



TABLE I  
Formulation of Mixes for One-Stage Vulcanization

| Mix <sup>a</sup> | NR  | XNBR | DIBDIS             | DIBTRI             | DIBTET             | DCHDIS             | DCHTRI             | DCHTET             |
|------------------|-----|------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 1                | 100 | —    | 4.338 <sup>b</sup> | —                  | —                  | —                  | —                  | —                  |
| 2                | —   | 100  | 4.338 <sup>b</sup> | —                  | —                  | —                  | —                  | —                  |
| 3                | 75  | 25   | 4.338 <sup>b</sup> | —                  | —                  | —                  | —                  | —                  |
| 4                | 50  | 50   | 4.338 <sup>b</sup> | —                  | —                  | —                  | —                  | —                  |
| 5                | 25  | 75   | 4.338 <sup>b</sup> | —                  | —                  | —                  | —                  | —                  |
| 6                | 100 | —    | —                  | 4.626 <sup>c</sup> | —                  | —                  | —                  | —                  |
| 7                | —   | 100  | —                  | 4.626 <sup>c</sup> | —                  | —                  | —                  | —                  |
| 8                | 75  | 25   | —                  | 4.626 <sup>c</sup> | —                  | —                  | —                  | —                  |
| 9                | 50  | 50   | —                  | 4.626 <sup>c</sup> | —                  | —                  | —                  | —                  |
| 10               | 25  | 75   | —                  | 4.626 <sup>c</sup> | —                  | —                  | —                  | —                  |
| 11               | 100 | —    | —                  | —                  | 4.914 <sup>d</sup> | —                  | —                  | —                  |
| 12               | —   | 100  | —                  | —                  | 4.914 <sup>d</sup> | —                  | —                  | —                  |
| 13               | 75  | 25   | —                  | —                  | 4.914 <sup>d</sup> | —                  | —                  | —                  |
| 14               | 50  | 50   | —                  | —                  | 4.914 <sup>d</sup> | —                  | —                  | —                  |
| 15               | 25  | 75   | —                  | —                  | 4.914 <sup>d</sup> | —                  | —                  | —                  |
| 16               | 100 | —    | —                  | —                  | —                  | 5.274 <sup>e</sup> | —                  | —                  |
| 17               | —   | 100  | —                  | —                  | —                  | 5.274 <sup>e</sup> | —                  | —                  |
| 18               | 75  | 25   | —                  | —                  | —                  | 5.274 <sup>e</sup> | —                  | —                  |
| 19               | 50  | 50   | —                  | —                  | —                  | 5.274 <sup>e</sup> | —                  | —                  |
| 20               | 25  | 75   | —                  | —                  | —                  | 5.274 <sup>e</sup> | —                  | —                  |
| 21               | 100 | —    | —                  | —                  | —                  | —                  | 5.562 <sup>f</sup> | —                  |
| 22               | —   | 100  | —                  | —                  | —                  | —                  | 5.562 <sup>f</sup> | —                  |
| 23               | 75  | 25   | —                  | —                  | —                  | —                  | 5.562 <sup>f</sup> | —                  |
| 24               | 50  | 50   | —                  | —                  | —                  | —                  | 5.562 <sup>f</sup> | —                  |
| 25               | 25  | 75   | —                  | —                  | —                  | —                  | 5.562 <sup>f</sup> | —                  |
| 26               | 100 | —    | —                  | —                  | —                  | —                  | —                  | 5.850 <sup>g</sup> |
| 27               | —   | 100  | —                  | —                  | —                  | —                  | —                  | 5.850 <sup>g</sup> |
| 28               | 75  | 25   | —                  | —                  | —                  | —                  | —                  | 5.850 <sup>g</sup> |
| 29               | 50  | 50   | —                  | —                  | —                  | —                  | —                  | 5.850 <sup>g</sup> |
| 30               | 25  | 75   | —                  | —                  | —                  | —                  | —                  | 5.850 <sup>g</sup> |

<sup>a</sup> All the mixes contain ZnO, 5 g; stearic acid, 2 g, sulfur, 0.5 g.

<sup>b</sup> Weight corresponds to 9 mmol DIBDIS.

<sup>c</sup> Weight corresponds to 9 mmol DIBTRI.

<sup>d</sup> Weight corresponds to 9 mmol DIBTET.

<sup>e</sup> Weight corresponds to 9 mmol DCHDIS.

<sup>f</sup> Weight corresponds to 9 mmol DCHTRI.

<sup>g</sup> Weight corresponds to 9 mmol DCHTET.

The characteristics of XNBR, Krynac-X 7.50 (Bayer Polymeres, France), are as follows: carboxylic acid, ~7%; monomer content, 27.3%; Mooney viscosity, ML<sub>(1+4)</sub> at 100°C, 49; total ash content, 0.21%; volatiles, 0.2%; specific gravity, 0.98. Natural rubber (RMA 1×) was procured from the local market.

### Preparation of vulcanizates

#### Single rubber vulcanizates

Requisite amounts of compounding ingredients were incorporated in previously masticated rubber on a Berstorff laboratory-size (203 × 102 mm) two-roll mixing mill. Finally, sulfur was added to the mix after cooling the mill. The stocks were cured under pressure at 160°C.

#### Blend vulcanizates

In the present investigation, two types of blending procedures were adopted: one-stage vulcanization

and two-stage vulcanization. The details of these procedures were discussed earlier.<sup>5</sup>

### Rheometric studies

Cure characteristics of rubber mixes were determined by Monsanto Oscillating Disk Rheometer, R-100, with 3° arc oscillation.

### Measurement of physical properties

Physical properties, such as modulus at 200% elongation and tensile strength, were measured according to ASTM D412-51T in an Amsler (Sweden) tensile tester. The hardness was determined according to ASTM D2240-85 by using a Shore-A durometer.

The procedure for the determination of age resistance and oil resistance of the vulcanizates was discussed earlier.<sup>5,11</sup>

**TABLE II**  
Cure Characteristics and Physical Properties of DIBDIS, DIBTRI, and DIBTET Accelerated One-Stage Vulcanizates Cured at 160°C

| Mix | Maximum torque<br>$R_x$ (Nm) | Scorch time<br>$t_2$ (min) | Optimum cure time<br>$t_{90}$ (min) | 200% Modulus (MPa)       | Tensile strength (MPa) | Elongation at break (%) | Hardness shore-A | Swelling index (Q) | Crosslinking value (1/Q) |
|-----|------------------------------|----------------------------|-------------------------------------|--------------------------|------------------------|-------------------------|------------------|--------------------|--------------------------|
| 1   | 2.45                         | 5.00                       | 12.0                                | 0.27 (0.39) <sup>a</sup> | 14.07 (1.01)           | 790 (350)               | 45 (52)          | 3.937              | 0.254                    |
| 2   | 4.80                         | 0.50                       | 20.5                                | 1.68 (1.93)              | 10.05 (9.80)           | 610 (500)               | 66 (70)          | 0.410              | 2.441                    |
| 3   | 2.30                         | 6.00                       | 12.5                                | 0.48 (0.65)              | 10.30 (5.60)           | 680 (480)               | 52 (56)          | 2.956              | 0.338                    |
| 4   | 2.42                         | 6.00                       | 14.5                                | 1.00 (1.55)              | 10.94 (7.25)           | 530 (450)               | 60 (63)          | 2.062              | 0.485                    |
| 5   | 2.80                         | 0.50                       | 16.5                                | 1.60 (1.92)              | 16.03 (12.36)          | 540 (460)               | 66 (70)          | 1.114              | 0.897                    |
| 6   | 3.50                         | 2.50                       | 6.0                                 | 0.63 (0.98)              | 15.10 (0.98)           | 670 (200)               | 52 (55)          | 3.140              | 0.318                    |
| 7   | 5.60                         | 0.50                       | 17.0                                | 1.70 (2.14)              | 10.51 (9.77)           | 470 (440)               | 66 (70)          | 0.390              | 2.561                    |
| 8   | 3.35                         | 2.50                       | 6.5                                 | 0.93 (1.49)              | 14.20 (4.24)           | 620 (340)               | 55 (58)          | 2.465              | 0.406                    |
| 9   | 3.40                         | 2.50                       | 8.5                                 | 1.41 (1.88)              | 15.54 (10.07)          | 530 (520)               | 62 (64)          | 1.804              | 0.554                    |
| 10  | 3.93                         | 0.25                       | 10.5                                | 1.80 (2.57)              | 18.36 (13.30)          | 520 (410)               | 66 (71)          | 0.956              | 1.046                    |
| 11  | 3.95                         | 1.50                       | 4.5                                 | 0.75 (-)                 | 16.10 (0.95)           | 650 (190)               | 55 (55)          | 3.105              | 0.322                    |
| 12  | 6.20                         | 0.25                       | 26.0                                | 1.72 (2.20)              | 11.06 (7.50)           | 460 (410)               | 66 (69)          | 0.376              | 2.660                    |
| 13  | 3.70                         | 3.00                       | 6.0                                 | 0.91 (1.54)              | 14.69 (3.10)           | 600 (300)               | 57 (60)          | 2.209              | 0.453                    |
| 14  | 3.80                         | 2.50                       | 7.5                                 | 1.40 (1.91)              | 15.64 (7.30)           | 510 (450)               | 60 (65)          | 1.660              | 0.602                    |
| 15  | 4.25                         | 0.25                       | 10.0                                | 1.70 (2.51)              | 20.18 (11.02)          | 530 (400)               | 66 (71)          | 0.874              | 1.144                    |

<sup>a</sup> Values in parentheses are the aged properties of the vulcanizates at  $(100 \pm 1)^\circ\text{C}$  for 72 h.

