Quantitative Analysis of Crosslinked Structure in Rubber Materials by Sulfur K-edge NEXAFS

Kensuke Shirode, Hitoshi Kawai, Hiroaki Oe, Norihiko Nakamura, Shinya Yagi

Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan
Research Dept. No. 1, Central Research Center, Toyo Tire Corporation, 3-10-1 Yato, Kawanishi, Hyogo 666-0131, Japan
Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

Corresponding author: yagi.shinya@c.mbox.nagoya-u.ac.jp

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Quantitative analysis of crosslinked structure in vulcanized rubber is not enough. There have been some methods based on mechanical properties but no methods to obtain only information on the crosslinked structure. We have solved that problem by curve fitting of sulfur K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra. NEXAFS is useful to determine the chemical structure of the target element. The crosslinked structure obtained by NEXAFS shows a high correlation with the orthodox method. We have established the useful method to assist the orthodox analysis results. We have clarified the relationship between heat resistance of rubber materials and crosslinked structure using NEXAFS in this study.

Keywords: S K-edge NEXAFS; Curve fitting; Rubber; Vulcanization; Crosslinked structure

I. INTRODUCTION

Vulcanization is one of the most important chemical reactions for rubber materials. This reaction is performed to form three-dimensional crosslinked structures by bridging carbon polymer chains with sulfur chains. The crosslinked structure is related to various mechanical properties, such as hardness, hysteresis loss, and modulus [1]. In particular, the length of the sulfur chain which bridges the polymer chains influences the rubber properties [2].

Figure 1 shows a schematic diagram of the crosslinked structure [3]. The crosslinked structure is distinguished according to the sulfur chain length Sx. The value x is the number of the sulfur atoms in the sulfur chain (monosulfide: x = 1, disulfide: x = 2, and polysulfide: x = 3–8). The sulfur chain length Sx is controlled by a ratio of a sulfur powder and vulcanization accelerators. The vulcanization accelerator has two major roles; a reduction of the vulcanization time and an increase in the crosslink density. The use of the vulcanization accelerator is essential to produce the rubber as industrial tire products. For example, the rubber vulcanized with a conventional vulcanization (CV) system, which consists of a high sulfur/vulcanization accelerator ratio, has a long sulfur chain and a good fatigue resistance. On the other hand, the rubber vulcanized with an efficient vulcanization (EV) system, which consists of a low ratio, has a short sulfur chain and a good heat resistant. A semi-EV system has a ratio and mechanical properties that are intermediate between the CV and EV systems. The swelling method is known well for investigating the sulfur chain length Sx. The degree of swelling and/or compressive properties of...
swollen rubber are converted to the crosslink density using a theoretical formula. Moreover, the sulfur chain length $S$ can be estimated in conjunction with reagents to cleave the sulfur chain with a specific length [4–6]. However, the swelling method has some problems. Firstly, the reagents to cleave the sulfur chain are dangerous. Secondary, rubber specimens subjected to the swelling method cannot be used for other analyses because the regents break the rubber structure. Thirdly, specifying the chain length of the polysulfide is not possible. Fourthly, the swelling method assumes that there is no C–C bond between the polymer chains, but there is no evidence that such an assumption is correct. Moreover, a previous study has shown the error in estimating the crosslink density due to the entanglement of the polymer [3]. Therefore, assessing only a crosslinked structure requires a new technique.

Recently, sulfur K-edge near-edge X-ray absorption fine structure (NEXAFS) has been used for analyzing the crosslinked structure. NEXAFS provides only information about the target element since the absorption edge of the target element is unique. An earlier study using NEXAFS has suggested that the crosslink density, the antioxidant, and the filler affect the degradation of the crosslinked structure [7]. Another previous study has shown that the shapes of NEXAFS spectra indicate the difference of the sulfur chain length $S$, formed by different vulcanization systems [8].

However, these studies have analyzed NEXAFS spectra by linear combination fitting and comparison of spectral shapes. It is hard to say that the spectra have been analyzed sufficiently. On the other hand, Yagi et al. have tried quantitative analysis by curve fitting of NEXAFS spectra [9]. The measurement sample is not a vulcanized rubber material but is vulcanized squalene that is a low molecular-weight compound having a structure similar to the rubber molecule. The change in each peak intensity as a function of a heat aging time was quantitatively shown, but the sulfur chain length $S$ has not yet been estimated. For analyzing a crosslinked structure in vulcanized rubber, we conduct a curve fitting analysis of NEXAFS spectra of vulcanized rubber. The purpose of this study is to obtain knowledge about the crosslinked structure by quantitative analysis using NEXAFS.

