

Cure Characteristics of Unaccelerated Sulfur Vulcanization of Epoxidized Natural Rubber

B. T. POH,* M. F. CHEN, and B. S. DING

School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

SYNOPSIS

The curing characteristics of unaccelerated sulfur vulcanization of ENR 25 and ENR 50 were studied in the temperature range from 100–180°C. The range of sulfur loading was from 1.5 to 6.5 phr. The scorch time was determined by Mooney Shearing Disk Viscometer whereas the initial cure rate, maximum torque, and reversion properties were obtained from the Moving Die Rheometer (MDR 2000). Results shows that ENR 25 gives a longer scorch time than ENR 50, an observation similar to that in an accelerated system reported earlier. For temperature < 120°C, scorch time depends exponentially on sulfur loading for both rubbers. However, this dependence diminishes as temperature is increased. This observation is attributed to the availability of activated sulfur molecules for vulcanization. The initial cure rate and maximum torque increases with increasing sulfur loading. ENR 50, however, exhibits higher value than ENR 25, suggesting faster cure in the former. For a fixed sulfur loading, reversion is a time and temperature-dependent phenomenon. It decreases with increasing sulfur loading because of the increase of cross-linking density for both rubbers studied. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Cure characteristics of epoxidized natural rubber (ENR) have been reported in recent years. Most of these studies involved the use of accelerated sulfur vulcanization systems.^{1–5} With regard to the cure characteristics of unaccelerated sulfur vulcanization of ENR, research work in this area seems scarce. Gelling et al.⁶ and Amu et al.⁷ reported briefly the sulfur vulcanization behavior of ENR 50 in the absence of an organic accelerator. They found that vulcanization of ENR 50 by sulfur alone is considerably faster than that of natural rubber. This observation is attributed to the additional activation when olefin and epoxide groups are in the same molecule.⁶ For sulfur loading up to 2.5 phr, it is observed that Mooney scorch time of ENR 50 decreases with an increase in sulfur concentration.⁷ A systematic study of the cure characteristics of unaccelerated sulfur vulcanization of ENR 25 and ENR 50, however, is not reported so far. It is thus the aim of this

paper to discuss some of our findings on this area of research, particularly, the scorch, cure, and reversion properties of ENR vulcanized by sulfur alone.

EXPERIMENTAL

Materials

ENR 25 and ENR 50 having 25 and 50 mol % of epoxidation, respectively, were used in this study and the technical specification of the rubbers was given in our previous paper.¹ Freshly supplied commercial grade sulfur was used as the vulcanizing agent for the rubbers.

Compounding

The range of sulfur loading used was from 1.5 to 6.5 phr. Mixing procedure was carried out in accordance with ASTM Designation: D 3184-80⁸ using a two-roll mill at 70 ± 5°C. The compound was then kept in a closed container maintained at 23 ± 3°C for 24 h before testing.

* To whom correspondence should be addressed.

Measurement

The scorch time of the compound was determined by Mooney Shearing Disk Viscometer and the testing procedure as described in ASTM D 1646-81⁹ was followed. For the determination of cure rate, maximum torque and reversion properties, Monsanto Moving Die Rheometer (MDR 2000) was used. The moving die frequency and oscillation amplitude were 1.66 Hz and $\pm 0.5^\circ$, respectively. The instrument was calibrated at 177°C by using an elastic torque standard of 20.98 in. lbs. The sample volume used for each testing was about 4 g.

RESULTS AND DISCUSSION

The results obtained from this study are discussed with respect to the scorch behavior, initial cure rate, maximum torque, and reversion properties of the unaccelerated sulfur vulcanization of ENR.

