Thiophosphoryl Disulfides as Crosslinking Agents for Chloroprene Rubber

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ABSTRACT: The objective of this investigation was the determination of a suitable substitute for ethylene thiourea (ETU), a well-known vulcanizing agent for polychloroprene rubber (CR). Unfortunately, ETU is a potent carcinogenic compound, and so its replacement is needed. The efficacy of several thiophosphoryl disulfides as crosslinking agents for CR, either alone or in combination with other compounds, was examined. It was shown that bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) and bis(dicyclohexyl)thiophosphoryl disulfide (DCHDIS), being ecofriendly, could be replacements. Additionally, these thiophosphoryl compounds were shown to provide significant antioxidant protection. CR vulcanizates containing DIPDIS or DCHDIS exhibited higher tensile strengths than those containing ETU. Bis(3-ethoxysilylpropyl) tetrasulfide imparted to CR vulcanizates a notable modulus, which was comparable to that obtained with ETU-cured products. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1913–1919, 2004

Key words: rubber; crosslinking; ageing; mechanical properties

INTRODUCTION

Ethylene thiourea (ETU)[1] produces an efficient curing system for polychloroprene by the participation[2] of active tertiary allylic chlorine. Because ETU has been reported to be a potent carcinogen,[3] an alternative accelerator[4–6] or crosslinking agent is being sought. Earlier investigations have shown that thiophosphoryl sulfides can react with the silanol groups of silica,[7] the carboxylic groups of carboxylated nitrile rubber,[8] and the diene rubbers.[9] Polychloroprene rubber (CR) contains reactive chlorine at the tertiary allylic position. In an exploratory study, it was noted that CR reacted with bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) and was vulcanized during the process. Because DIPDIS, as shown in a previous report, is ecofriendly, our attention has been drawn to the use of this multifunctional rubber additive as a safe curative[10] for CR. In this exploratory study, an attempt has been made to understand the chemistry of the vulcanization of CR with thiophosphoryl disulfides.

EXPERIMENTAL

Materials

CR (precrosslinked xanlhogen disulfide (XD)-grade Bayprene 215; Mooney viscosity of rubber (ML) [1+4] at 100°C = 50 ± 6, maximum total ash content = 1%,

density = 1.23 g/cm^3) was obtained from Bayer (Germany). DIPDIS, bis(dicyclohexyl)thiophosphoryl disulfide (DCHDIS), and bis(di-*n*-butyl)thiophosphoryl disulfide (DNBDIS) were prepared and purified according to the procedure as reported by Pimblott et al.[11] for the preparation of DIPDIS. ETU (technical-grade) was purchased from a local market. Analytical-reagent-grade zinc oxide, magnesium oxide, extra-pure-grade stearic acid, sulfur (mp = 118°C), carbon black (N550; Phillips Carbon Black, Durgapur, India), and processing oil (Elasto-710, IOC, Faridabad, India) were used in this study.

Isolation of *n*-butyl chloride and cyclohexyl chloride from the reaction of CR with DNBDIS and DCHDIS, respectively

DNBDIS (5 g) was incorporated into 50 g of previously masticated CR in a two-roll mill. The compound thus obtained was placed in a 250-cc, round-bottom flask with a condenser and a receiver containing chloroform. Ice-cold water was circulated through the condenser, and the flask was then heated at 160–170°C in an oil bath. The distillate was collected in the receiver, which was covered with the freezing mixture. The reaction was carried out for 60 min, and the strongly acidic chloroform solution thus obtained was washed with water until it was neutral. The neutral chloroform solution was then dried with anhydrous Na$_2$SO$_4$, and the dried solution was subjected to GLC analysis with a Hewlett–Packard 3398A gas chromatograph. All GLC analyses were carried out at 35°C with an Hewlett–Packard Innowax (1-μm) column. The chro-

