

Concentration Effect of Stearic Acid on Scorch Behavior of Epoxidized Natural Rubber

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SYNOPSIS

The effect of stearic acid on Mooney scorch time of epoxidized natural rubber (ENR 25 and ENR 50) and one grade of unmodified natural rubber (SMR L) was investigated in the concentration range of 0.5 to 14.5 phr. Other parameters, namely accelerator systems, temperature, and fillers (carbon black and silica), on the scorch property of ENR 25 in the presence of excess loading of stearic acid were also studied. Results indicate that scorch time increases with stearic acid loading for all the rubbers investigated, the rate of increase being fastest in ENR 50, followed by ENR 25 and SMR L. Mooney scorch time of ENR shows strong dependence on stearic acid loading for delay-action accelerators and at lower temperatures of vulcanization. For a fixed filler loading, the dependence of scorch time on stearic acid concentration is similar to that of gum stock. The retardation effect exhibited by excess stearic acid on the vulcanization of ENR may be attributed to complex formation of chelates and the reduction in activation of adjacent double bonds in ENR resulting from interaction between stearic acid and the epoxide group of ENR. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A small quantity of stearic acid (usually about 0.5–2 phr) is normally used as an activator in the study of vulcanization of natural rubber. However, the effect of excess stearic acid concentration on the vulcanization behavior of rubber has not been widely investigated. Coran^{1,2} carried out studies on the concentration effect of stearic acid on natural rubber. He found that the specific rate of vulcanization is decreased if the concentration of stearic acid is increased. This is attributed to the complex formation of chelates between zinc ions (brought into solution by stearic acid) and the accelerator, intermediate reaction products, or cross-link precursors. With regard to epoxidized natural rubber (ENR), there is no report on the effect of excess stearic acid on the curing characteristics of the rubber, especially its scorch properties. It is thus the aim of this article to describe some of our findings in this area of interest.

EXPERIMENTAL

Materials

SMR L, ENR 25, and ENR 50 having 0, 25, and 50 mol % of epoxidation, respectively, were used in this study. Five accelerators, MBT, TMTD, CBS, ZDMC, and DPG, were also used. The respective technical specifications of rubbers and accelerators are given in our previous papers.^{3,4} Oil furnace black (HAF grade having a surface area of about 70 m²/g) and precipitated silica (with a surface area of about 170 m²/g) were chosen as fillers. Other compounding ingredients such as zinc oxide, stearic acid, and sulfur were of commercial grade. All materials were freshly supplied and used without further purification.

Method

The formulation of rubber compound and mixing procedure were carried out in accordance to the method described by the American Society for Testing and Materials (ASTM), designation D 3184-80.⁵ However, in this study, the concentration of stearic

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acid used ranged from 0.5 to 14.5 phr. The concentration of fillers (HAF and silica) were varied from 10 to 40 phr. Mooney scorch time and cure index of the rubber compound were determined by a Mooney Shearing Disk Viscometer. Details regarding the testing procedure were outlined in our previous article.³

RESULTS AND DISCUSSION

In this study, the results are discussed with respect to the degree of epoxidation, types of accelerators, and fillers.

Effect of Epoxidation of Natural Rubber

The variation of Mooney scorch time with stearic acid concentration for unmodified natural rubber (SMR L grade), ENR 25, and ENR 50 is shown in Figure 1. Results indicate that scorch time increases with increasing stearic acid concentration for all the rubbers studied. For stearic acid concentration less than 1 phr, ENR 50 shows the shortest scorch time, followed by ENR 25 and SMR L. This observation is consistent with our previous study.⁴ However, for stearic acid concentration greater than 1 phr but less than 6 phr, ENR 50 showed a longer scorch

