

Effect of Bis(diisopropyl)thiophosphoryl Disulfide on the Covulcanization of Styrene–Butadiene Rubber and Ethylene–Propylene–Diene (Monomer) Blends

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ABSTRACT: Covulcanization of elastomer blends constituting styrene–butadiene rubber (SBR) and ethylene–propylene–diene (monomer) rubber (EPDM) was successfully performed in the presence of reinforcing fillers like carbon black and silica by using a multifunctional rubber additive, bis(diisopropyl)thiophosphoryl disulfide (DIPDIS). The polarity of EPDM rubber was increased by a two-stage vulcanization technique, which allowed the formation of rubber-bound intermediates. In this way the migration of both curatives and reinforcing fillers in the EPDM–SBR blend could be controlled and cure rate mismatch could be minimized. The process significantly improved the physical

properties of the blend vulcanizates. The phase morphology, as evident from the SEM micrographs, was indicative of the presence of a much more compact and coherent rubber matrix in the two-stage vulcanizates. Different accelerator systems were studied to understand better the function and effectiveness of DIPDIS in developing homogeneity in the blends of dissimilar elastomers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1231–1242, 2004

Key words: blends; crosslinking; bis(diisopropyl)thiophosphoryl disulfide (DIPDIS); two-stage vulcanization; fillers

INTRODUCTION

Acquisition of combinatorial and desirable features exhibited by vulcanizates of the component elastomers in a unique substance is the fundamental justification for blending two or more elastomers. Unfortunately and most commonly, however, it has been found that covulcanization leads to reduction in the mechanical strength of the vulcanizate compared with its expected values.^{1–4} The endothermic nature of blending and smaller entropic contribution, attributed to the high molecular weight of elastomers, leads to an immiscible system having overall positive free energy of mixing.^{5,6} Homogeneity of mixing and cure compatibility are the most relevant polymeric properties pertaining to elastomer blends and, although microheterogeneity is usually desirable to retain the individual properties of the respective elastomer components, maldistribution of crosslinks attributed to curative migration, filler, and plasticizer transfer are the subject of consideration regarding inferior covulcanization properties.^{7,8} Blends of elastomers differing in unsaturation levels usually suffer from cure-rate mismatch^{9,10} because of the differential solubility and reactivity of the curatives with the component elastomers. In this context blending of EPDM polymers

(having low unsaturation) with other diene rubbers like natural rubber (NR), styrene–butadiene rubber (SBR), and butadiene rubber (BR) (having high level of unsaturation) is the most intriguing and challenging aspect in the field of rubber research. It has been observed by earlier investigators that bis(diisopropyl)thiophosphoryl disulfide (DIPDIS), apart from its function as an accelerator and a sulfur donor, reacts with diene rubbers to form pendant groups along the backbone chain in the early stage of vulcanization.^{11,12} Recently, we observed that DIPDIS can be effectively applied as a coupling agent–*cum*–accelerator to covulcanize NR and ethylene–propylene–diene (monomer) rubber (EPDM) to obtain improved interfacial crosslinking.^{13,14} It is thus expected that DIPDIS would be very effective in producing coherent blends composed of EPDM and highly unsaturated SBR. The present article will focus primarily on the study of the cure behavior during the covulcanization of SBR–EPDM rubber blends containing reinforcing fillers and their vulcanizate properties in the presence of a thiophosphoryl disulfide compound. A two-stage vulcanization procedure was adopted to improve further the physical properties of the blends.

EXPERIMENTAL

Materials

The characteristics of styrene–butadiene rubber (Plioflex 1502, The Goodyear Tire and Rubber Co.,

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USA) used in the present investigation were as follows: bound styrene, about 23.5%; Mooney viscosity $ML_{(1+4)}$ at 100°C, 50; ash content, 0.8%; sp. gr., 0.94.

Ethylene-propylene-diene (monomer) rubber (Herlene 521, Herdillia Unimers Ltd., Unimers Ltd., Mumbai, India) was used, characterized as follows: Mooney viscosity $ML_{(1+4)}$ at 100°C, 45; E/P ratio, 52/48; ENB content, 5% by weight; sp. gr., 0.86.

Carbon black (HAF, N330) was obtained from Phillips Carbon Black Ltd. (Carbon Black Ltd. (Durgapur, India). Precipitated silica (Ultrasil VN3) of Degussa-AG (Germany) was used as obtained after heating at 105–106°C for 16 h. Analytical-grade paraffin oil (S. D. Fine Chemicals, Mumbai, India) was used as process oil. DIPDIS was prepared and purified according to the procedure reported by Pimblott and coworkers.¹¹ Commercial-grade dibenzothiazyl disulfide (MBTS; ICI, Rishra, India) and tetramethyl thiuram disulfide (TMTD; Nocil, Thane, India) were used after necessary purification. Other reagents used (isooctane, toluene, etc.) were of analytical grade.

Preparation of vulcanizates

One-stage rubber vulcanizates

Requisite amounts of compounding ingredients (ZnO, stearic acid, filler, and oil) were incorporated sequentially in previously masticated rubber (for pure rubber compound) or masticated and preblended rubbers on a Berstorff laboratory two-roll mixing mill size (203 × 102 mm) using a 25-min compounding cycle. Finally, the accelerator and sulfur were added to the mix after cooling the mill. The stocks were cured under pressure at 160°C to optimum cure (t_{90}).

Two-stage rubber vulcanizates

In this procedure requisite amounts of SBR and EPDM were first masticated separately. The whole amounts of ZnO, stearic acid, accelerator, and sulfur were incorporated into EPDM. The time (t) for the commencement of cure for the mix was calculated from the rheograph run at 160°C in a Monsanto Rheometer (R-100; Monsanto, St. Louis, MO). The compounded EPDM mix was then heated at 160°C in a hydraulic press for a predetermined time (t) to obtain the modified (grossly undercured) mix. Three different mixing sequences were studied thereafter. In the first mode fillers and process oil were mixed with modified EPDM mix to obtain the filled masterbatch and after that a requisite amount of masticated SBR was added to it to maintain the desired ratio. In the second sequence blending of modified EPDM with masticated SBR was done before the addition of filler. In the last mode all the filler was mixed with masticated SBR to obtain the filled masterbatch of SBR and after that requisite amount of modified EPDM was added to

obtain the desired mix. In the case of silica-loaded compounds no process oil was incorporated. The compounds were vulcanized under pressure at 160°C to optimum cure (t_{90}).

Measurement of physical properties

Physical properties such as modulus at 200% elongation and tensile strength of the vulcanizates were measured according to ASTM D412-92 after 24 h of maturation of the samples, using a tensile testing instrument (Amsler, Sweden). 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.

