

Photodegradation of Poly(ethylene 2,6-Naphthalate) Films

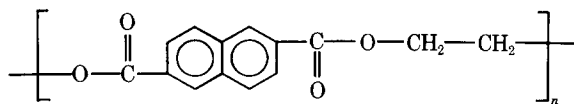
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Synopsis

Poly(ethylene 2,6-Naphthalate) films were irradiated in air by various light sources. By means of a spectral irradiator and a UV carbon arc, the most effective wavelength was determined as about 382 $m\mu$. For a wavelength shorter than 375 $m\mu$, the insolubilization reaction occurs only at the surface layer, while at 382 $m\mu$, the chain scission and insolubilization occur at the same time throughout the depth. Some observations on the change of the fluorescence spectra upon UV irradiation are described.

INTRODUCTION

Poly(ethylene 2,6-naphthalate) (PEN-2,6) is the condensation polymer of 2,6-naphthalenedicarboxylic acid with ethylene glycol and can be extruded into films:



When biaxially stretched, it gives colorless and transparent film with excellent physical and chemical properties, including weatherability.¹ Concerning the latter, some observations on the photochemical behavior of the PEN-2,6 films (MW about 20,000) in air are reported in this note.

WAVELENGTH DEPENDENCE

The absorption spectra of the PEN-2,6 films of thickness greater than 4 μ show a sharp rise at around 380 $m\mu$; they are entirely opaque in the wavelength region smaller than about 380 $m\mu$ but are transparent in the visible and near-ultraviolet greater than about 380 $m\mu$. The corresponding feature was observed through the exposure tests by a grating spectral irradiator (Japan Spectroscopic Co, Ltd, type CRM-FA); the coloration was most intensive at 382 \pm 7 $m\mu$, slight at less than 375 $m\mu$, and was not seen at greater

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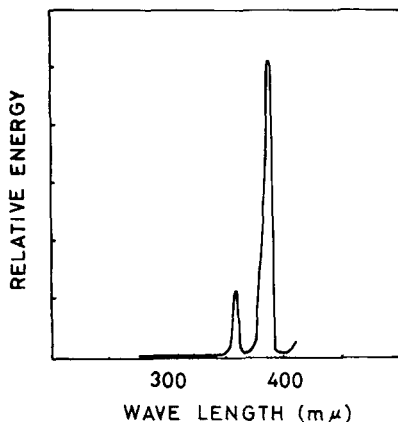


Fig. 1. Wavelength distribution of UV carbon arc.

than $389 \text{ m}\mu$. Thus, prolonged exposure of the PEN-2,6 films to visible light does not incur any deterioration of the properties.

For a wavelength smaller than $375 \text{ m}\mu$, exposure tests can be carried out by means of a high-pressure mercury lamp (Toshiba H-400P) combined with filters. The H-400P lamp emits spectra at $546, 436, 365, 578, 402, 313, 302, 297 \text{ m}\mu$ in the order of intensity and does not contain any light at $382 \pm 7 \text{ m}\mu$. For these short wavelengths, the light is completely absorbed in the very thin surface layer of the film, and the photochemical reaction is limited to take place at the surface. In fact, when the samples were irradiated by the mercury lamp for many hours, they gave rise to an insoluble fraction not dissolved in *o*-chlorophenol at 140°C for 40 min. The percentage of the insoluble fraction was higher if the thickness was thinner. Furthermore, the intrinsic viscosity of the soluble portion did not change from its original value regardless of the thickness. In other words, only the surface layer was subjected to the insolubilization reaction and the interior of the film was not affected by irradiation of light of less than $375 \text{ m}\mu$.

As we have seen, the PEN-2,6 films are colored most intensely at around $380 \text{ m}\mu$, where the light penetrates into the film deeply and causes a reaction throughout the entire depth. This is verified by the exposure experiments of a UV carbon arc (Shimazu Type CW-DW 3) which has an enormous intensity

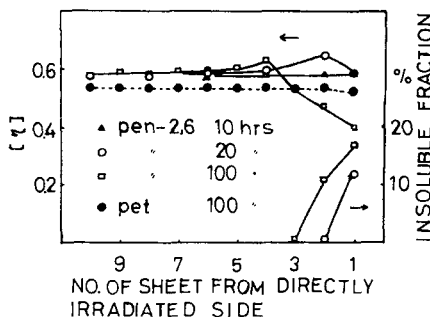


Fig. 2. Exposure of stacked sheets to UV carbon arc.