### Scanning electron microscopy (SEM) studies

SEM was carried out on the fractured surfaces of the specimens derived from tensile testing by using a scanning electron microscope (Hitachi, model S-415A) in accordance with the procedure given previously.<sup>5</sup>

## RESULTS AND DISCUSSION

### One-stage vulcanization with bis(diisobutyl) thiophosphoryl compounds

This section deals with the comparative study of the activities of various thiophosphoryl sulfides in the vulcanization of NR–XNBR blends. It is observed by us that bis(diisopropyl) thiophosphoryl di- and poly-

sulfides are capable of promoting chemical links between XNBR and NR.<sup>5</sup> Thus, two dissimilar phases are brought close to one another. From the proposed reaction scheme,<sup>5</sup> it is evident that the alkyl group ( $R$ ) of the thiophosphoryl compound plays an important role in interrubber crosslinking. Allowing for the efficiency of these thiophosphoryl compounds in the vulcanization<sup>4</sup> of rubber, only those compounds obtained with isobutyl alcohol and cyclohexyl alcohol will be considered here for studying their performance in the blends under investigation. Table I records the compositions of various mixes used in the present investigation and Table II provides information regarding the vulcanizing activity of these compounds. It is ev-

**TABLE III**  
Formulation of Mixes for Two-Stage Vulcanization Using DIBDIS, DIBTRI and DIBTET

| Mix                                                                       | 3'                | 4'                | 5'                | 8'                | 9'                | 10'               | 13'               | 14'               | 15'               |
|---------------------------------------------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| First stage                                                               |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| NR                                                                        | 75                | 50                | 25                | 75                | 50                | 25                | 75                | 50                | 25                |
| ZnO                                                                       | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 |
| Stearic acid                                                              | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 |
| DIBDIS                                                                    | 4.34 <sup>a</sup> | 4.34 <sup>a</sup> | 4.34 <sup>a</sup> | —                 | —                 | —                 | —                 | —                 | —                 |
| DIBTRI                                                                    | —                 | —                 | —                 | 4.63 <sup>b</sup> | 4.63 <sup>b</sup> | 4.63 <sup>b</sup> | —                 | —                 | —                 |
| DIBTET                                                                    | —                 | —                 | —                 | —                 | —                 | —                 | 4.91 <sup>c</sup> | 4.91 <sup>c</sup> | 4.91 <sup>c</sup> |
| S                                                                         | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               |
| Second stage (after preheating <sup>d</sup> compounded NR at first stage) |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| XNBR                                                                      | 25                | 50                | 75                | 25                | 50                | 75                | 25                | 50                | 75                |

<sup>a</sup> Weight corresponds to 9 mmol DIBDIS.

<sup>b</sup> Weight corresponds to 9 mmol DIBTRI.

<sup>c</sup> Weight corresponds to 9 mmol DIBTET.

<sup>d</sup> Preheating times ( $t$ ) for mixes 3', 4', 5', 8', 9', 10', 13', 14', and 15' at  $140^\circ\text{C}$  are 20, 19, 18, 6, 5.5, 4.5, 5.5, 5, and 4 min, respectively.

TABLE IV  
Cure Characteristics and Physical Properties of DIBDIS, DIBTRI, and DIBTET Accelerated Two-Stage Vulcanizates Cured at 160°C

| Mix | Maximum torque<br>$R_{\infty}$ (Nm) | Scorch time<br>$t_2$ (min) | Optimum cure time<br>$t_{90}$ (min) | 200% Modulus (MPa)       | Tensile strength (MPa) | Elongation at break (%) | Hardness shore-A | Swelling index (Q) | Crosslinking Value (1/Q) |
|-----|-------------------------------------|----------------------------|-------------------------------------|--------------------------|------------------------|-------------------------|------------------|--------------------|--------------------------|
| 3'  | 2.85                                | 1.75                       | 9.00                                | 0.60 (1.02) <sup>a</sup> | 13.67 (7.41)           | 670 (480)               | 53 (55)          | 2.605              | 0.384                    |
| 4'  | 3.15                                | 2.00                       | 9.00                                | 1.15 (1.63)              | 15.22 (11.66)          | 620 (480)               | 60 (64)          | 1.806              | 0.554                    |
| 5'  | 3.60                                | 1.25                       | 9.00                                | 1.92 (2.18)              | 17.00 (13.20)          | 570 (490)               | 67 (70)          | 0.942              | 1.061                    |
| 8'  | 3.40                                | 0.25                       | 4.50                                | 1.14 (1.62)              | 14.25 (7.00)           | 600 (400)               | 56 (58)          | 2.267              | 0.441                    |
| 9'  | 3.65                                | 0.75                       | 5.00                                | 1.55 (2.07)              | 16.41 (10.43)          | 530 (410)               | 62 (65)          | 1.588              | 0.630                    |
| 10' | 4.05                                | 0.25                       | 8.00                                | 1.83 (2.41)              | 20.15 (14.00)          | 580 (440)               | 66 (70)          | 0.860              | 1.163                    |
| 13' | 3.90                                | 0.50                       | 4.75                                | 1.40 (1.87)              | 15.70 (6.25)           | 590 (390)               | 56 (57)          | 1.994              | 0.502                    |
| 14' | 4.10                                | 0.50                       | 5.25                                | 1.67 (2.10)              | 17.81 (10.12)          | 510 (400)               | 61 (63)          | 1.520              | 0.658                    |
| 15' | 4.55                                | 0.25                       | 9.75                                | 1.82 (2.60)              | 22.21 (14.20)          | 500 (380)               | 66 (69)          | 0.800              | 1.251                    |

<sup>a</sup> Values in parentheses are the aged properties of the vulcanizates at  $(100 \pm 1)^{\circ}\text{C}$  for 72 h.

ident from the cure data (mixes 1–5) that DIBDIS rapidly reacts with XNBR. Its reaction with blends becomes slow as the proportion of XNBR decreases. Thus, the scorch times ( $t_2$ ) for mixes 3 and 4 increase, whereas the scorch time for mix 5 diminishes sharply. Mixes 6–10 provide  $t_2$  data (Table II) for DIBTRI-accelerated mixes. From the results, it may be inferred that the reaction of DIBTRI with the pure rubbers and their blends is faster than DIBDIS and very close to that of DIBTET (mixes 11–15).

It can be seen from Table II that as the number of sulfur atoms increases for the thiophosphoryl compounds, the optimum cure times ( $t_{90}$ ) generally decrease for the blends. The observed increase in  $t_{90}$  values for the 100% XNBR mix accelerated by thiophosphoryl compounds (mixes 2, 7, and 12) are due to the marching cure. The  $t_{90}$  values for marching cure are apt to increase.

The maximum torque ( $R_{\infty}$ ) values of the rubber vulcanizates as recorded by the rheometer increase in the following manner:

$$\text{DIBDIS} < \text{DIBTRI} < \text{DIBTET}$$

This is expected as the rates and also the levels of cure for diene rubbers become faster as the number of sulfur atoms increased in the thiophosphoryl compounds.<sup>2</sup> The rate of increase is greater for XNBR than for NR, and this is also true for XNBR-rich blends.

Similar to the  $R_{\infty}$  values, the modulus of the rubber vulcanizates increases with the proportion of S atoms in the thiophosphoryl sulfides. In these cases also, the stocks containing 100% XNBR (mixes 2, 7, and 12) exhibit highest modulus for each of the di-, tri-, and tetrasulfide-accelerated stock. The XNBR-rich blends (mixes 5, 10, and 15) also show significant increment in modulus. This is mainly due to the formation of metalcarboxylate crosslinkages<sup>12</sup> in the XNBR phase.

Table II also records the tensile data for mixes 1–15. The data indicate the increment of tensile property of the vulcanizates of NR or XNBR with the increase of S atom in the thiophosphoryl compounds. The most interesting feature is that for each thiophosphoryl compound it is seen that XNBR-rich blends exhibit higher tensile values and the blend (75:25::XNBR:NR) attains the highest tensile strength, which is superior to either of the

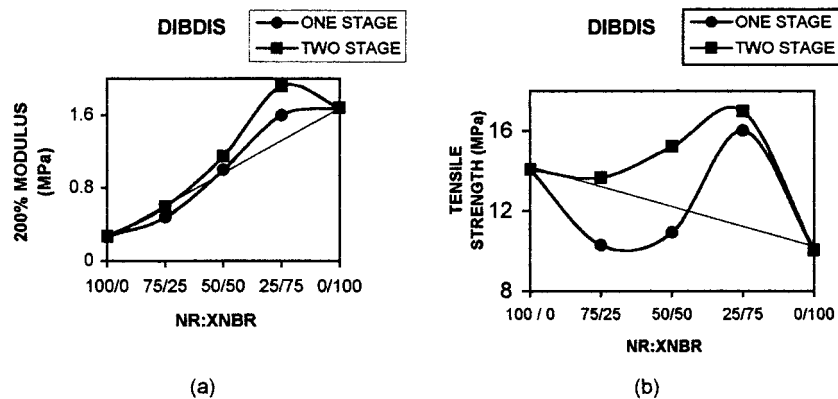


Figure 1 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DIBDIS.

