NR–EPDM Covulcanization: A Novel Approach

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ABSTRACT: Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) was used successfully as a novel coupling agent cum accelerator to co-vulcanize the elastomer blend comprising highly unsaturated natural rubber (NR) and ethylene propylene diene rubber (EPDM) of low unsaturation content. The blend vulcanizates produced exhibit improved physical properties that can be further enhanced by implementing a two-stage vulcanization technique, as well as by judicious selection of the NR-to-EPDM ratio. The results indicate coherency and homogeneity in the blend composition of two-stage vulcanizates. The cure-rate mismatch problem could thus be solved through the formation of rubber-bound intermediates with a multifunctional rubber additive (i.e., DIPDIS), thereby restricting the curative migration from lower to highly unsaturated rubber. The blend morphology as revealed by SEM studies accounts for significant improvement in physical properties, particularly in two-stage vulcanizates. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 800–808, 2001

Key words: cure-rate mismatch, NR–EPDM blend, rubber-bound intermediate, curative diffusion, bis(diisopropyl) thiophosphoryl disulfide (DIPDIS)

INTRODUCTION

Compounding of blends consisting of two or more elastomers has long been the useful method for achieving properties that a single elastomer lacks. However, it is a general trend that the physical properties of the vulcanized elastomer blends are inferior to those predicted by interpolation between the properties of the component elastomers.[1–3] Blends of elastomers having similar polarity and cure rate exhibit almost additive properties, but dissimilar elastomers result in blends with inferior properties.[4] This property failure has been ascribed mainly to three types of incompatibility that exist between dissimilar elastomers: (1) thermodynamic incompatibility involving phase separation on molecular scale[5,6]; (2) viscosity mismatch causing delay or even pre-

venting the formation of coherent blends[7,8]; and (3) cure-rate mismatch due to imbalance in unsaturation levels of the elastomers. Among these, viscosity mismatch can be improved through proper blending processes by adjusting the raw polymer viscosities, extender oil, and filler concentrations. Thermodynamic incompatibility can be alleviated to some extent by reducing the interfacial energy through the creation of microdomains and subsequent adhesion between the elastomeric phases or by crosslinking the phases across the interfaces during vulcanization.[9]

The present investigation deals with cure-rate mismatch, which reaches its extreme when the blends constitute high-unsaturated diene rubbers, including natural rubber (NR), SBR, and IR, and low-unsaturation rubbers, including IIR and ethylene propylene diene rubber (EPDM). It involves the migration of polar curatives from the low-unsaturation phase to a more polar high-unsaturation phase, further undercuring the low-unsaturation phase.[10–17] Ozone resistance of

high-diene rubber is improved significantly by the incorporation of EPDM elastomer.[3,18–22] But the crosslinking deficiency between the elastomeric phases exhibits poor static and dynamic mechanical properties,[16,19,23,24] and it has been shown that unvulcanized EPDM exists in the vulcanized blend with NR.[25]

Several approaches have been made to obtain a co-cured blend vulcanizate of NR–EPDM without sacrificing the physical properties by (1) increasing the unsaturation of EPDM elastomer so that the cure rate becomes at par with NR or other diene rubbers[26–29]; (2) curing with peroxide and polysulfide[29]; (3) halogenating[30] the rubber; (4) effecting partial prevulcanization[26,31]; (5) using accelerators with long hydrocarbon chains[19,32]; and (6) grafting accelerators or sulfur donors[23,33,34] or polydiene chains[35,36] in EPDM. Incorporation of lead dithiocarbamate into EPDM, before it is mixed with NBR, has been reported to yield an improved blend[10,14] vulcanizate. EPDM has been reported to react with N-chlorothioamides[37] to produce a macromolecular cure retarder, making it compatible with NR. EPDM modified with maleic anhydride[38] has been observed to produce blend vulcanizates of improved physical properties. The use of polyoctanomer (TOR)[39,40] and halobutyl rubber[41] as the compatibilizer for NR–EPDM has been cited.

