

NOTES

Luminescence from Thermally Oxidized Polypropylene in Relation to Its Light Stability

INTRODUCTION

The photo-oxidation of polyolefins is generally believed to be initiated by impurities introduced during polymerization and/or processing of the polymer.^{1,2} The main light-absorbing species are carbonyl groups, peroxides, aromatic compounds, diene/triene unsaturations, catalyst residues, and oxygen polymer charge transfer complexes. Thus, the photostability of a particular polymer may depend on the relative concentrations and efficiencies of these impurities.²

Studies by Scott and co-workers^{3,4} have shown that prolonged thermal oxidation of polypropylene reduces its photostability. A marked change in the ultraviolet embrittlement time occurred during the period where the carbonyl concentration, as determined by infrared spectroscopy, changed least. However, because of the rather high temperature and long processing times employed, a primary antioxidant (*tert*-butylcatechol) was incorporated in the polymer. This type of antioxidant would prevent formation of carbonyl groups while being ineffective to hydroperoxide formation.^{5,6} This would tend to favor the role of hydroperoxides as the main initiators in subsequent photochemical oxidation.

In recent studies,⁷⁻⁹ we reported on the behavior of luminescent carbonyl groups during the thermal and photochemical oxidation of polyolefins. Here, we have monitored their behavior during controlled thermal oxidation of polypropylene and examined the subsequent light stability of the polymer. In our experiments, no additives were incorporated that could influence the course of the thermal oxidation.

EXPERIMENTAL

Materials

Additive-free polypropylene (mainly isotactic) was supplied by I.C.I. Limited (Plastics Division).

Thermal Oxidation

Samples of polypropylene powder were heated at 130°C in air and in nitrogen for 15, 30, 45, 60, and 75 min and were then subsequently pressed into film (100 μ thickness) at 190°C for 1 min. These conditions were found satisfactory in our earlier studies.⁷⁻⁹

Photo-oxidation

The polyolefin films were photo-oxidized in a Xenotest-150 described earlier.^{7,9} Carbonyl formation at 1710 cm^{-1} was monitored by the means of the index

$$\log_{10} \frac{I_0}{I_t} / d \times 100$$

(where d = film thickness in μ) using a Perkin-Elmer Model 521 infrared spectrophotometer.

Luminescence Measurements

The fluorescence and phosphorescence spectra were recorded using a double grating (1200 lines/mm) Hitachi Perkin-Elmer MPF-4 spectrofluorimeter equipped with two R-446F photo-

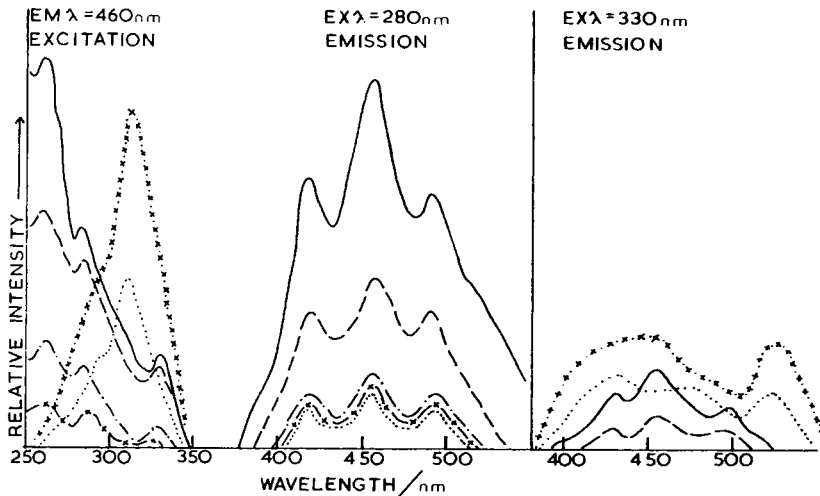


Fig. 1. Changes in the phosphorescence from polypropylene powder after (—) 0 min, (---) 15 min, (-·-) 30 min, (-X-X) 45 min, (.....) 60 min, and (·x·x·x) 75 min of heating in air at 130°C.

multiplier tubes. Phosphorescence lifetimes were obtained by coupling the sample intensity signal from the fluorimeter to a Tetrionix DM-64 storage oscilloscope.⁷⁻⁹

RESULTS AND DISCUSSION

The phosphorescence excitation and emission spectra of unstabilized polypropylene powder before thermal oxidation are shown in Figure 1. The excitation spectrum has three main maxima at about 260, 280, and 330 nm. The corresponding emission spectrum has maxima at about 415, 455, and 485 nm. Due to the superior resolving power of the instrument used here, we were

