

# Evaluation of Physical Properties and Curing Characteristics of Silica-Filled Ethylene–Propylene–Diene Terpolymer in the Presence of Chloroprene Rubber

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**ABSTRACT:** The effect of addition of chloroprene rubber (CR) on the dispersion of silica in EPDM (ethylene–propylene–diene terpolymer) was studied. It was observed that physical properties of the vulcanizates could be significantly increased at the EPDM : CR blend ratio of 92.5 : 7.5. SEM micrographs also indicated that incorporation of CR into

EPDM improves the network structure of the resulting vulcanizates. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 196–200, 2004

**Key words:** thiophosphoryl disulfide; polychloroprene rubber; dispersions; blends; silicas

## INTRODUCTION

Ethylene–propylene–diene terpolymer (EPDM) is widely used in wire and cable,<sup>1–3</sup> automotive radiator hose,<sup>4</sup> white sidewalls of tires,<sup>5,6</sup> and many other speciality applications because of its ability to accept high loading of fillers and excellent resistance to oxygen, ozone, and heat. Recently<sup>7</sup> more attention is being paid to mineral fillers like silica because of the high price of carbon black. Moreover, silica has the tendency to give less hysteresis loss than carbon black. Unfortunately, the compatibility of silica fillers with the polymer matrix is poor. It is difficult to obtain a good dispersion of silica in the polymer matrix because of the strong filler–filler interaction.<sup>8</sup> Silica has a number of hydroxyl groups,<sup>9</sup> which become responsible for the formation of strong hydrogen bonds with basic materials. The chlorine present in the polychloroprene rubber (CR) also forms hydrogen bonds with the hydroxyl group of silica. The use of silica as filler is further limited because of its adsorption of curatives. As a result there occurs reduction of both the scorch time and the crosslink density of silica-filled rubber vulcanizates. To overcome these difficulties a silane-coupling agent such as bis(3-triethoxysilylpropyl) tetra sulfide (TESPT)<sup>10–12</sup> is used to improve the filler dispersion and thus prevent adsorption of curatives on the silica surface. Recently<sup>13</sup> it has been reported that addition of a small amount of polychloro-

prene rubber into silica-filled natural rubber greatly improves the physical properties of the vulcanizates. Thus we became interested in studying the effect of CR on the dispersion of silica in EPDM vulcanizates. Moreover, it was our aim to determine the optimum concentration of CR for improving the oxidation resistance, oil resistance, and heat resistance properties<sup>14–17</sup> of silica-filled EPDM vulcanizates.

## EXPERIMENTAL

### Materials used

Polychloroprene rubber [Baypren 215; ML<sub>1+4</sub> (at 100°C), 50 ± 6; total ash content, max 1%; density, 1.23 gm/cm<sup>3</sup>; precrosslinked XD grade), used in the present investigation, was obtained from Bayer AG (Leverkusen, Germany). Ethylene–propylene–diene rubber (EPDM), Herlene 521, was from Herdillia Unimers Ltd., India. Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) was prepared in our laboratory and purified according to the procedure reported by Pimblott et al.<sup>18</sup> AR grade zinc oxide (E. Merck, Darmstrdt, Germany), magnesium oxide (E. Merck) extra-pure grade stearic acid (E. Merck), GR grade sulfur (E. Merck mp 118°C), and precipitated silica (Ultrasil VN 3, Degussa, Germany) were used in the present work.

