Thiophosphoryl Disulfides: Novel Coupling Agents for Styrene–Butadiene Rubber/Carboxylated Nitrile Rubber Blends

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SYNOPSIS

Thiophosphoryl disulfide was successfully used as a novel coupling agent to form a coherent blend comprising polar carboxylated nitrile rubber (XNBR) and nonpolar styrene–butadiene rubber (SBR) establishing close proximity between them through chemical bridging. The study reveals that XNBR in the presence of thiophosphoryl disulfide greatly improves the physical properties of SBR and thus acts as a reinforcing filler. It is noted that the physical properties of the vulcanizates obtained from the SBR-XNBR blend depend upon the SBR : XNBR ratio and the mode of cure. SEM studies corroborate the observed facts. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Earlier workers[1] observed that bis(diisopropyl) thiophosphoryl disulfide (DIPDIS), apart from its activity both as an accelerator and sulfur donor, can react with diene rubbers, such as cis 1,4-polyisoprene, and form pendent groups along the elastomeric chain in the early stage of vulcanization. Recently, it has been observed by us[2,3] that thiophosphoryl disulfides react with carboxylated nitrile rubber (XNBR) during vulcanization. Based on the above reactions DIPDIS was successfully used to form a blend[4] comprising polar XNBR and nonpolar NR through the chemical links between the two. It is expected that thiophosphoryl disulfides can also be effectively utilized to form a coherent blend comprising polar XNBR and nonpolar styrene–butadiene rubber (SBR). The objective of the present investigation was to prepare such novel blends of SBR and XNBR in the presence of thiophosphoryl disulfides and study the cure behavior of these blends as well as the vulcanizate properties under various conditions.

EXPERIMENTAL

Materials

DIPDIS and bis(dicyclohexyl) thiophosphoryl disulfide (DCHDIS) were prepared and purified according to the procedure reported earlier.[1-3] Commercial grade tetramethyl thiuram disulfide (TMTD) was used in the present investigation. Bis(N-oxydiethylene) disulfide (ODDS), supplied by the Monsanto Company was used as received. N-Oxydiethylene 2-benzothiazole sulfenamide (OBTS) obtained from ACCI, was used after necessary purification.

Carboxylated nitrile rubber, X7.50, was obtained from Polysar Ltd., France (highly carboxylated, monomer content 27.8%, ML − 1 + 4' at 100°C, 49, specific gravity 0.98, total ash content 0.21%, volatiles 0.2%). SBR 1502 was supplied by the B. F. Goodrich Company, Akron, OH (bound styrene 23.5%, ash content 1.5%, organic acid content 7.00–4.75%, soap content 0.50%, specific gravity 0.94, nonstaining and nondiscoloring).

Preparation of Vulcanizates and Measurement of Physical Properties

One Stage Vulcanization of SBR–XNBR Blends

SBR and XNBR were first masticated separately. Masticated XNBR was cut into pieces and added to

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previously masticated SBR. Requisite amounts of zinc oxide, stearic acid, DIPDIS/DCHDIS, DIPDIS + ODDS, DIPDIS + OBTS, and TMTD were incorporated in the SBR-XNBR mix on a Berstorff labmill of size 203 × 102 mm. Finally sulfur was added to the mix after cooling the mill. The stocks were cured under pressure at 160°C.

Two Stage Vulcanization of SBR-XNBR Blends

In this procedure requisite amounts of SBR and XNBR were first masticated separately. The whole amount of the compounding ingredients was incorporated in the SBR. A portion of this mix was cured at 140°C in a Monsanto Rheometer (R-100). The time (t) for the commencement of cure using this mix was noted from the rheograph. Some portion of this compounded SBR was then heated at 140°C in a hydraulic press for the predetermined time (t) when a grossly undercured SBR mix was obtained. The material was then mixed with a requisite amount of masticated XNBR/SBR in order to maintain the desired ratio of the two rubbers in their respective blends as mentioned later. The vulcanizates were obtained under pressure at 160°C.

Measurement of Physical Properties

The procedures for the measurement of physical properties such as modulus at 200% elongation, tensile strength, elongation at break, hardness, age resistance, oil resistance of vulcanizates by swelling, etc., were discussed earlier.[4]

Scanning Electron Microscopy (SEM) Studies

This was carried out on the fractured surfaces of specimens derived from tensile testing. The procedure was given previously.[4]

RESULTS AND DISCUSSION

Earlier, it was reported by Mori[5] that 6-dibutylamino-1,3,5-triazine-2,4 dithiol (DBAT) can co-vulcanize vinylidenefluoride-hexafluoropropane copolymer and acrylonitrile-butadiene rubber that have reactive groups and little compatibility. Close proximity in the interface of the two polymers through DBAT also showed better physical properties. Recently we established[4] that DIPDIS is capable of bringing about chemical links between NR (natural rubber) and XNBR and thus establishes close proximity between polar XNBR and nonpolar NR. This type of molecular arrangement is found to influence the physical properties of these blends. When using SBR instead of NR, it is expected that thiophosphoryl disulfides will also construct chemical bridges between polar XNBR and nonpolar SBR through the rubber bound intermediates of SBR, having pendent accelerator groups formed in the early part of vulcanization. The intermediates thus formed are likely to react with the —COOH groups of XNBR thereby forming the chemically linked coherent blend of SBR and XNBR. The reaction is schematically represented in Scheme 1.

One Stage Vulcanization

To start with, the cure behavior of compounded SBR (mixes 1–5), XNBR (mixes 6–10), and their blends (mixes 11–23), in accordance with the recipes presented in Table I. was studied. The data for the cure characteristics, obtained from the Monsanto Rheometer (R-100), are presented in Table II and the course of vulcanization reactions are depicted in Figures 1–5. The numbers shown on the curves correspond to those used for the mix formulation as presented in Table I.

From our recent investigations[3] regarding the reaction of different thiophosphoryl disulfides with XNBR, we have found that DCHDIS is the best curative cum accelerator for XNBR so far as physical properties are concerned. Therefore DCHDIS, in addition to DIPDIS, is included in the present study. It was further observed[6] that DIPDIS, in combinations with ODDS and OBTS, exhibits synergistic activity when used in the vulcanization of XNBR. An equimolar ratio of DIPDIS : ODDS or DIPDIS : OBTS was used in the present study because maximum activity with regard to physical properties was obtained at this ratio of the accelerators. TMTD, like DIPDIS, also functions as a sulfur donor,[7] but it does not react with —COOH groups of XNBR.[2] So it was thought that the inclusion of TMTD would help understanding of the function of DIPDIS in the vulcanization of SBR-XNBR blends.

The cure curves of compounded SBR (except for mix 5) are S shaped; for XNBR, in each case (except for mix 10) the cure curve is comprised of two distinct regions indicating the occurrence of two different types of cure.[2,3] TMTD, both with SBR and XNBR, gives typical steep cure curves of highest magnitude of R_∞ (characteristic of TMTD cure).