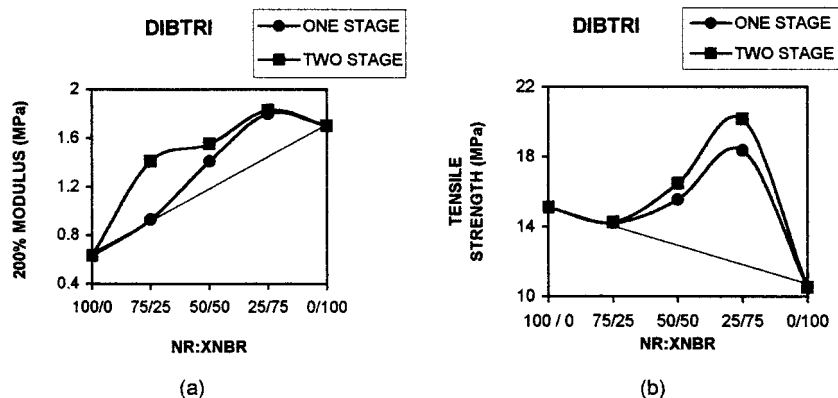


Figure 2 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DIBTRI.

pure elastomer. In elastomer blends, the mechanical integrity of an intercrosslinked morphology will usually lead to such superior performance.<sup>13–15</sup>

The elongation at break values, as can be seen from the table, diminish with the increase in S concentration in the thiophosphoryl compound. The minimum elongation values are, however, obtained with XNBR-rich vulcanizates.

Table II also provides Shore A hardness values of the vulcanizates derived from bis(diisobutyl) thiophosphoryl di-, tri-, and tetrasulfides. By comparing the hardness of the vulcanizates of NR and XNBR, it is found that the latter shows maximum hardness, whereas the blend vulcanizate rich in XNBR exhibits highest results which exceeds either of the individual elastomers for a particular thiophosphoryl compound.

In the swelling experiment, the vulcanizates were swollen in isooctane:toluene (70:30) medium for 48 h at  $30 \pm 2^\circ\text{C}$ . The swelling value,  $Q$ , defined as the grams of solvent per gram of rubber hydrocarbon, is readily calculated<sup>11</sup> from the expression:

$$Q = \frac{\text{Swollen weight} - \text{dried weight}}{(\text{Original weight} \times 100) / \text{Formula weight}}$$

where formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of rubber. A comparison of the crosslinking values was also made from the reciprocal of swelling values ( $1/Q$ ). The crosslinking data obtained from the swelling experiment of the vulcanizates from the single elastomer as well as from the blends have been shown in Table II. It is observed that XNBR swells less than NR. So, the blends containing higher amounts of XNBR are expected to swell less than those containing lesser amount of XNBR. Again, if the interrubber linkage exists at the interfacial region between XNBR and NR, then swelling restriction of the highly swollen NR phase occurs and this will certainly impart an additional influence on the swelling data. In our previous study,<sup>5</sup> it is observed that the blend containing 75% XNBR and 25% NR vulcanized with DIPDIS swells less than that vulcanized with tetramethyl-thiuram disulfide (TMTD). This is due to the fact that DIPDIS is capable of forming interrubber linkages at the interfacial region between XNBR and NR, but TMTD is not. This interrubber linkage is responsible for swelling restriction in the former case. In the present study, di-, tri-, and tetrasulfides of various thiophosphoryl com-

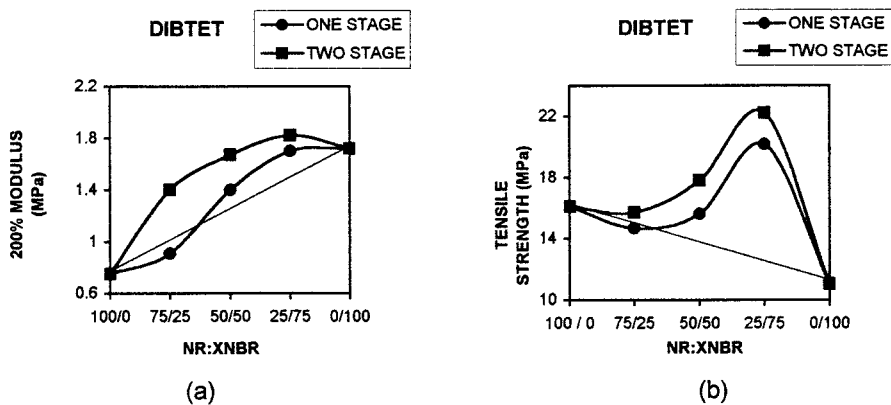
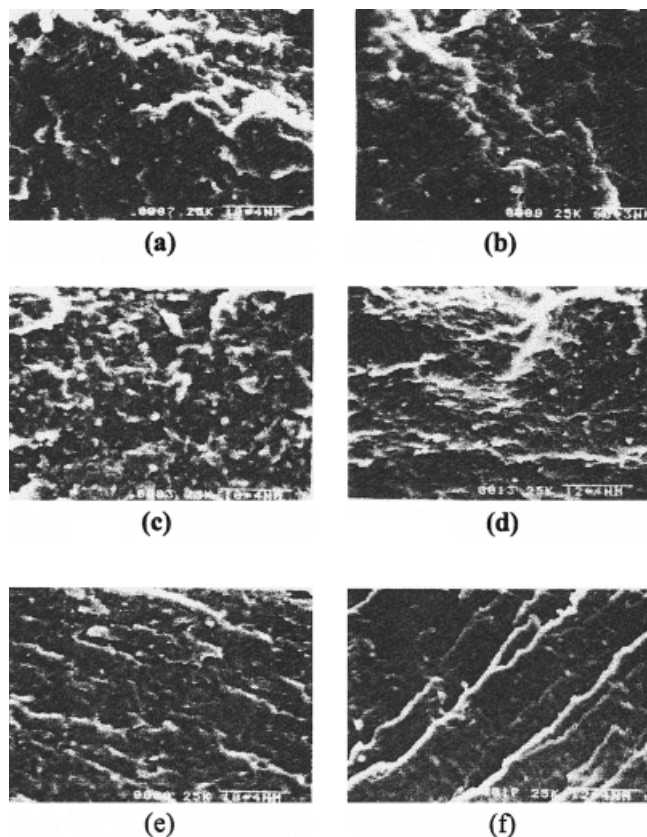


Figure 3 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DIBTET.



**Figure 4** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DIBDIS cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 300×; (b) NR : XNBR (75 : 25) blend (two stage) at 500×; (c) NR : XNBR (50 : 50) blend (one stage) at 300×; (d) NR : XNBR (50 : 50) blend (two stage) at 250×; (e) NR : XNBR (25 : 75) blend (one stage) at 300×; (f) NR : XNBR (25 : 75) blend (two stage) at 250×.

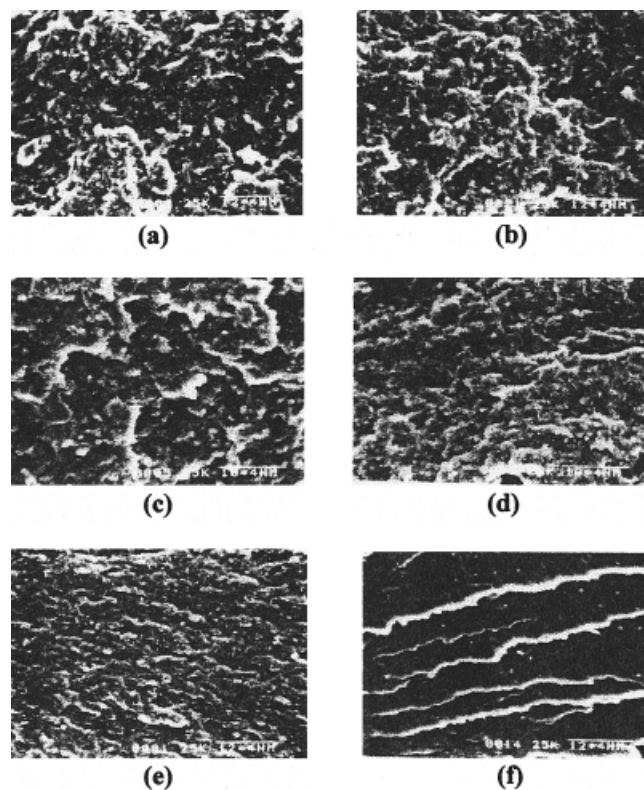
pounds are also capable of forming interrubber linkages which would certainly influence the swelling data ( $Q$ ) and hence crosslinking values ( $1/Q$ ). It is evident from the results that with the increasing amount of XNBR in the blend, the amount of crosslinks is also increasing. This indicates that more interrubber linkages are formed in the blends with an increasing amount of XNBR. The change in the concentration of crosslinks with the change in proportion of rubber in the blends accelerated with di-, tri-, and tetrasulfides of the various thiophosphoryl compounds is similar in nature.

