

Investigation of the extraction method for hexavalent chromium in plastic samples

Environmental concerns have risen to the top of the global agenda. One consequence is that the design and manufacture of products with minimal impact on humans and the environment is required. The European Union, for example, regulates and limits the use of four heavy metals, namely, lead (Pb), cadmium (Cd), mercury (Hg), and hexavalent chromium (Cr(VI)), and two types of brominated flame retardants (polybrominated biphenyls: PBB, polybrominated diphenyl ethers: PBDE), in electrical and electronic equipment put on the market after July 1, 2006. Directive 2002/95/EC (RoHS directive) governs the restriction on those hazardous substances in European member states; meanwhile, other regions of the world have put similar regulations in place [1]. Owing to these regulations, it is important for the manufacturer to analyze and control certain substances used in products and their materials. Only the oxidation state of the hexavalent species of chromium is regulated in the RoHS directive and therefore its analysis is challenging. Cr(VI) has been used for chromate conversion coatings of metals, pigments of polymers, and other applications in industrial products. However, no reliable determination method for Cr(VI) in polymers has yet been established. One of the reliability problems of Cr(VI) determination is the occurrence of unstable variance during analysis. The valence of chromium is known to be changed easily by the oxidation-reduction reaction. Cr(VI) may change into Cr(III) under acidic conditions, whereas Cr(III) may change into Cr(VI) under alkaline conditions. Therefore, a chemical analysis method that keeps Cr(VI) stable for the extraction process is required. IEC 62321 cites EPA 3060A as a pretreatment method for the quantitative analysis of Cr(VI) in polymer in the Informative Annex [2]. However, when we performed extraction tests of Cr(VI) in polyethylene (PE) powder following the EPA 3060A method, the recovery was very low, about 3%. When thermoplastics are heated, they become soft, changing from a solid state to a liquid state. Moreover, we have found that PE polymer is dissolved by some kinds of fatty acids. Using these properties, we applied liquid/liquid extraction methods for Cr(VI) in PE. We report the effective extraction method of using fatty acid for Cr(VI) in the most difficult polymers such as PE [3]. In particular, it was confirmed whether the valence of Cr changed or not in the extraction process, by XAFS analysis.

XAFS measurement using synchrotron radiation was performed at beamline **BL14B2**. For the

fluorescence yield method, a 19-element Ge solid-state detector was used. The intensity was normalized by using the average intensity from 6300 to 6500 eV in which negligible oscillation was observed.

The sample of PE containing Cr(VI) was made by adding lead chromate (PbCrO_4) or zinc chromate (ZnCrO_4) to PE. The Cr(VI) concentration was set to 1%. Five kinds of fatty acids (oleic acid, linoleic acid, nonanoic acid, octanoic acid and heptanoic acid) were selected as solvent with a boiling point of 200°C and melting point below room temperature. The PE samples containing Cr(VI) were heated with each fatty acid to obtain uniform solutions. These solutions were packed in polyethylene bags for XAFS measurement.

Chromium sulfate ($\text{Cr}_2(\text{SO}_4)_3$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were measured by XAFS as standard materials and the results are shown in Fig. 1. In the case of measuring Cr(VI)-containing samples, a pre-edge peak at 5992 eV was observed. This pre-edge peak corresponds to the electric dipole transition from the 1s core state to the p component in the d-p hybridized orbital [4]. We can judge whether chromium is hexavalent or not by confirming the presence of this pre-edge peak. The solutions of PE containing lead chromate dissolved by fatty acids were measured by XAFS. The results are shown in Fig. 2. In the case of using nonanoic acid, octanoic acid and heptanoic acid, the pre-edge peak intensity was lower than the intensity obtained when using oleic acid and linoleic acid. This indicates that the valence change from Cr(VI) to Cr(III) occurred in the dissolving process. The fatty acids have the carboxyl group (-COOH) in the molecular chain end,