The cure behavior of SBR in respect of R_∞, t_2, and t_{90} for various SBR compounded stocks (mixes 1–5) is very similar to that observed with NR-com-

(SBR)

(Thiophosphoryl disulfide)

(1)

(XNBR)   (XNBR)

(2)

(XNBR
moiety)

(SBR
moiety)
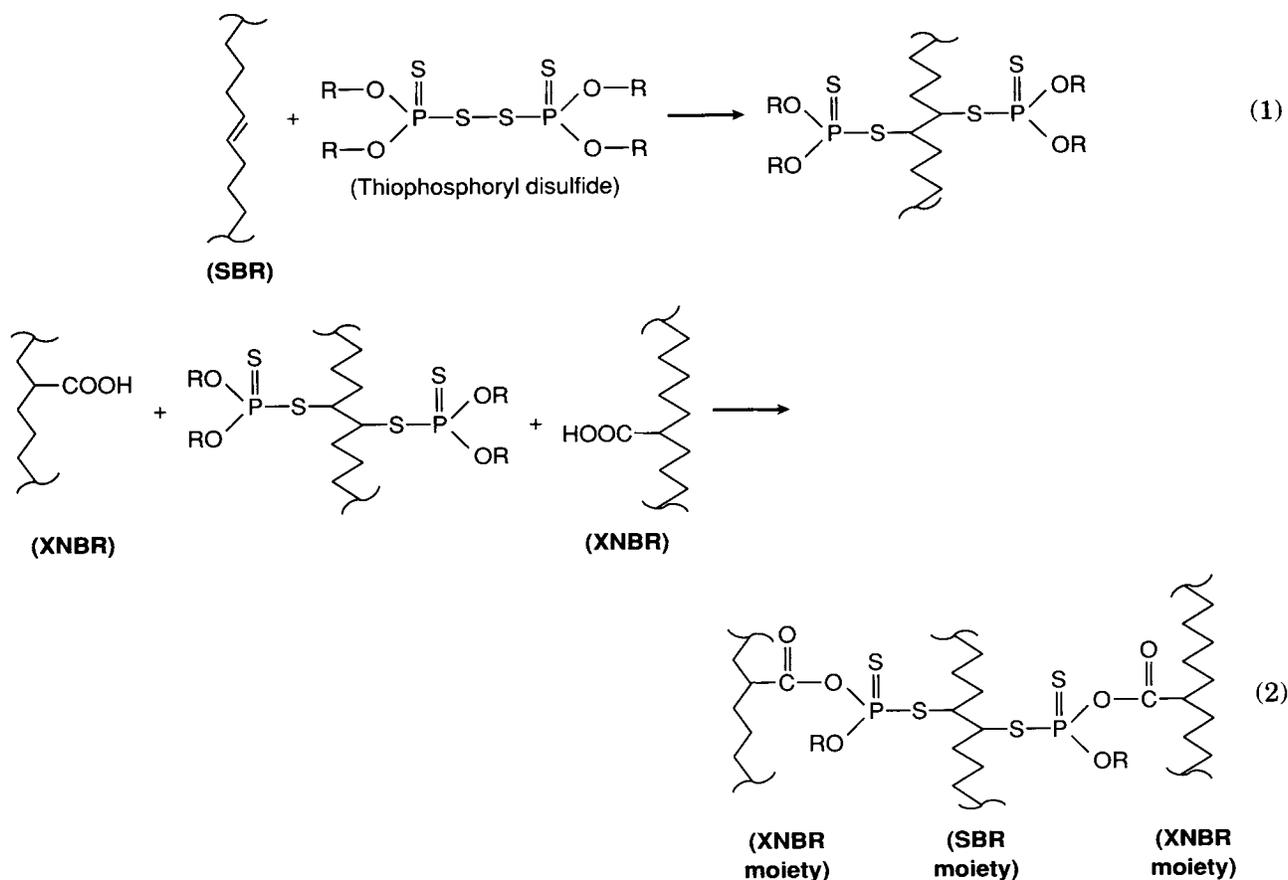
(XNBR
moiety)

Scheme 1 Reaction of thiophosphoryl disulfide with SBR and XNBR.

pounded stocks.[4] The cure behavior of XNBR in the presence of various thiophosphoryl disulfides including DIPDIS, DCHDIS, etc., was also reported previously.[2–4]

For the blends of XNBR and SBR (mixes 11–22) either with DIPDIS/DCHDIS or with the combinations of DIPDIS + ODDS and DIPDIS + OBTS, two distinct regions are also visible in the respective cure curves. It is evident from the cure curves that the extent of the first wavy region is dependent on the concentration of XNBR present in the blend(s) and, therefore, it is highest for those blends that comprise 75% XNBR and 25% SBR. It is also evident from the data that the R_α values of DIPDIS-compounded blends are very similar to those of DCHDIS-compounded blends; the blends of SBR and XNBR containing DIPDIS + ODDS or DIPDIS + OBTS show comparatively lower R_α values. The same trend is also observed for t_{90} values of the blends. The value of scorch time t_2, as expected, is low as well as more or less similar in all the cases irrespective of the blend composition and the type of thiophosphoryl disulfides or their combinations used. The cure behavior of mix 23 (TMTD

accelerated 75 : 25 XNBR : SBR) is different from that of mixes 13 and 16 having comparable compositions of rubber ingredients, but cure curves of entirely different nature, in this case showing the complete absence of two types of cure as seen in the other two cases (mixes 13 and 16).

The physical data obtained in one stage vulcanization are presented in Table III. The results indicate that modulus, tensile strength, hardness, and elongation at break values of SBR gum vulcanizates of mixes 1–4 are more or less the same and are extremely low. TMTD-accelerated SBR vulcanizate (mix 5) gives comparatively higher modulus, tensile strength, and hardness values but lower elongation at break value. XNBR vulcanizates (mixes 6–10) possess considerably higher modulus, tensile strength, and hardness values than those of SBR vulcanizates due to the conjoint effect of flexible metallocarboxylate crosslinks[8] and those arising from the reaction between —COOH groups of XNBR and thiophosphoryl disulfides. Elongation at break values of XNBR vulcanizates are also higher than those of SBR vulcanizates. Thiophosphoryl disulfides,[3] by virtue of their reactions with

Table I   Formulation of Mixes for One Stage Vulcanization

Mix	1	2	3	4	5	6	7	8	9	10	11
SBR	100	100	100	100	100	—	—	—	—	—	75
XNBR	—	—	—	—	—	100	100	100	100	100	25
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
DIP DIS	3.834[a]	—	—	—	—	3.834[a]	—	—	—	—	3.834[a]
DCH DIS	—	5.274[b]	—	—	—	—	5.274[b]	—	—	—	—
DIP DIS : ODDS (4.5 : 4.5)	—	—	2.979[c]	—	—	—	—	2.979[c]	—	—	—
DIP DIS : OBTS (4.5 : 4.5)	—	—	—	3.051[d]	—	—	—	—	3.051[d]	—	—
TMTD	—	—	—	—	2.16[e]	—	—	—	—	2.16[e]	—
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

	12	13	14	15	16	17	18	19	20	21	22	23
SBR	50	25	75	50	25	75	50	25	75	50	25	25
XNBR	50	75	25	50	75	25	50	75	25	50	75	75
ZnO	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2	2
DIP DIS	3.834[a]	3.834[a]	—	—	—	—	—	—	—	—	—	—
DCH DIS	—	—	5.274[b]	5.274[b]	5.274[b]	—	—	—	—	—	—	—
DIP DIS : ODDS (4.5 : 4.5)	—	—	—	—	—	2.979[c]	2.979[c]	2.979[c]	—	—	—	—
DIP DIS : OBTS (4.5 : 4.5)	—	—	—	—	—	—	—	—	3.051[d]	3.051[d]	3.051[d]	—
TMTD	—	—	—	—	—	—	—	—	—	—	—	2.16[e]
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

[a] Wt corresponds to 9 mM DIP DIS.
[b] Wt corresponds to 9 mM DCH DIS.
[c] Wt corresponds to (4.5 : 4.5) mM DIP DIS : ODDS.
[d] Wt corresponds to (4.5 : 4.5) mM DIP DIS : OBTS.
[e] Wt corresponds to 9 mM TMTD.

