Effect of Stearic Acid Concentration on the Reversion Behavior of Epoxidized Natural Rubber

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ABSTRACT: The effect of stearic acid concentration on the reversion behavior of epoxidized natural rubber (ENR 25 and ENR 50) was carried out in the temperature range of 150–180°C and 0.5–14.5 phr of stearic acid loading. Three common accelerators; namely, zinc dimethyldithiocarbamate (ZDMC), tetramethylthiuram disulfide (TMTD), and N-morpholinylbenzothiazole-2-sulfenamide (MBS) and conventional sulfur vulcanization system was used throughout the study. A Monsanto oscillating-disk rheometer was used to determine the reversion behavior of the rubber. Results indicate that for all the accelerators used, reversion decreases with increasing stearic acid concentration. The rate of decrease is more gradual up to about 6.5 phr of stearic acid, after which a rapid drop of reversion is observed for both ENR 25 and ENR 50. This observation is attributed to the increasing amount of mono- and disulfidic crosslinks as a result of desulfuration of polysulfidic crosslinks. The higher the stearic acid loading, the greater is the retardation effect on vulcanization; that is, more time is available for desulfuration. Increasing temperature would increase the reversion of the rubber vulcanizate because of the increase in thermal energy to decompose more crosslinks, including mono- and ether crosslinks for temperature higher than 160°C. ZDMC (an ultrafast accelerator) gives a higher reversion than MBS (a delay-action accelerator), because desulfuration occurs more slowly in the former system. The observed decrease in reversion as stearic acid concentration increases is technologically importance, because the aging property of the rubber vulcanizate is significantly improved. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1165-1169, 1999

Key words: reversion; rubber; accelerator; crosslink; desulfuration

INTRODUCTION

Reversion is a well-known phenomenon in the accelerated sulfur vulcanization of natural rubber. For most technological applications, reversion is undesirable. Kok¹ in his study of the effects of compounding variables of natural rubber, found that accelerators, which normally provide fast cure, cause more severe reversion than slower accelerators. The reversion behavior of epoxidized natural rubber (ENR) at low stearic acid concentration (2 phr) was investigated in the temperature range from 140 to 180°C in an accelerated sulfur vulcanization system.² It is concluded

that, below 160°C, reversion of ENR is associated with the decomposition of di- and polysulfidic crosslinks; whereas, above 160°C, additional breakdown of mono- and ether crosslinks occurs. The reversion property of unaccelerated sulfur vulcanization of ENR was also studied,³ and indicates that reversion decreases with increasing sulfur loading and is a time- and temperaturedependent phenomenon. However, there is no report on the systematic investigation of concentration effect of stearic acid on the reversion behavior of ENR, although its effect on Mooney scorch time of ENR has been reported,⁴ which shows that scorch time increases with stearic acid loading for all the rubbers studied, the rate of increase being fastest in ENR 50 followed by ENR 25 and SMR L. In view of the finding that stearic acid increases the scorch time—hence, increases the

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Figure 1 Variation of percentage reversion of ENR 25 with stearic acid loading in ZDMC-accelerated vulcanization system.

processing safety—it is interesting to explore its effect on the reversion behavior of ENR further. In this article, we report some of our findings on the concentration effect of stearic acid on the reversion behavior of two grades of ENR; namely ENR 25 and ENR 50.

EXPERIMENTAL

Materials

ENR 25 and ENR 50 having 25 and 50 mol % of epoxidation, respectively, were used as the base elastomers. The technical specification of the rubbers used is given in Table I of our previous paper.⁵ Three accelerators [zinc dimethyldithiocarbamate (ZDMC), tetramethylthiuram disulfide (TMTD), and *N*-morpholinylbenzothiazole-2sulfenamide (MBS)] having melting points of 250, 140, and 78°C, respectively, were used. These accelerators were freshly supplied by The Bayer Co. Other compounding ingredients, such as zinc oxide, stearic acid, sulfur, and poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), were of commercial grades and used without further purification.

