research papers

Structural analysis of sulfur in natural rubber using X-ray absorption near-edge spectroscopy

Wanwisa Pattanasiriwisawa,[a]* Jaruwan Siritapetawee,[b] Orasa Patarapaiboolchai[c] and Wantana Klysubun[a]

[a]National Synchrotron Research Center, 111 University Avenue, Muang, Nakhon Ratchasima 30000, Thailand, [b]College of Medicine and Public Health, Ubon Rajathanee University, Ubon Ratchathani 34190, Thailand, and [c]Faculty of Science, Prince of Songkla University, Songkhla 90112, Thailand. E-mail: wanwisa@nsrc.or.th

X-ray absorption near-edge spectroscopy (XANES) has been applied to natural rubber in order to study the local environment of sulfur atoms in sulfur crosslinking structures introduced in the vulcanization process. Different types of chemical accelerators in conventional, semi-efficient and efficient vulcanization systems were investigated. The experimental results show the good sensitivity and reproducibility of XANES to characterize the local geometry and electronic environment of the sulfur K-shell under various conditions of vulcanization and non-vulcanization of natural rubber. Several applications of XANES in this study demonstrate an alternative way of identifying sulfur crosslinks in treated natural rubber based on differences in their spectra and oxidation states.

Keywords: XANES; natural rubber; sulfur crosslinks.

1. Introduction

Natural rubber (NR) is a raw material that is widely used in a variety of industries owing to its outstanding properties such as its high stress at break, good tear resistance, low heat build up and good tack. NR consists of cis-1,4-polyisoprene forming an amorphous structure that undergoes rapid change into crystal form when stress is applied. This peculiarity, namely strain-induced crystallization (SIC), gives NR tensile strength, tear resistance and abrasion resistance. SIC is an interesting topic for polymer science and its industrial applications. For decades much NR research has been concentrated on SIC studies in order to understand the properties of rubber using several experimental techniques, such as X-ray scattering (Mitchell, 1984; Toki et al., 2002; Murakami et al., 2002; Tosaka et al., 2004; Ikeda et al., 2007), stress relaxation (Gent, 1961; Gent et al., 1998; Luch & Yeh, 1973), transmission electron microscopy (Toshiki et al., 2000), infrared spectroscopy (Lewis et al., 1995), nuclear magnetic resonance (NMR) (Lin et al., 2004) and dilatometry (Gent et al., 1998). In addition to SIC, there is also a key process known as vulcanization, a necessary treatment to form sulfur crosslinking in rubber. This vulcanization has also drawn much attention for its role in enhancing the elasticity of the rubber and governing other physical properties as well. Some research groups have carried out characterization of the crosslinks in NR using solid-state NMR (Boochathum & Chiewnawin, 2001; Boochathum & Prajudtake, 2001) and X-ray absorption spectroscopy (XAS)

(Chauvistré et al., 1992, 1997; Modrow et al., 2000; Hormes & Modrow, 2001).

In our studies, we are motivated by the fact that Thailand is the biggest rubber exporter in the world, but the rubber is mostly distributed as a raw material (rubber latex, rubber smoke sheets and rubber blocks). Thus improvement in the quality and development of NR products is necessary for Thailand in order to raise the value of rubber and hence the income of the country. Our rubber research is conducted at the molecular level using XAS techniques based on synchrotron radiation, which has recently become available in Thailand. The XAS facility, i.e. beamline 8 (BL8) and its XAS station (Klysubun et al., 2006, 2007), is located at the National Synchrotron Research Center (NSRC) in Nakhon Ratchasima province. We aim to analyze the molecular structure and crosslinks of sulfur for better understanding of the physical properties of rubber and to share our findings with the rubber research and industry in Thailand.

Making rubber products with suitable characteristics for individual use primarily depends on the vulcanization conditions which involve a number of variables such as type of chemical accelerator, amount of sulfur etc. A set of these variables is known as the rubber compounding recipe which is commercially secret. It also depends on the heating time during vulcanization (i.e. curing time). In general, there are three vulcanization systems: conventional vulcanization (CV system), efficient vulcanization (EV system) and semi-efficient vulcanization (semi-EV system). The CV system uses a lot of

sulfur and a little accelerator, the EV system uses a little sulfur and a lot of accelerator, while the semi-EV system is the intermediate system. Here we consider how to apply the X-ray absorption near-edge spectroscopy (XANES) technique for investigation of all these vulcanization systems with different types of accelerator, amounts of sulfur and curing times.