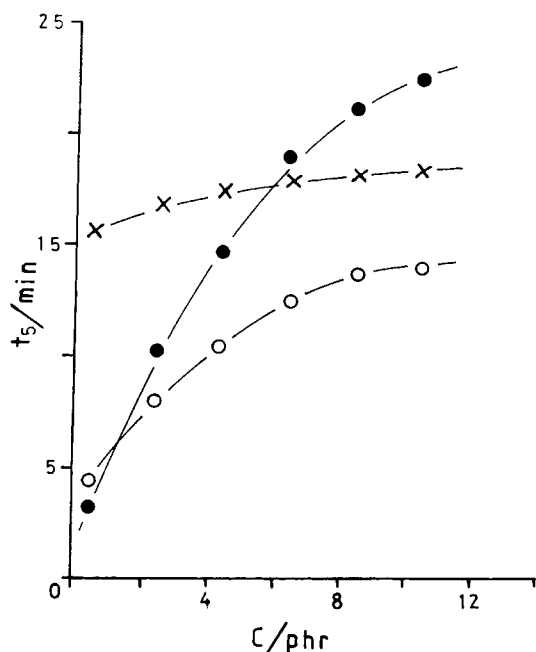


Figure 1 Variation of Mooney scorch time with stearic acid concentration for various rubbers at 120°C. (X) SMR L; (O) ENR 25; (●) ENR 50.

time compared to ENR 25 but still shorter than SMR L. Further loading of stearic acid beyond 6 phr results in ENR 50 exhibiting the longest scorch time among the rubbers investigated. This study clearly shows that the rate of increase in scorch time with stearic acid concentration depends greatly on the rubber, that is, the rate is fastest in ENR 50, followed by ENR 25 and SMR L.

For lower loading of stearic acid, ENR gives a shorter scorch time compared to SMR L. This is attributed to the activation of double bond by the adjacent epoxide group in ENR and additional cross-links resulting from the ring opening of the epoxide group in ENR.⁶ However, as the stearic acid concentration is increased, ENR indicates a greater rate of scorch delay compared to SMR L. This observation may be attributed to chelates formation^{1,2} and also due to the interaction between stearic acid and the epoxide group in ENR via hydrogen bonding that results in the "solvation" of the epoxide group in ENR. The solvation effect will reduce the activation of adjacent double bonds by the epoxide group in ENR, especially for ENR 50. This explanation is consistent with the observed increment in scorch time as shown in Figure 1 that indicates that increments in scorch time (Δt_5) between 0.5 and 10.5 phr of stearic acid loadings for ENR 50, ENR 25, and SMR L are 19.1, 9.8, and 2.9 min, respectively. The increment of scorch time in ENR 50 is nearly double that of ENR 25 because the mol % of the epoxide group in the former is twice that of the latter. This means that more solvation by excess stearic acid occurs in ENR 50 compared to ENR 25. In the case of SMR L where there is no epoxide group, the increase of scorch time with higher loading of stearic acid is associated mainly with the complex formation of chelates between the zinc ion (brought into solution by stearic acid) and accelerator, intermediate reaction products, or cross-link precursors.^{1,2}

Effect of Accelerators

Figure 2 shows the dependence of Mooney scorch time of ENR 25 on stearic acid concentration for different accelerators studied at 120°C. Except for ZDMC and TMTD, the other accelerators investigated (viz., MBT, DPG, and CBS) indicate a rapid increase in scorch time with an increase in stearic acid concentration up to about 8 phr of stearic acid loading, after which the scorch time seems to level off with further loading of stearic acid. This observation suggests that stearic acid behaves like a retardant when it is present in excess. In the case of MBT, the maximum stearic acid loading that can

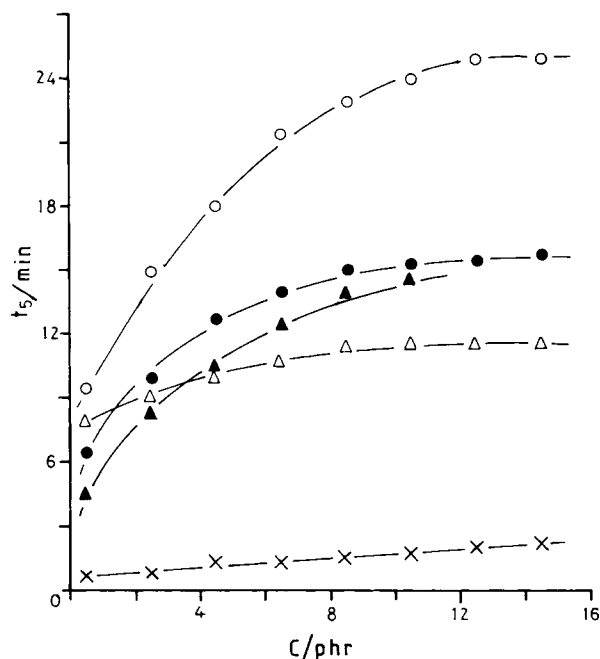


Figure 2 Variation of Mooney scorch time of ENR 25 with stearic acid concentration for various accelerators at 120°C. (○) CBS; (●) DPG; (▲) MBT; (△) TMTD; (X) ZDMC.