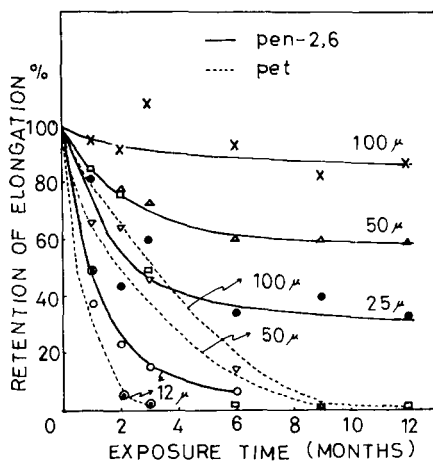


Fig. 3. Retention of elongation at break vs. exposure time for various thicknesses in case of outdoor exposure.

peak at 380–390 $m\mu$, as shown in Figure 1. Ten sheets of 12 μ films were stacked and exposed to the UV carbon arc for up to 100 hr. After the irradiation, the intrinsic viscosity and the insolubility of each film were measured. The result is shown in Figure 2. In this case, the reaction took place even at the layers which were away from the irradiated side more than 50 μ . The chain scission and insolubilization occurred at the same time there.

For comparison, poly(ethylene terephthalate) (PET), which is of similar structure as PEN-2,6 except for the substitution of a benzene ring instead of naphthalene, was examined concurrently. It has been known that the PET

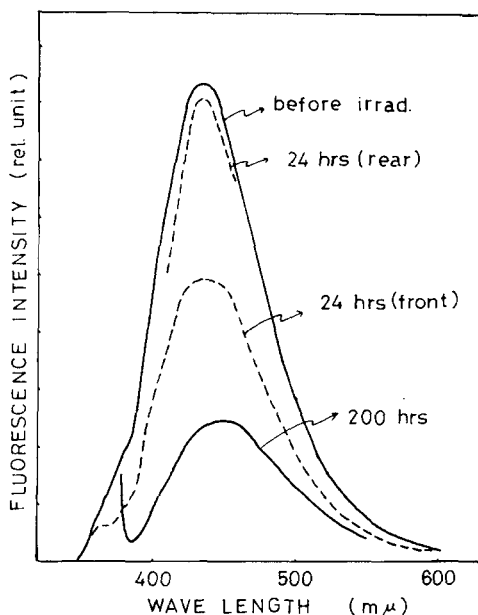


Fig. 4. Fluorescence spectra of PEN-2,6 films irradiated for various hours.

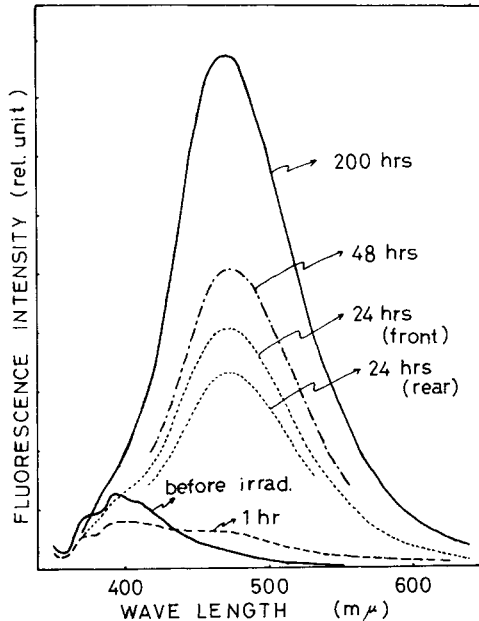


Fig. 5. Fluorescence spectra of PET films irradiated for various hours.

films have an absorption edge at $310\text{ m}\mu$ and degrade most by the irradiation of light of this wavelength.^{2,3,4} Actually, the molecular weight of PET films deteriorated severely by the irradiation of the mercury lamp which has spectra at $313\text{ m}\mu$, whereas they did not degrade much by exposure to UV carbon arc which did not contain any intensive spectra at around $310\text{ m}\mu$ as seen in Figure 1.

The Sunlight contains wavelengths of both 310 and $380\text{ m}\mu$ so that it affects both PET and PEN-2,6 films. In this case, the degradation was much more severe for PET than for PEN-2,6 films, as shown in Figure 3. In PET films, only chain scission occurred upon exposure to UV light and no insolubilization was found. The fact that PEN-2,6 films give rise to insoluble fractions but PET films do not, upon exposure to UV light, corresponds to the case of irradiation by electron beam or γ -ray.^{1,5}

FLUORESCENCE SPECTRA

PEN-2,6 and PET both emit fluorescence when excited by UV light as shown in Figures 4 and 5. These spectra changed in the following way upon exposure to UV light. Namely, PEN-2,6 films which have a strong fluorescence band at $435\text{ m}\mu$ ⁶ decreased in intensity after irradiation, whereas for PET the emission bands at 375 , 395 , and $410\text{ m}\mu$ decrease in intensity and, at the same time, a band grew at $470\text{ m}\mu$ as shown in Figures 4 and 5. It was also found that when the films were subjected to heat aging at 240°C , the emission band grew for both PEN-2,6 and PET at 435 and at $470\text{ m}\mu$, respectively. Thus, it is suggested that for PEN-2,6, the reaction products would be different for heat aging and for the UV exposure in air and also the reaction scheme would not be similar to that of PET.

More work is needed to elucidate the photoreaction mechanism of PEN-2,6.

References

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Received July 8, 1975

Revised September 25, 1975