

# Mooney Scorch Time and Cure Index of Epoxidized Natural Rubber in Presence of Sodium Carbonate

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**ABSTRACT:** The effect of sodium carbonate on the Mooney scorch time and cure index of epoxidized natural rubber (ENR 50) was studied with concentrations of 0–2 phr and 100–160°C temperatures. A conventional vulcanization system based on an ASTM formulation was used throughout the investigation on the gum and carbon black filled rubber compound. The results indicated that the scorch time and cure index for the gum and filled compounds increased to a maximum value at 0.15 phr of sodium carbonate, and further loading of sodium carbonate caused it to decrease. This observation was attributed to the neutralization of the residual acid in ENR 50 in the initial stage, thus reducing the formation of ether crosslinks via an acid-catalyzed ring-opening reaction with the epoxide group in ENR 50. However, as the sodium carbonate was increased beyond 0.15 phr, the excess sodium carbonate enhanced the vulcanization rate as shown by the drop of the scorch time and cure index. The peak maximum was more evident at lower temperature and its peak height decreased with increasing temperature, suggesting that the neutralization effect by sodium carbonate was overshadowed by the faster cure rate resulting from the availability of thermal energy to overcome the activation energy of vulcanization as the temperature was elevated. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1352–1355, 2001

**Key words:** scorch; cure; rubber; epoxide; sodium carbonate

## INTRODUCTION

We carried out several studies on the scorch and cure index of epoxidized natural rubbers (ENR) in an accelerated sulfur vulcanization system. These included the effects of epoxidation,<sup>1</sup> stearic acid,<sup>2</sup> and the accelerator/sulfur ratio<sup>3,4</sup> on the Mooney scorch time and cure index of ENR. The cure characteristics of unaccelerated sulfur vulcanization of ENR was also reported.<sup>5</sup> Basically, the scorch time and cure index of ENR have a significant dependence on the temperature of vulcani-

zation; degree of epoxidation of NR; and standard compounding ingredients such as stearic acid, carbon black, and accelerators. A systematic investigation was recently performed on the scorch and cure behavior of ENR in the presence of phenol- and amine-based antioxidants.<sup>6,7</sup> This study found that phenol-based antioxidants retard the vulcanization rate whereas the contrary was observed for the amine-based antioxidants. In view of the technological importance of scorch in rubber technology, we conducted further research in this field of interest by studying the concentration effect of sodium carbonate on the scorch and cure properties of ENR 50 because it is an effective base to improve the aging<sup>8</sup> and scorch problem<sup>9</sup> in rubber.

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## EXPERIMENTAL

An ENR having 50 mol % epoxidation (ENR 50) was used as the base elastomer. It was supplied by Guthrie Co. Its technical specifications were given in our previous article.<sup>1</sup> The accelerators used for the gum and filled compounds were 2-mercaptobenzothiazole and *N-tert-butyl-2-benzothiazyl sulfenamide* (TBBS), respectively. The sodium carbonate and other standard rubber chemicals were commercial grades and used without further purification. The standard test formulation based on ASTM D3184-89 was chosen and is shown in Table I. Mixing was carried out on a two-roll mill at  $70 \pm 5^\circ\text{C}$ , and the total times taken to complete one mixing cycle for the gum and carbon black filled compounds were 18 and 29 min, respectively. The sheeted rubber compound was then conditioned at  $23 \pm 2^\circ\text{C}$  for 24 h before testing on a Monsanto automatic Mooney Viscometer (MV 2000) in accordance with the procedure described by ASTM D1646-96a. The Mooney scorch time ( $t_5$ ) is defined as the time for an increase of 5 units above the minimum viscosity whereas the cure index ( $\Delta t_L$ ) is defined as the difference in time for an increase of 35 units above the minimum viscosity over  $t_5$  (i.e.,  $\Delta t_L = t_{35} - t_5$ ). The cure index defines the overall rate of cure.

