

# Natural Rubber–Ethylene-Propylene-Diene Rubber Covulcanization: Effect of Reinforcing Fillers

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**ABSTRACT:** Filled covulcanizates of elastomer blend comprising natural rubber (NR) and ethylene-propylene-diene rubber (EPDM) of commercial importance were successfully prepared by using a multifunctional rubber additive; namely, bis(diisopropyl)thiophosphoryl disulfide (DIPDIS). A Two-stage vulcanization technique further improved the physicochemical properties of the blend vulcanizates by restricting, through the formation of polar rubber bound intermediates, the migration of curative and filler from lower to highly unsaturated rubber. Scanning electron microscopy studies indicate homogeneity and coherency in the morphology of the two-stage vulcanizates. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1001–1010, 2002; DOI 10.1002/app.10361

**Key words:** filled vulcanizate; curative diffusion; natural rubber–ethylene-propylene-diene rubber blend, rubber-bound intermediate, bis(diisopropyl) thiophosphoryl disulfide

## INTRODUCTION

Co-curing of elastomeric blends comprising elastomers with different levels of unsaturation is a challenge to the scientists<sup>1–13</sup> and headache to the rubber compounders. It has been recently observed<sup>14</sup> in our laboratory that multifunctional additives, like bis(diisopropyl) thiophosphoryl disulfide (DIPDIS), can be successfully used as a coupling agent as well as accelerator to covulcanize highly unsaturated natural rubber (NR) and ethylene-propylene-diene rubber (EPDM) of low unsaturation content. In a NR–EPDM blend, the curatives usually migrate from EPDM to NR, thereby rendering the less polar EPDM phase drastically undercured.<sup>2, 15–20</sup> As a result, insufficient interfacial crosslinking occurs, which in turn results in poor static and dynamic mechan-

ical properties.<sup>1,14,21–24</sup> The main objective of the present investigation is to covulcanize NR–EPDM rubber blends containing reinforcing carbon black and silica so as to get blend vulcanizates with improved physicochemical properties for practical utility.

## EXPERIMENTAL

### Materials

NR (RMA IX) was purchased from local market. A.R grade zinc oxide (E. Merck), extra pure grade stearic acid (E. Merck), and G.R grade sulfur (E. Merck; mp, 118 °C) were used in the present work. EPDM (Herlene — 521; ENB content, 5% by wt., E/P ratio, 52/48; ML1+4 [100 °C] 45; total ash content, 0.15 %; specific gravity, 0.86 %) was obtained from Herdillia Unimers Ltd. (India). Carbon black (HAF, N-330) was obtained from Phillips Carbon Black Ltd. (Durgapur, W.B., India). Precipitated Silica (Ultrasil VN3) of De-

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gussa-AG (Germany) was used as obtained after heating at 105–106°C for 16 h. Analytical grade paraffin oil was used as process oil. DIPDIS was prepared and purified according to the procedure reported by Pimblott and co-workers.<sup>25</sup> Analytical grade isooctane (2,2,4-trimethyl pentane) and G.R grade toluene (E. Merck) were used.

### Preparation of Vulcanizates and Measurements of Physical Properties

#### *One-Stage Vulcanization of NR-EPDM Filled Blends*

NR and EPDM were first masticated separately and then mixed with each other. Requisite amounts of ZnO, stearic acid, carbon black (or silica), and process oil were added sequentially on a 203 × 102 mm Berstorff lab mill. The mix thus obtained was allowed to cool to room temperature, and the rolls were also allowed to cool. Finally, DIPDIS and sulfur were added to the mix on the cooled mill. The stocks were cured under pressure at 160°C.

#### *Two-Stage Vulcanization of NR-EPDM Filled Blends*

In this procedure, requisite amounts of NR and EPDM were first masticated separately. Then, specified amounts of ZnO, stearic acid, DIPDIS, and sulfur were incorporated in the EPDM. The time (*t*) for the commencement of cure for the mix was calculated from a rheograph run at 160°C in a Monsanto Rheometer (R-100). The compounded EPDM mix was then heated at 160°C in the hydraulic press for the predetermined time (*t*) to yield the grossly undercured mix. Carbon black and process oil (in the case of silica, no process oil was used) were first mixed with the EPDM mix and then the requisite amount of masticated NR was added to maintain the desired ratio. The vulcanizates were obtained under pressure at 160°C.

#### Measurement of Physical Properties

After maturing the vulcanizates for 24 h at ambient temperature, physical properties (e.g., modulus at 200% elongation and tensile strength) were measured according to ASTM D 412-92.

In the aging experiment, the vulcanizates were aged for 72 h at 100 ± 1 °C in a forced-air circulation oven. The aged specimens were then kept at room temperature for an additional 24 h before measuring modulus, tensile strength, elongation at break, etc.

In the crosslink-density measurement experiment, a weighed rubber sample was immersed in isooctane/toluene medium (70:30) for 48 h at ambient temperature (30 ± 2 °C). The rubber was removed, blotted as rapidly as possible with blotting paper, and weighed in a tared weighing bottle. After removal of the solvent under vacuum, the weight of the imbibed solvent was obtained. The swelling value *Q*, defined as the grams of solvent per gram of rubber hydrocarbon, is readily calculated with the following expression:<sup>26</sup>

$$Q = \frac{\text{Swollen wt} - \text{Dried wt}}{(\text{Original wt} \times 100)/(\text{formula wt})}$$

where formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of rubber. A comparison of the crosslinking values (1/*Q*) was also made from the reciprocal of swelling values.

