Cure Index and Activation Energy of Vulcanization of Natural Rubber and Epoxidized Natural Rubber Vulcanized in the Presence of Antioxidants

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ABSTRACT: The cure index and apparent activation energy of vulcanization of one grade of natural rubber (SMR L) and two grades of epoxidized natural rubbers (ENR 25 and ENR 50) were studied in the presence of three types of antioxidants [viz., 2,2′methylene-bis(4-methyl-6-tertbutylphenol) (AO 2246), poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), and *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD)] in the temperature range of 120–180°C by using a Monsanto automatic Mooney viscometer. Accelerated sulfur vulcanization system and up to 5 phr of antioxidant concentration was used throughout the investigation. Results indicate that both cure index and apparent activation energy of vulcanization are dependent on the type and concentration of the antioxidant used. AO 2246 (a phenol-based antioxidant) would retard vulcanization as reflected by the higher cure index and activation energy, an observation which is attributed to the solvation and steric hindrance effects of the antioxidant. On the contrary, both TMQ and IPPD (amine-based antioxidants) exhibit reverse behavior due to the catalytic effect of the antioxidants in generating more active sulfurating agents for vulcanization. In all cases, SMR L gives higher cure index and apparent activation energy than the corresponding ENR, a phenomenon which is associated with the activation of the adjacent double bond by epoxide group in the latter. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3234–3238, 2000

Key words: cure; activation; rubber; antioxidant; vulcanization

INTRODUCTION

We have reported the dependence of Mooney scorch time of natural rubber (SMR L) and epoxidized natural rubbers (ENR 25 and ENR 50) on concentration and types of antioxidants.[1] In the study, it was found that the scorch time of ENR increases with an increase in phenol-based antioxidant such as AO 2246, a retardation effect which is attributed to the solvation of epoxide ring of ENR by the phenolic group in AO 2246. This solvation effect is not significant in the case of SMR L. However, for the amine-based antioxidants such as *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD) and poly-2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), scorch time of SMR L and ENR is reduced by the antioxidants, a phenomenon which is associated with the enhancement effect of the amine-based antioxidants to catalyze the formation of the more active sulfurating agent. To understand further the role of antioxidants in the vulcanization of SMR L and ENR, we have extended the investigation to the cure index and activation energy of vulcanization of the three rubbers by using the same vulcanization system reported in our previous study on Mooney scorch time.[1]

EXPERIMENTAL

SMR L, ENR 25, and ENR 50 having 0, 25, and 50 mol % of epoxidation, respectively, were used as the base elastomers in this study. The antioxidants used were the same as in our previous investigation [i.e., 2,2′methylene-bis(4-methyl,6-tertbutylphenol) (AO 2246), TMQ, and IPPD]. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, and 2-mercaptobenzothiazole (MBT) were of commercial grades and used as supplied [Bayer (Malaysia) Co. Ltd.]. The compounding procedure, as described by ASTM D 3184–89,[2] was adopted. The base formulation for the rubber compound was: rubber, 100; zinc oxide, 6; sulfur, 3.5; stearic acid, 0.5; MBT, 0.5; antioxidant, variable. This recipe is the same as that used in our previous study[1] on the effect of antioxidants on Mooney scorch time of SMR L and ENR. The cure index of the rubber compound was determined by using a Monsanto automatic Mooney viscometer (MV 2000) according to the procedure described by ASTM D 1646–96a.[3] It is defined as the difference in time required for an increase of 35 units (t_{35}) above the minimum viscosity over that for an increase of five units (t_5), [i.e., cure index (Δt_L) = $t_{35} - t_5$]. The cure index defines the overall rate of cure.

RESULTS AND DISCUSSION

Cure Index

The cure index at 120°C for the three rubber compounds vulcanized in the presence of the phenol-
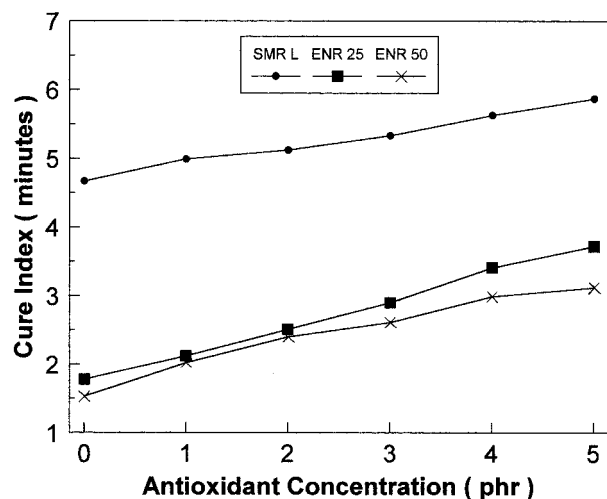

