Effect of Blend Ratio on Mooney Scorch Time of Rubber Blends

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ABSTRACT: The Mooney scorch times of three rubber blends [epoxidized natural rubber (ENR) 50/SMR L, ENR 50/styrene butadiene rubber (SBR), and Standard Malaysian Rubber SMR L/SBR] were studied in the temperature range of 120–160°C using an automatic Mooney viscometer. *N*-Cyclohexyl-2-benzothiazyl sulfenamide was used as the accelerator, and the rubber formulation was based on the conventional vulcanization system. Results for the blends investigated indicate that a negative deviation of scorch time from the interpolated value was observed, especially for temperatures lower than 130°C. This observation was attributed to the induction effect of the ENR 50 in the ENR 50/SMR L and ENR 50/SBR blends to produce more activated precursors to crosslinks, thus enhancing interphase crosslinking. To a lesser extent, SMR L also exhibited such an induction effect in the SMR L/SBR blend. At 120°C, maximum induction effect occurred at around a 40% blend ratio of ENR 50 and SMR L in the respective blends. For the filled stock at 140°C, carbon black exhibited less effect on the scorch property of the blends compared to silica. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1301–1305, 1998

Key words: scorch; blend; rubber; silica; carbon black

INTRODUCTION

Several scorch properties of rubber compounds involving a single component rubber have been reported.[1–4] Similar studies were also carried out by other research workers.[5–7] The rubbers studies in our previous works were SMR L, SMR 10, styrene butadiene rubber (SBR), and epoxidized natural rubber (ENR). Parameters such as rubber types, accelerators, and fillers that influence the scorch time of rubbers were systematically investigated. In the case of ENR, the effects of stearic acid[3] and sulfur concentration[4] on the scorch property were thoroughly studied. However, the scorch behavior of rubber blends was not reported before, although Bhownick and De[8] studied the effect of curing temperature and curing system on structure–property relations of rubber blends. Owing to the technological importance of rubber blends that enhance the physical properties of rubber vulcanizates and improve their processing behavior,[9] it is thus important to report our findings on the scorch behavior of some rubber blends.

EXPERIMENTAL

Materials

SMR L, ENR 50, and SBR were used as the elastomers and their respective technical specifications were given by previous articles.[1,2] Three types of blends were used: ENR 50/SMR L, ENR 50/SBR, and SMR L/SBR. For each blend, the blend ratio was varied from zero to 100%. *N*-Cyclohexyl-2-benzothiazyl sulfenamide (CBS) was used was the accelerator, and it was freshly supplied by

Table I   Recipes Used in Formulations

Ingredient	Gum Stock (phr)	Filled Stock (phr)
Rubber blend[a]	100	100
Zinc oxide	5	5
Sulfur	2.5	2.5
Stearic acid	2	2
CBS	0.6	0.6
Filler	—	Variable

phr, parts per hundred parts of rubber; (—) blend ratio for filled stock, 50/50.

[a] Blend ratio for gum stock, variable.

Bayer Company. Other compounding ingredients such as zinc oxide, stearic acid, and sulfur were of commercial grades. High abrasion furnace (HAF) grade carbon black (N330) and precipitated silica (vulcasil-S grade) were chosen as the fillers in the study of filled stock. The rubbers and the compounding ingredients were used without further purification.

Compounding and Testing

A conventional vulcanization system was used in the formulation of the rubber compounds. Table I shows the recipes used in the formulations.

The rubbers were preblended, and a standard mixing procedure as described by another study[1] was carried out using a two-roll mill at a temperature of 70 ± 5°C. For the gum stock, the total time taken to complete one mixing cycle was 18 min; for the black-filled compound, the total time taken was 29 min. The Mooney scorch time was determined by using a Monsanto automatic Mooney viscometer (MV 2000). The testing procedure was conducted according to the method described in ASTM D 1646-94.[10] The Mooney scorch time (t_5) is defined as the time required for an increase of 5 units above the minimum viscosity as determined from a plot of the Mooney viscosity versus time.

RESULTS AND DISCUSSION

In this study our main interest was to investigate the effects of blend ratio and fillers on the scorch behavior of rubber blends. The results obtained are discussed with respect to these two parameters.

Effect of Blend Ratio

Figure 1 shows the variation of Mooney scorch time of the ENR 50/SMR L blend with a blend ratio of ENR 50. Owing to the activation of an adjacent double bond by the epoxide group, the scorch time for ENR 50 is shorter than that of SMR L, which was observed in our previous study.[2] For all the temperatures investigated, the scorch time of the blend decreased with increasing ENR 50, especially for temperatures lower than 130°C where the drop in scorch time becomes more pronounced. At higher temperatures, the scorch time of the blend does not show significant dependence on the blend ratio because enough thermal energy is available to overcome the activation energy for vulcanization.

