Thesis Abstract

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1. Thesis Title

Study on Sulfur Cross-Linking of Isoprene Rubber *via* Dinuclear Bridging Bidentate Zinc/Stearate Complexes

2. Thesis Abstract

To reveal the sulfur cross-linking reaction of isoprene rubber, modern approaches such as synchrotron X-ray analysis and density functional theoretical (DFT) calculation were subjected. A network structure formed by a sulfur cross-linking reaction of isoprene rubber when *N*-(1,3-benzothiazol-2-ylsulfanyl) cyclohexanamine was used as an accelerator consists of the mesh network with low network-chain density and domain network with high network-chain density. In this thesis, the role of the dinuclear bridging bidentate zinc/stearate complexes which was formed in the mesh network was investigated, and the effect on the sulfur cross-linking reaction and sulfidic linkages was revealed.

This thesis consists of four chapters. Chapters 1 and 2 aim to the role of the dinuclear bridging bidentate zinc/stearate complexes on the sulfur cross-linking reaction, and chapters 3 and 4 aim to the evaluation of sulfidic linkages formed by the zinc dinuclear complexes. In chapter 1, clarification of the zinc dinuclear complexes during the sulfur cross-linking was conducted using *in situ* zinc K-edge X-ray absorption fine structure (Zn K-edge XAFS) spectroscopy, *in situ* infrared spectroscopy, and rheological measurement, along with DFT calculations. In chapter 2, on the basis of *in situ* Zn K-edge XAFS spectroscopy, the amounts of the zinc dinuclear complexes are quantitatively measured, and several byproducts are identified to explain the proposed mechanism. In chapter 3, using sulfur K-edge X-ray absorption near edge structure (S K-edge XANES) spectroscopy, the effect of solvent extraction was quantitatively determined. It was found that unreacted reagents prevent the correct evaluation of sulfidic linkages due to the presence of sulfur content. In addition, it was suggested that the zinc dinuclear complexes tend to generate the disulfidic linkages during reaction. In chapter 4, S K-edge XANES

spectroscopy revealed that disulfidic linkage was dominantly generated even though zinc stearate was used as an activator for sulfur cross-linking reaction instead of ZnO and stearic acid.

This thesis revealed that the dinuclear bridging bidentate zinc/stearate complexes play an important role in the sulfur cross-linking reaction of isoprene rubber.