

Cure and Mechanical Properties of Filled SMR L/ENR 25 and SMR L/SBR Blends

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ABSTRACT: The effect of blend ratio of natural rubber/epoxidized natural rubber (SMR L/ENR 25) and natural rubber/styrene-butadiene rubber (SMR L/SBR) blends on scorch time (t_2), cure time (t_{90}), resilience, hardness, and fatigue properties were studied in the presence of carbon black and silica. An accelerated sulfur vulcanization system was used throughout the investigation. The scorch and cure times of the rubber compound were assessed by using a Moving-Die Rheometer (MDR 2000). Resilience, hardness, and fatigue life were determined by using a Wallace Dunlop Tripsometer, a Wallace Dead Load Hardness Tester, and a Fatigue to Failure Tester, respectively. The results indicate that t_2 and t_{90} decrease with increasing ENR 25 composition in the SMR L/ENR 25 blend whereas both values increase with increasing SBR content in the SMR L/SBR blend. This observation is attributed to faster cure in ENR 25 and higher saturation in SBR. Resilience decreases with increase in % ENR and % SBR but hardness shows the reverse behavior in their respective blends. The fatigue life increases with % ENR, but it passes through a maximum with % SBR in the respective blends. In all cases, aging lowers the fatigue life, a phenomenon that is caused by the breakdown of crosslinks in the vulcanizate. Differences in all the observed values between carbon black-filled and silica-filled blends are associated with the varying degrees of interaction and dispersion of the two fillers in the rubber blend matrix. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 47–52, 2001

Key words: cure; resilience; hardness; fatigue; blend

INTRODUCTION

We have reported several studies on the cure and mechanical properties of rubber/rubber blends. These include the study of the effect of blend ratio on Mooney scorch time of rubber blends,^{1,2} tensile and tear properties of epoxidized natural rubber (ENR)/natural rubber (NR),^{2,3} and ENR 50/styrene-butadiene rubber (SBR) blends.⁴ Recently,

we have also reported a systematic investigation on the fatigue, resilience, and hardness properties of unfilled natural rubber (SMR L)/ENR 25 and SMR L/SBR blends⁵ which indicates that, before aging, fatigue life passes through a maximum at 50% ENR or SBR for both blends. This observation is attributed to the “synergistic” effect of mutual reinforcement due to strain-induced crystallization in the SMR L/ENR 25 blend whereas, for the SMR L/SBR system, compatibility accounts for the observed maximum. The resilience of both blends decreases with increasing blend ratio of ENR or SBR whereas the reverse behavior is obtained for the hardness property. Owing to the interesting blend properties exhibited by the un-

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Table I Technical Specifications of Carbon Black and Silica

	Silica	Carbon Black
Mean particle size (μm)	0.02	0.03
Surface area (m^2/g)	170	98.9
Density (g/cm^3)	2.2	1.8

filled SMR L/ENR 25 and SMR L/SBR blends, we have extended the study to the carbon black- and silica-filled blends. The cure and mechanical properties of the two filled blends obtained in this study are reported and discussed.

EXPERIMENTAL

Materials

One grade of natural rubber (SMR L), epoxidized natural rubber (ENR 25) and styrene-butadiene rubber (1502; Buna Hüls) were used as the elastomers. The accelerator and antioxidant used were *N*-cyclohexyl-2-benzothiazyl sulfenamide and *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine, respectively. Carbon black and precipitated silica were chosen as the fillers and their respective technical specifications are given in Table I. Other standard rubber compounding ingredients such as stearic acid, zinc oxide, and sulfur were of commercial grades and used without further purification.

Compounding and Cure Assessment

A typical formulation of rubber blend compound is shown in Table II. The rubbers were preblended, and the compounding procedure as described by the American Society for Testing and Materials ASTM D 3184-89 was adopted. Compounding was performed by using a two-roll mill maintained at $70^\circ \pm 5^\circ\text{C}$. The sheeted rubber compound was then conditioned at $23^\circ \pm 2^\circ\text{C}$ for 24 h before cure assessment on a Monsanto Die Rheometer (MDR 2000) operated at 150°C .