### Preparation of vulcanizates

Requisite amounts of MgO were incorporated in previously masticated CR on a Berstorff Laboratory (Berstorff GmbH, Hannover, Germany) two-roll mixing mill (size: 203 × 102 mm) at first. Zinc oxide, stearic acid, and silica were added sequentially in masticated

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TABLE I  
Formulations of the mixes and the Cure Characteristics of Silica-Filled Vulcanizates at 160°C

Ingredient property	Mix						
	1	2	3	4	5	6	7
CR	00.0	2.5	5.0	7.5	10.0	12.5	15.0
EPDM	100	97.5	95.0	92.5	90.0	87.5	85.0
ZnO	5	5	5	5	5	5	5
MgO	0	0.1	0.2	0.3	0.4	0.5	0.6
Stearic acid	2	2	2	2	2	2	2
Silica	30	30	30	30	30	30	30
DIPDIS <sup>a</sup>	3.834	3.834	3.834	3.834	3.834	3.834	3.834
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Maximum rheometric torque, $R_{\alpha}$ (N/m)	4.0	4.5	4.85	5.45	4.8	5.2	5.4
Scorch time, $t_2$ (min)	2.75	3.00	3.50	4.00	5.00	4.50	5.00
Optimum cure time, $t_{90}$ (min)	9.0	14.0	14.0	16.0	16.5	17.5	18.0

<sup>a</sup> Weight corresponds to 9 mmol bis(diisopropyl)thiophosphoryl disulfide.

EPDM. Finally, CR, with added MgO was mixed into the EPDM compounds using a 15-min total compounding cycle. The mixing mill was cooled by cold water circulation during mixing.

### Bound rubber determination

For the bound rubber determination<sup>19</sup> the solvents used were toluene and *n*-hexane. All compounds were stored at room temperature for 1 week before extraction. A weighed amount of compound (~ 0.2 g) was cut into small pieces of approximately 1 mm<sup>3</sup> and placed into a stainless steel wire cage of known weight. The cage was then immersed in 25 mL of toluene for 7 days at room temperature and the solvent was renewed after 3 days. Finally, the sample was kept in *n*-hexane for another day. After extraction, the compound and the cage wire were dried for 1 day in air at room temperature and then for 24 h in an oven at 105°C. The percentage (%) bound rubber of the polymer  $R_B$  was then calculated according to the following equation<sup>19</sup>:

$$R_B = \frac{W_{fg} - W[m_f(m_f + m_p)]}{W[m_p/(m_f + m_p)]} \times 100 \quad (1)$$

where  $W_{fg}$  is the weight of gel containing filler after extraction,  $m_f$  is the weight of the filler in the compound,  $m_p$  is the weight of polymer in the compound, and  $W$  is the weight of the specimen.

### Measurement of physical properties

Physical properties like modulus at 200% elongation and tensile strength of the vulcanizates were measured after 24 h of maturation according to ASTM D412-92. The hardness was determined according to ASTM D2240-85 using a Shore A durometer. In the ageing experiment, the vulcanizates were aged for

72 h at  $100 \pm 1^\circ\text{C}$  in a forced-air circulated oven. The aged specimens were then kept for a further period of 24 h at room temperature before measuring modulus, tensile strength, elongation at break, and hardness.

### Scanning electron microscopy (SEM)

Fractured surfaces of specimens derived from tensile testing were used for this study. The test specimens, after being kept in a desiccator for 24 h, were gold coated. SEM micrographs of the specimens were then taken using a scanning electron microscope (Model S-415 A, Hitachi, Osaka, Japan).

## RESULTS AND DISCUSSION

The formulations of the various compounds used in the present investigations are presented in Table I. We used 2.5 to 15 phr CR in silica-filled EPDM compounds to ascertain the optimum dose of CR for effective dispersion of silica. Curing characteristics of the rubber compounds are shown in Table 1 and the