### Two-stage vulcanization

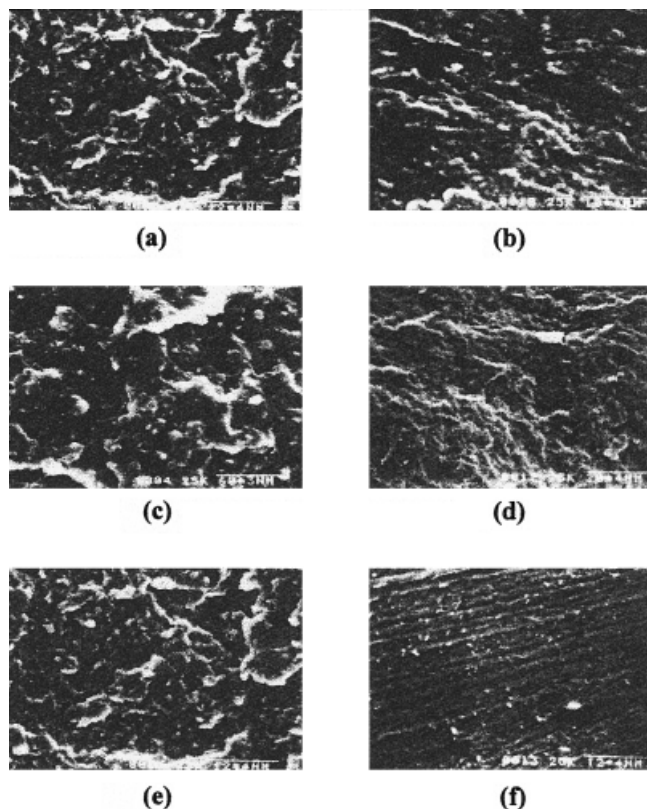
The importance of two-stage vulcanization using thiophosphoryl compounds was discussed in our previous studies<sup>5,16</sup> on elastomer blends. Hence, the study involving DIBDIS, DIBTRI, and DIBTET in two-stage vulcanization for the NR-XNBR blends becomes imperative to understand their role both as accelerator

and as coupling agent in vulcanization. Thus, several formulations were selected and these are presented in Table III. The cure and physical data for this two-stage vulcanization are given in Table IV. The most important and significant step in the two-stage vulcanization is the generation of rubber-bound moieties<sup>1,17</sup> from the accelerator complex with sulfur, etc. These rubber-bound moieties, which are the precursor<sup>18</sup> to the ultimate crosslinks, are responsible for subsequent vulcanization. Thus, owing to the prior formation of these rubber-bound moieties, a reduction in scorch safety occurs in two-stage vulcanization. Consequently, the optimum cure time decreases as compared to one-stage vulcanization. Also, there was the anticipated increase in the resultant torque and the modulus values. It is evident from the physical data of Table IV that the modulus at 200% elongation and tensile strength of all the vulcanizates are higher at two-stage vulcanization than those obtained in one-stage and these results clearly indicate the success of two-stage vulcanization.

However, it is difficult to draw any conclusion from the elongation-at-break values. The increase in hard-



**Figure 5** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DIBTRI cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 250×; (b) NR : XNBR (75 : 25) blend (two stage) at 250×; (c) NR : XNBR (50 : 50) blend (one stage) at 300×; (d) NR : XNBR (50 : 50) blend (two stage) at 300×; (e) NR : XNBR (25 : 75) blend (one stage) at 250×; (f) NR : XNBR (25 : 75) blend (two stage) at 250×.



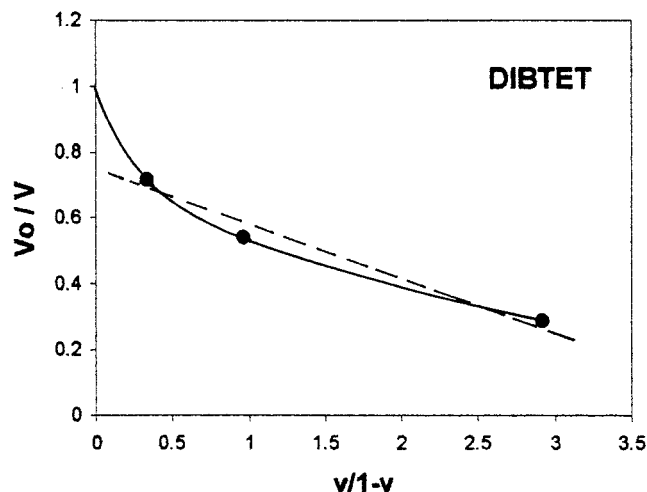
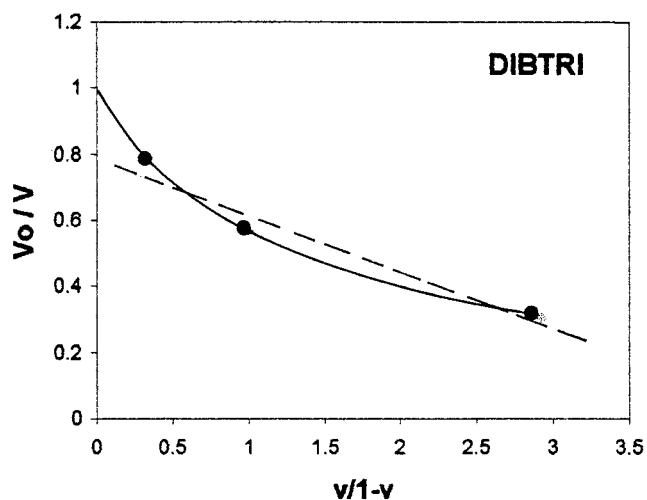
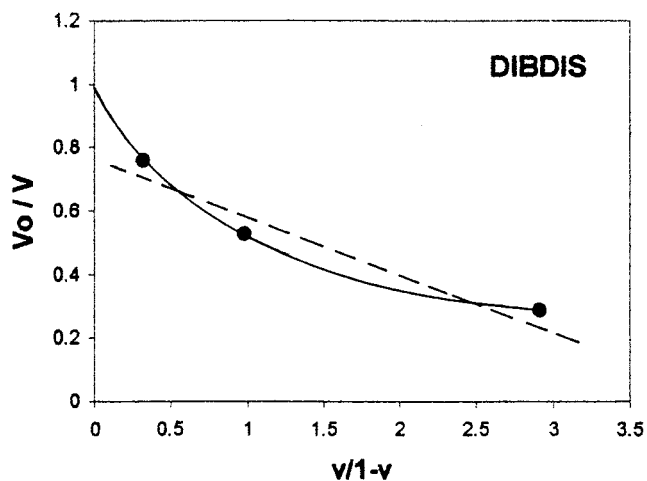
**Figure 6** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DIBTET cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 250×; (b) NR : XNBR (75 : 25) blend (two stage) at 300×; (c) NR : XNBR (50 : 50) blend (one stage) at 500×; (d) NR : XNBR (50 : 50) blend (two stage) at 150×; (e) NR : XNBR (25 : 75) blend (one stage) at 250×; (f) NR : XNBR (25 : 75) blend (two stage) at 250×.

ness (Shore A) for the vulcanizates in the two-stage vulcanization, in most of the cases, is marginal, although there are cases where hardness of the resulting vulcanizates remains unaltered.

The variation of tensile strength and 200% modulus values both in one-stage and in two-stage against blend composition in the presence of DIBDIS, DIBTRI, and DIBTET is shown in Figures 1-3, respectively, for easy and quick understanding of the discussion made so far. The figures clearly show a fair degree of synergism, which is at its maximum at the 25/75 NR/XNBR blend composition. In retrospect, this is, of course, an obvious claim that the blends under investigation are technologically compatible, having some degree of intermolecular interaction which is enhanced in the case of two-stage vulcanization.