In the crosslink-density measurement experiment, a weighed rubber sample was immersed in (70/30) isooctane-toluene medium for 48 h at ambient temperature ($30 \pm 2^\circ\text{C}$). The rubber was removed, blotted as rapidly as possible with blotting paper, and weighed in a 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, was readily calculated from the expression¹⁵

$$Q = \frac{\text{swollen wt.} - \text{dried wt.}}{(\text{original wt.} \times 100) / \text{formula wt.}}$$

where formula wt. 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

This was carried out on the tensile-fractured surfaces of the specimens that, 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-415A; Hitachi, Osaka, Japan).

RESULTS AND DISCUSSION

EPDM has been well established as a polymeric antiozonant.¹⁶ However, because of the nonpolar nature of the EPDM molecules curative migration^{17,18} and filler transfer¹⁹ occur from this phase to another diene rubber phase having higher unsaturation and polarity. This results in less-reinforced and undercured EPDM, along with overcured diene rubber matrix, which yields vulcanizates with poor mechanical properties

TABLE I
Formulations and Cure Characteristics of One-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R-100)

	Mix													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Formulation														
SBR	100	—	75	50	25	75	75	100	—	75	50	25	75	75
EPDM	—	100	25	50	75	25	25	—	100	25	50	75	25	25
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
N330	40	40	40	40	40	40	40	—	—	—	—	—	—	—
Silica	—	—	—	—	—	—	—	30	30	30	30	30	30	30
Process oil	5	5	5	5	5	5	5	—	—	—	—	—	—	—
DIPDIS ^a	3.834	3.834	3.834	3.834	3.834	—	—	3.834	3.834	3.834	3.834	3.834	—	—
MBTS ^a	—	—	—	—	—	2.988	—	—	—	—	—	—	—	2.988
TMTD ^a	—	—	—	—	—	—	2.160	—	—	—	—	—	—	2.160
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Cure characteristic ^b														
R_{∞} (Nm)	5.90	4.55	4.45	3.20	2.40	4.30	6.10	6.10	3.70	4.90	3.15	1.45	4.35	4.20
t_2 (min)	5.00	7.50	5.00	5.00	6.50	2.75	0.75	4.25	3.50	4.25	3.00	2.75	7.00	0.50
t_{90} (min)	16.50	30.00	17.75	18.50	21.00	12.50	11.00	12.25	10.50	10.75	9.00	8.00	30.75	2.50

^a Weight corresponds to 9 mmol DIPDIS/MBTS/TMTD.

^b $R_{\infty} = R_{\max} - R_{\min}$, t_2 = scorch time, t_{90} = optimum cure time.

attributed to lack of efficient interrubber crosslinking. Our objective was to enhance the polarity of the EPDM phase by reacting it with DIPDIS, which tends to improve interfacial crosslinking. To understand the effectiveness of DIPDIS in blends, two other conventional accelerators, MBTS and TMTD, were chosen and their results are compared.

One-stage vulcanization

Black-filled compounds

The recipes of mixes 1–7 are shown in Table I and the corresponding rheographs are depicted in Figure 1. Typical S-shaped curves are observed for all the mixes. It can be seen from the cure data (Table I) that DIPDIS is very effective in increasing the R_{∞} value of

SBR (mix 1), which is even higher than that of both NR¹⁴ and EPDM (mix 2). Evidently this suggests a better state of cure. However, the decreasing values of R_{∞} ($= R_{\max} - R_{\min}$) observed for the blends (mixes 3–5) with progressive increase in EPDM concentration are suggestive of a gradual deterioration of cure-state arising from severe curative and carbon black migration^{19,20} across the phase boundaries. It is evident from Table I that for SBR–EPDM (75 : 25) blend vulcanizates, DIPDIS-accelerated stock shows the highest scorch safety (t_2) and cure time (t_{90}) (compare the values of mix 3 with those of 6 and 7); TMTD-accelerated stock (mix 7) exhibits a characteristic high torque (R_{∞}) but very low scorch (t_2) value, whereas MBTS-cured stock (mix 6) shows the lowest R_{∞} and intermediate t_2 and t_{90} values.

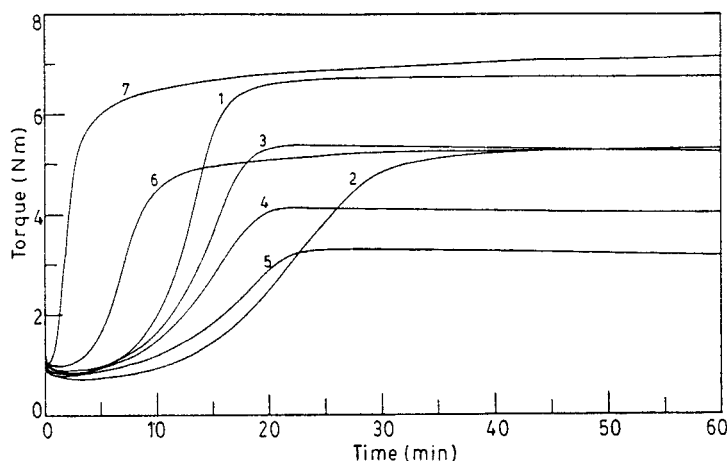


Figure 1 Rheographs of carbon black-filled vulcanizates (mixes 1–7) cured at 160°C.