Scorch Behavior

Figures 1 and 2 show the dependence of Mooney scorch time on sulfur loading for ENR 25 and ENR 50, respectively, at various temperatures of vulcanization in an unaccelerated sulfur system. For both the rubbers studied, the scorch time indicates strong exponential dependence on sulfur loading for temperature $< 120^\circ\text{C}$. At low temperature and low sulfur loading, the number of activated sulfur molecules

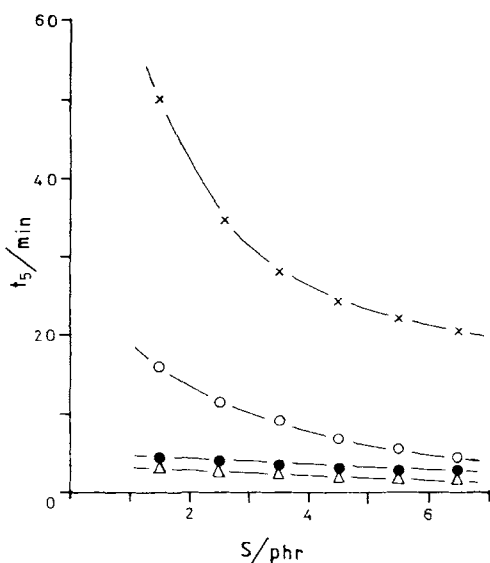


Figure 1 Variation of Mooney scorch time of ENR 25 with sulfur loading at various temperatures of vulcanization. X, 100°C; O, 120°C; ●, 140°C; Δ, 160°C.

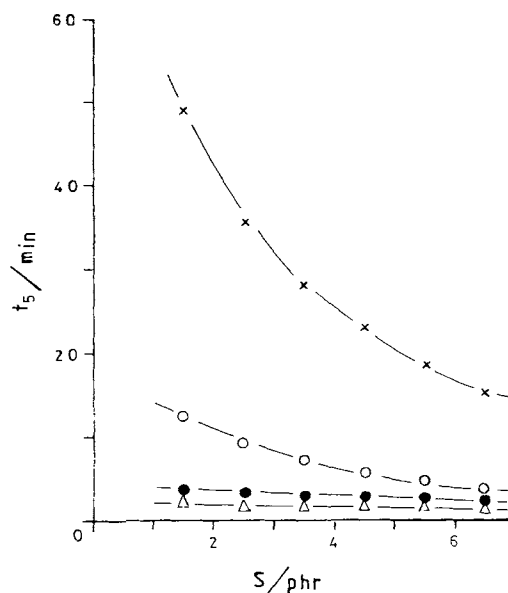


Figure 2 Variation of Mooney scorch time of ENR 50 with sulfur loading at various temperatures of vulcanization. Symbols as in Figure 1.

necessary for cross-linking is less; thus, longer scorch time is observed. However, as the sulfur concentration is increased, there are more activated sulfur molecules available for cross-linking, as reflected by the decrease in scorch time. At higher temperature of vulcanization, even at low sulfur loading, there are enough number of activated sulfur molecules for cross-linking; thus scorch time remains virtually independent of sulfur concentration for temperatures higher than 140°C.

A comparison of scorch behavior between accelerated and unaccelerated sulfur vulcanization for the ENR rubbers is shown in Figure 3. For the accelerated sulfur vulcanization system where the sulfur content is 3.5 phr, the scorch time data was obtained from our previous study.¹ For both vulcanizing systems, an exponential decrease in Mooney scorch time with increasing temperature was obtained. The scorch time for unaccelerated sulfur vulcanization system indicates a much higher value compared with that in an accelerated sulfur vulcanization system. As in the case of accelerated sulfur vulcanization,¹ the scorch time of ENR 25 is greater than that of ENR 50 in unaccelerated sulfur vulcanization. This is attributed to the presence of more epoxide groups in ENR 50, hence greater activation of adjacent double bond by the epoxide group compared with ENR 25. However, as the temperature of vulcanization is increased, the difference in scorch time between ENR 25 and ENR 50 narrows because more