#### Scanning Electron Microscopy (SEM) Studies

SEM analysis was carried out on the tensile fractured surfaces of the specimens, which were gold coated after being kept in a desiccator for 24 h. SEM photographs of the specimens were then taken with a Hitachi scanning electron microscope (model S-415A).

## RESULTS AND DISCUSSION

#### One-Stage Vulcanization of Carbon Black Filled Compounds

The compositions of mixes 1–5 are given in Table I, and the courses of vulcanization for the different recipes are depicted in Figure 1. Typical S-shaped cure curves are seen in all the cases.

Physical data for the vulcanizates of carbon black filled mixes 1–5 are shown in Table II. It can be seen from Table II (mixes 3 – 5) that modulus, tensile strength, and elongation at break lie well below the additive line joining that of the respective properties of the pure elastomeric compounds (mixes 1 and 2). The blends rich in NR content exhibit comparatively better results, which can be well explained by inefficient co-cure, due to curative migration and filler transfer,<sup>27</sup> as well the lower unsaturation (thus less polar) of EPDM compared with the high unsaturation (thus more polar) of NR. Generally unsat-

**Table I** Formulation and Cure Characteristics of Mixes of One-Stage Vulcanizates Measured at 160°C with a Monsanto Rheometer (R-100)

Formulation/Cure Characteristic	Mix									
	1	2	3	4	5	6	7	8	9	10
NR	100	—	75	50	25	100	—	75	50	25
EPDM	—	100	25	50	75	—	100	25	50	75
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
HAF (N 330)	40	40	40	40	40	—	—	—	—	—
Silica (Pptd.)	—	—	—	—	—	30	30	30	30	30
Process oil	5	5	5	5	5	—	—	—	—	—
DIPDIS	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Maximum rheometric torque, $R_{\infty}$ (Nm)	4.75	4.55	4.70	3.60	2.20	4.95	3.70	4.15	2.75	1.05
Scorch time, $t_2$ (min)	4.00	7.50	4.00	4.75	5.00	3.25	3.50	3.00	3.00	3.00
Cure time (min)	10.00 <sup>b</sup>	30.00 <sup>b</sup>	13.00	15.00	20.00	6.75 <sup>b</sup>	10.50 <sup>b</sup>	6.00 <sup>b</sup>	6.50 <sup>b</sup>	6.50 <sup>b</sup>

<sup>a</sup> Weight corresponds to 9 m mol DIPDIS.

<sup>b</sup> Values corresponds to the optimum cure time ( $t_{90}$ ).

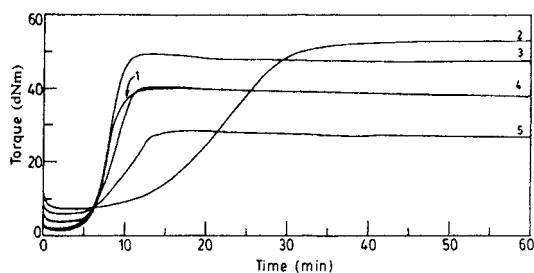
uration of the NR polymer is the driving force governing the carbon black distribution.<sup>28</sup> All these factors lead to further weakening of the already weakly reinforced EPDM phase by the dearth of polar curatives. Evidently, vulcanizates with poor physicochemical properties are being produced.

The age-resistance behavior is expected to improve as the proportion of EPDM in the blends is increased. This phenomenon can be easily visualized from the retention of tensile strength and elongation at break values after aging. The crosslinking value ( $1/Q$ ) gives the relative measurement of the crosslinking density of the polymer matrix. In mix 3, this value is surprisingly high in view of the fact that all the blend compounds (mixes 3–5) were cured for longer period than their respective optimum cure time ( $t_{90}$ ) to

facilitate mold opening and to get more predictable vulcanizates. These blend compositions, when cured up to their respective  $t_{90}$ , remained partially undercured, and the measurement of the physical properties became erroneous because of high surface imperfections and irregularities. In the case of mixes 4 and 5, severe weight losses were observed (results are shown in brackets, Table II) in the swelling experiment, rendering the experiment unsuitable for these compounds. This result indicates that a significant proportion of rubber matrix remains unvulcanized due to the curative migration in the one-stage vulcanizates rich in EPDM content.