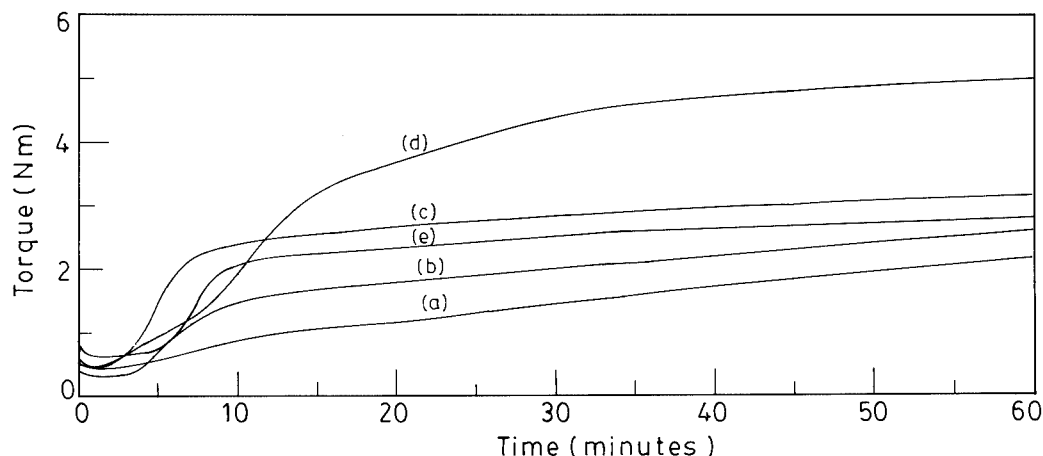*Correspondence to:* D. K. Basu (psudkb@mahendra.iacs.res.in).

Figure 1 Rheographs of CR containing (a) no additive; (b) only DIPDIS (9 mmol phr); (c) only ZnO (5 phr); (d) DIPDIS (9 mmol phr), ZnO (5 phr), MgO (4 phr), and stearic acid (2 phr); and (e) only TESPT (2 phr).

matogram clearly indicated the presence of n-butyl chloride in the distillate. Similarly, the presence of cyclohexyl chloride could be detected in the distillate with DCHDIS instead of DNBDIS.

Preparation of the vulcanizates

Requisite amounts of MgO, stearic acid, the filler, and the oil were incorporated sequentially into previously masticated rubber on a Berstorff laboratory two-roll mixing mill (203 mm × 102 mm) (Hanover, Germany) with a 15-min compounding cycle. Finally, the accelerator, sulfur, and ZnO were added to the mix. The stocks were cured under pressure at 160°C to the optimum cure [for the optimum cure time (t_{90})]. For the gum study, MgO, stearic acid, the accelerator, sulfur, and finally ZnO were added with a 10-min compounding cycle. The mixing mill was cooled by water circulation during compounding.

Measurement of the physical properties

Physical properties such as the modulus, tensile strength, and elongation at break of the vulcanizates were measured according to ASTM D 412-92 after 24 h of maturation of the same. The hardness was determined according to ASTM D 2240-85 with a shore A durometer. In the aging experiment, the vulcanizates were aged for 72 h at 100 ± 1°C in a forced-air-circulated oven. The aged specimens were then kept for 24 h more at room temperature before the modulus, tensile strength, elongation at break, and hardness were measured.

RESULTS AND DISCUSSION

The course of vulcanization of CR in the presence of a thiophosphoryl disulfide (i.e., DIPDIS) is depicted in Figure 1. Figure 1(a) traces the thermal vulcanization of raw CR, whereas Figure 1(b) traces the course of CR

vulcanization in the presence of DIPDIS. The influence of zinc oxide on the rate and extent of cure is shown in Figure 1(c). The cure behavior of CR in Figure 1(d) in the presence of different rubber additives clearly points out the vulcanization activity of DIPDIS. It appears that the active chlorine atoms of CR react with alkoxy groups present in DIPDIS and form crosslinks during the cure. A plausible mechanism for the reaction between CR and thiophosphoryl disulfide is presented in Scheme 1.

The liberation of alkyl chloride (RCl), as shown in Scheme 1, is established by the heating of CR with DCHDIS and by the subjection of the liberated reaction product (after necessary processing) to GLC analysis (see the Experimental section), which confirms the presence of cyclohexyl chloride (RCl), as proposed in Scheme 1.

