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# The Effect of Accelerator/Sulphur Ratio on the Cure Time and Torque Maximum of Epoxidized Natural Rubber

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The cure time of accelerated sulphur vulcanization of Epoxidized Natural Rubber (ENR 25) was studied while one grade of unmodified natural rubber – Standard Malaysian Rubber Light (SMR L) was used as a control. Five accelerators, *viz.* 2-mercaptobenzothiazole (MBT), tetramethylthiuram disulphide (TMTD), zinc dimethyldithiocarbamate (ZDMC), *N*-tert-butyl-2-benzothiazylsulphenamide (TBBS) and diphenylguanidine (DPG) were used in the study and the vulcanization systems used were conventional vulcanization (CV), semi-efficient vulcanization (semi-EV) and efficient vulcanization (EV). Monsanto Moving-Die Rheometer (MDR 2000) was used to determine the cure time in the temperature range of 100–180°C. The results indicate that cure time decreases exponentially with increasing temperature for the two rubbers studied. At a fixed curing temperature, ENR 25 shows shorter cure time compared to that of SMR L. This has been attributed to the activation of the double bond by the adjacent epoxide group in ENR 25. Studies of the effect of varying amounts of MBT at a fixed sulphur concentration show that cure time decreases as the accelerator concentration increases. ENR 25 shows higher torque maximum than SMR L. This observation can be related to the oxirane group which is bulky and thus accounts for increased glass transition temperature with increase in the level of epoxidation. Of the vulcanization systems, CV shows the highest torque maximum followed by semi-EV and then EV. This trend can be attributed to the amount of active sulphurating agent which increases with increasing accelerator concentration. It was also found that the influence of accelerator/sulphur ratio becomes less significant as vulcanization temperature increases.

**Keywords:** Epoxidized natural rubber (ENR 25); natural rubber (SMR L); cure time; torque maximum; accelerator/sulphur ratio; accelerator types; temperature

## INTRODUCTION

Epoxidized natural rubber (ENR) is a new polymer offering unique properties. Studies on the cure characteristics of accelerated-sulphur vulcanization of ENR are limited to scorch and reversion behaviour [1–4], cure index and activation energy [5]. Most of the studies on ENR concentrate on its physical and mechanical properties [6–12] or its blends [13–16]. Our previous paper on the scorch behaviour [3] showed that ENR 25 shows shorter scorch time compared with natural rubber (NR). This has been attributed to the activation of the double bond by the oxirane group. It was also found that the influence of accelerator/sulphur ratio become less significant as vulcanization temperature increases. Poh *et al.* [4] showed that the time-dependent reversion behaviour of ENR is similar to that of unmodified NR. Another paper [5] showed that the cure index depends on the accelerators and vulcanization systems. Highly substituted accelerators (*e.g.* TBBS) tend to give a higher cure index and apparent activation energy which suggested that steric hindrance plays an important role in accelerated sulphur vulcanization of rubbers.

While the few studies conducted so far on the cure characteristics of accelerated-sulphur vulcanization of ENR are limited to scorch and reversion behaviour, studies on cure time and torque maximum of different vulcanization systems are rather limited. In view of the importance of curing characteristics of epoxidized natural rubber, it is the aim of this study to describe further some of the findings involving the cure time and torque maximum.

## EXPERIMENTAL

### Materials

Epoxidized natural rubber with 25 mol % epoxidation (ENR 25) and natural rubber grade SMR L were obtained from Kumpulan Guthrie Berhad., Malaysia. Five accelerators MBT, TMTD, ZDMC, DPG and TBBS were supplied by Bayer. The technical specifications of the rubbers and accelerators were given in our previous paper [3]. Carbon black (330), silica (vulkasil-S) and calcium carbonate having a surface

area of 70 m<sup>2</sup>/g, 170 m<sup>2</sup>/g and 22 m<sup>2</sup>/g and partical size of 30 nm, 19 nm and 75 nm respectively were chosen as the fillers, with loading ranged from 0–60 phr. Other compounding ingredients such as zinc oxide, stearic acid and sulphur were of commercial grade. All the materials were freshly supplied and used as received.

## Method

Compounding was done in accordance with the method described by ASTM Designation D 3184-89 [17] using a two-roll mill at 70 ± 5°C and total time taken to complete one mixing cycle was 18 min. for the gum stock and 29 min. for the filled stock. The concentrations of sulphur and the accelerators were varied to ascertain different vulcanization systems *i.e.* CV, semi-EV and EV [3]. The compound was then kept in a close container maintained at 23 ± 3°C for 24 h before testing.

## Measurement

The cure times of the compounds were determined with the Monsanto Moving-Die Rheometer (MDR 2000). The moving die frequency and oscillation amplitude were 1.66 Hz and ± 0.5° 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 4.0 g.

## RESULT AND DISCUSSION

### Effect of Rubbers

Figures 1–3 show the variation of cure time with temperature for SMR L and ENR 25 by using three different vulcanization systems. An exponential decrease of cure time with increasing temperature is shown by the rubbers studied. The three systems used, *i.e.* CV, semi-EV and EV systems show the same characteristics. SMR L shows more gradual cure behaviour than the ENR 25 for all the three vulcanization systems. This observation can be explained that as the

