Mooney Scorch Time of Epoxidized Natural Rubber

B. T. POH* and B. K. TAN

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

SYNOPSIS

The scorch property of accelerated sulfur vulcanization of three grades of epoxidized natural rubber (viz. ENR 10, ENR 25, and ENR 50) was studied by using Mooney Shearing Disk Viscometer in the temperature range of 100–180°C. Effects of accelerator types, concentration of accelerator, and carbon black on ENR 10 were also determined. Results obtained indicate a similar scorch behavior as that reported earlier for SMR L. However, some differences in the magnitude of scorch times in the temperature and concentration studies are observed between ENR and SMR L. These differences are attributed to the activation of a double bond by the adjacent epoxide group in ENR, the effect being more significant for a higher degree of epoxidation of natural rubber. In the case of ENR 50, differential scanning calorimetry measurement suggests that additional crosslink occurs via a ring-opening reaction at about 155°C. Based on first-order reaction kinetics, the apparent activation energy of vulcanization for the rubbers studied is estimated and discussed.

INTRODUCTION

Epoxidized natural rubber (ENR) is obtained by chemical modification of natural rubber latex (*Hevea brasiliensis* type) with peracetic acid.[1] This type of chemically modified natural rubber has been the subject of recent research interest after the realization that ENR has shown some physical properties similar to those of synthetic rubbers. Most studies of ENR concentrate mainly on its physical and mechanical properties,[2–5] vulcanization, and aging behavior.[6,7] Recently, a study on the blend properties of ENR with plasticized poly(vinyl chloride) was also reported.[8] However, there is very limited study on the scorch behavior of ENR, particularly its temperature dependence of scorch time. Thus, it is our aim in this paper to report some of our findings in this field of interest.

EXPERIMENTAL

Materials

ENR 10, ENR 25, and ENR 50 having 10, 25, and 50 mol % of epoxidation, respectively, were supplied

by Rubber Research Institute of Malaysia (RRIM). Technical specification of the ENR used as given by the supplier is shown in Table I.

Six accelerators were used in this study. Except for diphenylguanidine (DPG), which has a melting point of 145°C, supplied by Monsanto Company, the technical specification of the other five accelerators is as was given in our previous paper.[9] All the accelerators used were freshly supplied by the respective suppliers. High-abrasion furnace (HAF) grade carbon black was used as the filler. It was also supplied by RRIM and has a surface area of 65–70 m^2/g. Other compounding ingredients such as zinc oxide, stearic acid, and sulfur were of commercial grades. The rubbers and all the compounding ingredients were used without further purification.

Method

Formulation of the accelerated sulfur vulcanization for both the gum stock and black-filled stock was the same as that described in our previous study on natural rubber (SMR grade) and SBR.[9] Similarly, rubber compounding and procedure for the determination of Mooney scorch time and cure index using a Mooney shearing disk viscometer were also carried out in accordance to the method described in our earlier investigation.[9] To study the thermal behavior of each of the rubbers used, differential

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Table I   Technical Specification of ENR

	ENR 10	ENR 25	ENR 50
Glass transition temperature (°C)	−60	−45	−20
Specific gravity	0.94	0.97	1.03
Mooney viscosity, $M_{L,1+4}$ (100°C)	90	110	140

scanning calorimetry (DSC) measurement was conducted by using a Perkin-Elmer DSC-2. Samples (10–15 mg) were encapsulated in aluminium holders and heated at a rate of 20°C/min under nitrogen from 100 to 200°C. The area of any peak observed was measured by the planimetry method. Indium was used as the calibration standard.

RESULTS AND DISCUSSION

Results obtained are discussed with respect to the effect of epoxidation of natural rubber, types and concentration of accelerators, and effect of carbon black on the Mooney scorch time of ENR.

