

Novel Method for Preparation of Carboxylated Nitrile Rubber–Natural Rubber Blends Using Bis(diisopropyl)Thiophosphoryl Polysulfides

NITYANANDA NASKAR, SUBHAS CHANDRA DEBNATH, DIPAK KUMAR BASU

Polymer Science Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Received 14 March 2000; accepted 10 June 2000

ABSTRACT: Bis(diisopropyl)thiophosphoryl trisulfide (DIPTRI) and bis(diisopropyl)thiophosphoryl tetrasulfide (DIPTET) are successfully used as a novel coupling agent and accelerator, respectively, to covulcanize an elastomer blend comprising polar carboxylated nitrile rubber (XNBR) and nonpolar natural rubber (NR). These compounds are capable of forming a chemical link between these dissimilar rubbers to produce a technologically compatible blend as judged by a swelling experiment. The blend vulcanizates thus produced exhibit enhanced physical properties that can further be improved by adopting the two-stage vulcanization technique and also by judicious selection of the NR:XNBR ratio. The blend morphology assessed by scanning electron microscopy micrographs accounts for significant improvement in the physical properties of the blend vulcanizates, particularly in two-stage vulcanization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1725–1736, 2001

Key words: coupling agent; natural rubber–carboxylated nitrile rubber blend; technological compatibility; bis(diisopropyl)thiophosphoryl trisulfide; bis(diisopropyl)thiophosphoryl tetrasulfide

INTRODUCTION

Successful use was reported for bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) as a coupling agent¹ to produce a compatible blend of two dissimilar rubbers like natural rubber (NR) and carboxylated nitrile rubber (XNBR) through the formation of interfacial bonds.¹ The network structure thus produced exhibited improved physical properties than that of either pure component. A comparison of the curing characteristics of the thiophosphoryl di-, tri-, and tetrasulfides as sulfur donors² for diene rubbers made by the earlier researchers revealed that as the number of sulfur atoms increased in the thiophosphoryl com-

pounds the rates and the levels of cure also became higher and higher. In an earlier exploratory study we observed that thiophosphoryl polysulfides significantly enhanced the tensile strength of the vulcanizates obtained from styrene–butadiene rubber (SBR)–XNBR blends.³ Based on the above observations we became interested in investigating the effect of bis(diisopropyl)thiophosphoryl tri- and tetrasulfides (DIPTRI and DIPTET) in the vulcanization of NR–XNBR blends because both of these components play a significant role in the formation of interfacial crosslinks between the elastomer phases.

EXPERIMENTAL

Materials

The DIPTRI and DIPTET were synthesized and purified according to the procedure reported by

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

Journal of Applied Polymer Science, Vol. 80, 1725–1736 (2001)
© 2001 John Wiley & Sons, Inc.

Table I Formulation of Mixes for One-Stage Vulcanization

Mix	1	2	3	4	5	6	7	8	9	10
NR	100	—	75	50	25	100	—	75	50	25
XNBR	—	100	25	50	75	—	100	25	50	75
ZnO	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
DIPTRI	4.12 ^a	4.12 ^a	4.12 ^a	4.12 ^a	4.12 ^a	—	—	—	—	—
DIPTET	—	—	—	—	—	4.41 ^b	4.41 ^b	4.41 ^b	4.41 ^b	4.41 ^b
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

^a This weight corresponds to 9 mmol DIPTRI.

^b This weight corresponds to 9 mmol DIPTET.

Pimblott et al.² The characteristics of the XNBR (Krynac-X7.50) were as follows: about 7% carboxylic acid; 27.3% monomer content; Mooney viscosity $ML_{(1+4)}$ at 100°C, 49; 0.21% total ash content; 0.2% volatiles; specific gravity 0.98. The NR (RMA 1X) was procured from a local market.

Methods

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. 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.¹

Measurement of Physical Properties

Physical properties like the modulus at 200% elongation and tensile strength of the vulcanizates were measured according to ASTM D412-51T in an Amsler tensile tester. The hardness

was determined according to ASTM D2240-85 using a Shore A durometer.

The procedure for the determination of age resistance and oil resistance of the vulcanizates was discussed earlier.^{1,4}

Scanning Electron Microscopy (SEM) Studies

SEM studies were carried out on the tensile fractured surfaces by using a scanning electron microscope (model S-415A, Hitachi) in accordance with the procedure given previously.¹

RESULTS AND DISCUSSION

One-Stage Vulcanization

The formulations of the mixes (using DIPTRI and DIPTET) for one-stage vulcanization are presented in Table I. The cure data for the mixes containing DIPTRI and DIPTET in one-stage vulcanization (mixes 1–10) are recorded in Table II and the rheographs of the above mixes depicting the course of vulcanizations are shown in Figures 1 and 2. The numbers representing the curves correspond to those used for the mix formulations as presented in Table I. As can be seen from Table II, DIPTRI/DIPTET-accelerated XNBR stock is

Table II 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
R_{α} (Nm)	3.80	5.50	3.30	3.40	3.65	3.95	6.30	3.50	3.60	4.10
t_2 (min)	1.00	0.50	2.00	0.75	0.50	1.50	0.50	2.00	2.00	0.50
t_{90} (min)	3.50	10.0	5.00	6.25	7.25	4.00	11.0	5.00	6.00	7.50

R_{α} , maximum rheometric torque; t_2 , scorch time; t_{90} , optimum cure time.

