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Investigation of crosslink structure of natural rubber during vulcanization using X-ray absorption near edge spectroscopy

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Abstract

The X-ray absorption near edge spectroscopy technique (XANES) has been applied to determine the crosslinking structure of natural rubber (NR) during sulfur vulcanization process. The NR samples were prepared using DCBS as an accelerator at different sulfur to DCBS ratios (from 0.26 to 6.67). The results showed that with increasing cure time from t_c50 to t_c70, t_c90 and t_c100 the position of sulfur peak shifted to higher energy. This implied that the amount of polysulfidic crosslink gradually decreased with increasing cure time. This result supported the crosslinking mechanism proposed in the literature at which the polysulfidic crosslink is dominating at initial curing stage. Moreover, when rubber was over-cured for 20 min, the amount of polysulfidic crosslink further decreased indicating by shifting of sulfur peak to high energy. The effect of sulfur to accelerator ratio on the crosslink structure was also elucidated by XANES. The results showed that the position of sulfur peak passed through the lowest energy with the increasing of the sulfur to DCBS ratios. It means that the amount of polysulfidic crosslink was not simply correlated with the sulfur to accelerator ratios. It passed through maximum with increasing sulfur to accelerator ratio. This caused the reversion resistance of rubber no longer directly proportional to the sulfur to accelerator ratio. The result from this study indicated that XANES technique is a prospective tool to investigate the crosslink structure of sulfur cured rubber.

1. Introduction

Vulcanization/crosslinking or curing is a process which transforms rubber from a high molecular weight liquid into elastic solid by chemically linking rubber chains to form “infinite network”. There are different vulcanization systems available such as sulfur, peroxide, difunctional molecules, etc. Among them, the sulfur vulcanization is the most feasible curing system because of a low cost process. To improve efficacy of sulfur curing, sulfur must be used in combination with one or more accelerators (e.g. sulfenamides, thiazoles, thiuram sulfides, etc.) and an activator system, as for instance soluble zinc and fatty acid [1]. This network is formed by a mixture of mono-, di- and poly-sulfidic crosslinks [2,3]. The sulfur crosslinks structure is dramatically related to the physical and thermal properties of the rubber which is depended strongly on amount and type of curing ingredients. Therefore, the specific properties of the accelerated sulfur cured rubber can be achieved by simply adjusting curing packages. However, when the accelerated sulfur cured rubbers especially natural rubber are either further heated after reaching the optimum vulcanization or used at high temperature service conditions, they will begin to exhibit what is commonly known as reversion. Once rubber has begun to revert, many of its desirable properties are lost. The simplistic reason for this phenomenon is a deterioration of the crosslink networks in the vulcanizates. The degradation of linkages is mainly from polysulfidic linkages [2]. This is attributed to their low heat stability. Therefore, to obtain the cured rubber with high reversion resistance, the rubber compound giving less polysulfidic linkages was favourable. There have been many attempts try to assess the relationship between the rubber formula and the crosslink structure [1,3-13]. In general, it has been believed that the resultant networks with the high proportion of polysulfidic linkages which are more susceptible to deterioration from heat are obtained when the high sulfur to accelerator ratio is used and vice versa. To evaluate the crosslink structure during sulfur vulcanization, there is only a chemical treatment available [13]. However, this method is very difficult and causes strongly unpleasure smell.

The main investigation is focused on the crosslink structures of the resultant networks. Currently, many research groups have used X-ray absorption near edge structure (XANES) spectroscopy at the sulfur *K*-edge with synchrotron radiation as a potential tool for analysis of the sulfur crosslinks [1,3-12]. However, there is no study focused on the change of sulfur crosslinks during vulcanization and reversion process in NR. The aim of this study is to evaluate the sulfur

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crosslink structure during initial, fully and over curing state using XAS. Then we wish to elucidate the vulcanization characteristic of NR which can be a great advantage for development of the rubber product in Thailand.

2. Experimental

2.1 Rubber compounding

The series of natural rubber (NR) compounds was prepared. The weight ratios of sulfur to DCBS accelerator were ranged from 0.26 to 6.67. The formulation of NR vulcanizate is listed in Table 1. All formulations were comprised of a common base composition of 100 phr of NR, 8 phr of ZnO, 1 phr of stearic acid, 1 phr of TMQ and 1 phr of 6PPD. The rubber was mixed with chemicals using a laboratory internal mixer with a fill factor of 0.7, a temperature of 50°C and a rotor speed of 50 rpm by a two-stage sequential procedure. NR was first masticated for 1 min before the ZnO was added and then continuously mixed for 2 min. The remaining chemicals (stearic acid, TMQ and 6PPD) were added and mixed for 2 min. Finally, the compound was dumped, giving a total heated mixing time for the first step of 5 min, and cooled down to room temperature. For the second stage, the compound was put back into the heated mixer and then mixed with the curatives (sulfur and DCBS) for an additional 3 min, giving a total second stage heated mixing time of 4 min. Then, the compound was taken out and sheeted off with a two-roll mill to ~5 mm thickness. These rubber sheets were stored at room temperature for 16-24 h. before curing.