Effect of Epoxidation of Natural Rubber

Figure 1 shows the variation of Mooney scorch time with temperature for SMR L,[9] ENR 10, ENR 25, and ENR 50. The exponential decrease of scorch time with increasing temperature is exhibited by the rubbers studied. This exponential behavior can be explained by the exponential dependence of the rate of reaction on temperature as discussed in our pre-
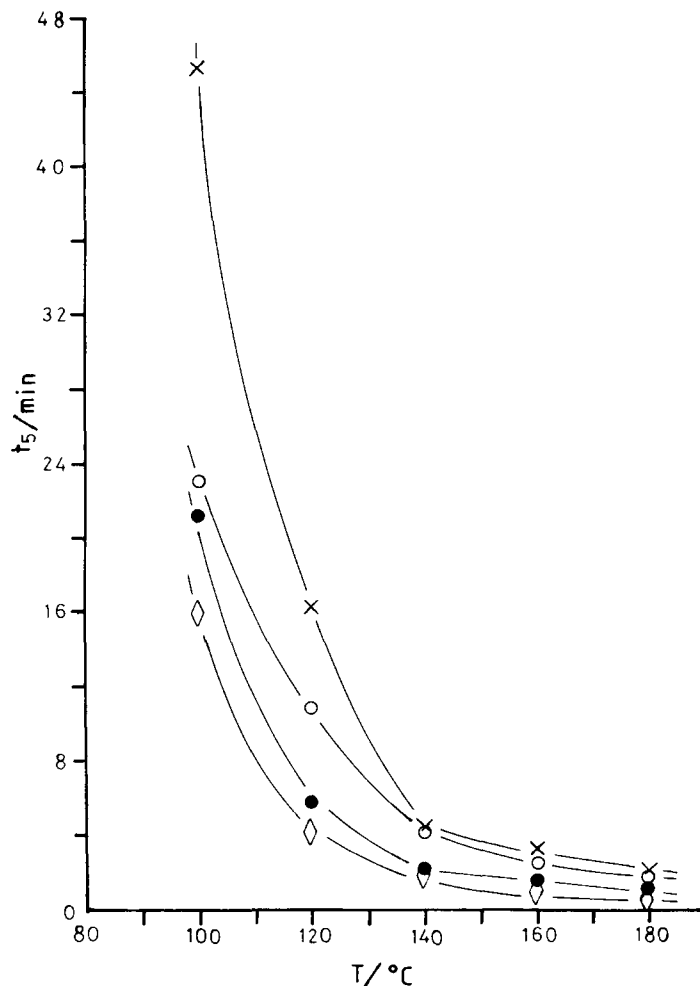
Figure 1   Variation of Mooney scorch time with temperature for the various types of ENR. SMR L is included for comparison purposes. (×) SMR L; (○) ENR 10; (●) ENR 25; (◇) ENR 50.
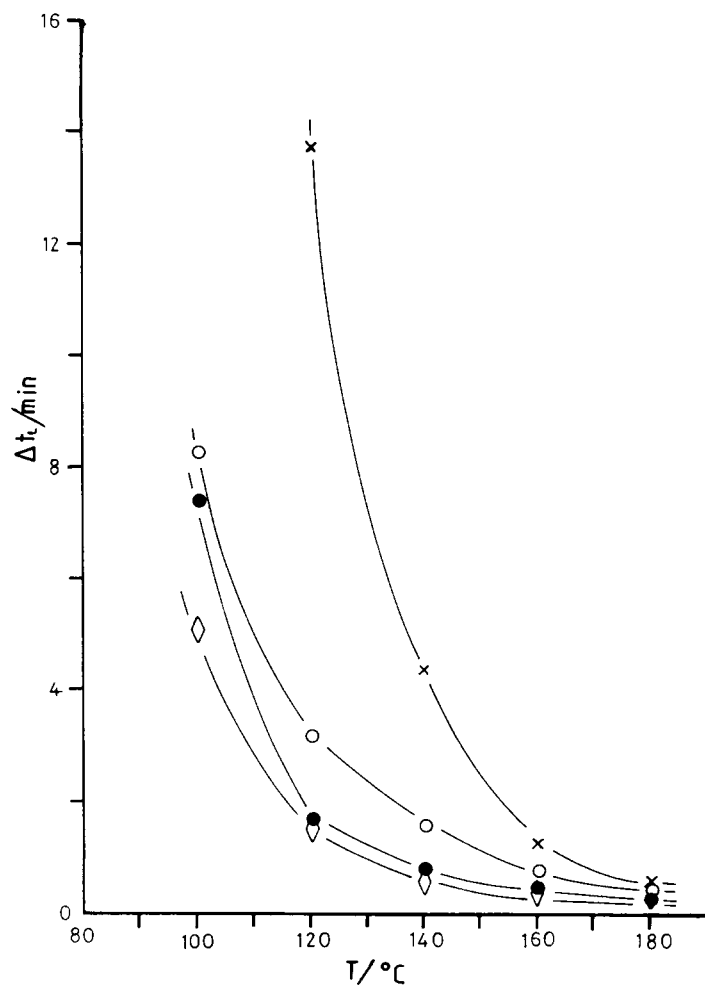
Figure 2   Variation of cure index with temperature for the various types of ENR. SMR L is included for comparison purposes. Symbols as in Figure 1.

