Vulcanization reaction of squalene and \( S_8 \) powder studied by Sulfur K-edge NEXAFS under liquid phase

S Yagi\(^1,2,3\), Y Menjo\(^2\), C Tsukada\(^3\), S Ogawa\(^2\), G Kutluk\(^3\), H Namatame\(^3\) and M Taniguchi\(^3\)

\(^1\)Green conversion section, EcoTopia Science Institute, Nagoya University, Nagoya 464-8603, JAPAN
\(^2\)Graduate School of Engineering, Nagoya University, Nagoya 464-8603, JAPAN
\(^3\)Synchrotron radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, JAPAN

E-mail: s-yagi@nucl.nagoya-u.ac.jp

Abstract. Vulcanized rubber materials are useful in our surroundings. However, detail structure and reaction are not revealed even in present. Since squalene molecule possesses some same properties compared with natural rubber, we have prepared the samples of vulcanized squalene at 140 °C for several hours. To understand the vulcanization reaction, sulfur K-edge NEXAFS measurements have been carried out for the vulcanized squalene under liquid phase with He-path system and fluorescence detection mode. Moreover, we have tried curve fitting analysis of NEXAFS spectra. The results indicate that the squalene has been vulcanized by the \( S_8 \) molecule at 140 °C and the \( S_8 \) molecule length is shortened from 8 to 5-6 after the vulcanization reaction.

1. Introduction
Vulcanization reaction has been invented by C. Goodyear in 1839 [1]. Natural rubber is vulcanized by sulfur powder and the vulcanized rubber materials have been used historically in our surroundings. The rubber materials possess unique physical properties such as high elasticity and restoring force, and can be used to the bio-functional materials. Furthermore, the rubber materials are also considered to apply to bio-implant because it is chemically stable. For example, the vulcanized rubber, which possesses some interactions with the solid state surface, can be used in many industrial fields. Therefore, the vulcanized rubber has many possibilities and is paid attention in recent years.

Though the natural rubber consists of polymers of the organic compound isoprene (cis-C\(_5\)H\(_8\)), the natural rubber includes minor impurities of other organic compounds as protein and fatty acid molecules. It is thought that the properties of rubber materials are influenced greatly by the existence of both the structural difference and the impurities. Therefore, the control of the properties of the rubber materials is very difficult [2,3,4].

The rubber materials are produced by heating the mixture of raw rubber classified in terms of high polymerized hydrocarbon compound, sulfur powder (\( S_8 \)) and other added materials. The \( S_8 \) reacts with the carbon chains in the raw rubber. This reaction is called "bridged reaction". The physical properties of the rubber materials depend upon the three-dimensional structure by the bridged reaction. Generally, the reaction and the structure are known as “vulcanization reaction” and “bridge structure”, as shown in figure 1, respectively. Even in present time, the mechanism of the vulcanization reaction has not
been firmly resolved. In that sense, we are thinking the vulcanization reaction is complex. To understand the vulcanization reaction and the bridge structure is important to synthesize the vulcanized rubber materials. However, it is very difficult to mix the vulcanization reaction reagent with the raw rubber in the laboratory by its high viscosity.

Squalene has some specific properties, which are liquid phase hydrocarbon compound, same monomer of natural rubber and less impurities. Take into account of those factors, we propose the squalene instead of the raw rubber in this study. But there is a few manuscripts written about the vulcanization reaction with the squalene [5,6]. The purpose of this study is to understand the vulcanization reaction for the bridge structure with reaction time variation using sulfur K-edge NEXAFS (near-edge X-ray absorption fine structure) measurement.

![Figure 1. Schematic view of vulcanized rubber and bridge structure by Sx (x=1-8).](image1)

![Figure 2. Photographic view of vulcanized squalene with polyethylene film cell for NEXAFS measurement.](image2)

2. Experimental

The reagents of the squalene (2.5 g: KATAYAMA CHEMICAL INDUSTRIES Co., LTD.) and the S8 powder (50 mg: KATAYAMA CHEMICAL INDUSTRIES Co., LTD.) were mixed into closed vials under Ar atmosphere to avoid the air oxidation. The mixed samples were stirred at 140 °C for several hours (0, 3, 6, 9 and 12 h). Sulfur K-edge NEXAFS measurement of the vulcanized squalene samples was carried out by fluorescence X-ray yield mode using the atmospheric XAFS measurement system with He-path at the BL-3 on HiSOR [7] and the BL6N1 on Aichi Synchrotron Radiation Center (AichiSR) beamlines. Those soft X-ray beamlines were used the InSb(111) crystals in the monochromator system. Especially, the synchrotron facility of the electron storage ring in AichiSR was operated at the top-up mode. The photon energy was calibrated on the assumption that the first peak of K2SO4 powder appears at 2481.70 eV. The fluorescence yield detections at BL-3 and BL6N1 were employed using a UHV-compatible gas-flow type proportional counter with P-10 gas (10 % CH4 in Ar) and a SDD (silicon drift detector), respectively. We used polyethylene film cell with about 12 μm thickness for liquid samples, as shown in figure 2. In fact, a slight sulfate contaminant such as SO3 and/or SO4 was observed in the film cell. However, because the sulfur component amount contained in the measurement sample was large, a large problem did not occur. The sulfur K-edge NEXAFS spectrum for the contaminants of SO3 and SO4 of the film cell were shown in figure 3.
3. Results and discussion