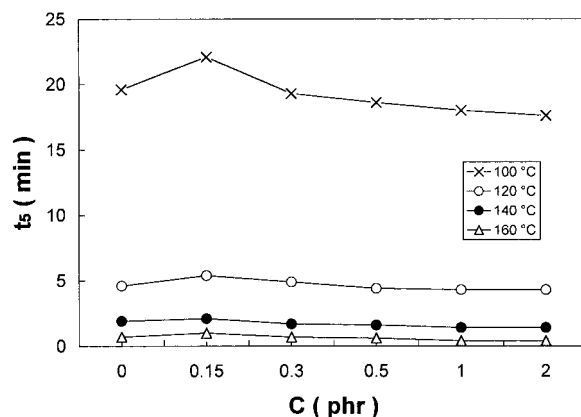
## RESULTS AND DISCUSSION

The dependence of the  $t_5$  of the ENR 50 gum compound on the concentration of sodium carbonate for various temperatures of vulcanization is

**Table I Formulation for Gum and Carbon Black Filled Compound**

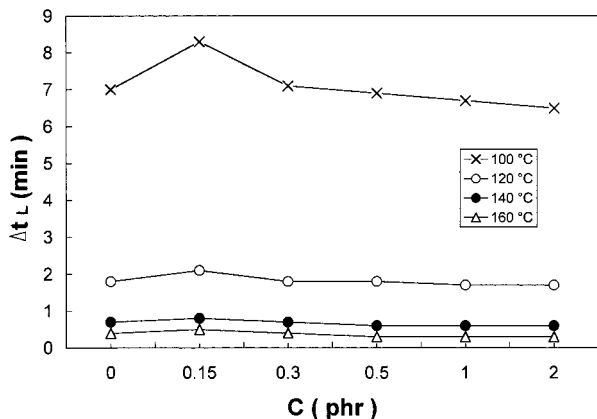
Ingredient	Gum Recipe (phr)	Filled Recipe (phr)
ENR 50	100	100
Zinc oxide	6.00	5.00
Sulfur	3.50	2.25
Stearic acid	0.50	2.00
MBT	0.50	—
HAF N330	—	35.00
TBBS	—	0.70
Sodium carbonate	Variable <sup>b</sup>	Variable <sup>b</sup>

phr, parts per hundred of rubber; variable, 0, 0.15, 0.3, 0.5, 1, or 2.



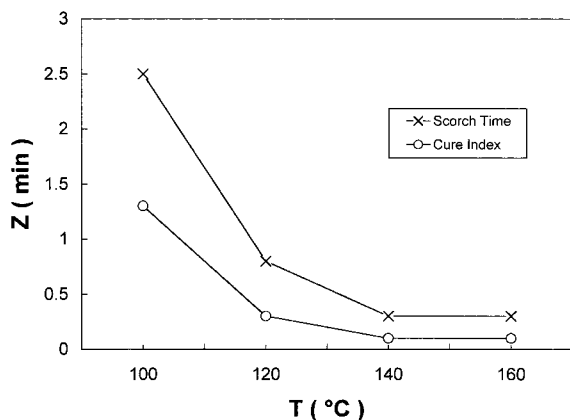
**Figure 1** The variation of the Mooney scorch time ( $t_5$ ) of gum ENR 50 with the sodium carbonate concentration (C) for various temperatures of vulcanization.

shown in Figure 1. For a temperature lower than  $120^\circ\text{C}$ , the  $t_5$  indicated a maximum value at 0.15 phr of sodium carbonate; after that it decreased with a further increase in sodium carbonate loading. Below 0.15 phr, sodium carbonate neutralized the residual acid that was trapped inside the ENR 50 during coagulation of the rubber, thus avoiding the formation of ether crosslinks via an acid-catalyzed ring-opening reaction of the epoxide group<sup>9,10</sup> in the ENR 50. This meant that the scorch time was increased to a maximum at 0.15 phr of sodium carbonate because ether crosslinks were not formed due to the absence of acids in the rubber. However, as the sodium carbonate concentration was further increased, the excess sodium carbonate acted as a base that enhanced the rate of vulcanization, thus lowering the scorch time as shown in Figure 1. Most probably, the mechanism of cure enhancement was similar to that reported for carboxylate ions.<sup>11</sup> In this case the occupation of vacant zinc orbitals by carbonate ions should weaken the Zn-S binding and hence increase the nucleophilicity of the mercaptide sulfur atoms in the complexes, thus facilitating the formation of the active sulfurating reagent that activates the formation of crosslinking in the rubber. However, as the temperature was increased, the maximum decrease indicated faster cure as a consequence of the availability of thermal energy to overcome the activation energy of vulcanization that was reported in our previous study.<sup>1</sup> In other words, the effect of neutralization by sodium carbonate in preventing the formation of initial ether crosslinks was overshadowed by the faster cure rate as the temperature of vulcanization was increased. In fact, for a temperature