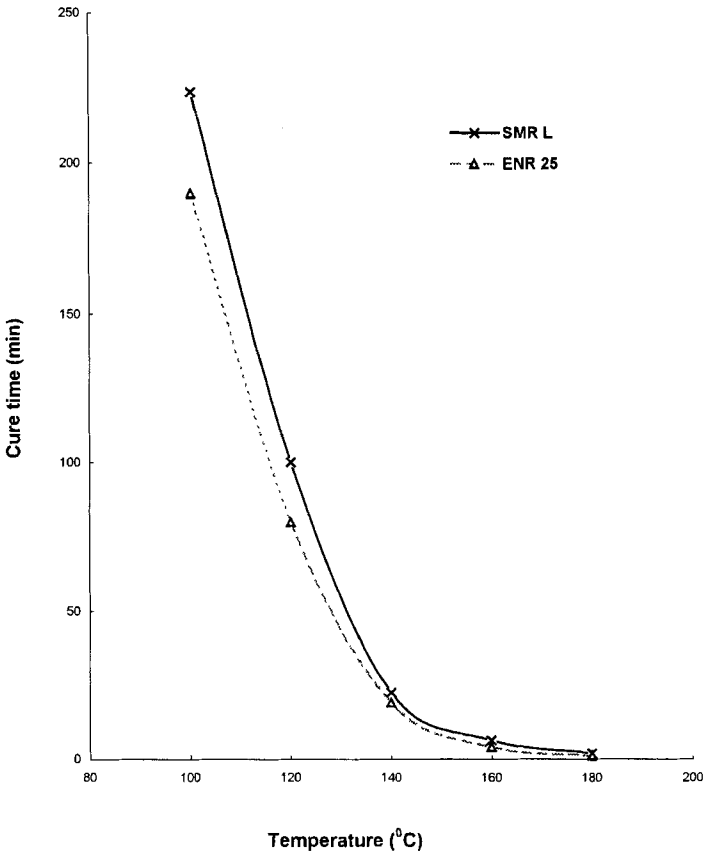


FIGURE 1 Temperature dependence of cure time for ENR 25 and SMR L compounds cured with MBT accelerated CV system.

temperature of curing is increased, there is sufficient thermal energy to cause faster curing. Also, the mobility of the rubber chain is increased, and this would mean that the probability of crosslinking is increased. It is observed that the rate of increase of cure time is greater for SMR L than ENR 25.

For temperature less than 160°C, the cure time increases steadily with decreasing temperature. But, for temperature greater than 160°C, a rapid increase in initial rate of cure time is observed. The higher cure rate above 160°C may be attributed to the thermal energy available to crosslinking. The cure rate slows down due to the formation of more

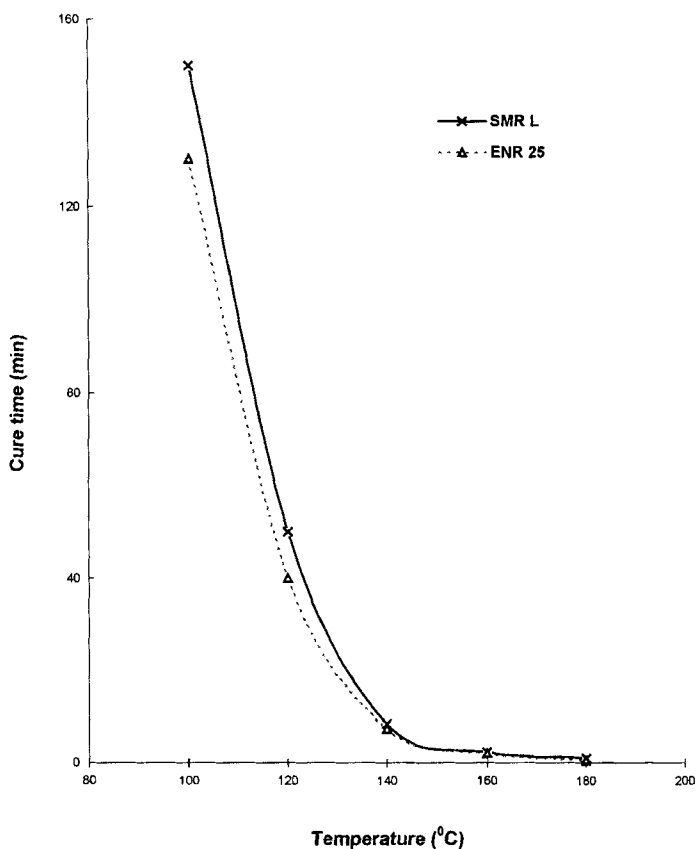


FIGURE 2 Temperature dependence of cure time for ENR 25 and SMR L compounds cured with MBT accelerated semi-EV system.

stable monosulphidic crosslinks from desulphuration of a polysulphidic crosslink [18, 19] as cure time increases. In the case of ENR 25, due to the activation of the double bonds by the adjacent epoxide groups, a faster rate of vulcanization is observed [1], leading to shorter cure time.

### Effect of Accelerators

The variation of cure time with temperature for SMR L and ENR 25 for the various accelerators in CV system are shown in Figure 4. In all the accelerators studied, ZDMC shows the shortest cure time. On the