Measurement of Resilience, Hardness, and Fatigue Life

The rubber test samples were prepared by the compression molding method according to the respective cure times determined by the MDR 2000

at 150°C . The resilience of the rubber samples was determined by a Wallace Dunlop Tripsometer in accordance with the procedure described by BS 903: part A8. The dropping angle of the pendulum was 45° and the rebound angle (θ) was read directly from the dial. The % resilience was calculated based on the following equation:

$$\% \text{ resilience} = (1 - \cos \theta)/(1 - \cos 45^\circ) \times 100$$

where θ is the rebound angle.

A Wallace Dead Load Hardness Tester was used for the hardness measurement, and the method described by BS 903: part A26 was followed. The reading for the hardness test was recorded as international rubber hardness degree.

With regard to the fatigue life determination, the sample was prepared in the form of a dumbbell which was cut from a vulcanized rubber sheet of 1.5-mm thickness using a BS Type E dumbbell cutter. A Monsanto Fatigue to Failure Tester operating at 100 rpm was used to determine the fatigue life. The extension ratio was varied from 2.0 to 2.4. Six test specimens were used for each rubber sample and the number of cycles required to break the test piece was recorded automatically on the equipment. The average fatigue life (N) of each sample was computed by using the Japan Industrial Standard formula as shown below:

$$N = 0.5A + 0.3B + 0.1(C + D)$$

where A is the highest reading followed by B , C , and D .

Table II A Typical Formulation of Rubber Compound

Ingredient	Recipe (phr) ^a
Rubber blend ^b	100
Filler ^c	20
Zinc oxide	5
Stearic acid	2
Sodium carbonate	0.3
CBS	1.5
IPPD	2
Sulphur	1.5

CBS, *N*-cyclohexyl-2-benzothiazyl sulfenamide; IPPD, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine.

^a Parts per hundred parts of rubber.

^b Blend ratio for SMR L/ENR 25 and SMR L/SBR (0 : 100, 25 : 75, 50 : 50, 75 : 25, 100 : 0).

^c Carbon black or silica.

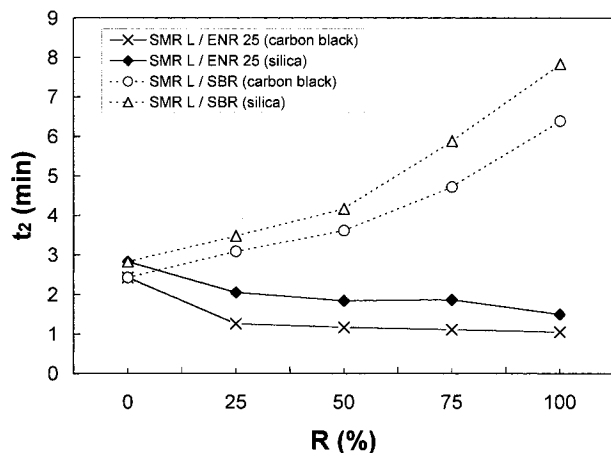


Figure 1 Dependence of scorch time (t_2) on blend ratio of ENR 25 or SBR (R) for filled rubber blends cured at 150°C.

Aging tests were also performed on the fatigue property of the blends. The dumbbell-shaped rubber samples were aged in an air oven at 100°C for 48 h, then removed from the oven and allowed to condition at room temperature for at least 16 h before fatigue measurements were conducted.