vious paper.[9] However, it is observed that the rate of decrease of scorch time is greatest for ENR 50, followed by ENR 25, ENR 10, and SMR L. For a fixed temperature, SMR L gives the longest scorch time, followed by ENR 10, ENR 25, and ENR 50. The differences in scorch time between all the rubbers narrow down for temperature greater than 160°C. One interesting observation that arises from this study is the fact that the Mooney scorch time of SMR L (which contains more double bonds than do the others) is greater than that of ENR, especially at a lower temperature of study, i.e., 120°C and below. One possible explanation is that ENR contains epoxide groups that activate the adjacent double bonds, thus increasing the rate of crosslinking and, subsequently, shortening the scorch time. The epoxide-activated double bonds are distributed randomly along the polymer molecule, since it has been shown by NMR spectroscopy studies that epoxidation reaction is a random process in both homo-

geneous solution and in latex particles of natural rubber.[10] The mechanism of crosslinking via double bond of the rubber molecule has been explained in our previous study.[9] The higher the concentration of the epoxide group in the rubber chain, the stronger is the activation of the adjacent double bond. This is shown by the shortest scorch time of ENR 50 compared to the other ENR studied. Gelling and Morrison[6] also observed this type of additional activation when olefin and epoxide groups are in the same molecule. Similar temperature-dependence behavior on cure index (defined as $\Delta t_L = t_{35} - t_5$) is also observed. This is shown in Figure 2.

To ascertain the thermal behavior of ENR, particularly at high temperature, differential scanning calorimetry (DSC) measurement was carried out on the rubbers, the thermograms of which are shown in Figure 3. Except for ENR 50, the other two ENR do not indicate any significant endothermic peak around 155°C. The endothermic peak of ENR 50
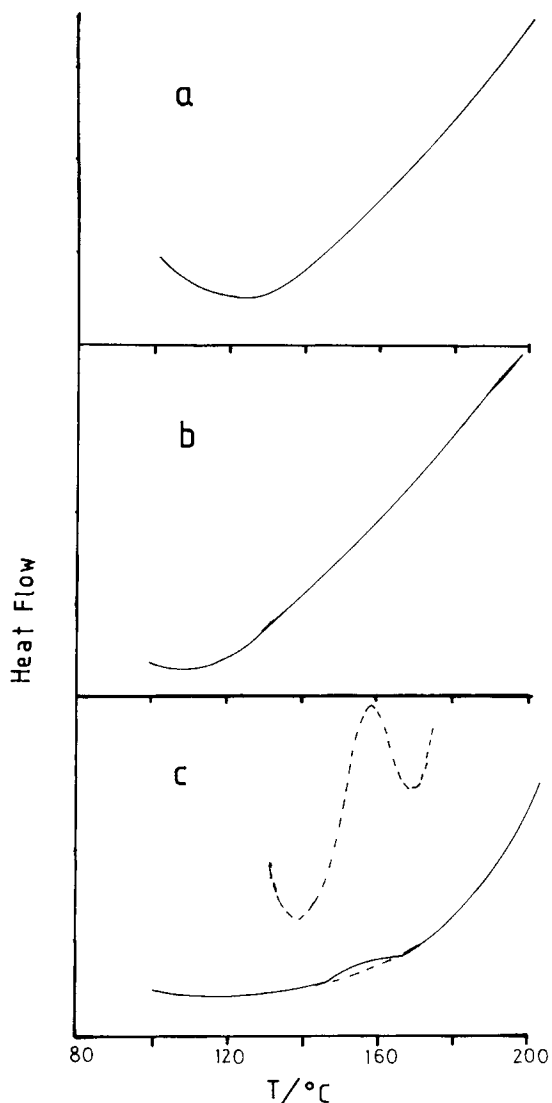
Figure 3 DSC thermograms with a heating rate of 20°C/min under nitrogen for the three grades of ENR. (a) ENR 10; (b) ENR 25; (c) ENR 50.

becomes more obvious as the range sensitivity is increased. We attribute this endothermic event to the ring opening of the epoxide group in ENR 50 at 155°C. As reported earlier by Gelling and Morrison[6] on aging of ENR, acid-catalyzed ring-opening reaction of epoxide groups occurs with the formation of ether crosslinks. This additional crosslink through the acid-catalyzed ring-opening also accounts for the shorter scorch time observed in ENR 50. The enthalpy of ring-opening of the epoxide group as determined by the peak area is estimated to be 0.045 cal/g.

In the case of ENR 10 and ENR 25, DSC measurement on the two rubbers does not indicate any

endothermic peak around 155°C, as shown in Figure 3(a) and (b), respectively. This observation may be due to the lower concentration of epoxide groups in the two rubbers. If ring-opening does occur, the number of groups is so small that it is impossible to detect them using the present DSC equipment.