TABLE II
Physical Properties of the One-Stage Vulcanizates Cured at 160°C^a

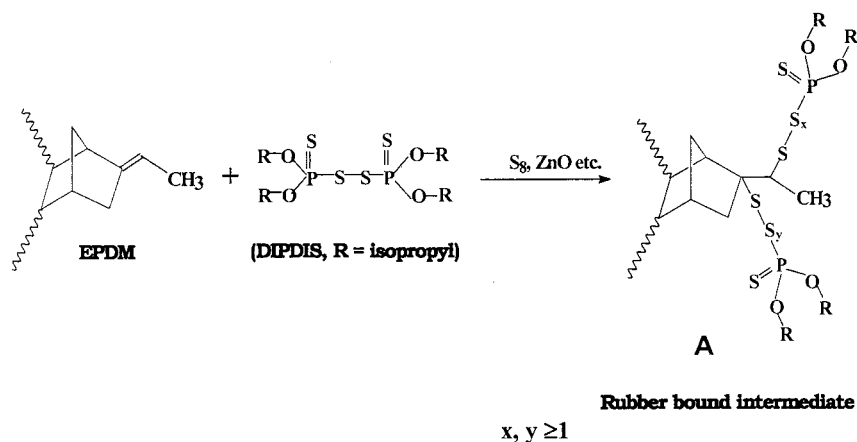
Property	Mix													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
200% Modulus (MPa)	3.100 (4.613)	3.948 (6.224)	3.482 (4.981)	3.007 (4.000)	— (—)	2.128 (4.273)	4.432 (6.796)	1.112 (1.628)	0.824 (1.431)	1.266 (1.624)	1.193 (1.402)	— (—)	0.781 (1.083)	1.637 (2.333)
Tensile strength (MPa)	18.95 (17.16)	18.13 (15.08)	12.88 (11.13)	5.47 (6.00)	2.48 (3.07)	10.23 (9.01)	8.41 (7.11)	15.19 (14.18)	12.91 (13.08)	10.33 (8.28)	4.41 (3.68)	0.75 (0.83)	8.31 (7.84)	9.24 (5.65)
Elongation at break (%)	565 (430)	530 (400)	410 (335)	236 (225)	176 (165)	515 (395)	335 (225)	810 (735)	1020 (730)	675 (630)	600 (490)	175 (185)	815 (715)	590 (370)
Hardness (Shore A)	60 (65)	66 (69)	61 (65)	63 (68)	65 (70)	60 (64)	64 (67)	62 (65)	60 (64)	61 (66)	65 (67)	— (—)	60 (63)	64 (66)
Crosslinking value (1/Q)	0.527 [8.35]	0.396 [9.35]	0.463 [8.50]	— [18.08]	— [24.55]	0.383 [8.71]	0.422 [7.32]	0.499 [4.67]	0.208 [6.70]	0.208 [5.81]	0.418 [24.51]	— [42.11]	0.313 [6.43]	0.383 [5.16]

^a Values in parentheses are aged values (aging done at 100 ± 1°C for 72 ± 1 h). Values in square brackets are %loss in weight during the swelling experiment.

Physical data for the vulcanizates of mixes 1–7 are presented in Table II. It can be seen that modulus, tensile strength, and elongation at break values for DIPDIS-cured blends (mixes 3–5) lie below the additive line, which corresponds to the respective properties of the constituent elastomers (mixes 1 and 2). As the proportion of EPDM is increased in the blend (mixes 4 and 5) the physical properties deteriorate because of the nonuniform distribution of crosslinks between the constituent elastomeric phases. Higher unsaturation of the diene polymers (here SBR) is the driving force governing the carbon black distribution.⁷ The EPDM-rich rubber matrix becomes deficient in curatives and fillers, as they migrate from EPDM (less polar) to the comparatively more polar SBR phase. These phenomena lead to the formation of less-reinforced and severely undercured EPDM matrix along with overcured SBR domains having higher carbon black concentration. The net result is the formation of vulcanizates exhibiting significantly deteriorated physical properties. It is evident from Table II that the vulcanizate from TMTD-accelerated stock (mix 7)

shows the highest modulus and hardness values (characteristics of TMTD cure) but the lowest tensile strength and elongation at break values compared to those of DIPDIS- and MBTS-accelerated blend vulcanizates (mixes 3 and 6, respectively). The tensile strength for the DIPDIS-accelerated vulcanizates is highest, whereas maximum elongation at break value is obtained for MBTS-cured stocks.

The rubber-bound intermediate **A** (as shown in Scheme 1), formed by the reaction of DIPDIS and EPDM molecules at the early stage of vulcanization, might behave as a very active crosslinking precursor and subsequently promote the interfacial crosslinking through coupling with SBR molecules. It is believed that interrubber linking is polysulfidic in nature²¹ and DIPDIS could form di- or polysulfidic linkages in the presence of elemental sulfur.^{22,23} The linkages facilitate crosslink slippage and thus impart good tensile strength,²⁴ which was observed in our case. TMTD is reported to function as a sulfur donor.²⁵ It forms predominantly monosulfidic links that are incapable of exhibiting crosslink slippage. The vulcanizates are



Scheme 1 Probable reaction of DIPDIS with EPDM in the presence of ZnO and S.

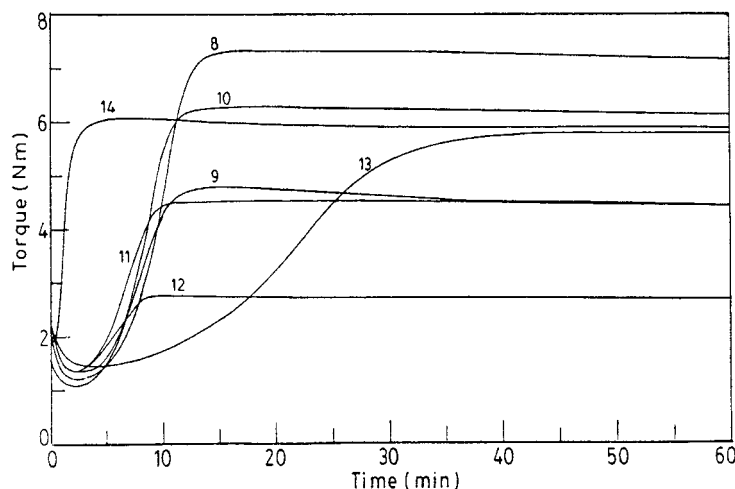


Figure 2 Rheographs of silica-filled vulcanizates (mixes 8–14) cured at 160°C.

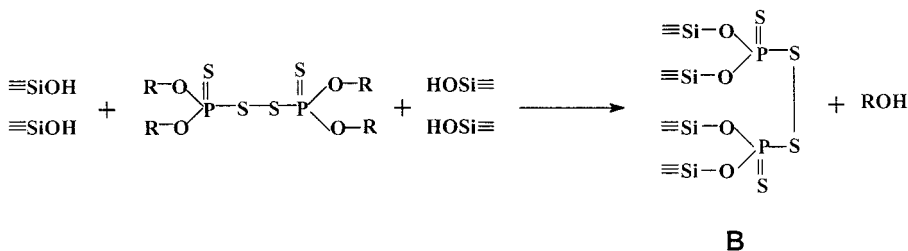
thus likely to show low tensile strength but high modulus.

The reciprocal of swelling index ($1/Q$) presented in Table II gives relative assessment of crosslink density of the polymer matrix. It can be seen that the vulcanizate from mix 1 gives the highest value. However, in the case of blend compositions with a higher fraction of EPDM (mixes 4 and 5) significant weight loss occurs during the swelling experiment. As a result the $1/Q$ values could not be obtained. This is indicative of the gross undercuring of the blends concerned. The DIPDIS-accelerated blend vulcanizate (mix 3) shows a significantly high $1/Q$ value, indicating a rather high degree of crosslinking.