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	11
Maximum rheometric torque, R_∞ (Nm)	4.75	4.70	4.70	4.30	5.45	4.95	4.80	5.40	4.88	5.80	4.20
Scorch time, t_2 (min)	7.00	6.00	6.50	8.00	1.75	1.00	1.75	1.00	1.00	1.00	1.50
Optimum cure time, t_{90} (min)	19.00	24.00	17.50	24.00	5.25	17.00	20.50	16.00	14.00	16.50	23.00

	12	13	14	15	16	17	18	19	20	21	22	23
Maximum rheometric torque, R_∞ (Nm)	4.10	4.60	4.35	4.47	4.70	4.40	4.15	4.30	3.50	3.10	3.90	5.35
Scorch time, t_2 (min)	1.50	1.50	1.50	1.50	1.75	1.50	1.25	1.25	1.25	1.25	1.25	1.00
Optimum cure time, t_{90} (min)	21.50	20.00	21.00	21.50	19.00	15.00	14.50	14.50	17.50	16.00	14.50	4.75
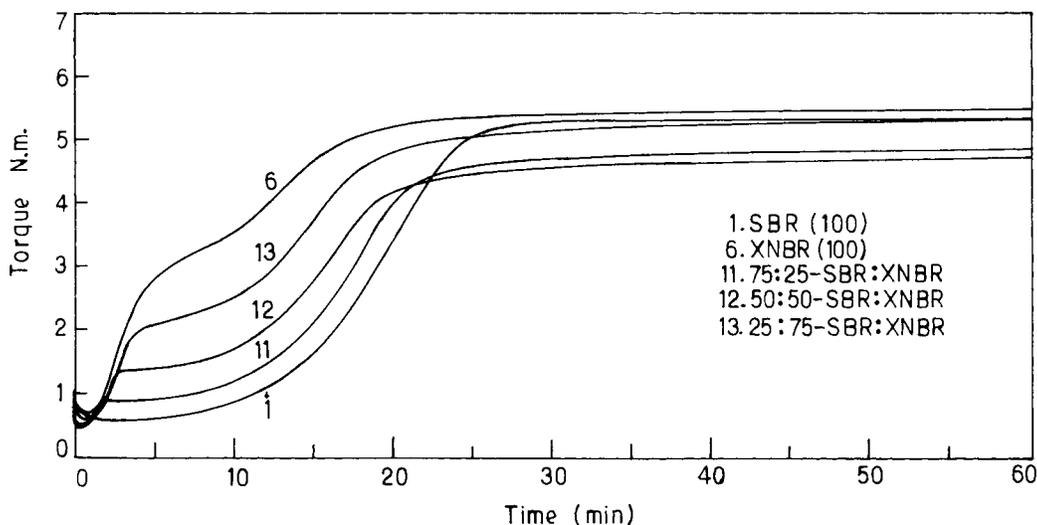
Figure 1   Rheographs of mixes 1, 6, 11–13 (Table I) cured at 160°C.

—COOH groups of XNBR, give rise to new types of flexible[3,4,9] di- or polysulfidic linkages that are capable of facilitating crosslink slippage and thus impart good tensile strength. Among the thiophosphoryl disulfides studied so far, DCHDIS[3] is found to have the highest modulus and tensile strength for XNBR vulcanizates because of its capability to generate additional amounts of flexible polysulfidic linkages of the type —COOP(S)—S—S$_n$—S—P(S)OOC—. This is also reflected in the present case. Binary combinations of DIPDIS + ODDS as well as DIPDIS + OBTS yield vulcanizates that show significant modulus and tensile values as these combinations generate synergism during vulcanization of XNBR. TMTD-accelerated XNBR vulcanizate shows the lowest tensile strength. This

phenomenon may be explained as due to the incapability of TMTD to react with the —COOH groups of XNBR and thus providing no di- or polysulfidic crosslinks of the above mentioned types. Moreover, the fast curing TMTD forms monosulfidic links that evidently do not exhibit crosslink slippage.

It can be seen from the results presented in Table III that for the blend vulcanizates derived from DIPDIS or DCHDIS, the modulus, tensile strength, and hardness values are also extremely good. It seems that interrubber linking, arising from the reaction between —COOH groups of XNBR and thiophosphoryl disulfide fragments pendent to SBR, according to Scheme 1, is the key factor for the observed effect. This type of flexible linking[4,9] facilitates crosslink slippage and thus imparts enhanced
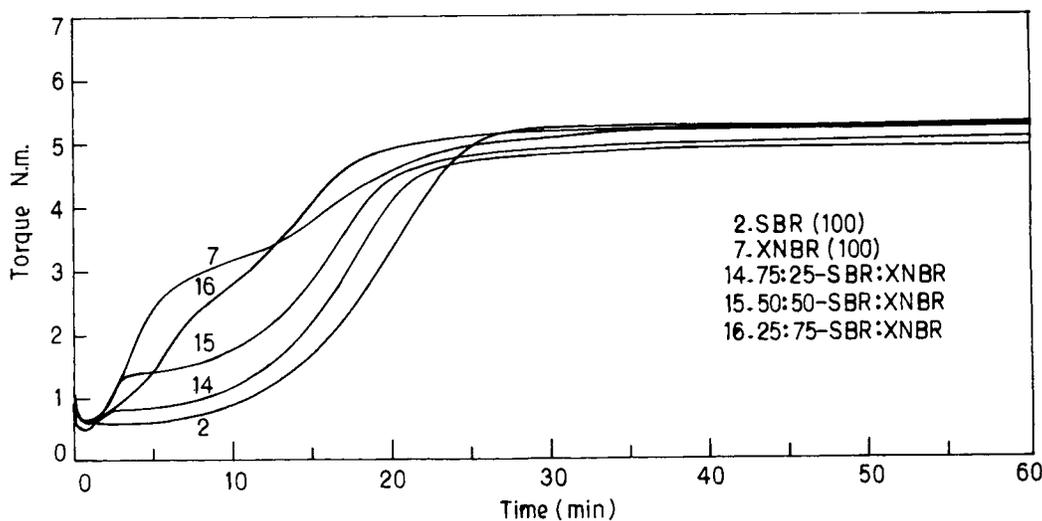
Figure 2   Rheographs of mixes 2, 7, 14–16 (Table I) cured at 160°C.
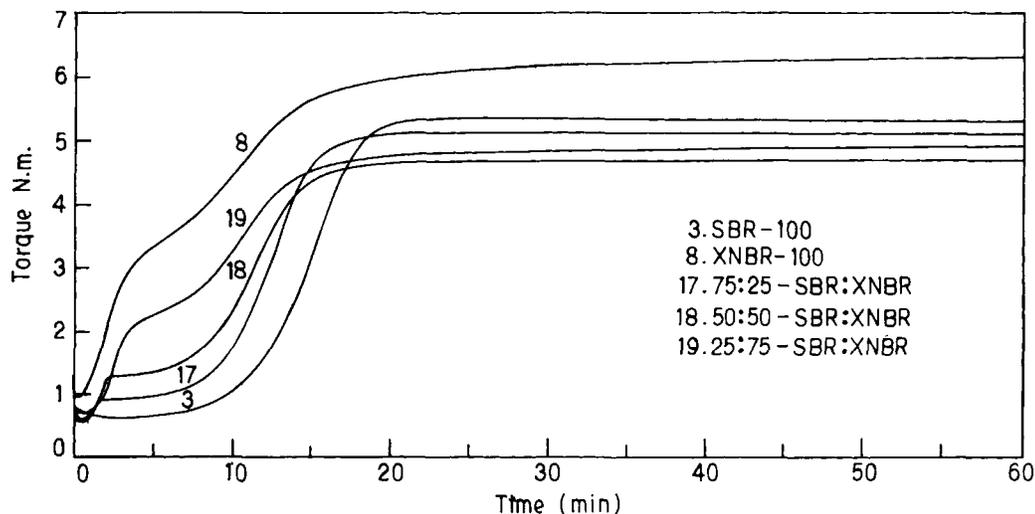
Figure 3 Rheographs of mixes 3, 8, 17–19 (Table I) cured at 160°C.

tensile strength. The interrubber crosslinks of the type mentioned above, conjointly with metallocarboxylate crosslinks, are responsible also for significant modulus as well as hardness values of the vulcanizates derived specially for 50 : 50 and 75 : 25 XNBR : SBR blends. Table III also records the data of elongation at break that show that the values progressively decrease from 75 : 25 SBR : XNBR to 25 : 75 SBR : XNBR vulcanizates.