It was earlier shown that thiophosphoryl disulfides obtained from methanol, ethanol, isopropyl alcohol, n-butyl alcohol, and cyclohexyl alcohol,[12] either alone or in combination with other accelerators, could be used as accelerators for carboxylated nitrile rubber vulcanization. However, very little is known about these rubber additives, which can be used as accelerators and curatives for CR vulcanization. Therefore, some studies were carried out with bis(dimethyl)thiophosphoryl disulfide (DMDIS), DIPDIS, DNBDIS, and DCHDIS to provide a clear understanding of the cure behavior of these compounds. In all these sulfurless vulcanizations, ZnO, MgO, and stearic acid were added. The rheographs are shown in Figure 2. Stockcontaining DNBDIS developed the lowest torque. The vulcanizing activity of DMDIS was better than that of DNBDIS. The activity of DIPDIS, in this respect, was noteworthy among the three, whereas the activity for DCHDIS was undoubtedly the best. The investigations carried out so far clearly point out the reaction of the alkoxy groups of thiophosphoryl sulfides with the active chlorine atoms of CR.

POLYCHLOROPRENE

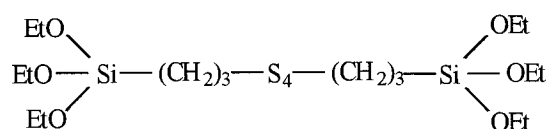THIOPHOSPHORYL
DISULFIDE

Scheme 1
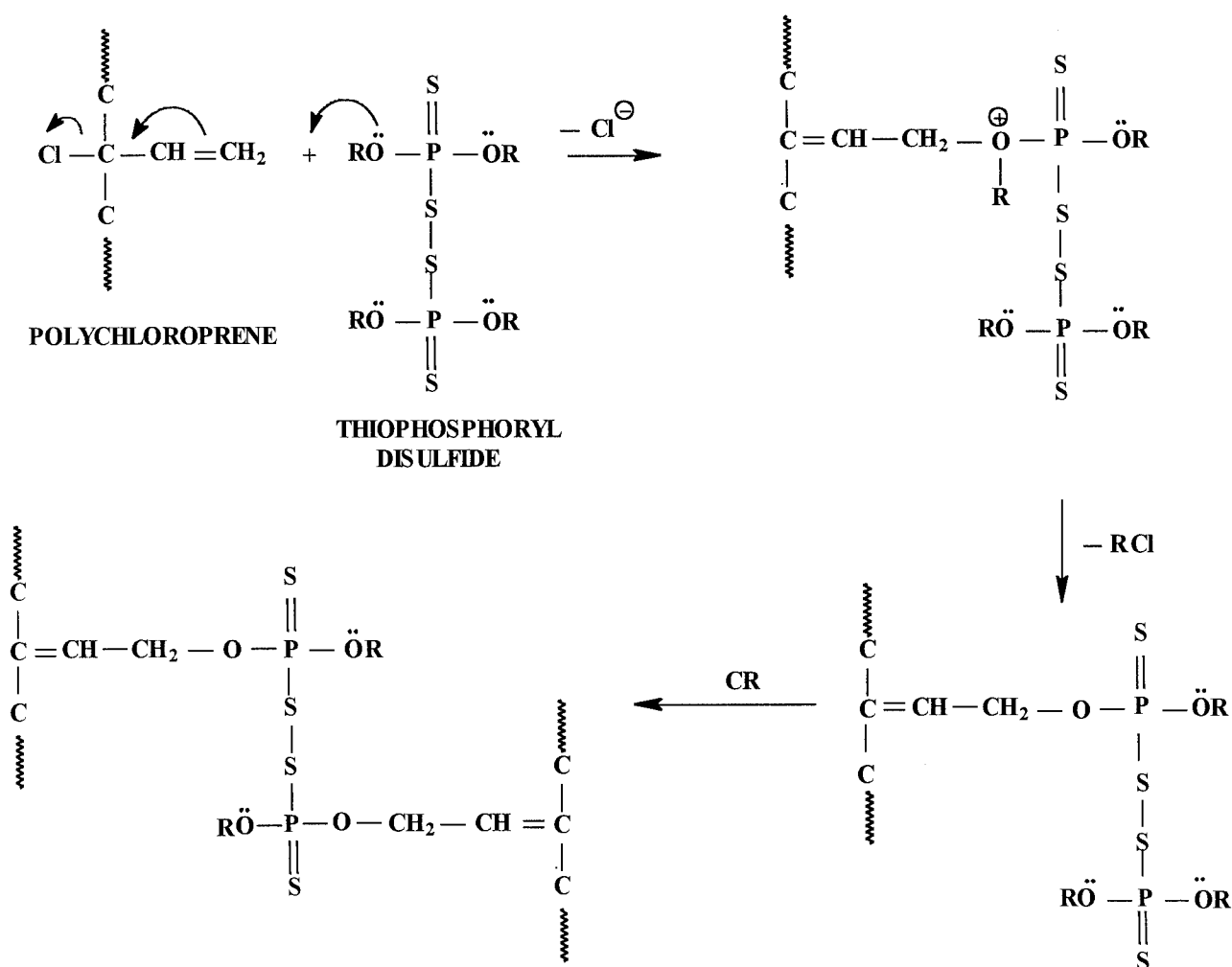
To justify this proposition, we incorporated another compound, bis(3-ethoxysilylpropyl) tetrasulfide (TESPT; also known as Si69), which had a structural similarity to the thiophosphoryl disulfides, into CR, as shown in mix 5 (Table I):
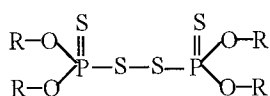
Thiophosphoryl disulfide