#### Aged properties of the vulcanizates

Thiophosphoryl disulfides were shown to yield a substantial amount of zinc dithiophosphates<sup>1</sup> (ZDP) *in*



**Figure 7** Kraus plots of NR-XNBR blends in the presence of DIBDIS, DIBTRI, and DIBTET.

TABLE V  
Cure Characteristics and Physical Properties of DCHDIS, DCHTRI, and DCHTET accelerated One-Stage Vulcanizates Cured at 160°C

| Mix | Maximum torque<br>$R_x$ (Nm) | Scorch time<br>$t_2$ (min) | Optimum cure time<br>$t_{90}$ (min) | 200% Modulus (MPa)       | Tensile strength (MPa) | Elongation at break (%) | Hardness shore-A | Swelling index (Q) | Crosslinking value (1/Q) |
|-----|------------------------------|----------------------------|-------------------------------------|--------------------------|------------------------|-------------------------|------------------|--------------------|--------------------------|
| 16  | 3.50                         | 4.50                       | 11.5                                | 0.50 (0.54) <sup>a</sup> | 12.99 (2.00)           | 690 (350)               | 52 (52)          | 3.301              | 0.303                    |
| 17  | 4.70                         | 0.75                       | 19.0                                | 1.63 (2.15)              | 12.01 (11.98)          | 540 (450)               | 65 (71)          | 0.385              | 2.596                    |
| 18  | 3.10                         | 6.00                       | 13.5                                | 0.78 (1.04)              | 13.79 (8.31)           | 630 (500)               | 55 (55)          | 2.533              | 0.395                    |
| 19  | 3.20                         | 5.00                       | 15.5                                | 1.17 (1.73)              | 14.80 (10.10)          | 570 (500)               | 60 (61)          | 1.645              | 0.608                    |
| 20  | 3.50                         | 0.50                       | 17.5                                | 1.48 (2.56)              | 20.40 (15.5)           | 560 (440)               | 65 (70)          | 0.960              | 1.041                    |
| 21  | 3.60                         | 2.50                       | 5.50                                | 0.50 (.59)               | 14.10 (.74)            | 750 (240)               | 52 (46)          | 3.176              | 0.315                    |
| 22  | 5.50                         | 0.75                       | 16.5                                | 1.72 (2.43)              | 12.42 (12.65)          | 430 (410)               | 65 (70)          | 0.380              | 2.631                    |
| 23  | 3.25                         | 3.00                       | 7.0                                 | 0.99 (1.20)              | 15.20 (4.40)           | 620 (360)               | 56 (56)          | 2.426              | 0.412                    |
| 24  | 3.45                         | 3.00                       | 8.0                                 | 1.39 (2.26)              | 16.44 (11.20)          | 570 (400)               | 60 (63)          | 1.598              | 0.626                    |
| 25  | 3.70                         | 0.25                       | 10.5                                | 1.68 (3.18)              | 22.12 (18.10)          | 620 (400)               | 66 (70)          | 0.912              | 1.097                    |
| 26  | 3.70                         | 1.50                       | 4.0                                 | 0.58 (—)                 | 15.36 (0.51)           | 700 (180)               | 51 (48)          | 3.015              | 0.332                    |
| 27  | 6.20                         | 0.75                       | 19.5                                | 1.82 (2.80)              | 12.99 (8.91)           | 480 (340)               | 66 (72)          | 0.375              | 2.666                    |
| 28  | 3.50                         | 2.50                       | 5.5                                 | 1.00 (1.33)              | 15.88 (3.66)           | 630 (280)               | 55 (56)          | 2.066              | 0.484                    |
| 29  | 3.70                         | 2.50                       | 7.50                                | 1.39 (2.21)              | 17.18 (8.86)           | 520 (350)               | 62 (64)          | 1.494              | 0.669                    |
| 30  | 4.10                         | 0.50                       | 10.0                                | 1.68 (3.30)              | 24.27 (13.66)          | 580 (310)               | 66 (70)          | 0.810              | 1.234                    |

<sup>a</sup> Values in parentheses are the aged properties of the vulcanizates at  $(100 \pm 1)^\circ\text{C}$  for 72 h.

*situ*, which actively play the role of effective antioxidant.<sup>19,20</sup> So, it may be reasonably expected that DIBDIS-, DIBTRI-, and DIBTET-accelerated mixes would contain significant amounts of ZDP. It was thus decided to investigate the aging behavior of the vulcanizates derived from these accelerators. The results are shown in parentheses in Table II in connection with the physical data obtained in one-stage vulcanization. It is found from the table that modulus at 200% elongation for all the vulcanizates increases during the 72-h aging at  $100^\circ\text{C}$ . This is, however, expected. It is evident from the results that the aged property of the vulcanizates with regard to tensile strength is very poor for NR or NR-rich vulcanizates, where a drastic drop in strength is observed. However, the XNBR and

XNBR-rich vulcanizates containing metalcarboxylate crosslinkages<sup>12</sup> significantly resist this deleterious effect of aging. The fall in tensile strength is seen to be maximum in the case of tetrasulfide (DIBTET). This is probably due to the formation of polysulfidic crosslink, which undergoes oxidative degradation.<sup>21</sup>

The elongation at break values are severely affected for NR or NR-rich stock. XNBR-rich components resist the fall in elongation values. Similar to modulus, the hardness of all the vulcanizates increases during aging. The aged properties of the vulcanizates in two-stage vulcanization are shown in Table IV (values given in parentheses). The modulus and hardness of all the vulcanizates in two-stage vulcanization increase during aging as observed in one-stage vulcani-

TABLE VI  
Formulation of Mixes for Two-Stage Vulcanization Using DCHDIS, DCHTRI, and DCHTET

| Mix                                                                                | 18'               | 19'               | 20'               | 23'               | 24'               | 25'               | 28'               | 29'               | 30'               |
|------------------------------------------------------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| First stage                                                                        |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| NR                                                                                 | 75                | 50                | 25                | 75                | 50                | 25                | 75                | 50                | 25                |
| ZnO                                                                                | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 | 5                 |
| Stearic acid                                                                       | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 | 2                 |
| DCHDIS                                                                             | 5.27 <sup>a</sup> | 5.27 <sup>a</sup> | 5.27 <sup>a</sup> | —                 | —                 | —                 | —                 | —                 | —                 |
| DCHTRI                                                                             | —                 | —                 | —                 | 5.56 <sup>b</sup> | 5.56 <sup>b</sup> | 5.56 <sup>b</sup> | —                 | —                 | —                 |
| DCHTET                                                                             | —                 | —                 | —                 | —                 | —                 | —                 | 5.85 <sup>c</sup> | 5.85 <sup>c</sup> | 5.85 <sup>c</sup> |
| S                                                                                  | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               | 0.5               |
| Second stage<br>(after preheating <sup>d</sup><br>compounded NR<br>at first stage) |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| XNBR                                                                               | 25                | 50                | 75                | 25                | 50                | 75                | 25                | 50                | 75                |

<sup>a</sup> Weight corresponds to 9 mmol DCHDIS.

<sup>b</sup> Weight corresponds to 9 mmol DCHTRI.

<sup>c</sup> Weight corresponds to 9 mmol DCHTET.

<sup>d</sup> Preheating times ( $t$ ) for mixes 18', 19', 20', 23', 24', 25', 28', 29', and 30' at  $140^\circ\text{C}$  are 20, 19, 18, 5, 4.5, 3, 4.5, 4, and 3 min, respectively.



TABLE VII  
Cure Characteristics and Physical Properties of DCHDIS, DCHTRI, and DCHTET Accelerated Two-Stage Vulcanizates Cured at 160°C

| Mix | Maximum torque<br>$R_x$ (Nm) | Scorch time<br>$t_2$ (min) | Optimum cure time<br>$t_{90}$ (min) | 200% Modulus (MPa)       | Tensile strength (MPa) | Elongation at break (%) | Hardness shore-A | Swelling index (Q) | Crosslinking value (1/Q) |
|-----|------------------------------|----------------------------|-------------------------------------|--------------------------|------------------------|-------------------------|------------------|--------------------|--------------------------|
| 18' | 3.30                         | 1.50                       | 8.00                                | 0.85 (1.38) <sup>a</sup> | 15.58 (12.00)          | 630 (480)               | 56 (56)          | 2.182              | 0.458                    |
| 19' | 3.35                         | 1.00                       | 7.00                                | 1.25 (2.07)              | 16.65 (14.50)          | 590 (490)               | 62 (65)          | 1.540              | 0.650                    |
| 20' | 3.90                         | 1.25                       | 12.50                               | 1.58 (2.74)              | 23.35 (20.20)          | 620 (500)               | 68 (69)          | 0.860              | 1.162                    |
| 23' | 3.45                         | 0.75                       | 4.75                                | 1.17 (1.64)              | 16.07 (9.45)           | 610 (400)               | 56 (58)          | 2.109              | 0.474                    |
| 24' | 3.70                         | 0.75                       | 5.75                                | 1.92 (2.24)              | 19.02 (14.26)          | 580 (430)               | 60 (63)          | 1.495              | 0.669                    |
| 25' | 4.20                         | 1.00                       | 7.50                                | 2.32 (3.00)              | 24.81 (20.00)          | 530 (440)               | 67 (70)          | 0.840              | 1.190                    |
| 28' | 3.65                         | 0.75                       | 5.00                                | 1.26 (1.33)              | 18.04 (3.11)           | 600 (300)               | 56 (56)          | 1.930              | 0.518                    |
| 29' | 3.85                         | 0.50                       | 6.00                                | 1.83 (2.24)              | 21.11 (10.37)          | 540 (380)               | 61 (63)          | 1.435              | 0.697                    |
| 30' | 4.90                         | 1.00                       | 9.50                                | 2.55 (3.16)              | 27.37 (18.33)          | 590 (340)               | 70 (73)          | 0.722              | 1.385                    |

<sup>a</sup> Values in parentheses are the aged properties of the vulcanizates at  $(100 \pm 1)^\circ\text{C}$  for 72 h.

zation. A fall in the tensile strength values are observed for the aged vulcanizates. However, the degree of decrease is comparatively less than that seen in one stage. Stocks rich in XNBR generate vulcanizates in two-stage that are resistant, to some extent, to the harmful effect of oxidation.

