformly absorbed throughout the film and reaches the rear surface. Thus, since the transmission IR records the bulk properties of the material, the IR absorption differences observed



in this work for irradiations with the two filters would be expected to be negligible.

The close similarities in the curves for the per cent elongation (Fig. 2) and the fluorescence emission (Fig. 5) with the front-surface ATR measurements of the  $\text{—COOH}$  endgroups seem to suggest that the physical properties and fluorescence build-up in PET are associated with surface reactions. According to the Griffith Crack theory,<sup>20,21</sup> the tensile strength is a property which is a function of the material (as reflected in Young's modulus) and its surface and also a function of the size of flaws in the sample. Since the surface energy is a measure of the resistance of the material to the initiation of fracture, it is therefore an index of the limiting tensile properties of the material. Thus this correlation observed between the tensile strength and the surface deterioration as measured by ATR and fluorescence appears consistent with fracture propagation from the surface when tension is applied to the polymer.<sup>22</sup> The physical deterioration of the surface can be accounted for by assuming that the photochemical reactions give rise to chain scissions and consequently smaller polymer molecules. These smaller fragments may then regroup and result in structural modifications of the polymer, especially within the surface layer. These morphologic changes would be reflected in the physical properties of the polymer.<sup>23</sup> Examination by electron microscopy indicates that prolonged irradiation does result in the formation of surface cracks,<sup>24</sup> as a result of an extensive restructuring of the surface.

Thus, it may be confirmed that the critical wavelength for the photochemical degradation of PET corresponds to approximately 310 nm. Irradiation at shorter wavelengths results in rapid deterioration in the physical properties of the polymer as a result of the surface (but not the bulk) of the polymer film undergoing major photochemical modification. This is to be expected, of course, because of the wavelength region in which PET absorbs strongly.

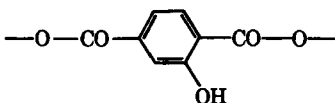
The ability for light of wavelength longer than 315 nm to be absorbed and cause photochemical degradation is indicated by the results obtained with the 1-64 filter (cut-off 315 nm) (Fig. 4). These data indicate that prolonged exposure to the long-wavelength UV radiation causes a build-up in the fluorescent material and an increase in the concentration of  $\text{—COOH}$  endgroups both in the bulk of the material and at both the front and rear surfaces of the film. The comparable surface spectra changes observed at both the front and the rear surface of the film are clear indications of a long wavelength surface reaction comparable to that observed using xenon-arc and carbon-arc irradiation.<sup>1</sup> The slightly higher changes observed on the front surface in comparison to the rear surface may be accounted for by the attenuation of the light beam on passing through the film sample. The importance of oxygen in this long-wavelength degradation of PET is at present under investigation by performing irradiations under vacuum and comparing the results with those obtained in air.

The nature of the irradiation environment has been shown (Table II) to markedly affect the nature and extent of deterioration of the physical

and chemical properties of PET. In the majority of previous investigations, normal atmospheric irradiation conditions have been used, when it would be expected that oxidation reactions may be important. For oxidative conditions it could be predicted that radicals produced as a result of photolytic cleavage, or subsequent hydrogen abstraction, would react with oxygen to give peroxy radicals capable of further reaction. Thus, owing to the presence of oxygen, it may be expected that radical recombination resulting in crosslinks could be reduced. When irradiations were performed under vacuum or in nitrogen atmosphere, crosslinking was observed to have occurred to such an extent that material insoluble in *o*-chlorophenol was observed. Irradiations performed in an oxygen-containing atmosphere, however, gave films completely soluble in *o*-chlorophenol, with lower intrinsic viscosities, indicating that chain scission had occurred. Thus, the assumption that oxygen suppresses crosslinking appears to be valid for the data presented here. This is consistent with the findings of Stephenson<sup>5,7</sup> and Marcotte,<sup>9</sup> who both observed the formation of gels on irradiating under vacuum, although Stephenson also reported no gel formation in a nitrogen atmosphere. The close agreement obtained in this work between irradiations in nitrogen and under vacuum, however, suggests similar processes are taking place in both environments. The fact that no gel was observed on irradiation in a 5-torr air atmosphere (Table II) seems to suggest that only a small trace of oxygen is required to inhibit the crosslinking reactions sufficiently to prevent the formation of insoluble material.