Figure 1   Variation of cure index with AO 2246 concentration for the various rubbers, studied at 120°C.
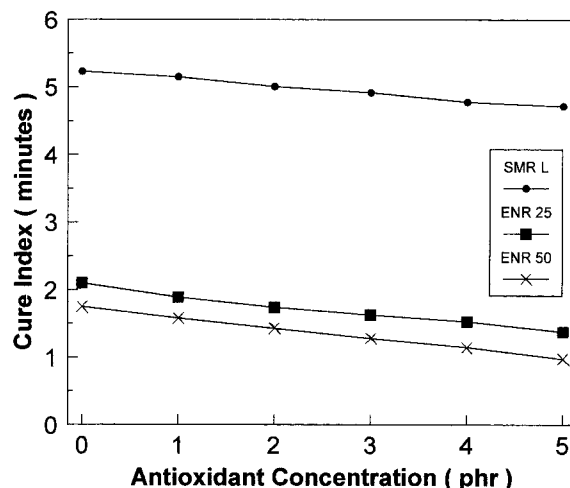

Figure 2   Variation of cure index with TMQ concentration for the various rubbers, studied at 120 °C.

based antioxidant (AO 2246) is shown in Figure 1. The cure index increases with an increase in antioxidant concentration for the rubbers studied. This implies that AO 2246 retards the vulcanization rate, an observation similar to that reported for the effect of AO 2246 on Mooney scorch time of SMR L and ENR.[1] This retardation phenomenon is attributed to the steric hindrance and solvation of epoxide ring by phenol group of AO 2246, which reduces the activation of the double bond in ENR. In the case of SMR L, where there is no epoxide group, the increase in cure index with AO 2246 is associated with the steric hindrance of the bulky groups in AO 2246. This steric effect would retard the formation of active sulfurating agents, a reaction intermediate necessary for vulcanization. The extra solvation effect in ENR is reflected by the steeper slope for both ENRs as compared to SMR L as shown in Figure 1. For a fixed concentration of AO 2246, SMR L gives a longer cure index, followed by ENR 25 and ENR 50. This observation is due to the presence of epoxide groups which activate the adjacent double bonds in ENR and hence enhances the vulcanization rate; the effect is more significant in ENR 50 than ENR 25.[4] In SMR L, where there is no such activation of double bond, the cure index is much higher than that of ENR. The role of two amine-based antioxidants (i.e., TMQ and IPPD) on the cure index of the rubbers studied is shown in Figures 2 and 3, respectively. Contrary to that observed for AO 2246, the cure index in the presence of TMQ and IPPD indicates a decline in value as the concentration of the antioxidant is increased. This enhancement effect of amine-based antioxidants such as TMQ and IPPD
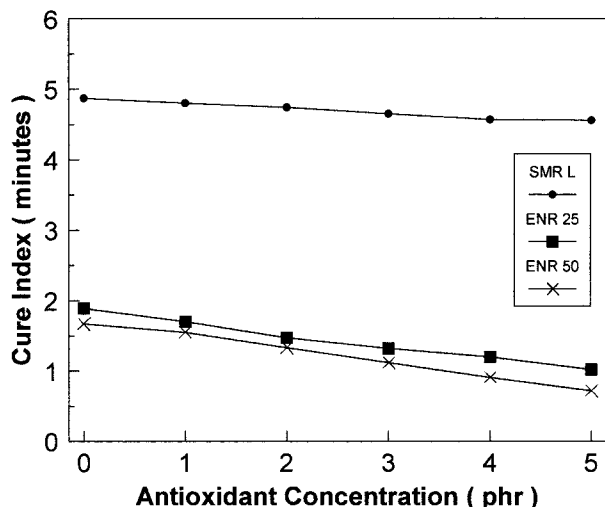
Figure 3 Variation of cure index with IPPD concentration for the various rubbers, studied at 120 °C.

in catalyzing the formation of active sulfurating agent[5] would increase the cure rate, hence reduces the cure index. Because TMQ and IPPD have a hydrogen bonding site (—NH), they can also solvate the epoxide group of ENR. However, this solvation effect is overshadowed by the catalytic effect of TMQ and IPPD (both amine-based antioxidants) in generating more active sulfurating agents necessary for vulcanization. Hence, the cure index of ENR decreases as the concentration of amine-based antioxidant is increased. Amines form external ligands that occupy the vacant zinc orbitals.[5] This occupation should weaken Zn—S binding and hence increase the nucleophilicity of the mercaptide sulfur atoms in the complexes and thus facilitate the formation of the active sulfurating reagent. In the case of a phenol-based antioxidant such as AO 2246, no external ligand is formed due to the presence of the oxygen atom, which carries two lone pairs of electrons. Also, the oxygen atom is more electronegative than nitrogen atom.

