

CHANGES IN BEHAVIOR OF FLAME RETARDANTS IN ACRYLONITRILE-BUTADIENE-STYRENE AND POLYCARBONATE RESINS BY WEATHERING TESTS

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Introduction

Flame retardants (FRs), which are chemicals used in preventing combustion and/or delaying of the spread of fire after ignition on materials, are used in polymers since the 1960s¹⁻³. FRs may contain halogens (chlorine and bromine), phosphorus, aluminum, and magnesium, or antimony trioxide (Sb₂O₃), etc.². Particularly, organochlorine, organobromine, and organophosphate FRs have been widely used in commercial plastics of electric and electronic equipment³. However, it has become of concern such that plastics have been recognized as the main source of environmental contamination with these compounds because plastics can release the FRs⁴. Besides, the releases of FRs, plastics are not readily managed throughout the supply chain. Under such situations, it is desired to accurately manage the behavior of FRs contained in the plastics. For accurate management of the behavior of FR, plastics including FRs such as reference materials are needed. Consequently, we prepared quality control (QC) plastic samples including appropriate FRs with sufficient concentrations as plastic disks⁵. FRs included in the QC plastic samples were dechlorane plus (DP; organochlorine; 500 mg/kg), tetrabromobisphenol A (TBBPA; organobromine; 1000 mg/kg), triphenyl phosphate (TPhP; organophosphate; 1000 mg/kg), and/or Sb₂O₃ (inorganics; 500 mg/kg) in either acrylonitrile-butadiene-styrene (ABS) or polycarbonate (PC) resins. As a result, it was obvious that our QC plastic samples were prepared properly, and are applicable to elucidate the behaviors of FRs throughout the supply chain. Based on the results mentioned above, some weathering tests were performed in accordance with the ISO 4892 series to investigate the decomposition/vaporization/elution of organic and inorganic FRs in the QC plastic samples. In this study, we report the changes in behavior of FRs analyzed by gas chromatography/mass spectrometry (GC/MS) in weathered QC plastic samples. In addition, polymers and elements arising from these plastic samples were also evaluated by Fourier transform infrared (FTIR) and by energy dispersive X-ray fluorescence (ED-XRF) spectrometry.

Materials and methods

The QC plastic samples (ABS or PC resin including three organic FRs or four FRs) were artificially weathered by an accelerated xenon arc weathering test in accordance with ISO 4892 part 2⁶. The tests were performed in a Super Xenon Weather Meter SX2D-75 (Suga Test Instruments, Japan). Test conditions of the Weather Meter are as follows; black panel temperature (63±3) °C, relative humidity (50±5) %, a cycle of 18 min water spray and 102 min dry period or no water spray, weathering time 200 h with a UV-light intensity of 180 W/m² (300 to 400 nm). The condition of the tests was assumed to be similar to the sunlight exposure of approximately half a year⁷.

For GC/MS analysis, ABS or PC disk was respectively freeze-pulverized with a CryoMill (Verder Scientific, Germany). DP from AccuStandard (USA), TBBPA from Kanto Chemical (Japan), and TPhP from AccuStandard were used in this study. For organic FRs, each pulverized sample (0.1 g) was weighed in a PP tube. After addition of *p,p'*-DDE (Wako Pure Chemical Industries, Japan) as the surrogate solution [prepared using toluene (Wako Pure Chemical Industries)], the dissolution of the sample was performed with 10 mL tetrahydrofuran (Kanto Chemical) for 60 min using an ultrasonication equipment, and this condition was validated elsewhere⁸. The solutions obtained were cleaned-up by precipitation with *n*-hexane (Wako Pure Chemical Industries) on ABS or PC resin, then, *p,p'*-DDD (Wako Pure Chemical Industries) as the syringe spike solution (prepared using toluene) was added to the cleaned solution. An Agilent Technologies (USA) 6890 GC equipped with a DB-17MS column (15 m × 0.25 mm i.d., 0.15 μm film thickness; Agilent Technologies), and a 5975B MSD was used for end determination. The analysis was performed using on-column injection mode, and the injection volume was 0.1 μL. Helium was used as the carrier gas (1.5 mL/min) and inlet temperature was set as oven track mode. Organic FRs were monitored with EI ionization and SIM or Scan mode. Column oven temperature was programmed from 50 °C (2 min) to 300 °C at a rate of 20 °C/min with a final hold time of 10 min. DP, TBBPA, and TPhP were quantified by internal standard method. DP was quantified as the sum of the peak area for *syn*- and *anti*-DP.