Figure 1 also shows that the observed scorch time of the blend deviates negatively from the calculated value based on the interpolation between the scorch time of the two component elastomers. The difference in scorch time between observed and calculated values is denoted by Z:

$$Z = t_5 \text{ (observed)} - t_5 \text{ (interpolated)}$$

A plot of Z versus the blend ratio of ENR 50 for various temperatures of vulcanization is indicated in Figure 2. The negative deviation of scorch time from the interpolated value is attributed to the induction effect of ENR 50 on SMR L molecules that causes an overall increase in the rate of crosslinking of the blend. Probably more activated precursors to crosslinks[11] are formed as a result of the activation of the double bond by the epoxide
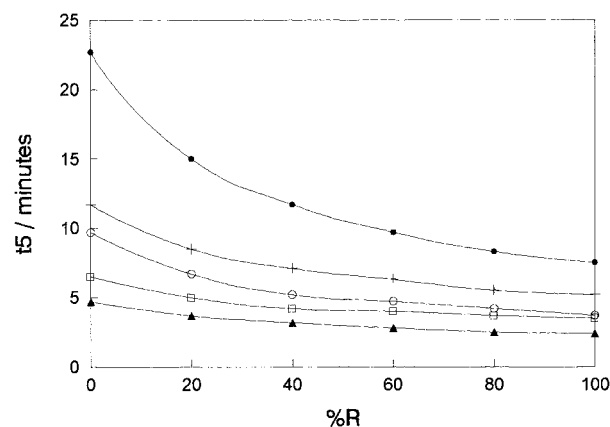

Figure 1   Variation of Mooney scorch time of the ENR 50/SMR L blend with the blend ratio of ENR 50 (% R) for various temperatures of vulcanization: (●) 120°C, (+) 130°C, (○) 140°C, (□) 150°C, and (▲) 160°C.
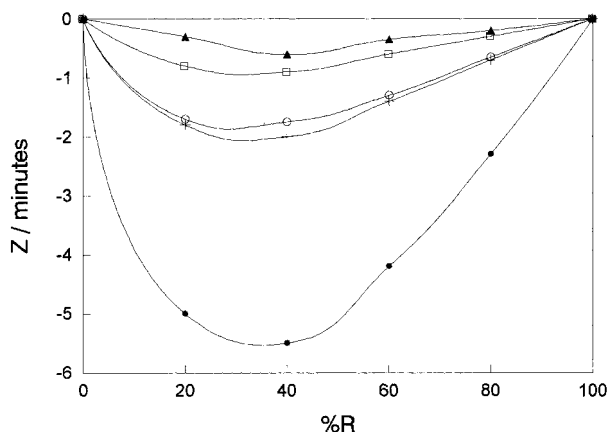
Figure 2 Variation of the difference in Mooney scorch time between the observed value and interpolated value (Z) of the ENR 50/SMR L blend with the ratio of ENR 50 (% R) for various temperatures of vulcanization. The symbols are as in Figure 1.

Figure 3 Variation of Mooney scorch time of the ENR 50/SBR blend with the blend ratio of ENR 50 (% R) for various temperatures of vulcanization. The symbols are as in Figure 1.

group.[2] The availability of the activated precursors will accelerate vulcanization not only between ENR 50 molecules, but also induces faster interphase crosslinking between ENR 50 and SMR L molecules. The development of interphase crosslinking has also been observed by several research workers,[12–15] even with polymers of significantly different solubility parameters.[15]

The deviation of scorch time from the interpolated value is greatest at 120°C, suggesting that the induction effect of ENR 50 is more significant at a lower temperature of vulcanization. However, as temperature is increased, the Z value decreases and approaches the interpolated value. This observation is associated with the decreasing effect of the activated double bond in ENR 50 as temperature is increased; that is, enough thermal energy is available to overcome the activation energy of vulcanization, and the induction effect of ENR 50 becomes less important. Figure 2 also shows that the maximum deviation from the interpolated value occurs at around a 40% blend ratio of ENR 50 for all temperatures studied. At this blend ratio the induction effect of the activated double bond in ENR 50 is most significant in enhancing faster interphase cure between ENR 50 and SMR L rubber molecules. As the blend ratio of ENR 50 is further increased, the induction effect diminishes as the blend becomes more ENR 50 dominant.