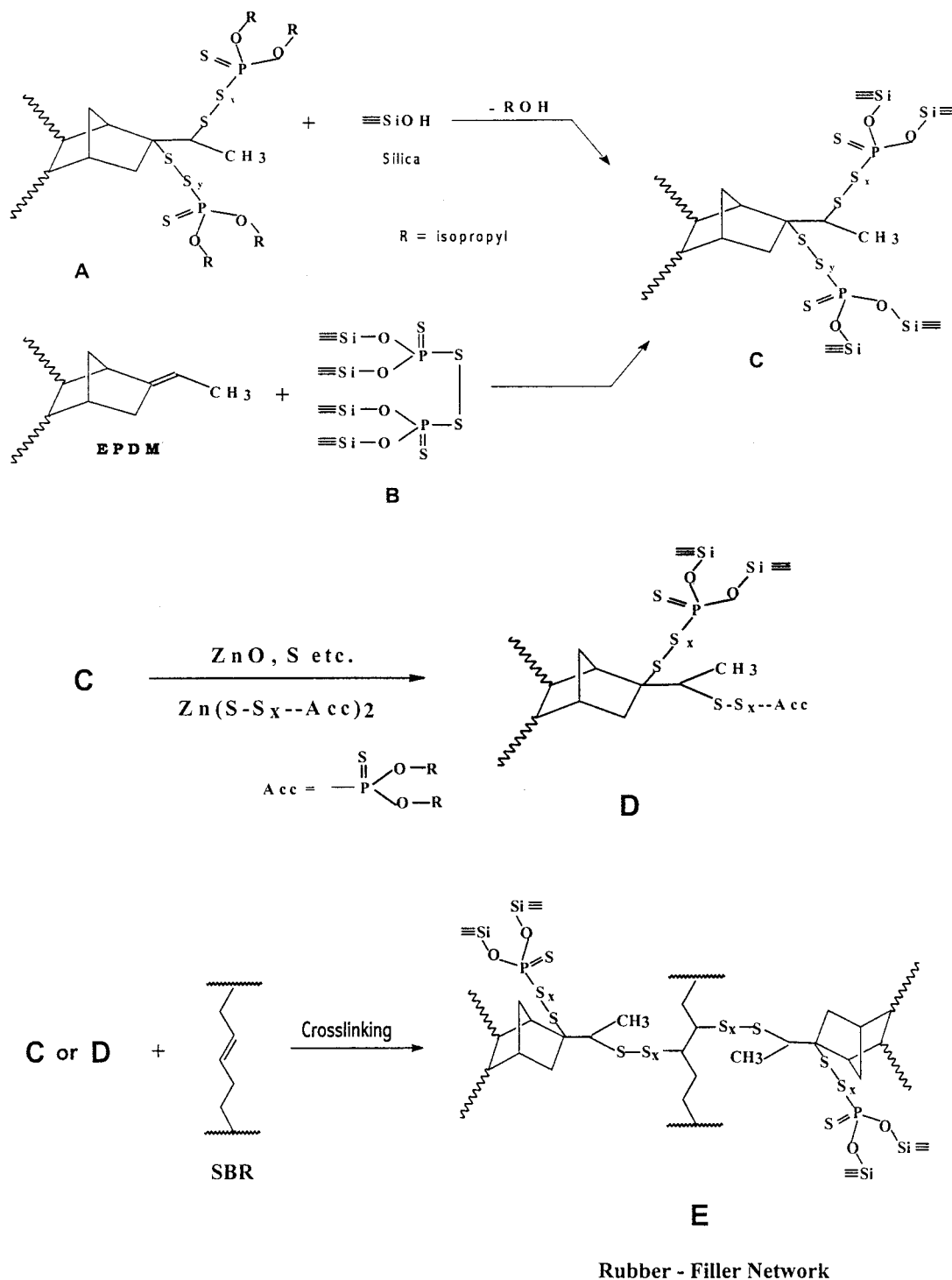
It can be seen from Table II that all the vulcanizates acquire resistance to heat and oxidation (values given in parentheses) even in the absence of any antioxidant. It is well known that about 30% of EPDM is required with other diene rubbers (blends) to impart substantially better ageing and ozone resistance than the corresponding control compounds fully protected with conventional antioxidants or antiozonants.^{26,27} The inherent property of SBR²⁸ and EPDM³ to resist thermo-oxidative degradation is further facilitated by antioxidant shielding²⁹ provided by zinc diisopropylthiophosphate (ZDP),^{11,12,30} which is formed in the medium (Scheme 1).

Silica-filled compounds

Silica adsorbs polar curatives, resulting in a vulcanizate having a poor state of cure.³¹ As can be seen from Figure 2 all the compositions (mixes 8–14, Table I) give S-shaped rheographs. Interestingly, a faster cure rate is observed in all compositions compared to that of the black-filled vulcanizates of similar composition (Fig. 1), except MBTS-cured stock (mix 13). It can be seen that the vulcanizate containing solely SBR (mix 8) shows a higher R_{∞} value than that of its counterpart containing HAF black (mix 1). This is not true in the case of EPDM containing reinforcing silica (compare mix 9 with mix 2), however, where a decrease in R_{∞} is observed. The extent of cure, as revealed from the R_{∞} values (Table I), clearly indicates the activating influence of DIPDIS for the silica-filled blend enriched with SBR (mix 10) compared to that of MBTS (mix 13) or TMTD (mix 14). Silica normally retards cure,³¹ although in the presence of DIPDIS fast curing was observed as evinced from the t_2 values (Table I). It is suggested that the component formed from DIPDIS (A, Scheme 1) reacts with silanol groups (Si—OH) of silica particles to form compounds B³² (Scheme 2) and C (Scheme 3) respectively, with the elimination of isopropyl alcohol. The high reactivity of these substances might explain the fast curing nature, which



Scheme 2 Reaction of silica with DIPDIS.



Scheme 3 Some probable reactions of DIPDIS in the curing of EPDM and SBR in the presence of silica.

facilitates rubber–filler interaction at the early stage of vulcanization and subsequent formation of the proposed rubber–silica network (E, Scheme 3). In this context, DIPDIS acts as a rubber–filler coupling agent by attaching filler particles onto the rubber chain through primary valence bonds.