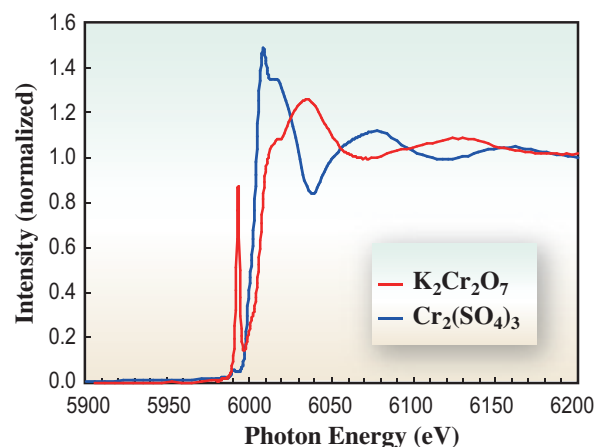


Fig. 1. XAFS spectra of Cr standard materials.

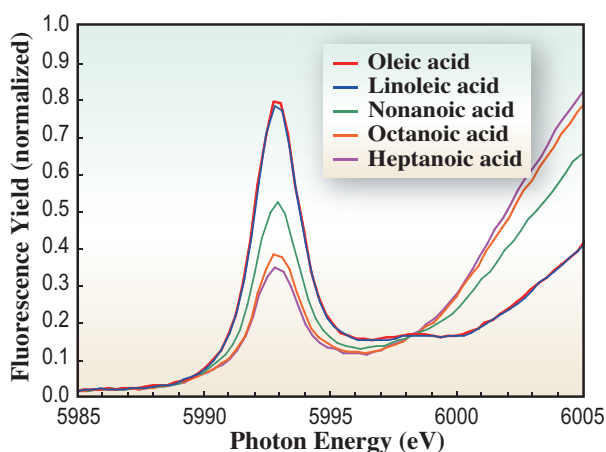


Fig. 2. XAFS spectra of lead chromate containing plastics dissolved by five kinds of fatty acids.

and the carboxyl group is acid. The valence change of Cr(VI) is thought to be attributable to this acid character. For the PE sample containing zinc chromate, the results are shown in Fig. 3. Similarly to the case of lead chromate, the pre-edge peak intensity was low in the cases of dissolution by nonanoic acid, octanoic acid and heptanoic acid. From the above results, it was found that linoleic acid and oleic acid are suitable for dissolving PE without changing the valence of Cr. It is thought that oleic acid and linoleic acids have long carbon chains, and therefore, the valence of Cr is not changed. However, the viscosity

of the solution dissolved by oleic acid became higher with lower temperature. Therefore, we investigated the extraction method using only linoleic acid. The PE sample containing lead chromate was dissolved by linoleic acid and then added to KOH solution to extract Cr(VI). The concentration of Cr(VI) in KOH solution was measured by diphenylcarbazide colorimetry. The calculated recovery relative to the amount of added Cr(VI) of about 80% was achieved, which was much higher than the recovery obtained by the EPA 3060A method. This method enables us to determine the concentration of Cr(VI) in polymer samples.

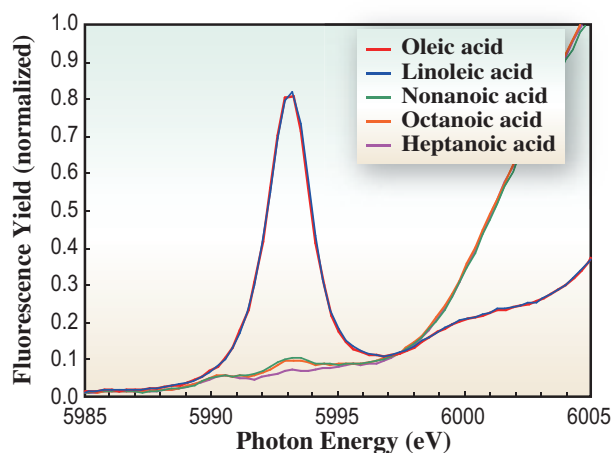


Fig. 3. XAFS spectra of zinc chromate containing plastics dissolved by five kinds of fatty acids.

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