The investigations carried out thus far for the preparation of fruitful NR–EPDM blends involve cure-rate mismatch, which still a great concern for practical purposes. It would be our endeavor to mitigate this adverse effect in the presence of a multifunctional additive, namely bis(diisopropyl)-thiophosphoryl disulfide (DIPDIS), using a new vulcanization technique.

EXPERIMENTAL

Materials

NR (RMA IX) was purchased from the local market. A.R-grade zinc oxide (ZnO) (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 weight, *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). DIPDIS was prepared and purified according to the procedure reported by Pimblott and coworkers.[42] Analytical-grade Iso-octane (2,2,4-trimethyl pentane) (S.D. Fine Chemicals Ltd., India) and G.R-grade Toluene (E. Merck) were used.

Preparation of Vulcanizates and Measurements of Physical Properties

One-stage vulcanization of NR–EPDM blends: NR and EPDM were first masticated separately. Masticated EPDM was cut to pieces and added to previously masticated NR. Requisite amounts of ZnO, stearic acid, and DIPDIS were incorporated in the NR–EPDM mix on a Berstorff lab mill of size 203 × 102 mm. Finally, sulfur was added to the mix on the cooled mill. The stocks were cured under pressure at 160°C.

Two-stage vulcanization of NR–EPDM blends: In this procedure, requisite amounts of NR and EPDM were first masticated separately. The whole amounts of compounding ingredients were incorporated in EPDM. A portion of this mix was run at 160°C in a Monsanto Rheometer (R-100). The time (*t*) for the commencement of cure for the mix was noted from rheograph. The remaining portion of the compounded EPDM was then heated at 160°C in the hydraulic press for the predetermined time (*t*), when a grossly undercured EPDM mix was obtained. The material was then mixed with requisite amount of masticated NR in order 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 such as modulus at 200% elongation and tensile strength were measured according to ASTM D412-51T.

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 a further period of 24 h at room temperature before measuring modulus, tensile strength, elongation at break, and other features.

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 ± 2°C). The rubber was removed, blotted 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

Table I   Formulation of Mixes and Cure Characterisitics of One-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R-100)

Components	Mix				
	1	2	3	4	5
NR	100	—	75	50	25
EPDM	—	100	25	50	75
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
DIPDIS	3.834[a]	3.834[a]	3.834[a]	3.834[a]	3.834[a]
S	0.5	0.5	0.5	0.5	0.5
Maximum rheometric torque,					
R_∞ (Nm)	4.40	4.15	3.30	2.50	1.55
Scorch time, t_2 (min)	3.50	10.50	3.50	2.50	5.00
Optimum cure time, t_{90}					
(min)	11.00	42.00	9.50	11.25	14.25

NR, natural rubber; EPDM, ethylene–propylene–diene rubber; DIPDIS, diisopropylthiophosphoryl disulfide; S, sulfur.
[a] Weight corresponds to 9 mmol DIPDIS.

value Q, defined as the grams of solvent per gram of rubber hydrocarbon, is readily calculated from the expression[43]

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

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

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

RESULTS AND DISCUSSION

The formulations of various rubber mixes employed in the present investigation are presented in Tables I and III. With the objective of controlling curative diffusion from the nonpolar to polar elastomer, an attempt has been made to make EPDM more polar through its reaction with DIPDIS, which is evidently reactive to NR and other synthetic rubbers.[42,44] Although EPDM

used in the present investigation has a low unsaturation content (~5%), it can be reasonably expected that it will react with DIPDIS and yield rubber-bound intermediate in accordance with reaction schemes I and II.

In order to justify this proposition, vulcanization of the blend was carried out in two distinctly different ways: one-stage and two-stage vulcanization.