Compounding and Testing

The base formulation for the rubber compound was: rubber, 100; zinc oxide, 5; accelerator, 0.5; sulfur, 2.5; antidegradant (TMQ), 2; stearic acid, variable (0.5–14.5). The mixing procedure as described by the American Society for Testing and Materials (ASTM)-Designation D 3184-89⁶ was followed. A Monsanto oscillating-disk rheometer (Model 100) was used to determine the reversion property of the rubber compound, because rheometer torque is found to be suitable as an indicator of reversion behavior of rubber.¹ The testing procedure, as described in ASTM designation D 2084-93,⁷ was used. The sensitivity of the equipment was calibrated by using a torque standard (AT 001). It was calibrated for the use of a 3° arc rotor to obtain greater sensitivity in the measurement. A circular test specimen of about 30-mm diameter and 11.5-mm thickness was used. The percentage reversion (*R*) is defined as:

$$R = (T_{\rm max} - T_{\rm 30}) 100 / (T_{\rm max} - T_{\rm min})$$

where $T_{\text{max}} = \text{maximum torque}$, $T_{\text{min}} = \text{mini-mum torque}$, and $T_{30} = \text{torque at 30 min after the maximum torque on the rheograph.}$

RESULTS AND DISCUSSION

The effect of stearic acid concentration on the percentage reversion (R) of ENR 25 and ENR 50 is shown in Figures 1 and 2, respectively, for the ZDMC-accelerated vulcanization system. For a fixed temperature, percentage R decreases gradually with increasing stearic acid concentration up to about 6.5 phr of stearic acid, after which, a sudden drop of percentage R is observed with further increase in stearic acid loading. The decrease in reversion is attributed to the increase in mono- and disulfidic crosslinks resulting from the desulfuration of polysulfidic crosslinks as stearic acid loading is increased. In the presence of ex-



Figure 2 Variation of percentage reversion of ENR 50 with stearic acid loading in ZDMC-accelerated vulcanization system.



Figure 3 Variation of percentage reversion of ENR 25 with stearic acid loading in TMTD-accelerated vulcanization system.

cess of stearic acid, solvation of epoxide groups by stearic acid molecules occurs; thus, decreases the activation of adjacent double bond in ENR, as reflected by the longer scorch time at higher stearic acid loading.⁴ This means that more time is available for the desulfuration process to occur during vulcanization. This observation is very similar to the reversion behavior of accelerated sulfur vulcanization involving slower accelerator; for example, MBTS and MBT, which cause crosslinks to form at slower rates, but these crosslinks desulfurate more rapidly to give the more stable mono- and disulfidic crosslinks.¹ As temperature increases, percentage R also increases correspondingly for all the stearic acid concentration studied. For temperature greater than 160°C, in addition to the breakdown of diand polysulfidic crosslinks, additional breakdown from mono- and ether crosslinks in ENR occurs.² Morrison et al.⁸ also reported that for polyisoprene, the thermal breakdown of monosulfide crosslinks and pendent groups must be considered for temperature greater than 160°C. The reversion behavior of ENR in the presence of excess stearic acid for the TMTD-accelerated system is shown in Figures 3 and 4 for ENR 25 and ENR 50, respectively. Again, percentage R decreases steadily with increasing stearic acid concentration because of the formation of more monoand disulfidic crosslinks as a result of greater desulfuration of polysulfidic crosslinks. In fact, in the case of ENR 50 studied at 150°C, no reversion is detected at 14.5 phr of stearic acid, suggesting that, at high stearic acid concentration, the crosslinks are predominantly mono- and ether



Figure 4 Variation of percentage reversion of ENR 50 with stearic acid loading in TMTD-accelerated vulcanization system.

types, which are not decomposed at 150°C. However, for temperature higher than 160°C, reversion still occurs, even at high stearic acid loading, confirming our previous explanation that, for temperature higher than 160°C, breakdown of mono- and ether crosslinks takes place. Similar reversion behavior is also observed for the MBSaccelerated system, as shown in Figures 5 and 6 for ENR 25 and ENR 50 respectively. The delayed-action nature of MBS accelerator coupled with the solvation effect of stearic acid enhances the desulfuration process. This is particularly seen at temperatures under 160°C. In fact, at 150°C, no reversion is observed for all the stearic acid concentrations studied for the two grades of



Figure 5 Variation of percentage reversion of ENR 25 with stearic acid loading in MBS-accelerated vulcanization system.



Figure 6 Variation of percentage reversion of ENR 50 with stearic acid loading in MBS-accelerated vulcanization system.

ENR. However, for temperatures above 160° C, reversion occurs because of the breakdown crosslinks, including mono- and disulfidic ones, as pointed out earlier. The severity of breakdown increases as temperature is further increased, as reflected by the higher percentage R values at 180° C, where enough thermal energy is available to cause decomposition of crosslinks, thus giving rise to higher reversion.