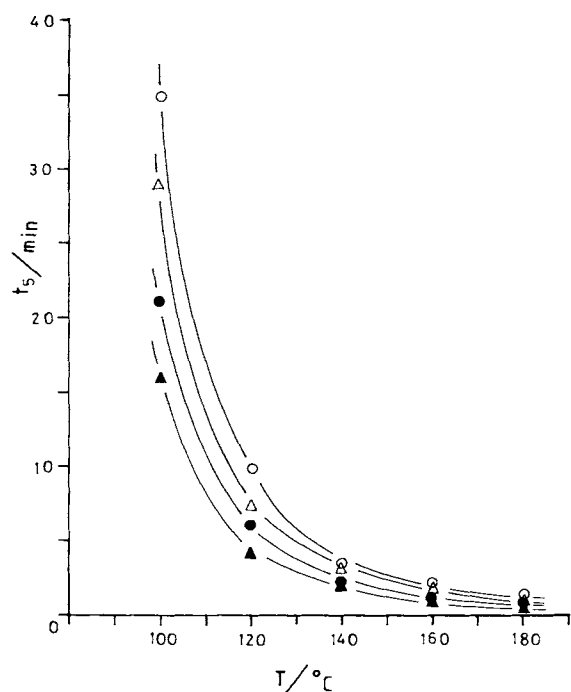


Figure 3 Temperature dependence of Mooney scorch time for the accelerated and unaccelerated systems at 3.5 phr of sulfur loading. Unaccelerated system: ○, ENR 25; △, ENR 50; accelerated system: ●, ENR 25; ▲, ENR 50.

activated sulfur molecules are available for cross-linking because of the increase in thermal energy. Also, for temperature $> 155^{\circ}\text{C}$, additional cross-link due to ring-opening reaction occurs.¹

For the temperature range studied, Mooney scorch time for the unaccelerated system is always longer than that of accelerated system. In the accelerated sulfur vulcanization system, the presence of other compounding ingredients—especially the accelerators—helps to form the active sulfurating agents that would enhance cross-linking; thus shorter scorch time is observed.^{10,11} The difference in scorch time between accelerated and unaccelerated systems is more significant at lower temperature because of the lower number of activated sulfur molecules available for vulcanization. However, as the temperature is increased, this difference narrows. This is attributed to the greater increase in the number of activated sulfur molecules in the unaccelerated system.

Initial Cure Rate and Maximum Torque

The initial cure rate (r), maximum torque (τ_{max}), and reversion (R) properties of unaccelerated sulfur vulcanization of ENR were determined by

Monsanto Moving Die Rheometer (MDR 2000). A typical MDR rheograph for the unaccelerated system is shown in Figure 4. Figure 5 shows the variation of the initial cure rate of ENR with sulfur loading at 150°C . The initial cure rate increases with increasing sulfur loading. This is attributed to the increase in the number of activated sulfur molecules available for cross-linking. In the case of ENR 25, the initial cure rate increases steadily with sulfur loading, whereas for ENR 50 a more gradual increase is observed, especially for sulfur content higher than 4.5 phr. The nonlinear increase of cure rate for sulfur loading greater than 4.5 phr in ENR 50 is most probably due to the limited availability of cross-linking sites (i.e., activated double bonds). Thus, the limiting value of cure rate is reached earlier in ENR 50 compared with ENR 25, which has a higher degree of unsaturation than the former. However, for a fixed sulfur loading, owing to the higher epoxidation in ENR 50 and hence greater activation of adjacent double bond, a faster cure rate is noted in ENR 50, which is more polar than ENR 25.