### Two-Stage Vulcanization of Carbon Black-Filled Compounds

The distribution of filler particles in elastomer blends is undoubtedly determined by a combination of complex factors, including mixing procedure, relative polymer viscosities, unsaturation, polarity, and the ability of an elastomer to wet and form strong attachments to the filler. In two-stage vulcanization, it could be reasonably expected that accelerator fragments get anchored onto the EPDM backbone (Scheme 1),<sup>14</sup> thereby rendering the EPDM more polar because of the pendant moieties of DIPDIS. However, with the



**Figure 1** Rheographs of mixes 1–5 cured at 160 °C.

**Table II** Physical Properties of the One-Stage Vulcanizates Cured at 160°C<sup>a</sup>

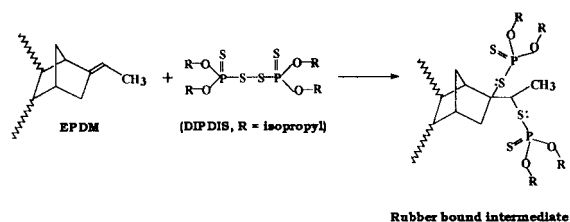
Physical Property	Mix									
	1	2	3	4	5	6	7	8	9	10
200%										
Modulus (MPa)	3.397 (4.233)	3.948 (6.224)	4.121 (4.118)	3.441 (—)	— (—)	1.407 (1.958)	0.824 (1.431)	1.564 (1.823)	0.983 (—)	— (—)
Tensile strength (MPa)	17.40 (9.08)	18.13 (15.08)	11.03 (5.58)	4.54 (3.34)	1.24 (1.337)	17.71 (7.14)	12.91 (13.08)	8.84 (2.76)	2.25 (0.81)	0.50 (—)
Elongation at break (%)	476 (310)	530 (400)	375 (245)	245 (155)	130 (120)	670 (480)	1020 (730)	595 (285)	425 (145)	108 (—)
Hardness (Shore A)	56 (60)	66 (69)	60 (63)	62 (65)	65 (67)	57 (59)	60 (64)	60 (62)	61 (63)	56 (—)
Crosslinking value (1/Q)	0.380 [6.61]	0.396 [9.35]	0.404 [6.75]	— [30.79]	— [44.57]	0.342 [2.42]	0.208 [6.70]	0.392 [13.82]	— [32.14]	— [47.25]

<sup>a</sup> Values in ( ) are aged values (aging done at 100 ± 1°C for 72 ± 1 h); values in [ ] are % loss in weight during the swelling experiment.

incorporation of carbon black into that modified EPDM matrix (to form EPDM–black masterbatch), the filler transfer to the favored NR phase would be restricted. Careful control of mixing of rubber additives and subsequent vulcanization is thus apt to generate better co-cured and coherent blends with much improved physicochemical properties. In reality, these better blends could be achieved. The composition and preparation of the blends in two-stage vulcanization, where the EPDM/DIPDIS ratio in mixes 3', 4', and 5' was progressively increased, are shown in Table III. At first, the filler incorporation time was adjusted for three different sequencings of mixing to produce blends of similar composition (mixes 4', 4'a, and 4'b; Table IV). The results indicate that the modified-EPDM recipe (mix 4') provides vulcanizates that exhibit the best physical properties. Hence, this sequence of mixing of rubber additives was maintained throughout the experiment (see Experimental). The cure curves of the mixes are shown in Figure 2. In all the cases, the  $R_{\infty}$  values are much higher than that of correspond-

ing one-stage values (mixes 3, 4, and 5; Table I). It is evident that both  $t_2$  and  $t_{90}$  are reduced significantly.

The physical properties of the vulcanizates obtained from mixes 3', 4', and 5' during two-stage vulcanization are recorded in Table V. The samples were cured up to their respective  $t_{90}$ . In all the cases, significant improvement in tensile strength and elongation at break are observed compared with one-stage vulcanization; however, modulus and crosslinking values show an opposite trend because of the longer cure time used for the one-stage samples. Evidently, this procedure produced higher crosslink density within the individual components of the elastomeric phases, thereby resulting in higher modulus values for the one-stage vulcanizates. But, because of the absence of interfacial crosslinking between the elastomers forming the blend, tensile strength and elongation at break values decrease in one-stage blend vulcanizates. It seems that hardness values for the vulcanizates remain almost unaltered with respect to the one-stage vulcanizates. The blend vulcanizates from mix 3' exhibit highest modulus, tensile strength, elongation at break, and 1/Q values. Moreover, the tensile strength and elongation at break values transcend that of the component elastomers by a significant amount. It is also evident that the vulcanizates exhibit least weight loss in the swelling experiment. All these results can be explained in light of the curative fixation on the EPDM backbone. This fixation, in fact, lowers filler transfer

**Scheme 1** Reaction of DIPDIS with EPDM.

**Table III Formulation of Mixes and their Cure Characteristics of Two-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R100)**

Stage/Cure Characteristic	Formulation	Mix					
		3'	4'	5'	8'	9'	10'
First stage	EPDM	25	50	75	25	50	75
	ZnO	5	5	5	5	5	5
	Stearic acid	2	2	2	2	2	2
	DIPDIS	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>	3.834 <sup>a</sup>
	S	0.5	0.5	0.5	0.5	0.5	0.5
Second stage (after preheating <sup>b</sup> compounded EPDM at first stage)	HAF	40	40	40	—	—	—
	Silica	—	—	—	30	30	30
	P. Oil	5	5	5	—	—	—
	NR	75	50	25	75	50	25
Maximum rheometric Torque, $R_{\infty}$ (Nm)		5.85	5.20	3.45	5.35	4.75	3.20
Scorch time, $t_2$ (min)		2.25	2.50	2.00	1.75	2.00	1.25
Optimum cure time, $t_{90}$ (min)		6.50	7.75	8.25	4.50	5.00	4.75

<sup>a</sup> Weight corresponds to 9 m mol DIPDIS.

