



Free-volume hole size evaluated by positron annihilation lifetime spectroscopy in the amorphous part of poly(ethylene terephthalate) degraded by a weathering test



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ABSTRACT

The degradation of poly(ethylene terephthalate) (PET) was investigated through a weathering test by using a xenon weather meter. The degraded structure was evaluated by means of gel permeation chromatography (GPC), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and positron annihilation lifetime spectroscopy (PALS). The GPC results indicated a decrease of number average molecular weight and a broadening of polydispersity with the degradation of PET, probably due to chain scission and some networking reactions. The DSC results indicated that the crystallinity index was changed through the weathering test. However, the change of crystallinity was poorly correlated with the progress of degradation. In the $\tan \delta$ measurement by DMA, suppression of molecular mobility during the degradation was implied by the increase in T_g with increasing exposure time. The PALS results revealed that the free-volume hole size decreased with increasing exposure time. The decrease in the free-volume hole size can be attributed to the interaction between functional groups produced by hydrolysis or photochemical chain scission. The change of properties and structure in the amorphous part of PET was found to be correlated with the progress of the degradation in the weathering test.

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1. Introduction

Recently, the massive dissemination of photovoltaic cells has stimulated demand for durability evaluation of the materials that are comprised in the devices. In particular, the weatherability of the polymeric materials is important in the assessment of the product lifetime. Poly(ethylene terephthalate) (PET) has been commonly applied as the back sheet of photovoltaic devices, and is a major focus of research on weatherability [1–3]. Degradation of PET, which is used as a material in commodity products such as drink bottles, has been extensively investigated with respect to material recycling [4,5]. Because the major recycling method for PET involves a melting process, heat degradation has attracted the attention of many researchers. On the other hand, the degradation of PET by weathering conditions has also been examined by several researchers, especially in terms of photochemical degradation [6–10]. Since the degraded structure is expected to depend on the degradation conditions, precise structural analysis of the degraded

material is essential to understand the degradation mechanism and the weatherability of PET.

Structural alterations during the degradation, such as the chain scission of PET molecules and the change in crystallinity, have been investigated using techniques including infrared absorption spectroscopy (IR), differential scanning calorimetry (DSC), X-ray diffraction, etc. [11–13]. According to these studies, chain scission by hydrolysis [14,15] or photochemical reaction [8–10] produces low molecular weight polymer chains. The crystallization enhancement was explained by the production of these low molecular weight polymer chains. However, direct evaluation of the structural changes in the amorphous part of PET remains an open question. The development of amorphous structure analysis is expected to help in obtaining a comprehensive understanding of the PET degradation in combination with the analysis of molecular structure and crystal structure.

Positron annihilation lifetime spectroscopy (PALS), which can evaluate the free-volume hole size of amorphous materials, is known as an effective analytical method for PET [16–19]. In this study, systematic structure analyses on the molecular, crystal, and amorphous parts of the PET degraded in weathering tests were conducted by means of gel permeation chromatography (GPC),

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DSC, dynamic mechanical analysis (DMA), and PALS. The amorphous-structure alteration is discussed in comparison with the molecular- and the crystal-structure alteration. The correlation between the structural alterations and the progress of degradation is also discussed.

2. Experimental

2.1. Samples and weathering test

The Lumirror[®] S10 (50 μm film, Toray Industries Inc. Japan) was employed as a test sample. The weathering test was performed using a 7.5 kW super xenon weather meter (SX75, Suga Test Instruments, Japan) until the tensile strength of the specimen was decreased to less than half of the initial value. The weathering test conditions were: irradiance of 180 W/m^2 , black panel temperature of 63 $^{\circ}\text{C}$, and humidity of 50%. The sampling of the specimen was conducted at 0, 24, 48, 72, 96, 144, and 192 h. The weathering test was eventually stopped after 192 h. Tensile tests of PET films were performed using an Autograph AG 01000B tester (Shimadzu, Japan) at room temperature, RT, with dumbbell shape specimens. The grip distance was 50 mm, the gage length was 25 mm, and the test speed was 2 mm/min. The results of the tensile tests are shown in Fig. 1. The tensile strength was defined as maximum stress of the tensile test. The tensile strength and elongation at break values are the average values of 3–4 measurements.