Activation Energy

Assuming first-order reaction kinetics for the cross-linking process, an Arrhenius plot was carried out in order to obtain the apparent activation energy of vulcanization. In this case, the reciprocal of cure index was plotted against the reciprocal of temperature as shown in Figure 4. Straight-line plots are observed for SMR L and ENR 10 for the temperature range studied. This implies that only the same vulcanization mechanism involving double-bond reaction occurs. The estimated apparent activation energy for SMR L and ENR 10 are obtained from the slope of the linear plot, as shown in Figure 4. The respective values are 21.5 and 12.4 kcal/mol. These values have the same order of magnitude as reported by other workers. Scheele[11] reported an activation energy of about 19.5 kcal/mol, whereas Dogadkin and Shershnev[12] obtained a value of about 21 kcal/mol for the MBT-accelerated sulfur vulcanization. The lower value of apparent activation energy for ENR 10 as obtained in this study is obviously due to the presence of epoxide groups that activate the adjacent double bonds, thus lowering the activation energy of vulcanization. However, for ENR 25 and ENR 50, a straight-line plot is not observed, but curves having an increasing slope with decreasing temperature are obtained in both cases. This suggests that the apparent activation energy of vulcanization is a function of temperature. It decreases with increasing temperature as indicated by the slope of the curve, which becomes more gradual with increasing temperature. A transition of slopes occurs at about 155°C ($10^3/T = 2.34$ K^{-1}), which suggests that more than one type of mechanism is involved in the vulcanization of ENR 25 and ENR 50. Most probably, above 155°C, crosslinking via activated double-bond and acid-catalyzed ring-opening reaction occurs simultaneously in the two rubbers, the rate of which is faster in ENR 50. However, below 155°C, the mechanism of crosslinking involves mainly the activated double bonds. From Figure 4, the estimated apparent activation energy for ENR 25 varies from 8.7 to 12.4 kcal/mol, whereas that of ENR 50 ranges from 7.2 to 12.4 kcal/mol. The lower activation energy of vulcanization at a higher temperature of study can be at-
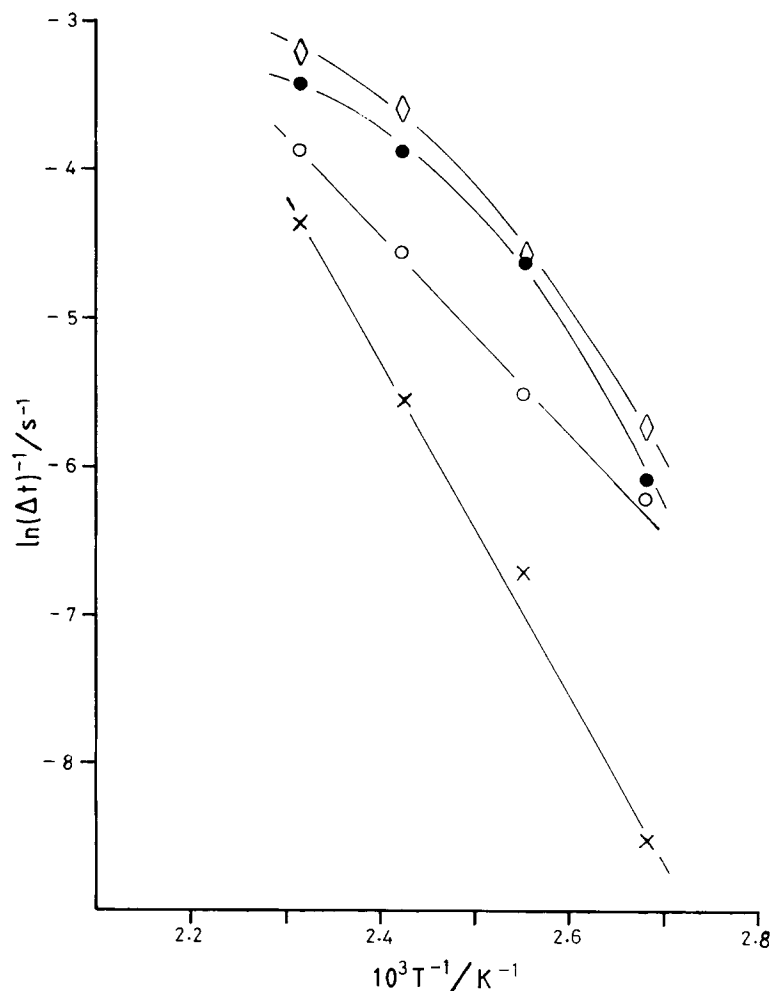
Figure 4   Arrhenius plot to determine the apparent activation energy of vulcanization for the rubbers studied. Symbols as in Figure 1.

tributed to the simultaneous crosslinking via an activated double-bond and epoxide ring-opening reaction that leads to the formation of an ether crosslink.