Bis-(3-triethoxysilylpropyl) tetrasulfide (TESPT)

Vulcanization occurred, and the curing activity of Si69 fell between those of DMDIS and DNBDIS. The compositions of the various rubber mixes used in this investigation are shown in Table I, which also includes the cure data of the corresponding mixes. It was difficult to obtain the exact t_{90} value because of the marching cure caused by the curatives. For the sake of convenience, t_{90} values were arbitrarily calculated on the basis of a 60-min cure time, and these are also recorded in Table I. It is evident from the results that

CR vulcanizates derived from both DIPDIS and DCHDIS accelerators produced close physical data.

Effect of the concentration of thiophosphoryl disulfide on the CR cure

Figure 3 shows that as the concentration of DCHDIS was increased from 6 to 9 mmol phr, both the rate of the reaction and the torque were markedly increased. However, beyond 9 mmol phr, an adverse effect was ob-
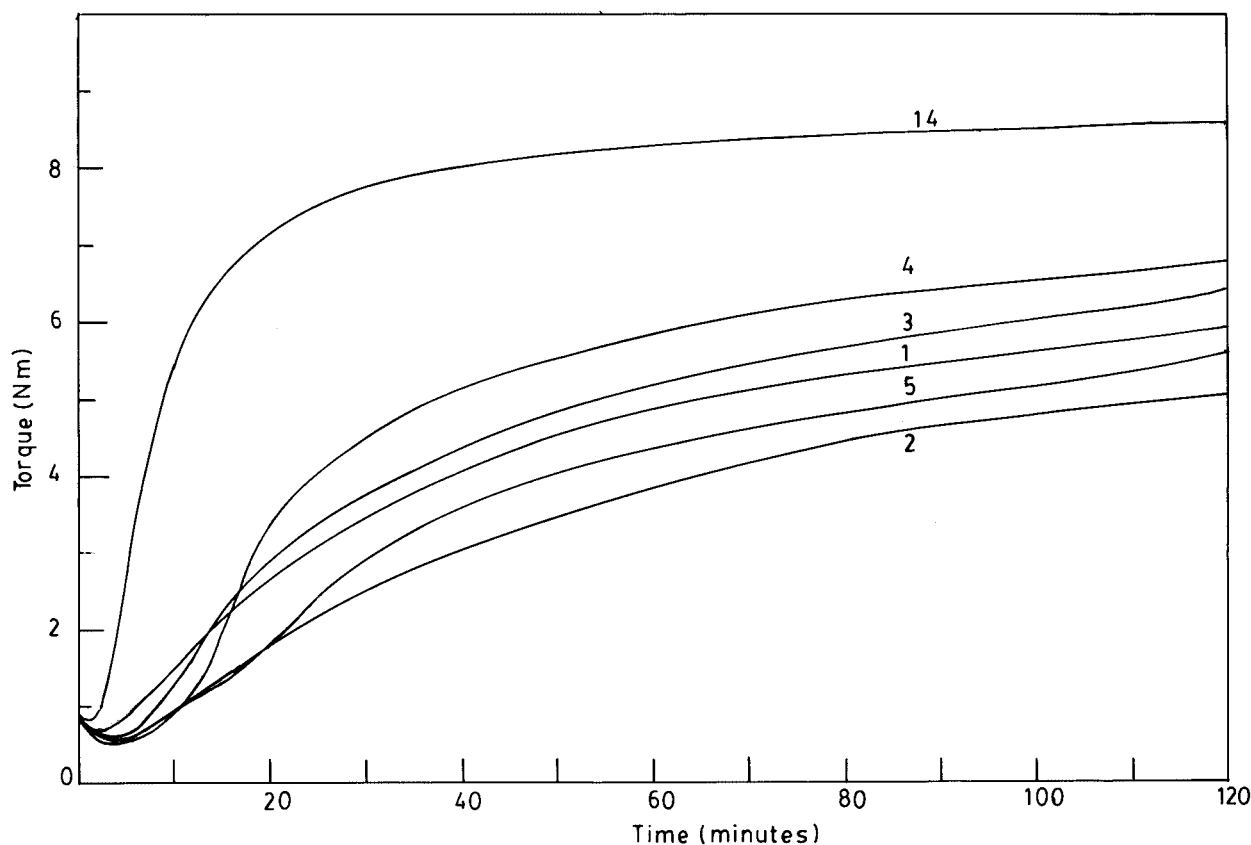
Figure 2 Rheographs of mixes 1–5 and 14 cured at 160°C.