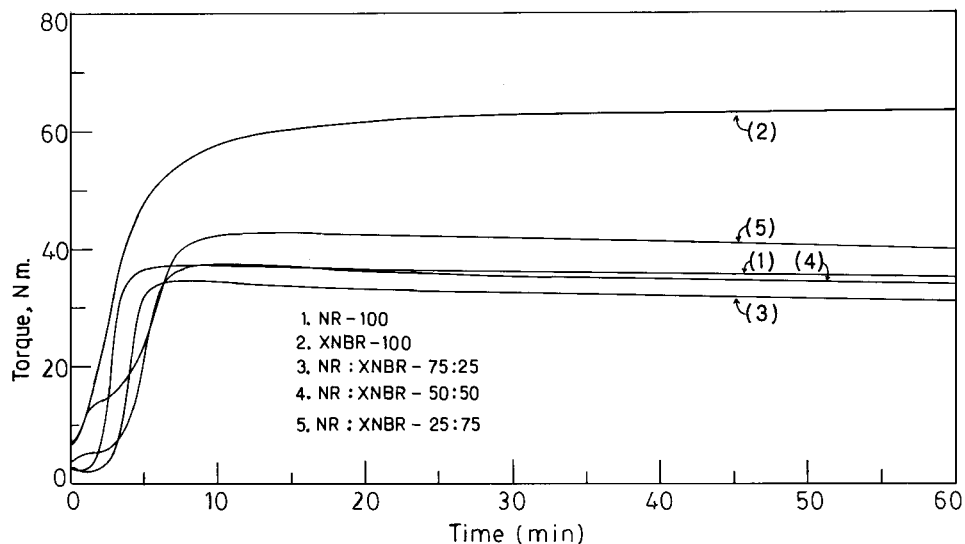


Figure 1 Rheographs of mixes 1-5 (Table I) cured at 160°C.

more scorchy than NR stock (compare mixes 1 with 2 and 6 with 7). The reaction of XNBR both with DIPTRI and DIPTET under experimental conditions was very fast and thus the recipes exhibited low values for the scorch time (t_2) for XNBR. However, this was not reflected in the optimum cure time (t_{90}). This was evidently due to the marching cure of XNBR stocks. As expected DIPTRI-accelerated stock of XNBR exhibited higher torque than the corresponding NR stock. For the blends where NR was progressively replaced by XNBR and the resulting mixes were cured with DIPTRI, the t_2 value decreased. Note

also from the table that the t_{90} values progressively increased with the increase in the concentration of XNBR in the blend. The optimum cure time values of the three blends fell in between the 100% NR and 100% XNBR formulations. The cure curves of 100% NR and 100% XNBR were of the typical S shape (Fig. 1). However, the situation was quite different for the blends: in each case (except for mixes 3 and 8) the cure curves comprised two distinct regions, indicating the occurrence of two different types of cure.^{5,6} The maximum torque value (R_α) of the blend vulcanizates cured with DIPTRI (mixes 3-5), which can be

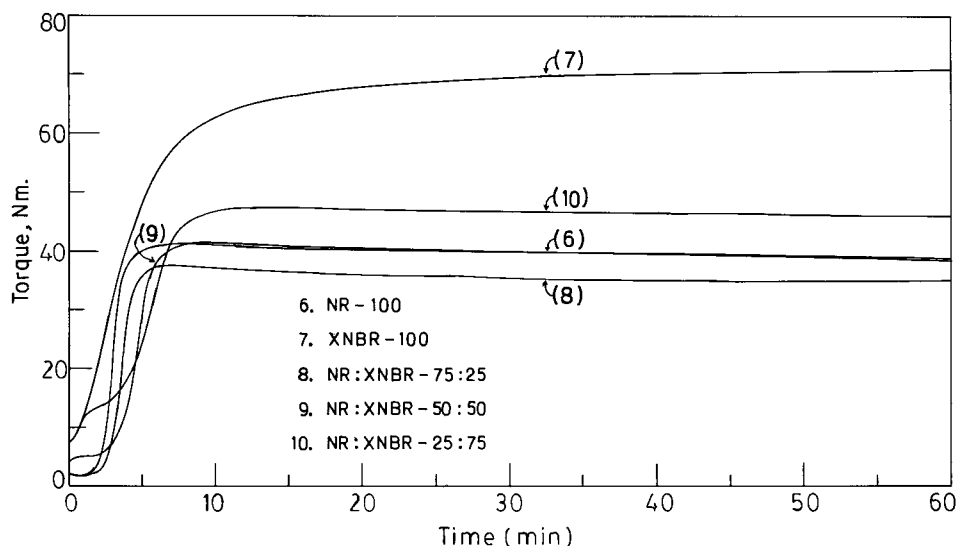


Figure 2 Rheographs of mixes 6-10 (Table I) cured at 160°C.

seen from Table II, fell below the one obtained with 100% NR.

The results obtained with DIPTET under identical conditions (mixes 6–10) were similar to those obtained with DIPTRI with some minor variations. However, the torque values for the combinations cured with DIPTET were higher compared to those obtained with DIPTRI. This was expected because DIPTET contains a larger amount of sulfur than DIPTRI. It was reported² that DIPTRI and DIPTET both act as sulfur donors for diene rubber; the rates and the levels of cure also became faster as the number of S atoms increased in the thiophosphoryl compounds (compare the rheographs of Fig. 1 with those of Fig. 2).

The physical properties of the blend vulcanizates usually become poor because of the heterogeneous character of most of the compositions. However, interrubber crosslinking^{7–10} brought about during vulcanization enhances the physical properties of elastomer blends.

It was reported^{1,3} previously that thiophosphoryl disulfide imparts pronounced increase in physical properties by promoting interrubber coupling during vulcanization of NR–XNBR and SBR–XNBR blends. Thiophosphoryl polysulfides are thus expected to act favorably as their counterparts (thiophosphoryl disulfides) do. Table III records the physical data of the blend vulcanizates using DIPTRI and DIPTET in onestage vulcanization. The results indicated that the modulus values of NR vulcanizates (mixes 1 and 6) obtained either with DIPTRI or with DIPTET were more or less the same but were considerably lower than that obtained with XNBR vulcanizates under identical conditions (mixes 2 and 7). It is evident from the table that DIPTRI/DIPTET-cured vulcanizates from NR–XNBR blends exhibited a gradual increase in modulus as the proportion of NR was progressively replaced by XNBR. However, this was expected because XNBR produces vulcanizates¹¹ of high modulus that are due to the formation of metalcarboxylate crosslinking. The tensile strength values of NR vulcanizates obtained either with DIPTRI or with DIPTET (compare the value of mix 1 with that of mix 6) was almost the same, but differences appeared in the presence of XNBR (mixes 2 and 7). The tensile strength values for the blend vulcanizates provided some interesting information. For incompatible blends the physical properties, especially the tensile strength, was likely to decline. But in this case, because of interphase crosslinking, it can be seen that most of the blends (mixes