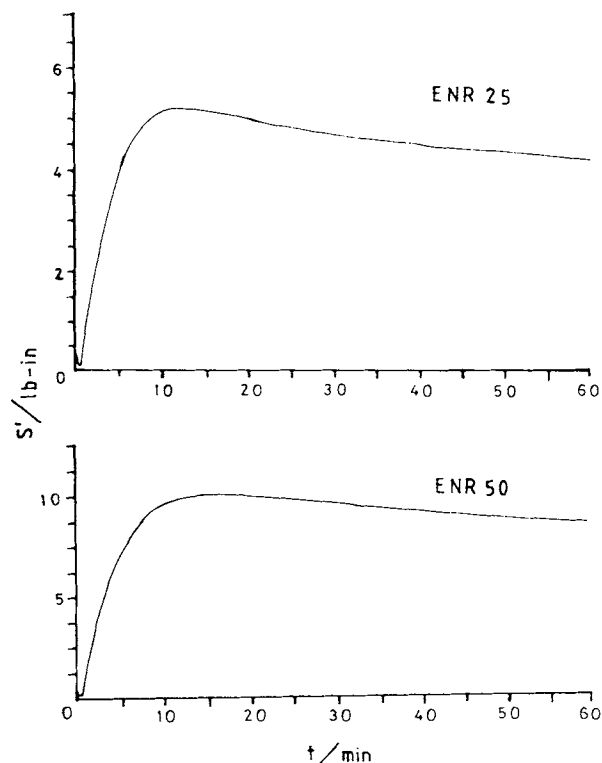


Figure 4 Two typical MDR rheographs at 160°C showing the time-dependence behavior of the elastic torque (S') component in an unaccelerated system for ENR 25 and ENR 50. Sulfur loading is 3.5 phr.

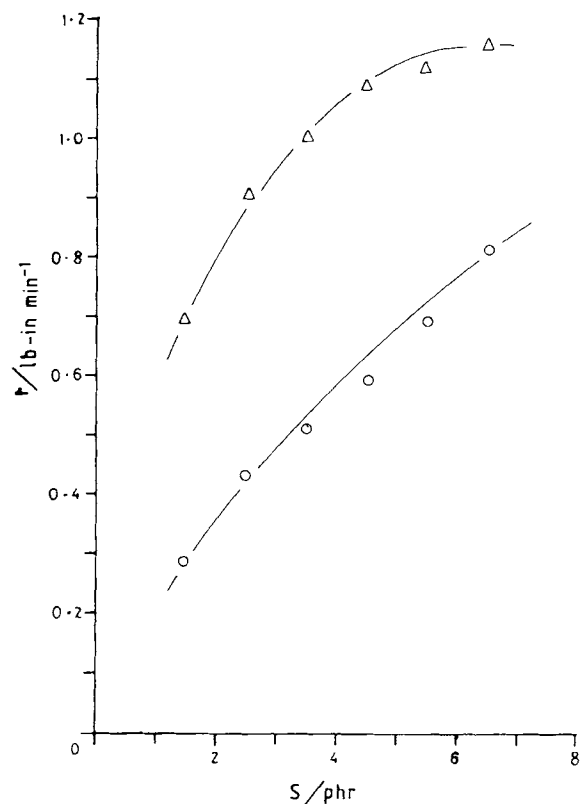
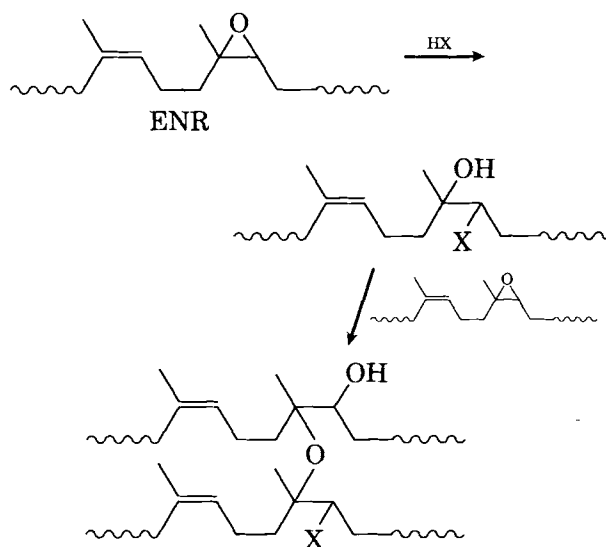


Figure 5 Variation of initial cure rate (r) with sulfur loading at 150°C. O, ENR 25; Δ, ENR 50.