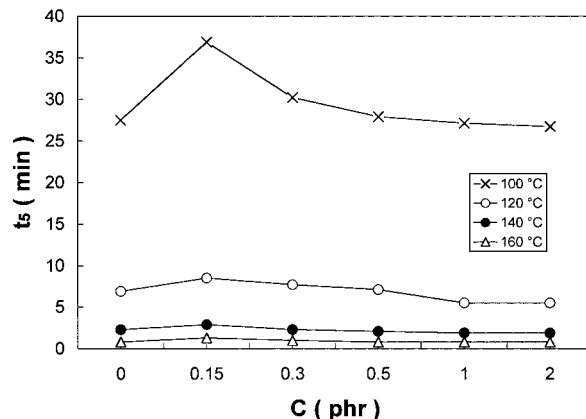


**Figure 2** The variation of the cure index ( $\Delta t_L$ ) of gum ENR 50 with the sodium carbonate concentration ( $C$ ) for various temperatures of vulcanization.

greater than 140°C, the  $t_5$  was essentially independent of the sodium carbonate concentration. Even though the sodium carbonate influence on the  $t_5$  was found to be negligible at higher temperatures of vulcanization, the incorporation of sodium carbonate into the ENR compound was still necessary to improve the tensile strength of ENR cured via a conventional sulfur vulcanization system.<sup>9</sup> Besides, sodium carbonate helps the normal functioning of prevulcanization inhibitors<sup>9</sup> if the latter is added to the rubber compound. The dependence of the  $\Delta t_L$  of ENR 50 on the concentration of sodium carbonate is shown in Figure 2. Again, at a lower temperature of vulcanization, a maximum was obtained at 0.15 phr of sodium carbonate, which was attributed to the neutralization of residual acid to prevent the for-

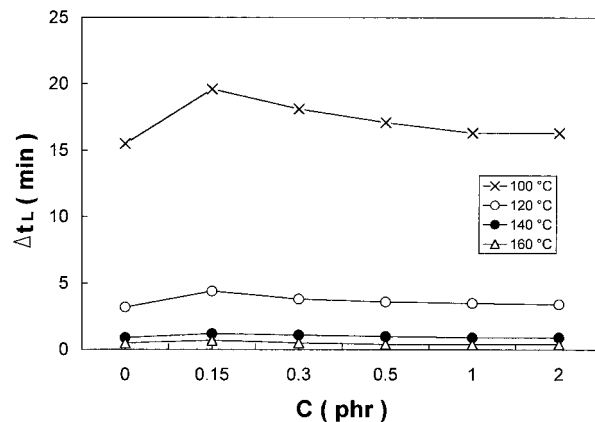


**Figure 3** The temperature dependence of the difference between the maximum and control values ( $Z$ ) of the scorch time and cure index for gum ENR 50.

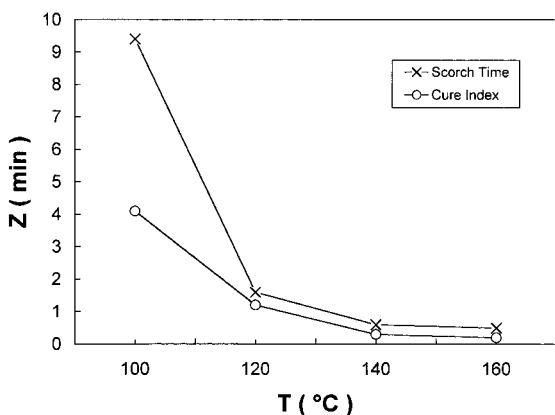


**Figure 4** The variation of the Mooney scorch time ( $t_5$ ) of carbon black filled ENR 50 with the sodium carbonate concentration ( $C$ ) for various temperatures of vulcanization.