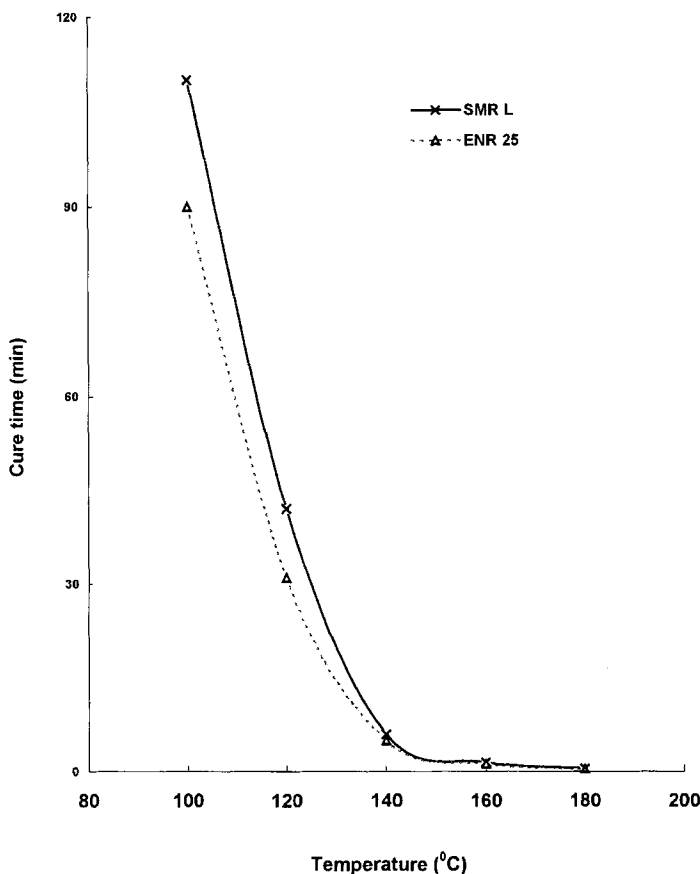


FIGURE 3 Temperature dependence of cure time for ENR 25 and SMR L compounds cured with MBT accelerated EV system.

other hand DPG shows the longest cure time. It was found that DPG is decomposed at vulcanization temperature with the formation of ammonia, aniline, tetraphenylmelamine and triphenyldicarbamine [20, 21]. The presence of DPG with sulphur, leading to the formation of polysulphide compounds and polysulphide crosslinks in the vulcanizates [21] may cause longer cure time. During DPG - accelerated vulcanization, DPG produces a large amount of polysulphides. On the other hand, ZDMC and TMTD show shorter cure time. Because the

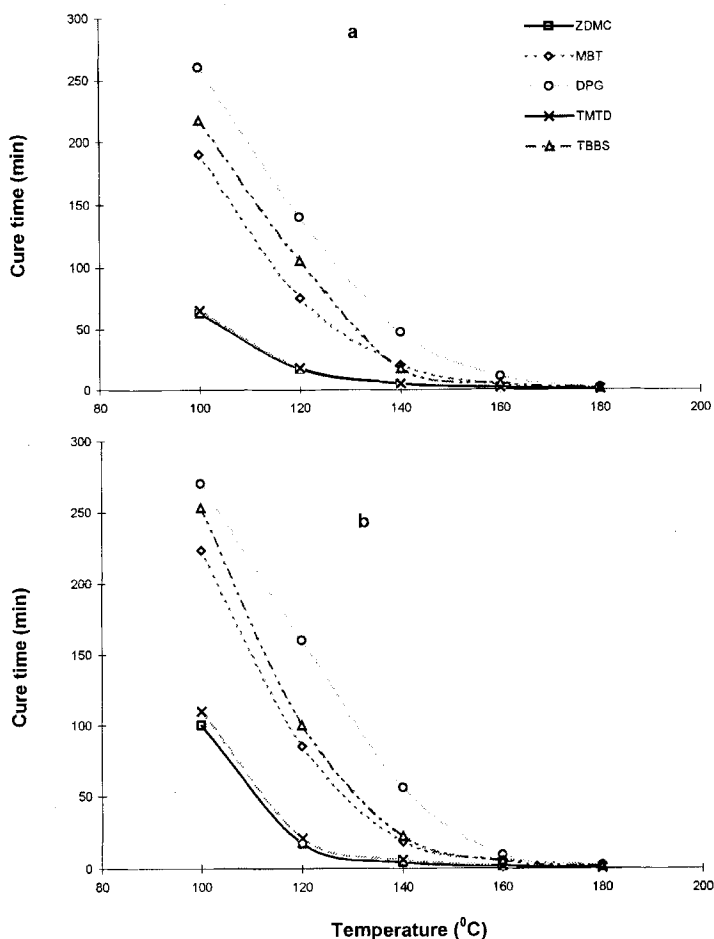


FIGURE 4 Variation of cure time with temperature for (a) ENR 25 and (b) SMR L compounds cured with different accelerators (CV system).

accelerators belongs to the “ultra fast” accelerators class, they produce intermediate sulphurating reagents (chelate) which are more active [22], and due to the lower activation energy of vulcanization they show shorter cure time. The accelerators can be arranged in the order of increasing cure time as follows:

$$\text{ZDMC} < \text{TMTD} < \text{TBBS} < \text{MBT} < \text{DPG}$$



The variation of cure time with temperature for SMR L and ENR 25 for the various accelerators in semi-EV system are shown in Figure 5. In all the accelerators studied, ZDMC shows shortest cure time than the others. On the other hand DPG shows the longest cure time,