served. This behavior was somewhat peculiar. The wavy nature of the cure curves for 12 and 15 mmol phr indicated two distinct types of vulcanization of CR in the presence of DCHDIS. It may be that in the presence of a large amount of DCHDIS, intramolecular linking, along with gains in intermolecular crosslinking, began. It is evident from the rheographs that the optimum concentration of DCHDIS for crosslinking CR was 9 mmol phr,

and this concentration of the thiophosphoryl disulfides was used in this investigation.

Effect of the temperature on CR crosslinking in the presence of DCHDIS

Figure 4 depicts the rheographs for the CR vulcanizations carried out at 150, 160, and 170°C. With an

TABLE I
Formulations and Cure Characteristics of CR Vulcanizates at 160°C

	Mix													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
MgO	4	4	4	4	4	4	4	4	3	2	1	—	4	4
DMDIS	3.402[a]	—	—	—	—	—	—	—	—	—	—	—	—	—
DNBDIS	—	4.320[a]	—	—	—	—	—	—	—	—	—	—	—	—
DIPDIS	—	—	3.834[a]	—	—	—	—	—	3.834[a]	3.834[a]	3.834[a]	3.834[a]	—	—
DCHDIS	—	—	—	5.274[a]	—	5.274[a]	—	5.274[a]	—	—	—	—	—	—
TESPT	—	—	—	—	2	—	2	2	—	—	—	—	—	—
S	—	—	—	—	—	0.5	0.5	0.5	—	—	—	—	—	—
ETU	—	—	—	—	—	—	—	—	—	—	—	—	—	0.92[a]
R_∞ (Nm)	5.2	4.5	5.45	5.75	4.8	6.6	5.8	7.1	5.65	5.7	5.85	5.8	33	7.8
t_2 (min)	1.50	2.25	2.5	2.75	3.0	3.5	3.0	3.5	2.25	1.75	1.5	1.5	2.5	1.0
t_{90} (min)	41	45	39	38	45	42	37.5	44	35	35	35	33	42	16

[a] The weight corresponds to 9 mmol of DMDIS, DNBDIS, DIPDIS, DCHDIS, or ETU. All the mixes contained 5 phr ZnO and 0.5 phr stearic acid.
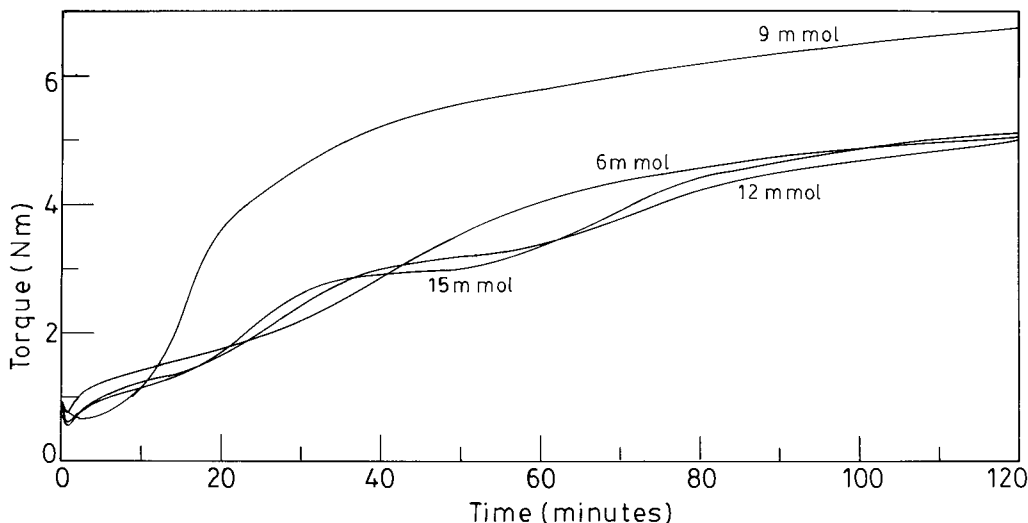
Figure 3 Rheographs of CR mixes containing different concentrations of DCHDIS cured at 160°C. The mixes contain 4 phr MgO, 0.5 phr stearic acid, and 5 phr ZnO.