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

Mix	1	2	3	4	5	6	7	8	9	10
200% Modulus (MPa)	0.57 (0.78)	1.40 (2.18)	0.69 (1.28)	0.87 (1.81)	1.38 (2.44)	0.57 (0.68)	1.67 (2.30)	0.87 (1.32)	1.14 (2.11)	1.44 (2.68)
Tensile strength (MPa)	15.2 (1.2)	11.8 (10.0)	14.4 (6.7)	15.7 (11.2)	18.5 (16.3)	15.4 (0.7)	12.0 (8.7)	14.8 (3.4)	16.7 (9.8)	20.5 (13.1)
Elongation at break (%)	770 (300)	600 (400)	730 (390)	650 (420)	640 (420)	700 (220)	550 (360)	680 (280)	610 (390)	620 (390)
Swelling index	2.78	0.35	2.30	1.62	0.96	2.47	0.32	2.22	1.52	0.90
Crosslinking value	0.36	2.90	0.43	0.62	1.05	0.40	3.07	0.45	0.66	1.11
Hardness Shore A	54 (55)	65 (71)	55 (57)	58 (62)	66 (71)	55 (56)	64 (70)	55 (60)	60 (65)	65 (70)

The values in the parentheses are the aged properties of the vulcanizates at 100 ± 1°C for 72 h.

3-5 and 8-10) showed improved strength over the parent components. The highest increment in tensile strength was exhibited when the blends contained 75% XNBR (mixes 5 and 10). However, this was expected because the concentration of reactive centers for crosslinking continued to increase with the increase of the XNBR percentage. Actually, in these cases the preponderance of metal-carboxylate crosslinks¹¹ and new types of di- or polysulfidic crosslinks^{1,3} (arising from the reaction between the —COOH groups of XNBR and thiophosphoryl sulfides) occurred and the conjoint effect of these flexible crosslinks was responsible for the higher tensile values of these blends. These types of flexible linkages are capable of facilitating crosslink slippage^{1,3,12} and thus impart good tensile strength. The corresponding elongation at break values for the mixes (3-5 and 7-10) pointed out that with the progressive increase of XNBR concentration in the blend the values diminished and approached the limiting value of the parent XNBR component, the highest value being exhibited by the NR component (mixes 1 and 6). Shore A hardness values are also included in Table III. NR vulcanizates attained the lowest value (mixes 1 and 6) and that for blend vulcanizates containing 75% XNBR became the highest. It is necessary to mention here that the modulus and hardness reflect the extent of crosslinking. In this case the highest crosslinking values ($1/Q$) were exhibited by the XNBR vulcanizates (mixes 2 and 7). Surprisingly, the blend vulcanizate containing 25% NR/75% XNBR provided the highest Shore A hardness value, although its crosslinking value was much below that of 100% XNBR. The reason is that XNBR is polar and is therefore very resistant to a solvent or fuel, which is nonpolar. Thus, the crosslinking value as obtained in the procedure was likely to be very high. Hence, the true picture for the extent of crosslinking for the XNBR fractions of the blend may provide an enhanced value for the crosslinking. The blend vulcanizates (mixes 5 and 10) containing 25% NR are likely to imbibe a significant quantity of solvent or fuel for which the crosslinking value appreciably diminishes.

In regard to DIPTET-accelerated blends (mixes 6-10), the physical data (Table III) generally exhibited higher values than those obtained with DIPTRI-accelerated blends. This was expected because the rates and the levels of cure became faster as the number of sulfur atoms increased in the thiophosphoryl compounds.

Two-Stage Vulcanization

The primary object of two-stage vulcanization is to create a congenial atmosphere for the generation of more rubber bound intermediates that will subsequently take part in interrubber crosslinking of NR and XNBR separately from taking part in the sulfur crosslinking. This can be achieved by increasing the concentration of DIPTRI or DIPTET in the NR and preheating the resulting NR compound for a predetermined time. From this point the second stage of vulcanization begins. The pendent moieties of DIPTRI/DIPTET, which are bound to the NR backbone, then are allowed to react with the —COOH groups of XNBR. The resultant interrubber linking effected by thiophosphoryl polysulfides (DIPTRI and DIPTET) is likely to generate a coherent mass that is apt to give higher modulus and hardness and lower elongation at break as compared to those obtained in one-stage vulcanization. Again the interrubber linking arising from thiophosphoryl polysulfides is flexible^{1,3,12} because of the presence of (XNBR moiety)—COOP(S)—S_n—(NR moiety)—S_n—P(S)OOC—(XNBR moiety). Thus, it may be reasonably expected that the resulting vulcanized matrix will be flexible and exhibit improved tensile strength. Table IV shows the composition and preparation of the blends in two-stage vulcanization. For two-stage vulcanization of NR-XNBR blends, two most important factors, preheating time and preheating temperature, are to be considered carefully to obtain maximum concentration of the anticipated rubber bound intermediate at the first stage. Figures 3 and 4 represent the cure curves at the second stage in two-stage vulcanization of blends using DIPTRI and DIPTET, respectively. Table V provides the cure data of DIPTRI and DIPTET accelerated NR-XNBR blends in two-stage vulcanization. It is evident from a comparison between Table II and Table V that scorch times (t_2) for the blend vulcanizates are generally more reduced in two-stage vulcanization than in one-stage vulcanization because the components responsible for vulcanization are already present here. This is also true for reducing the optimum cure times (t_{90}). As expected, the torque values increased to some extent. Also, it can be seen from Table V that the vulcanizates from DIPTET-accelerated stocks exhibited higher torque values than the corresponding DIPTRI-accelerated vulcanizates.