<sup>b</sup> Preheating times ( $t$ ) for all the mixes at 160°C are 10 min.

from EPDM to NR. Other blends (mixes 4' and 5') also showed enhancement in properties with respect to their one-stage values. The age-resistance properties of the blend vulcanizates are also improved significantly with the increase in EPDM content in the blend. Remarkable improvement in physical properties is observed in the case of the vulcanizates of mix 5'. In the one-stage process, these vulcanizates dissolved significantly during the swelling experiment. In the case of the 1:1 blend (mix 4'), the tensile strength value crossed the much-desired barrier of 10 MPa, which is considered to be the threshold value of industrial applications. Thus, a well co-

cured, coherent, and industrially viable carbon black-filled blend system could be achieved from the two rubbers. This system differs greatly from unsaturation levels and thus overcomes the adverse effects of curative and filler migration.

#### One-Stage Vulcanization of Silica Filled Compounds

Silica is not generally used for the reinforcement of EPDM-based compounds because it adsorbs the organic (polar) curatives and thus retards cure. EPDM itself is slow curing because of its low level of unsaturation. We incorporated silica in the

**Table IV Cure Characteristics and Physical Properties of Two-Stage 50 : 50 (NR-EPDM) Black-Filled Vulcanizates with Different Mixing Sequence and Cured at 160°C**

Mix <sup>a</sup>	Maximum Rheometric Torque, $R_{\infty}$ (Nm)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
4'	5.20	3.001	12.70	530
4'a	4.30	1.950	6.99	540
4'b	5.05	2.632	10.30	450

<sup>a</sup> 4; Compounded mass containing EPDM, ZnO, stearic acid, DIPDIS, and S is preheated and then HAF and P.oil are incorporated to get carbon black masterbatch into which masticated NR is finally added.

4a; Compounded mass containing EPDM, ZnO, stearic acid, HAF, P.oil, DIPDIS, and S preheated to get EPDM-carbon black masterbatch into which is incorporated masticated NR.

4b; Compounded mass containing EPDM, ZnO, stearic acid, DIPDIS, and S is first preheated followed by incorporation of masticated NR. The blend thus obtained is loaded with HAF and P.oil.

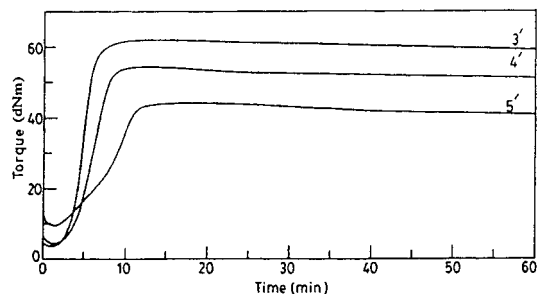


Figure 2 Rheographs of mixes 3'–5' cured at 160 °C.

NR–EPDM blend to make it more suitable for other nonblack applications. Recipes of several silica-filled compounds and their respective cure characteristics are presented in Table I (mixes 6–10). Typical S-shaped curves (Figure 3) are obtained in all the cases. It is interesting to note that faster cure rate is observed with silica than with gum<sup>14</sup> and black-filled vulcanizates of similar composition (Figure 1). This difference might be explained by the reaction between the fragments of DIPDIS and the silanol (Si-OH) groups present at the silica surfaces. The isopropyl moiety (-OR) in DIPDIS reacts with the silanol group of silica through the elimination of isopropyl alcohol (Scheme 2),<sup>29</sup> facilitating the rubber-filler interaction and thus resulting in faster curing.

Physical data of the mixes 6–10 are shown in Table II. The vulcanizates obtained solely from EPDM (mix 7) show lower modulus, tensile strength, and  $1/Q$  but higher elongation at break value than their counterparts containing HAF (mix 2). This behavior is also manifested in the blend compositions (mixes 8–10). EPDM elastomers in general have very high capacity for fillers and oil extenders; this has been attributed to the chain entanglement of the long, supple molecules of EPDM that readily occlude or “en-

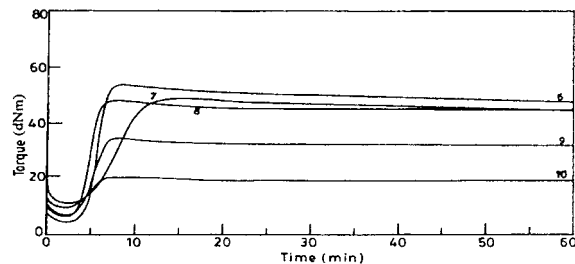


Figure 3 Rheographs of mixes 6–10 cured at 160 °C.

