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Rapid evaluation of photo, thermal and oxidative degradation of high impact polystyrene by a xenon lamp-based online ultraviolet irradiation-pyrolysis-GC/MS system

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ABSTRACT

Photo, thermal and oxidative degradation behaviors of high impact polystyrene (HIPS) containing butadiene rubber (BR) were evaluated by online ultraviolet irradiation-pyrolysis (UV/Py)-GC/MS system with a micro-UV irradiator. Volatile degradation products evolved during UV irradiation at 60 °C in air were identified and quantified through online GC/MS measurements. Formation of some typical volatiles from the HIPS sample during 1 h irradiation, such as benzaldehyde, acetophenone and benzoic acid originating from PS and 2-propenal from BR, clearly indicates the contribution of oxidative reactions in the polymer chains. Moreover, the residual HIPS samples after irradiation up to 12 h were characterized by evolved gas analysis-mass spectrometry (EGA-MS). The observed EGA thermograms clearly showed not only lower temperature shifts of onset and peak top of gas evolution, but also peak broadening compared with that of the original HIPS sample, reflecting some structural changes in HIPS polymer chains during the irradiation. Furthermore, the degradation behavior of HIPS by the micro-irradiator was compared with that obtained by the conventional accelerated degradation test using a Xe weather meter. The observed EGA profile of HIPS irradiated by the Xe weather meter for 300 h showed the equivalent temperature shift and broadening to that for the residual HIPS after 1 h irradiation by the micro-UV irradiator. This result suggests that the micro-UV irradiator in UV/Py-GC/MS system might achieve the comparable degradation processes of polymeric materials much more rapidly compared with the conventional accelerated degradation test methods.

1. Introduction

High impact polystyrene (HIPS) containing several percent of butadiene rubber (BR) component to enhance its impact strength is widely used in many application fields including housing materials for electrical appliances and office automation equipment, and food packages. However, HIPS gradually deteriorates with time by various external factors such as sun light, heat, air, and moisture, leading to color changes and lowering of mechanical properties. Therefore, it is important to evaluate the degree and mechanisms of degradation of HIPS using weatherability tests. So far mechanical, morphological and thermal properties of HIPS were studied by natural weathering test for long period of 8760 h [1], in which remarkable morphological changes were observed especially at the surface of the materials along with the dramatic loss in mechanical properties. On the other hand, the chemical analysis approaches for the deteriorated HIPS have been conducted mainly using infrared spectroscopy [2,3]. Furthermore, the microwave-assisted extracts from the recycled HIPS were analyzed by gas chromatography (GC)/mass spectrometry (MS), in which a wide variety of oxidized products were identified to be those originated from both PS and BR phases [4].

For weatherability tests of polymeric materials, outdoor exposure tests and various types of accelerated degradation tests are generally used; however, the former tests generally require weeks to months, or even years, and even in the accelerated methods several hundred hours of test periods are often necessary. Moreover, little has been reported on direct analysis of volatile compounds from polymer samples evolved during degradation process, although changes in the chemical structures in the degraded samples subjected to the weathering tests can be

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evaluated to some extent. Only some limited attempts to study volatile compounds evolved during the degradation process of polymer samples have been reported by using MS [5] and GC [6].

To compensate for the shortcoming of the conventional testing methods, authors have developed an online ultraviolet irradiation-pyrolysis (UV/Py)-GC/MS system [7] in which a micro-UV irradiator based on a xenon (Xe) lamp is equipped in the pyrolysis (Py)-GC/MS system using a vertical microfurnace pyrolyzer. The system allows online analysis of volatile products formed from the sample materials during their photo, thermal and oxidative degradation process caused by the micro-UV irradiator at any desired temperature in various atmosphere including air. Further, the residual degraded sample can be analyzed by evolved gas analysis (EGA)-MS or Py-GC/MS which have been widely utilized for the practical characterization of polymeric materials [8–10].

By using this technique, UV-induced degradation behaviors of typical synthetic polymers such as polystyrene, polycarbonate and polypropylene have been studied [7]. Moreover, photo, thermal, and oxidative degradation of acrylic coating paint samples used for house exterior walls were evaluated by EGA-MS through the comparison of the thermograms of UV irradiated samples obtained both by the micro-UV irradiator in UV/Py-GC/MS and a metal halide weather meter [11]. The observed thermograms showed a good correlation between the two methods and demonstrated that UV/Py-GC/MS greatly shortened the time required for the weatherability tests.

In this work, the photo, thermal, and oxidative degradation of HIPS were studied by UV/Py-GC/MS in which the online GC/MS analysis of volatile products formed from the HIPS sample during UV irradiation and the EGA-MS of the residual materials after the irradiation were complementarily performed. Furthermore, the thermograms observed by EGA-MS of the HIPS sample irradiated by the micro-UV irradiator were compared with those of the irradiated surfaces of HIPS plate samples deteriorated by the Xe weather meter to evaluate the correlation between the two weathering processes.