FTIR experiment was performed using a Thermo Fisher Scientific Nicolet 6700 FTIR spectrometer (USA) equipped with a Smart iTR™ Attenuated Total Reflectance. All samples were measured from 4000 to 650 cm^{-1} . A total of 32 background and sample scans were measured for each sample. Data were collected with a temperature-stabilized deuterated triglycine sulfate (DTGS) KBr detector.

A Shimadzu XRF Raynu EDX-720 (Japan) was used for evaluation of four elements using plastic disks. Operating conditions of ED-XRF spectrometer for Cl ($K\alpha$), Br ($K\alpha$), P ($K\alpha$), and Sb ($L\alpha$) are as follows; X-ray irradiation from lower side of sample, Rh target (air cooling), tube voltage 15 kV, tube current 800 μA , Al filter, vacuumed sample chamber, X-ray irradiated diameter to sample 10 mm, measurement time 9999 sec. The NMIJ CRM 8110-a (certified reference material of polystyrene resin) and BCR-680 (certified reference material of polyethylene resin, IRMM, France) were used as a reference.

Results and discussion:

FTIR spectra of QC plastic samples

FTIR spectra were obtained from both original and weathered QC plastic samples, and compared. As Figure 1, the ABS spectra significantly changed by the weathering test. The absorbance peaks of butadiene group (around 900 cm^{-1}) in the original ABS resin were disappeared in the weathered ABS resin. This result was in good agreement with published data⁹. On the other hand, there was no significant difference for PC resin.

GC/MS results of QC plastic samples

We compared the concentration of FRs between original and weathered QC plastic samples. Figure 2 shows the relative concentrations when analytical results from the original QC plastic samples are 1. In this study, there was no significant difference for the concentrations of each FRs with or without water spray. This may be because the FRs were kneaded into the resin rather than being coated to the resin surface. However, measurement standard deviations from FRs in the QC plastic samples weathered seemed to be relatively larger than those in the original samples. In each FR, the obtained results had a number of common points between ABS and PC resins. The concentration of TPhP did not change through the weathering tests, while the concentration of TBBPA changed and decreased obviously (approximately 30 to 40 %). Organobromine FRs including TBBPA have been known to be photodegraded and pyrolyzed, thus, this behavior was also observed. In addition, as for the result of Scan analysis, a degradation product, tribromobisphenol A, was detectable in the QC plastic samples weathered in this study. On the other hand, the behavior of DP was different from that of TBBPA and TPhP. The concentrations of DP in ABS resin decreased slightly (approximately 10 %) despite the fact that the concentrations of DP in PC resin did not change. Moreover, a degradation product, $[\text{DP}-1\text{Cl}+1\text{H}]^{10}$, was detectable in the ABS resin weathered on Scan analysis. PC resin has a relative excellent property on weather resistance rather than ABS resin¹¹, thus, a property such as the prevention of photodegradation of DP in weathered PC resin may occur. Obtained results for ABS and PC resins did not depend on whether Sb_2O_3 was included or not.

ED-XRF spectra of QC plastic samples

We focused on the results of DP and TBBPA obtained by GC/MS analysis on ABS resins. The chlorine arising from DP and bromine arising from TBBPA were evaluated by ED-XRF spectrometry to elucidate the relationship of two FRs and the elements in the ABS resins. Figure 3 shows the relative intensities of the chlorine and bromine between the original and weathered ABS resins. As a result, for the bromine, the relative intensities were in agreement within the accepted limits of measurement standard deviations from ED-XRF analysis. On the other hand, there was a significant difference between the original and weathered ABS resins. From the results of GC/MS and ED-XRF analyses, the behaviors of DP/chlorine and TBBPA/bromine in ABS resin may be different.