RESULTS AND DISCUSSION

Scorch and Cure Time

Figures 1 and 2 show the variation of scorch time (t_2) and cure time (t_{90}), respectively, with blend ratio (R %) of ENR 25 or SBR in the carbon black- and silica-filled SMR L/ENR 25 and SMR L/SBR blends. It can be seen that for SMR L/ENR 25

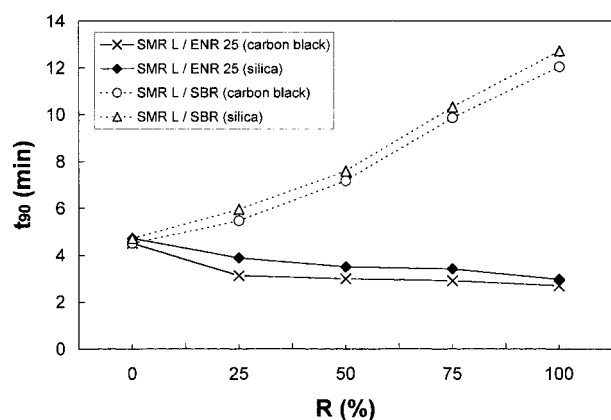


Figure 2 Dependence of cure time (t_{90}) on blend ratio of ENR 25 or SBR (R) for filled rubber blends cured at 150°C.

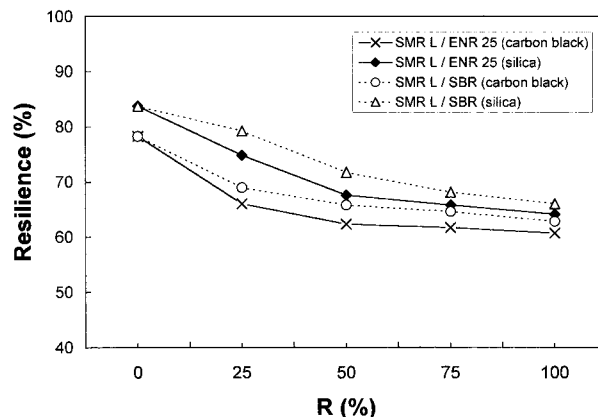


Figure 3 Variation of resilience with blend ratio of ENR 25 or SBR (R) for the filled rubber blends.

blends, t_2 and t_{90} decrease with increasing ENR 25 composition in the blend. We have reported⁶ that, due to the activation of adjacent double bond by the epoxide group in ENR, the scorch time and cure time are shorter than that of SMR L. However, for SMR L/SBR blends, t_2 and t_{90} increase with increasing SBR composition in the blend. SBR, which has fewer double bonds than SMR L, cures slower than SMR L, thus longer scorch and cure times were observed as SBR composition increased in SMR L/SBR blends. Figures 1 and 2 also show that, for the same rubber blend, the silica-filled system exhibits longer t_2 and t_{90} than those of the carbon black-filled blends. Compared with carbon black, precipitated silica is hydrophilic in nature⁷ and it interacts strongly with rubber, especially with a polar rubber like ENR 25.⁸ Germain and Machurat⁹ and Wagner¹⁰ also reported that silica adsorbs certain rubber ingredients such as stearic acid and accelerators. This phenomenon would decrease the number of active sulfurating agents, hence increasing the t_2 and t_{90} of the blends.

Resilience and Hardness

The effect of blend ratio on resilience and hardness of filled SMR L/ENR 25 and SMR L/SBR blends is shown in Figures 3 and 4, respectively. It can be seen that, for both systems, resilience decreases with increasing ENR 25 or SBR composition in the blends. The reverse behavior is obtained for the hardness property. We have observed a similar trend for SMR L/ENR 25 and SMR L/SBR gum blends.⁵ The resilience and low temperature behavior of SBR vulcanizate are inferior to those of natural rubber¹¹ whereas in-

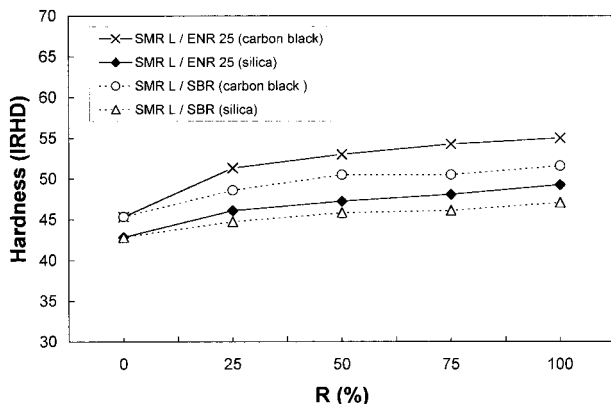


Figure 4 Variation of hardness with blend ratio of ENR 25 or SBR (R) for the filled rubber blends.