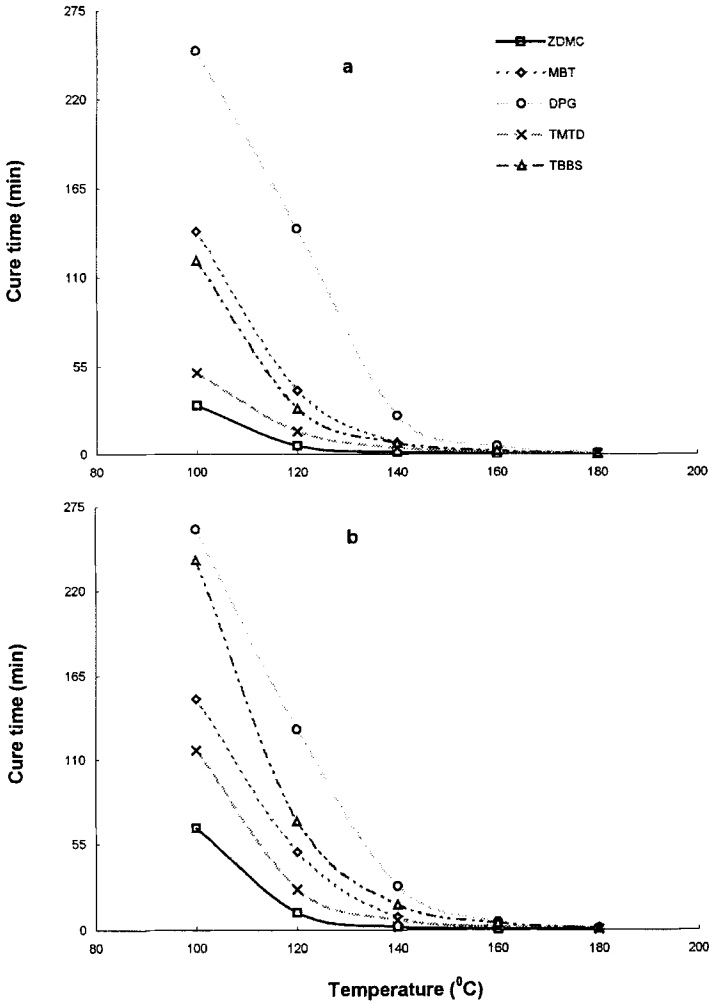


FIGURE 5 Variation of cure time with temperature for (a) ENR 25 and (b) SMR L compounds cured with different accelerators (semi-EV system).

Similar observations have been explained above in the case of CV vulcanization system. In the case of TMTD, the dependence of cure time is more obvious than that of ZDMC. This may be attributed to the slower rate of crosslinking by TMTD due to the formation of ZDMC as the reaction intermediate in TMTD accelerated vulcanization [23,24]. The accelerators can be arranged in the order of increasing cure time as shown for the CV system.



The variation of cure time with temperature for SMR L and ENR 25 for the various accelerators in EV system are shown in Figure 6. In all the accelerators studied, ZDMC shows the shortest cure time with increasing temperature. The longest cure time observed with the sulphenamide type of accelerator *i.e.* TBBS. This observation may be due to the slower rate of disappearance of the sulphenamide accelerator and its apparent immediate reaction product with sulphur [25]. On the contrary, ZDMC is an "ultrafast" type of accelerators and the short cure time observed is probably due to the lower activation energy of vulcanization, apart from its direct function as a catalyst for producing the initial polysulphidic crosslinked network. ZDMC also involves itself specifically in the formation of monosulphides [22]. In this system excess TMTD may cause lower rate of cure, because during the TMTD accelerated sulphur vulcanization, tetramethylthiuram polysulphide (TMTP) is formed [26]. This gives rise to mainly low sulphur rank TMTP. TMTP reacts with the rubber chain and, consequently, pendent groups of low sulphur rank are formed [27]. The accelerators can be arranged in the order of increasing cure time as follows:



In all the accelerators studied, as shown in Figures 4–6, as temperature is increased, the difference in cure time for the various accelerator systems narrows down. At temperatures greater than 160°C, the cure time for each accelerator system tends to a limiting value; *i.e.*, it does not depend greatly on the temperature. This observation is due to the sufficient thermal energy available to

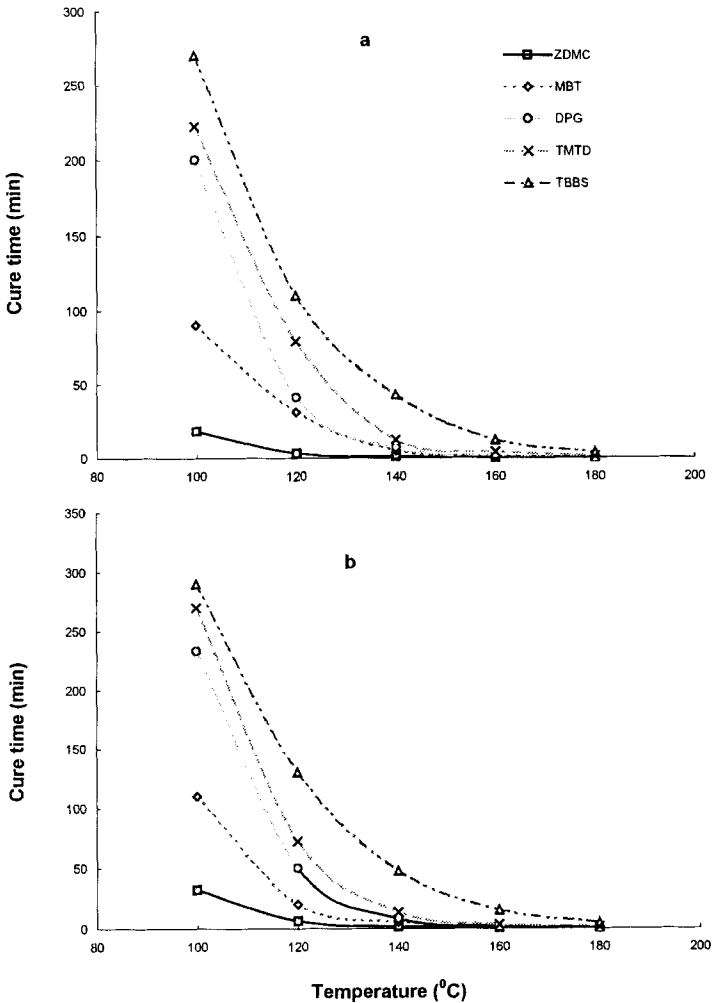


FIGURE 6 Variation of cure time with temperature for (a) ENR 25 and (b) SMR L compounds cured with different accelerators (EV system).

overcome the activation energy of vulcanization at temperatures greater than 160 $^{\circ}\text{C}$  as explained earlier for other vulcanization systems. It can therefore be inferred that the accelerators behave similarly at higher temperatures irrespective of the type of vulcanization system involved.