Eventually, the behaviors of DP, TBBPA, TPhP in ABS or PC resin weathered may be (respectively) characterized using data from GC/MS and ED-XRF analyses. However, it is necessary to understand the change in concentrations of total elements and to diversify the condition of weathering tests such as UV-light intensity, temperature, humidity, cycle of water spray, and weathering time for more detailed discussion.

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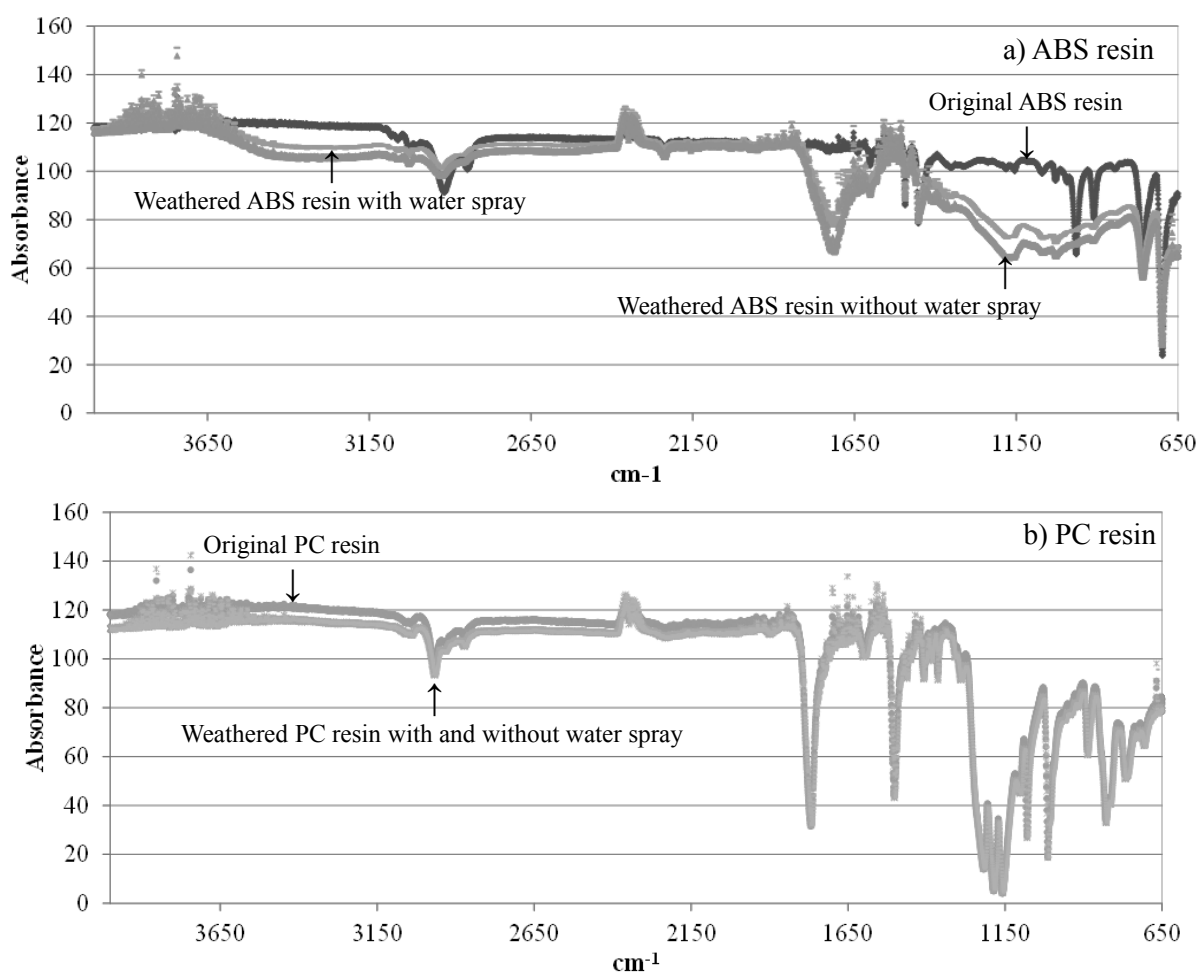