Figures 7 and 8 compare the reversion behavior of ENR 25 and ENR 50 at 160°C for various accelerators used in this study. For fixed stearic acid loading, it is noted that ZDMC consistently gives the highest value, followed by TMTD and MBS for all the stearic acid loadings. ZDMC, being an "ultrafast" accelerator, desulfurates more



Figure 7 Variation of percentage reversion of ENR 25 with stearic acid loading for the various accelerator systems at 160°C.



Figure 8 Variation of percentage reversion of ENR 50 with stearic acid loading for the various accelerator systems at 160°C.

slowly, thus forming more polysulfidic crosslinks than the other two accelerators. On the other hand, desulfuration of the MBS (a delayed-action accelerator) system is relatively faster, hence giving rise to more stable mono- and disulfidic crosslinks, as shown by the lower reversion. The rate of desulfuration in the TMTD-accelerated system is intermediate between ZDMC and MBS. The decrement of percentage R from 0.5 phr to 14.5 phr of stearic acid concentration is given in Table I for the various accelerators studied at 160°C.

From Table I, it is obvious that the solvation effect of excess stearic acid is most significant in ZDMC-accelerated vulcanization system, as shown by the higher value of ΔR , especially for ENR 25. The excess stearic acid effectively retards the cure rate of the ultrafast accelerator (ZDMC) by solvation mechanism,⁴ thus providing more time for the desulfuration of polysulfidic crosslinks to the more stable mono- and disulfidic types. In the case of the delayed-action accelerator (MBS), it is already a slow accelerator, and the presence of excess stearic acid does not markedly influence the cure rate; that is, the retarding ef-

Table IDecrement in Percentage R (ΔR)between 0.5–14.5 phr of Stearic Acid

Accelerator	ENR 25 $(\Delta R, \%)$	ENR 50 (ΔR , %)
ZDMC	22.1	18.2
TMTD	17.0	16.0
MBS	9.9	10.3



Figure 9 Comparison of percentage reversion between ENR 25 and ENR 50 at 160°C and 6.5 phr of stearic acid loading for the various accelerator systems.

fect is not significant, as indicated by the lowest value of ΔR . The concentration effect of stearic acid on the TMTD-accelerated system is intermediate between the ultrafast and delayed-action accelerators.

The reversion behavior between ENR 25 and ENR 50 at 160°C and 6.5 phr of stearic acid concentration is shown in Figure 9. For the three accelerators studied, ENR 25 consistently shows higher reversion values than ENR 50. This observation is attributed to the higher density of crosslink in the former because of the presence of more double bonds in ENR 25. Because there are more crosslinks in ENR 25, more breakdown occurs, and higher reversion is observed. This finding is in agreement with our previous $study^2$ at low loading of stearic acid; that is, 2 phr. The difference in percentage R between ENR 25 and ENR 50 is 1.7, 1.1, and 2.6% for ZDMC, TMTD, and MBS systems, respectively. The higher value exhibited by the MBS-accelerated system is associated with the greater catalytic action of the MBS transformation product,^{1,8} as compared to the other accelerators used in this study.

CONCLUSION

From this investigation of the effect of stearic acid concentration on the reversion behavior of ENR 25 and ENR 50, the following conclusions can be drawn. First, for all accelerators and temperatures studied, reversion of ENR decreases gradually up to about 6.5 phr of stearic acid loading, after which a sudden drop of reversion with further loading of stearic acid is observed. This observation is attributed to the increasing effect of solvation of epoxide groups that retards the curing process as stearic acid concentration increases. This means that more time is available for the desulfuration of polysulfidic crosslinks to the more stable mono- and disulfidic crosslinks. Thus, the aging property of ENR can be improved by using excess stearic acid concentration, which is technologically significant. Second, for a fixed temperature of study, ZDMC-accelerated system gives the highest reversion, followed by TMTD and MBS systems for all the range of stearic acid investigated. This is attributed to slow desulfuration of ZDMC (an ultrafast accelerator) as compared to the other two accelerators. However, the decrement in percentage R between 0.5 to 14.5 phr of stearic acid loadings is greatest in ZDMC, because the effect of cure retardation resulting from the solvation by excess stearic acid is more significant in an ultrafast accelerator such as ZDMC as compared to a delayed-action accelerator, such as MBS. Third, ENR 25 indicates a higher reversion compared with ENR 50 at high stearic acid loading, an observation very similar to that reported for low stearic acid concentration²; that is, 2 phr. This observation is explained by the higher density of crosslinks in ENR 25, because it contains more double bonds than ENR 50. At 160°C and 6.5 phr of stearic acid content, the variation is between 1.1 to 2.6% reversion between the two rubbers for the three accelerators studied.

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