Table 1. Rubber formulation.

Composition (phr)					
NR; 100 phr, ZnO; 8 phr, Stearic acid; 1 phr, TMQ; 1 phr, 6PPD; 1 phr					
Sulfur (S)	1.40	2.63	3.36	4.00	5.00
DCBS	3.50	2.25	1.75	1.25	0.75
S/DCBS ratio	0.26	1.17	1.92	3.20	6.67

2.2 Cure characterization

The cure kinetics of rubber compounds were determined at 155°C using a Moving Die Rheometer (MDR), in accordance with the method described by ASTM D5289-95. Since the cure time (t_c100) was taken as the time to reach maximum torque, and reversion refers to the loss of crosslinked density associated with over curing, then the rheometer torque was used as an indicator of reversion behavior. There were two parameters used to indicate the reversion behavior of the NR compound. The first one was the range of plateau region before the torque started to decrease. And the second one was the reversion rate taking from the initial slope of the decreasing torque.

2.3 Preparation of rubber vulcanizate for XANES evaluation

All rubber compounds were then compression molded into 200 µm films in a hydraulic press at 155°C according to their t_c(50), t_c(70), t_c(90), t_c(100) and t_c(100)+20 min. The obtained rubber sheet was immersed into 100 ml of chloroform overnight to remove the residual unlinked sulfur containing molecules that may interfere the absorption of sulfur atom of the crosslink. Then, the treated rubber sheet was taken out and rinsed twice with 50 ml of fresh chloroform and then left at room temperature until completely dry. To avoid any degradation that may influence the XANES spectrum around the *K*-edge of sulfur due to the lack of anti-degrading, the X-ray absorption measurement of the treated rubber was evaluated no more than two days after the chloroform treatment.

2.4 XANES measurement

The XANES experiment was carried out at BL8 of the Synchrotron Light Research Institute (SLRI) in Thailand. Each sample was stuck to a 6 x 20 mm sample holder. The photon energy was selected using a Si (111) double crystal monochromator. All XANES spectra around the *K*-edge of sulfur were taken using two ionization chambers, before and after the sample. The ionization chamber which is place before and after sample was filled with 37 and 200 mbar N_2 gas for the sulfur *K*-edge measurements, respectively. The sample chamber was filled with He gas and separated from the two ionization chamber by a polypropylene window. The white line of ferrous sulfate ($FeSO_4$) was used for the calibration at 2481.4 eV around the sulfur *K*-edge absorption. Measurements were performed in Transmission mode. All XANES spectra were averaged and normalized using the IFEFFIT software version 1.2.11 [14].

3. Results and discussion

Figure 1 shows a cure curve of NR compound at the S/DCBS ratio of 6.67 when testing at 155°C. It was found that the torque increased with increasing cure time. This indicated that crosslink density increased with increasing cure time. Moreover, after reaching maximum torque further heating rubber caused the decreased torque. This can be implied that the crosslink density was reduced.

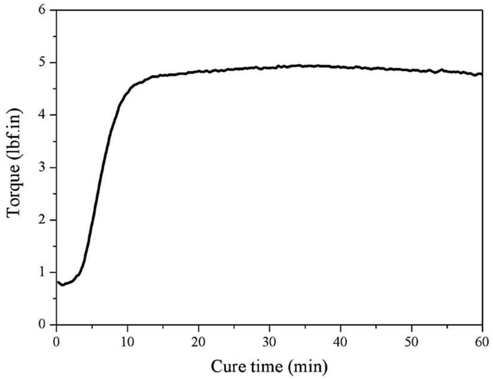

Figure 1. MDR cure curve of NR cured at the S/DCBS ratio of 6.67when testing at 155°C.