There is reason to believe that this interrubber linking is basically polysulfidic in nature. This can be proved otherwise. Instead of incorporating sulfur and DIPDIS separately into a blend mix of 75 : 25 XNBR : SBR (mix 13, Table II), when a preheated (6 min at 140°C) mixture of DIPDIS and sulfur (in the same proporation as before) was added to the same blend mix under identical conditions, it was

found that modulus value fell marginally (from 2.00 to 1.88 MPa) and tensile strength increased notably (from 17.03 to 19.63 MPa). When a mixture of DIPDIS and sulfur is heated, polysulfides are potentially formed that expectedly increase the extent of formation of polysulfidic inter-rubber linkages of the type (XNBR moiety)COOP(S) — S_n — (SBR moiety) — S_n — P(S) OOC — (XNBR moiety) resulting in enhancement of tensile strength value.

Once again, the physical properties of the vulcanizates obtained from blends (mixes 11–22) in the presence of thiophosphoryl disulfides can be explained from the consideration of viscosities of SBR and XNBR. The viscosity of XNBR is higher than that of SBR. So during vulcanization[10] it is likely that SBR would flow first and encapsulate XNBR. In the process, the fragments of thiophosphoryl di-
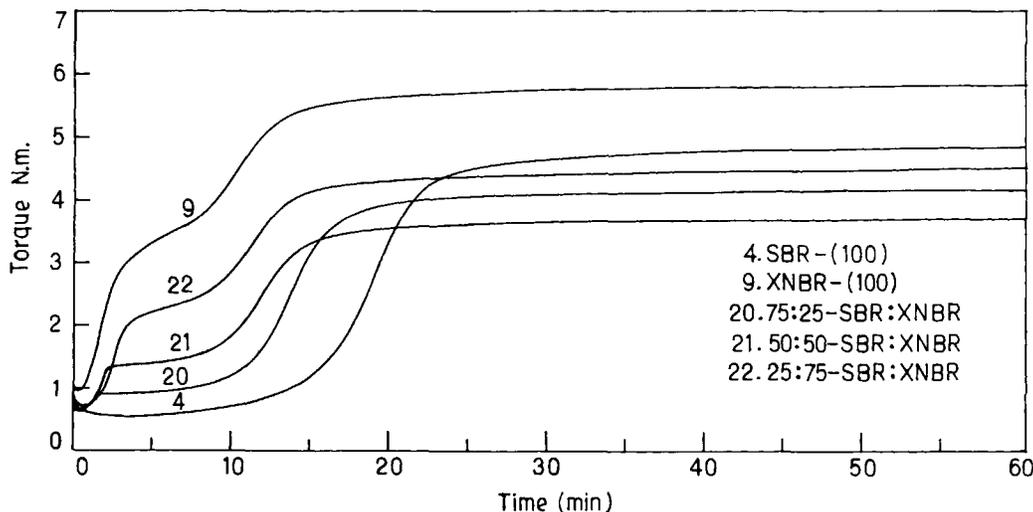
Figure 4 Rheographs of mixes 4, 9, 20–22 (Table I) cured at 160°C.
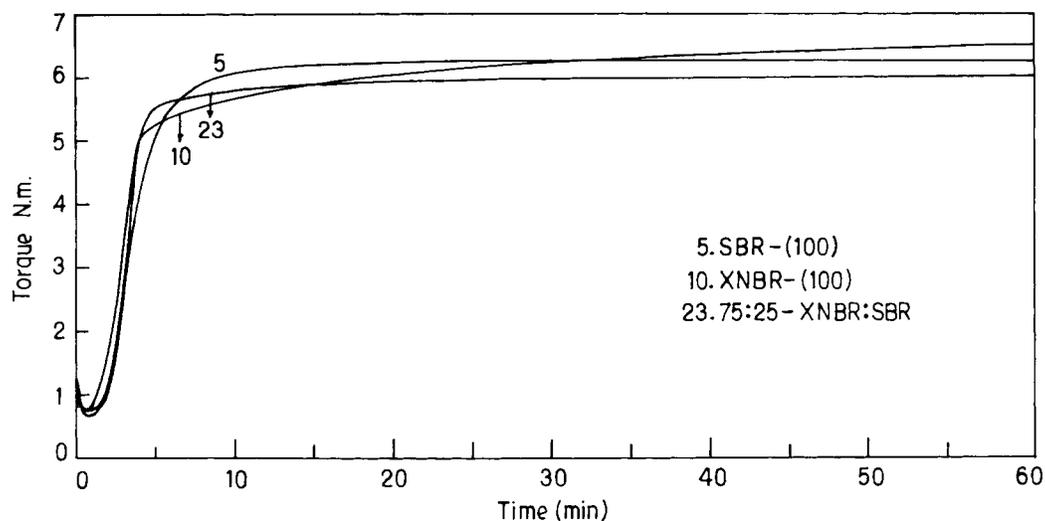
Figure 5   Rheographs of mixes 5, 10, 23 (Table I) cured at 160°C.

sulfide linked with the SBR backbone happen to combine with the pendent —COOH groups, dispersed along the XNBR chain (Scheme 1). This chemical union brings the two polar and nonpolar rubbers closer for the further reaction to take place.

It is evident from the data presented in Table III that in all the cases of SBR–XNBR blends, particularly for 50 : 50 and 25 : 75 SBR : XNBR, the extremely poor modulus and tensile values of the vulcanizates solely obtained with SBR are so im-