2. XAS and BL8 at the Siam Photon Laboratory

XAS measures the probability that a photon is absorbed by the sample as a function of its energy. A spectrum obtained using the XAS technique can be separated into two parts, XANES and EXAFS (extended X-ray absorption fine structure). XANES is useful for identifying chemical forms (as fingerprints) and oxidation states as well as studying valence states (Prange *et al.*, 2002) and symmetry of unoccupied orbitals, whereas EXAFS, appearing as an oscillation seen above the absorption edge (Rosolen & Abbate, 2001), is useful for analysis of local atomic structure. XAS is non-destructive to the sample and can be used with various types of sample, *e.g.* solid (Polian *et al.*, 1989; Lytle *et al.*, 1990), liquid (George & Gorbaty, 1989; Filipponi & Di Ciico, 1995) and gas (Hitchcock *et al.*, 1986; Sze *et al.*, 1988).

For XAS research conducted in Thailand, Siam Photon Laboratory provides an experimental facility at BL8. It has been open for external users since 2006. XAS spectra in the *K*- and *L*-edge regions of several atoms can be measured in both transmission and fluorescent modes. A photograph of the XAS station at BL8 is shown in Fig. 1. The available photon energy ranges from 1830 to 9000 eV using three types of monochromating crystal interchangeably: Si(111), InSb(111) and Ge(220). For rubber samples, *K*-shell absorption of sulfur is of interest at a photon energy around 2472 eV given by Si(111) crystals.

3. Experiments

There were three types of chemical accelerator used in our studies: CBS (*N*-cyclohexyl-2-benzothiazole sulphenamide),
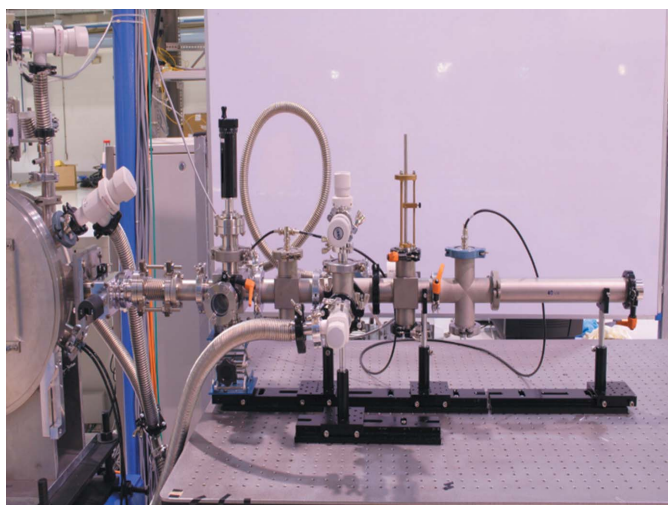

Figure 1
Photograph of the experimental station for transmission-mode XAS.

MBT (2-mercaptobenzothiazole) and TMTD (tetramethyl thiuram disulfide). Three sets of rubber sheet samples were prepared. The first set of samples was obtained by mixing NR with varying amounts (measured in parts per hundred of rubber unit, phr) of MBT accelerator, and sheeting on a two-roll mill. Vulcanization did not occur in this set. The second set of samples was prepared by adding the NR with each accelerator compound at 5 phr. After sheeting on a two-roll mill, the samples were molded at 443 K for 90 min. Although heat and pressure were involved, vulcanization did not occur in the absence of additional sulfur. The third set of samples used the same accelerators as for the second set. Three vulcanization systems were prepared: CV, EV and semi-EV system, with accelerator-to-sulfur phr ratios of 1:2.5, 4:2.1 and 2.5:1.7, respectively. Vulcanization of all systems was induced by heating at 443 K.