One-Stage Vulcanization

The cure and physical data related to the gum vulcanizates of NR and EPDM, as well as their blends, are presented in Tables I and II. To start with, the cure behavior of compounded NR (mix 1), EPDM (mix 2), and their blends (mixes 3–5), in
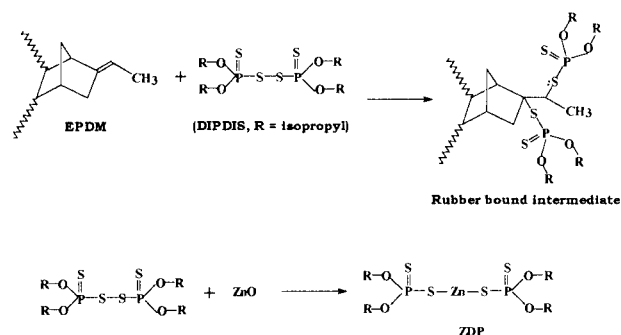
Scheme I   Reactions of bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) with ethylene propylene diene rubber (EPDM) and zinc oxide (ZnO).
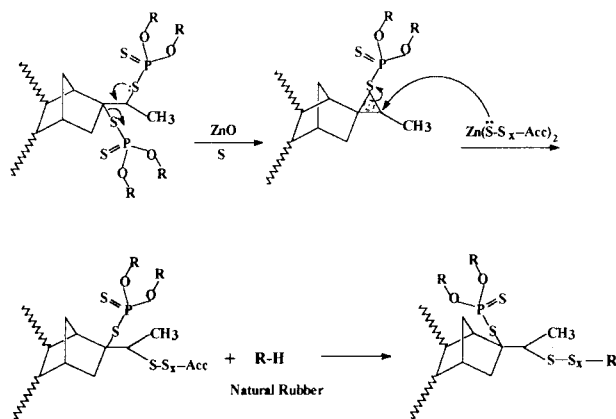
Scheme II Reactions of the rubber-bound intermediates during co-curing with natural rubber (NR).

accordance with their recipes presented in Table I, was studied. The data pertaining to the cure characteristics, obtained from Monsanto Rheometer (R-100), are presented in Table I, and the course of vulcanization reaction is depicted in Figure 1. The numbers shown on the curves correspond to those used for the formulations recorded in Table I. It can be seen from the cure data (Table I) that DIPDIS is capable of raising the R_∞ values of both NR and EPDM. The intermediate formulations (mixes 3–5), however, show decreasing trends in R_∞ as the proportion of NR is decreased progressively in the blend. The reaction of DIPDIS with NR, as can be seen from the rheograph, is faster than that with EPDM. This has been attributed to the low level of unsaturation in EPDM, as reflected in the cure curves of pure NR and the mixes enriched with NR (mixes 1, 3, and 4). This effect is also apparent in the lower values of both scorch time (t_2) and optimum cure time (t_{90}).

The physical data obtained in one-stage vulcanization are presented in Table II. The results indicate that modulus values are rather high for pure elastomers. EPDM has substantially high modulus that owes to the high base hardness of the elastomer itself. The blend vulcanizates have decreasing trend in modulus with increase in the concentration of EPDM. This could be well explained by the fact that with the same amount of curatives in all the blends, the EPDM phase with a higher EPDM-to-NR ratio suffers from proportionally more curative migration from EPDM to NR phase leaving the EPDM phase further undercured (low intra-rubber crosslinking). This leads to the formation of vulcanizates that exhibit lower modulus, tensile strength, elongation at break and crosslinking value. The results also indicate inefficient co-curing due to the poor interfacial crosslinking among the constituent elastomers of the blend. This effect is also pronounced in the tensile strength and elongation at break values. EPDM (mix 2) has very low tensile strength and elongation at break, which is quite expected. In the present investigation, a high accelerator-to-low sulfur ratio has been used, which primarily favors monosulfidic crosslinks in the network exhibiting lower values of tensile strength and elongation at break.[45]