be investigated is about 10.5 phr because above that concentration, the viscosity of the rubber compound decreases causing a slippage of the rotor in the Mooney viscometer. This behavior is attributed to the plasticization effect of the excess stearic acid.

The increment of Mooney scorch time (Δt_5) for the corresponding increase in stearic acid loading from 0.5 to 10.5 phr for the various accelerators studied is given in Table I.

Table I shows that Δt_5 depends greatly on the types of accelerators used, with "ultrafast" accelerators (e.g., ZDMC) giving the lowest value and delay-action accelerator (e.g., CBS) indicating the highest Δt_5 value. ZDMC, which can be regarded as a soluble zinc mercaptide species that is internally chelated,⁷ forms an active sulfurating complex easily and thus enhances the cross-linking rate of ENR 25. This is reflected by the slight dependence of Mooney scorch time on stearic acid concentration because of the faster cross-linking rate of ZDMC, that is, the lower activation energy of vulcanization. Thus, solvation by excess stearic acid does not significantly affect the scorch time of ZDMC-accelerated sulfur vulcanization. In the case of TMTD, the dependence of Mooney scorch time on stearic acid concentration is more obvious than that of ZDMC. This may be attributed to the slower rate of cross-

linking by TMTD due to the formation of ZDMC as the reaction intermediate in TMTD accelerated sulfur vulcanization.^{8,9} The presence of excess stearic acid would probably slow down the formation of the reaction intermediate ZDMC.

In the case of the medium fast accelerators DPG and MBT, significant dependence of Mooney scorch time on stearic acid loading is observed as indicated by the respective Δt_5 values. This finding suggests that solvation of the epoxide group by excess stearic acid, resulting in the reduction of the activation of the adjacent double bond in ENR, is significant as reflected by the increase of scorch time as stearic acid loading increases. The largest Δt_5 value, however, is observed in the CBS-accelerated system. The scorch delay exhibited by CBS allows time for more solvation of the epoxide group by excess stearic acid. Also, the formation of carboxylate ligands to the zinc atom of the intermediate reaction product may occur prior to cross-linking of ENR 25. Owing to these two factors, a strong dependence of Mooney scorch time on stearic acid loading is observed when CBS is used as the accelerator.

Effect of Temperature of Vulcanization

The dependence of Mooney scorch time of ENR 25 with stearic acid concentration for various temperatures of vulcanization is shown in Figure 3. Results indicate that scorch time strongly depends on stearic acid concentration only at lower temperatures of vulcanization, 120°C and below, whereas for temperatures greater than 140°C, the dependence becomes less significant. The increment in scorch time between 0.5 and 14.5 phr of stearic acid is 74.1, 15.5, 3.9, and 1.1 min for 100, 120, 140, and 160°C, respectively. At higher temperatures of vulcanization, enough thermal energy is available to overcome the activation energy of vulcanization even at higher loading of stearic acid where the activation of adjacent double bonds in ENR is significantly reduced due to the solvation effect of the epoxide group. At lower temperatures of vulcanization, the effects of