XANES measurements were carried out at BL8 using synchrotron radiation from the Siam Photon Laboratory storage ring operated at 1.2 GeV electron beam energy and an electron beam current of about 100 mA. A Si(111) double-crystal monochromator was used for selecting the photon energy. The energy resolution ($\Delta E/E$) was around 10^{-4}. Each treated rubber sheet of all sample sets was cut and placed on a 12 mm × 6 mm sample holder. The photon beam size was 10 mm × 1 mm. All XAS spectra around the *K*-edge of sulfur were recorded using two ionization chambers. They were filled with air at 60 mbar and located before and after the sample to record the incoming and transmitted photon beam intensity. The photon energy was calibrated in the region around the sulfur *K*-edge absorption using the maximum of the absorption peak (white line) of zinc sulfate ($ZnSO_4$) powder at 2481.4 ± 0.1 eV (Prange *et al.*, 2002). All of the XANES spectra were averaged and normalized using *IFEFFIT* software, version 1.2.7 (Ravel & Newville, 2005).

4. Results and discussion

Fig. 2 shows the XANES spectra of the *K*-edge of sulfur in rubber samples with different amounts of MBT (1–4 phr), along with the spectrum of the standard chemical compound of MBT. The spectral features in each spectrum are similar. The pre-edge peak and the main absorption peak appear at 2469.8 eV and 2472.7 eV, respectively. The peak height increased with the amount of MBT simply owing to the increase in sulfur content. It is noted that the XANES spectrum of sulfur in the sample also resembles that of sulfur in the standard chemical compound of MBT. This result confirms that the oxidation state of sulfur does not change, meaning that neither the linkage nor the sulfur crosslinks occur by only increasing the amount of accelerator. It also shows that XANES has the capability for quantitative analysis of a sample, such as determining the amount of MBT in NR.

Fig. 3 shows XANES spectra of NR with three types of accelerator: CBS, MBT and TMTD. The thicknesses of the rubber sheets are all the same. The XANES spectra of CBS- and MBT-containing NR have similar characteristics because they have similar molecule structures, *i.e.* heterocyclic. The
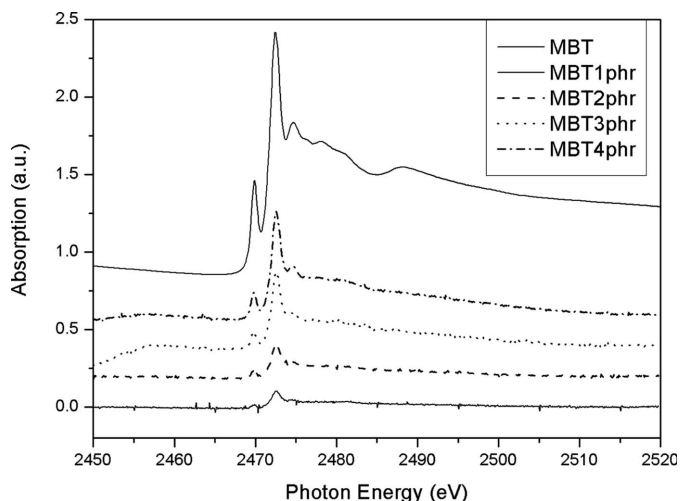
Figure 2
Sulfur *K*-edge XANES spectra with various amounts of sulfur from MBT, and the MBT standard chemical compound.
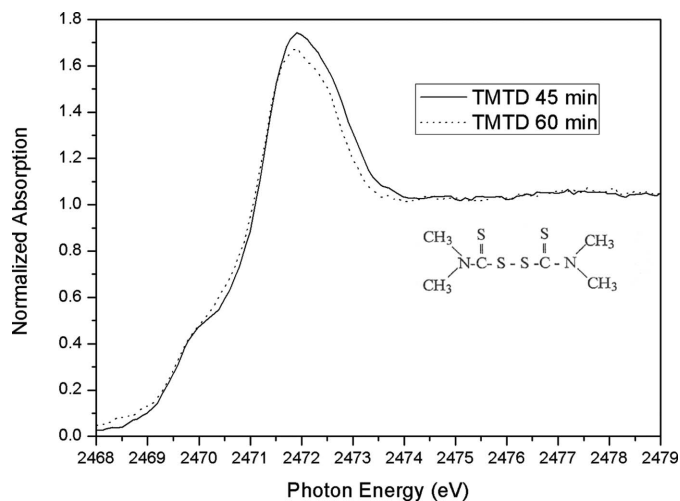