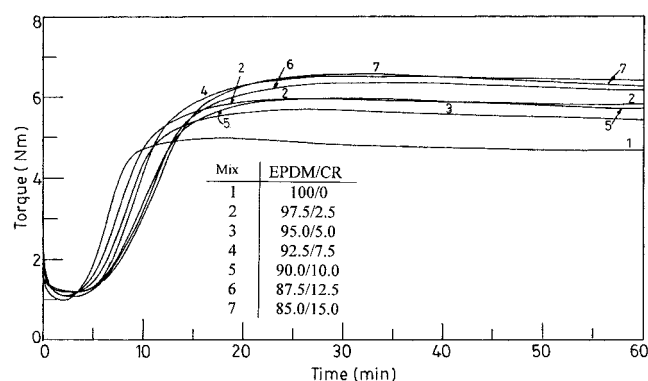
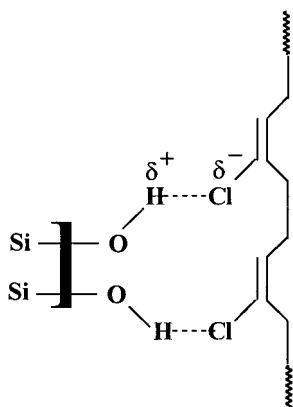


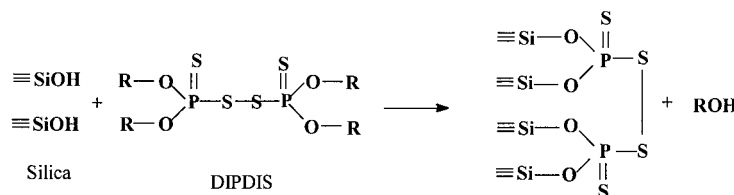
Figure 1 Rheographs of silica-filled vulcanizates cured at 160°C.



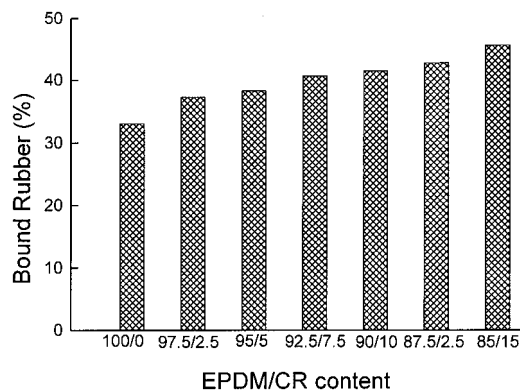
**Scheme 1** Interaction between chloroprene rubber and silica.

courses of vulcanization are depicted in Figure 1. It is evident from the results that, with the increase in the proportion of the CR content in a silica-filled EPDM rubber system, maximum rheometric torque increases initially and then decreases. The maximum value is obtained at 7.5 phr of CR content. This increase of torque is attributed to the formation of crosslinks and thus the difference in torque is very closely related to the crosslink density. The greater the difference in torques, the higher the crosslink density.<sup>20–22</sup> The differences in torques of the compounds containing CR on the whole are higher than those of compounds without CR, which indicates that the adsorption of curatives on the silica surface could be reduced by incorporation of CR (Scheme 1 and Scheme 2). Because EPDM is a nonpolar rubber and CR is a polar rubber, the compatibility of the latter with EPDM is poor. On the contrary CR is more compatible with silica. Thus the silica surface is likely to be more covered with CR in the compounds. Consequently, the amount of curatives adsorbed on the silica surface is reduced.

It is evident from the results (Table I, mixes 1–7) that the scorch time of the compounded rubber increases with the increase in CR content. This is also true for optimum cure time. This can be explained on the basis of the difference in the number of reactive sites on the rubbers. A sulfur crosslinking reaction occurs on allylic carbon. The allylic carbons on the EPDM and reactive CR repeat units number 3 and 2, respectively.



**Scheme 2** Interaction between silica and bis(diisopropyl)thiophosphoryl disulfide.



**Figure 2** Plot of amount of bound rubber against chloroprene rubber content.

Therefore, much more time is required to complete the crosslinking reaction as the CR content increases.

In the bound rubber experiment it was found that bound rubber increased significantly with the increase of CR content (Fig. 2), a result that implies that silica particles are preferentially adsorbed on CR than on EPDM. This may be ascribed to the fact that CR contains the electronegative chlorine atom that may form a hydrogen bond with the silanol group of silica, as shown in Scheme 1.