Crosslinking value ($1/Q$) shown in Table II also corroborates these observations. In the case of mix 4, significant weight loss (>50%) was observed in the swelling experiment for determining the $1/Q$ value; specimens from mix 5 were almost dissolved in the solvent rendering this experiment unsuitable for these compositions. This indicates the presence of significant amount of unvulcanized rubber matrices particularly at higher EPDM contents due to the curative migra-

Table II   Physical Properties of One-Stage Vulcanizates Cured at 160°C

Mix	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslinking Value ($1/Q$)
1	0.562 (0.320)	13.56 (4.59)	730 (345)	46 (38)	0.338 [4.13]
2	0.850 (1.050)	1.30 (1.05)	330 (200)	55 (57)	0.313 [6.37]
3	0.547 (0.300)	10.01 (5.08)	705 (510)	47 (45)	0.264 [6.40]
4	0.395 (0.464)	1.75 (1.41)	530 (315)	a	— [51.4]
5	0.171 (0.190)	0.29 (0.28)	460 (415)	a	—

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

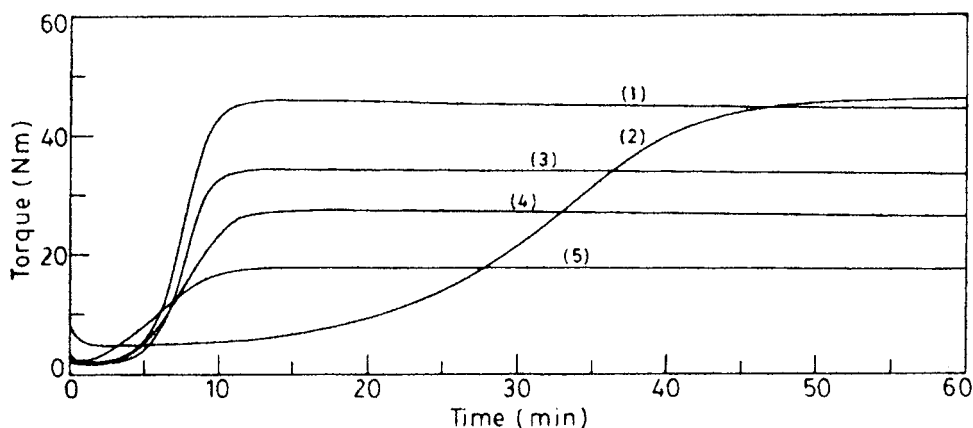a Hardness could not be determined due to the undercured state of the vulcanizates.

Figure 1 Rheographs of mixes 1–5 (Table I) cured at 160°C.

tion from one rubbery phase to the other. Nevertheless, the results appear to indicate that the most favorable condition persists in the case of mix 3, where the weight loss is comparable with the pure rubber constituents, though much reduced $1/Q$ value was observed. This evidently generates vulcanizates of highest modulus, tensile strength and elongation at break among the blends.

Vulcanizates obtained from EPDM are resistant to heat and oxidation due to the low unsaturation level and absence of any unsaturation in the backbone chain. DIPDIS – accelerated NR vulcanizates possess high thermal and thermal oxidative stability due to the formation of zinc diisopropyldithiophosphate (ZDP) in situ.[42] So it is expected that the blends would also exhibit this

phenomenon even in absence of any antioxidant in the composition. Actually this is observed in the retention of modulus and tensile strength values (Table II) of vulcanizates aged for 72 h at 100°C, particularly for the pure EPDM and EPDM – rich blends (mixes 2 and 5). Although mix 5 has the highest concentration of EPDM, it suffers from the worst curative migration, leaving the major bulk of the mix undercured. This is reflected in the reduced R_∞, modulus, and tensile strength values of the blend vulcanizates.