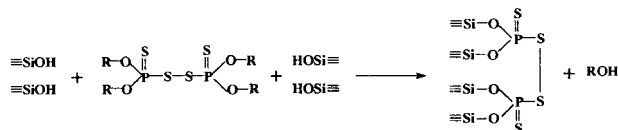
trap” large volumes of oil and filler.<sup>30</sup> Obviously, the phenomenon demands higher loading than the one employed in the present study. High elongation at break value is the characteristic of silica-loaded compounds. It can be seen from the data presented in Table II that EPDM-rich blend vulcanizates exhibit poor properties. All the blend compositions like HAF-loaded ones also suffer from significant weight loss in the swelling experiment. It is evident that inefficient interfacial crosslinking between NR and EPDM occurs in the case of silica-filled systems subjected to one-stage vulcanization, where both curative and filler migration from EPDM to NR phase occurs during vulcanization. Distribution of silica in the NR matrix is facilitated by the interaction of the protein component of NR with the hydroxylated surface of the precipitated silica.<sup>31</sup> As the mixing progresses, the viscosity of the NR phase is reduced gradually. Thus, highly polar silica opts for its migration from high viscosity EPDM to low viscosity NR phase. The situation is worst in the case of mix 10, which cannot be cured properly even by increasing the cure-time.

Age-resistance behavior of the blend vulcanizates is not good, as expected from the viscosity and cure-rate mismatch of the elastomers. All the blend mixes were cured up to their respective  $t_{90}$

Table V Physical Properties of Two-Stage Vulcanizates Cured at 160 °C<sup>a</sup>

Mix	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslinking Value ( $1/Q$ )
3'	3.557 (4.386)	21.61 (12.49)	555 (375)	60 (62)	0.387 [6.26]
4'	3.001 (4.231)	12.70 (9.18)	530 (350)	61 (65)	0.348 [8.11]
5'	2.425 (3.505)	9.02 (8.95)	595 (435)	63 (67)	0.274 [10.06]
8'	1.711 (1.924)	18.04 (8.15)	690 (575)	60 (61)	0.362 [2.44]
9'	1.297 (1.863)	11.52 (8.83)	724 (592)	61 (64)	0.255 [4.65]
10'	1.002 (1.586)	7.85 (5.93)	825 (730)	62 (65)	0.170 [6.12]

<sup>a</sup> Values in ( ) are aged values (aging done at  $100 \pm 1^\circ\text{C}$  for  $72 \pm 1$  h); values in [ ] are % loss in weight during the swelling experiment.



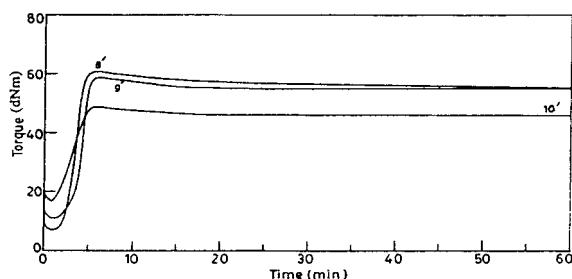
**Scheme 2** Reaction of Silica with DIPDIS.

because of the early reversion shown in the cure study (Figure 3). The blend vulcanizates from mixes 9 and 10 thus suffered from insufficient cure.

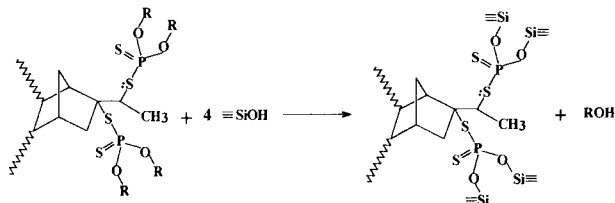
### Two-Stage Vulcanization of Silica Filled Compounds

The EPDM-silica masterbatch technique is also employed here to inhibit the filler transfer from the EPDM to the NR phase. The recipes and cure characteristics of the two-stage vulcanizates (mixes 8', 9' and 10') are shown in Table III. At first, the EPDM is modified with DIPDIS and then silica is incorporated into it to form the EPDM-SiO<sub>2</sub> masterbatch. In all the blends, both  $t_2$  and  $t_{90}$  values diminished further with respect to their one-stage values (Figure 4). This result indicates that much of the reactive pendant DIPDIS fragment-silica complex formed initially (Scheme 3) boosts up the vulcanization reaction. Because the early reversion (like one-stage system) still persists, it is inferred that a thermally stable network is not formed in the rubber matrix with silica particles. The increase in  $R_\infty$  values is indicative of higher crosslinking density compared with the one-stage values.

Physical data for the vulcanizates obtained from mixes 8', 9', and 10' (Table V) show much improved modulus, tensile strength, and elongation at break compared with one-stage values (mixes 8, 9, and 10; Table II). The values for the percent weight losses are much less than the corresponding values at one-stage (Table II). The