mation of ether crosslinks in ENR 50 as explained earlier. In order to compare the peak height at 0.15 phr of sodium carbonate with respect to the control sample (without sodium carbonate) for various temperatures of vulcanization, the difference in the  $t_5$  or  $\Delta t_L$  between the maximum and control values was computed and denoted as  $Z$ , which is shown in Figure 3. From the plot it is obvious that for the scorch time and cure index the  $Z$  indicated the highest value at a low temperature and it dropped drastically with increasing temperature of vulcanization as more thermal energy was available to overcome the activation energy of vulcanization, thus eclipsing the effect of sodium carbonate on the  $t_5$  and  $\Delta t_L$  of ENR 50.



**Figure 5** The variation of the cure index ( $\Delta t_L$ ) of carbon black filled ENR 50 with the sodium carbonate concentration ( $C$ ) for various temperatures of vulcanization.



**Figure 6** The temperature dependence difference between the maximum and control values ( $Z$ ) of the scorch time and cure index for carbon black filled ENR 50.

Figure 3 also shows that the  $Z$  value was consistently higher for the  $t_5$  compared to that of the  $\Delta t_L$ . This observation may be ascribed to the greater effect of sodium carbonate in the initial stage of vulcanization where the scorch time was measured.

The corresponding results for the  $t_5$ ,  $\Delta t_L$ , and  $Z$  values for the carbon black filled ENR 50 are shown in Figures 4, 5, and 6, respectively. For a fixed loading of TBBS there were maximum values of  $t_5$  and  $\Delta t_L$  observed at 0.15 phr of sodium carbonate for the various temperatures studied. This observation was attributed to the initial neutralization of residual acid by the sodium carbonate, which prevented the formation of ether crosslinks that would shorten the  $t_5$  of the rubber compound. The maximum decreases with increasing temperature of vulcanization suggested the diminishing effect of sodium carbonate as the temperature was elevated, as indicated by the decreasing  $Z$  values in Figure 6.

## CONCLUSION

The scorch time and cure index for gum and carbon black filled ENR 50 increased with increasing

sodium carbonate loading up to 0.15 phr at temperatures lower than 120°C; both values decreased with further additions of sodium carbonate. This observation was attributed to the sodium carbonate neutralization of the residual acid in ENR 50, which prevented the initial ether crosslinking via acid-catalyzed ring opening of the epoxide group in ENR 50. However, beyond 0.15 phr of sodium carbonate the presence of the excess base enhanced the rate of vulcanization and lowered the scorch time and cure index of the rubber. At a higher temperature of vulcanization the neutralization effect of sodium carbonate was eclipsed by the faster cure rate resulting from the availability of thermal energy to overcome the activation energy of vulcanization.

## REFERENCES

- Poh, B. T.; Tan, B. K. *J Appl Polym Sci* 1991, 42, 1407.
- Poh, B. T.; Tang, W. L. *J Appl Polym Sci* 1995, 55, 537.
- Sadequl, A. M.; Ishiaku, U. S.; Ismail, H.; Poh, B. T. *Eur Polym J* 1998, 34, 51.
- Sadequl, A. M.; Ishiaku, U. S.; Poh, B. T. *Eur Polym J* 1999, 35, 711.
- Poh, B. T.; Chen, M. F.; Ding, B. S. *J Appl Polym Sci* 1996, 60, 1569.
- Poh, B. T.; Te, C. S. *J Appl Polym Sci* 1999, 74, 2940.
- Poh, B. T.; Te, C. S. *J Appl Polym Sci* 2000, 77, 3234.
- Amu, A.; Ismail, K. A. R. K.; Dulngali, S. Some Aspects on Processing and Ageing of Epoxidized Natural Rubber. In Preprint of the International Rubber Conference, Rubber Research Institute of Malaysia. Kuala Lumpur, Malaysia, 1985.
- Baker, C. S. L.; Gelling, I. R.; Newell, R. *Rubber Chem Technol* 1985, 58, 67.
- Baker, C. S. L.; Gelling, I. R. *Rubber World* 1985, 191(3), 15.
- Bateman, L., Ed. *The Chemistry and Physics of Rubber-Like Substances*; Applied Science: London, 1963; p 534.