Two-Stage Vulcanization

Our objective was to increase the concentration of the rubber-bound intermediates through the incorporation of adequate amount of DIPDIS in

Table III   Formulation of Mixes and Cure Characterisitics of Two-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R-100)

	Mix	3′	4′	5′
First stage	EPDM	25	50	75
	ZnO	5	5	5
	Stearic acid	2	2	2
	DIPDIS	3.834[a]	3.834[a]	3.834[a]
	S	0.5	0.5	0.5
Second stage (after preheating[b] compounded EPDM at first stage)	NR	75	50	25
Maximum rheometric torque, R_∞ (Nm)		4.45	4.10	3.15
Scorch time, t_2 (min)		1.75	2.25	2.00
Optimum cure time, t_{90} (min)		6.25	7.00	8.25

EPDM, ethylene–propylene–diene rubber; ZnO, zinc oxide; DIPDIS, diisopropylthiophosphoryl disulfide; S, sulfur; NR, natural rubber.

[a] Weight corresponds to 9 mmol DIPDIS.

[b] Preheating times (t) for all mixes at 160°C are 10 min.
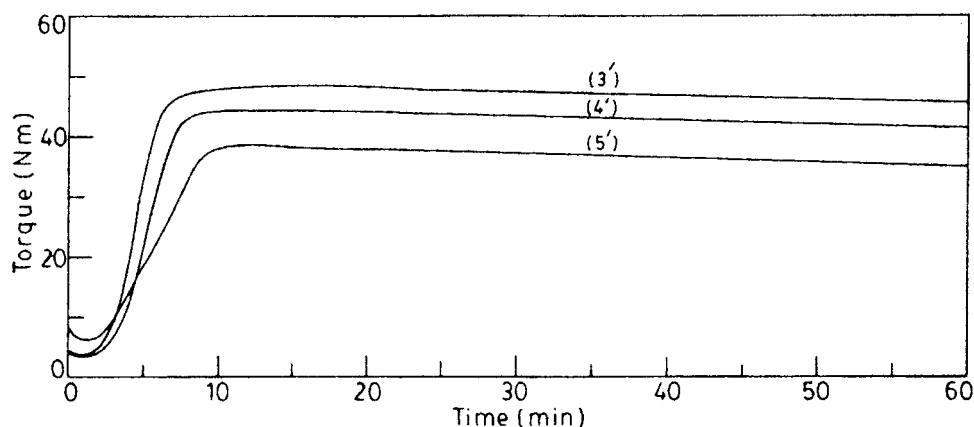
Figure 2   Rheographs of mixes 3′–5′ (Table III) cured at 160°C.

EPDM, followed by heating for a predetermined period, in accordance with the procedure as described in the experimental section for two-stage vulcanization.[46,47] The grossly undercured material obtained in the first stage favorably contains a higher amount of reactive fragments compared with that in one-stage vulcanization. The intermediates thus formed are expected to combine with NR in the second stage of the procedure, the resultant effect being the generation of more inter-rubber linkages and formation of novel rubber blends of significantly improved physical properties.

Table III presents the composition and cure characteristics of the blends in two-stage vulcanization, with DIPDIS-to-EPDM ratio varied to obtain the desired results. As expected the R_∞ values of the blend vulcanizates increase with the increased DIPDIS concentration, followed by reduction in t_2 and t_{90} values. Figure 2 presents the cure curves of the two-stage vulcanization. Each blend was preheated for 10 min and the physical properties of the vulcanizates

(mixes 3′, 4′, and 5′) in two-stage vulcanization are shown in Table IV. In all cases, there is a significant improvement in modulus, tensile strength, elongation at break, and crosslinking value ($1/Q$) over those obtained in one-stage vulcanization of the corresponding blends. The weight losses in the swelling experiment are also comparable to that of the pure mixes (mixes 1 and 2), indicating adequate degree of vulcanization in the elastomeric blends. In the case of mix 5′, the weight loss is slightly higher, signifying a lower level of cure. It is evident from the physical data that the vulcanizate of mix 3′ exhibits the highest tensile strength, elongation at break, and $1/Q$ value. The modulus and hardness values do not support this, however, because EPDM, as already mentioned, has a higher base hardness than NR (Table II, mixes 1 and 2). Further, in two-stage vulcanization, the EPDM phase itself is well cured (higher intra-rubber crosslinking) by restricting the curative migration from the EPDM to NR phase. Regarding the percentage increment of

