

Chemical bonding states of synthetic rubbers based on SBR

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Adding a filler to a compound can significantly change the mechanical properties of the compound. The mechanical property changes are estimated to be caused by an nm-size bound-rubber structure formed between the filler particles. Using styrene-butadiene rubber as a compound and silica as a filler, micro absorption spectra were measured by STXM to obtain the chemical bonding state of the bound rubber structure. The obtained spectra around the C-K absorption edge showed that: a spectral difference related to the compound difference, and a spectral difference originated from the structural difference.

1 Introduction

Synthetic rubber materials adding a filler material such as carbon black to an elastomer material can significantly change the mechanical properties of the elastomer: stress properties, tensile strength, and abrasion resistance [1]. The factors of the changes in mechanical properties are not well understood, but the type and the number of filler particles to obtain the desired mechanical properties are known empirically. The structure of the synthetic rubber material differs at each scale and exhibits a hierarchical structure [2-4]. Among the hierarchical structure, we presume that the chemical-bonding- and the 3D- structure of the bound-rubber structure formed between filler particles determine the overall mechanical properties.

To clarify the chemical bonding state of the bound rubber structure, it has been performed that quantification of the solvent insoluble fraction by the solvent swelling method and structural analysis using the swelling state by the small-angle scattering method [2]. These findings are average of the structural data since the size of the bound rubber structure is the order of 10 nm observed under an electron microscope. When considering the case of silica as a filler as an example of the chemical bonding state of the synthetic rubber material, it is expected that chemical species such as silanol groups in silica, functional groups in the elastomer material, and silane coupling agents added to the elastomer material are involved in the chemical bonding between the fillers [1]. If the chemical bonding state and spatial distribution of the bound rubber structures can be clarified by measuring the absorption spectra of the bound rubber structures, the origin of the mechanical property improvements will be understood. We would like to accomplish this by measuring nm-scale absorption spectra using STXM.

In this study, we will add filler materials and/or reagents to elastomer materials the mechanical properties are known, then the chemical states of the bound rubber structure and its spatial distribution will be measured using the STXM. We believe that this process will clarify the origin of the mechanical properties.

2 Experiment

The compounds of the measurement sample were styrene-butadiene rubber (SBR) to which reagents and vulcanization agents were added. Next, silica was added to the compounds, and finally, a coupling material was added to the compounds with silica.

After kneading the respective materials, cross-linked materials were prepared and then sectioned using an ultramicrotome. Each section was mounted on a microgrid and then fixed in a sample holder for STXM. Compounds that SBR was changed to a modified SBR were also subjected to the same treatment, and the results were compared with those of samples based on native SBR. All the measurement time per point was fixed as 2 msec. As a result of preliminary measurement under the same field of view, since the structures in the sample changed with time by STXM measurement at a spot diameter smaller than 100 nm, STXM measurement was carried out at a spot diameter of 100 nm which the structure did not change within the measurement time.

The measured STXM spectral image sets were transformed into optical density image sets, then the image sets were subjected to principal component analysis and separated into spectral structures and noise components. New spectral image sets were created using the separated spectral structures. Cluster analysis was made for the new spectral image sets, and the correspondences were obtained between spectral- and spatial-distribution-structures.

3 Results and Discussion

In the measurement result of the C-K absorption edge, it was found that (1) a change in the spectral shape was observed with or without the modification of SBR (FIG. 1), and (2) the structure around the vacancies formed in the samples (structure A in FIG. 2) showed a similar spectral shape regardless of the reagents. In addition, a comparison of the optical microscope images suggests that a part of structure B in FIG. 2 includes the fillers with the bound rubber structure (Structure B and C in FIG. 2).

Based on peak shapes and the energy positions of reference materials, the spectral difference between the elastomer materials designated as bars in Fig. 1 is originated from: peak A is a transition to the π^* orbital of

the C=C bond, peak B is a transition to the C-H* bonding, and peaks C and C' are transitions to the σ^* orbitals of the C bonds [5]. The peak structures were commonly observed in all samples, although their spectral intensities were different for each sample and there were also differences in the presence or absence of microstructures.

The observed spectral structure of the region containing the fillers was that derived from C- and H-bonds. The measurement of the O-K absorption edge will be necessary adding to that of the C-K absorption edge to separate the structure based on the expected silanol group, and the measurement of the S-L_{2,3} absorption edge will be necessary to separate the structure based on each reagent.

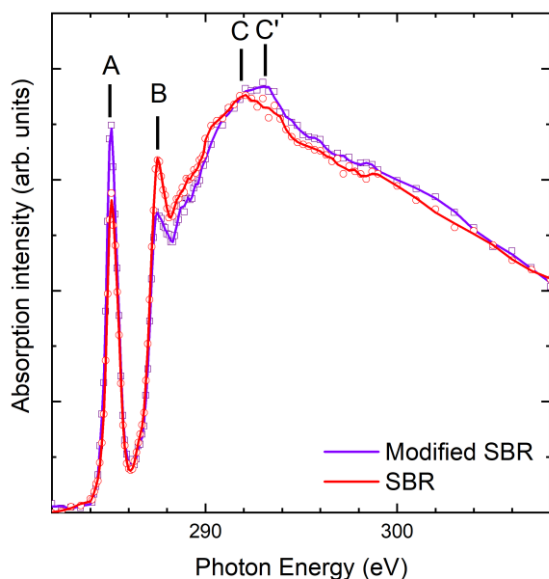


Figure 1: C-K edge spectra of SBR and modified SBR with the same-filler and reagents. Spectral intensities are normalized by the background intensity. Curves are smoothing results for a guide to see.

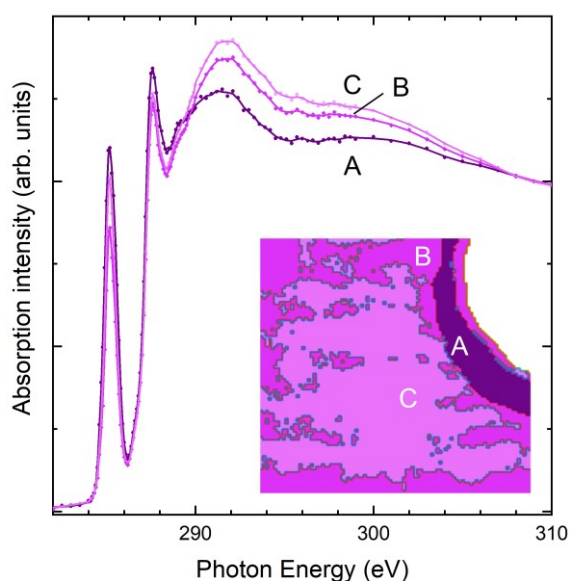


Figure 2: Separation result of spatial and spectral structure of the sample in which silica was added as the filler to SBR. The C-K absorption edge spectra corresponding to the structure A, B, and C color-coded in the figure are indicated by their corresponding colors and symbols. The image size in the figure is $7 \times 7 \mu\text{m}^2$. The space in the upper right of the image is the void in the sample.

Acknowledgment

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