### Effect of Sulphur/Accelerator Ratio (Vulcanization Systems)

In this study, MBT was used to investigate the effect of accelerator to sulphur ratio which in practical compounding can be translated to CV, semi-EV and EV vulcanization systems. Based on the observed behaviour of MBT accelerated vulcanizates in Figures 1–3 and 4–6, the general trend is that cure time decreases in the order CV > semi-EV > EV. This observation is illustrated further with the cure study involving MBT/S ratios shown in Figure 7.

The variation of cure time of SMR L and ENR 25 with MBT concentration for various temperatures of curing is shown in Figure 7. The results indicate that the cure time strongly depends on MBT concentration at lower temperatures of vulcanization, *i.e.* 120°C and below, whereas for temperatures greater than 140°C, the dependence becomes less significant. At higher temperatures of vulcanization, enough thermal energy is available to overcome the activation energy of vulcanization. The range of MBT concentration was from 0.5 to 4.0 phr. Again Figure 7 shows that cure time in an accelerated sulphur system is higher at low MBT concentration. This may be due to a decrease in active sulphurating agents. Above the 2.0 phr. MBT concentration, it shows almost the same cure rate, because above that concentration, the viscosity of the rubber compound decreases. According to Bateman [22], MBT influences the cure time by involving itself directly in the interaction with molecular sulphur in order to produce intermediates which are active sulphurating reagents. The amount of active sulphurating reagent increases with increasing MBT concentration; thus cure time decreases and eventually tends to a constant value. It can be seen also from Figures 7a and 7b that due to the activation of double bonds by epoxide groups, ENR 25 compounds show shorter scorch time compared to that of SMR L compounds.

However, the generalization that cure time decreases with increase in accelerator concentration cannot be extended to all the accelerators investigated as shown in Figures 8 and 9. No regular pattern of behaviour can be seen although the highest cure time is shown by the EV system for some accelerators such as TBBS and TMTD in both rubbers. This suggests that the mechanism of cure in these accelerators is entirely different from that of MBT as discussed in the preceding

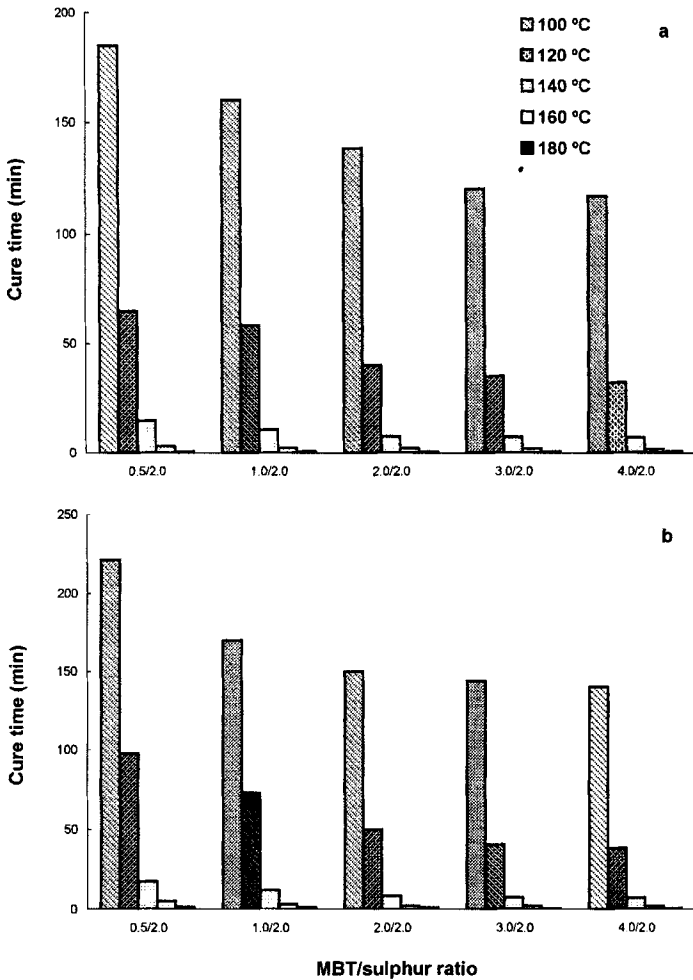


FIGURE 7 The dependence of cure time on MBT concentration at different temperatures (a) ENR 25 (b) SMR L.

section. This is so since different accelerators are known to behave differently in each rubber compound (22).

In Figures 8 and 9, the studies were conducted at three reference temperatures *i.e.* 100°C, 140°C and 180°C denoting low, medium and high temperatures respectively. It is obvious that the differences