Figure 4
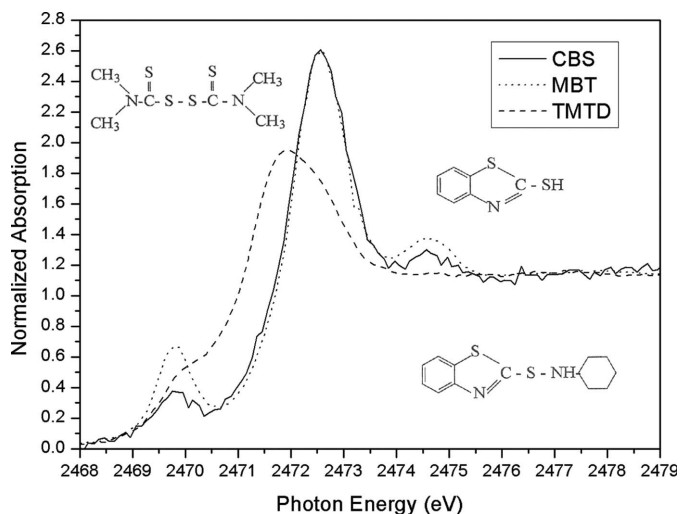Sulfur *K*-shell XANES spectra using TMTD in NR with different curing times.

Figure 3
Sulfur *K*-shell XANES spectra with different accelerators, CBS, MBT and TMTD, in NR.

maximum peaks for CBS- and MBT-containing NR are observed at 2472.7 eV. This corresponds to the σ^* (S—C) resonance. The pre-edge peak is also observed in CBS- and MBT-containing rubber at 2469.8 eV. For TMTD-containing NR, the XANES spectrum differs from the others. It shows a maximum peak at a lower photon energy, *i.e.* 2471.8 eV, as compared with those of CBS and MBT. This peak can be assigned to the σ^* (S—S) resonance. The assignments of the σ^* resonance peaks are based on the studies of Hitchcock *et al.* (1986), Sze *et al.* (1988) and George & Gorbaty (1989).

The XANES technique can also be used explicitly for monitoring the influence of curing time. In Fig. 4 we compare the sulfur *K*-edge XANES spectra of TMTD-containing NR after 45 min and 60 min of curing time. The height of the S—S resonance peak is decreased when the curing time is increased. The accelerators (TMTD) added in the vulcanization of NR act as sulfur donors so vulcanization may occur during the

curing process. The overcuring time can be seen by the increasing height of the absorption peak as the curing time increases. Then the rubber undergoes overcuring reversion and the elasticity is decreased. This result is similar to the degrading of rubber by thermal oxidation (Modrow *et al.*, 2000). These results will be useful for optimizing the curing time in the vulcanization process in our future work.

Figs. 5 and 6 show the *K*-edge XANES of sulfur among the three vulcanization systems of CV, EV and semi-EV. In general, the absorption structures are similar, showing the S—C resonance peak. This peak shifts to lower photon energy from the EV system to the semi-EV system to the CV system. The peak shift is in the same manner for both CBS and MBT accelerators used in the vulcanization. The peak shift is related to the number of sulfur atoms bonded in the crosslink or the bond length as previously reported by Chauvistré *et al.* (1997) and Hormes & Modrow (2001). The absorption peak of the XANES spectrum is shifted to a lower photon energy when the number of sulfur C—S_x—C (x = 1, 2, 3, 4) chains increases (Chauvistré *et al.*, 1997; Hormes & Modrow, 2001). In this study it is found that sulfur tends to make a longer crosslink when the system is changed from EV to semi-EV to CV. It can be concluded that in the EV and CV systems the crosslink type is likely to be monosulfidic and polysulfidic, respectively, whereas in the semi-EV system there is a mixture of both monosulfidic and polysulfidic crosslinks. In addition, vulcanization with MBT, based on the peak shift, may yield longer sulfur crosslinks than vulcanization with CBS. Radiation damage may not effect the samples because the shift of the absorption peak is based on the σ^* (S—X) resonance in NR (Chauvistré *et al.*, 1992) and the XANES spectrum of the sulfur chain (C—S_x—C) in NR (Chauvistré *et al.*, 1997; Hormes & Modrow, 2001).