### Solvent resistance

XNBR is notable for its unique oil- and solvent-resistance property, whereas that for NR is rather poor. In the case of blends, the interface crosslinking between NR and XNBR is likely to influence this property. Thus, the swelling behavior of the blend vulcanizates is expected to shed some light in this regard. Table II records swelling data which provide the solvent resistance of vulcanizates obtained with DIBDIS, DIBTRI, and DIBTET in one-stage vulcanization. It is evident that the NR vulcanizates exhibit poor resistance whereas, as expected, those derived from XNBR are quite resistant to solvent. NR-XNBR blends having 25 : 75 ratio (mixes 5, 10, and 15) do exhibit enhancement of solvent resistance in the presence of DIBDIS, DIBTRI, and DIBTET, although this is much lower

than that obtained solely with XNBR. It can be seen from the data that with the rise in the proportion of XNBR in the blend, the solvent resistance property (1/Q values) of the NR-XNBR vulcanizates increases. This property is further enhanced in the two-stage vulcanization process. It may be reasonably expected that the interfacial crosslinks cause swelling restriction<sup>22</sup> of the highly swollen phase. The swelling data for the blend vulcanizates obtained with DIBDIS, DIBTRI, and DIBTET in the two-stage vulcanization are recorded in Table IV. The data clearly indicate that the oil-resistance property of the blend vulcanizates in two-stage increases in the same manner as in one-stage vulcanization, but the values of 1/Q are increased further. These higher 1/Q values suggest the formation of more interfacial crosslinks between the elastomer phases in two-stage vulcanization.

### Scanning electron microscopy

The morphology of the blend vulcanizate arising from the polar and nonpolar rubbers is greatly influenced by the coupling agent through the introduction of

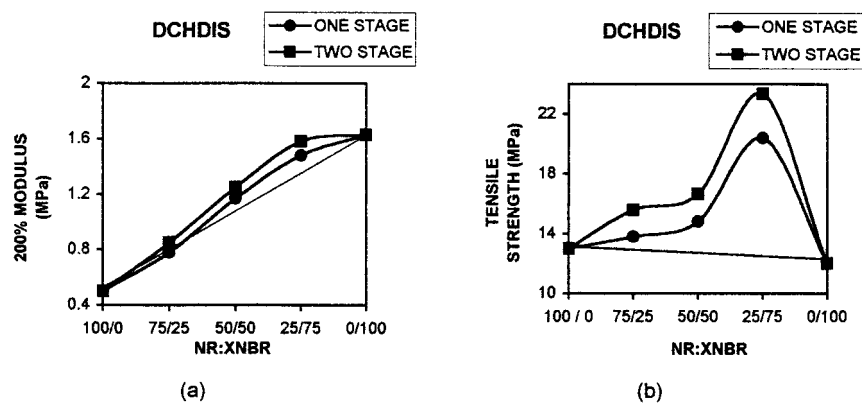


Figure 8 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DCHDIS.

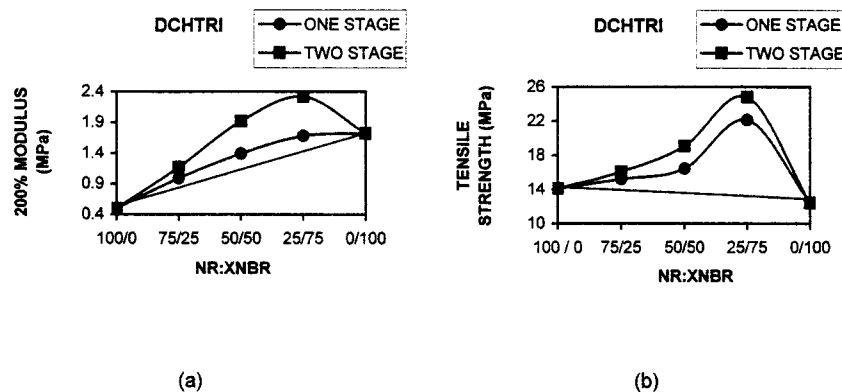


Figure 9 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DCHTRI.

interface crosslinking, which is apt to generate some orientations in the rubber matrix. It was thought that SEM study will shed some light in this regard. So, some SEM investigations were carried out on the tensile-fractured surfaces of the blend vulcanizates obtained in the presence of DIBDIS, DIBTRI, and DIBTET. It is found that the micrographs of 100% NR and 100% XBNR vulcanizates obtained in the presence of di-, tri-, and tetrasulfides of various thiophosphoryl compounds are more or less the same. Hence, these micrographs are considered redundant and only those of the blend vulcanizates concerned with one-stage and two-stage vulcanization are presented. Figures 4-6 represent SEM micrographs of DIBDIS-, DIBTRI-, and DIBTET-accelerated NR-XBNR blend vulcanizates, respectively. Micrographs derived from these three accelerated systems indicate similarity in the architecture for the respective matrices obtained in one-stage and two-stage vulcanization processes.

Figure 4(a,c,e) is the micrographs of tensile-fractured surfaces of the vulcanizates of mixes 3, 4, and 5 (Table I) obtained from one-stage vulcanization. It is visible from the surface texture that the phase distribution is improved and the orientation of the rubber matrix becomes more ordered as the proportion of XBNR is increasing in the blend. Figure 4(b,d,f) is the

SEM micrographs of the corresponding blend vulcanizates obtained from two-stage vulcanization. These micrographs exhibit more ordered orientation of the rubber matrix than those obtained from one-stage vulcanization. It is also observed that the two-stage vulcanizate matrices are more homogeneous and compact than those formed in one-stage vulcanization. This observed coherency between the two rubbers accounts for the improvement in the mechanical properties of the vulcanizates of mixes 3', 4', and 5' over mixes 3, 4, and 5, respectively. In the case of Figure 4(f), the long ridge lines indicative of reinforcement could be seen. These special architectures perhaps account for the superior physical properties of mix 5'.

The SEM micrographs presented in Figures 5 and 6 clearly indicate the similarity in architecture as stated earlier. So, the features of these micrographs can be explained in the same light as before.

The existence of interfacial linking between NR and XBNR in the presence of DIBDIS, DIBTRI, and DIBTET can also be established from the Kraus plot<sup>23</sup> following the equation:

$$V_0/V = 1 - M(v/1 - v)$$

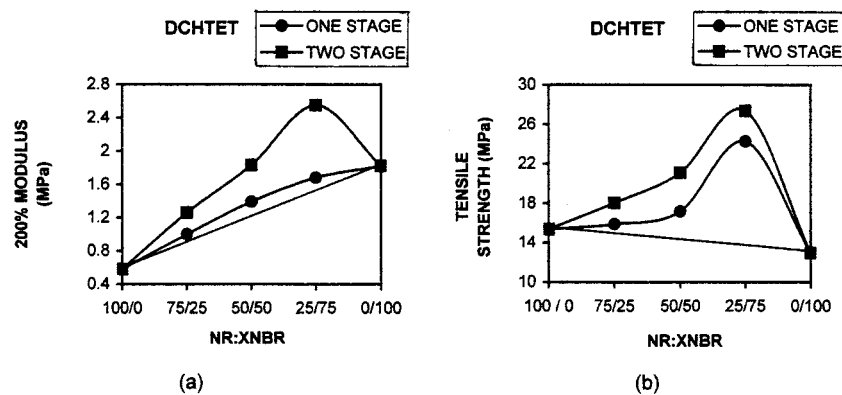
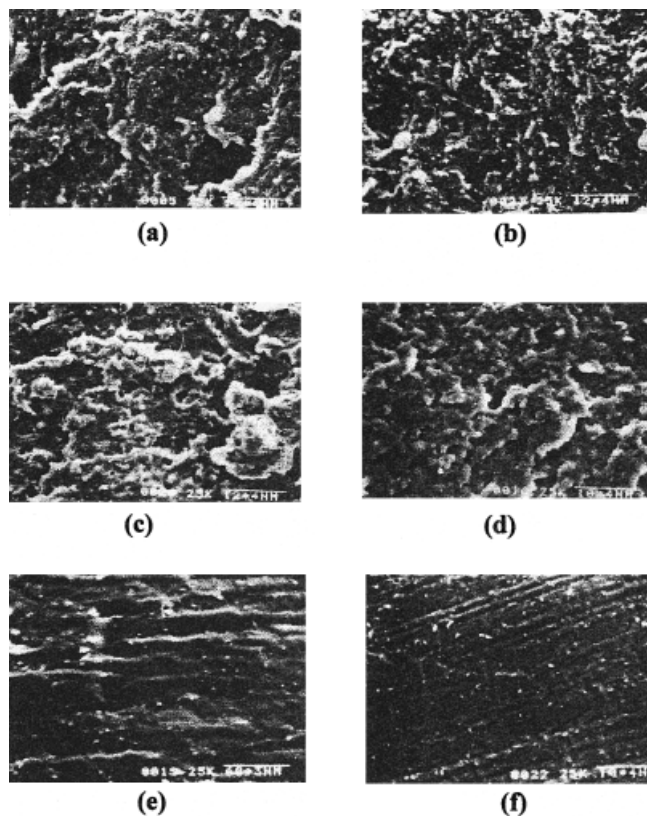


Figure 10 Variation of (a) 200% modulus and (b) tensile strength against blend composition in the presence of DCHTET.