Fig. 1 FTIR spectra from ABS (a) and PC resin (b) before and after weathering tests

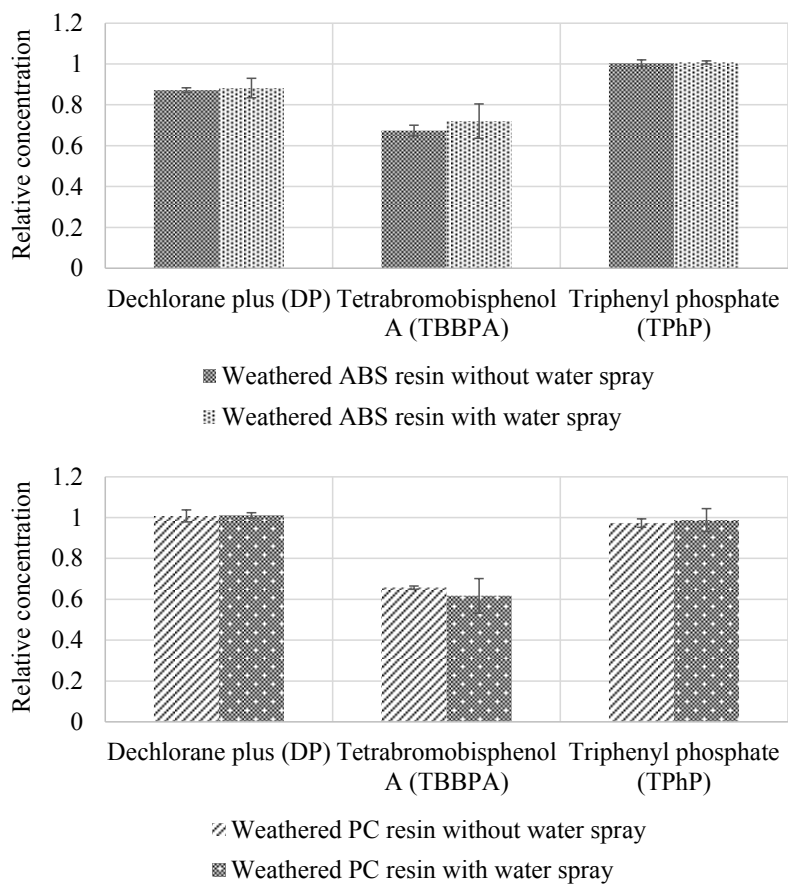


Fig. 2 Relative concentrations of FRs in weathered ABS and PC resins with or without water spray when analytical results of FRs in original ABS or PC resin is 1. Error bar represents measurement standard deviations of FR analysis.

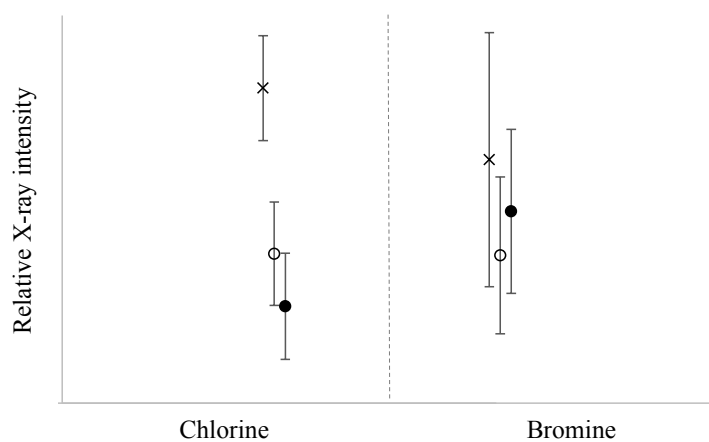


Fig. 3 Relative X-ray intensities of chlorine and bromine in original (x) and weathered QC samples (o, without water spray; •, with water spray) when X-ray intensities of the NMIJ CRM 8110-a is 1. Error bar represents measurement standard deviations of FR analysis.