Knowledge of the chemical bonding in a system helps us to understand its mechanical properties. For example, the chemical bonding in polysulfidic crosslinks provides rubber products with good mechanical properties but it is not good
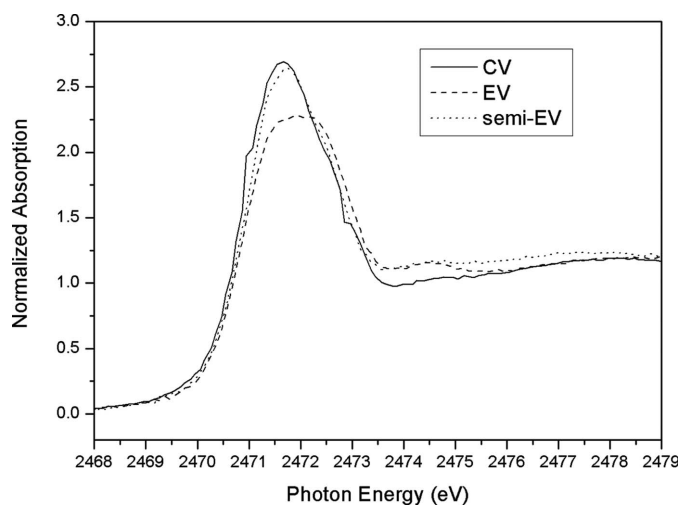
Figure 5
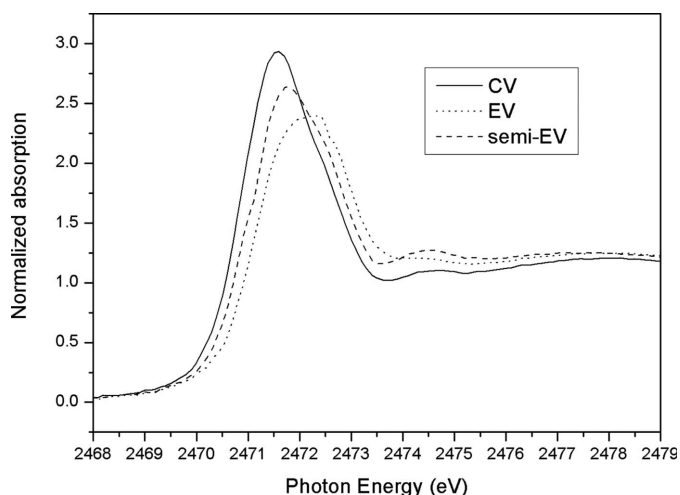Sulfur vulcanization system using CBS accelerator.

Figure 6
Sulfur vulcanization system using MBT accelerator.

for heat resistance; and *vice versa*, chemical bonding in monosulfidic crosslinks does not provide a rubber product with good mechanical properties, though it is good for heat resistance.

5. Conclusion

Various applications of XANES in the field of structural and quantitative analysis of the sulfur *K*-shell have been employed to study natural rubber for better understanding of its chemical and physical properties. XANES can be used to distinguish sulfur in non-vulcanization and vulcanization systems in natural rubbers. It can also identify the sulfur crosslinks in the vulcanization system. This result determines the method in using synchrotron application in rubber

research. Further work is required in designing a sample holder for stretching rubber products as we would like to find out more on the influences of physical changes, *i.e.* stretching and thermal effects on the inner structure of rubber.