A similar scorch behavior was observed for the ENR 50/SBR blend as shown in Figure 3. The scorch time decreases exponentially with an increasing ENR 50 blend ratio. The decrease is more significant at a lower temperature of vulcaniza-
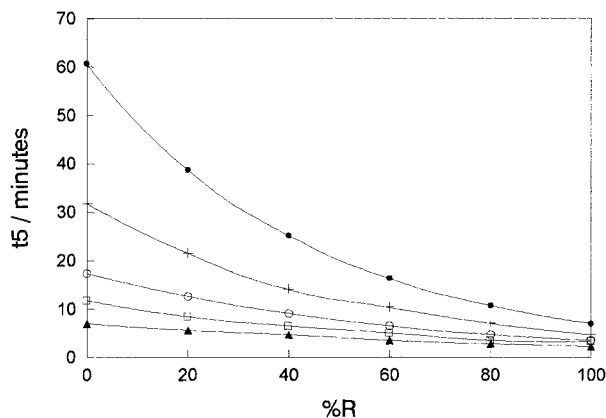
tion (i.e., for a temperature lower than 130°C). Figure 4 shows the dependence of scorch time of the SMR L/SBR blend on the blend ratio of SMR L. In this case the scorch time decreases with increasing SMR L composition. SMR L, which has more double bonds than SBR, cures faster than SBR; thus, a shorter scorch time is observed in the former. Based on the same explanation as in the ENR 50/SMR L blend, the induction effect of SMR L molecules enhances interphase crosslinking between SBR and SMR L molecules, resulting in a lower scorch time of the blend than the interpolated value. However, as the temperature is increased, the scorch time of the blend approaches the interpolated value, an observation similar to the previous two blends.
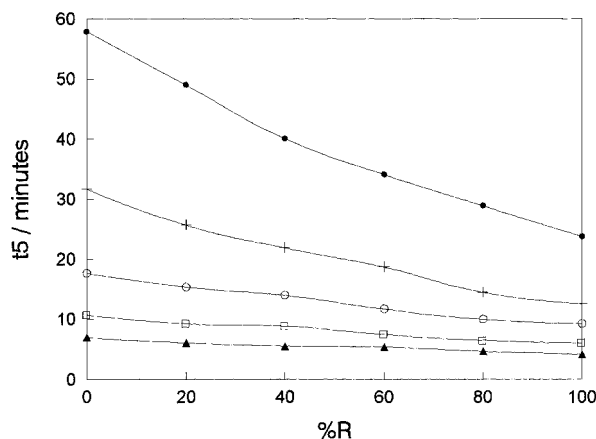

Figure 4 Variation of Mooney scorch time of the SMR L/SBR blend with the blend ratio of SMR L (% R) for various temperatures of vulcanization. The symbols are as in Figure 1.
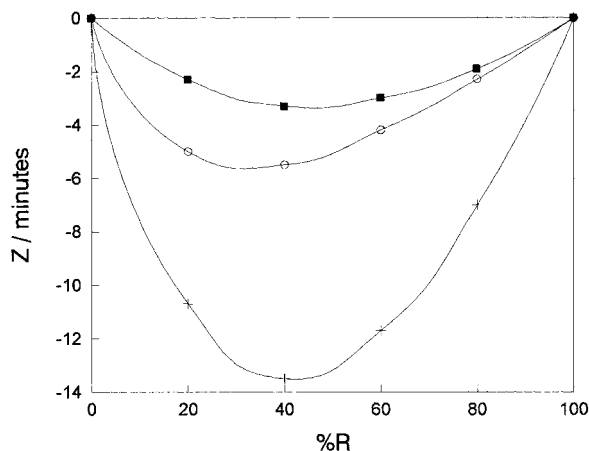
Figure 5 Comparison of the Z values for the various blends at 120°C. The blend ratio (% R) on the x axis indicates the composition of the first component rubber in the blend. (○) ENR 50/SMR L, (+) ENR 50/SBR, and (■) SMR L/SBR.

The difference in scorch time from the interpolated value for the three blends studied at 120°C is summarized in Figure 5. The ENR 50/SBR blend gives the greatest deviation, followed by the ENR 50/SMR L and SMR L/SBR blends. In the ENR 50/SBR and ENR 50/SMR L blends, the maximum deviation occurs at around a 40% blend ratio of ENR 50, whereas for the SMR L/SBR blend it occurs at around a 40% blend ratio of SMR L. Figure 5 suggests that the induction effect of ENR 50 is greater compared to SMR L. This observation is attributed to the presence of an epoxide group in the ENR 50, which activates the adjacent double bond; hence, more activated precursors to crosslinking are formed.