Table I Δt_5 for Various Accelerators

Accelerator	Δt_5 (min)
ZDMC	1.1
TMTD	3.5
DPG	8.8
MBT	9.8
CBS	14.5

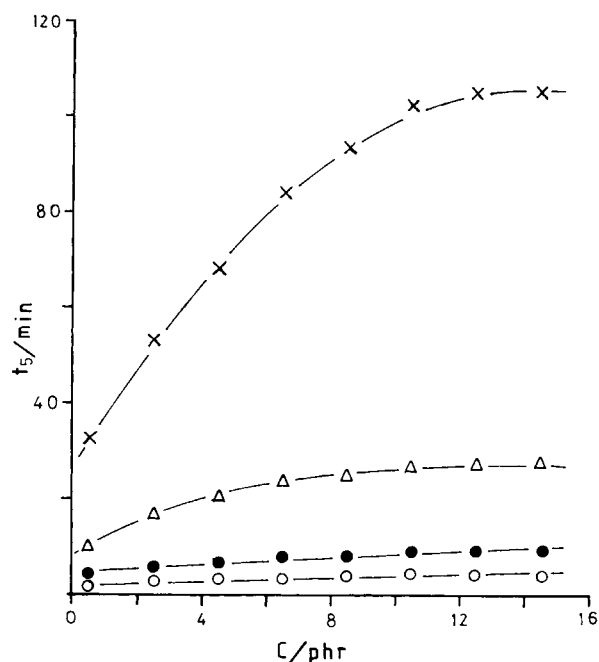


Figure 3 Variation of Mooney scorch time of ENR 25 with stearic acid concentration for various temperatures of vulcanization. Accelerator used is CBS. (X) 100°C; (Δ) 120°C; (\bullet) 140°C; (\circ) 160°C.

chelation and reduction of activation of adjacent double bonds in ENR become significant as exhibited by the strong dependence of scorch time on stearic acid concentration. Similar behavior is also observed for the cure index ($\Delta t_L = t_{35} - t_5$) plot as shown in Figure 4. A strong dependence of cure index on stearic acid concentration is obtained at lower temperatures of vulcanization. By using the cure index data and assuming first-order kinetics, an Arrhenius plot is carried out as shown in Figure 5 for four stearic acid loadings, 0.5, 4.5, 8.5, and 12.5 phr. All four plots indicate curves of increasing slope with decreasing temperatures suggesting change of vulcanization mechanisms from low temperatures to higher temperatures of vulcanization. This observation is consistent with our result reported in our previous study⁴ for a single concentration of stearic acid where MBT is used as the accelerator. From the Arrhenius plot, a range of apparent activation energy is estimated and given in Table II.

The order of magnitude of the apparent activation energy is comparable to that reported earlier where MBT was used as the accelerator.⁴ For each loading of stearic acid, a range of E_a was observed. This is associated with the change in vulcanization mechanism of ENR from low to higher temperatures of vulcanization. Table II indicates that the end values

(especially the lower end value) of E_a increase with increasing stearic acid loadings. This observation may be attributed to two factors, the increasing chelation effect of zinc ions as a result of increasing solution of zinc ions by stearic acid, and the decreasing activation of adjacent double bonds in ENR due to solvation of epoxide groups as the stearic acid loading is increased.

Effect of Fillers

In this study, two fillers, high-abrasion furnace (HAF) grade carbon black and precipitated silica, were used. Figure 6 shows the variation of Mooney scorch time of ENR 25 with stearic acid concentration in the presence of carbon black. It was observed that for the four carbon black loadings studied, all the plots exhibited an increase in scorch time with increasing stearic acid concentration. This observation is similar to the results for the gum stock reported earlier in the article. For a fixed stearic acid concentration, the scorch time of ENR compound decreases with increasing loading of carbon black. This result is consistent with our earlier findings reported in the previous study.⁴ As explained before, the role of carbon black is to activate the