**Figure 4** Rheographs of mixes 8'-10' cured at 160°C.



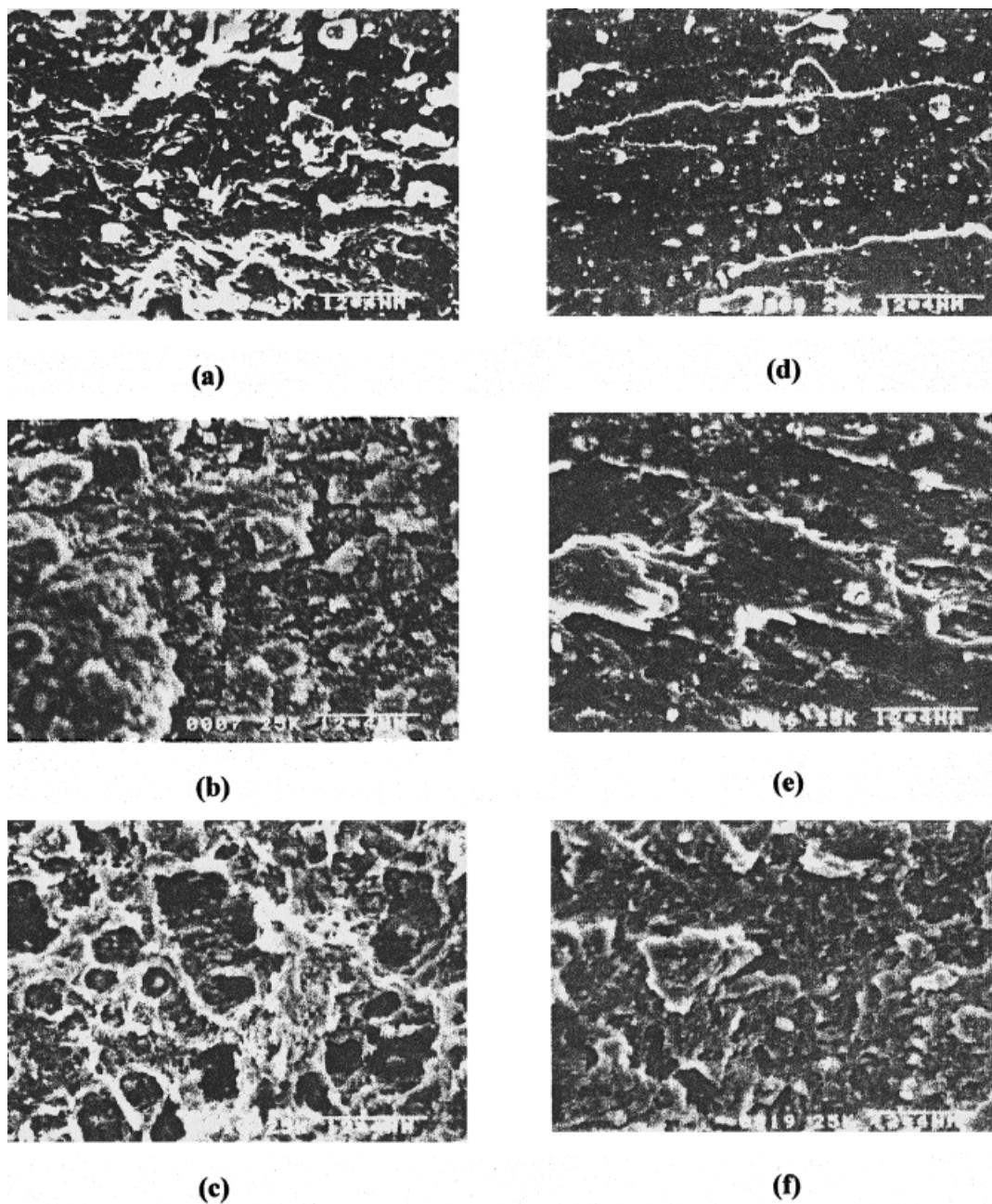
**Scheme 3** Reaction of Silica with pendant DIPDIS fragments.

results indicate that the age-resistance behavior of the blend vulcanizates is significant for the vulcanizates formed in two-stage process. The early reversion occurs not solely because of the polymer chain scission. Destruction of the polymer-filler linkages by prolonged dynamic shearing stress during rheometric study should be taken into account. In the static aging study, these linkages are believed to be unaffected in the absence of any dynamic mechanical stresses, and the observed lowering of the physicochemical values is attributable to the chain scission caused by oxidation at elevated temperature. In the early stage of vulcanization, pendant DIPDIS fragments might react with silica to form large EPDM-DIPDIS(fragment)-SiO<sub>2</sub> aggregates (Scheme 3), which in turn facilitates the reaction with NR. Improvement in the physical properties of the vulcanizates is thus believed to be the outcome of the interfacial crosslinking. Addition of silica in the modified EPDM makes the latter substantially polar and in this way restricts the filler transfer to the NR phase. All these facts lend support to the formation of coherent and homogeneous blend systems of practical importance.

### SEM Studies

SEM studies were performed to reveal the compactness and coherency of the rubber matrix formed by the chemical bonding between NR and EPDM in the presence of DIPDIS. Samples were prepared according to the procedure given in the experimental section.

Figures 5(a-c) represent SEM micrographs of DIPDIS accelerated and carbon black-filled blend vulcanizates of NR and EPDM (one-stage) in different proportions (mixes 3, 4, and 5, Table I) and Figures 5(d-f) depict the corresponding micrographs of two-stage vulcanizates (mixes 3', 4', and 5', Table III). It is evident from the figures that the state of dispersion progressively deteriorates from Figure 5a to 5c (the number and size of