Table VI records the physical data of DIPTRI- and DIPTET-accelerated blends (mixes 3'-5' and

Table IV Formulation of Mixes for Two-Stage Vulcanization

	Mix	3'	4'	5'	8'	9'	10'
First stage	NR	75	50	25	75	50	25
	ZnO	5	5	5	5	5	5
	Stearic acid	2	2	2	2	2	2
	DIPTRI	4.12 ^a	4.12 ^a	4.12 ^a	—	—	—
	DIPTET	—	—	—	4.41 ^b	4.41 ^b	4.41 ^b
	S	0.5	0.5	0.5	0.5	0.5	0.5
Second stage ^c	XNBR	25	50	75	25	50	75

^a Weight corresponds to 9 mmol DIPTRI.

^b Weight corresponds to 9 mmol DIPTET.

^c After preheating compounded NR at first stage. Preheating times (*t*) for mixes 3', 4', 5', 8', 9', and 10' at 140°C are 2.5, 2, 2, 3, 3, and 2 min, respectively.

8'–10'). Comparing the modulus values of DIPTRI-accelerated stocks with the corresponding values derived from DIPTET, it can be seen that DIPTET-accelerated vulcanizates show higher modulus values than those obtained in the presence of DIPTRI. This trend was also noticed for the tensile strength, elongation at break, and hardness of the vulcanizates. Generally speaking, the hardness of the blend vulcanizates derived from DIPTRI and DIPTET occupied intermediate positions as compared to NR and XNBR vulcanizates. The high modulus and tensile strength, the low elongation at break, and swelling values obtained from the blend vulcanizates as presented in Table VI manifest the efficacy of the blend containing 75% XNBR and 25% NR (mixes 5' and 10').

The variation of the tensile strength and 200% modulus values in one-stage and two-stage vulcanizations against the blend composition in the presence of DIPTRI and DIPTET is shown in Fig-

ures 5 and 6, respectively. The figures clearly show a fair degree of synergism, which is at its maximum with 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 two-stage vulcanization.

Aging Characteristics of Blend Vulcanizates

XNBR is noted for its age resistance because of the formation of metalcarboxylate crosslinks in the network. It is thus expected that the presence of XNBR would impart some beneficial effect upon the aged vulcanizates of the rubber blends. So it was our objective to examine the aging behavior of the NR–XNBR blend vulcanizates. It can be seen from Table III that all the aged samples (values given in parentheses) obtained in one-stage vulcanization exhibited a progressive

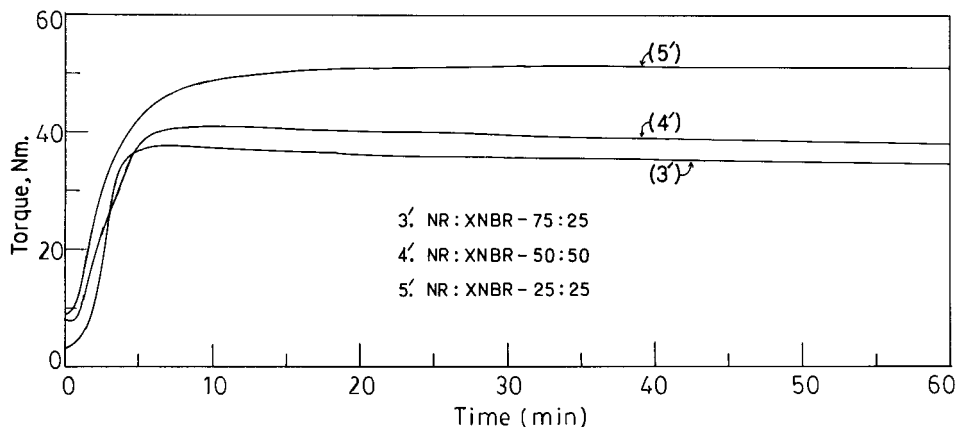


Figure 3 Rheographs of mixes 3'–5' (Table III) cured at 160°C (second stage).

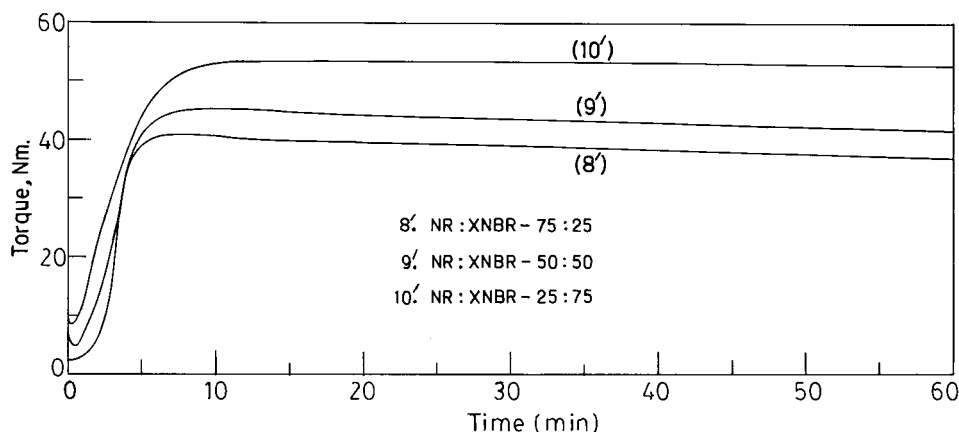


Figure 4 Rheographs of mixes 8'–10' (Table III) cured at 160°C (second stage).

increment of the modulus values as the concentration of XNBR in the blend was gradually increased. It is interesting to note that the aged vulcanizates from DIPTRI- and DIPTET-accelerated blends containing 75% XNBR and 25% NR (mixes 5 and 10, respectively) showed higher modulus values than those obtained with 100% XNBR (mixes 2 and 7). This was also true for the tensile strength but the values diminished rapidly during aging with the increase in NR content. It can be seen from Table III that for the combination (75:25/XNBR:NR, mix 5) the fall in tensile strength during aging was minimal. However, a greater fall in tensile strength was exhibited by DIPTET-accelerated vulcanizates. The aging behavior of DIPTET-accelerated vulcanizates in one-stage vulcanization was similar to that obtained with DIPTRI-accelerated vulcanizates. As usual the modulus of all the vulcanizates increased during aging while a fall in tensile strength was noticed.