### II. EXPERIMENTAL

Table 1 shows the composition of three measurement samples. Each component is given in the unit of parts per 100 parts of rubber, which is defined as a weight of the materials for 100 g of rubber and is a common expression in the field of rubber industries. Table 2 shows details of the used materials for the samples. The materials in Table 1 were mixed under mechanical shear using an internal mixer. Obtained mixtures were sheeted using an open roll and pressed under 10 MPa and 160°C by a hydraulic oil press. The vulcanization reaction progresses together with heating and pressing. The vulcanization time was determined to be 90% of the time to reach maximum torque on a rheometer. The rheometer is a device for judging the progress of vulcanization by measuring the change of torque during heating [1]. The accelerated aging test was conducted to clarify the relationship between the sulfur chain length $S$, and the heat resistance. The rubber samples were aged inside of a gear oven at 120°C for 9, 21, 42, 120, and 168 h.

Previous studies have shown that the solvent extraction of vulcanized rubber before the NEXAFS measurement is important [10]. All samples were extracted with acetone and toluene prior to the measurement. NEXAFS spectra (2465–2485 eV) were obtained by the partial fluorescence yield with a He-path system. This measurement was performed at the beamline BL6N1 in Aichi Synchrotron Radiation Center. A silicon drift detector (SDD, SHI Co., Ltd.)

| Material                  | Sample  | A     | B     | C     |
|---------------------------|---------|-------|-------|-------|
| Styrene-butadiene rubber  |         | 100   | 100   | 100   |
| Carbon black N339         |         | 30    | 30    | 30    |
| Zinc oxide                |         | 2     | 2     | 2     |
| Stearic acid              |         | 1     | 1     | 1     |
| Sulfur ($S$)              |         | 2     | 1     | 0.5   |
| Vulcanization accelerator |         | 1     | 2     | 4     |

| Vulcanization system      | CV      | Semi-EV | EV    |
|---------------------------|---------|----------|-------|
| Sulfur chain length $S$    | long    | middle   | short |

$^a$ N-cyclohexyl-2-benzothiazolesulfenamide

Table 2: Details of the used materials.

| Material                  | Product name    | Manufacturer                                      |
|---------------------------|-----------------|---------------------------------------------------|
| Styrene-butadiene rubber  | SBR 1502        | JSR Corporation                                   |
| Carbon black N339         | Seast KH        | Tokai Carbon Co., Ltd.                            |
| Zinc oxide                | Zinc Oxide #2   | Mitsui Mining & Smelting Co., Ltd.                |
| Stearic acid              | LUNAC S-20      | Kao Corporation                                   |
| Sulfur ($S$)              | 5% oil-put finely powdery sulfur | Tsurumi Chemical Industry Co., Ltd. |
| Vulcanization accelerator | SANCELER CM     | Sanshin Chemical Industry Co., Ltd.              |

$^a$ N-cyclohexyl-2-benzothiazolesulfenamide
was placed at the 90-degree position with respect to the incident X-ray. The rubber sample size was 3 mm × 5 mm × 1 mm. The maximum detection depth of measurements is about 40 μm. The detection depth was estimated based on the density and the composition of rubber without sulfur (S₈) and the vulcanization accelerator.

In the tensile test, dumbbell-shaped specimens were elongated at a tensile speed of 500 mm min⁻¹, and stress-strain curves were measured to obtain the elongation at break. In the swelling method, a strip-shaped test piece was immersed in toluene, and the swelling weight was measured. The swelling weight was converted to the total crosslink density using the equation shown in the previous study [11] based on the Flory-Rehner equation [12]. The rubber test specimens were immersed in a n-hexanethiol/piperidine solution to cleave di- and polysulfide chains. The swelling weight in toluene of the rubber test specimens after cleaving the sulfur chains was measured. The crosslink density was obtained by conversion of the swelling weight. The ratio of di- and polysulfide to all crosslinked structures was estimated from the ratio of the crosslink density before and after cleaving the sulfur chains.