Figure 3 shows sulfur K-edge NEXAFS spectra for the vulcanized squalene samples reacted at 140 °C for several hours and the background of contaminants described in Experimental section. All NEXAFS spectra, except BG, are normalized by the edge-jump value. Moreover, an inset is also shown by magnified photon energy area. The structures of BG spectrum mean that some sulfur contaminants as thiol and sulfate are existing in the cell membrane, but the amount of those contaminants are extremely little. Thus we conclude that the BG structures never affect the NEXAFS spectra of vulcanized squalene. In our study, though we have detected the sulfur signals by use of the fluorescence detector, usually this detection method produces a self-absorption effect [8,9,10]. According to the self-absorption effect, the peak intensity is including some error. The first peak is observed at 2471.8 eV in start phase, which means the reaction time for vulcanization is 0 hour in figure 3. The peak intensity is approximately 4.4 compared with the edge-jump value. This value is almost same as the result reported by I.J. Pickering et al. and G.N. George et al. [11,12]. This comparison indicates that our NEXAFS spectra include little the self-absorption effect in spite of using the fluorescence detection. Thus, the S₈ materials are existing under highly dispersed condition in the squalene. In other words, when someone obtains XAFS spectra of highly dispersed molecularly or atomically by means of the fluorescence detection, there is no self-absorption effect.

The first peak at 2471.8 eV is assigned to the transition from sulfur 1s to anti-bonding molecular orbital σ*(S-S). But this peak position is not same as the position of S₈ powder of 2471.6 eV, which is not shown in figure 3. It is thought that the bond length of S-S in S₈ powder in squalene matrix is slightly shorter than that of S₈ powder in vacuum. The first peak shifts to 2472.2 eV continuously with reaction time in 12 hours. In addition, the peak position after 12 hours does not match the position of the monosulfide vulcanized squalene of σ*(S-C) at 2472.8 eV reported by S. Inoue et al. [13]. This
result means that the chemical state of vulcanized squalene after 12 hours is not single chemical state, but the mixed materials of S₈ and monosulfide states. Considering that the intensity of the peak is decreased gradually proportional to the reaction time, the spectrum change means the specific reaction. Concretely, the reduce of first peak intensity and the shift of peak position suggest the decrease of the number of S-S bond and the creation of S-C bond.

It is necessary to carry out the curve fitting of the NEXAFS spectra to estimate quantitatively the decrease and the increase the peak intensities correspond to the S-S or S-C bond element. The curve fitting needs the energy position of ionization potential of sulfur 1s level. Usually the ionization potential is measured by means of XPS (X-ray photoelectron spectroscopy) technique. But we cannot measure the chemical state of the sulfur, since our samples are liquid phase. Thus, we have performed the curve fitting about the simple XAFS spectrum of the S₈ powder dispersed into squalene. The result of the curve fitting for the S₈ powder dispersed into squalene at 120 °C, not shown here, the ionization potential position is estimated to be 2476.0 eV. Therefore, we have tried to the curve fitting of all NEXAFS spectra by use of the energy value of 2476.0 eV as a step function. Since the S-S and S-C bonds in the vulcanization reaction exist under liquid environment, we have adopted an asymmetric Gaussian peak in curve fitting analyses.

Figure 4 shows a typical sulfur K-edge NEXAFS spectrum, which is of the vulcanized squalene at 140 °C for 9 hours, and the result of curve fitting. Three peak components, which are assigned as σ*(S-S), σ*(S-C) and σ*(S-O) resonances from lower photon energy side, have been extracted. Two peaks of σ*(S-S) and σ*(S-C) are originated from the S8 source and the vulcanized bridge structure, respectively. In addition, unfortunately we have observed the σ*(S-O) peak, which are occurred by the oxidation reaction with some contaminants of water in squalene and/or air.

We have performed the curve fitting of NEXAFS spectra for all vulcanized squalene at 140 °C and extracted the intensities of three peak components related to S-S, S-C and S-O bonds. Those results are shown in figure 5. We have carried out the normalization which sum of the three peak components is to be 1.0. Judging from the results of curve fitting, the peak intensity of S-S bond decreases gradually in proportional to the reaction time. On the other hand, the S-C peak intensity increases. These results mean that the vulcanization reaction is occurring at the carbon of squalene. When the fitting line related with the S-S bond is extrapolated, the peak intensity approaches 0.6. It seems that this value means the 8 value of S₈ becomes 5 (S₅) or 6 (S₆).
4. Conclusion

We have prepared the samples of vulcanized squalene at 140 °C for several hours instead of the vulcanized rubber materials. The sulfur K-edge NEXAFS spectra for the samples have been obtained under liquid phase with He-path system and fluorescence detection mode. All NEXAFS spectra have not shown very little the self-absorption effect. Judging from the results of curve fitting of NEXAFS spectra, the squalene has been vulcanized by the $S_8$ molecule at 140 °C. In addition, the $S_8$ molecule length is shortened from 8 to 5-6 in proportional to the reaction time. It can be said that the sulfur K-edge NEXAFS analysis using He-path system is very powerful tool to understand the bridge structure of vulcanization reaction.

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