Types of Accelerators

In accelerated sulfur vulcanization, accelerators are used to increase the rate of vulcanization and also to improve the physical properties of the vulcanizate. Scorch time and cure rate of rubber compounds depend greatly on the types of accelerators used. In this study, we have used several types of commercial accelerators to investigate the effect of accelerator types on the Mooney scorch time of ENR 10. ENR 10 was chosen because we are interested in studing the effect of activated double bonds by epoxide groups on scorch time and complications arising

from ring-opening reaction at high temperature is avoided. Six accelerators belonging to various types of accelerators were used in the investigation. The results are shown in Figure 5. The exponential decrease of scorch time with increasing temperature is observed for all the accelerators studied. Except for ZDMC, the other accelerators show a greater rate of decrease of scorch time with increasing temperature. The longer scorch time observed for the sulfenamide type of accelerator (viz. CBS and TBBS) can be explained by the Coran's kinetic scheme for scorch delay,[13] i.e., a slower rate of disappearance of the sulfenamide accelerator and its apparent immediate reaction product with sulfur. On the contrary, ZDMC belongs to the "ultrafast" type of accelerator and the short scorch time observed is probably due to lower activation energy of vulcanization.
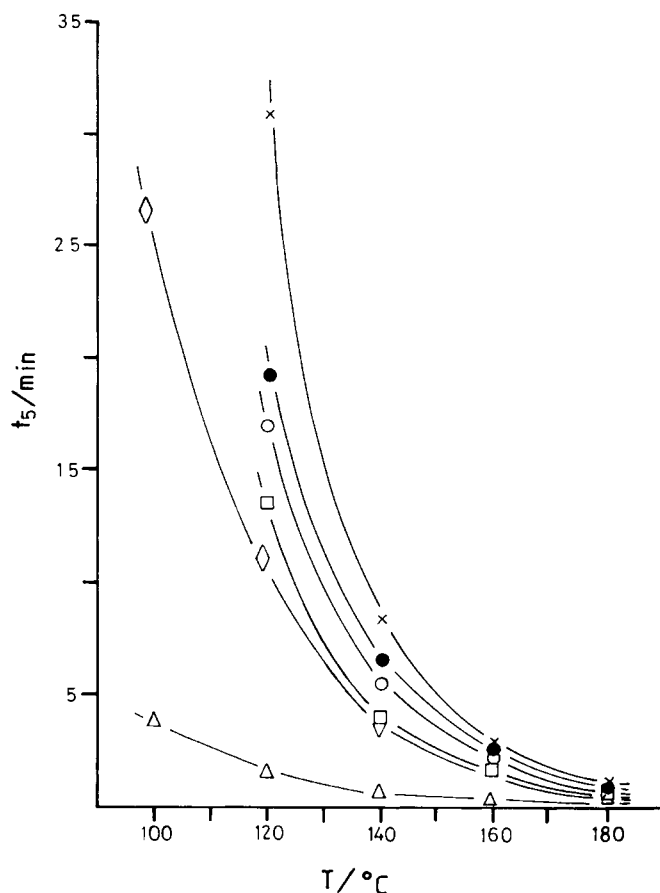
Figure 5 Variation of Mooney scorch time with temperature in ENR 10 for the various accelerators. (×) TBBS; (●) CBS; (○) TMTD; (□) DPG; (◊) MBT; (△) ZDMC.

Owing to the activation of double bonds by the adjacent epoxide groups, the scorch time of ENR 10 is lower compared to that of SMR L reported previously[9] for the same accelerators used. This is consistent with our earlier argument that activation of double bonds lowers the apparent activation energy of vulcanization, thus shortening the scorch time. As in the case of SMR L, the difference in scorch time for the various accelerators studied narrows down as temperature increases, i.e., above 160°C. At higher temperatures, the thermal energy supplied can easily overcome the apparent activation energy for the various types of accelerators investigated. The order of accelerator arranged in decreasing scorch time is as follows:

TBBS > CBS > TMTD > DPG > MBT > ZDMC

which is similar to that reported previously for SMR L.[9]