The physical data of the silica-filled vulcanizates for mixes 8–14 are presented in Table II. The low modulus

and high elongation at break values are quite expected of silica-loaded stocks. DIPDIS-cured blends, rich in EPDM (mixes 11 and 12), exhibit poor tensile strength, which is similar to that of HAF-filled stocks (mixes 4 and 5). In these cases too the significant weight loss in swelling experiments indicates the presence of considerable amounts of unvulcanized rubber. Migration of polar silica particles and curative molecules from the

TABLE III
Formulations and Cure Characteristics of Two-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R100)

	Mix													
	3'	4' ^a	4' ^a b	4' ^b c	5'	6'	7'	10'	11' ^a	11' ^a b	11' ^b c	12'	13'	14'
First stage														
EPDM	25	50	50	50	75	25	25	25	50	50	50	75	25	25
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2	2	2
DIPDIS ^d	3.834	3.834	3.834	3.834	3.834	—	—	3.834	3.834	3.834	3.834	3.834	—	—
MBTS ^d	—	—	—	—	—	2.988	—	—	—	—	—	—	2.988	—
TMTD ^d	—	—	—	—	—	—	2.160	—	—	—	—	—	—	2.160
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Second stage (after preheating ^e compounded EPDM at first stage)														
N330	40	40	40 ^a	40 ^b	40	40	40	—	—	—	—	—	—	—
Silica	—	—	—	—	—	—	—	30	30	30 ^a	30 ^b	30	30	30
Process oil	5	5	5 ^a	5 ^b	5	5	5	—	—	—	—	—	—	—
SBR	75	50	50 ^a	50 ^b	25	75	75	75	50	50 ^a	50 ^b	25	75	75
Cure characteristic ^f														
R _∞ (Nm)	6.20	5.05	5.25	5.30	3.85	6.35	6.95	5.75	4.95	4.80	4.80	3.30	4.45	5.40
t ₂ (min)	2.50	3.00	3.00	2.25	2.00	1.25	0.25	2.25	1.50	2.00	2.00	1.75	3.00	0.25
t ₉₀ (min)	12.50	12.50	12.50	12.75	14.25	16.00	5.50	7.00	5.50	6.00	6.30	5.75	24.00	4.00

^a HAF (with process oil) or silica masterbatches of preheated (modified) EPDM compound are mixed with SBR.

^b HAF (with process oil) or silica are added to the preblends of SBR and modified EPDM compound

^c HAF (with process oil) or silica masterbatches of SBR are mixed with modified EPDM compound,

^d Weight corresponds to 9 mmol DIPDIS/MBTS/TMTD.

^e Preheating times (*t*) at 160°C are 10 min (DIPDIS and MBTS mixes) and 1 min (TMTD mixes).

^f R_∞ = R_{max} - R_{min}; t₂ = scorch time; t₉₀ = optimum cure.

EPDM phase leading to inefficient cure might well explain these observations. For SBR-EPDM (75/25) blend vulcanizates, the stock containing TMTD (mix 14) exhibits the highest modulus and lowest elongation at break values among the different cure systems, whereas the tensile strength is highest for DIPDIS (mix 10), but lowest for MBTS (mix 14). DIPDIS provides the highest 1/*Q* value among the blend vulcanizates (compare mix 10 with mixes 13 and 14). This is corroborated by the results shown in square brackets for the weight loss during swelling experiments.

The age-resistance of the vulcanizates containing DIPDIS, attributed to the *in situ* formation of ZDP during vulcanization, is notable. However, for TMTD-cured stock (mix 14) there is a significant reduction in tensile strength and elongation at break values in spite of the efficient vulcanization (EV) system used. However, MBTS-cured stock (mix 13) provides better results in this respect. The increase in modulus for TMTD-cured vulcanizates (mix 14) may be attributable to the further formation of rigid monosulfidic linkages through postcuring. On the other hand, the increase in modulus for DIPDIS-cured vulcanizate could be accounted for by the conversion of flexible di- or polysulfidic linkages to monosulfidic ones.

Two-stage vulcanization

During vulcanization accelerator fragments become attached to the rubber chain to form pendant groups,

which function as the precursors to crosslink formation.^{25,33} The objective of two-stage vulcanization (TSV) is to graft the accelerator moieties onto the EPDM backbone, so that its migration to other rubber phase is restricted. The subsequent enhancement of polarity attributed to the higher concentration of rubber-bound intermediates having polar pendant accelerator fragments (rubber-bound intermediate **A**, Scheme 1) enables the EPDM phase to restrict filler migration. This grossly undercured material is expected to combine with SBR at a later stage. Because of the steric effect imparted by the bulky moiety in **D** (Scheme 3), crosslinking within the EPDM matrix (**D-D** linking) is not facile. On the other hand, **D-SBR** (interfacial) interaction would be energetically more feasible and thus paves the way for the formation of coherent blend systems having improved physical properties.

The composition of the blends and their rheological parameters in two-stage vulcanization are given in Table III. Here the DIPDIS-to-EPDM ratio was varied (mixes 3'-5' and 10'-12') to achieve the desired results. MBTS and TMTD were also incorporated into some blend systems (mixes 6', 7', 13', and 14') to compare the effectiveness of DIPDIS. For different blend compositions the preheating time was adjusted to obtain the maximum level of rubber-bound intermediates at the first stage. Three modes of mixing sequences were followed to ascertain the filler/oil in-

TABLE IV
Cure Characteristics and Physical Properties of Two-Stage 1:1 (SBR-EPDM) Filled Vulcanizates Cured at 160°C with Different Mixing Sequences

Mix	Filler	R_{∞}^a (Nm)	200% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Crosslinking value ^b (1/Q)
4'	N330	5.05	2.385	12.60	480	61	0.469 [8.21]
4'a	N330	5.25	3.685	10.72	400	62	0.436 [8.77]
4'b	N330	5.30	3.802	9.89	370	63	0.390 [9.83]
11'	Silica	4.95	1.461	11.76	715	63	0.330 [5.19]
11'a	Silica	4.80	1.582	10.79	675	65	0.302 [5.54]
11'b	Silica	4.80	1.701	9.87	645	66	0.284 [5.96]

^a $R_{\infty} = R_{\max} - R_{\min}$.

^b Values in square brackets are %loss in weight during the swelling experiment.

corporation time (see Experimental section). The cure characteristics and physical data of two-stage vulcanizates from EPDM-SBR blends (1 : 1) having HAF and silica fillers are shown in Table IV (mixes 4'-4'b and mixes 11'-11'b). In both cases the modified EPDM-filler masterbatches (mixes 4' and 11') imbued vulcanizates with the highest order of tensile strength, elongation at break, and 1/Q values and so this sequence of mixing was followed in the remaining experiments. Figures 3 and 4 depict the rheographs of the mixes containing HAF and silica, respectively. It can be seen from the results that the R_{∞} values of the two-stage vulcanizates are distinctly higher than those of the corresponding one-stage ones (Table I). At this stage both t_2 and t_{90} , as expected, were reduced, whereas the t_{90} values of MBTS-accelerated blend (mix 6') and TMTD-accelerated stock (mix 14') were increased. It is evident from the rheographs that DIPDIS-accelerated formulations containing silica (mixes 10'-12') attain almost a plateau after reaching maxima. These phenomena can be explained by following the probable reaction paths as shown in Scheme 3. Component C,

formed initially (Scheme 3), is transformed into component D, which ultimately forms the rubber-filler network (E). Shortening of the cure time and improvement in physical properties may be attributable to the conversion of component C to the rubber-silica network (E), although the subsequent reduction of torque might be attributable to the thermomechanical instability of this rubber-filler network (E). Both MBTS and TMTD exhibit typical marching cure, indicating clearly their different modes of vulcanization reaction.