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

| Mix | 200% Modulus (MPa) | Tensile Strength (MPa) | Elongation at Break (%) | Hardness Shore-A | Aged in Air, 72 h at 100°C | | | Swelling Index, Q | Crosslinking Value, $1/Q$ |
					Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)		
1	0.57	1.01	380	51	0.87	0.99	270	2.2603	0.4424
2	0.60	1.05	350	52	0.89	0.99	260	2.1800	0.4587
3	0.63	1.16	380	53	0.93	1.20	320	1.9801	0.5050
4	0.57	1.06	420	51	0.73	1.09	320	2.1204	0.4716
5	1.02	1.33	280	55	1.11	1.17	200	1.8301	0.5464
6	1.46	11.65	600	65	1.80	10.27	500	0.3246	3.0803
7	1.72	16.98	600	68	2.42	16.10	510	0.3123	3.2020
8	1.68	18.26	600	68	2.19	16.96	450	0.2914	3.4317
9	1.75	18.88	580	69	2.15	18.98	480	0.2873	3.4806
10	1.53	4.11	430	66	2.76	6.77	350	0.3500	2.8571
11	1.04	7.32	550	57	1.55	6.38	410	1.6829	0.5942
12	1.90	15.29	530	70	2.57	13.16	350	1.1500	0.8695
13	2.00	17.03	510	71	2.86	15.13	380	0.6840	1.4619
14	1.21	7.54	570	58	1.69	6.20	480	1.6680	0.5995
15	1.96	16.10	550	70	2.69	15.50	480	1.1140	0.8976
16	2.09	18.18	540	71	3.10	17.90	460	0.6400	1.5625
17	0.81	7.55	600	55	1.54	5.21	410	1.6450	0.6079
18	1.27	12.24	550	62	2.26	11.42	420	1.1800	0.8474
19	1.76	16.77	530	68	2.53	17.10	440	0.7070	1.4144
20	0.78	7.16	590	54	1.38	6.40	430	1.7152	0.5830
21	1.43	12.47	550	63	2.30	13.96	420	1.2600	0.7936
22	1.72	17.85	520	68	2.62	16.85	420	0.7120	1.4044
23	1.57	7.11	500	64	2.35	7.48	400	1.7531	0.5704
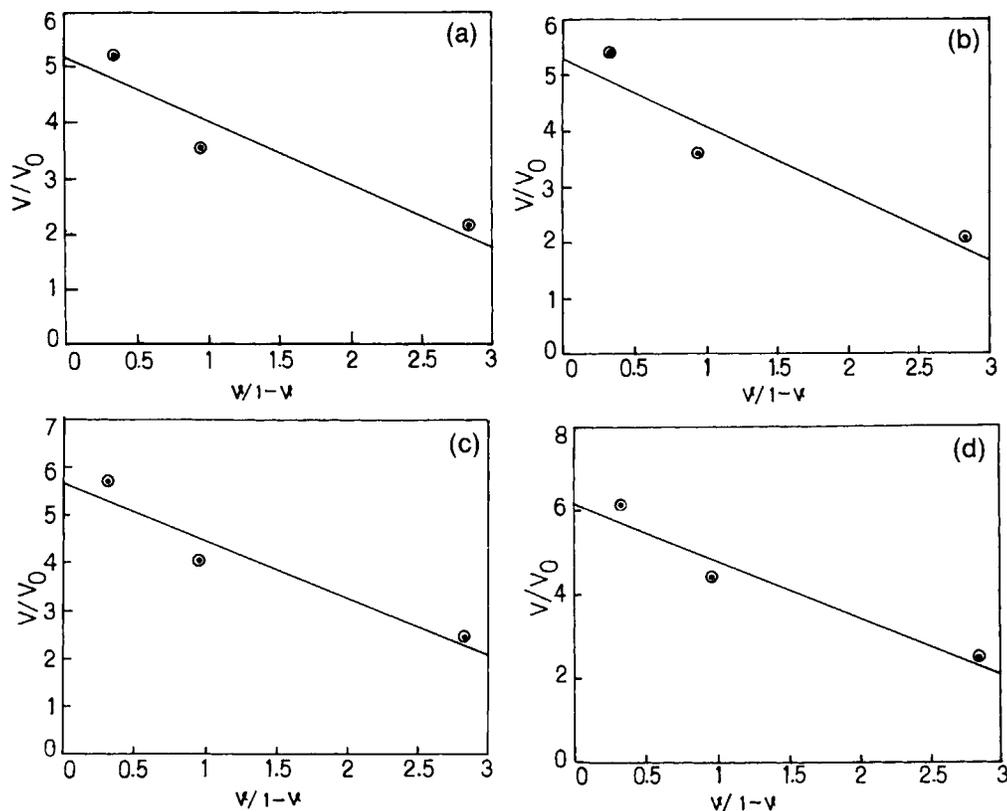
Figure 6 Kraus plots of SBR-XNBR blends in the presence of (a) DIPDIS; (b) DCHDIS; (c) DIPDIS : ODDS; (d) DIPDIS : OBTS.

proved that XNBR may be regarded as a reinforcing filler for SBR. It is reflected in the results that the modulus and tensile strength of the vulcanizates depend on the XNBR–SBR blend ratios and the most favorable condition for the reaction according to Scheme 1 persists in the XNBR : SBR blend ratio of 75 : 25. As regards the modulus and tensile strength of the vulcanizates derived from the blends containing DCHDIS (mixes 14–16), it can be seen that the values are somewhat superior to those ob-

tained with DIPDIS (mixes 11–13). When binary combinations of DIPDIS + ODDS (mixes 17–19) and DIPDIS + OBTS (mixes 20–22) are used to prepare SBR–XNBR blends, it is found that in these cases the tensile values are more or less similar to the previous cases (i.e., DIPDIS/DCHDIS compounded blends) for 75 : 25 or 25 : 75 SBR–XNBR blends (compare tensile values of mixes 11 and 14 with those of mixes 17 and 20 and tensile values of mixes 13 and 16 with those of mixes 19 and 22), but

Table IV   Formulation of Mixes for Two Stage Vulcanizates

	Mix	11'	12'	13'
First stage	SBR	75	25	25
	ZnO	5	5	5
	Stearic acid	2	2	2
	DIP DIS	3.834[a]	3.834[a]	3.834[a]
	S	0.5	0.5	0.5
Second stage (after preheating[b] compounded SBR at first stage)	XNBR	25	50	75
	SBR	—	25	—

[a] Wt corresponds to 9 mM DIP DIS.

[b] Preheating time (t) for mixes 11', 12', 13', at 140°C are 8, 15, and 15 min, respectively.

become surprisingly lower for 50 : 50 blends (compare tensile values of mixes 12 and 15 with those of mixes 18 and 21). Here, the modulus values are unexpectedly lower for all the cases than those obtained for DIPDIS/DCHDIS accelerated blend vulcanizates (compare modulus values of the vulcanizates of mixes 17–22 with those of mixes 11–16). The tensile strength values of pure XNBR vulcanizates, derived either from (DIPDIS + ODDS) or (DIPDIS + OBTS) accelerated combinations, are even higher than those of the blends comprising 75% XNBR and 25% SBR with the same binary combinations (compare the tensile strength values of the vulcanizates of mixes 8 and 9 with those of mixes 19 and 22). The reason is the decrease in the concentration of XNBR in the stock. From a comparison of the physical data of the vulcanizates obtained from mixes 13, 16, 19, and 22 with that of mix 23, it appears that both modulus and tensile strength of TMTD-accelerated blend vulcanizates (mix 23) are extremely low as compared to those obtained in the above mentioned combinations. This is due to the incapability of TMTD to react with —COOH groups of XNBR and the consequent absence of inter-rubber linking (Scheme 1).

