

In-situ S K-edge XAFS study of rubber compound in the heating process by using the conversion electron yield method

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Adding sulfur to a natural rubber and heating is known to be an important process of the rubber manufacturing to enhance the elasticity of the rubber. In the process, called ‘vulcanization’, sulfur works to make bridging between molecular chains to form a molecular network structure. Although many studies have been done to clarify the reaction mechanism, the details are not clear yet. Recently we studied the mechanism at the XAFS beamline, BL-10 in the SR center [1]. S K-edge XAFS spectra were taken sequentially at 140 °C with the partial fluorescence yield (PFY) mode by using silicon drift detector (SDD). The sulfide bond formation through S cross-linking was revealed qualitatively. However, it is noted that the PFY mode is rather bulk sensitive and the surface structure has not been clarified yet.

The total electron yield (TEY) mode is usually adopted to obtain surface XAFS, but it sometimes suffers from charging effect in the case of an insulating sample, such as rubbers. To overcome this problem, we developed the conversion electron yield (CEY) method and applied it to investigate the surface behavior of the rubber compound in the heating process. Figure 1 shows S K-edge XAFS spectra of an untreated rubber, taken simultaneously with the TEY and CEY modes. The TEY spectrum is very noisy because of the serious charging effect.

Isoprene rubber was mixed with N-cyclohexyl-2-benzothiazole sulfonamide (CBS),

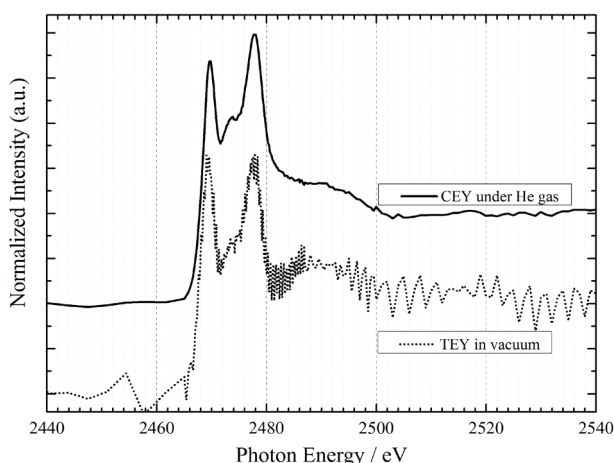


Figure 1. The spectra of an untreated rubber, obtained by the CEY and TEY method.

stearic acid, zinc oxide and sulfur into the isoprene compound by double roller. The sample prepared was mounted on a sample holder made of SUS304, because SUS304 prevents chemical reaction between sample and sample holder. Subsequently, the sample was installed in the atmosphere pressure helium gas chamber of BL-10. The experimental setup is shown in Fig. 2. For the CEY method, a metal grid was set in front of the sample holder by about 20 mm, and -300 V was applied to the grid to pull He^+ ions. The sample leak current was measured with a pico-ammeter.

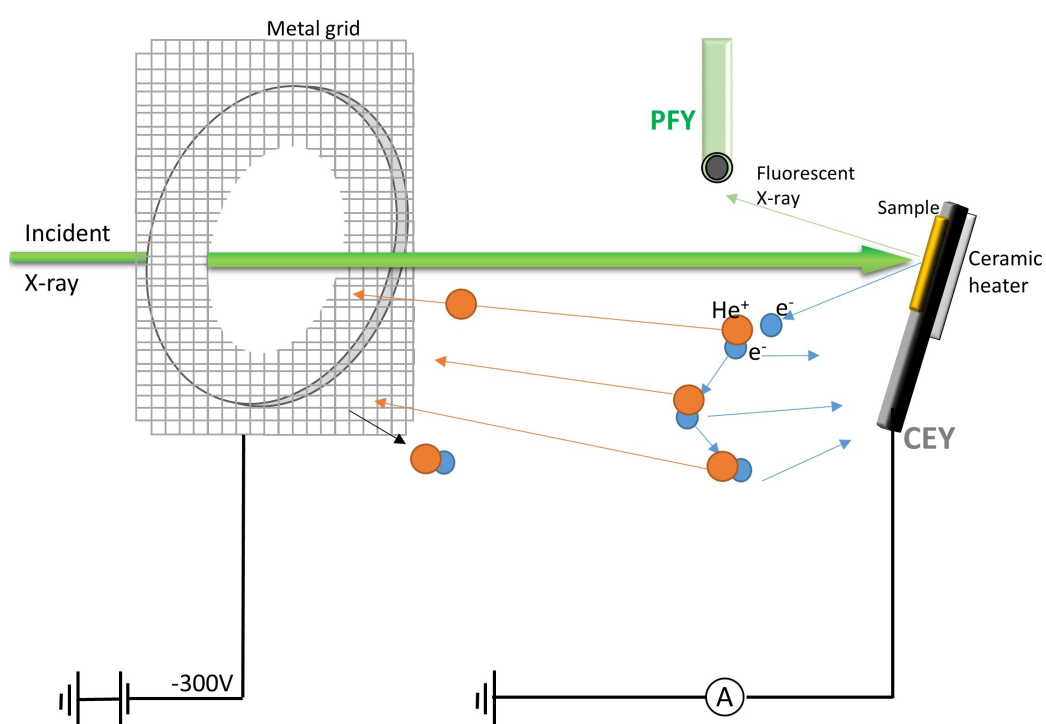


Figure 2. A schematic drawing of the CEY experimental setup. High energy Auger electrons ejected from the sample collide He atoms one after another and generate many He^+ ions and electrons in the process of losing the energy. He^+ ions thus produced are accelerated to the metal grid and remained electrons are pulled back to the sample. As a result, the TEY spectrum with the leak current measurement has an opposite polarity of the conventional one.