increase in the temperature, the torque increased. The values for the extent of crosslinking [revealed via the maximum rheometric torque (R_∞)] obtained at 160 and 170°C were very close to one another. This was also true for the rate of reaction, as shown by the rheographs. On the basis of this curing behavior, 160°C was chosen as the optimum temperature for this study.

The requisite additives were incorporated into CR, as listed for mix 5 (Table I). It is evident from the rheographs presented in Figure 2 that thiophosphoryl disulfide and Si69 can bring about the cure of CR in a similar fashion, differing only in degree.

Effect of sulfur on the vulcanization of CR

It is evident from the cure data obtained with DCHDIS and sulfur that sulfur enhanced the ultimate torque

(mixes 4 and 6, Table I). This was also true for Si69-accelerated stock (mixes 5 and 7). As expected, ETU provided a very fast and flat cure in comparison with DCHDIS or Si69 even in the presence of sulfur (cf. curves 6 and 7 with curve 14, Fig. 2). Moreover, both DCHDIS and Si69 provided more scorch safety than ETU. To enhance the cure rate and ultimate torque, we formulated a mix that contained DCHDIS, sulfur, and Si69 (mix 8). This composition exhibited an R_∞ value that was very near to that obtained with ETU. However, t_{90} values in all these cases (mixes 6–8) were always much higher than the t_{90} value of the ETU-cured stock (mix 14).

Effect of MgO on the CR cure

The concentration of MgO was varied from 0 to 4 phr in the formulations (mixes 3, 9, 10, 11, and 12, Table I).
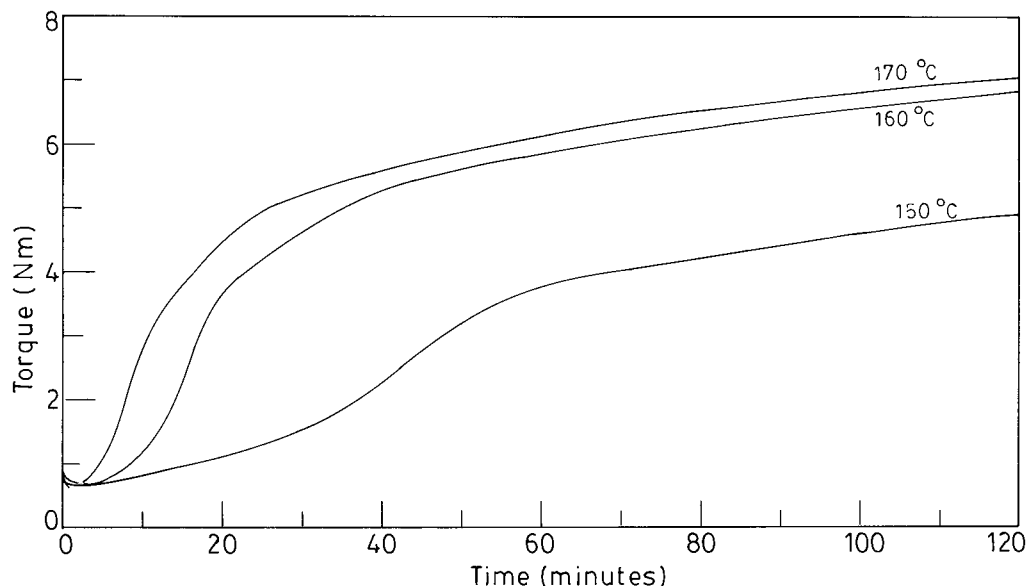

Figure 4 Rheographs of mix 4 at different temperatures.