Table IV   Physical Properties of Two-Stage Vulcanizates Cured at 160°C

Mix	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness (Shore A)	Crosslinking Value ($1/Q$)
3′	0.726 (0.677)	14.23 (7.51)	760 (485)	47 (50)	0.322 [4.17]
4′	0.764 (0.784)	8.58 (4.95)	697 (450)	50 (53)	0.268 [6.81]
5′	0.782 (1.146)	4.05 (3.74)	607 (480)	52 (55)	0.205 [10.57]

Values in parentheses are aged values (aging done at 100 ± 1°C for 72 ± 1 h). Values in square brackets are percentage loss in weight during the swelling experiment.
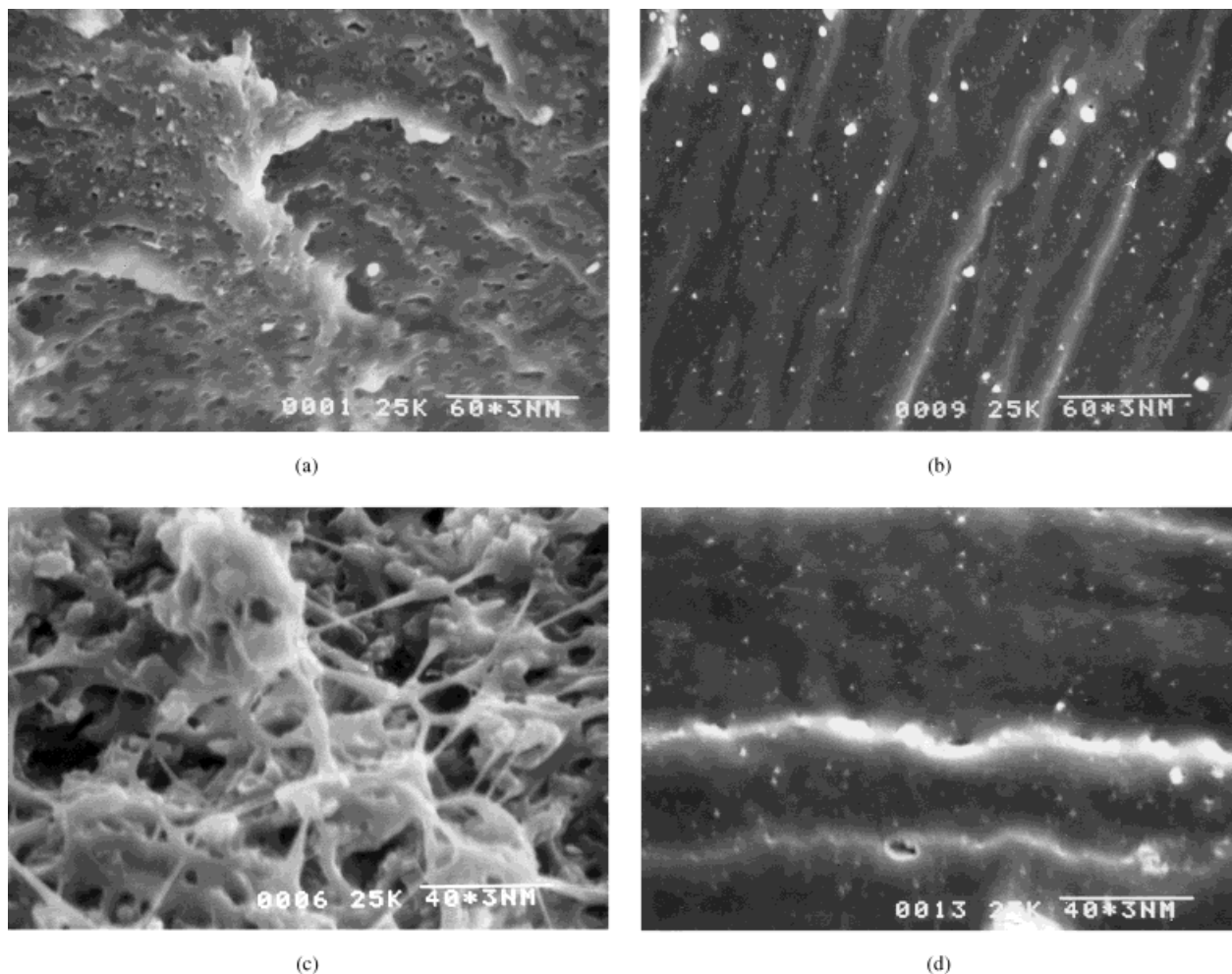
Figure 3 Scanning electron micrographs of tensile fractured surfaces of the vulcanizates cured at 160°C; (a) 75 25 unsaturated natural rubber–ethylene propylene diene (NR–EPDM) blend (one-stage) at 500 $\times$; (b) 75 : 25 NR–EPDM blend (two-stage) at 500 $\times$; (c) 50:50 NR–EPDM blend (one-stage) at 750 $\times$; (d) 50:50 NR–EPDM blend (two-stage) at 750 $\times$.