III. RESULTS AND DISCUSSION

A. Method of curve fitting of sulfur K-edge NEXAFS spectra

Figure 2 shows the NEXAFS spectra of the unaged samples A, B, and C. These spectra have two peaks. The first peak has different positions depending on the samples and is located between 2472 and 2473 eV. The second peak is located at 2481.8 eV regardless of the samples. The second peak is assigned to SO₄²⁻ by a NEXAFS spectrum of ZnSO₄. There is a possibility that ZnSO₄ is formed, as the Zn element is present in the rubber samples. However, it cannot be confirmed only from the S K-edge NEXAFS spectra. The unaged samples give different energies of the first peak; A: 2472.2 eV, B: 2472.4 eV, and C: 2472.8 eV. We measured NEXAFS spectra of the sulfur powder and L-cysteine as the standard samples having S–S and S–C bonds, respectively. The peaks corresponding to the S–S and S–C bonds appear at 2471.8 and 2473.0 eV, respectively. Since the first peaks for all three samples are close to the peaks of the S–S and S–C bonds, it is suggested that the first peak is related to the crosslinked structure. If the crosslinked structures are formed in rubber samples according to the relationship between the vulcanization system and the sulfur chain length Sₙ as shown in Table 1, sample A should have a long sulfur chain and sample C should have a short sulfur chain. The long sulfur chain has more S–S bonds than that with the short sulfur chain. Thus, it is assumed that the NEXAFS spectra of the rubber sample with the long sulfur chain have the first peak close to the S–S bond. Sample A has the first peak located close to the S–S bond and the first peak of sample C is located close to the S–C bond. The first peak position corresponds to the relationship between the vulcanization system and the sulfur chain length Sₙ. Therefore, the first peak position shows the sulfur chain length Sₙ. The quantitative analysis of the sulfur chain length Sₙ requires determining the quantity of S–S and S–C peak intensities.

We try curve fitting of the NEXAFS spectra to analyze the spectra quantitatively. Curve fitting has been performed with six Gaussian functions. Those components are assigned to the S–S bond, the S–C bond, the S–O bond, SO₂, SO₃²⁻, and multiple and/or single scatterings. The crosslinked structure is composed of the S–S and S–C bonds as shown in Figure 1. Since polymer chains always exhibit micro Brownian motion at room temperature, it is expected the intense motion of the sulfur chains connecting with polymer chains. On the other hand, a previous study has shown that the change of the bonding length causes the change of the peak position and the full width at half maximum (FWHM) in the NEXAFS spectrum albeit the same chemical bond [13]. The vibration of the internuclear bond is known to result in skewed absorption peaks, and these peaks can be approximated by an asymmetric Gaussian function [13]. The asymmetric Gaussian function is composed of the summation of the symmetric one having an increase in the FWHM with increasing the photon energy. Replacing the FWHM of a symmetric Gaussian function to a linear function has been proposed to make an asymmetric Gaussian function easily [13]. We consider that the bond length of the sulfur chain is affected by the micro Brownian motion of the polymer chain so that the asymmetric Gaussian function is defined for the S–S bond. The asymmetric Gaussian function is adjusted by the FWHM exhibiting the linear function based on the NEXAFS spectrum of the sulfur powder. The peak position and the FWHM of the S–C bond are based on the NEXAFS spectrum of L-cysteine. The previous studies have shown that sulfur oxides exist in rubbers before the accelerated aging test [10] and the amount of the sulfur oxides increases with heat aging [7, 14]. From a spectral comparison among vulcanized rubber, the standard samples, and a previous study [15], the peak position and the FWHM of the S–O bond and SO₂ are estimated. The peak position and the...
FWHM of the $\text{SO}_4^{2-}$ are determined based on the NEXAFS spectrum of ZnSO$_4$. The five components except for the S–S bond are reproduced by symmetric Gaussian functions. All peak positions and the values of the FWHM are configured from the NEXAFS spectra of the standard samples. Moreover, the excitation from the S 1s orbital to the continuum band is described by a step function using a Sigmoid function. The continuum originates from multiple molecular bond components and has different leading-edge positions. The continuum must have a step shape in theory. However, it is hard to determine the leading-edge positions experimentally. The Sigmoid function in this study has a wide step-width to approximate the step shape. We make the universal Sigmoid function that can be used for all samples.