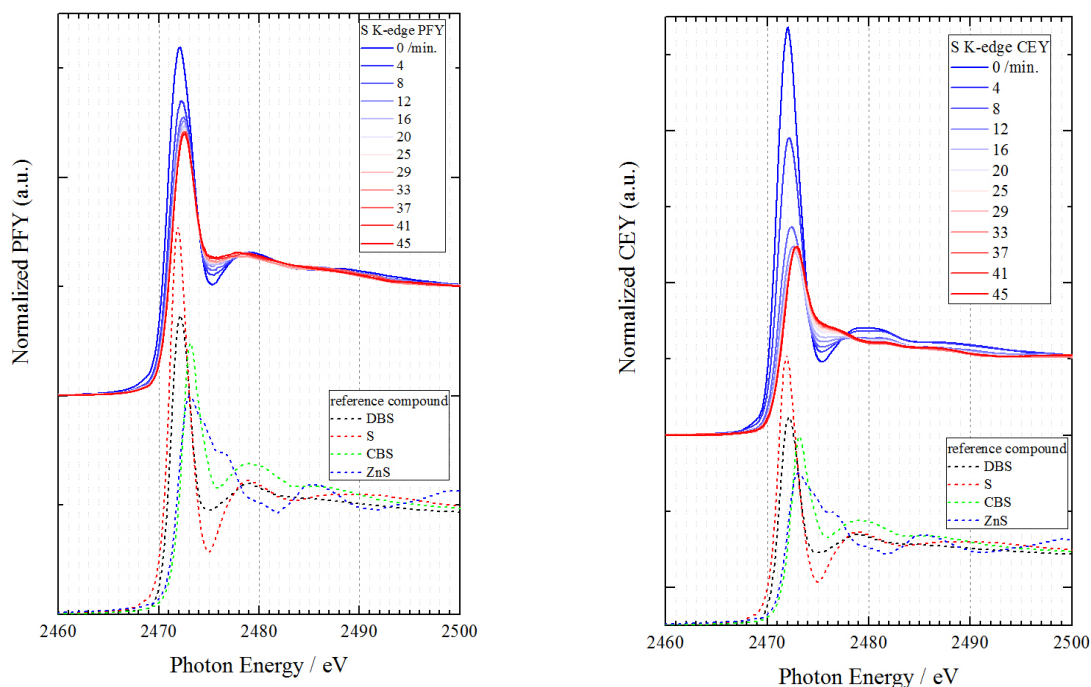


Figure 3. The in-situ XAFS spectra obtained by (a) PFY (b) and CEY method. All heating and XAFS measurement time was 45 minutes. The lower spectra are reference spectra of CBS, di-sulfide (DBS), sulfur (S) and zinc sulfide (ZnS).

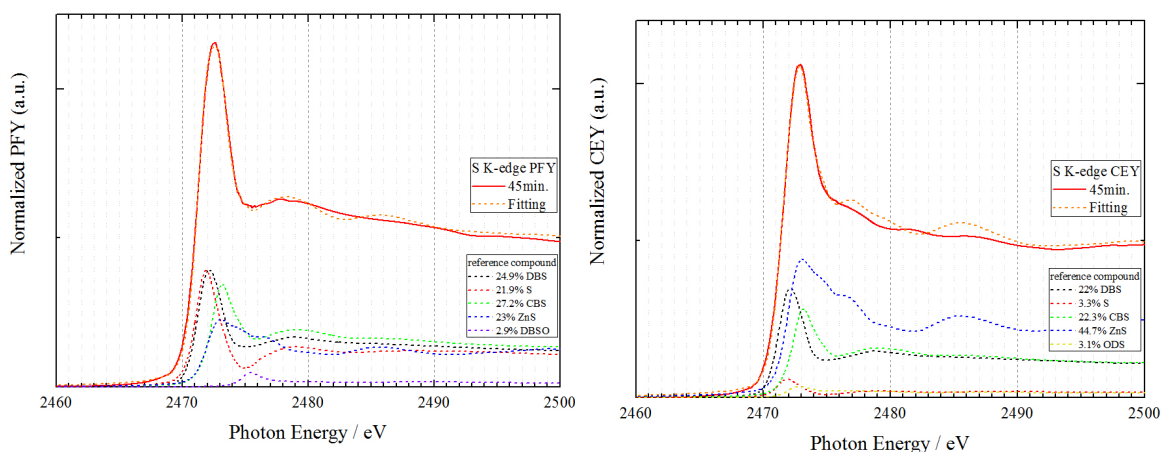


Figure 4. The in-situ XAFS spectra obtained by (a) PFY (b) and CEY method at 45 minutes. The broken line named Fitting is linear combination fitting of reference spectra showed lower position in each graph. ODS indicates mono-sulfide bond, and DBSO indicates di-n-butyl sulfoxide.

We found a clear difference between the PFY and CEY spectra. The spectra of rubber compound heated for 45 minutes were analyzed by the linear combination fitting of the reference spectra of the possible constituents, as shown in Fig.4. Note that the element sulfur is reduced significantly in the surface region. It probably occurred due to sublimation of sulfur or diffusion of sulfur into the bulk.

S K-edge XAFS spectra of the sample were taken sequentially at 140 °C, both with the CEY and PFY modes. Figure 3 shows the changes of the PFY and CEY spectra as a function of elapsed time; the white line shifts to higher energy, and the bump at 2478 eV smears out gradually.

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The present work also demonstrates that the CEY mode is very effective for taking XAFS spectra of insulating samples and that the simultaneous use of the PFY and CEY modes is a powerful tool to probe surface and bulk of a sample.

Reference

- [1] Y. Ikeda et al. Project for Creation of Research Platforms and Sharing of Advanced Research Infrastructure (R1247)