The data for the physical properties of the aged vulcanizates obtained in two-stage vulcanization are recorded in Table VI. The values are given in parentheses for the respective properties. It is

evident that during aging the modulus increased with the increase of XNBR concentration. The tensile strength of the aged samples also declined, which is usual in this case. However, the fall in tensile strength for the NR-rich combination accelerated by DIPTRI (mix 3', Table VI) was low compared to that (mix 3, Table III) obtained in one-stage vulcanization. For other combinations (mixes 4' and 5') the percentage fall in tensile strength was almost similar to that obtained in one stage, although the values of tensile strength retained after aging were distinctly higher. The aged vulcanizates of DIPTET-accelerated stocks (mixes 8', 9', and 10') in two-stage vulcanization behaved similarly.

The elongation at break values during aging as shown in Table III and Table VI were usually low for DIPTRI- and DIPTET-accelerated vulcanizates, depending upon the composition of the blend and the type of vulcanization procedure (one stage or two stage).

As can be seen from Table III and Table VI, the hardness of the blend vulcanizates increased during aging with the proportion of XNBR in the blend for both the DIPTRI- and DIPTET-accelerated vulcanizates. As usual, the vulcanizates containing 75% XNBR attained the highest values.

The increase in modulus during aging is a common phenomenon. The fall in tensile strength for the vulcanizates containing polysulfidic linkages might be due to depletion¹³ of flexible polysulfidic linkages that are thermolabile and thus are decomposed during accelerated aging. In this process additional sulfur from the polysulfides is capable of forming further crosslinkages, the result being the enhancement of the modulus and hardness. Actually, this was also observed in our case.

Table V Cure Characteristics of Two-Stage Vulcanizates at 160°C Using Monsanto Rheometer (R-100)

Mix	3'	4'	5'	8'	9'	10'
R_{α} (Nm)	3.40	3.60	4.10	3.85	4.05	4.50
t_2 (min)	0.75	0.50	0.25	1.00	0.75	0.25
t_{90} (min)	4.00	5.00	7.00	4.25	5.00	6.50

R_{α} , maximum rheometric torque; t_2 , scorch time; t_{90} , optimum cure time.

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

Mix	3'	4'	5'	8'	9'	10'
200% Modulus (MPa)	0.81 (1.42)	1.02 (1.82)	1.60 (2.36)	0.95 (1.69)	1.21 (1.97)	1.70 (2.61)
Tensile strength (MPa)	15.8 (10.3)	17.0 (12.3)	21.5 (19.0)	16.5 (5.0)	18.6 (10.6)	23.1 (16.2)
Elongation at break (%)	720 (450)	630 (430)	600 (430)	650 (330)	650 (400)	610 (410)
Swelling index	2.19	1.52	0.84	2.10	1.42	0.75
Crosslinking value	0.45	0.66	1.19	0.47	0.70	1.34
Hardness Shore A	56 (58)	59 (63)	65 (71)	55 (60)	60 (65)	68 (72)

The values in the parentheses are the aged properties of the vulcanizates at $100 \pm 1^\circ\text{C}$ for 72 h.

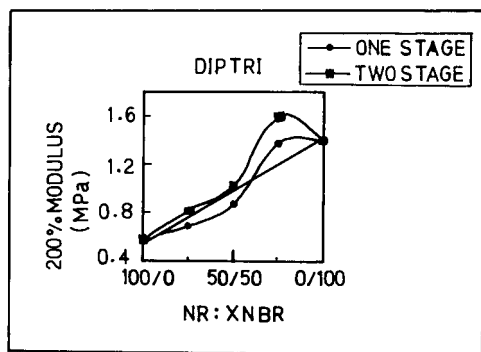
Solvent Resistance

XNBR is notable for its unique oil and solvent resistance property, while that for NR is rather poor. In blends the interface crosslinking between NR and XNBR is likely to influence this property. Thus, the swelling behavior of the blend vulcanizates was expected to cast some light in this regard. The swelling value, Q , defined as the grams of solvent per gram of rubber

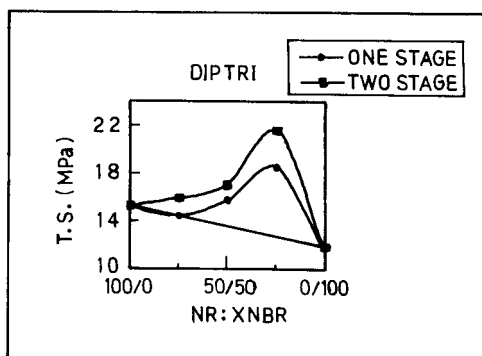
hydrocarbon, is readily calculated⁴ from the expression

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{\frac{\text{original weight} \times 100}{\text{formula weight}}}$$

where formula weight is the total weight of rubber plus compounding ingredients based on 100

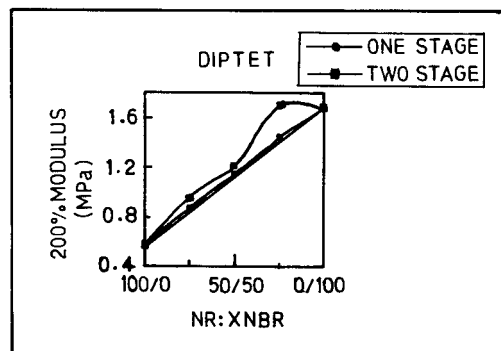


(a)

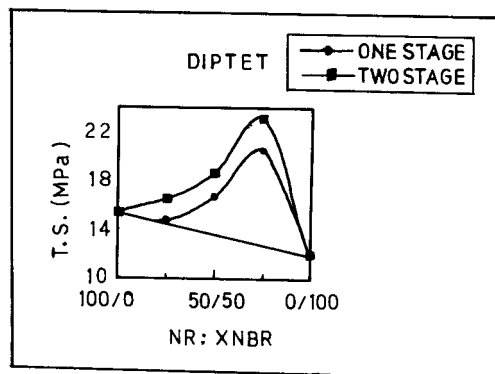


(b)

Figure 5 The variation of the (a) 200% modulus and (b) tensile strength against the blend composition in the presence of DIPTRI.