TABLE II
Physical Properties of the CR Vulcanizates Cured at 160°C

	Mix													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
200% modulus (MPa)	0.82	0.78	0.86	1.13	0.95	1.21	1.09	1.58	0.85	0.89	0.89	0.83	0.47	1.61
	(1.10)	(1.09)	(1.52)	(1.77)	(1.41)	(2.04)	(1.92)	(1.84)	(1.25)	(1.16)	(1.23)	(1.24)	(1.06)	(1.67)
Tensile strength (MPa)	5.91	5.25	3.65	5.22	5.48	4.52	5.42	3.97	4.95	5.03	5.65	5.60	4.89	2.84
	(6.06)	(5.65)	(3.96)	(5.16)	(2.79)	(3.15)	(3.58)	(2.84)	(4.09)	(3.38)	(2.98)	(2.06)	(2.58)	(1.85)
Elongation at break (%)	700	692	593	530	543	514	600	445	570	590	595	600	756	355
	(612)	(595)	(460)	(480)	(480)	(365)	(390)	(280)	(490)	(505)	(420)	(240)	(525)	(205)
Hardness (shore A)	52	52	53	53	52	53	52	55	52	52	52	52	45	58
	(54)	(54)	(55)	(56)	(54)	(60)	(58)	(58)	(54)	(55)	(55)	(55)	(52)	(60)

The values in parentheses are aged values (aging was done at $100 \pm 1°C$ for 72 ± 1 h).

It can be seen in Table I that R_∞ gradually increased as the proportion of MgO decreased from 4 to 1 phr. However, the reverse was true for the scorch time (t_2) and t_{90}. The physical properties, with respect to the modulus, tensile strength, elongation at break, and hardness of CR vulcanizates, are recorded in Table III (shown later). Under the experimental conditions, MgO had very little influence on the modulus values of the vulcanizates. However, the tensile strength values of the vulcanizates indicated that with up to 3 phr MgO in the formulation, there was hardly any variation of the strength, but afterward, the fall was significant.

No such change in the elongation at break could be seen. In fact, more or less constant values for elongation were observed. This was also true for hardness values. Investigations[13,14] carried out on model compounds of CR revealed that compounds containing diene and triene structures were formed in the medium. The CR backbone might have contained these structures in the presence of MgO. This modification of the backbone of CR was prone to oxidative degradation. Consequently, we performed aging tests of the vulcanizates. The results are shown in Table II. The modulus of the vulcanizates containing up to 3 phr MgO remained almost constant during aging but increased significantly when 4 phr MgO was present in the formulation. The tensile strength values for the vulcanizates containing a small amount of MgO decreased sharply during aging. However, with the increase in the MgO concentration from 3 to 4 phr, the tensile strength of aged vulcanizates was retained to a great extent. During aging, however, these were smaller than the unaged samples. Like the modulus, the hardness of the vulcanizates increased to some extent. The results indicated that DIPDIS had a distinct influence on the vulcanization of CR, being a multifunctional rubber additive. Apart from taking a direct role as a crosslinker, it acted as the accelerator for sulfur vulcanization, compensating for some evil effects arising from oxidative degradation by the introduction of sulfur crosslinks in the modified CR

backbone (due to diene–triene transformation). Furthermore, it can act as an antioxidant,[15,16] obviously providing protection against the degenerative process.