**Figure 11** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DCHDIS cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 250×; (b) NR : XNBR (75 : 25) blend (two stage) at 250×; (c) NR : XNBR (50 : 50) blend (one stage) at 250×; (d) NR : XNBR (50 : 50) blend (two stage) at 300×; (e) NR : XNBR (25 : 75) blend (one stage) at 500×; (f) NR : XNBR (25 : 75) blend (two stage) at 300×.

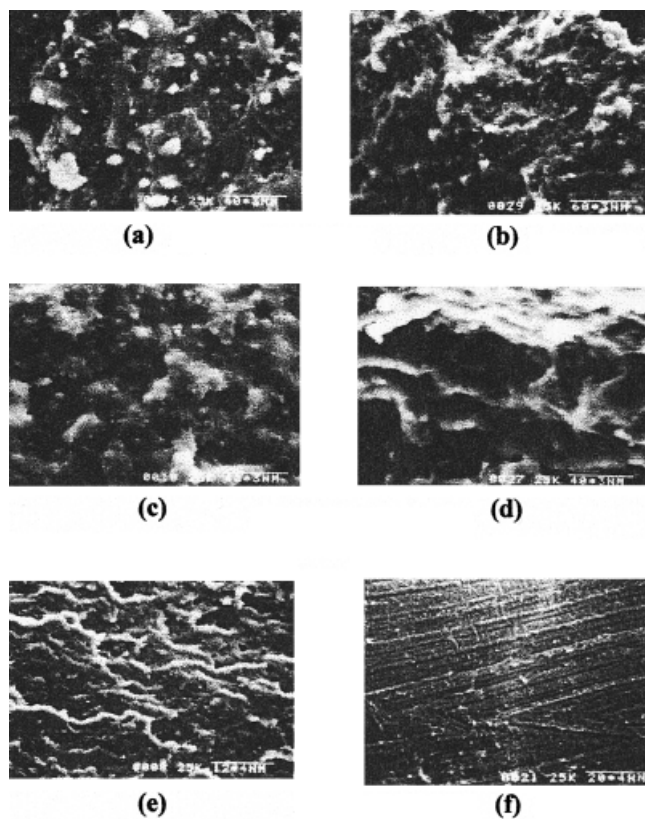
where  $V_0$  and  $V$  are the volume fraction of NR in the swollen pure NR vulcanizate and NR-XNBR blend vulcanizate, respectively,  $v$  is volume fraction of XNBR in the blend vulcanizates, and  $M$  is a parameter depending on  $V_0$  and the extent of swelling restriction. The vulcanizates were swollen in isooctane : toluene (70 : 30) medium. The plots of  $V_0/V$  against  $v/1 - v$  have been depicted in Figure 7. According to the Kraus equation, these plots form straight lines with an intercept of 1.0 on the  $y$ -axis. It is evident that the lines passing through the points deviate from linearity and cut the  $y$ -axis at 1.0. However, if straight lines are drawn, the intercept acquires a value lying between 0.7 and 0.8. Whatever may be the nature of the plots, the slopes are negative in all the cases, which suggests the formation of strong interrubber bonds.

#### One-stage vulcanization with bis(dicyclohexyl) thiophosphoryl compounds

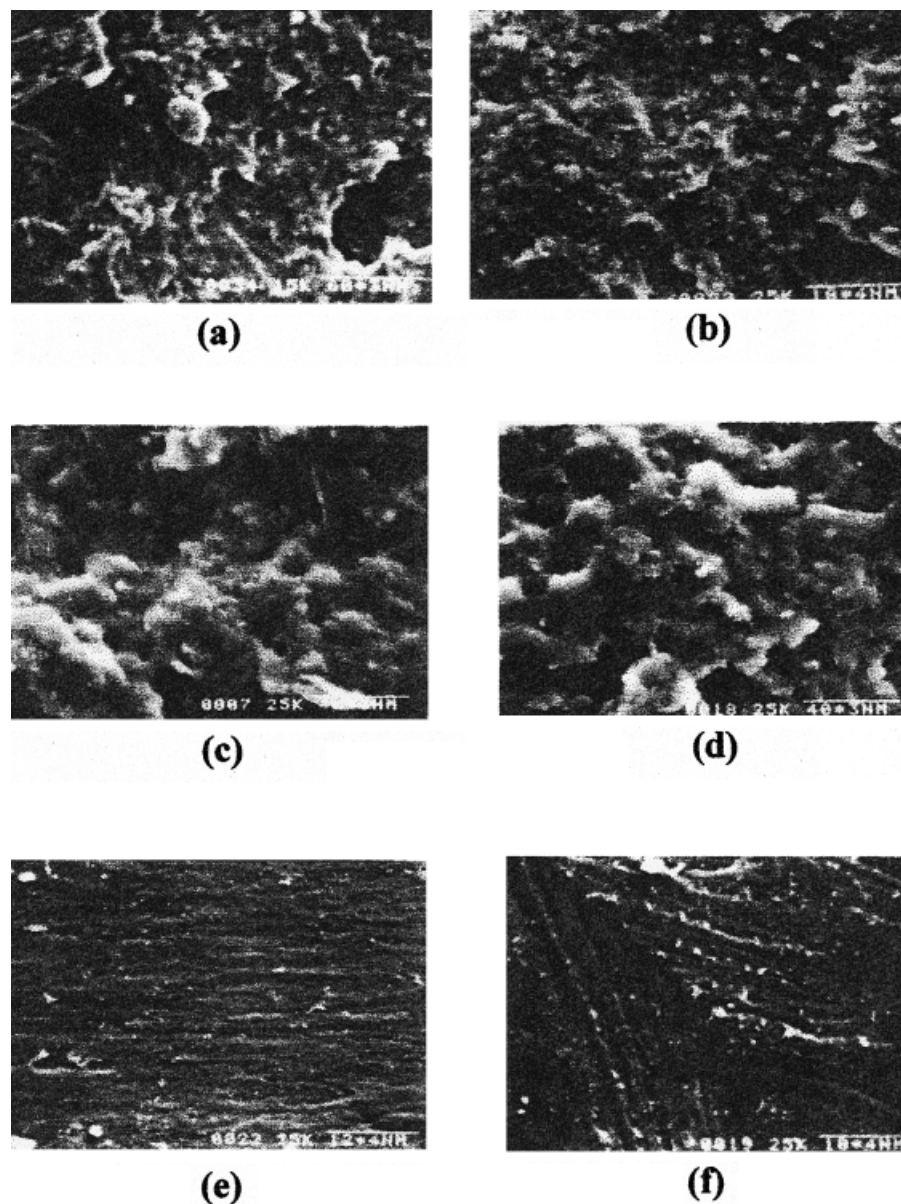
The compositions of the various mixes employed in the present investigation are shown in Table I. The

cure data obtained in the presence of di-, tri-, and tetrasulfides of bis(dicyclohexyl) thiophosphoryl compounds in the vulcanization of NR, XNBR, and their blends are presented in Table V through mixes 16–30.

It is evident from the table that DCHDIS, DCHTRI, and DCHTET react sharply with XNBR and hence there is no difference in the  $t_2$  values (mixes 17, 22, and 27; Table V). However, for NR (mixes 16, 21, and 26), we find a sharp fall in  $t_2$  values. With the gradual replacement of NR with XNBR, there occurs an initial rise in  $t_2$  (mixes 18, 19, 23, 24, 28, and 29) and thereafter an abrupt fall in XNBR-rich stocks (mixes 20, 25, and 30). The optimum cure time ( $t_{90}$ ) for NR when vulcanized with DCHDIS, DCHTRI, and DCHTET are seen to diminish with the introduction of higher polysulfides (mixes 16, 21, and 26). This is not so with XNBR vulcanization. In this case, we observe initial fall and then rise in  $t_{90}$  value (mixes 17, 22, and 27). The blends of NR and XNBR combine the individual effects, and thus, in XNBR-rich formulations (mixes 20, 25, and 30), highest values for optimum cure time are observed. It is apparent from the data that the  $R_\infty$  (max-



**Figure 12** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DCHTRI cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 750×; (b) NR : XNBR (75 : 25) blend (two stage) at 500×; (c) NR : XNBR (50 : 50) blend (one stage) at 750×; (d) NR : XNBR (50 : 50) blend (two stage) at 750×; (e) NR : XNBR (25 : 75) blend (one stage) at 250×; (f) NR : XNBR (25 : 75) blend (two stage) at 150×.