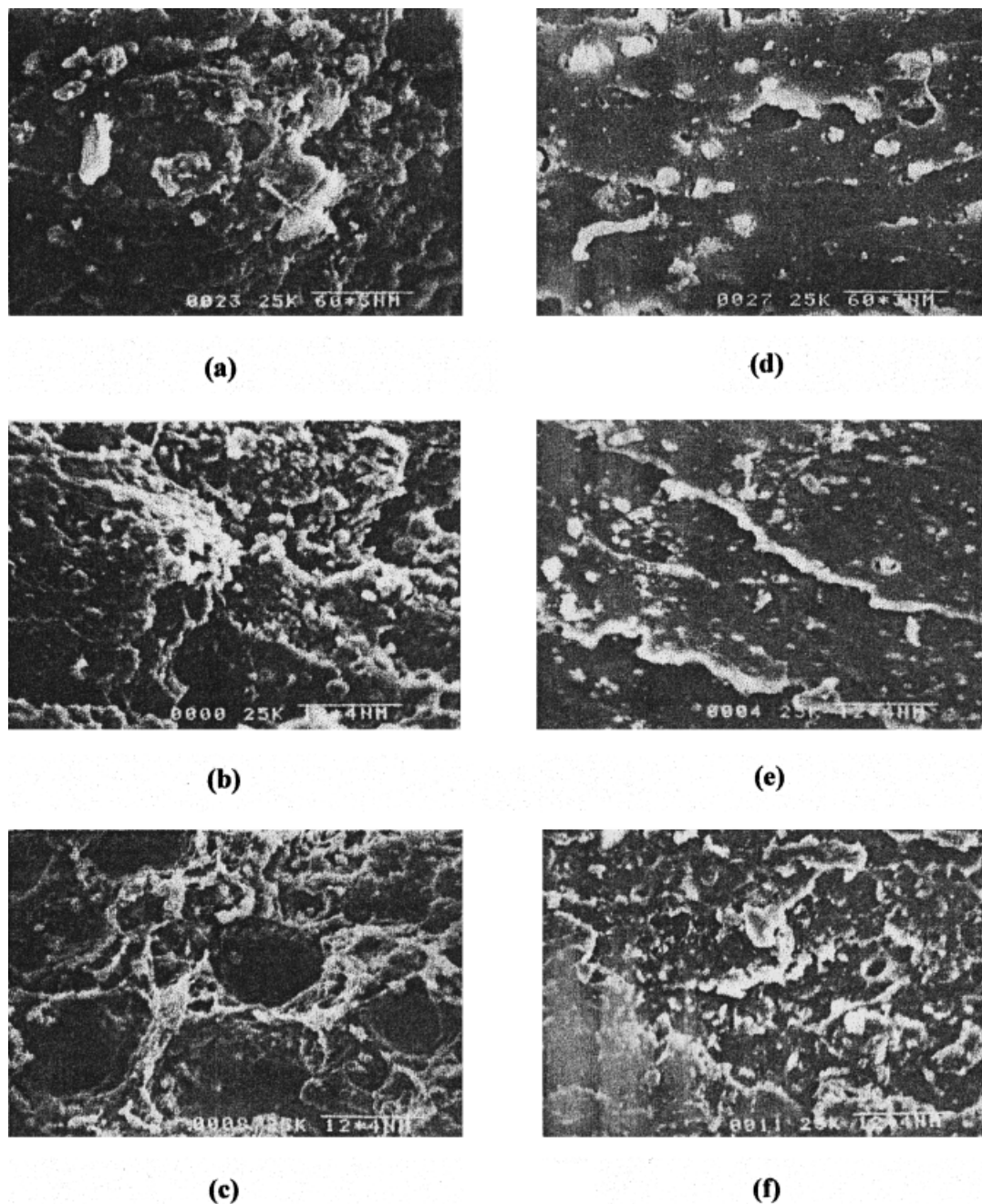


**Figure 5** SEM micrographs of tensile fractured surfaces of the black-filled vulcanizates cured at 160°C: (a) 75:25 NR-EPDM blend (one-stage) at 250 $\times$ ; (b) 50:50 NR-EPDM blend (one-stage) at 250 $\times$ ; (c) 25:75 NR-EPDM blend (onestage) at 250 $\times$ ; (d) 75:25 NR-EPDM blend (two-stage) at 250 $\times$ ; (e) 50:50 NR-EPDM blend (two-stage) at 250 $\times$ ; (f) 25:75 NR-EPDM blend (two-stage) at 250 $\times$ .

the vacuoles are progressively increased). This trend is also manifested in the decrease in mechanical properties (mixes 3-5, Table II). Figure 5c poses the worst situation, with lots of big vacuoles, a shattered surface, and little coherency in the blend.

The micrographs of two-stage vulcanizates exhibit a high degree of ordered orientation of the rubber matrix where ridge lines (lines of reinforcement) are evident, especially in cases of Figure 5d and Figure 5e (mixes 3' and 4', Table III). It is evident that the two-stage vul-





**Figure 6** SEM micrographs of tensile fractured surfaces of the silica-filled vulcanizates cured at 160°C: (a) 75:25 NR-EPDM blend (one-stage) at 500 $\times$ ; (b) 50:50 NR-EPDM blend (one-stage) at 250 $\times$ ; (c) 25:75 NR-EPDM blend (one-stage) at 250 $\times$ ; (d) 75:25 NR-EPDM blend (two-stage) at 500 $\times$ ; (e) 50:50 NR-EPDM blend (two-stage) at 250 $\times$ ; (f) 25:75 NR-EPDM blend (two-stage) at 250 $\times$ .

canization further reduces the number of vacuoles, significantly rendering the vulcanizate matrix more homogeneous and compact. This enhancement of coherency between the two rubbers accounts for the improvement in the phys-

icochemical properties of the vulcanizates of mixes 3', 4', and 5' compared with mixes 3, 4, and 5 respectively.