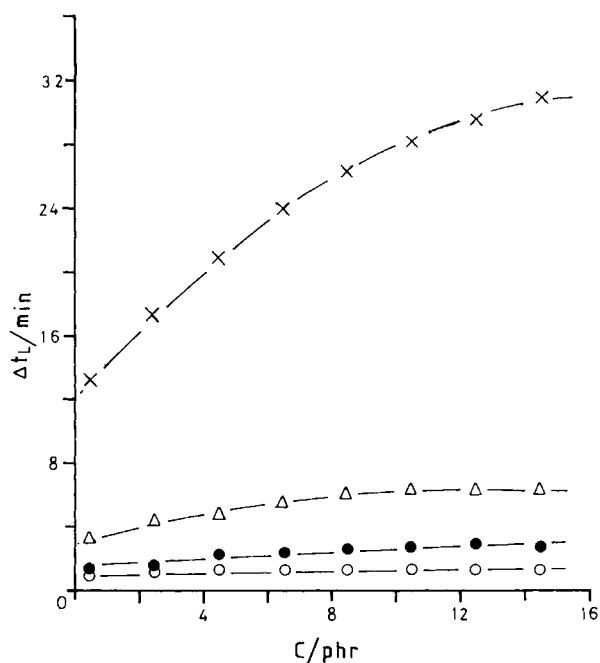


Figure 4 Cure index of ENR 25 versus stearic acid concentration for various temperatures of vulcanization. Accelerator used is CBS. (X) 100°C; (Δ) 120°C; (\bullet) 140°C; (\circ) 160°C.

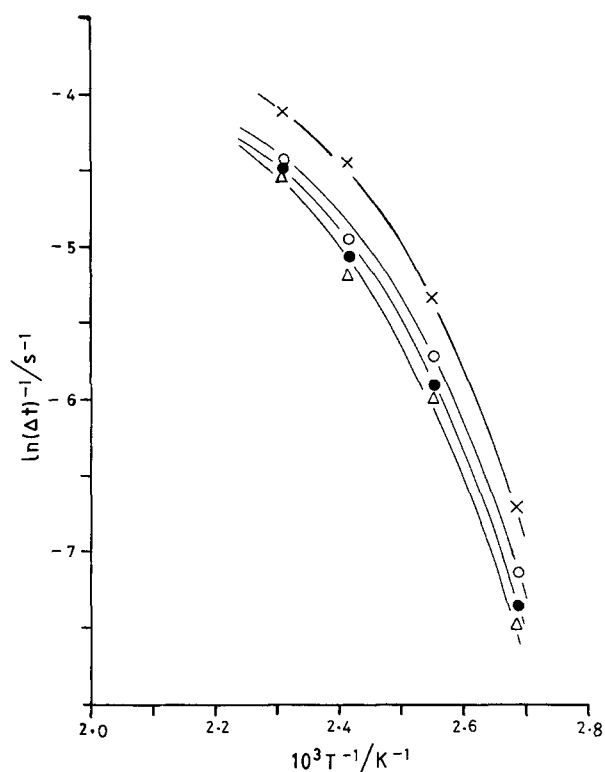


Figure 5 Arrhenius plot using the data from Figure 4 for various stearic acid concentrations. (X) 0.5 phr; (O) 4.5 phr; (●) 8.5 phr; (Δ) 12.5 phr.

vulcanizing process through the 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.¹⁰ Thus, scorch time decreases with increasing carbon black loading.

The effect of silica on scorch time of ENR 25 is shown in Figure 7. For a fixed loading of silica, the scorch time increases with increasing stearic acid concentration similar to that observed for carbon black. However, for a fixed loading of stearic acid,

Table II Apparent Activation Energy of Vulcanization (E_a) for Various Concentrations of Stearic Acid

Stearic Acid Concn. (phr)	E_a (kcal/mol)
0.5	9.4–20.1
4.5	10.0–20.1
8.5	10.6–20.6
12.5	11.1–20.6

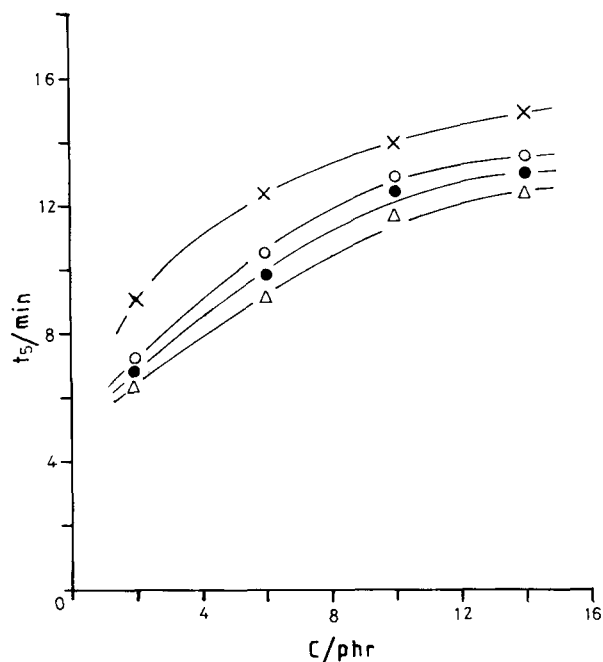


Figure 6 Variation of Mooney scorch time of ENR 25 with stearic acid concentration for various loadings of HAF carbon black at 120°C. (X) 10 phr; (O) 20 phr; (●) 30 phr; (Δ) 40 phr.