creasing epoxidation increases the glass transition temperature (T_g) which in turn results in decreasing the resilience, reduced air permeability, higher hysteresis, and better wet traction.^{12,13} SBRs are copolymers of butadiene and styrene. The presence of styrene groups would act as harder blocks to increase the degree of hardness of SMR L/SBR blends. The presence of epoxide group makes ENR harder than SMR L and is responsible for the increasing hardness of the SMR L/ENR 25 blends. For the same rubber blend at a fixed blend ratio, carbon black-filled blends exhibit lower resilience and higher hardness than the silica-filled ones. It can be seen from Table I that, although the average particle size of silica is smaller than that of carbon black, the carbon black-filled blends show lower resilience and higher hardness than silica-filled blends. This may be attributed to the weak silica-rubber interphase interaction and poor filler dispersion compared with carbon black.¹⁴ Figures 3 and 4 also indicate that, for the same filler systems and at a fixed blend ratio, SMR L/ENR 25 blends show lower resilience and higher hardness than SMR L/SBR blends. This observation might be attributed to better filler-rubber interphase interaction in SMR L/ENR 25 blends compared with SMR L/SBR blends, particularly between silica and ENR 25.

Fatigue Life

The effect of blend ratio (R) on the fatigue life (N) of carbon black-filled blends is shown in Figure 5 at an extension ratio of 2. For the SMR L/ENR 25 blend, N increases steadily with R before and after aging. This observation is attributed to the

higher fatigue life of ENR 25 compared with SMR L as a result of higher degrees of saturation and hysteresis in the former. Young¹⁵ and Gent¹⁶ reported that oxidation in rubber contributes to the fatigue crack growth in air and the rate is increased in the presence of ozone. Because ENR 25 contains fewer double bonds than SMR L, less oxidation occurs in the former. The higher hysteresis in ENR, as a result of higher T_g in ENR 25, also contributes to the higher fatigue life in ENR 25. The T_g s for SMR L and ENR 25 are -69° and -48°C , respectively.¹⁷ After aging, the N values are lower because of the breakdown of crosslinks, especially the polysulfidic ones.^{8,18} In the case of the SMR L/SBR blend before aging, N increases with R up to a maximum value at 50% SBR in the blend, after which N decreases with increase in % SBR in the blend. This positive deviation of observed N values from ideality can be associated with the compatibility of SMR L and SBR, both of which are nonpolar in nature. At 50% SBR, maximum compatibility occurs as reflected by the maximum N values observed, as shown in Figure 5. However, because of the irregular structure of the SBR chain, the rubber is noncrystallizable upon stretching. Thus, N drops drastically after the maximum value as SBR becomes the dominant rubber component. After aging, N shows a lower value than that of the unaged sample, a phenomenon similar to that observed for the SMR L/ENR 25 system which was discussed above. No maximum value is obtained in this case and the fatigue life decreases gradually with % SBR. The breakdown of crosslinks of vulcanizate after aging coupled with the noncrystallizability of SBR ac-

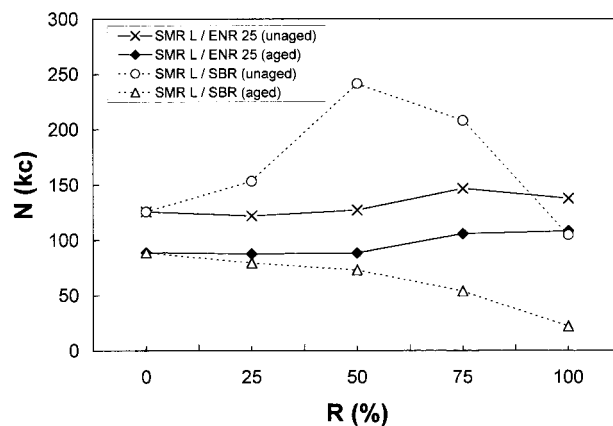


Figure 5 Variation of fatigue life (N) with blend ratio of ENR 25 or SBR (R) for the carbon black-filled rubber blends before and after aging at 100°C for 48 h. The extension ratio is 2.