(a)



(b)

Figure 6 The variation of the (a) 200% modulus and (b) tensile strength against the blend composition in the presence of DIPTET.

parts of rubber. A comparison of the crosslinking values was also made from the reciprocal of the swelling values. Table III records swelling data that provide the solvent resistance of vulcanizates obtained with DIPTRI and DIPTET in one-stage vulcanization. It is evident that the NR vulcanizates exhibited poor resistance while those derived from XNBR showed quite significant results, as expected. This property was however not pronounced in the 50:50 NR-XNBR blends containing either DIPTRI or DIPTET. NR-XNBR blends having a 25:75 ratio (mixes 5 and 10) did exhibit enhancement of solvent resistance in the presence of both DIPTRI and DIPTET, although this was 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 increased. This property was further enhanced in the two-stage vulcanization process. It may be reasonably expected that the interfacial crosslinks caused swelling restriction of the highly swollen phase. The swelling data for the blend vulcanizates obtained with DIPTRI and DIPTET in two-stage vulcanization are recorded in Table VI. The data clearly indicated that the oil resistance property of the blend vulcanizates in two-stage vulcanization increased in the same manner as in one-stage vulcanization, but the values of $1/Q$ were increased further. These higher $1/Q$ values suggested the formation of more interfacial crosslinks between the elastomer phases in two-stage vulcanization.

SEM Studies

The interfacial linking between NR and XNBR in the presence of thiophosphoryl polysulfides is apt to form a compact and coherent rubber matrix. So, SEM studies were considered to throw some light in this regard and thus tensile fractured surfaces of the vulcanizates derived from thiophosphoryl polysulfide-accelerated blends of NR-XNBR were chosen for the study. Figure 7(a-f) depicts micrographs of DIPTRI-accelerated blend vulcanizates in one-stage and two-stage vulcanizations. It is evident from the micrographs that as the proportion of XNBR increased from 25 to 75% in the blend the state of dispersion was progressively improved and a reduction in vacuoles occurred. This was true for both one-stage and two-stage vulcanizates. However, the SEM micrographs in two-stage vulcanization exhibited more

homogeneous surfaces than those obtained in one stage. Here unidirectional ripples were also observed in XNBR-rich combinations. All these facts accounted for the significant enhancement of physical properties for the DIPTRI-accelerated vulcanizates, especially in two-stage vulcanization. Figure 8(a-f) represents the tensile fractured micrographs of DIPTET-accelerated NR-XNBR blend vulcanizates. The micrographs indicated the similarity in the architecture with those obtained from DIPTRI-accelerated vulcanizates in both one-stage and two-stage vulcanization.

In our previous study³ with SBR-XNBR blends accelerated with thiophosphoryl disulfides we observed the appearance of strong lines in the SEM micrographs of tensile fractured surfaces of rubber vulcanizates. It was suggested that chemical bonding between SBR and XNBR conferred ordered orientation of the rubber matrix, the outcome of which was the occurrence of these lines. In the present study with NR and XNBR in the presence of thiophosphoryl polysulfides we believe that a similar reaction took place between these two rubbers.

In order to investigate further the formation of interfacial bonds between the elastomer phases, swelling experiments in connection with Kraus plots were carried out.

For filled systems, the rubber-filler interaction caused swelling restrictions of the elastomer network. Similarly, in a vulcanized binary rubber blend, if interfacial bonds exist, the lightly swollen dispersed phase restricts the swelling of the highly swollen continuous phase. Thus, a situation existed that was analogous to the rubber-filler concept and a similar mathematical and graphical analysis could be applied.¹⁴ The lightly swollen dispersed phase was considered as a filler. The methods of analysis, assumptions, calculations, and plotting of the swelling data following the analogous filler systems of Kraus¹⁴ were detailed by Zapp.¹⁵

The blend vulcanizates under investigation swollen in isoctane:toluene (70:30) medium can be treated by the Kraus equation¹⁴:

$$V_0/V = 1 - Mv/1 - v$$

where V_0 is the volume fraction of NR in the swollen gel of the pure NR vulcanizate, V is the volume fraction of NR in the swollen NR-XNBR blend vulcanizate, v is the volume fraction of XNBR in the blend vulcanizates, and M is a pa-