scorch time increases with increasing silica loading, a finding contrary to that observed for carbon black. Precipitated silica that contains about 10–14% water is hydrophilic in nature.^{11,12} Owing to the presence of polar groups in silica and ENR, a strong interaction exists between silica and ENR as reflected by the high level of reinforcement of ENR by silica.¹³ Therefore in this study, the increase in scorch time with silica loading may be explained by the interaction between surface active groups in silica and epoxide groups in ENR via hydrogen bonding, thus decreasing the activation of adjacent double bonds in ENR.

CONCLUSION

From this study, the following conclusions can be drawn.

1. For all the rubbers studied, Mooney scorch time increases with increasing stearic acid concentration. At high loading of stearic acid, greater than 6 phr, ENR 50 exhibits the longest scorch time, followed by ENR 25 and SMR L, an observation that is the reverse of that reported in our previous study⁴ for low

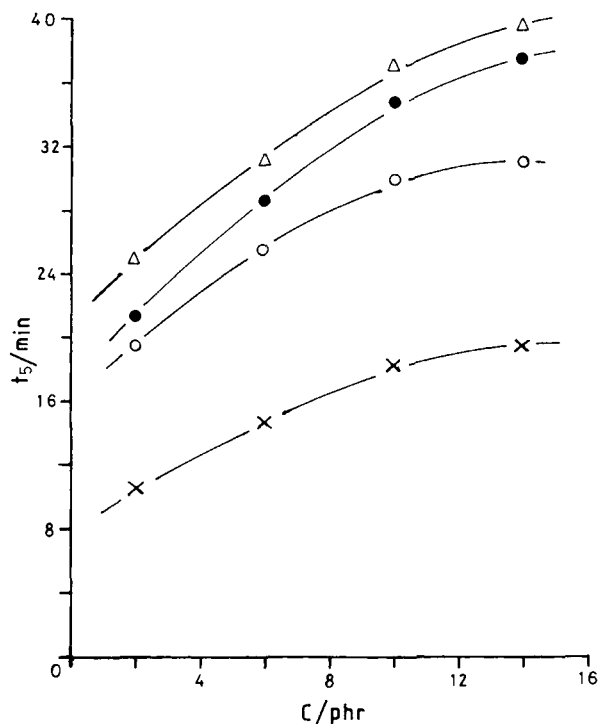


Figure 7 Variation of Mooney scorch time of ENR 25 with stearic acid concentration for various loadings of precipitated silica at 120°C. (X) 10 phr; (O) 20 phr; (●) 30 phr; (Δ) 40 phr.

loading of stearic acid. The increase in scorch time of ENR in the presence of excess stearic acid is mainly attributed to the solvation of epoxide groups by the excess stearic acid, thus reducing the activation of adjacent double bonds in ENR. In the case of SMR L, the observed increase in scorch time is associated with the chelate formation between zinc ions (brought into solution by stearic acid) and accelerator, intermediate reaction product, or cross-link precursors.

2. A strong dependence of scorch time on stearic acid concentration is observed for delay-action accelerator systems, for example, CBS and at lower temperatures of vulcanization, less than 120°C. For the delay-action accelerator, the extent of solvation of epoxide groups is greater, whereas at lower temper-

atures of vulcanization, less thermal energy is available to overcome the activation energy for cross-linking.

3. The scorch behavior of filled ENR in the presence of excess stearic acid is similar to that of the gum stock. However, for a fixed stearic acid concentration, scorch time of ENR decreases with increasing carbon black loading but it increases with increasing silica loading. Carbon black activates the vulcanizing process, whereas silica interacts strongly with ENR, thus reducing the activation of adjacent double bonds in ENR.

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