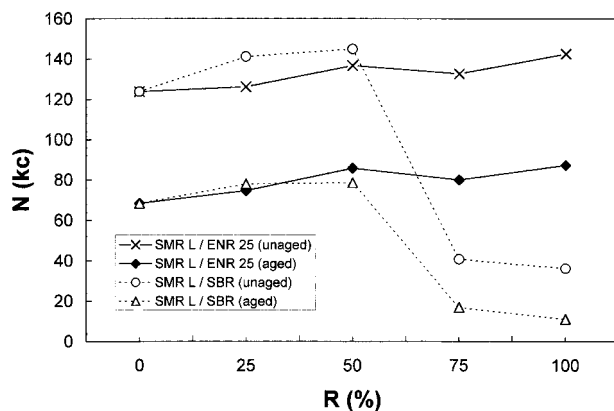


Figure 6 Variation of fatigue life (N) with blend ratio of ENR 25 or SBR (R) for the silica-filled rubber blends before and after aging at 100°C for 48 h. The extension ratio is 2.

counts for the lower N values in the SMR L/SBR blend system.

Figure 6 shows the effect of blend ratio on the fatigue life of the blends in the presence of silica. Again, N values of the SMR L/ENR 25 blend increase with % ENR 25, an observation which is similar to the carbon black-filled blend. For the SMR L/SBR blend, the N value increases with SBR composition up to 50% blend ratio, after which a drastic drop is observed. For both systems, the corresponding N values of the blends are decreased after aging because of the thermal degradation of crosslinks. One interesting finding is that, above 75% R , the SMR L/ENR 25 system consistently exhibits higher N values than that of the SMR L/SBR system before and after aging. This observation is ascribed to the stronger interaction between silica (a polar filler) and the polar ENR 25, especially at higher compositions of ENR. However, the nonpolar SBR interacts weakly with a polar filler such as silica to give a weaker vulcanizate as shown in Figure 6, especially at higher SBR composition. The overall effect of aging on the respective N values is represented as a % retention of fatigue life after aging at 100°C for 48 h as shown in Figure 7. For both carbon black- and silica-filled vulcanizates, the SMR L/ENR 25 system consistently indicates higher % retention values than the SMR L/SBR blend. This observation may be attributed to the crystallizability of both SMR L and ENR 25 when the rubbers are subjected to cyclic tensile stress. On the contrary, the noncrystallizable SBR succumbs to earlier failure upon repeated tensile stress. Figure 7 also shows that % retention of the

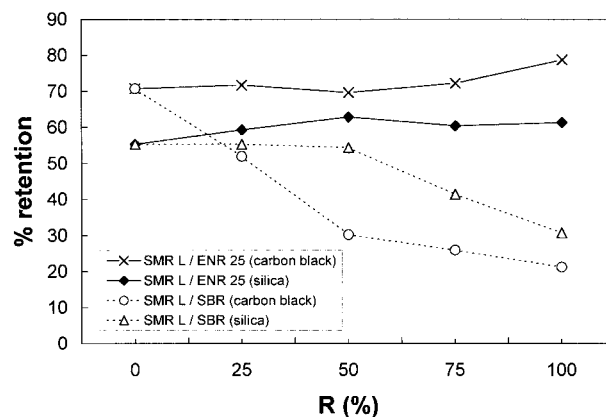


Figure 7 Percent retention of fatigue life versus blend ratio of ENR 25 or SBR (R) for the filled rubber blends after aging at 100°C for 48 h.

