

2005A0894-RI-np-TU

BL19B2

XAFS analysis of residual Sb Catalysis in PET polymers by fluorescent X-ray detection  
Kazunari Shiozawa(15854), Tomoyoshi Sasakawa(15276), Masayoshi Aoki(17000)  
Mitsui Chemical Analysis & consulting Service Inc.(mc-Anac)

### Introduction

Polyethylene terephthalate (PET) is widely used many common convenience products as transparent polymer. PET is made by using antimony compounds as polymerization catalyst. In PET, Sb of residual catalyst remained between about 100 to 300ppm(wt). It was thought that state of residual Sb influenced quality of PET polymer. So, XAFS analysis of residual Sb in PET were planned. But, in transmission mode of XAFS measurements, specially thick samples were need to gain the sufficient edge jump for XAFS analysis of low concentration element. Then, we used fluorescence method of XAFS measurements.

### Experimental

PET contained about 200wtppm Sb is molded as 2 or 3mm thickness flat plate. For transmission mode, these plates cut at small peaces of 1cm square. And we made rod of about 20cm length layered these small peaces. Another way, for fluorescence measurements, we use one plate. Sb metal,  $\text{Sb}_2\text{O}_3$  and Sb triacetate were prepared as standard materials. XAFS measurements were carried out at BL19B2 with Si(111) double crystal monochromator and Rh-coated mirror. Sb K-edge XAFS spectra for PET were collected at fluorescence mode using 19-elements Ge solid state detector and transmission mode, and for standard materials were recorded at transmission mode only. XAFS data were analyzed by REX2000(Rigaku Co.).

### Result and Discussion

Figure 1 and Figure 2 shows Sb K-edge X-ray absorption profile at transmission and fluorescence mode respectively. In these result, it was found that fluorescent XAFS profile stood comparison with transmitted it. It was clearly seen that fluorescence mode has advantage over transmission mode in XAFS analysis of residual Sb Catalysis in PET for easy sample preparation. Figure 3 shows EXAFS Fourier transforms(FT) for PET and standard materials. Sb(III) standard materials ( $\text{Sb}_2\text{O}_3$ , Sb triacetate) were clearly observed first and second nearest FT peak. But, Sb in PET was only observed first nearest one assigned Sb-O distance. Figure 4 shows XANES region of Sb K-edge profile. In this result, absorption energy was same at all.

Shape of absorption profile was similar between Sb(III) standard materials ( $\text{Sb}_2\text{O}_3$ , Sb triacetate) and Sb in PET. Therefore, residual Sb in PET was guessed Sb(III). But, due to only Sb-O first nearest peak at PET was existed in FT analysis, the local environment of Sb in PET was different from Sb(III) standard materials ( $\text{Sb}_2\text{O}_3$ , Sb triacetate).

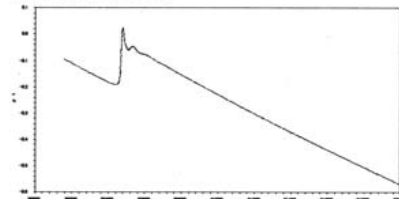


Figure 1 Sb K-edge XAFS profile of transmission mode at PET

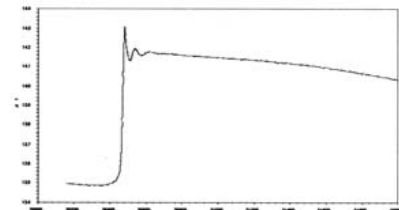


Figure 2 Sb K-edge XAFS profile of fluorescence mode at PET

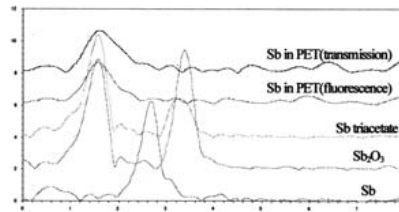


Figure 3 Fourier transforms analysis for PET and standard materials

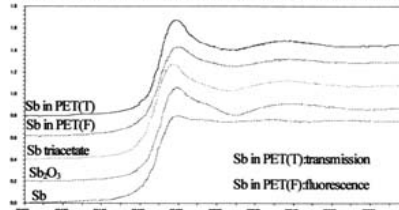


Figure 4 XANES region of Sb K-edge profile

2005A0895-RI-np-TU

BL19B2

## Chemical State of Ca in Calcium Silicate Complex Oxide Studied by XAFS

S. Matsuno<sup>1</sup> (7649), J. Kikuma<sup>1</sup> (15726), T. Araki<sup>1</sup> (16957), Y. Mitamura<sup>1</sup> (16287),  
H. Matsuyama<sup>1</sup> (16614) and T. Honma<sup>2</sup> (2073)

1) Asahi KASEI Corporation, 2-1, Samejima, Fuji, 416-8501

2) JASRI, 1-1-1, Kouto, Mikazuki, Sayou-gun, Hyogo, 679-5198

The major hydration product of Portland cement is an amorphous calcium silicate hydrate (C-S-H), which is thought to be a poorly organized layered structure related to tobermorite. C-S-H composition varies over a wide range of Ca/Si ratios (from 0.6 to 2.0) accompanied by structural changes depending on the composition. This study investigates the relationship between variations in Ca/Si ratios and chemical state of Ca in C-S-H gels.

XAFS experiments were carried out at the beamline BL19B2. The incident X-ray was obtained by a double-crystal Si(111) monochromator. The higher harmonics in the incident beam were eliminated by detuning and by using two Rh-coated mirrors set at 7 mrad. EXAFS spectra of Ca in Ca/Si=0.6 after detune is shown in Fig 1.

We measured Ca K-edge XAFS of C-S-H gels of Ca/Si=0.6, 1.0, 1.4 with transmission mode. Figure 2 shows radial structure functions derived from EXAFS spectra. The peak of 0.19nm is corresponding to Ca-O. There are not great differences in radial structure function. The further analysis is in progress.

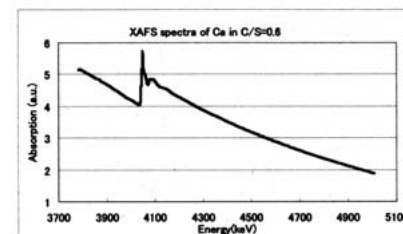


Fig. 1 EXAFS spectra of Ca in Ca/Si=0.6 after detuning

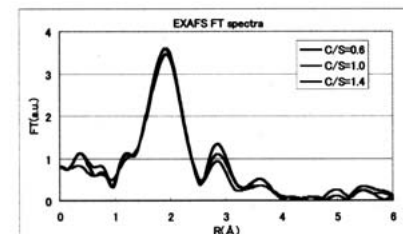


Fig. 2 Radial structure functions of Ca-K EXAFS