Vulcanizates obtained from SBR are found to have good age resistance properties when these are obtained in the presence of DIPDIS, DCHDIS, or binary mixtures of DIPDIS + ODDS and DIPDIS + OBTS as seen from the results presented in Table III. The inherent property of SBR[11] to resist the thermooxidative degradation of rubber is further supported by the antioxidant coverage[12] provided by zinc dithiophosphate[1,13,14] (ZDP) formed *in situ*. XNBR vulcanizates are resistant to heat and oxidation due to the presence of metallocarboxylate

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

Mix	11'	12'	13'
Maximum rheometric torque, R_∞, (N·m)	4.10	4.30	4.50
Scorch time t_2 (min)	3.50	2.00	2.00
Optimum cure time, t_{90} (min)	22.00	16.00	17.00

linkages.[8,15] The presence of thiophosphoryl disulfides also acts as an additive factor to cause further improvement in the age resistance property of XNBR through the generation of ZDP *in situ*.[4] In this case nonconventional di- or polysulfidic crosslinks (arising from the reaction between —COOH groups of XNBR and thiophosphoryl disulfide), conjointly with metallocarboxylate crosslinks, give notable heat and oxidative aging resistance as shown in Table III. Thus it was expected that the blends of SBR and XNBR would also exhibit significant heat and age resistance properties. Actually this is observed from the results presented in Table III. Here all the blends of SBR and XNBR either in the presence of thiophosphoryl disulfides (DIPDIS or DCHDIS) or in the presence of equimolar proportions of the component accelerators, viz., DIPDIS, ODDS, OBTS, etc., exhibit a good degree of retention of original tensile strength values irrespective of the blend composition. As expected, the modulus values of all the vulcanizates increased and the values for elongation at break fell.[7,16,17]

The oil resistance property of XNBR is notable while that of SBR is rather poor. The chemical linkage between SBR and XNBR is likely to influence
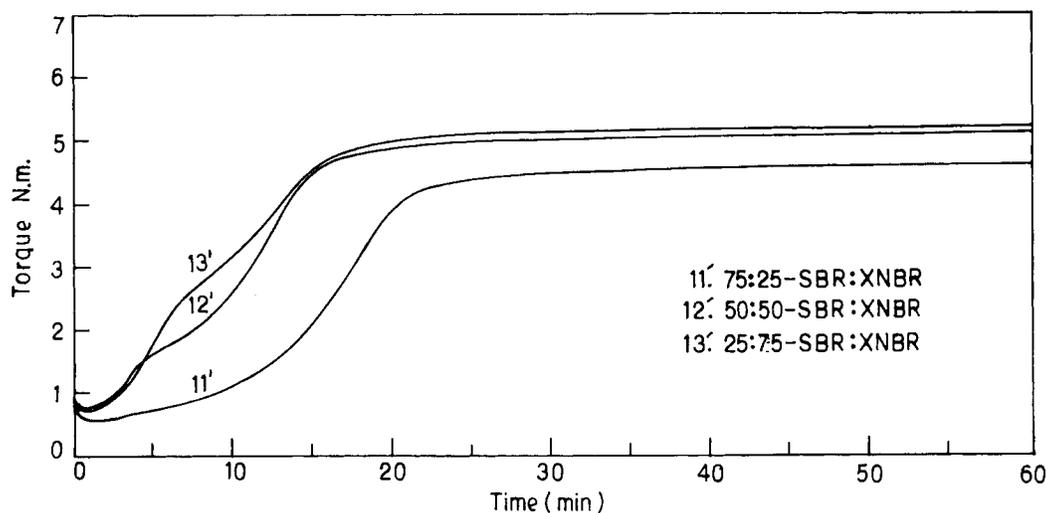
Figure 7   Rheographs of mixes 11'–13' (Table IV) cured at 160°C (second stage).

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

| Mix | 200% Modulus (MPa) | Tensile Strength (MPa) | Elongation at Break (%) | Hardness Shore-A | Aged in Air, 72 h at 100°C | | | Swelling Index, Q | Crosslinking Value, 1/Q |
					Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)		
11'	1.10	8.22	580	59	1.69	7.35	450	1.0800	0.9259
12'	2.07	17.46	570	71	2.74	16.08	440	0.6800	1.4705
13'	2.33	21.63	550	75	2.96	20.45	450	0.4900	2.0408

this property. The swelling index Q (see Experimental) was expected to shed some light in this regard. The results are given in Table III. It is evident from Table III that DCHDIS-accelerated vulcanizates of XNBR (mix 7) exhibit the best oil resistance property followed by DIPDIS-accelerated vulcanizates of XNBR (mix 6). The vulcanizates of XNBR containing DIPDIS + ODDS (mix 8) or DIPDIS + OBTS (mix 9) also show significant oil resistance behavior. Blends of SBR and XNBR, in each case, exhibit excellent oil resistance properties that are very dependent upon the concentration of XNBR in the blend. In this regard swelling indices of DCHDIS- and DIPDIS-compounded blends are very close to each other followed by those of DIPDIS + ODDS and DIPDIS + OBTS compounded blend vulcanizates. The results are suggestive of the formation of inter-rubber linkages between XNBR and SBR through thiophosphoryl disulfides as coupling agents. This aspect becomes more clear from the data obtained with TMTD-accelerated SBR–XNBR blend (mix 23), the vulcanizate of which exhibits poor resistance to swelling even though the blend contains an XNBR : SBR ratio of 75 : 25 for which highest properties are generally observed in other cases (see Q values of mixes 13, 16, 19, and 22). One probable explanation for this deficiency arises from the existence of noncoherent domains of SBR and XNBR lacking in interrubber linking as depicted in Scheme 1. It is evident from the results that higher values of $1/Q$ as observed for the vulcanizates derived from the mixes 13, 16, 19, and 22 suggest the formation of chemical links between SBR and XNBR.

The formation of interpolymer bonds (at the interfacial region) between SBR and XNBR Kraus plots[18] of SBR–XNBR blends swollen in isooctane : toluene (70 : 30) medium were investigated as shown in Figure 6 in accordance with the equation

$$\frac{V}{V_0} = -\frac{av}{1-v}$$

where V_0 and V are the swelling weights in isooctane : toluene, of XNBR vulcanizates and that of SBR–XNBR blend vulcanizates, respectively, and v is the volume fraction of XNBR in the blend vulcanizates. In Kraus plots, (i.e., V/V_0 vs. $v/1 - v$) when the slope of the line is negative there is strong interpolymer interaction. Again, the positive slope indicates no interaction between the two rubbers. In the present investigation the slopes of the lines obtained from several SBR–XNBR blends were found to be negative and these provided information regarding the formation of strong interrubber bonds in the presence of DIPDIS, DCHDIS, equimolar DIPDIS + OBTS combination, and equimolar DIPDIS + ODDS combination.

Two Stage Vulcanization

Earlier[4] we adopted this technique while blending XNBR and NR. It was observed that the two stage vulcanization process provides more insight into the chemistry of vulcanization reaction during the formation of the blend of XNBR with a nonpolar diene rubber like NR in the presence of DIPDIS.

The objective of two stage vulcanization is to increase the concentration of rubber-bound intermediates having pendent DIPDIS fragments along the polymer backbone of SBR, to a maximum level. This can be achieved by increasing the concentration of DIPDIS in SBR and preheating the resulting SBR compound for a predetermined time. From this point the second stage of vulcanization begins. The pendent moieties of DIPDIS, bound to the SBR backbone, then are made to react with the —COOH groups of XNBR. The resultant effect is thus the generation of more interrubber linkages and formation of novel blends having improved physical properties.