Physical data for the vulcanizates obtained from mixes 3'-7', which contain HAF, and mixes 10'-14' containing silica are given in Table V. In all cases the tensile strength, elongation at break, and 1/Q values were substantially improved compared to one-stage values (Table II), except in the case of MBTS (mix 13') and TMTD (mix 14') cured silica-filled stocks. The modulus values of cured stocks containing carbon black and DIPDIS (mixes 3' and 4') decreased compared to one-stage values (mixes 3 and 4, Table II). SBR constitutes the continuous phase in mixes 3 and 3' (see Tables I and II). Now, the SBR phase of mix 3' was

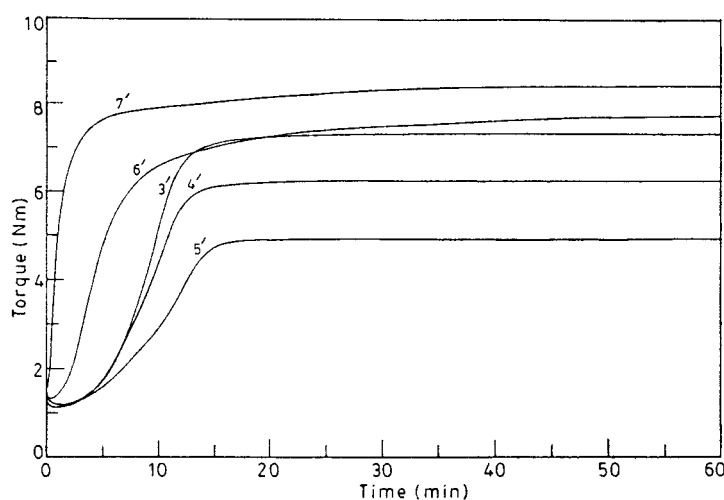


Figure 3 Rheographs of carbon black-filled vulcanizates (mixes 3'-7') cured at 160°C (second stage).

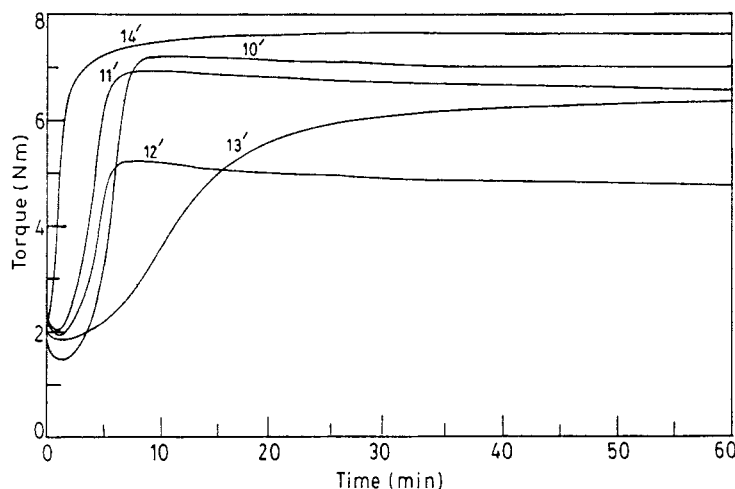


Figure 4 Rheographs of silica-filled vulcanizates (mixes 10'–14') cured at 160°C (second stage).

constrained to contain lesser amounts of carbon black and curatives, which were subjected to restricted migration from EPDM to SBR phase in TSV; thus the continuous phase became less reinforced. The observed decrease in modulus may be thus explained. At the same time, however, the higher tensile strength and elongation at break may be attributed to the efficient interrubber crosslinking, where polysulfidic crosslinks play a vital role.²¹ For mixes 4 and 4' a similar argument holds, although here the proportion of SBR and EPDM is equal. Silica, which is much more polar than furnace blacks, migrates to the SBR phase in sufficient amounts to overcome the imposed restriction, the resultant effect being the manifestation of higher reinforcement in TSV compared to that at one-stage vulcanization.

The blend vulcanizates from mixes 3' and 10' provided the best values of tensile strength and $1/Q$ for HAF- and silica-filled compounds, respectively, and in this respect DIPDIS-cured stocks exhibited much bet-

ter performance over that of the corresponding MBTS- and TMTD-cured stocks (compare physical data for the vulcanizates of mix 3' with the corresponding values for mixes 6' and 7' and for mix 10' with mixes 13' and 14', Table V). Moreover, the tensile strength values of the vulcanizates (SBR and EPDM in the proportion of 75 : 25) cured by DIPDIS exceeded those of the component elastomers by a substantial degree [compare mix 3' with mixes 1 and 2 (Table II) and mix 10' with mixes 8 and 9 (Table II)]. In the first stage of the TSV all the curatives were deliberately incorporated into the EPDM matrix and thus the lesser the portion of EPDM in the blend vulcanizates, the higher the concentration of effective rubber-bound intermediates (pendant DIPDIS fragments). Actually this was observed. Weight losses during the swelling experiment were also reduced, particularly in the case of EPDM-rich two-stage vulcanizates [compare mixes 4, 5, 11, and 12 (Table II) with mixes 4', 5', 11', and 12' (Table V), respectively]. The results indicate efficient

TABLE V
Physical Properties of Two-Stage Vulcanizates Cured at 160°C^a

Mix	200% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Crosslinking value ^b ($1/Q$)
3'	2.879 (4.670)	22.66 (21.92)	565 (440)	60 (65)	0.504 [6.67]
4'	2.385 (3.821)	12.60 (13.24)	480 (395)	61 (64)	0.469 [8.21]
5'	1.845 (2.605)	7.45 (9.57)	415 (375)	63 (67)	0.352 [10.98]
6'	3.047 (4.821)	16.94 (14.59)	685 (525)	62 (65)	0.414 [8.91]
7'	4.393 (7.688)	13.41 (13.26)	440 (335)	64 (67)	0.458 [7.01]
10'	1.681 (1.915)	18.52 (15.41)	775 (655)	61 (64)	0.469 [4.83]
11'	1.461 (1.726)	11.76 (10.93)	715 (625)	63 (65)	0.330 [5.89]
12'	1.134 (1.550)	5.35 (6.52)	655 (605)	62 (66)	0.224 [9.78]
13'	1.299 (1.367)	13.09 (10.22)	880 (825)	60 (62)	0.329 [5.29]
14'	2.604 (3.089)	14.17 (9.31)	655 (555)	65 (68)	0.384 [3.77]

^a Values in parenthesis are aged values (ageing done at $100 \pm 1^\circ\text{C}$ for 72 ± 1 h).