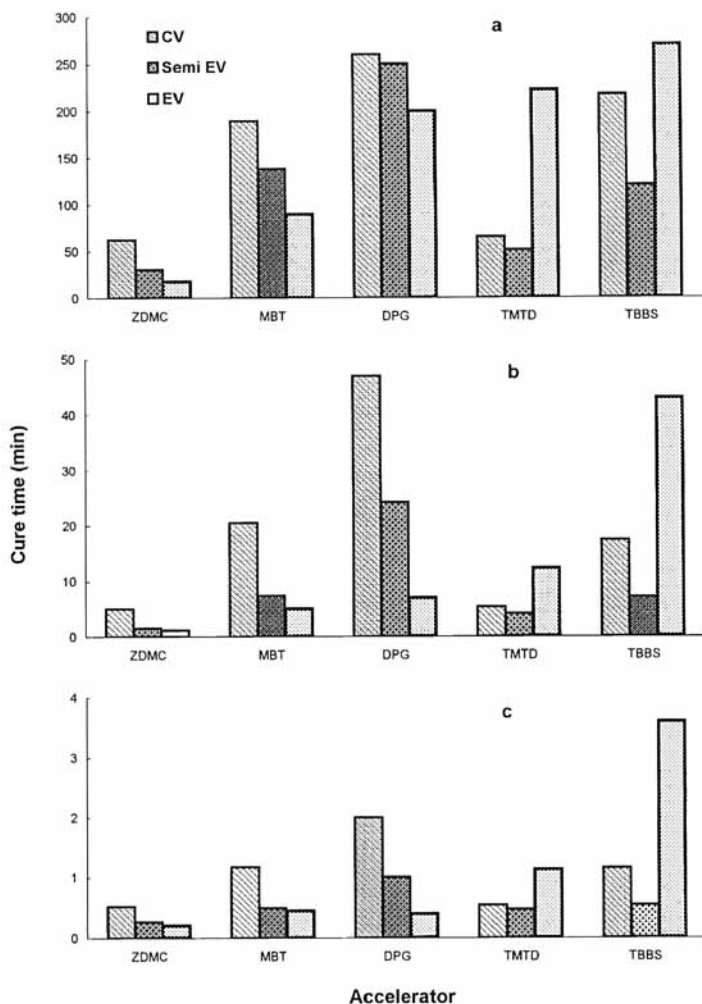


FIGURE 8 The variation of cure time with vulcanization systems in ENR 25 compounds for different accelerators at (a) 100°C (b) 140°C and (c) 180°C.

among the accelerators are more pronounced at lower temperatures (Figs. 8a and 9a) while the differences become drastically reduced with increase in temperature to the extent that at very high temperatures, the differences are almost insignificant (Figs. 8b and 9b at 140°C, 8c

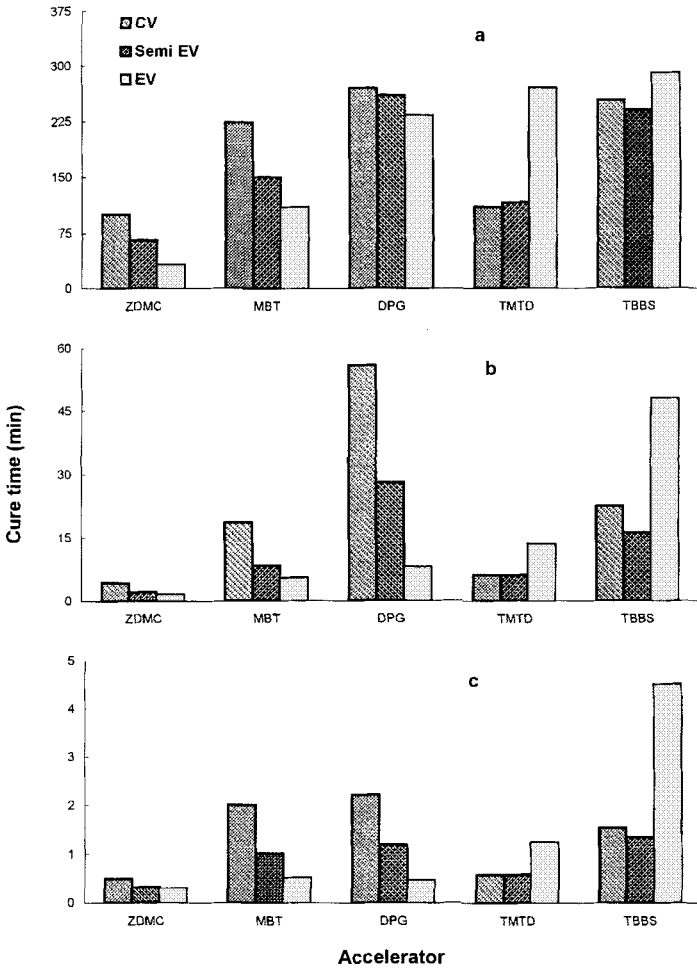


FIGURE 9 The variation of cure time with vulcanization systems in SMR L compounds for different accelerators at (a) 100°C (b) 140°C and (c) 180°C.

and 9c at 180°C). It could therefore be inferred that sulphur/accelerators ratio or vulcanization system does not play a significant role in determining cure behaviour at very high temperatures. It is also shown that the influence of accelerator type is equally not so significant. These observations could be attributed to the very low activation energy at very high temperatures.

### Effect of Fillers

Table I shows the effect of different filler loadings on the cure characteristics of ENR 25 and SMR L vulcanizates. The semi-EV system was chosen, rather than other vulcanization systems, because it is suitable for ENR [7]. It can be seen that cure time increased with increasing silica filler loadings for SMR L and ENR 25 vulcanizates, whereas the cure time for both carbon black and  $\text{CaCO}_3$ -filled SMR L and ENR 25 vulcanizates show falling and rising trends with increasing filler loading. The difference in cure time may be attributed to the fact that each type of filler possesses different filler properties *viz.* surface area, surface reactivity and particle size. Filler reinforcement is controlled by numerous interrelated factors [28, 29]. Here stress is mainly governed by particle size. It was found that the cure effect is also dependent on the accelerator systems and the type of elastomer [30].