Figure 2 shows the *K*-edge XANES of sulfur in natural rubber (NR) compounds cured with various cure times. The cure time (t_cx) is referred to time at which the rubber is crosslinked up to x%. For this study, the t_c50, t_c70, t_c90 and t_c100 were 6 min 54 s, 7 min 33 s, 10 min 30 s, and 36 min 56 s, respectively. The result designated that the increased cure time has affected on the linkages of the NR vulcanizates. As can be seen, the increased cure time caused the shift of the XANES peak. Chauvistré *et al.*, 1997; Hormes & Modrow, 2001 reported that the peak shift is related to the number of sulfur atoms bonded in the crosslink or the bond length and the absorption peak of XANES spectrum is shifted to a lower photon energy when the number of sulfur C-S_x-C (x=1, 2, 3, 4) is increased. In order to confirm this phenomenon, the XANES spectrum of L-cysteine (-SH) and L-cystine (S-S) used as standard reference compounds are investigated and shown in Figure 3. The peak of XANES of L-cysteine (-SH) located at higher photon energy than that of L-cystine (S-S). The result of this study was comparable to that of Hitchock *et al.* [15], Sze *et al.* [16] and George & Gorbaty [17] as well. This can confirm that the shift of sulfur peak to the different location related to the change in sulfur rank.

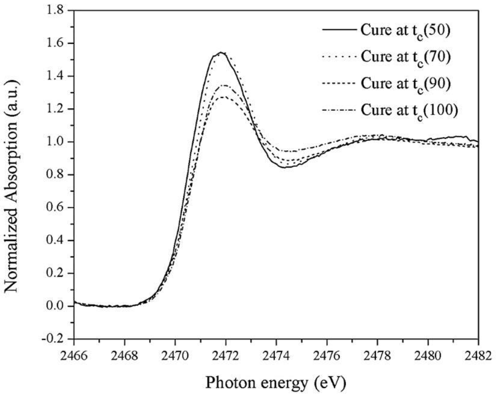

Figure 2. XANES spectra of sulfur cured NR compound at various cure times when testing at 155°C.

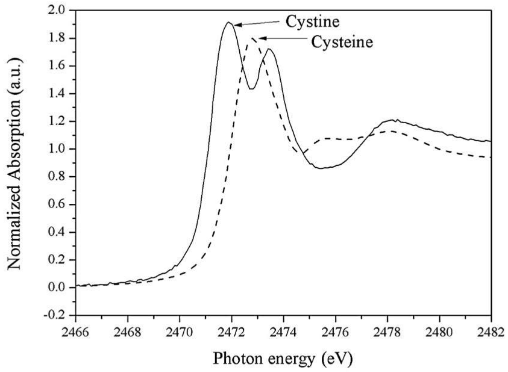

Figure 3. Sulfur peak in XANES spectra of L-cysteine (-S-H) and L-cystine (S-S).

In this study it was found that the peak of XANES of the NR compound cured with the shortest cure time (t_c50) located at the lowest photon energy (~2471.7 eV) which can be inferred that the networks of this NR vulcanizate mainly consisted of the longest crosslink (polysulfidic crosslink). However, when increasing cure time, the position of sulfur peak shifted to higher energy. This implied that the amount of polysulfidic crosslink gradually decreased with increasing cure time. This result supported the crosslinking mechanism proposed in the literature at which the polysulfidic crosslink is dominating at initial curing stage. Then, these polysulfidic crosslinks are transformed to shorter linkages via shortening of linkages with additional crosslink called as desulfuration.

Furthermore, Figure 4 compared the *K*-edge XANES of rubber cured at $t_c(100)$ with that of rubber over-cured for 20 min. It can be clearly seen that the over-curing caused the sulfur peak shift to even higher energy. In accordance with the cure curve, this can be indicated that the over-curing caused the destruction of polysulfidic linkages called as reversion. The underlying reason for breaking down of polysulfidic linkages was due to their lower bond dissociation energy than that of shorter ones. Therefore, only the shorter linkages were left or survived after reversion. As result, these shorter linkages were dominant, thus causing the over-cured rubber to show a sulfur peak of XANES at the higher energy.

Figure 5 shows the effect of sulfur to accelerator ratios on the *K*-edge XANES of sulfur in natural rubber (NR) compounds cured with DCBS at 155°C for $t_c(100)$. In general, it has been believed that vulcanizates cured with the high sulfur to accelerator ratio is more susceptible to reversion. This is due to their structures are consisted of a high proportion of polysulfidic linkages. Therefore, the vulcanizates cured with different sulfur to accelerator ratios will show sulfur peak in XANES at different photon energy. Interestingly, it was found here that the increase of the sulfur to accelerator ratios initially caused the peak of XANES shift to the lower photon energy and then back to higher photon energy again. It is inferred that the amount of polysulfidic linkages passed through the maximum with the increase of sulfur to accelerator ratio. The result here indicated that the relation between the sulfur to accelerator ratio and the distribution of sulfur linkages was not directly proportional.