^b Values in square brackets are %loss in weight during the swelling experiment.

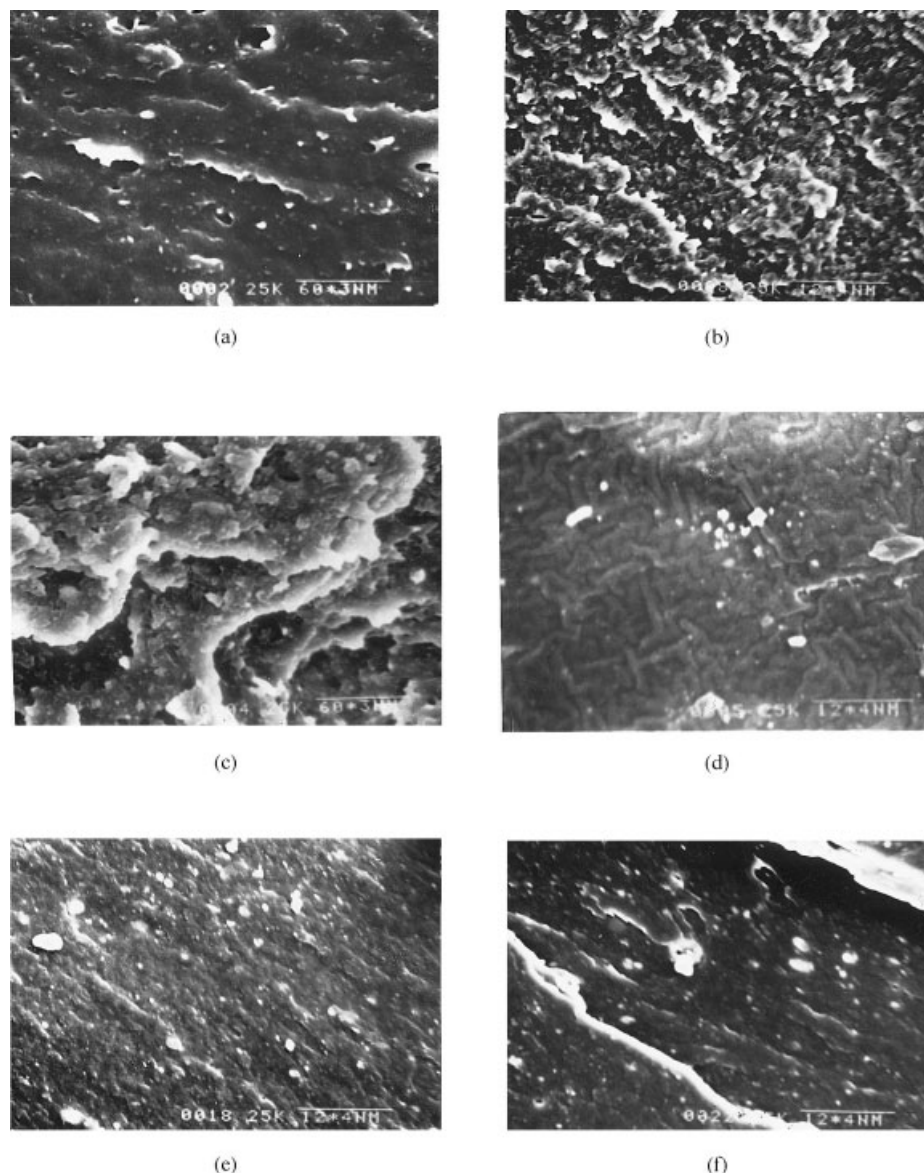


Figure 5 SEM micrographs of tensile-fractured surfaces of the carbon black-filled vulcanizates cured at 160°C: (a) 75 : 25 SBR-EPDM blend (one stage) at $\times 250$; (b) 50 : 50 SBR-EPDM blend (one-stage) at $\times 250$; (c) 25 : 75 SBR-EPDM blend (one-stage) at $\times 250$; (d) 75 : 25 SBR-EPDM blend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

co curing. From the results of the age-resistance behavior of the vulcanizates (mixes 3'-7', Table V) it is observed that the physical properties after ageing for the carbon black-filled vulcanizates are quite high. Ageing behaviors of the mixes containing DIPDIS, MBTS, and TMTD (mixes 10', 13', and 14', Table V) were very close to one another. Here significant increases in modulus and hardness were observed. The observed reduction in tensile strength and elongation at break in the static ageing experiments may be attributable to the shortening of crosslinks after the elimination of sulfur under experimental conditions. SBR and EPDM become hardened during ageing because of the formation of stiffer monosulfidic linkages,

which are initially flexible, at the expense of di- or polysulfidic crosslink network.³⁴ This hardening of the rubber is associated with the increase in the modulus, but at the same time the tensile strength and elongation at break values decrease rapidly. The overall enhancement of physical properties in the presence of DIPDIS is indicative of the formation of polymer-silica interaction by the pendant DIPDIS fragments grafted onto the EPDM backbone. Addition of fillers in the modified EPDM converts the rubber matrix further polar because of the polar-polar interaction between polymer molecules and filler particles, thus restricting the movement of filler across the phase boundaries. This is true for black filler also because