The fastest cure time for calcium carbonate ( $\text{CaCO}_3$ ) filled SMR L and ENR 25 compounds may be due to the lower surface area. In general, a faster cure rate is obtained with fillers having a low surface area and high moisture content [31]. It can be seen that carbon black filled SMR L and ENR 25 compounds have shorter cure times compared to silica filled compounds. According to Kraus [32], carbon black can promote the accelerator dissociation into reactive species and catalyze the formation of hydrogen sulphide which can activate the sulphur vulcanization system. Studies by Fetterman [33] on the influence of silica on cure behaviour of rubber found that the impact

TABLE I Cure time ( $t_{90}$ ) of different-filled ENR 25 and SMR L compounds at 140°C for SMR L

% Filler (phr)	0	15	30	45	60
carbon black	9.75	12.5	14.0	13.25	11.25
silica	9.75	13.25	20.5	28.5	35.0
$\text{CaCO}_3$	9.75	11.25	9.0	7.75	8.25
for ENR 25					
carbon black	9.0	9.0	9.25	7.25	7.0
silica	9.0	12.25	14.75	22.5	28.0
$\text{CaCO}_3$	9.0	8.75	7.0	6.0	6.5

Base formulation of the rubber compound: Rubber, 100; zinc oxide, 6; stearic acid, 2; sulphur, 2; MBT, 2 phr; and filler variable.



on cure retardation is directly proportional to the surface area of silica and the functionality of sulphur is dependent on both the particle size and total content of silica. Nasir *et al.* [30] reported that the cure retardation can be attributed to a silica – accelerator interaction. The silica reacts with zinc oxide and subsequently reduces the reactivity of zinc which in turn slows down the reactivity of sulphur.

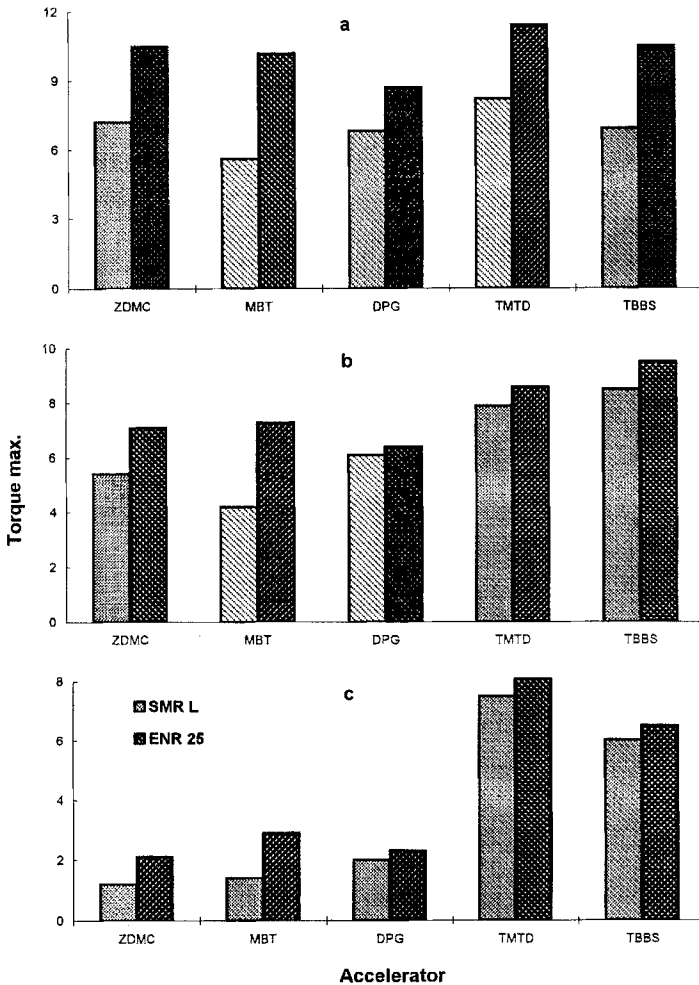


FIGURE 10 The variation of torque maximum with different accelerators and different vulcanization systems at 140°C (a) CV, (b) semi-EV and (c) EV.

## Torque Maximum

Figure 10 shows the variation of torque maximum with different accelerators and different vulcanization systems. For all the three vulcanization systems, ENR 25 shows higher torque maximum than SMR L. This observation can be explained in terms of the oxirane group which is bulky and this accounts for increased glass transition temperature with increase in the level of epoxidation [34]. ENR 25 contains epoxide groups that activate the adjacent double bonds, thus a faster cure of vulcanization is observed [35].

In all the vulcanization systems, CV shows the highest torque maximum followed by semi-EV and EV system. This observation can be explained that the accelerator reacts with sulphur and zinc oxide to form active sulphurating agent [22]. This is followed by reaction with rubber molecules giving rise to crosslinking. The amount of active sulphurating agent increases with increasing accelerator concentration thus more crosslinks are formed and shorter torque maximum is observed as shown in Figure 10.

## CONCLUSION

1. Cure time decreases exponentially with increasing temperature for both the rubbers studied. For a fixed temperature of curing, SMR L indicates the higher cure time than ENR 25 in all vulcanization systems studied. This is attributed to the activation of double bonds by the adjacent epoxide group in ENR 25 molecule.
2. In all the accelerators studied, as temperature is increased, the difference in cure time for the various accelerator systems narrows down. At temperature greater than 160°C, the cure time for each accelerator system tends to a limiting value, *i.e.* it does not depend much on the temperature. This suggests that at temperature greater than 160°C, the activation energy is lower compared to that at temperature less than 160°C. It can therefore be inferred that the accelerators behave similarly at higher temperatures irrespective of the type of vulcanization system involved. In all the vulcanization systems ZDMC shows the shortest cure time, but DPG shows the longest cure time in CV and semi-EV systems. On the other hand TBBS shows the longest cure time in EV system.