Effect of Accelerator Concentration

MBT has been chosen to investigate the concentration dependence behavior of the accelerator on scorch time of ENR 10 because it is a commonly used accelerator. Figure 6 shows the variation of scorch time with increasing accelerator concentration. For temperatures below 140°C, scorch time of ENR 10 indicates a strong dependence on the accelerator concentration, whereas for temperatures greater than 140°C, the dependence becomes less significant. This is because at higher temperature, enough thermal energy is supplied to overcome the apparent activation energy of vulcanization for all the accelerator concentrations studied. The rate of reaction is also faster. On the other hand, at lower temperature of study, the rate of reaction is slower and scorch time depends on the amount of active sulfurating agents formed, especially at lower concentrations of accelerator. The amount of active sulfurating agents increases with increasing accel-
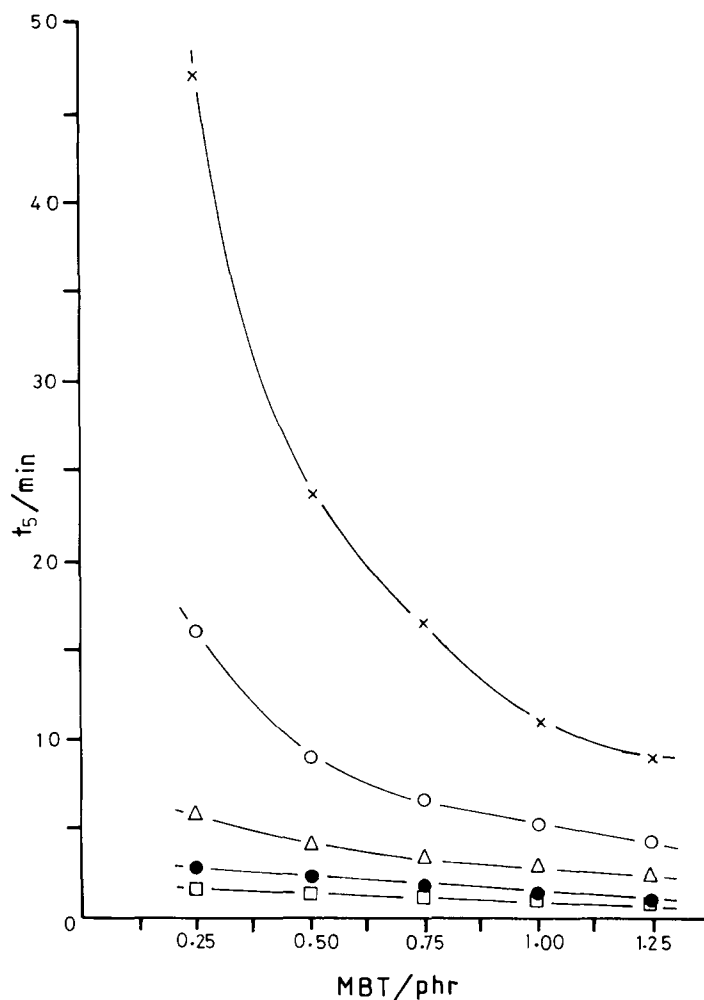
Figure 6 Variation of Mooney scorch time of ENR 10 with MBT concentration for various temperatures of curing. (×) 100°C; (○) 120°C; (△) 140°C; (●) 160°C; (□) 180°C.

erator concentration; thus, scorch time decreases and eventually tends to a constant value. The overall reaction mechanism to form a crosslink is similar to that described in our previous paper[9] except that because of the activation of a double bond by the epoxide group, the overall rate of vulcanization is faster; thus, the corresponding scorch time is shorter compared to that of SMR L reported earlier.

The % difference in scorch time (R) between SMR L and ENR 10 for 100 and 120°C is shown in Figure 7. The % difference in scorch time for 140 and 160°C is negligibly small; thus, it is not plotted in Figure 7. The % difference in scorch time (R) is defined as