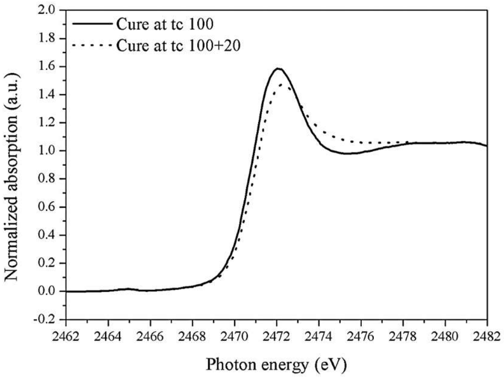

Figure 4. Comparison of XANES spectra of sulfur cured NR compound cured at $t_c(100)$ with at $t_c(100)+$ 20 min when testing at 155°C.

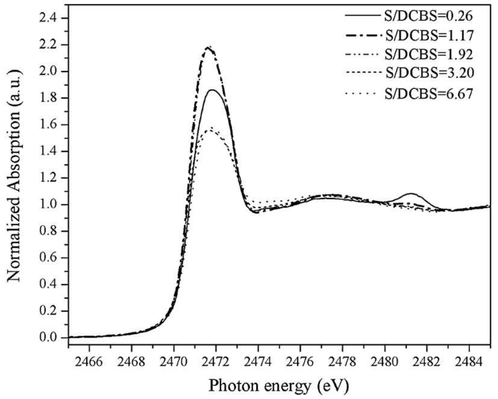

Figure 5. XANES spectra of NR compounds cured with various sulfur to DCBS ratios when testing at 155°C.

Figure 6 show the correlation amongst the sulfur to accelerator ratios, photon energy (E_0) of XANES peak, reversion resistance of NR cured with DCBS. It is known that the peak shift is related to the number of sulfur atoms bonded in the crosslink or the bond length. The photon energy of XANES peak is taken from the vulcanizate cured at t_c100. The vulcanizates with low reversion resistance is indicated by the one with the short plateau region and high reversion rate. The result revealed that the vulcanizate showing XANES peak at the lowest photon energy had the lowest reversion resistance. This was because its network was mainly consisted of polysulfidic crosslink. Besides using XANES technique to investigate the effect of cure time on the crosslink structure, this study also showed that this technique can be used to determine the reversion resistance of sulfur cured rubber.

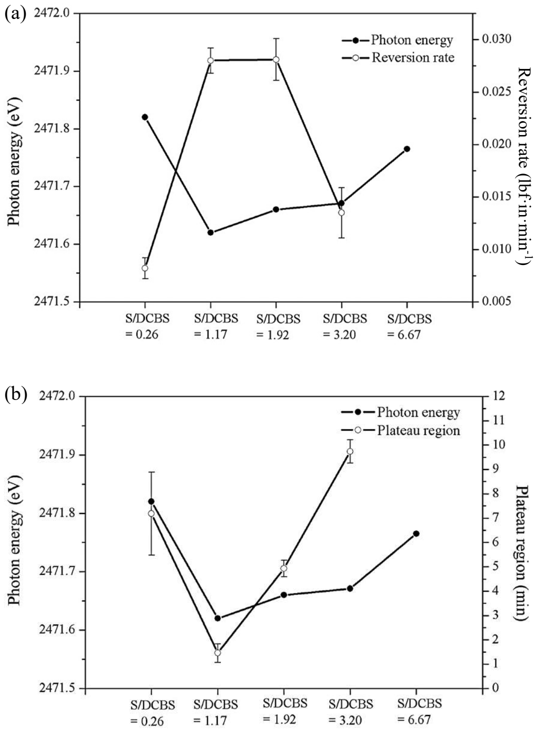

Figure 6. Relation amongst the sulfur to accelerator ratios, the position of XANES peak and (a) reversion rate and (b) plateau region of sulfur cured NR compounds.

4. Conclusions

When using sulfur to crosslink the rubbers, it can lead to various crosslink structures. Significantly, the crosslink structure is one of the most important factors controlling mechanical and thermal properties of the rubbers. This preliminary study showed that XANES can be a useful technique to determine the crosslink structure during both vulcanization and reversion process. The XANES spectra revealed that the change of crosslink structures of the sulfur cured NR compounds when varying the cure times and the sulfur to accelerator ratios. This result will lead us to understand more about vulcanization mechanism and be able to describe the relationship between rubber formula and the mechanical properties of the resultant rubber.

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