

Initial Process in the Radiation-induced Degradation of Poly(ethylene terephthalate) Detected by Fluorescence Measurements

Hideyuki Itagaki,* Masato Sakurai, and Ryo Nakazawa

*Department of Chemistry, Faculty of Education, Shizuoka University
836 Ohya, Shizuoka 422, JAPAN*

Keywords: fluorescence, oxidation, γ -ray, radiolysis, photolysis

1. Introduction

The use of the luminescent method guarantees high sensitivity, therefore the method can be employed for monitoring small chemical and physical changes in material products [1,2]. Poly(ethylene terephthalate)(PET) is one of the most resistible materials against the irradiation of γ -ray and UV light. However, there is no effective tools to assess the first stage of the degradation under a small amount of irradiation dose.

The fluorescence behavior of PET solid had not been clarified until we studied the PET films prepared by using a spin-casting method [3,4], which provides most reproducible films with identical physical properties. We found that the fluorescence of PET solid reflected whether the main-chain phenylene ring was in the crystal region or the amorphous one by comparing them with the information about the crystallinities obtained by the measurements of differential scanning calorimetry, IR absorption and density. Consequently, the fluorescence of PET films was found to consist of three species, i.e., one at 390 nm for phenylene ground state dimer [5-7], another at 370 nm for phenylene moiety in amorphous region, and the third at 330 nm for phenylene moiety in crystal region. Since the fluorescence properties of PET solids have become clearer, next we have tried to apply fluorescence spectroscopy to the study on the initial stage in the radiation-induced degradation of PET solids. The aim of the present work is (i) to show that the fluorescence

measurement is quite effective to observe the initial process of PET degradation and (ii) to clarify the cause of the degradation process induced by the γ -ray irradiation.

2. Experimental

The PET samples studied in this work were obtained by cutting out a flat rectangle (80 mm long and 13 mm wide) from commercial colorless PET bottles for soft drinks and were washed thoroughly with methanol. Samples sealed into Pyrex tubes were irradiated at room temperature with γ -rays from a ^{60}Co source at Radiochemistry Research Laboratory of Shizuoka University for a relatively small amount of dose and at Institute of Scientific and Industrial Research of Osaka University for a greater amount of irradiation dose. Fluorescence spectra and fluorescence excitation spectra were measured on a Hitachi F-4500 spectrofluorometer at room temperature. Films were set at 45° to the exciting beam. IR absorption spectra were measured on a Perkin Elmer 1720X FT IR spectrophotometer with resolution of 2 cm^{-1} .

3. Results and Discussion

There is no large difference in IR absorption spectra of PET films irradiated with γ -rays in aerated state compared to original films, up to 520 kGy, which was the maximum dose of the present work. Thus, the PET films were not degraded at all from the standpoint of IR spectroscopy. However, Fig. 1 shows that the PET films were found to be

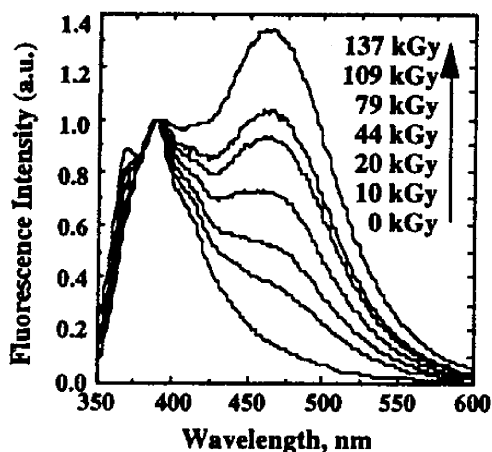


Fig. 1 Fluorescence spectra of PET films irradiated with γ -rays normalized at 390 nm (excitation wavelength is 336 nm).

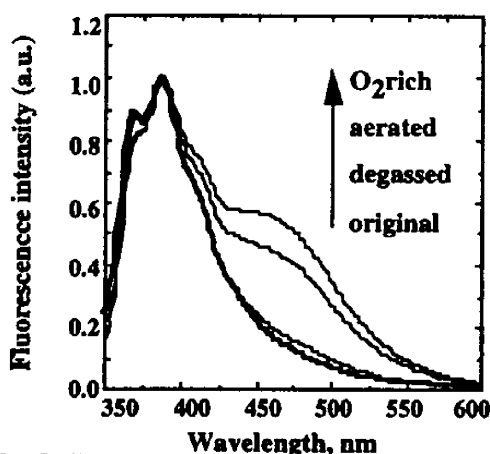


Fig. 2 Influence of oxygen on the radiation-induced degradation of PET films. All the fluorescence spectra are normalized at 390 nm (excitation wavelength is 336 nm).

damaged from the standpoint of fluorescence spectroscopy. An original PET film only exhibits the fluorescence due to ground state dimer of phenylene moieties (370 and 390 nm). However, new emission with a peak at 465 nm appears after the irradiation of γ -ray. The excitation spectrum for this new emission has a peak at 400 nm. The intensity of the new luminescence is perfectly proportional to the dose amount of γ -ray.

In order to examine the cause to produce the emissive component, we studied the influence of oxygen on its formation. Fig. 2 shows the fluorescence spectra of PET films after the irradiation with 15 kGy of γ -ray under degassed, aerated, and oxygen-rich conditions. Without oxygen, the fluorescence spectra did not change so much after the γ -ray irradiation. A greater amount of oxygen was found to give birth to the product whose emission peak is 465 nm. In conclusion, the

degradation process shown in Fig. 1 is due to oxidation reaction induced by the γ -ray irradiation.

The chemical structure of this product is unfortunately unknown at present because the IR spectroscopy could not detect it even after the irradiation of 520 kGy. Thus, we only speculate this structure by comparing the emission spectra of some candidate compounds. Edge et al. investigated the change in luminescence of PET when degraded at melt temperatures [8]. In their thermal decomposition experiments, hydroxylated phenylene groups were suggested to be produced and to be a cause of yellowing: diethyl-2,5-dihydroxyterephthalate, one of model compounds, shows fluorescence whose peak is around 460 nm. The reaction to form hydroxylated phenylene group can take place under our experimental conditions where PET and oxygen are irradiated with γ -rays.

4. Conclusion

We have successfully presented that the fluorescence spectroscopy can be employed as an effective tool to detect the initial process in radiation-induced degradation of PET solids, while no change was observed for the IR absorption spectra. The fluorescence spectra of the PET irradiated with γ -rays show that oxygen should take part in the degradation process, yielding an emissive phenylene derivative.

References

1. H. Itagaki, K. Horie and I. Mita, *Prog. Polym. Sci.* **15** (1990) 361.
2. H. Itagaki, *Fluorescence Spectroscopy*, in *Handbook of Polymer Sciences* (ed. T. Tanaka), Academic Press, in press.
3. H. Itagaki, Y. Inagaki and N. Kobayashi, *Polymer* **37** (1996) 3553.
4. H. Itagaki, *J. Luminescence* **72-74** (1997) 435.
5. N. S. Allen and J. F. McKeller, *Makromol. Chem.* **179** (1978) 523.
6. D. J. Hemker, C. W. Frank and J. W. Thomas, *Polymer* **29** (1988) 437.
7. M. F. Sonnenschein and C. M. Roland, *Polymer* **31** (1990) 2023.
8. M. Edge, R. Wiles, N. S. Allen, W. A. McDonald and S. V. Mortlock, *Polym. Degrad. Stab.* **53** (1996) 141.