Figure 3 shows an example of a typical curve fitting result for unaged sample A–C and sample A aged for 168 h. The summation of six Gaussian functions and Sigmoid functions corresponds to the NEXAFS spectra. Thus, the number of the chemical bonds can be compared among the samples by curve fitting of the NEXAFS spectra. Focusing on the peaks of the sulfur oxides, they are observed even in the unaged sample. It is suggested that a part of sulfur is oxidized during the vulcanization reaction. The number of the S–S and S–C bonds related to the crosslinked structure can be obtained by curve fitting of the NEXAFS spectrum. To understand the difference of the sulfur chain length $S_x$ among the rubber samples, we have tried to calculate the sulfur chain length $S_x$ from the result of curve fitting. When all sulfur chains are the same length, one sulfur chain certainly consists of two S–C bonds to connect the sulfur chain to the polymer chain. The number of the S–S bonds, which are formed between two S–C bonds, changes depending on the sulfur chain length $S_x$. For example, if the number $x$ of the sulfur atom in the sulfur chain length $S_x$ is three, the sulfur chain consists of two S–C bonds and two S–S bonds. If the number $x$ is four, the sulfur chain consists of two S–C bonds and three S–S bonds. The number of the S–S and S–C bonds thus provides the number $x$ of the sulfur atom in the sulfur chain length $S_x$. The number of the S–S and S–C bonds can be estimated by the peak intensity obtained from curve fitting of the NEXAFS spectra. As a result, the number $x$ of the sulfur atom in the sulfur chain length $S_x$ can be written by the following equation,

$$x = 2R + 1$$

where $R$ is the ratio of the NEXAFS intensities ($I$) of the S–S and S–C bond peaks ($I_{S-S}/I_{S-C}$). We analyze the ageing time dependence of the sulfur chain length $S_x$ in vulcanized rubber by the curve fitting method of the NEXAFS spectra.

B. Analysis of sulfur chain length

Figure 4 shows the relationship between the number $x$ of the sulfur atom in the sulfur chain length $S_x$ of aged samples and the heat aging time. The number $x$ of the sulfur atoms in the sulfur chain length $S_x$ is calculated from the peak ratio of the NEXAFS spectra.
and the heat aging time. The $x$ values of unaged samples are 3.6 (sample A), 3.2 (B), and 2.4 (C). The order of $x$ corresponds to the relationship between the vulcanization system and the sulfur chain length $S$, as shown in Table 1. The value $x$ gets smaller with increasing heat aging time for all three samples. The decreasing rate of the $x$ value is large up to 42 h and is small after 42 h. The degradation speed of sample A, which has the largest number $x$ in the unaged sample, is larger than that of sample C. This is because the bond dissociation energy of the S–S bond in the long sulfur chain (C–S–S–S–S–C) is smaller than that in the short sulfur chain (C–S–S–C) [16]. Moreover, the degradation speed slows down with increasing the heat aging time due to the decrease of the number of the S–S bonds that are weak to heat. The relationship between the vulcanization system and sulfur chain length $S$, has confirmed using the NEXAFS spectra. The relationship has been known previously but is clarified as a clear numerical value by spectroscopy.

C. Comparison of sulfur K-edge NEXAFS and mechanical property

Figure 5 shows the relationship between the retention rate of elongation at break and the retention rate of the number $x$ of the sulfur atom in the sulfur chain length $S_x$. The elongation at break ($E_b$) is a physical property obtained from the stress-strain curve. If the rubber materials do not elongate by heat aging, $E_b$ for the rubber material has a low value. Consequently, the $E_b$ ratio of the aged sample to the unaged sample (the retention rate of $E_b$) is used as an indicator of the heat resistance in the rubber material field [17]. The retention rate of the number $x$ is estimated in the same manner as the retention rate of $E_b$. Therefore, the unaged samples are plotted at the retention rate of $E_b$ of 100 and the retention rate of the number $x$ of 100, which is shown as an origin point in Figure 5. The retention rate of $E_b$ and the $S_x$ value decrease with increasing the heat aging time. Comparison of the 168-h aged samples shows that the retention rates of $E_b$ and $x$ of sample C, having the small initial $x$ value, are higher than those of samples A, having the large initial $x$ value. This result is consistent with the general result in the rubber industrial field. The short sulfur chain contributes to improve the heat resistance [2]. The relationship between the sulfur chain length and the heat resistance is mentioned in Section III.B. The short initial sulfur chain is effective in suppressing the reduction of $E_b$ by heat aging. The retention rates of $E_b$ and $x$ show a high correlation in each vulcanization system; the coefficients of determination $R^2$ are 0.96 (sample A), 0.96 (B), and 0.95 (C). The slope value of the approximate straight line is almost the same regardless of the vulcanization systems. Therefore, the retention rate of $x$ greatly affects the retention rate of $E_b$. It is well-known that there is a relationship between the crosslinked structure and the heat resistance. However, it is important that this fact is confirmed by the quantitative analysis based on the chemical state analysis using NEXAFS. Furthermore, it is also notable that the approximate straight lines do not go through the origin point. This suggests that there are some influential factors other than the sulfur chain length $S_x$, such as the scission of the polymer chain, the recombination of the polymer (the C–C bond), and the crosslink density.