The physical properties of the vulcanizates for mixes 1–7 are recorded in Table II. It is seen that, like torque, the modulus at 200% elongation of the vulcanizates increases with the increase in CR concentration and attains a maximum value at 7.5 phr of CR in the EPDM mix, after which a decrease is observed. This is attributed to the fact that crosslink density of the rubber vulcanizate increases with the increase in CR content up to 7.5 phr of CR and therefore a greater load is required for 200% elongation. The tensile strength of the vulcanizates behaves similarly. It is evident from the results that the elongation at break value gradually diminishes, attaining a minimum value at 7.5 phr CR with the incorporation of CR into the EPDM matrix. The decrease in the value of elongation at break is mainly a consequence of higher crosslink density of the rubber vulcanizate with increase in the CR content. The hardness value increases very slowly. This can also be explained from results of the swelling experiment. It is evident from the swell-

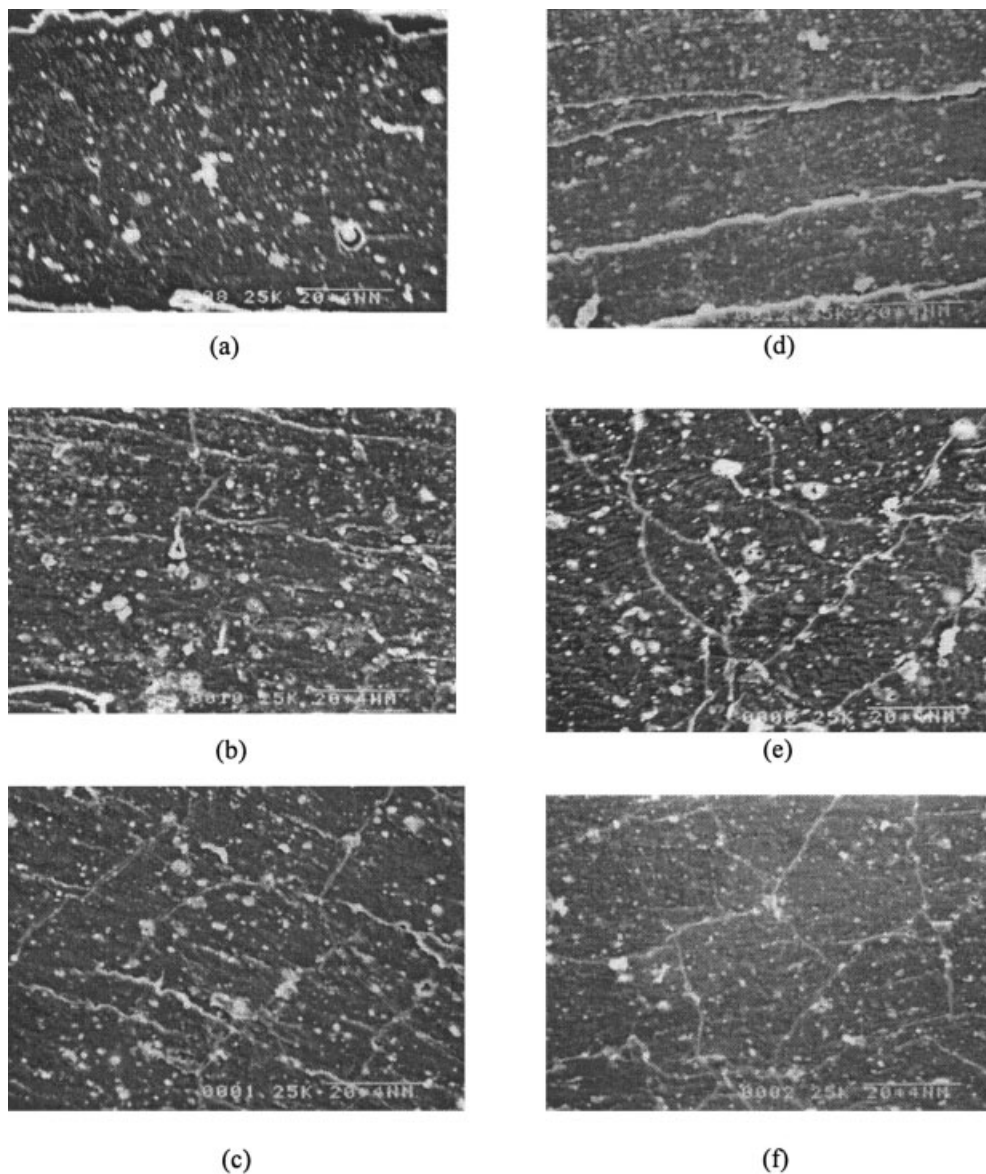
TABLE II  
Physical Properties of the One-Stage Silica-Filled Vulcanizates