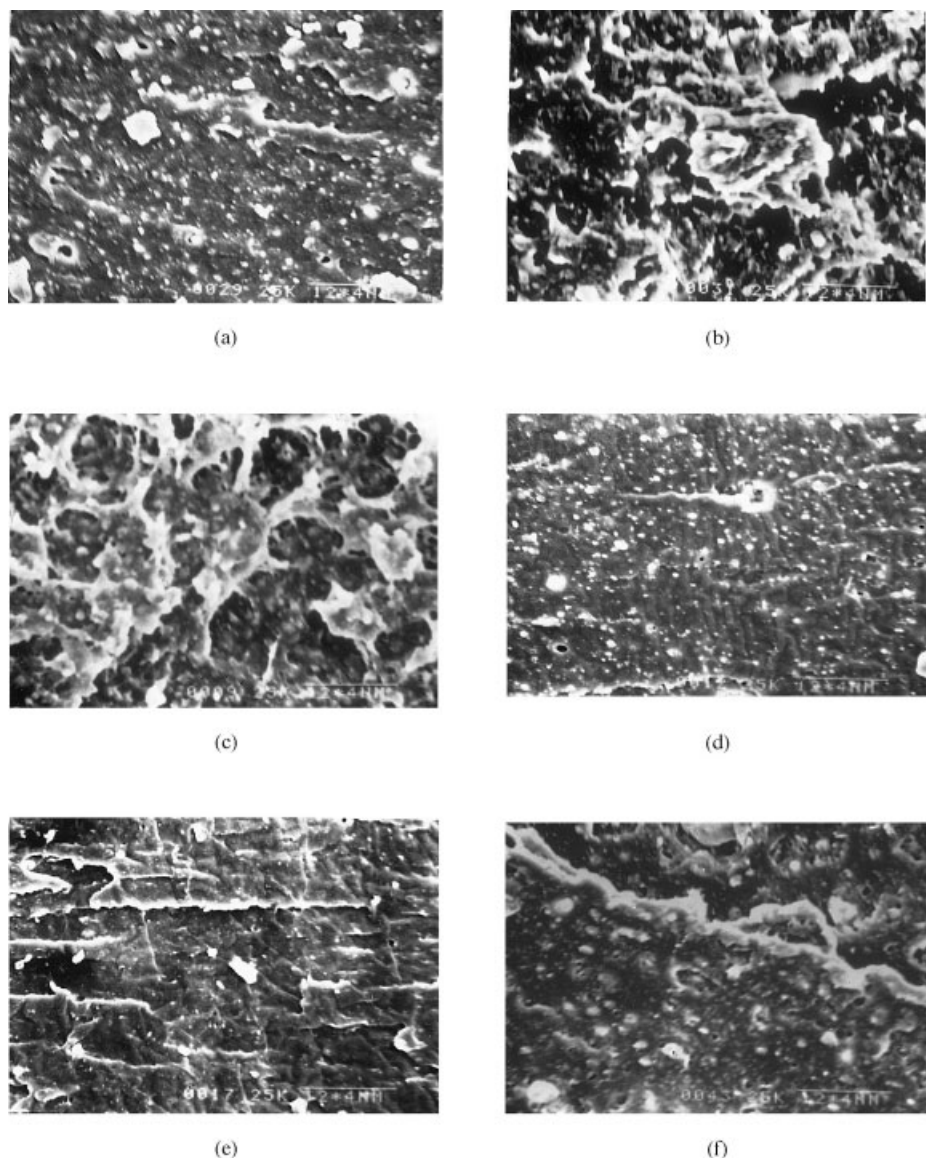


Figure 6 SEM micrographs of tensile-fractured surfaces of the silica-filled vulcanizates cured at 160°C: (a) 75 : 25 SBR–EPDM blend (one-stage) at $\times 500$; (b) 50 : 50 SBR–EPDM blend (one-stage) at $\times 250$; (c) 25 : 75 SBR–EPDM blend (one-stage) at $\times 250$; (d) 75 : 25 SBR–EPDM blend (two-stage)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

furnace black contains several organic functional groups at the surface³⁵ that are responsible for polymer–filler interaction.

SEM studies

SEM studies were expected to corroborate the physical data and provide the visual evidence regarding phase morphology of the blend systems. Tensile-fractured surfaces of DIPDIS-accelerated blend vulcanizates derived from both one-stage and two-stage vulcanization processes were studied (see Experimental section). Figure 5(a)–(c) illustrate SEM micrographs of DIPDIS-accelerated and carbon black–filled blend vul-

canizates of SBR and EPDM (one-stage) in the proportion of 75 : 25, 50 : 50, and 25 : 75, respectively (mixes 3, 4, and 5, Table I). Figure 5(d)–(f) represent corresponding micrographs obtained in the two-stage vulcanization (mixes 3', 4', and 5', Table III).

It is clearly visible from the surface texture that the phase segregation enhances as we progress from Figure 5(a) to Figure 5(c) and the situation becomes worst in the case of Figure 5(c). The number and the size of the vacuoles suggest least coherency among all the carbon black–filled compositions because of the lack of chemical bridging at the interphase of component elastomers, which is reflected in the poorest physico-chemical performances (mix 5, Tables I and II) among

the blends. Some degree of architectural homogeneity is found in Figure 5(a) and this corroborates the best performance among the blends obtained from one-stage vulcanization.

It is evident from the micrographs of two-stage vulcanizates [Fig. 5(d)–(f)] that superior dispersion compared to that of those shown in micrographs [Fig. 5(a)–(c)] is obtained. Moreover, the appearance of the strong ridge lines indicates a higher degree of compactness and homogeneity. The highest order of orientation is observed in the case of Figure 5(d). Evidently this accounts for the superior physical properties of the blend vulcanizate (mix 3'). The highly compact intermeshing network character of elastomer coils imparts a high order of coherency in the rubber matrix and thus reduces the amorphous behavior of the system. This type of orientation gradually disappears with the increment of the EPDM fraction [Fig. 5(e), (f)] in the blend and the reduction of the physical properties thus observed (mixes 11' and 12', Tables III and IV).

Figure 6(a)–(c) and Figure 6(d)–(f) represent DIPDIS-cured micrographs of silica-filled one-stage (mixes 10, 11, and 12, Table I) and two-stage (mixes 10', 11', and 12', Table III) blend vulcanizates, respectively. Here, a similar trend is observed as that for carbon black-filled vulcanizates. The more highly shattered surface in Figure 6(a) and larger and higher number of vacuoles in Figure 6(b) and (c) are in conformity with inferior mechanical performances than those of the corresponding carbon black-filled vulcanizates (compare the physical data of mixes 3, 4, and 5 with mixes 10, 11, and 12 in Tables I and II, respectively). This condition improved significantly in the case of two-stage vulcanizates and the appearance of ridge lines indicated an ordered intermeshing network. All these are manifested in the enhanced physical properties of the two-stage vulcanizates over those of the one-stage systems [compare the physical properties of the vulcanizates from mixes 10, 11, and 12 (Table II) with those from 10', 11', and 12' (Table V)].

CONCLUSIONS

It appears from the foregoing investigation on SBR–EPDM covulcanization that efficient interfacial crosslinking could be achieved by the judicious selection of SBR–EPDM ratio, concentration of DIPDIS in the compound, and the mode of mixing and vulcanization. The mechanical properties could be further improved by two-stage vulcanization. The enforced restriction on filler transfer and curative migration and concomitant development of coherency and homogeneity in the blend matrix, as evident from the SEM micrographs, corroborate the results obtained so far. It is evident that MBTS and TMTD fail to match

the performance of DIPDIS, which is a proven coupling-*cum*-curing agent for elastomer blends. However, further studies are required to gain better insight into the mode of actions of DIPDIS in the rubber–filler network.

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