D. Comparison of sulfur K-edge NEXAFS and swelling method

Figure 6 shows a comparison of the quantitative analysis results in the crosslinked structure obtained by the NEXAFS analysis and the swelling method. The number $x$ of the sulfur atom in the sulfur chain length $S_x$ is obtained from NEXAFS. The swelling method can distinguish up to three forms of the crosslinked structure, i.e., monosulfide, disulfide, and polysulfide. The distinguishable crosslinked struc-

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**Figure 5:** Relationship between retention of elongation at break and the number $x$ of the sulfur atom in the sulfur chain length $S_x$. The retention rate is a change rate of the aged sample relative to the unaged sample. The retention rates of $E_b$ and $S_x$ in three samples are decreased with heating.

**Figure 6:** A comparison of quantitative analysis results in crosslinked structure obtained by the S K-edge NEXAFS analysis and the swelling method. The value $y$ is the ratio of di- and polysulfide to all crosslink structures.
tured depends on the used reagent. In this study, the ratio of
disulfide and polysulfide to the crosslinked structure
(monosulfide, disulfide, and polysulfide) is estimated and
defined as the ratio $y$. For each vulcanization system, the
quantitative results of the NEXAFS analysis and the swell-
ning method have a high correlation; the coefficient of deter-
mination $R^2$ are 0.93 (sample A), 0.87 (B), and 0.75 (C).
However, the correlation is low with $R^2 = 0.66$ when all data
points of three vulcanization systems are taken into account.
The swelling method can distinguish monosulfide, disulfide,
and polysulfide but cannot clarify the chain length of poly-
sulfide. For example, degradation of sulfur chain from $S_3$ to
$S_4$ cannot be clarified. The crosslink density, which is esti-
mated using the swelling method, is based on the degree of
swelling. The degree of swelling is also affected by cross-
linked structures other than the sulfur chain. For example,
the polymer chain is modified due to the scission or recom-
bination of the polymer. In contrast, it is an advantageous
point that NEXAFS can acquire only information on the
focused element. Moreover, the correlation of the quantita-
tive results of NEXAFS and the swelling method is en-
hanced if the data of the long-aged samples (120 and 168 h)
are excluded. The coefficient of determined $R^2$ are 0.99
(sample A), 0.99 (B), and 0.98 (C). It is suggested that the
damage of the polymer in the long-aged samples causes the
change of the correlation.

When the straight lines through the data points in Figure 6
are extrapolated to the ratio $y$ of 0 in the horizontal axis,
they do not cross the vertical axis at 1.0 but at points larger
than 1. If the swelling method and NEXAFS show the same
quantitative result of the crosslinked structure, the straight
lines in Figure 6 ideally pass the point “1” at $y = 0$, but the
straight lines do not give the ideal result. The swelling
method assesses the entire rubber structure because the
crosslinked structure and the polymer influence the degree
of the swell. NEXAFS estimates the only crosslinked struc-
ture from the chemical state of sulfur. We have emphasized
that these methods have different viewpoints.

IV. CONCLUSION

We have developed the curve fitting method for the S
K-edge NEXAFS spectra to analyze the crosslinked struc-
ture in vulcanized rubber. Our method can distinguish the
chemical bonds in the rubber materials such as S–S, S–C,
S–O–, SO$_2$–, and SO$_3$–. The crosslinked structure in vulcan-
ized rubber is estimated as the number $x$ of the sulfur atom
in the sulfur chain length $S$, based on the S–S and S–C peak
intensities. The crosslinked structure in vulcanized rubber has
only been estimated by the proportion of monosulfide,
disulfide, and polysulfide so far. Our results are in good
agreement with standard analytical methods such as the
swelling method and the mechanical property tests. There-
fore, the curve fitting method of the NEXAFS spectra can be
used for the analysis of the crosslinked structure. We have
revealed that the relationship between the sulfur chain length
S, and the heat resistance of the rubber materials. The sulfur
chain length $S$, estimated by NEXAFS can be an indicator
of the heat resistance for rubber products. In the analysis by
NEXAFS, the crosslinked structure can be determined by
the chemical state of sulfur. It is quite different from the
conventional methods which verifies the change in mechan-
ic properties.

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