For two stage vulcanization of SBR–XNBR blends, two factors, preheating time and preheating temperature, are of utmost importance to ob-
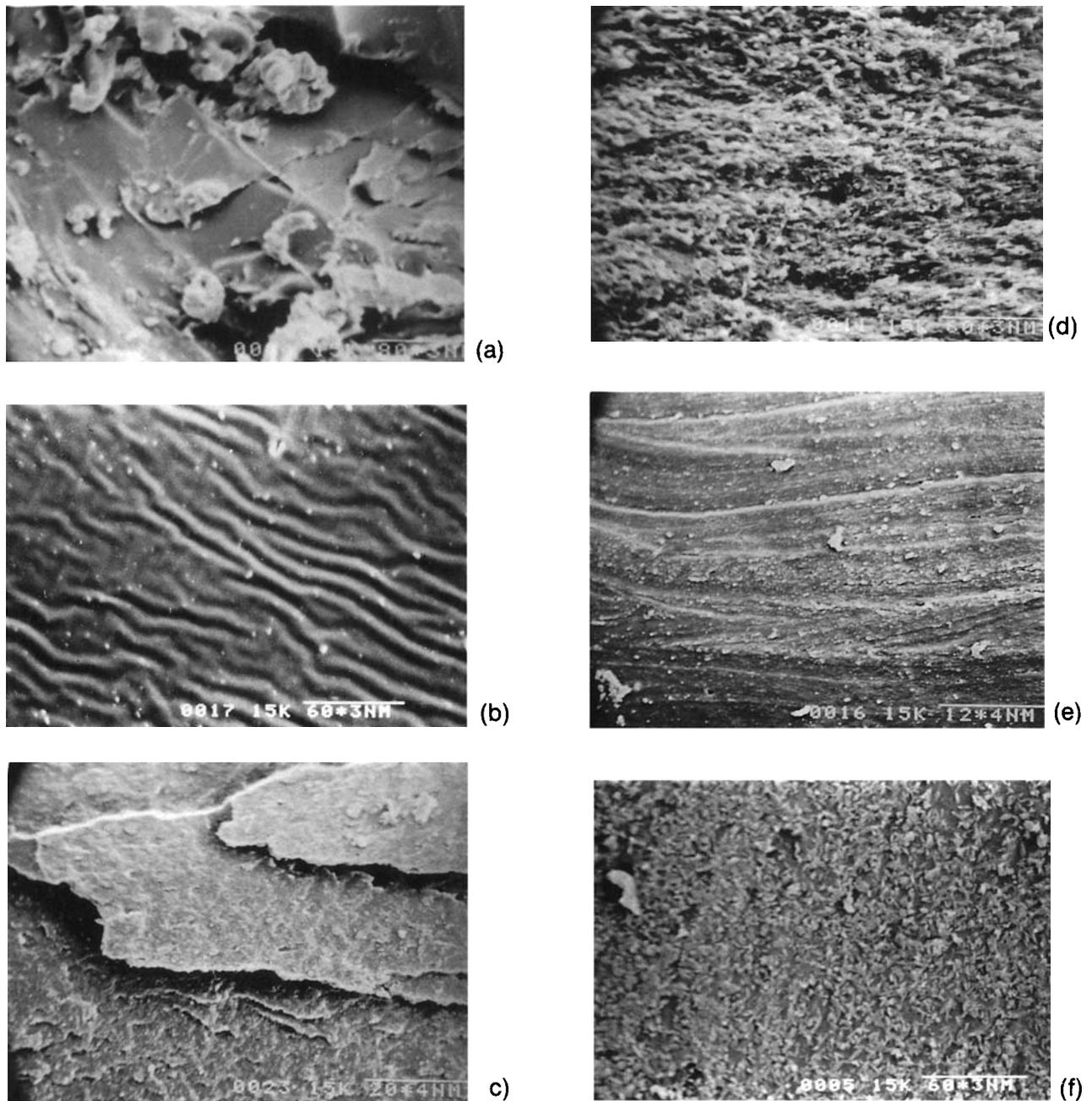
Figure 8 SEM micrographs of tensile fractured surfaces of the vulcanizates cured at 160°C. (a) SBR containing DIPDIS at 380×; (b) XNBR containing DIPDIS at 500×; (c) 75 : 25 SBR : XNBR blend containing DIPDIS (one stage) at 150×; (d) 50 : 50 SBR : XNBR blend containing DIPDIS (one stage) at 500×; (e) 25 : 75 SBR : XNBR blend containing DIPDIS (one stage) at 250×; (f) 25 : 75 SBR : XNBR blend containing TMTD (one stage) at 500×; (g) 75 : 25 SBR : XNBR blend containing DIPDIS (two stage) at 750×; (h) 50 : 50 SBR : XNBR blend containing DIPDIS (two stage) at 500×; (i) 25 : 75 SBR : XNBR blend containing DIPDIS (two stage) at 500×.

tain maximum concentration of the anticipated rubber-bound intermediate at the first stage. First of all, the preheating temperature is optimized at 140°C and then the preheating time is also ad-

justed for different blend compositions (see Experimental).

Table IV shows the composition and preparation of the blends in two stage vulcanization. It can be

(g)

(h)

(i)
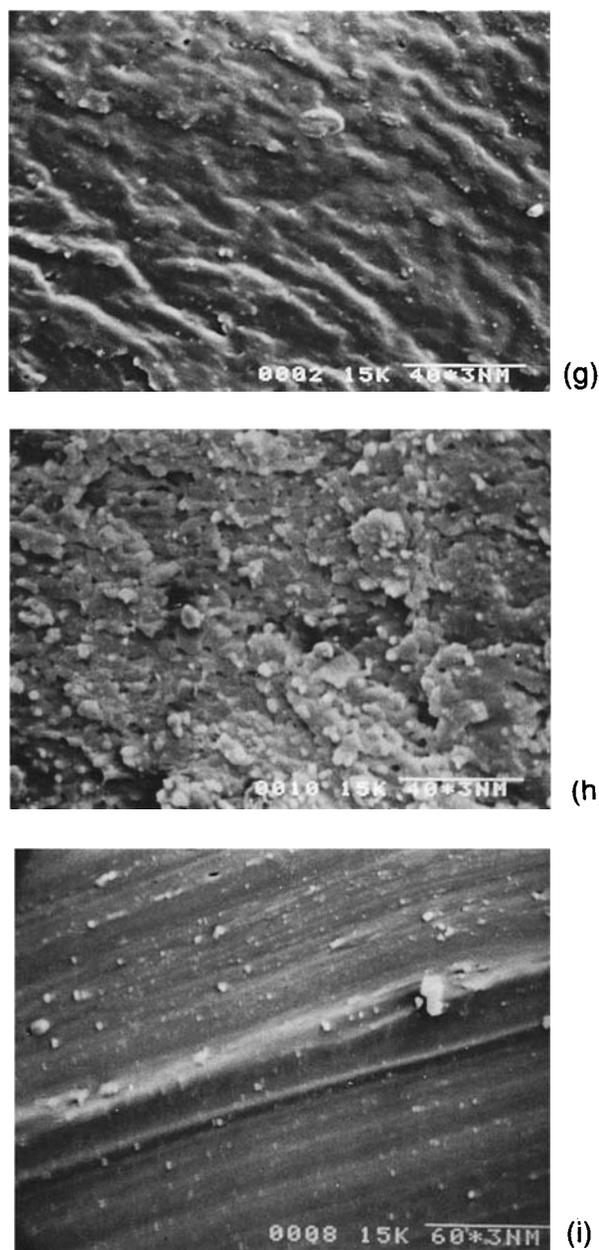
Figure 8 *(Continued from the previous page)*

seen from Table IV that DIPDIS : SBR ratio in mixes 11', 12', and 13' is progressively increased to obtain the desired results.

It can be seen from Table IV that in mix 12' (50 : 50 SBR : XNBR blend) only half of the requisite amount of SBR was added at the first stage (contrary to the case of mix 11' or 13' where a full amount of SBR was added at the first stage). At the second stage, the remaining portion of SBR was added along with the requisite amount of XNBR. This variation in technique adopted for the above mentioned composition can be explained in the following way.

