Analysis of variation of sulfidic linkages during vulcanization

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1. Introduction

A lot of rubber products have been extensively used in our society and most of them are prepared by a cross-linking reaction. Among the cross-linking reactions, sulfur cross-linking, namely, vulcanization is the most traditional and important reaction to give a three-dimensional network structure to rubber products.[1] It is well-known that a mixture of several kinds of sulfidic linkages is formed in the vulcanizates during the reaction. Mechanical and thermal resistances of the vulcanizates are drastically affected by a sequence of the sulfidic linkages. Therefore, it is important to analyze the sulfidic linkages in rubber material science, and sulfur K-edge X-ray absorption near edge structure (S K-edge XANES) measurement has also been utilized for the characterization[2]. However, most studies were not enough, because arguments about unreacted sulfur curing reagents were not accomplished. In this study, thus, the S-XANES measurement was conducted for solvent-extracted vulcanizates.

2. Experiments

Isoprene rubber (IR) compounds were prepared on a two-roll mill by mixing with 0.5 parts per one hundred rubber by weight (phr) of zinc oxide, 2 phr of stearic acid, 1 phr of *N*-(1,3-benzothiazol-2-ylsulfanyl) cyclohexanamine, and 1.5 phr of elemental sulfur (S_8). Cure behavior of the IR compound was measured at 140 °C by using a curelastometer. Thin films of about 0.2 mm thickness were prepared by heat-pressing at 140 °C for 18, 22, 26, 30, and 40 min according to a variation of torque obtained from the cure measurement. The obtained films were subjected to solvent extractions using a mixed solvent of chloroform and acetone twice and tetrahydrofurn twice at 25 °C for 24 hours, respectively. Reference samples of mono-, di-, and polysulfidic linkages were prepared by mixing octadecyl sulfate (ODS), dibenzyl disulfidic (DBS), and S_8 with IR, respectively. S K-edge XANES measurement was performed at r.t. by using a transmittance mode in BL10, SR center of Ritsumeikan University.

3. Results and discussion

Fig. 1(A) shows S K-edge XANES spectra of the samples which were prepared by varying the heat-pressing times. It can be seen that the S K-edge XANES spectra of IR samples showed similar peak top positions observed around 2472 eV. In case of the reference samples, peak top positions were observed at 2473.02, 2472.42, and 2472.24 eV for mono-, di-, and polysulfidic linkages, respectively. Therefore, the result shown in Fig. 1(A) suggests that a disulfide type is a main one for the sulfidic linkages formed in the samples.

The peak top positions are plotted against the time of heat-pressing with the curing curve in Fig. 1(B). It was detected that the peak position shifted to the lower energy from 18 – 22 min and followed by shifting to the higher energy after 22 min. The former may be ascribable to an effect of oxidation of sulfidic linkage by an evidence of an oxidation peak observed around 2482 eV. The latter is ascribed to a reversion of the vulcanization, i.e., a cleavage of sulfidic linkages from polysulfide/disulfide types to disulfide/monosulfide types. Effect of fraction of poly-, di- and mono-sulfidic linkages on the mechanical properties of the vulcanizate will be reported elsewhere.

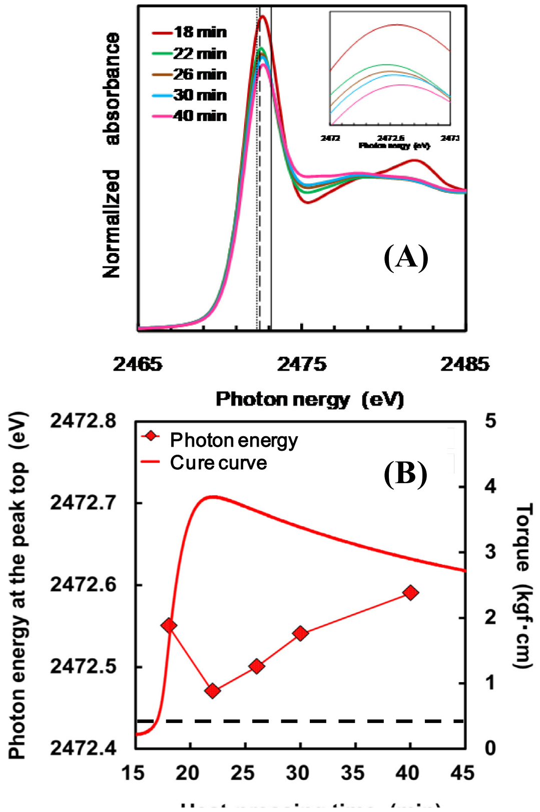

Fig.1 (A) S K-edge XANES spectra of the samples. Dotted, dashed and solid lines indicate the peak top positions of mono-, di- and polysulfidic linkages determined by using the reference samples, respectively. The inset displays spectra around peak top energies. (B) Relationship between the cure curve and the peak top energy at each heat-pressing time. The dashed line is the energy of the peak top of disulfidic linkage.

References

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[2] For examples, R. Chauvistré, et al., *Kautsch. Gummi Kunstst.*, **45**, 808(1992).