SMR L/ENR 25 system is essentially quite independent of blend ratio compared with SMR L/SBR systems for both filler systems. This means that the former blend system is more resistant to aging than the latter, particularly for blend ratios greater than 50%.

The effect of extension ratio on the fatigue life for both blend systems is shown in Figures 8 and 9 for SMR L/ENR 25 and SMR L/SBR blends, respectively, before aging. It is obvious that the N values decrease with extension ratio for all the systems studied. This observation is attributed to the higher cyclic tensile stress experienced by the vulcanizate as the extension is increased from 2 to 2.4.

CONCLUSIONS

Several findings are obtained from this investigation on the cure and mechanical properties of

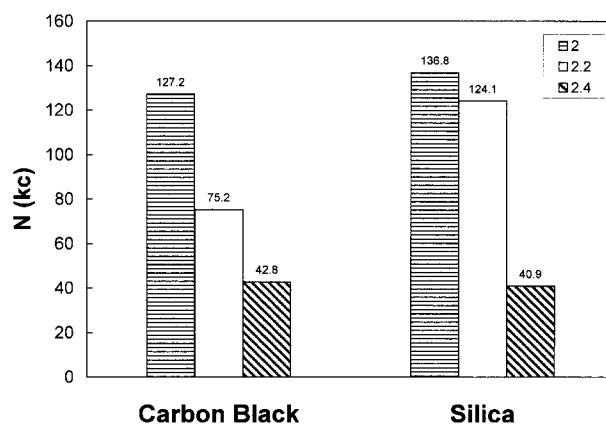


Figure 8 Comparison of fatigue life (N) of filled SMR L/ENR 25 blend for the various extension ratios before aging.

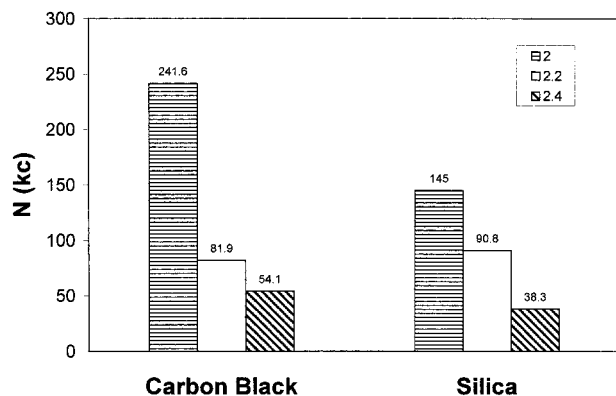


Figure 9 Comparison of fatigue life (N) of filled SMR L/SBR blend for the various extension ratios before aging.

SMR L/ENR 25 and SMR L/SBR blends. These can be summarized as follows:

1. Scorch time and cure time decrease with increasing % ENR 25 in the SMR L/ENR 25 blend, whereas it increases with % SBR in the SMR L/SBR system. This observation is attributed to the faster cure in ENR 25—attributed to the activation of adjacent double bond by epoxide group in the rubber—and slower cure rate of SBR which contains fewer double bonds than SMR L. The silica-filled system consistently shows higher values than carbon black-filled blends.
2. Resilience decreases with increasing % ENR 25 and % SBR in the respective blends, but hardness indicates the reverse behavior. The higher T_g of ENR 25 and the presence of styrene group in SBR accounts for the increase in hardness and lower resilience in the blends.
3. Fatigue life increases with % ENR 25 in the SMR L/ENR25 blend, an observation which is attributed to the higher fatigue life of ENR 25. For the SMR L/SBR system,

it passes through a maximum value at 50% SBR as a consequence of better compatibility between SMR L and SBR. Aging decreases the fatigue life of the blends because of the breakdown of crosslinks in the vulcanizate with the SMR L/ENR 25 blend, indicating better aging resistant than the SMR L/SBR system. In all cases, fatigue life decreases with extension ratio as a result of higher cyclic tensile stresses.

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