The presence of styrene groups along the polymeric backbone of SBR hinders the reaction of DIPDIS with SBR. As a result, there may occur a shortfall in the concentration of rubber-bound intermediate as compared to that obtained with NR[4] on the previous occasion. This effect is very pronounced in the case of the equimolar mixture of XNBR and SBR. To circumvent this difficulty, 25 g of SBR in the first stage contained the whole amount of different ingredients in order to enhance the DIPDIS : SBR ratio and thus the rubber-bound intermediate. The mix thus obtained was preheated at 140°C for the predetermined period of time and the resulting grossly undercured mass was then mixed with the remaining 25 g of SBR along with 50 g of XNBR as shown in Table IV.

This technique, however, failed in the case of 75 : 25 SBR : XNBR blend (mix 11', Table IV) containing an even higher amount of SBR as compared to that in mix 12'. It is believed that a substantial amount of SBR incorporated in the final stage significantly lowers the effective concentration of the rubber-bound intermediate that ultimately impairs the formation of interrubber crosslinkages.

Figure 7 represents the cure curves at the second stage in two stage vulcanization of blends. Table V represents the cure characteristics of two stage vulcanizates of blends. From a comparison of the cure data of one stage vulcanizates blends (mixes 11, 12, 13 of Table II) with those of two stage vulcanizates blends (mixes 11', 12', 13' of Table V), it can be seen that R_∞ values for all the blends remain more or less the same in both cases while the values of scorch safety for the blends are slightly increased in the two stage vulcanization process. The values of optimum cure time of two stage vulcanizates of all the XNBR : SBR blends diminish as compared to those derived in one stage vulcanization.

The physical properties of the vulcanizates derived from mixes 11', 12', and 13' in two stage vulcanization are shown in Table VI. In all cases there is significant improvement in modulus and tensile strength values than those obtained in one stage vulcanization blends. As expected, the vulcanizates of mix 13' exhibit the highest modulus, tensile strength, and hardness. This trend is also maintained in the age resistance and solvent resistance behavior of the vulcanizates.

SEM

The chemical bonding between SBR and XNBR in the presence of thiophosphoryl disulfide is apt to form a compact and coherent rubber matrix. So, SEM studies were considered to reveal this fact. In

this regard the tensile fractured surfaces of DIPDIS-accelerated vulcanizates of SBR, XNBR, and their blends derived from both one stage and two stage vulcanization processes were studied.

Figure 8(a,b) shows tensile fractured surfaces of SBR and XNBR vulcanizates in the presence of DIPDIS (mixes 1 and 6, Table I). Figure 8(c–e) represent SEM micrographs of DIPDIS-accelerated blends of SBR and XNBR in the proportion of 75 : 25, 50 : 50, and 25 : 75, respectively (mixes 11, 12, and 13, Table I). Figure 8(f) provides a SEM micrograph of TMTD-accelerated SBR–XNBR blend (25 : 75) (mix 23, Table I); Figure 8(g–i) depicts SEM micrographs of the blends of SBR and XNBR obtained in two stage vulcanization (mixes 11', 12', 13', Table IV).

The SEM micrograph of SBR vulcanizate shows loose blocks of rubber segments appearing as shattered surfaces and thus explains the observed poor mechanical properties of SBR. The fractured surface of XNBR vulcanizate exhibits unidirectional ripplings appearing as a compact and homogeneous surface and thus is responsible for the good mechanical properties of the vulcanizates.

From Figure 8(c–e) it is evident that for SBR-XNBR blends, the state of dispersion is progressively improved (the number of vacuoles are progressively reduced) as we go from Figure 8(c) to 8(e). In fact a good degree of homogeneity is found for the blend having an SBR : XNBR ratio of 25 : 75, suggestive of very good mechanical properties of the vulcanizates of mix 13. From a comparison of Figure 8(e) and 8(f) for example, DIPDIS- and TMTD-accelerated SBR–XNBR (25 : 75) blend vulcanizates obtained in one stage vulcanization, it is clear that the vulcanizates of mix 23 contain a considerably larger number of vacuoles indicating a poor state of dispersion of SBR in XNBR. This inhomogeneity in the micrograph clearly suggests the absence of chemical bonding in the SBR–XNBR blend in the presence of TMTD. This is also manifested in the poor mechanical properties of the vulcanizates of mix 23 as compared to those of mix 13. In the latter case, chemical bonding between SBR and XNBR confers some ordered orientation of the rubber matrix thereby generating strong lines of reinforcement as visualized through the development of parallel lines during tensile fracture of the vulcanizates [Fig. 8(e)].

The effect of two stage vulcanization can be envisaged from the comparison of the SEM micrographs of one stage vulcanizates blends with those of two stage vulcanizates of SBR–XNBR blends for example, by comparing Figure 8(c), 8(d), and 8(e) with 8(g), 8(h), and 8(i), respectively. It is evident

that the two stage vulcanization further reduces the number of vacuoles, giving a superior dispersion state of the two rubbers and renders the vulcanized rubber matrix more homogeneous and more compact. This enhancement of coherency between the two rubbers accounts for the improvement in the physical properties of the vulcanizates of mixes 11', 12', and 13' over mixes 11, 12, and 13, respectively. In fact the development of extremely strong and thick lines of reinforcement in the tensile fractured surface of the vulcanizate of mix 13' [Fig. 8(i)] explains its excellent mechanical properties.

REFERENCES

1. J. G. Pimblott, G. Scott, and J. E. Stuckey, *J. Appl. Polym. Sci.,* **19,** 865 (1975).
2. T. Biswas, N. Naskar, and D. K. Basu, *Kautschuk Gummi Kunststoffe,* **46,** 125 (1993).
3. T. Biswas, S. K. Mandal, and D. K. Basu, *Kautschuk Gummi Kunststoffe,* **47,** 508 (1994).
4. N. Naskar, T. Biswas, and D. K. Basu, *J. Appl. Polym. Sci.,* **52**(8), 1007 (1994).
5. K. Mori, *Rubber Chem. Technol.,* **60,** 822 (1987).
6. T. Biswas and D. K. Basu, unpublished data.
7. L. Bateman, C. G. Moore, M. Porter, and B. Savile, in *The Chemistry and Physics of Rubber-Like Substances,* L. Bateman, Ed., Maclaren and Sons Ltd., London, 1963, Chap. 15, 449.
8. H. P. Brown, *Rubber Chem. Technol.,* **36,** 931 (1963).
9. L. Bateman, J. I. Cunneen, C. G. Moore, L. Mullins, and A. G. Thomas, in *The Chemistry and Physics of Rubber-Like Substances,* L. Bateman, Ed., Maclaren and Sons Ltd., London, 1963, Chap. 19, p. 715.
10. D. R. Paul and J. W. Barlow, *J. Macromol. Sci.-Rev. Macromol. Chem.,* **C18**(1), 109 (1980).
11. W. M. Saltman, *Rubber Technology,* M. Morton, Ed., Van Nostrand Reinhold, New York, 1973, Chap. 7, p. 178.
12. A. J. Burn, *Tetrahedron,* **22,** 2153 (1966).
13. J. G. Pimblott, G. Scott, and J. E. Stuckey, *J. Appl. Polym. Sci.,* **23,** 3621 (1979).
14. S. Kaucharik and M. Pospisil, *Sb. Vys. Sk. Chem.-Technol.,* **S5,** 293 (1981).
15. S. K. Chakraborty, A. K. Bhowmick, and S. K. De, *J. Appl. Polym. Sci.,* **26,** 4011 (1981).
16. A. Kaehl, *Rubber Chem. Technol.,* **43,** 651 (1976).
17. R. N. Dutta, M. M. Das, D. K. Basu, and A. K. Chaudhuri, *Rubber Chem. Technol.,* **57,** 879 (1984).
18. G. Kraus, *J. Appl. Polym. Sci.,* **7,** 861 (1963).