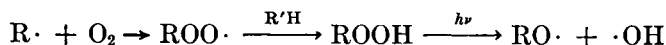
Increases in the —COOH endgroup concentration, as measured by IR absorption, were observed in all irradiation experiments in all environments. Thus, —COOH is probably produced as a result of a primary photolytic process. The fact that larger amounts of —COOH endgroups were observed for irradiations in an oxygen-rich atmosphere, however, indicates that they may also be produced as a result of subsequent oxidation processes, in addition to the primary photolytic ones.

A comparison of the fluorescence emission spectra (Fig. 6) and the UV absorption spectra (Fig. 7) of the films irradiated in oxidative and non-oxidative conditions further verifies the differences observed with the different environments. When irradiations were performed in the absence of oxygen, there was a distinct yellowing of the films, which is evident from the UV spectra, while no fluorescent material was observed to be formed. When irradiations were performed in an oxygen-containing system, however, only a slight discoloration was observed, but a fluorescent compound absorbing at 340 nm (evident also in UV spectra) was formed (Fig. 6). The fluorescence emission spectrum of this compound with an emission band at 460 nm (excitation 340 nm) is consistent with the presence of the monohydroxy species



observed previously<sup>1</sup> and identified by Pacifici.<sup>11</sup>

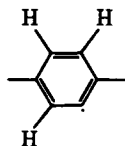
The formation of this compound may be explained on the basis of a photo-oxidative mechanism involving peroxy radicals and hydroperoxides, a well-established mechanism of photo-oxidation in polymeric materials:<sup>25</sup>



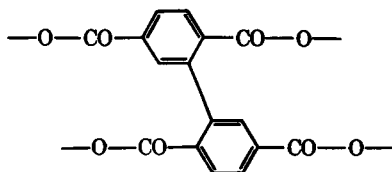
The hydroxyl radical so formed may then be able to substitute on the phenylene ring to give the above monohydroxy compound.

In the absence of oxygen, such a mechanism is not possible, and this explains the absence of fluorescent material in samples irradiated in nitrogen and under vacuum. Under these nonoxidative conditions, however, discoloration is observed, as is evident from the stronger absorption of the irradiated films in the visible region of the spectrum. The exact nature of this colored material is as yet unknown, but it is possibly due to the formation of a conjugated system within the polymer.

Based on ESR spectra, Marcotte<sup>9</sup> has postulated the formation of the radical

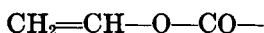


as a possible consequence of hydrogen abstraction on irradiating under vacuum. He concluded that crosslinking of such a radical may occur to give a structure such as



If hydrogen abstraction from the benzene ring is a feasible reaction under the irradiation conditions being employed, a build-up in these biphenyl residues may be sufficient to account for the coloration developed on irradiating in nonoxidative environments.

The possible formation of vinyl species such as



on irradiation<sup>26</sup> has also been proposed<sup>27</sup> as a likely precursor to color formation.

In conclusion, these results clearly indicate that while degradation occurs during the irradiation of PET under vacuum and in nitrogen, air, and oxygen, the overall mechanisms involved in oxidative and nonoxidative irradiation environments are different. The possibilities of the primary processes being the same in both cases are not ruled out, but the evidence

suggests that alternate secondary processes are involved in the two cases. From the investigation of the effect of wavelength on the decomposition, it may be concluded that it is the strong absorption by PET of wavelengths less than 310 nm which is mainly responsible for the rapid decomposition of the polymer at these wavelengths. Light of wavelength above 315 nm is, however, still capable of causing deterioration in the polymer, though longer irradiation times are required.

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