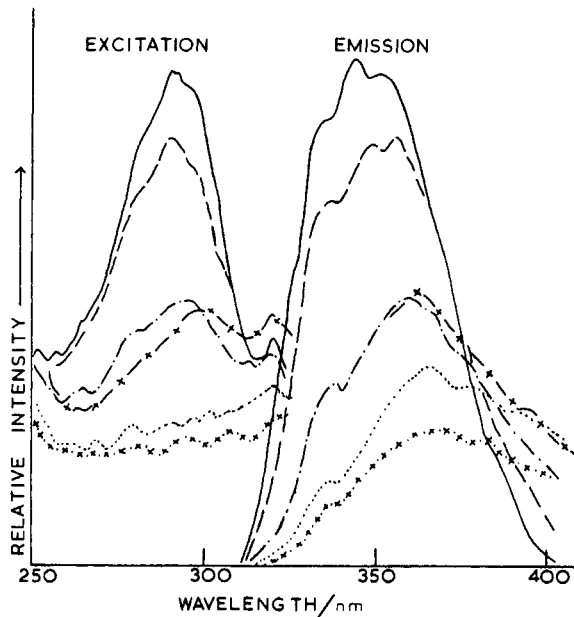


Fig. 2. Changes in the fluorescence from polypropylene powder after (—) 0 min, (---) 15 min, (-·-) 30 min, (-x-x) 45 min, (.....) 60 min, and (·x·x·x) 75 min of heating in air at 130°C.

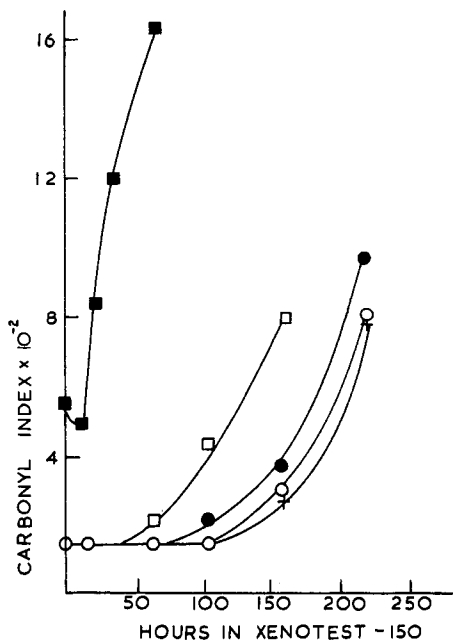


Fig. 3. Carbonyl index vs. hours of irradiation in Xenotest-150 for polypropylene film after (+) 0 min, (O) 15 min, (●) 30 min, (□) 45 min, and (■) 60 min of heating in air at 130°C.

able to distinguish more clearly the component bands in the emission spectra reported on earlier.⁷⁻⁹ Also, as found earlier, variation of the excitation wavelength produces a shift in the emission λ_{\max} and lifetime. The phosphorescence emission lifetime is also batch dependent.⁹ For the polypropylene sample under investigation here, the emission lifetime at 455 nm varied from 1.60 sec to 0.60 sec, exciting over the wavelength range of 280 to 330 nm, respectively. The presence of two or more species appears to be responsible for the emissions.^{8,9}

The fluorescence excitation and emission spectra of the same sample of unstabilized polypropylene powder are shown in Figure 2. Here, the excitation spectrum has its maximum at about 295 nm. The corresponding emission spectrum has its maximum at about 345 nm. Therefore, the differing fluorescence and phosphorescence excitation spectra from the same polypropylene sample clearly indicate that the same light absorbing species cannot be responsible for both emissions.

Heating the polypropylene powder at 130°C for different periods of time, up to 45 min, resulted in an overall reduction in both the fluorescence and phosphorescence intensities (Figs. 1 and 2). However, after heating the polymer for periods greater than this, the phosphorescence intensity increased at wavelengths longer than 450 nm and a new excitation band appeared at 310 nm. Over this same period of change in the phosphorescence emission spectrum from the polymer, the fluorescence showed no such significant change (Fig. 2). Only with the appearance of these longer-wavelength phosphorescent species did we observe an increase in the infrared absorbance at about 1710 cm^{-1} . Further, the above changes in both fluorescence and phosphorescence occurred only when the polymer was heated in the presence of oxygen. The zero time absorbance at 1710 cm^{-1} (Fig. 3) indicates that trace carbonyl-type impurities are present in the polymer initially.

Figure 3 shows that on subsequent photo-oxidation of the polypropylene samples which had been thermally oxidized for periods of up to 45 min, a gradual decrease occurred in the time to the onset of carbonyl group formation as observed by infrared spectroscopy (i.e., the induction period). However, with the polymer sample which had been heated for 60 min, no induction period was observed, showing, therefore, a marked reduction in light stability. Samples which had been heated for periods greater than this were extremely brittle and consequently difficult to assess in terms of their photochemical stability.

The fact that on thermal oxidation a new phosphorescence excitation spectrum appears above about 300 nm and that, when this spectrum is observed, the onset of photochemical oxidation begins suggests that the two observations are related. Earlier work indicates that phosphorescence from polypropylene in the wavelength range of 400–500 nm is due to light emission from impurity carbonyl groups.¹⁰ Thus, the above evidence is in accord with the view that these new phosphorescent species which absorb in the ultraviolet region of sunlight participate in the photochemical oxidation of the unstabilized polymer.⁷⁻⁹

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