The mechanism of TMQ and IPPD in catalyzing the formation of active sulfurating agent (B) from the accelerator complex (A) is shown below:
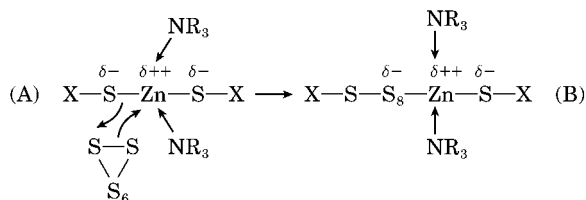
where NR_3 and S_8 represent the amine-based antioxidant and sulfur ring, respectively.

As in the case of AO 2246, SMR L exhibits higher cure index than ENR for a fixed antioxidant concentration as a result of the activation of double bonds by epoxide groups in the latter. Figure 4 compares the cure index of the various antioxidants for each rubber studied, which indicates that AO 2246 gives the highest cure index, followed by TMQ and IPPD. This order is slightly different from that reported for the dependence of the same antioxidants on Mooney scorch time,[1] where reverse order occurs between TMQ and IPPD. The difference in order between cure index and scorch time may be attributed to overall faster cure in IPPD as cure index is a measure of overall rate of cure, whereas Mooney scorch time is an indication of resistance to premature vulcanization.[6] The shorter cure index of rubber compound in the presence of IPPD is probably due to the effectiveness of IPPD in catalyzing the formation of active sulfurating agent because it contains two amine groups which are situated along the main chain as compared to TMQ. The cyclic ring where the amine group of TMQ is situated does not facilitate the easy formation of ligand with the vacant zinc orbitals.

Apparent Activation of Vulcanization

To understand further the kinetics of sulfur vulcanization in the presence of antioxidants, an Arrhenius plot is carried out to determine the apparent activation of vulcanization, where the reciprocal of cure index was plotted against the reciprocal of temperature, assuming first-order kinetics for the crosslinking process.[4] A typical
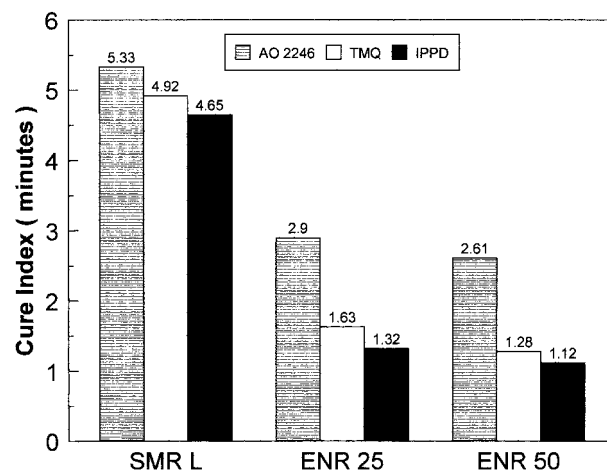

Figure 4 Comparison of cure index at 3 phr of antioxidants for the various rubbers, studied at 120 °C.
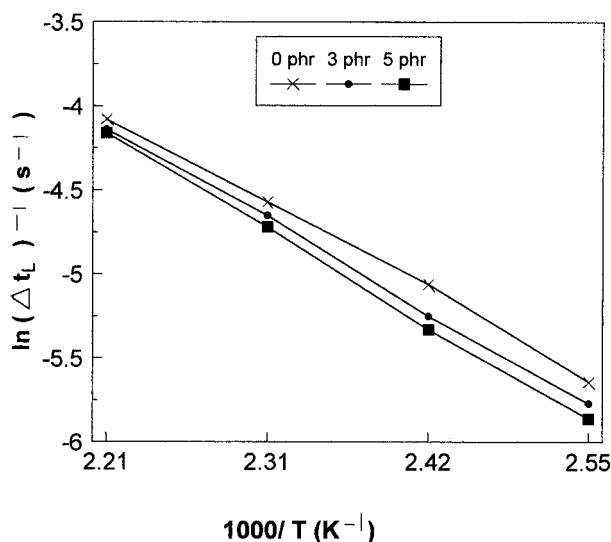
Figure 5 A typical Arrhenius plot for SMR L vulcanized in the presence of AO 2246.