physical properties, mixes enriched with EPDM (mixes 4′ and 5′) show phenomenal results, indicating significant co-curing. Tensile strength and elongation at break values of mix 3′ even surpassed the values of individual component elastomers (mixes 1 and 2). The results indicate that the hardness of the vulcanizates remained almost unchanged and age resistance was also observed to follow the same trend as other physical properties.

All these findings might be explained by assuming the chemical reaction of pendant DIPDIS at the EPDM backbone at the first stage of the two-stage vulcanization so as to reduce the migration of the curatives to NR phase readily (especially at high temperature of vulcanization). This restricted migration of a portion of the curatives leads to the improved co-curing which brings about enhanced physical properties of NR–EPDM blend vulcanizates. These are depicted in schemes 1 and 2.

SEM Studies

SEM studies were considered to throw some light regarding the compactness and coherency of rubber matrix resulted from DIPDIS accelerated NR–EPDM blend. Samples were prepared in according to the procedure given in the experimental section.

Figure 3 displays the one- and two-stage vulcanizates. The fractured surfaces of the one-

stage vulcanizates [Fig. 3(a) and (c)] contain numerous vacuoles indicative of noncoherency among NR and EPDM in these regions; this results in poor mechanical properties of the vulcanizates of mixes 3 and 4 (Tables I, II). By contrast, Figure 3(b) and (d) indicate architectural homogeneity, accounting for the good physical properties of mixes 3′ and 4′ (Tables III, IV), respectively. The enhancement of physical properties can be visualized from the comparison of the micrographs. The ridge lines are highly visible in two-stage vulcanizates (micrographs based on Fig. 3). It is further evident that, in two-stage vulcanization, the number of vacuoles are reduced significantly and this results in the formation of compact rubber matrix.

CONCLUSIONS

The investigations carried out for the vulcanization of NR–EPDM binary blends suggest that the physical properties of the vulcanizates could be significantly improved by the judicious selection of NR-to-EPDM ratio and the concentration of DIPDIS in the compound. These properties can further be improved by two-stage vulcanization. The preliminary study regarding SEM indicates coherency between NR and EPDM phases in the blend vulcanizates and corroborates the reaction of DIPDIS at the interface of dissimilar elastomeric domains. However, further investigations remain to be carried out in order to understand clearly the mechanism of the reaction of DIPDIS and the mode of linking in the blend of NR and EPDM.

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