XAFS Analysis of O K-edge of the Rubber for Metal Adhesion in Tire

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Steel wires are used in tires to improve the durability and performances. A small amount of fatty acid cobalt salt is contained in the rubber for metal adhesion, which improves the adhesiveness with the steel wire and the wet-heat adhesive property. According to the XAFS measurement, it was found that cobalt salt reacts with sulfur in rubber and cobalt sulfide (CoS) forms after the vulcanizing. However, it is not clarified whether the fatty acid cobalt dissociates and becomes cobalt hydroxide during rubber mixing, and the chemical state of fatty acid cobalt after vulcanization. The knowledge of the dissociation of cobalt species is important to predict the quality of rubber during the storage in the uncured state. Clarifying chemical state of fatty acid after vulcanization is useful to control vulcanization reaction and improve durability. In this study, O K-edge XAFS measurement was carried out to clarify the chemical state of fatty acid cobalt before and after rubber mixing, and after vulcanization.

Synthetic isoprene rubber not containing fatty acids was used because natural rubber has fatty acids. Considering the sensitivity of XANES measurements, 10phr of cobalt stearate as the fatty acid cobalt was added to the isoprene rubber. Furthermore, carbon black and zinc oxide were mixed at 150°C, and then sulfur and a vulcanization accelerator were mixed at below 100°C. Further vulcanization was carried out at 160°C for 20 minutes to prepare a cured rubber. The XANES measurements at O K-edge were carried out at BL-11 of the SR Center at Ritsumeikan University by partial fluorescence yield (PFY) mode. We measured the uncured rubber after high-temperature mixing (150°C) and the cured rubber after vulcanization with the reference samples of cobalt stearate, cobalt hydroxide, stearic acid and zinc stearate.

Figure 1 shows O K-edge XANES spectra of the uncured rubber, cobalt stearate, and cobalt hydroxide. For the uncured rubber, the sharp peak at 532 eV is observed, which position is with the spectrum in cobalt stearate. On the other hand, the spectrum of cobalt hydroxide which is considered to be formed as a dissociated state has the broadening structure from 535 to 545 eV, which is not found in the uncured rubber. The high-intensity peak at 535 and 538 eV of the uncured rubber is observed, which corresponds to the zinc oxide contained in rubber. From these results, it is found that cobalt stearate does not dissociate in uncured rubber because sulfur does not exist at high temperature mixing.

Figure 2 shows the O K-edge XANES spectra of the cured rubber, stearic acid and zinc stearate. During vulcanization, stearic acid and zinc combine to form the characteristic structure [1]. The sharp peaks in the cured rubber, stearic acid, and zinc stearate locate at 532.1, 531.8 and 532.4 eV, respectively. The peak at 536 eV is due to zinc oxide in the rubber. From these results, zinc stearate and stearic acid are contained in the rubber for metal adhesion after vulcanization.

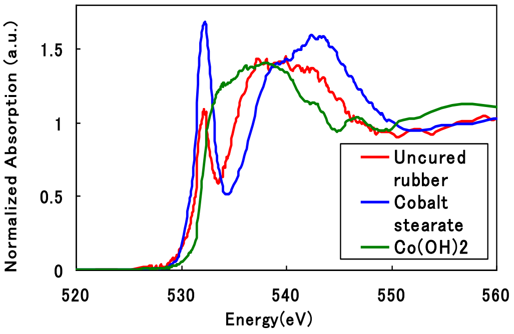

Fig. 1 O K-edge XANES spectra of the uncured rubber after mixing at 150 °C.

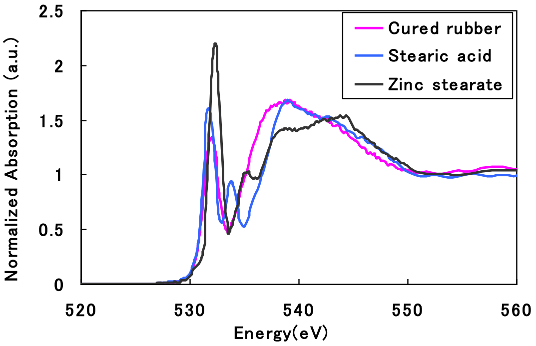

Fig. 2 O K-edge XANES spectra of the cured rubber.

Reference

(1) Y. Ikeda *et al.*, *Macromolecules*, **2015**, 48(3), 462-475.