Figure 7 Apparent activation energy of vulcanization of rubbers for various loadings of TMQ.

plot is shown in Figure 5 for SMR L cured at 120, 140, 160, and 180°C with and without AO 2246. The apparent activation energy of vulcanization is obtained from the slope of the straight line plot for 0, 3, and 5 phr of antioxidant. Figure 6 illustrates the effect of AO 2246 on the apparent activation energy of vulcanization for SMR L, ENR 25, and ENR 50. It is noted that the activation energy increases gradually with loading of AO 2246 for each rubber studied (i.e., AO 2246 retards the rate of cure). This observation is consistent with our earlier discussion that cure index increases (slower cure) with increasing AO 2246
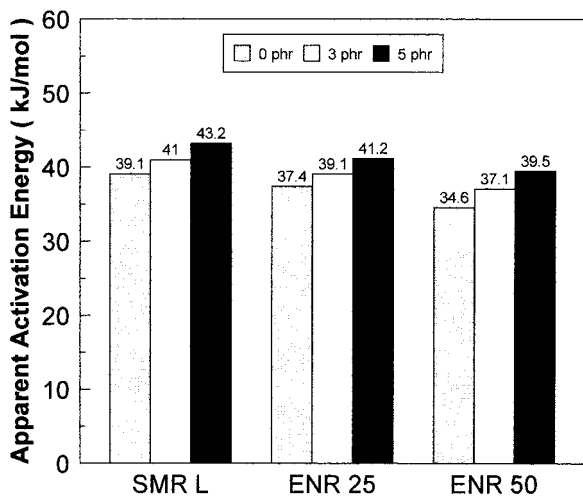
concentration. The increase in activation energy with AO 2246 is again attributed to the solvation of epoxide group in ENR and steric hindrance in the case of SMR L by AO 2246. However, on the contrary, TMQ and IPPD exhibit decreasing activation energy of vulcanization with increasing loading of the antioxidants for the three rubbers studied, as shown in Figures 7 and 8, respectively. This means that cure enhancement occurs in the presence of TMQ and IPPD. The amine-based antioxidants (TMQ and IPPD) catalyze the formation of more active sulfurating agent which in turn accelerates the vulcanization of rubbers. Hence, the apparent activation energy of vulcani-

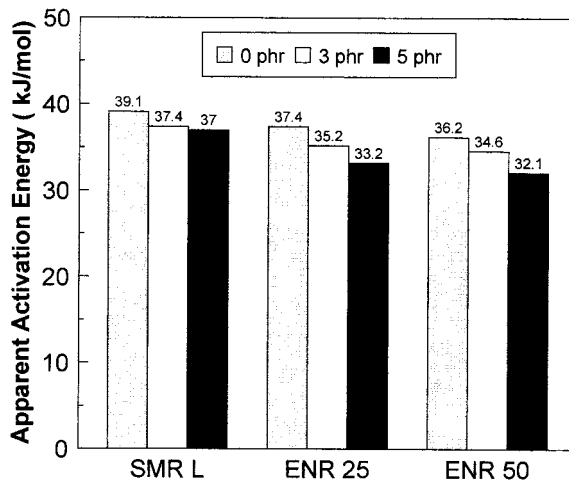**Figure 6** Apparent activation energy of vulcanization of rubbers for various loadings of AO 2246.

Figure 8 Apparent activation energy of vulcanization of rubbers for various loadings of IPPD.

zation and cure index is correspondingly reduced. In all cases, for a fixed loading of antioxidant, the order of decreasing apparent activation energy of vulcanization of the rubbers is as shown below:

SMR L>ENR 25>ENR 50

which has the same order as that reported and discussed for Mooney scorch time of the rubbers[4]

CONCLUSION

From this study, the following conclusions can be made.

(1) Cure index increases with AO 2246 loading, whereas it decreases with TMQ, and IPPD concentration with IPPD showing greater decrease than TMQ. This observation is attributed to the steric hindrance of AO 2246 and in the case of ENR, the extra effect of solvation of epoxide group in ENR also contributed to the increase in cure index. For TMQ and IPPD (both are amine-based antioxidants) systems, the antioxidant catalyzes the formation of active sulfurating agent and hence cure enhancement is observed. For a fixed amount of antioxidant loading, SMR L consistently exhibits higher cure index than ENR, a phenomenon which is associated with the role of the epoxide-activated double bond in the latter.

(2) The apparent activation energy of vulcanization also depends on the type and concentration of antioxidant used. It correlates well with the cure index (i.e., apparent activation energy increases with AO 2246 loading but decreases with TMQ and IPPD concentration for all the rubbers studied). This observation can also be explained by the retardation effect of AO 2246 and cure enhancement effect of TMQ and IPPD in the MBT-accelerated sulfur vulcanization. Both these effects becomes more significant as the antioxidant concentration is further increased. In all cases, SMR L gives higher apparent activation energy compared to the corresponding values in ENR.

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