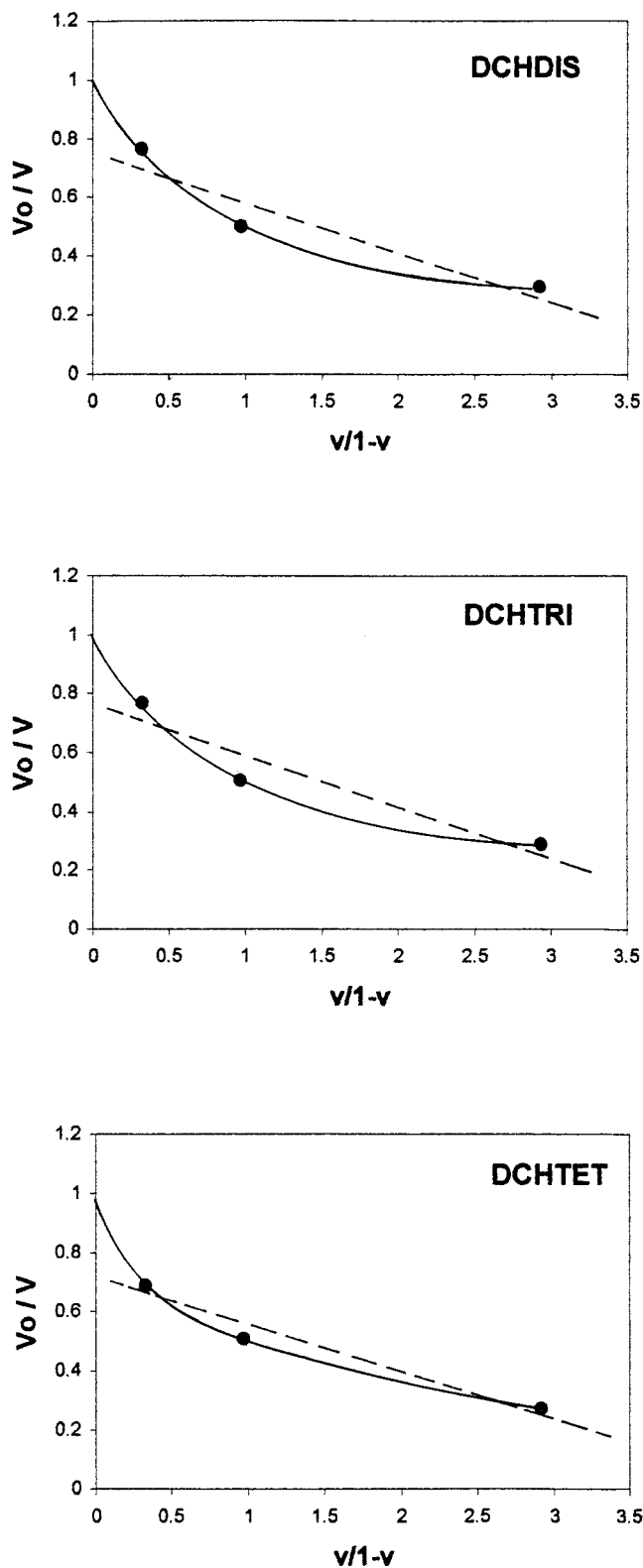
**Figure 13** SEM micrographs of tensile-fractured surfaces of the vulcanizates containing DCHTET cured at 160°C; (a) NR : XNBR (75 : 25) blend (one stage) at 500×; (b) NR : XNBR (75 : 25) blend (two stage) at 300×; (c) NR : XNBR (50 : 50) blend (one stage) at 750×; (d) NR : XNBR (50 : 50) blend (two stage) at 750×; (e) NR : XNBR (25 : 75) blend (one stage) at 250×; (f) NR : XNBR (25 : 75) blend (two stage) at 300×.

imum torque) values for DCHDIS-, DCHTRI-, and DCHTET-accelerated NR stocks (mixes 16, 21, and 26) are nearly the same, whereas there is progressive increase in the case of XNBR (mixes 17, 22, and 27). The intermediate compositions also exhibit this trend in  $R_x$  values with the progressive increase in XNBR concentration in the blend.

The modulus values of DCHDIS-, DCHTRI-, and DCHTET-accelerated vulcanizates increase in the order shown below:



It seems that the extra S atom is responsible for bringing about this change (mixes 16–30). The modulus values for the vulcanizates of XNBR-rich combinations are high, as can be seen from Table V. The tensile strength of the blend vulcanizates are notable. Similar to the modulus, the tensile strength of the vulcanizates follows the same order and the highest activity is exhibited by the XNBR-rich formulations (mixes 20, 25, and 30). It is reported<sup>13–15</sup> that introduction of interphase crosslinking in the blend vulcanizates usually leads to such superior property. The results indicate that the concentration of interphase crosslinking increases as the number of sulfur atoms increases in the thiophosphoryl compounds.



**Figure 14** Kraus plots of NR-XNBR blends in the presence of DCHDIS, DCHTRI, and DCHTET.

The elongation at break values are generally low for XNBR or XNBR-rich vulcanizates, whereas those for NR or NR-rich compositions are sufficiently high.

The hardness values are usually low for NR or NR-rich compounds but significantly high for XNBR or XNBR-rich vulcanizates. This is also true for the crosslinking brought about by DCHDIS, DCHTRI, and DCHTET.

The physical data of the aged vulcanizates obtained from DCHDIS-, DCHTRI-, and DCHTET-accelerated stocks are shown in Table V (the values are given in parentheses). Similar to bis(diisobutyl) thiophosphoryl di- and polysulfides, the modulus and hardness of the vulcanizates obtained in the presence of DCHDIS, DCHTRI, and DCHTET increase during hot air aging at  $100 \pm 1^\circ\text{C}$  for 72 h. Similarly, the tensile strength is affected drastically for NR or NR-rich vulcanizates, whereas the vulcanizates from XNBR or XNBR-rich formulations are capable of resisting this deleterious effect of aging to some extent. The changes with respect to elongation at break brought about during aging for the DCHDIS-, DCHTRI-, and DCHTET-accelerated vulcanizates are found to be similar in nature when compared with those effected by DIBDIS, DIBTRI, and DIBTET (compare the aged physical data of Table II with the corresponding data of Table V).

### Two-stage vulcanization

The compositions of mixes employed in two-stage vulcanization are shown in Table VI and the cure and physical data are recorded in Table VII. In the two-stage vulcanization, the compounds (mixes 18'-20', 23'-25', and 28'-30') to be vulcanized are deliberately made enriched with rubber-bound intermediates,<sup>5</sup> which ultimately take part in cure and thus the process becomes fast. Hence, scorch times and optimum cure times are reduced and the torque values of the vulcanizates are likely to increase. Actually, this was observed. The modulus and tensile strength values of the blend vulcanizates (compare the values in Table V with those in Table VII) in two-stage are increased significantly than those in one-stage. Significant improvement in the aged property with respect to tensile strength is observed due to the formation<sup>16</sup> of more interrubber linkages in two-stage vulcanization.

The variation of tensile strength and 200% modulus values both in one-stage and in two-stage against blend composition in the presence of DCHDIS, DCHTRI, and DCHTET is shown in Figures 8-10, respectively, for easy and quick understanding of the discussion made so far. The figures clearly show a fair degree of synergism, which is at its maximum at the 25/75 NR/XNBR blend composition. This study further lends support to the fact that technologically compatible blend vulcanizates having some degree of enhanced intermolecular interaction could be obtained from two-stage vulcanization.

### Solvent resistance

The solvent-resistance property of the vulcanizates derived from NR, XNBR, and their blends in the presence of DCHDIS, DCHTRI, and DCHTET in one-stage and two-stage is recorded in Tables V and VII, respectively. The results are similar to those obtained with bis(diisobutyl) thiophosphoryl compounds, but the difference is only in degrees.

### Scanning electron microscopy

The effectiveness of bis(dicyclohexyl) thiophosphoryl di- and polysulfides with regard to coupling activity could be judged from SEM. In this study, only the blend vulcanizates were included. The micrographs of 100% NR and XNBR are excluded for reasons mentioned earlier. The SEM micrographs of the tensile-fractured surface of the NR-XNBR blend vulcanizates derived from DCHDIS, DCHTRI, and DCHTET are depicted in Figures 11, 12, and 13, respectively. Micrographs (a), (c), and (e) of all these figures are of one-stage blend vulcanizates, whereas micrographs (b), (d), and (f) represent those obtained from two-stage vulcanization. The micrographs of two-stage vulcanizates in all cases exhibit much ordered orientation of the rubber matrix where steady ridge lines on the surface are observed.

The interfacial linking between NR and XNBR through the coupling agents (DCHDIS, DCHTRI, and DCHTET) and thus the occurrence of coherence between the two dissimilar rubbers can also be indirectly established by plotting  $V_0/V$  against  $v/(1 - v)$  in the well-known Kraus<sup>23</sup> plots shown in Figure 14, where

distinctly negative slopes appear, which indicate the presence of crosslinking between the elastomer phases.

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