$$R = \frac{(t'_5 - t_5)}{t'_5} \times 100\%$$

where t'_5 and t_5 are the Mooney scorch time of SMR L and ENR 10, respectively. t'_5 is obtained from our previously reported data.[9] For a fixed accelerator concentration, Figure 7 shows that R is greater for 100°C compared to that of 120°C. This is because at higher temperature more thermal energy is available to overcome the apparent activation energy of SMR L and ENR 10. Also, the effect of activated double bonds by the epoxide group on the scorch time becomes less significant at a higher temperature of vulcanization, thus narrowing down the difference in scorch times for both rubbers. For a fixed temperature, it is observed that R increases with increasing MBT concentration. This may imply that the rate of formation of an active sulfurating agent in ENR 10 is faster compared to that in SMR L as accelerator concentration is increased. Hence, the rate of decrease of scorch time in ENR 10 is faster
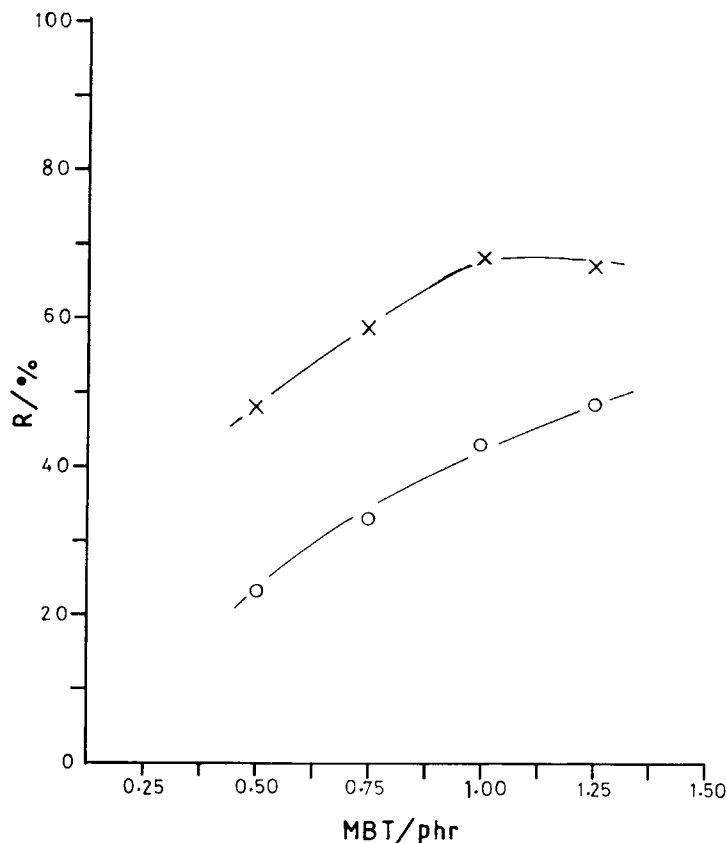
Figure 7   A plot of % difference in scorch time between SMR L (Ref. 9) and ENR 10 (*R*) vs. MBT concentration. (×) 100°C; (○) 120°C.

compared to that in SMR L, which is shown by the higher *R* values for higher accelerator concentration.

Effect of Carbon Black

In a carbon black-filled rubber compound, the function of carbon black is to reinforce and improve the physical properties of the rubber vulcanizate. Carbon black also affects the scorch properties of rubbers. Our previous study[9] on SMR L shows that addition of a high-abrasion furnace (HAF) grade carbon black will decrease the scorch delay, the effect being more evident at lower temperatures of curing. At higher temperatures, scorch time does not depend greatly on the carbon black concentration.

Similar carbon black concentration dependence behavior is also observed in our present study on ENR 10 as shown in Figure 8. HAF grade carbon black is also used in this investigation. Results indicate that scorch time of ENR 10 exhibits less carbon black concentration dependence, even at a lower temperature of curing (i.e., 120°C in this case) compared to the corresponding behavior in SMR L. Again, this may be explained by the effect of acti-

vation of double bonds by epoxide groups in ENR 10, thus supplementing the role played by carbon black in activating the vulcanizing process, i.e., through promotion of hydrogen sulfide formation and the rupture of S—N linkage when heated with sulfenamides in rubber, either in the presence or absence of other compounding ingredients.[14]

Figure 9 shows the % difference in scorch time (*R*) between SMR L and ENR 10 as a function of carbon black concentration. For both temperatures plotted, *R* decreases with increasing carbon black concentration, the rate being faster for 120°C compared to that of 140°C. For a fixed carbon black concentration, *R* is higher at lower temperatures. However, as carbon black concentration increases, the *R* value at 120°C approaches that of 140°C. This is shown by the difference in *R* values, which is 23% at 10 phr of carbon black and 5% at 50 phr of carbon black. One possible explanation is that at lower carbon black concentration ENR 10 gives a shorter scorch time compared to SMR L due to the epoxide-activated double bond in the former. However, as the concentration of carbon black increases, the role
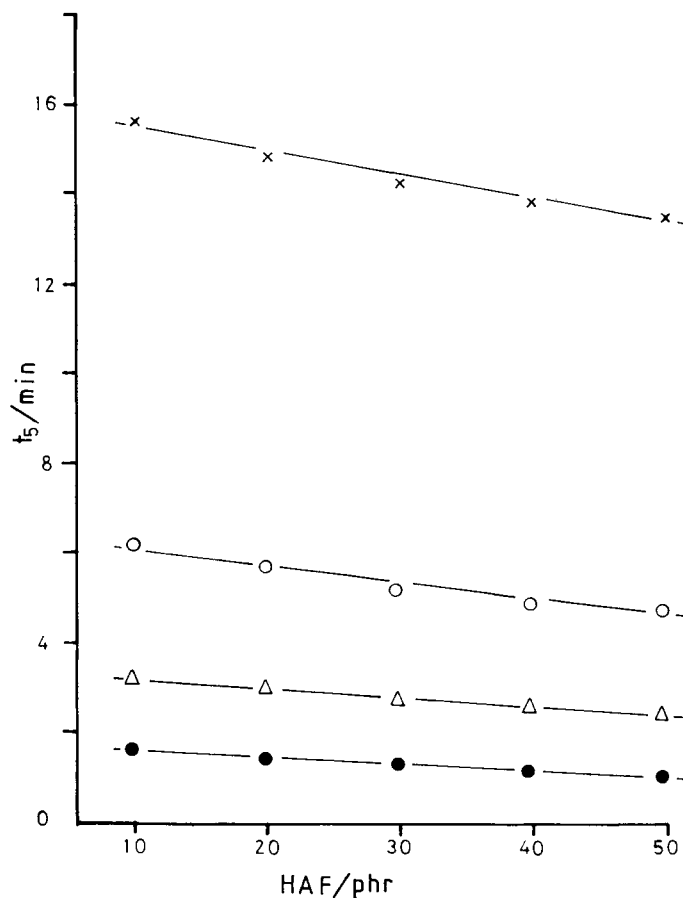
Figure 8   Variation of Mooney scorch time of ENR 10 with HAF concentration for various temperatures of curing. ($\times$) 120°C; ($\bigcirc$) 140°C; ($\triangle$) 160°C; ($\bullet$) 180°C.