This finding reinforces the evidence that unaccelerated sulfur vulcanization involves a polar chain process.¹²

Figure 6 shows the variation of maximum torque at 150°C with sulfur loading for the ENR studied. As in the case of the initial cure rate, ENR 50 exhibits a higher value of maximum torque compared with ENR 25. This observation is associated with the faster cure in ENR 50 due to the greater activation of adjacent double bond by the epoxide group in the rubber. In other words, for both vulcanizates to have the same maximum torque, more sulfur loading is needed in ENR 25. One interesting observation is that maximum torque in ENR 25 varies linearly with sulfur loading, whereas for ENR 50, it shows a slight positive deviation from linearity. This observation may be explained by the faster cure and additional ether cross-link due to ring-opening reaction⁶ in ENR 50 as torque is an indication of the degree of cross-linking in a rubber. The chemical reaction equation for the acid-catalyzed epoxy ring-opening reaction to form ether cross-link in ENR is shown below:



where HX is the acid from oxidation of sulfides produced during vulcanization.⁶

Reversion

Reversion is an important phenomenon in sulfur vulcanization of natural rubber. In this study, the percentage reversion (R) is defined as

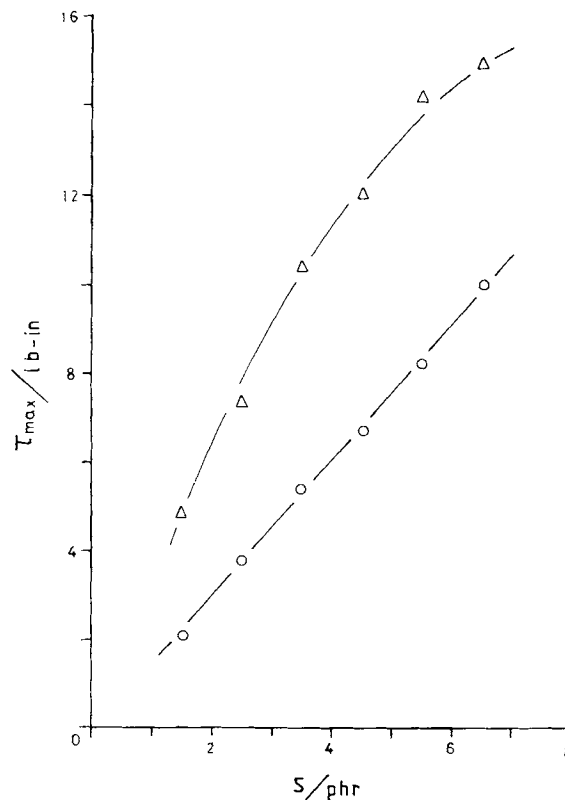


Figure 6 Variation of maximum torque (τ_{\max}) with sulfur loading at 150°C. Symbols as in Figure 5.

$$R = (\tau_{\max} - \tau_t)100/(\tau_{\max} - \tau_{\min})$$

where τ_{\max} , τ_{\min} , and τ_t are maximum torque, minimum torque, and torque at t minutes, respectively.

The time dependence of the reversion behaviour of ENR 25 for the various sulfur loading at 160°C is indicated in Figure 7. The observation that reversion increases with time of vulcanization is similar to that of an accelerated sulfur vulcanization for ENR⁵ and natural rubber.¹³ Figure 7 also shows that reversion in an unaccelerated sulfur system is higher at low sulfur loading. This may be due to insufficient cross-linking and reversion is mainly caused by thermal degradation of the main chain. However, as sulfur loading is increased beyond 3.5 phr, lower reversion is observed because of the increase in cross-linking density.

The temperature dependence of reversion of ENR 25 after 30 min from maximum torque at various sulfur loadings is shown in Figure 8. For a fixed sulfur loading, increase in temperature is accompanied by an increase in reversion. This is explained by the greater rate of decomposition of the rubber vulcanizate. As in the case of time dependence study, reversion increases with decreasing sulfur loading for