References

Boochathum, P. & Chiewnawin, S. (2001). *Eur. Polym. J.* **37**, 429–434.
Boochathum, P. & Prajudtake, W. (2001). *Eur. Polym. J.* **37**, 417–427.
Chauvistré, R., Hormes, J., Brück, D., Sommer, K. & Engels, H. W. (1992). *Kautsch. Gummi. Kunstst.* **45**, 808–813.
Chauvistré, R., Hormes, J., Hartmann, E., Etzenbach, N., Hosch, R. & Hahn, J. (1997). *Chem. Phys.* **223**, 293–302.
Filipponi, A. & Di Ciico, A. (1995). *Phys. Rev. B*, **51**, 12322–12336.
Gent, A. N. (1961). *J. Appl. Polym. Sci.* **6**, 433–441.
Gent, A. N., Kawahara, S. & Zhao, J. (1998). *Rubber Chem. Technol.* **71**, 668–768.
George, G. N. & Gorbaty, M. L. (1989). *J. Am. Chem. Soc.* **111**, 3182–3186.
Hitchcock, A. P., Horsley, J. A. & Stöhr, J. (1986). *J. Chem. Phys.* **85**, 4835–4848.
Hormes, J. & Modrow, M. (2001). *Nucl. Instrum. Methods Phys. Res. A*, **467–468**, 1179–1191.
Ikeda, Y., Yasuda, Y., Makino, S., Yamamoto, S., Tosaka, M., Senoo, K. & Kohjiya, S. (2007). *Polymer*, **48**, 1171–1175.
Klysubun, W., Sombunchoo, P., Wongprachanukul, N., Tarawarakarn, P., Klinkhico, S., Chaiprapa, J. & Songsiriritthigul, P. (2007). *Nucl. Instrum. Methods Phys. Res. A*, **582**, 87–89.
Klysubun, W., Tarawarakarn, P., Sombunchoo, P., Klinkhico, S., Chaiprapa, J. & Songsiriritthigul, P. (2006). *AIP Conf. Proc.* **879**, 860–863.
Lewis, E. L. V., Bower, D. I. & Ward, I. M. (1995). *Polymer*, **36**, 4741–4752.
Lin, W., Bian, M., Yang, G. & Chen, Q. (2004). *Polymer*, **45**, 4939–4943.
Luch, D. & Yeh, G. S. Y. (1973). *J. Polym Sci.* **11**, 467–486.
Lytle, F. W., Laan, G. V. D., Greegor, R. B., Larson, E. M., Violet, C. E. & Wong, J. (1990). *Phys. Rev. B*, **41**, 8955–8963.
Mitchell, G. R. (1984). *Polymer*, **25**, 1562–1572.
Modrow, H., Zimmer, R., Visel, F. & Homes, J. (2000). *Kautsch. Gummi. Kunstst.* **53**, 328–337.
Murakami, S., Senoo, K., Toki, S. & Kohjiya, S. (2002). *Polymer*, **43**, 2117–2120.
Polian, A., Itie, J. P., Dartyge, E., Fontaine, A. & Tourillon, G. (1989). *Phys. Rev. B*, **39**, 3369–3373.
Prange, A., Chauvistré, R., Modrow, H., Hormes, J., Trüper, H. G. & Dahl, C. (2002). *Microbiology*, **148**, 267–276.
Ravel, B. & Newville, M. (2005). *J. Synchrotron Rad.* **12**, 537–541.
Rosolen, J. M. & Abbate, M. (2001). *Solid State Ion.* **139**, 83–88.
Sze, K. H., Brion, C. E., Tronc, M., Bodeur, S. & Hitchcock, A. P. (1988). *Chem. Phys.* **121**, 279–297.
Toki, S., Sics, I., Ran, S., Liu, L., Hsiao, B. S., Murakami, S., Senoo, K. & Kohjiya, S. (2002). *Macromolecules*, **35**, 6578–6584.
Tosaka, M., Murakami, S., Poompradub, S., Kohjiya, S., Ikeda, Y., Toki, S., Sics, I. & Hsiao, B. S. (2004). *Macromolecules*, **37**, 3299–3309.
Toshiki, S., Kohjiya, S., Tosaka, M. & Tsuji, M. (2000). *Rubber Chem. Technol.* **73**, 926–937.