3. Cure time in an accelerated sulphur system is higher at low MBT concentrations. This may be due to the decrease of active sulphurating agents. MBT influences the cure time by involving itself directly in the interaction with molecular sulphur in order to produce intermediates which are active sulphurating reagents. The amount of active sulphurating reagent increases with increasing MBT concentration; thus cure time decreases and eventually tends to a constant value.
4. ENR 25 and SMR L vulcanizates show increases in cure time with increasing silica filler loading, whereas the cure time for both carbon black and  $\text{CaCO}_3$  filled ENR 25 and SMR L vulcanizates show falling and rising trends with increasing filler loading. The difference in cure time may be attributed to the filler related parameters such as surface area, surface reactivity and particle size. The fastest cure time of  $\text{CaCO}_3$ -filled ENR 25 and SMR L compounds may be due to the lower surface area. Silica-filled vulcanizates show longer cure time than carbon black-filled vulcanizates. The cure retardation can be attributed to silica-accelerator interaction. The silica reacts with zinc oxide and subsequently reduces the reactivity of zinc which slows down the reactivity of sulphur.
5. From this study, ENR 25 shows higher torque maximum than SMR L. This observation can be explained that the oxirane group is bulky and this accounts for increased glass transition temperature with increase in the level of epoxidation. A faster cure of ENR 25 vulcanization is observed, due to the activation of double bonds by the epoxide group in the rubber.

In all the vulcanization systems, CV shows the highest torque maximum followed by semi-EV and EV. This difference is attributed to the amount of active sulphurating agents which increases with increasing accelerator concentration, thus more crosslinks are formed and shorter torque maximum is observed.

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## References

- [1] Poh, B. T. and Tan, B. K. (1991). *J. Appl. Polym. Sci.*, **42**, 1407.
- [2] Poh, B. T. and Tang, W. L. (1995). *J. Appl. Polym. Sci.*, **55**, 537.
- [3] Sadequl, A. M., Ishiaku, U. S., Ismail, H. and Poh, B. T. (1998). *Eur. Poly. J.*, **34**, 51.
- [4] Poh, B. T., Kwok, C. P. and Lim, G. H. (1995). *Eur. Poly. J.*, **31**, 223.
- [5] Sadequl, A. M., Ishiaku, U. S. and Poh, B. T. (1998). *Eur. Poly. J.* (in press).
- [6] Baker, C. S. L., Gelling, I. R. and Newal, R. (1985). *Rubb. Chem. Tech.*, **58**, 67.
- [7] Gelling, I. R. (1985). *Rubb. Chem. Tech.*, **58**, 86.
- [8] Gelling, I. R. and Morrison, N. J. (1985). *Rubber Chem. Tech.*, **58**, 243.
- [9] Nasir, M., Poh, B. T. and Ng, P. S. (1989). *Eur. Poly. J.*, **25**, 267.
- [10] Davis, C. K. L., Wolfe, S. V., Gelling, I. R. and Thomas, A. G. (1983). *Polymer*, **24**, 107.
- [11] Ishiaku Hanafi Ismail, U. S., Arinab, A. R. and Ishak, Z. A. M. (1997). *Intern. J. Polymeric Mater.*, **36**, 39.
- [12] Sadequl, A. M., Ishiaku, U. S. and Poh, B. T. (1998). *Intern. J. Polymeric Mater.* (in press).
- [13] Varughese, K. T., De, P. P., Senyl, S. K. and De, S. K. (1989). *J. Appl. Poly. Sci.*, **37**, 2537.
- [14] Nasir, Z. A. and Ratnam, C. T. (1989). *J. Appl. Poly. Sci.*, **38**, 1219.
- [15] Margaritis, A. G. and Kalfoglou, M. K. (1987). *Polymer*, **28**, 497.
- [16] Ishiaku, U. S., Nasir, M. and Mohd Ishak, Z. A. (1994). *J. Vinyl Technol.*, **16**, 226.
- [17] Annual Book of ASTM Standards (1994). Vol. 09.01, Rubber, Natural and Synthetic - General Test Methods, Carbon Black, Designation D 3184-89, ASTM, Philadelphia, p. 451.
- [18] Thompson, J. and Watts, J. T. (1966). *Trans. Inst. Rubber Ind.*, **42**, T173.
- [19] McSweeney, G. P. and Morrison, N. J. (1983). *Rubber Chem. Tech.*, **56**, 337.
- [20] Moore, C. G. and Saville, R. W. (1955). *Rubber Chem. Tech.*, **28**, 92.
- [21] Dogadkin, B. A. and Pavlov, N. N. (1961). *Doklady Akad. Nauk SSSR*, **138**, 5.
- [22] Bateman, L. Ed. (1963). *The Chemistry and Physics of Rubber-like Substances*, pp. 449-561 Applied Science, London.
- [23] Scheele, W. and Franck, A. (1959). *Rubber Chem. Tech.*, **32**, 139.
- [24] Duchacek, E. V. (1974). *J. Appl. Poly. Sci.*, **18**, 125.
- [25] Coran, A. Y. (1964). *Rubber Chem. Tech.*, **37**, 689.
- [26] Geysler, M. and McGill, W. J. (1995). *J. Appl. Poly. Sci.*, **55**, 215.
- [27] Geysler, M. and McGill, W. J. (1996). *J. Appl. Poly. Sci.*, **60**, 431.
- [28] Medalia, A. I. (1972). *Rubber Chem. Tech.*, **45**, 1171.
- [29] Cotten, G. R. (1987). *Plast. Rubb. Applic.*, **7**, 173.
- [30] Nasir, M., Poh, B. T. and Ng, P. S. (1988). *Eur. Poly. J.*, **24**, 961.
- [31] Wagner, M. P. (1976). *Rubber Chem. Tech.*, **49**, 703.
- [32] Kraus, G. (1965). *Reinforcement of Elastomers*, 1st ed., Interscience, New York, p. 342.
- [33] Fetterman, M. Q. (1973). *Rubber Chem. Tech.*, **46**, 927.
- [34] Morrison, N. J. and Porter, M. (1984). *Rubber Chem. Tech.*, **57**, 63.
- [35] Poh, B. T., Chen, M. F. and Ding, B. S. (1996). *J. Appl. Poly. Sci.*, **60**, 1569.