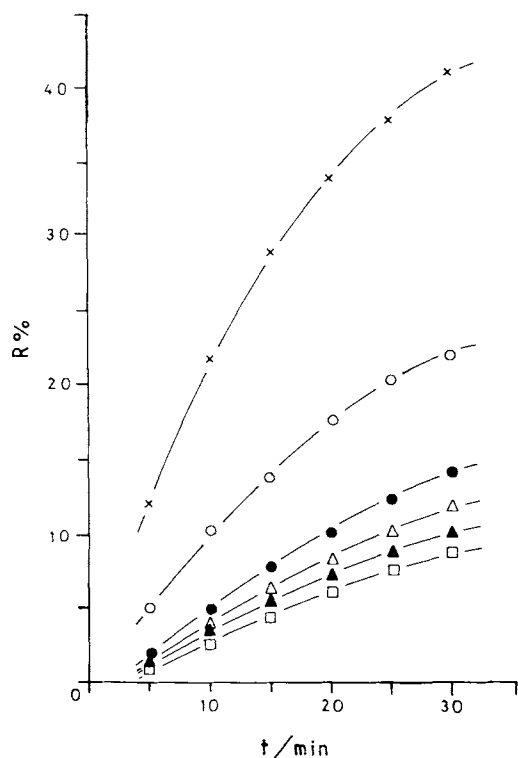


Figure 7 Time dependence behavior of percentage reversion ($R\%$) for ENR 25 at 160°C for various sulfur loadings (phr). \times , 1.5; \circ , 2.5; \bullet , 3.5; Δ , 4.5; \blacktriangle , 5.5; \square , 6.5.

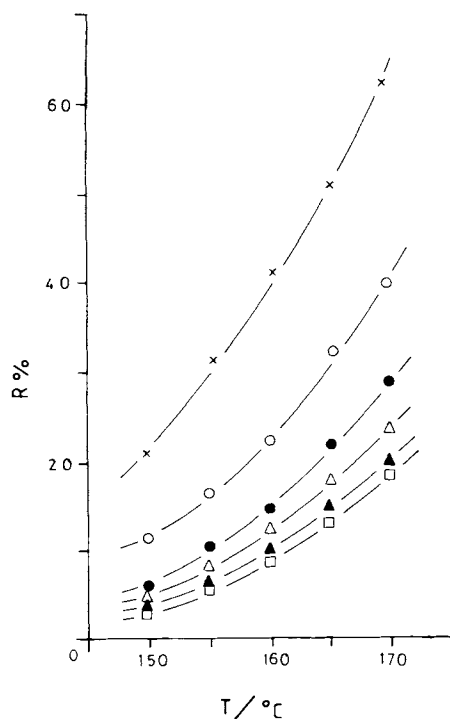


Figure 8 Temperature-dependent behavior of percentage reversion ($R\%$) for ENR 25 after 30 min from maximum torque for various sulfur loadings. Symbols as in Figure 7.

a fixed temperature of vulcanization. This observation is again mainly attributed to the thermal breakdown of the main chain for sulfur loading less than 3.5 phr.

The reversion behaviour between ENR 25 and ENR 50 at 160°C after 30 min from maximum torque is shown in Figure 9. For both rubbers studied, reversion decreases with increasing sulfur loading. The reversion in ENR 25 indicates a higher value compared with ENR 50—more significant at low sulfur loading—an observation similar to that reported for the accelerated system.⁵ However, this difference narrows as sulfur loading is increased. In fact, at 6 phr of sulfur loading, both rubbers exhibit similar reversion value. The higher reversion in ENR 25 at low sulfur loading is attributed to the lower cross-linking density and reversion is mainly caused by the thermal degradation of main chain as described previously. In the case of ENR 50, because of the greater activation of double bond by the epoxide group, higher cross-linking density is obtained and thus reversion is lower than ENR 25. However, as sulfur loading is increased, the number of activated sulfur molecules available for cross-linking is correspondingly increased. This means that more cross-linking occurs until both rubbers attain similar