	Mix <sup>a</sup>						
	1	2	3	4	5	6	7
200% Modulus (MPa)	0.80 (1.64) <sup>b</sup>	1.39 (1.72)	1.43 (1.91)	1.51 (1.95)	1.29 (2.08)	1.31 (2.41)	1.43 (2.61)
Tensile strength (MPa)	12.82 (11.50)	13.99 (12.11)	15.12 (10.17)	17.23 (12.02)	16.57 (11.25)	14.07 (10.34)	15.25 (9.35)
Elongation at break (%)	1150 (680)	820 (700)	860 (600)	800 (500)	820 (580)	790 (500)	710 (470)
Hardness (Shore A)	62 (65)	63 (65)	63 (67)	64 (67)	64 (67)	65 (68)	65 (68)
Crosslinking value (1/Q)	0.21 [6.70] <sup>c</sup>	0.25 [6.10]	0.35 [5.32]	0.42 [4.37]	0.38 [3.21]	0.40 [3.18]	0.45 [3.08]

<sup>a</sup> All samples were cured at 160°C.

<sup>b</sup> Values in parentheses are aged values.

<sup>c</sup> Values in square brackets are percentage of loss in weight during the swelling experiment.



**Figure 3** SEM micrographs of tensile fractured surfaces of the silica-filled vulcanizates cured at 160°C: (a) EPDM at  $\times 150$ ; (b) 97.5 : 2.5 EPDM : CR blend at  $\times 150$ ; (c) 95 : 5 EPDM : CR blend at  $\times 150$ ; (d) 92.5 : 7.5 EPDM : CR blend at  $\times 150$ ; (e) 87.5 : 12.5 EPDM : CR blend at  $\times 150$ ; (f) 85 : 15 EPDM : CR blend at  $\times 150$ .



ing data (Table II) that with the increase in CR content the swelling value ( $Q$ ) decreases [i.e. crosslinking value ( $1/Q$ ) increases with the increase in CR content]. It is also observed that percentage of weight loss during swelling experiments decreases as CR content increases.

The strength of the EPDM matrix under discussion is very much dependent on the dispersion of  $\text{SiO}_2$ . It was thought that scanning electron microscopy (SEM) studies would provide further evidence of this phenomenon. Micrographs of the tensile fractured surfaces for the various mixes are presented in Figure 3(a)–(f). It is evident from Figure 3(b)–(f) that network structures appear with the incorporation of CR. The vulcanizate without CR has a very poor dispersion of silica [Fig. 3(a)]. At 7.5 phr CR in EPDM, matrix ridgelines appear [Fig. 3(d)]. These lines cause reinforcement of the resulting vulcanizates. The micrographs corroborate the observed improvement in the physical properties, which in turn is caused by the facile distribution of silica in the rubber matrix.

The results of ageing experiments are shown in Table II. From the table it is evident that the 200% modulus increases for all the vulcanizates, whereas tensile strength declines dramatically. Percentage retention of tensile strength decreases with the increase in the CR content. This decrease in tensile strength is attributed to the presence of double bonds of CR, which are very much prone to oxidative degradation during prolonged ageing. On the other hand, the saturated backbone of EPDM resists oxidative degradation. Elongation at break values also decrease during ageing. The hardness values increase during ageing, as expected. From the swelling data (Table II) it is obvious that the crosslinking value ( $1/Q$ ) increases with the increase in CR content. As the crosslinking value increases, the rubber matrix becomes tough, and thus percentage retention of both 200% modulus and tensile strength decreases, although retention of 200% modulus is higher compared to that of the tensile strength.