2. Experimental

2.1. Sample

HIPS (HT50; PS Japan) containing 6.3% of BR component was used as the test sample. A dichloromethane solution of the HIPS sample (2 μg/ml) was prepared and a 10 μl aliquot of the solution (equivalent to 20 μg of HIPS) was placed in a sample cup having two side-openings for UV/Py measurement. Dichloromethane was then evaporated and a thin film of HIPS (a few micrometers in thickness) deposited on the bottom of the sample cup was subjected to UV/Py-GC/MS measurement. In addition, plated samples (70 mm × 50 mm × 3.3 mm thickness) of the same HIPS were prepared and subjected to Xe weather meter tests (wavelength: 320–700 nm, intensity: 34 mW/cm^2, 63 °C). After 100 and 300 h of irradiation, about 20 μg each of the HIPS sample scraped off from the degraded surface of the plate was subjected to EGA-MS measurement.

2.2. Analysis of volatiles evolved during degradation process

A Xe lamp-based micro-UV irradiator (UV-1047Xe, wavelength: 280–450 nm, intensity: 700 mW/cm^2; Frontier Laboratories, Japan) was used for UV irradiation in UV/Py-GC/MS system [7]. The sample cup depositing HIPS film was attached to the end of an optical fiber cable of the irradiator and was inserted into the vertical microfurnace pyrolyzer (multi-shot pyrolyzer EGA/PY-3030D, Frontier Laboratories, Japan) directly coupled to the split/splitless injector of a GC/MS (QP-2010 Plus, Shimadzu, Japan). Air was used as an atmospheric gas during the UV irradiation in the pyrolyzer set at 60 °C at a flow of 10 ml/min. With the GC oven door kept open, volatile degradation products from HIPS sample were introduced into a metal capillary separation column (Ultra ALLOY$^+$-1, polydimethylsiloxane, $L = 30$ m, id = 0.25 mm, df = 0.5 μm, Frontier Laboratories, Japan) in split mode with a split ratio of 1/10 and were cryo-trapped during the irradiation by immersing the head of the column (ca. 20 cm from the injector) in a 300 ml Dewar containing liquid nitrogen. When the UV irradiation was finished, the atmospheric gas for the UV/Py system was switched to helium, then the furnace temperature was raised to 250 °C with setting the temperature both of Py/GC interface and GC injection port at 250 °C, volatile compounds occluded in the HIPS matrix were thermally desorbed and were introduced into the head of the separation column immersed in liquid nitrogen, so that desorbed compounds were added to volatiles trapped in advance during the UV irradiation. Once the thermal desorption was completed, the separation column was drawn out of the liquid nitrogen trap, and then the GC/MS analysis of the trapped degradation products was started with the GC oven door closed.

In GC/MS analysis, GC oven temperature was ramped from 40 to 240 °C at the rate of 20 °C/min. Helium was flowed at the rate of 1 ml/min in column as a carrier gas (in split mode with total flow rate 50 ml/min). MS was operated in EI mode at 70 eV with a scan range set to 29–300 amu.

2.3. Analysis of residual polymer after UV irradiation

To evaluate the change in the polymer microstructure upon UV irradiation EGA-MS measurements of HIPS samples before and after the irradiation were performed. A deactivated metal capillary tube (UADTM-2.5N, $L = 2.5$ m, id = 0.15 mm, Frontier Laboratories, Japan) was set in the UV/Py-GC/MS system, in place of the separation column, to observed the EGA profiles (thermograms) of the HIPS samples [12]. The sample cup containing the deteriorated HIPS film after UV irradiation was set in the pyrolyzer and heated from 100 to 700 °C at a heating rate of 20 °C/min under a helium flow at 50 ml/min. The evolved gases were continuously introduced through Py/GC interface (at 200–300 °C) and GC split injection port (split ratio 1/50) into the capillary transfer tube kept at 300 °C and connected directly to the MS ion source (in EI mode with MS scan range of 29–600 amu). The control HIPS sample without irradiation, weighed 20 μg, was similarly subjected to EGA-MS measurement. Furthermore, as for the reference HIPS plate samples, about 20 μg of the irradiated surface by the weather meter was also measured under the same EGA-MS conditions to observe thermograms for comparison.

2.4. Size-exclusion chromatography

The number-average molecular weights (M_n) and the molecular weight dispersity (M_w/M_n) of the HIPS samples were estimated by size-exclusion chromatography (SEC) on a SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards.

3. Results and discussion

3.1. Volatile degradation products formed by UV irradiation

Fig. 1 shows chromatograms of volatile compounds evolved from thin film HIPS samples exposed at 60 °C in air for 1 h, (a) without and (b) with UV irradiation by the micro-UV irradiator in the online UV/Py-GC/MS. As shown in Fig. 1(a), without UV