2.2. GPC

Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (M_w/M_n) were measured by GPC at 40 $^{\circ}\text{C}$ using the Shodex GPC LF-404 column (Showa Denko, Japan) with a flow rate 0.15 mL/min. The sample solution (0.1% w/v) was made using 5 mM sodium trifluoroacetate in hexafluoro-2-isopropanol as the solvent. The calibration was done with the polystyrene standard.

2.3. DSC

The melting point (T_m) and the heat of fusion (ΔH) were measured using a SII DSC 7200 (Hitachi High-Tech Science, Japan). The sample was encapsulated in an aluminum pan and scanned at 10 $^{\circ}\text{C}/\text{min}$ from 20 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$. The first heating cycle data were used for analysis in order to avoid an influence of heat history. The ΔH was divided by the equilibrium melting enthalpy ($\Delta H_0 = 140 \text{ J/g}$) to obtain the crystallinity index (α , equation (1)) [20–22].

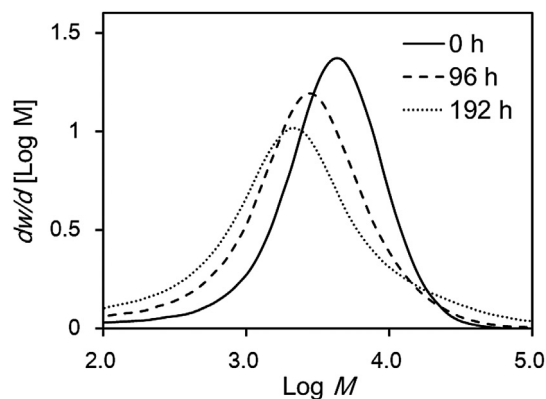


Fig. 2. GPC elution curves of the PET samples after 0, 96, and 192 h exposure.

$$\alpha = \frac{\Delta H}{\Delta H_0} \times 100 \quad (1)$$

2.4. DMA

The specimen for DMA was a 20 mm \times 5 mm strip of PET made using a cutting die. The DMA measurement was carried out from 0 $^{\circ}\text{C}$ to 200 $^{\circ}\text{C}$ on a DMA Q800 (TA instruments, US) at 1 Hz and a heating rate of 3 $^{\circ}\text{C}/\text{min}$, while applying a strain of 0.1%.

2.5. PALS

In PALS, the lifetime of *ortho*-positronium (*o*-Ps), the triplet state of a bound positron and electron, is measured to evaluate the size of free-volume holes. The relationship between *o*-Ps lifetime, τ_3 [ns], and the radius, R [nm], of a spherical free-volume hole is expressed based on the Tao-Eldrup model as follows in equation (2), [23–26].

$$\tau_3 = 0.5 \left[1 - \frac{R}{R + 0.166} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + 0.166}\right) \right]^{-1} \quad (2)$$

Details on the principles and the instrumentation of PALS system have been reported in a previous paper [27].

The PALS measurement was performed using a PALS 200A (Fuji-Imvac, Japan) slow positron pulse beam system at RT, with incident positron energies (E) of 1, 5, and 10 keV. The mean implantation depths of positrons from the PET surface, which are related to the density of PET ρ (1.40 g/cm^3) as well as E , were estimated to be 29 nm at $E = 1$ keV, 375 nm at $E = 5$ keV, and 995 nm at $E = 10$ keV.

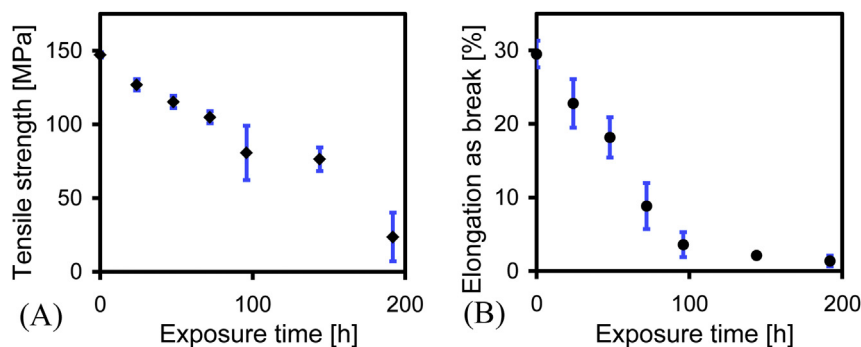


Fig. 1. (A) Tensile strength and (B) elongation at break as a function of exposure time obtained by means of a tensile test. The sizes of the markers include the experimental uncertainties in the case that uncertainty is not displayed.

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