of epoxide-activated double bonds becomes less significant. On the contrary, the concentration effect of carbon black becomes the dominating factor, especially at lower temperatures of curing. Hence, R decreases with increasing carbon black concentration, the rate being faster at lower temperatures of curing.

CONCLUSION

Comparison between the present study of ENR and that of SMR L reported earlier[9] gives the following conclusions:

1. Mooney scorch time decreases exponentially with increasing temperature for all the rubbers studied. For a fixed temperature of curing, SMR L indicates the longest scorch time, followed by ENR 10, ENR 25, and ENR 50. This is attributed to the activation of double bonds by the adjacent epoxide group in ENR,

the effect being more evident as the degree of epoxidation increases. Additional crosslinks may come from the ring-opening of the epoxide group as revealed by DSC measurement on ENR 50.

2. Mooney scorch time of ENR depends on the types of accelerator used. The order of accelerator arranged in decreasing scorch time is similar to that of SMR L.[9]

3. As in the case of SMR L, the Mooney scorch time of ENR 10 studied indicates concentration dependence on MBT and high-abrasion grade carbon black. The dependence behavior is more evident for temperatures lower than 140°C. Also, at lower temperatures of curing, SMR L shows a higher scorch time than does ENR 10. However, the differences in scorch times between the two rubbers narrow down as temperature is increased because more thermal energy is supplied to overcome the activation energy in both cases.

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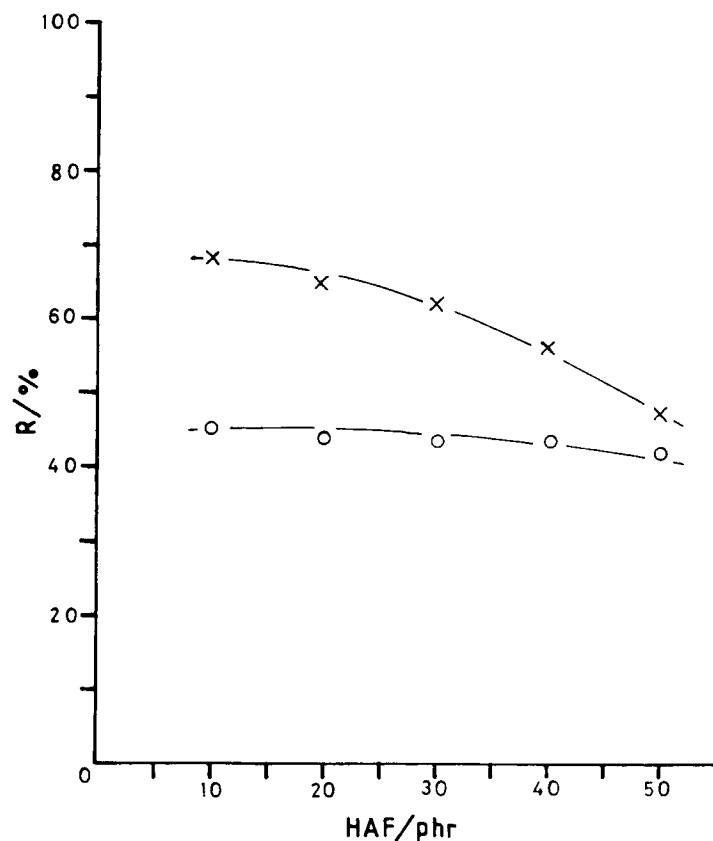
Figure 9 A plot of % difference in scorch time between SMR L (Ref. 9) and ENR 10 (R) vs. HAF concentration. (×) 120°C; (○) 140°C.

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