Effect of carbon black on CR vulcanization brought about by DCHDIS and a silane coupling agent

In this preliminary investigation, the effectiveness of DCHDIS and a silane coupling agent (Si69) was studied for practical purposes. This study was concerned with carbon black (N550) only. The progressive addition of DCHDIS, sulfur, Si69, and ETU (NA-22) was performed so that we could understand their individual effects on the resulting CR vulcanizates. The compositions of the mixes are shown in Table III, which also contains the cure data. With the addition of S and TESPT, the rheometric torque was increased. The highest R_∞ value was, however, obtained with the stock (mix 14′) that contained only ETU. t_2 did not significantly vary for carbon black filled vulcanizates in comparison with DCHDIS-cured gum stock. Even the addition of sulfur did not change the t_2 value of the filled stock (cf. the t_2 values of mix 4′ and mix 6′ in

TABLE III
Formulation of CR Mixes and Their Cure Characteristics at 160°C

	Mix			
	4′	6′	8′	14′
DCHDIS	5.274[a]	5.274[a]	5.274[a]	—
TESPT	—	—	2	—
NA-22	—	—	—	0.92[a]
S	—	0.5	0.5	—
R_∞ (Nm)	6.5	8.6	9.8	11.4
t_2 (min)	2	2	4	1.00
Cure time (min)	42[b]	44[b]	46[b]	20[b]

All of the mixes contained 100 phr CR, 4 phr MgO, 5 phr ZnO, 0.5 phr stearic acid, 5 phr processing oil, and 30 phr carbon black (N550).
[a] Weight corresponds to 9 mmol of DCHDIS or NA-22.
[b] Values correspond to t_{90}.

TABLE IV
Physical Properties of the Carbon Black Filled CR Vulcanizates Cured at 160°C

Mix	100% modulus (MPa)	200% modulus (Mpa)	300% modulus (Mpa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (shore A)
4'	1.50 (2.23)	4.06 (5.49)	6.92 (10.55)	18.00 (15.84)	515 (415)	60 (67)
6'	1.93 (3.00)	7.41 (10.40)	14.39 (—)	17.02 (16.65)	370 (280)	65 (70)
8'	2.54 (4.01)	8.02 (11.93)	14.32 (—)	17.15 (16.07)	323 (215)	68 (70)
14'	2.42 (4.04)	9.12 (13.11)	— (—)	14.13 (10.11)	270 (200)	70 (73)

Values in parenthes are aged values (aging was done at $100 \pm 1°C$ for 72 ± 1 h).

Table III). Moreover, the data presented in Table III show that TESPT in the presence of sulfur offered some sort of scorch safety. The cure effected by ETU was so fast that the t_2 value remained the same in both gum and carbon black filled stocks. The t_{90} values for the filled stocks increased to some extent with respect to that observed in the corresponding gum stocks. The physical data for carbon black filled stocks (mixes 1–4) are provided in Table IV. The moduli of the vulcanizates are presented in three ways (i.e., 100, 200, and 300) to provide an idea of the polymer–filler interaction. DCHDIS played a vital role and provided protection for all the vulcanizates obtained from mixes 4', 6', and 8' against failure during the measurement of the 300% modulus. The vulcanizates from ETU-accelerated stock did not survive the test. Mandal and Basu[17] observed a similar enhancement of the modulus at 300% elongation for silica-filled natural rubber vulcanizates containing TESPT. This phenomenon was explained by the rubber–filler interaction.[1] In this study, DCHDIS reacted with CR and the various reactive groups present in carbon black. The enhancement of the modulus at 300% elongation[19,20] observed in this study thus could be explained. It was evident from the results that the presence of sulfur or TESPT greatly improved the modulus of the CR vulcanizates. It was evident that the tensile strength for the DCHDIS-accelerated vulcanizates from both gum and carbon black filled stocks slightly decreased. This observation was somewhat peculiar. For obvious reasons, the elongation at break fell because of the incorporation of carbon black. However, the hardness of the filled vulcanizates increased.

The accelerated aging test, as usual, indicated an increase in the modulus values for all the vulcanizates. Although the tensile strength of the ETU-accelerated vulcanizates deteriorated during aging, that for other samples (mixes 4', 6', and 8') containing thiophosphoryl sulfide remained more or less unaltered for reasons mentioned earlier. Like the modulus, the hardness of all the CR vulcanizates loaded with carbon black increased during aging.

CONCLUSIONS

The multifunctional activities of thiophosphoryl disulfide (an accelerator, crosslinking agent, and antioxidant) strongly suggest that thiophosphoryl disulfides, either alone or in combination with other rubber additives, can be used as safe accelerators and curatives for CR. However, the higher cure time, compared with that of ETU, is a deterrent to its practical application. Therefore, efforts are being made to solve this problem. The adverse effect of MgO (which is usually observed in aging tests of CR vulcanizates containing ETU) could be ameliorated through the use of these disulfides.

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