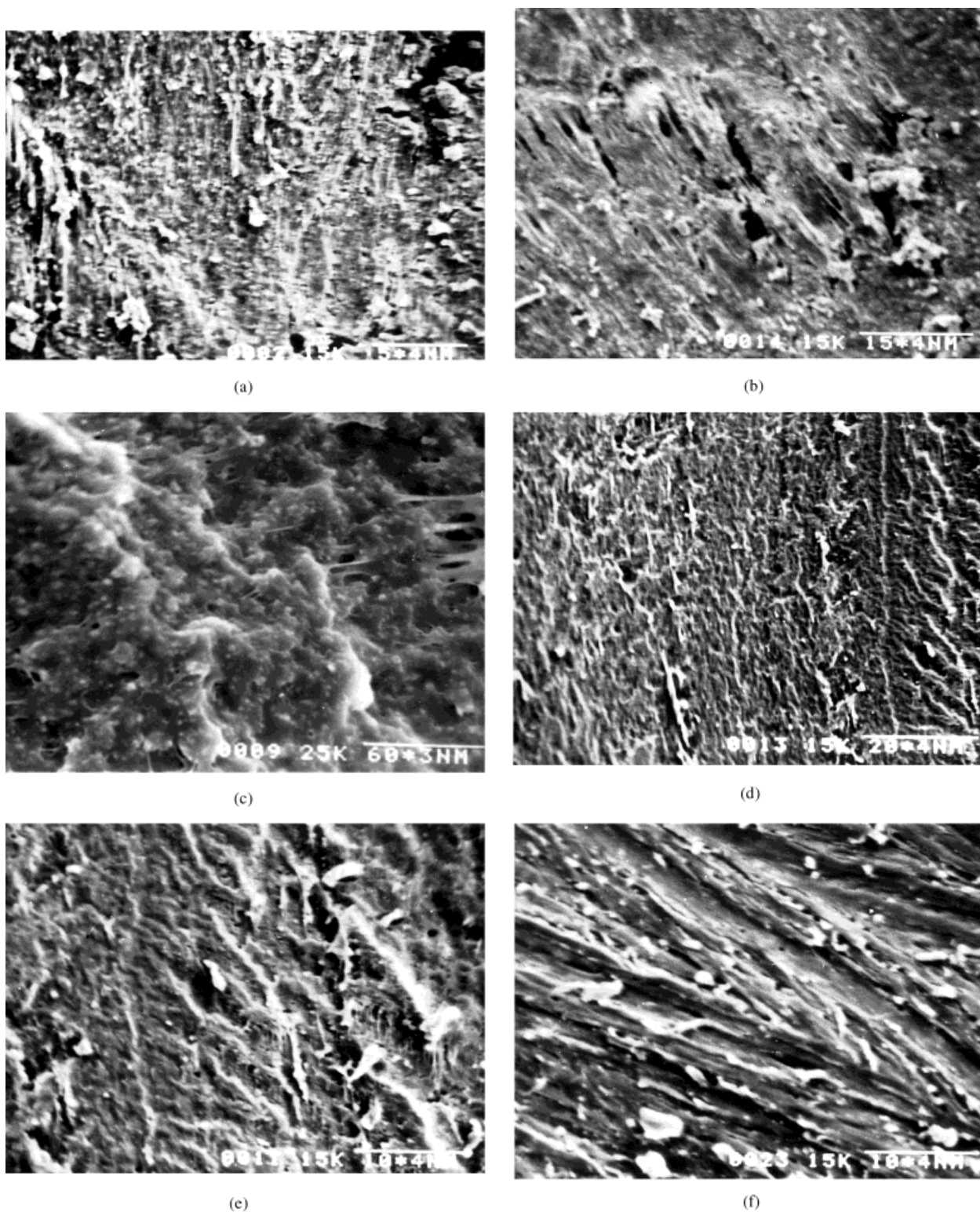


Figure 7 SEM micrographs of the tensile fractured surfaces of the vulcanizates containing DIPTRI cured at 160°C: (a) NR:XBNR (75:25) blend (one stage) at an original magnification of 200×, (b) NR:XBNR (75:25) blend (two stage) at an original magnification of 200×, (c) NR:XBNR (50:50) blend (one stage) at an original magnification of 500×, (d) NR:XBNR (50:50) blend (two stage) at an original magnification of 150×, (e) NR:XBNR (25:75) blend (one stage) at an original magnification of 300×, and (f) NR:XBNR (25:75) blend (two stage) at an original magnification of 300×.