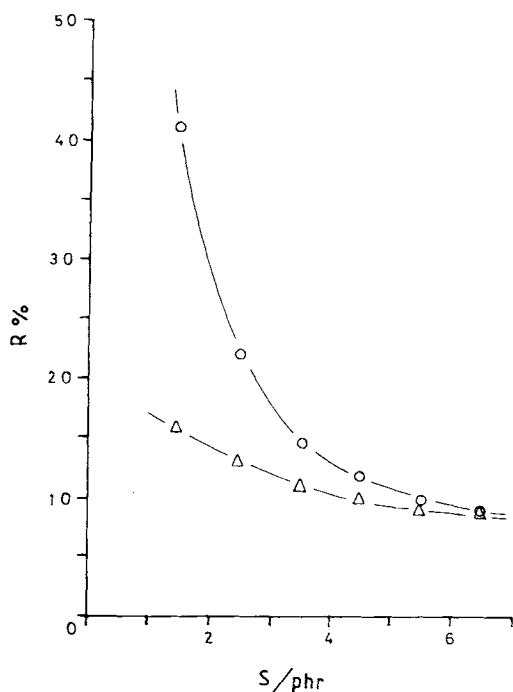


Figure 9 A comparison in reversion behavior between ENR 25 and ENR 50 at 160°C after 30 min from maximum torque for various sulfur loadings. Symbols as in Figure 5.

cross-linking density as reflected by the reversion value at 6 phr of sulfur loading.

CONCLUSION

From this study, the following conclusion can be drawn:

1. Mooney scorch time of ENR 25 and ENR 50 in an unaccelerated sulfur vulcanization indicates strong exponential dependence on sulfur loading for temperature < 120°C. However, for a higher temperature, scorch time for both rubbers is virtually independent of sulfur concentration. This observation is attributed to the availability of activated sulfur molecules for vulcanization. The scorch time for unaccelerated system is longer than that of an accelerated one because of the enhancement effect of the active sulfurating agent of the latter.
2. The initial cure rate and maximum torque increases with increasing sulfur loading for

both rubbers. However, ENR 50 exhibits higher values than ENR 25. This is associated with the faster cure in ENR 50 due to the greater activation of double bond by the epoxide group in the rubber.

3. Reversion in an unaccelerated system is a time and temperature-dependent phenomenon. It increases with increasing time and temperature of vulcanization. At low sulfur loading, reversion shows a higher value that is attributed to insufficient cross-linking. ENR 25 exhibits a higher reversion compared to ENR 50, and observation similar to that reported for the accelerated system.⁵

REFERENCES

1. B. T. Poh and B. K. Tan, *J. Appl. Polym. Sci.*, **42**, 1407 (1991).
2. C. S. L. Baker, I. R. Gelling, and R. Newell, *Rubber Chem. Technol.*, **58**, 67 (1985).
3. M. Nasir and C. H. Choo, *Eur. Polym. J.*, **25**, 355 (1989).
4. B. T. Poh and W. L. Tang, *J. Appl. Polym. Sci.*, **55**, 537 (1995).
5. B. T. Poh, C. P. Kwok, and G. H. Lim, *Eur. Polym. J.*, **31**, 223 (1995).
6. I. R. Gelling and N. J. Morrison, *Rubber Chem. Technol.*, **58**, 243 (1985).
7. A. Amu, K. A. R. Ku Ismail, and S. Dulngali, *Preprint of International Rubber Conference, Kuala Lumpur, Malaysia*, 1985.
8. *Annual Book of ASTM Standards 1981, Part 37, Rubber, Natural and Synthetic-General Test Methods, Carbon Black, Designation D 3184-80*, ASTM, Philadelphia, p. 697.
9. *Annual Book of ASTM Standards 1981, Part 37, Rubber, Natural and Synthetic-General Test Methods, Carbon Black, Designation D 1646-81*, ASTM, Philadelphia, p. 410.
10. L. Bateman, Ed., *The Chemistry and Physics of Rubber-like Substances*, Applied Science, London, 1963, p. 532.
11. C. H. Lee and B. T. Poh, *J. Appl. Polym. Sci.*, **30**, 71 (1985).
12. L. Bateman, Ed., *The Chemistry and Physics of Rubber-like Substances*, Applied Science, London, 1963, p. 486.
13. C. M. Kok, *Eur. Polym. J.*, **23**, 611 (1987).

Received April 11, 1995

Accepted August 13, 1995