## CONCLUSIONS

This investigation was mainly concerned with the dispersion of silica in EPDM in the presence of CR. The physical properties of the vulcanizates and the SEM

micrographs validate the beneficial effect of CR when incorporated at a somewhat low concentration. The reactions involved in the process of vulcanization however, are very complex, particularly when DIPDIS and CR are present in the reaction medium, given that silica reacts with both of them. This aspect will be dealt with in a future communication.

## References

1. Blodgett, R. B.; Fisher, T. G. *Trans AIEE Power Apparatus Syst* 1963, 82.
2. Mound, G. B.; Rybczynski, W. K. *Wire J* 1970, April, 51.
3. Canaud, C.; Sens, M. A.; Visconte, L. L. Y.; Nunes, R. C. R. *Kautsch Gummi Kunstst* 2001, 54, 56.
4. Daugherty, J. P.; Kehn, J. T. In: *Proceedings of the 94th Meeting of the Rubber Division, American Chemical Society, Atlantic City, NJ, Sept. 10–13, 1968; Paper no. 31.*
5. Herzlich, H. J.; Ostrander, W. M.; Thompson, L. C. In: *Proceedings of the 99th Meeting of the Rubber Division, American Chemical Society, Miami Beach, FL, April 27–30, 1971, Paper no. 16.*
6. Wingrove, D. E.; In: *Proceedings of the 122nd Meeting of the Rubber Division, American Chemical Society, Chicago, IL, Oct. 5–7, 1982.*
7. Hoffman, J. *Chem Market Rep* 2002, May 20.
8. Wagner, M. P. *Rubber Chem Technol* 1976, 49, 703.
9. Byers, J. T. *Rubber World* 1998, 38, 219.
10. Hashim, A. S.; Azahari, B.; Ikeda, Y.; Kohjiya, S. *Rubber Chem Technol* 1998, 71, 289.
11. Ranney, M. W.; Pagano, C. A. *Rubber Chem Technol* 1971, 44, 1080.
12. Vondracek, P.; Capka, M.; Schatz, M. *J Appl Polym Sci* 1979, 24, 1619.
13. Choi, S.-S. *J Appl Polym Sci* 2002, 83, 2609.
14. Johnson, P. R. *Rubber Chem Technol* 1976, 49, 650.
15. Bauchwitz, P. S. In: *Chloroprene; Standen, A., Ed.; Kirk-Othmer Encyclopedia of Chemical Technology; Interscience: New York, 1964; Vol. 5, p. 215.*
16. Hargreaves, A., II; Thompson, D. C. *Chlorobutadiene Polymer; Encyclopedia of Polymer Science and Technology; Wiley: New York, 1965; Vol. 3, p. 707.*
17. Murray, R. M.; Thompson, D. C. *The Neoprenes; Elastomer Chemical Department, E. I. du Pont de Nemours and Co.: Wilmington, DE, 1963.*
18. Pimblott, J. G.; Scott, G.; Stuckey, J. E. *J Appl Polym Sci* 1975, 19, 865.
19. Wolff, S.; Wang, M. J.; Tan, E. H. *Rubber Chem Technol* 1993, 66, 163.
20. Parks, C. R.; Brown, R. J. *Rubber Chem Technol* 1976, 49, 233.
21. Morrison, N. J.; Porter, M. *Rubber Chem Technol* 1984, 57, 63.
22. Mouri, H.; Tonosaki, Y. In: *Proceedings of the 152nd Meeting of the Rubber Division, American Chemical Society, Washington, DC, 1997; Paper no. 65.*