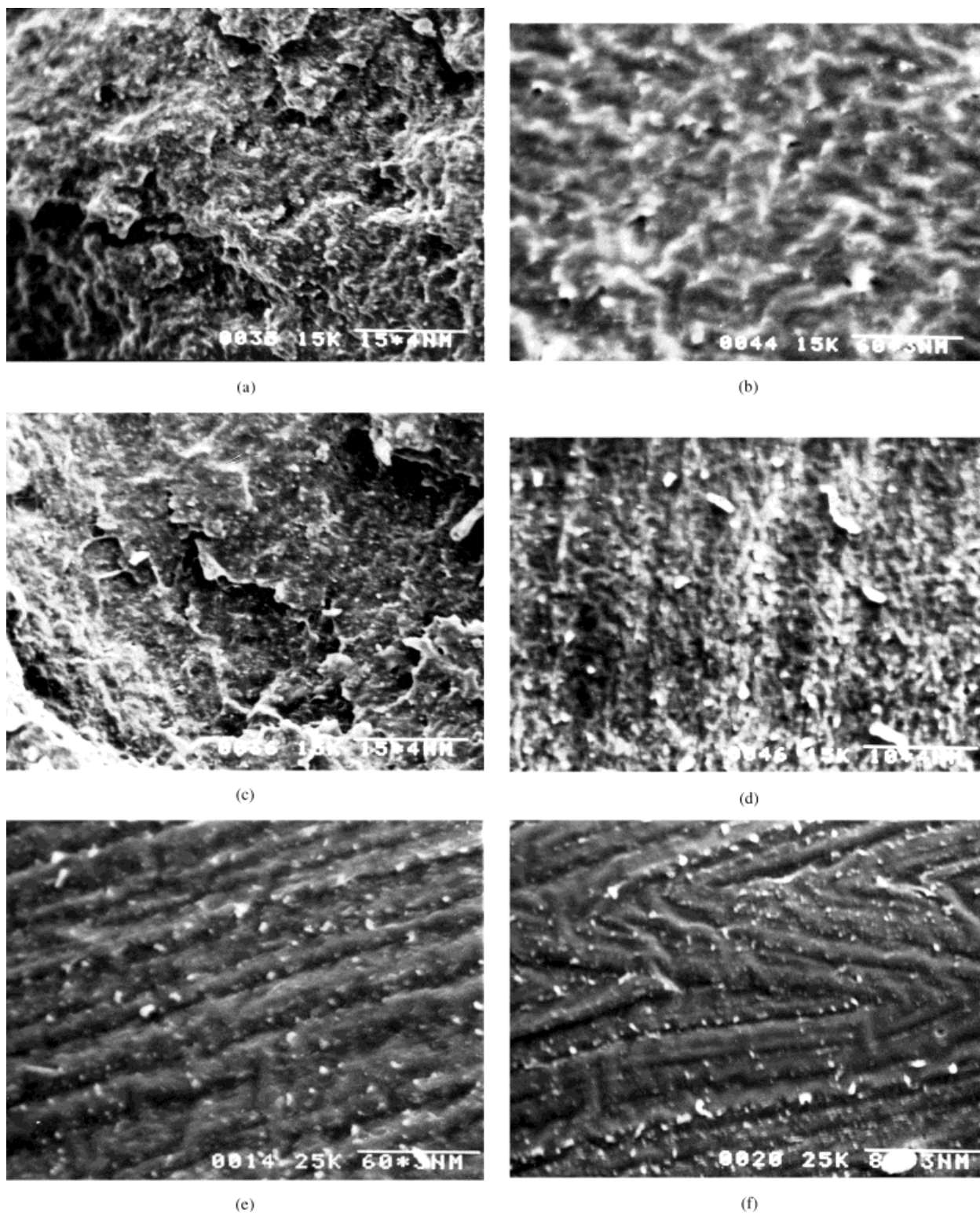


Figure 8 SEM micrographs of tensile fractured surfaces of the vulcanizates containing DIPTET cured at 160°C: (a) NR:XNBR (75:25) blend (one stage) at an original magnification of 200 \times , (b) NR:XNBR (75:25) blend (two stage) at an original magnification of 500 \times , (c) NR:XNBR (50:50) blend (one stage) at an original magnification of 200 \times , (d) NR:XNBR (50:50) blend (two stage) at an original magnification of 500 \times , (e) NR:XNBR (25:75) blend (one stage) at an original magnification of 500 \times , and (f) NR:XNBR (25:75) blend (two stage) at an original magnification of 380 \times .

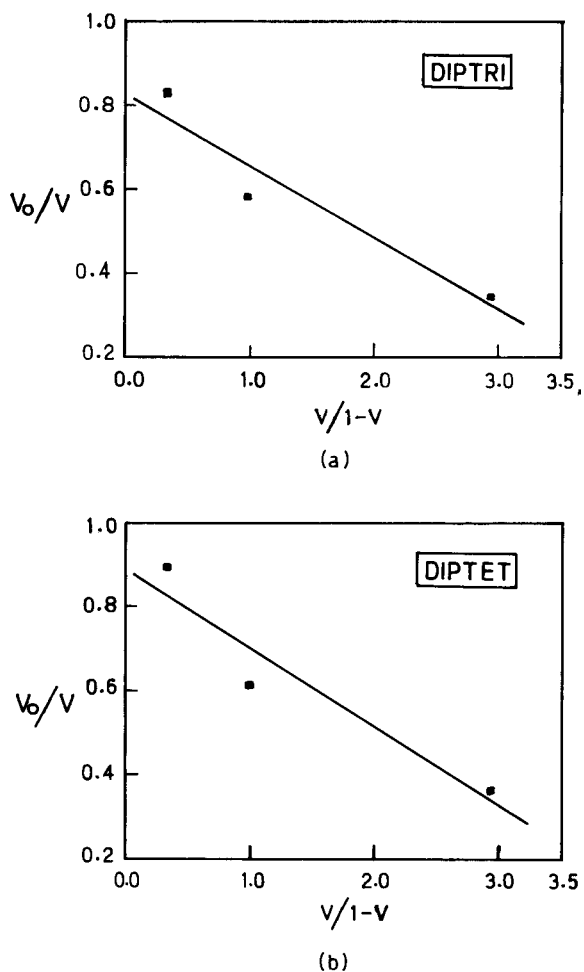


Figure 9 Kraus plots of NR-XNBR blends in the presence of (a) DIPTRI and (b) DIPTET.

parameter depending on V_0 and the extent of swelling restriction. Kraus plots (i.e., plots of V_0/V vs. $v/1-v$) form straight lines with slope $-M$. If no strong bonds exist between the two polymer phases, there is no swelling restriction by the lightly swollen phase; V_0/V remains near unity

and the slope M is near zero. On the other hand, if strong interfacial bonds cause swelling restrictions, slope M becomes negative. In the present investigation the slopes of the lines obtained from several NR-XNBR blends, as shown in Figure 9, were found to be negative and these corroborated the suggestion pertaining to the formation of strong interrubber bonds.

REFERENCES

1. Naskar, N.; Biswas, T.; Basu, D. K. *J Appl Polym Sci* 1994, 52, 1007.
2. Pimblott, J. G.; Scott, G.; Stuckey, J. E. *J Appl Polym Sci* 1979, 23, 3621.
3. Biswas, T.; Naskar, N.; Basu, D. K. *J Appl Polym Sci* 1995, 58, 981.
4. Parks, C. R.; Brown, R. J. *Rubber Chem Technol* 1976, 49, 233.
5. Biswas, T.; Naskar, N.; Basu, D. K. *Kautsch Gummi Kunstst* 1993, 46, 125.
6. Biswas, T.; Mandal, S. K.; Basu, D. K. *Kautsch Gummi Kunstst* 1994, 47, 508.
7. Mitchell, J. M. *Rubber Plast News* 1985, June 3, 18.
8. Zapp, R. L. *Rubber Chem Technol* 1973, 46, 251.
9. Bauer, R. F. *Polym Eng Sci* 1982, 22, 130.
10. Ahagon, A.; Gent, A. N. *J Appl Polym Sci Phys* 1975, 13, 1285.
11. Brown, H. P. *Rubber Chem Technol* 1963, 36, 931.
12. Bateman, L.; Cunneen, J. I.; Moore, C. G.; Mullins, L.; Thomas, A. G. In *The Chemistry and Physics of Rubber-Like Substances*; Bateman, L., Ed.; Maclaren & Sons Ltd.: London, 1963; p 715.
13. Bateman, L.; Moore, C. G.; Porter, M.; Saville, B. *The Chemistry and Physics of Rubber-Like Substances*; Bateman, L., Ed.; Maclaren & Sons Ltd.: London, 1963; Chapter 15.
14. (a) Kraus, G. *J Appl Polym Sci* 1963, 7, 861; (b) Kraus, G. *Rubber Chem Technol* 1964, 37, 6.
15. Zapp, R. L. *Multicomponent Polymer Systems*; Advances in Chemistry Series 99; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1971; Chapter 6, p 68.