Figures 6(a-c) and (d-f) depict SEM micrographs of DIPDIS-accelerated and silica-filled

one-stage (mixes 8, 9, and 10, Table I) and two-stage (mixes 8', 9', and 10', Table III) blend vulcanizates of NR and EPDM, respectively. In this case, the same arguments as used for carbon black-filled vulcanizates are applicable. But, compared with the carbon black-filled vulcanizates, much larger vacuoles (compare Figure 6c with Figure 5c) could be seen in the micrographs, and these vacuoles amply demonstrate their poorer physicochemical properties. In this case also, micrographs show much more compactness and coherency two-stage compared with one-stage vulcanizates, suggesting efficient chemical bonding across the rubber interface in the NR-EPDM blend.

## CONCLUSIONS

Investigations regarding covulcanization of NR-EPDM blends with reinforcing fillers suggest curing. The resultant improvement in physicochemical properties could be achieved by proper adjustment of the NR-EPDM ratio, mixing sequence of the compounding ingredients, and finally the mode of vulcanization. Enhancement in the properties is affected by restricting curative as well as filler migration from the EPDM to the NR phase. The SEM micrographs indicate interfacial chemical bridges in the blend vulcanizates and thus corroborate the results obtained so far. However, further investigations are necessary for better understanding of the reactions in the silica filled compounds.

## REFERENCES

1. Baranwal, K.C.; Son, P.N. *Rubber Chem Technol* 1974, 47, 88.
2. Mastromatteo, R.P.; Mitchell, J.M.; Brett, Jr., T.J. *Rubber Chem Technol* 1971, 44, 1065.
3. Morrissey, R.T. *Rubber Chem Technol* 1971, 44, 1025.
4. Coran, A.Y. *Rubber Chem Technol* 1988, 61, 281.
5. Hopper, R.J. *Rubber Chem Technol* 1976, 49, 341.
6. Shulman, C.B. *Rubber Chem Technol* 1986, 59, 180.
7. Tinker, A.J. *Proc Int Rubber Con.*, 1994, Moscow, Russia, Sept 26–Oct 1, 1994, p.180 (MRPRA publication 1511).
8. Itsuro, F.; Masao, M. (Sumitomo Chemical Company, Ltd) *Ger Offen.* 2,045,574, (March, 1971).
9. Yasui, S.; Hirooka, M.; Oshima, T. (Sumitomo Chemical Company). *U.S. Pat.* 3,649,573 (March 14, 1972).
10. Hashimoto, K., et al. *Nippon Gomu Kyokaishi* 1970, 43, 652.
11. Lohmar, J. *Kautchuk Gummi Kunststoffe* 1986, 39, 1065.
12. Young, D.G.; Kresge, E.N.; Wallace, A.J. *Rubber Chem Technol* 1982, 55, 428.
13. Chang, Y.; Shin, Y.; Chun, H.; Nah, C. *J Appl Polym Sci* 1999, 73, 749.
14. Ghosh, A.K.; Debnath, S.C.; Naskar, N.; Basu, D.K. *J Appl Polym Sci* 2001, 81, 800.
15. vanAmerongen, G.J. *Rubber Chem Technol* 1964, 37, 1065.
16. Gardiner, J.B. *Rubber Chem Technol* 1968, 41, 1312.
17. Whittington, W.H. *Rubber Ind* 1976, 9, 151.
18. Guillaumond, F. *Rubber Chem Technol* 1976, 49, 105.
19. Woods, M.E.; Davidson, J.A. *Rubber Chem Technol* 1976, 49, 112.
20. Shershnev, V.A. *Rubber Chem Technol* 1982, 55, 537.
21. Sutton, M.S. *Rubber World* 1964, 149(5), 62.
22. Baldwin, F.P.; Ver Strate, G. *Rubber Chem Technol* 1972, 45, 709.
23. Blumel, H.; Kerrutt, G. *Kautschuk Gummi Kunststoffe* 1971, 24, 517.
24. vanDuin, M.; Kraus, J.C.J.; Snedinga, J. *Kautschuk Gummi Kunststoffe* 1993, 46, 455.
25. Pimblott, J.G.; Scott, G.; Stuckey, J.E. *J Appl Polym Sci* 1975, 19, 865.
26. Parks, C.R.; Brown, R.J. *Rubber Chem Technol* 1976, 49, 233.
27. Callan, J.E.; Hess, W.M.; Scott, C.E. *Rubber Chem Technol* 1971, 44, 814.
28. Hess, W.M.; Herd, C.R.; Vegvari, P.C. *Rubber Chem Technol* 1993, 66, 329.
29. Mandal, S.K.; Datta, R.N.; Das, P.K.; Basu, D.K. *J Appl Polym Sci* 1988, 35, 987.
30. Callan, J.E.; Topcik, B.; Ford, F.P. *Rubber World* 1965, 151(6), 60.
31. Hess, W.M.; Scott, C.E.; Callan, J.E. *Rubber Chem Technol* 1967, 40, 371.