Effect of Fillers

In this study two fillers [i.e., HAF grade carbon black (N330) and silica] were used in the formulation. Figure 6 shows the variation of scorch time with carbon black loading at 140°C for ENR 50/SMR L and SMR L/SBR blends. This temperature of 140°C was chosen to study the effect of fillers because natural rubber is normally vulcanized at this temperature. For the ENR 50/SMR L blend, the scorch time was virtually independent of carbon black loading, an observation similar to that reported for SMR L at 140°C.[1] The result indicates that the catalytic effect of carbon black at 140°C does not influence the scorch behavior of the blend because sufficient thermal energy is available for vulcanization at this temperature.
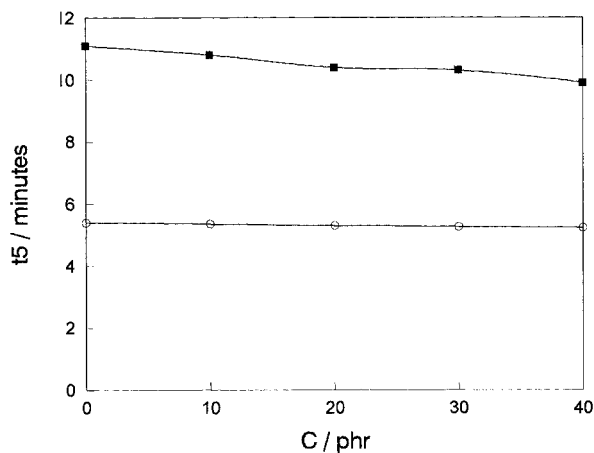

Figure 6 Dependence of Mooney scorch time of the blend on carbon black loading at 140°C. (○) ENR 50/SMR L and (■) SMR L/SBR.

However, for the SMR L/SBR blend, due to its slower cure rate relative to the ENR 50/SMR L blend, the catalytic effect of carbon black becomes significant as reflected by the gradual decrease in scorch time with the increase in carbon black concentration.

The scorch behavior for the two blends studied at 140°C in the presence of silica is shown in Figure 7. Scorch time increases with increasing silica loading for both blending systems, a different observation than with carbon black. Precipitated silica is hydrophilic in nature[16] and it interacts strongly with rubber, especially with a polar rubber like ENR 50.[17] Besides, silica also adsorbs certain rubber ingredients such as stearic acid and accelerators.[18] This phenomenon would de-
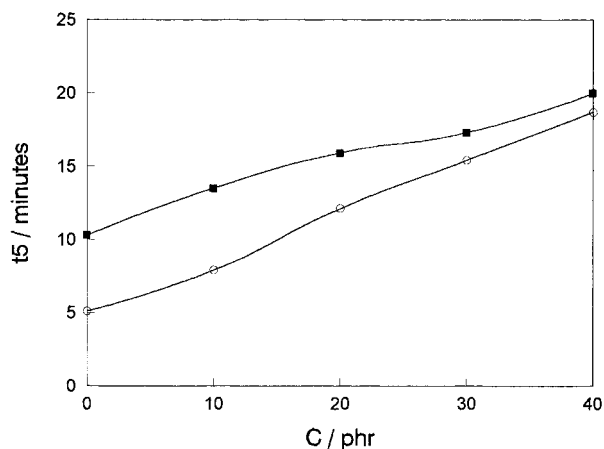

Figure 7 Dependence of Mooney scorch time of the blend on silica loading at 140°C. The symbols are as in Figure 6.

crease the number of active sulfurating agents, hence increasing the scorch time of the blend. The combined effects of the strong interaction with rubber and adsorption of certain rubber ingredients by precipitated silica account for the steady increase in scorch time for both blends. The stronger interaction of precipitated silica with ENR 50 is reflected by the faster rate of increase of scorch time in the ENR 50/SMR L blend compared to that of the SMR L/SBR blend.

CONCLUSION

From this study, the following conclusions can be drawn:

1. For the ENR 50/SMR L and ENR 50/SBR blends, the Mooney scorch time decreases with an increasing ENR 50 blend ratio, especially for temperatures lower than 130°C; for the SMR L/SBR blend, it decreases with increasing SMR L blend ratio. This negative deviation from the interpolated value is attributed to the induction effect of ENR 50 and SMR L to produce more activated crosslink precursors, thus enhancing interphase crosslinking in the respective blends. However, this induction effect becomes less significant with increasing temperature because enough thermal energy is available for vulcanization.

2. The scorch time of the ENR 50/SBR blend gives the greatest deviation from the interpolated value, followed by ENR 50/SMR L and SMR L/SBR blends where maximum deviation occurs at around a 40% blend ratio of ENR 50 in the ENR blends and a 40% blend ratio of SMR L in the SMR L/SBR blend. This observation is attributed to the greater induction effect in ENR 50 compared to SMR L as a result of the activation of the double bond by the epoxide group in the former.

3. At 140°C and a fixed blend ratio, the scorch time of the ENR 50/SMR L blend is independent of carbon black loading whereas for the SMR L/SBR blend the catalytic effect of carbon black causes a gradual decrease in scorch

time of the latter blend. On the other hand, precipitated silica increases the scorch time of both blends. This observation is attributed to the strong interaction with rubber and adsorption of certain rubber ingredients by precipitated silica, the combined effects being more pronounced in the ENR 50/SMR L blend due to the polar nature of ENR 50.

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