Polymer Blend: A Novel Method for the Preparation of a Natural Rubber–Carboxylated Nitrile Rubber Blend

NITYANANDA NASKAR, TAPASI BISWAS, and DIPAK KR. BASU*

Polymer Science Unit, Indian Association for the Cultivation of Science Jadavpur, Calcutta 700032, India

SYNOPSIS

Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) can be successfully used to form a blend comprising polar carboxylated nitrile rubber (XNBR) and nonpolar NR through a chemical link between the two. It is revealed from the study that the physical properties of the vulcanizates obtained from the NR-XNBR blend could be significantly improved by the judicious selection of the NR:XNBR ratio. These properties can further be improved by two-stage vulcanization as described in the procedure. The SEM study reveals that it is possible to form a coherent blend of NR and XNBR in the presence of DIPDIS. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

It has been observed that bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) reacts with carboxylated nitrile rubber (XNBR) during vulcanization.[1] Earlier workers also observed that DIPDIS, apart from its activity both as accelerator and sulfur donor, can react with NR and form pendent groups along the elastomeric chain in the early stage of vulcanization.[2] It was thought that on the basis of these reactions DIPDIS could be effectively utilized to form a predominantly coherent rubber blend comprising nonpolar NR and polar XNBR. The objective of the present work was to find the conditions for optimum reaction between XNBR and NR in the presence of DIPDIS, to investigate the cure behaviour of such an NR–XNBR blend, and to study the properties of the vulcanizates derived from these blends.

EXPERIMENTAL

Materials

DIPDIS was prepared and purified according to the procedure reported by Pimblott and co-workers.[2]

Commercial grade tetramethylthiuram disulfide (TMTD) was used in the present investigation. Carboxylated nitrile rubber, Krynac 221 (highly carboxylated with medium acrylonitrile content; mL-1 + 4' at 100°C, 50; total ash content 0.7%, nonstaining antioxidant; specific gravity 0.98) was obtained from Polysar Ltd. (Sarnia, Canada). Natural rubber (RMA 1X) was purchased from the local market.

Preparation of Vulcanizates and Measurement of Physical Properties

One-Stage Vulcanization of NR–XNBR Blend

NR and XNBR were first masticated separately. Masticated XNBR was cut to pieces and added to previously masticated NR. Requisite amounts of ZnO, stearic acid, and DIPDIS/TMTD were incorporated in the NR–XNBR mix on a Berstorff lab mill 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 NR–XNBR Blends

In this procedure requisite amounts of NR and XNBR were first masticated separately. The whole amount of compounding ingredients was incorporated in NR. A portion of this mix was cured at 160°C in a Monsanto Rheometer (R-100). The time

(t) for the commencement of cure, using this mix was noted from the rheograph. A portion of the compounded NR was then heated at 160°C in a hydraulic press for this predetermined time (t) where a grossly undercured NR mix was obtained. The material was then mixed with the requisite amount of masticated XNBR in order to maintain the desired ratio. The vulcanizates were obtained under pressure at 160°C.

## Measurement of Physical Properties

After keeping the vulcanizates for 24 h at ambient temperature, physical properties like modulus at 200% elongation and tensile strength were measured according to ASTM D412-51T.

In the aging experiment, the vulcanizates obtained at optimum cure were aged for 72 h at 100 ± 1°C in an oven provided with forced air circulation. The specimens thus aged were kept for a further period of 24 h at room temperature before measuring modulus, tensile strength, elongation at break, etc.

In the swelling experiment, a weighed rubber sample was immersed in (70 : 30) isooctane-toluene medium for 48 h at ambient temperature, 30 ± 2°C. The rubber was removed, blotted quickly with filter paper, and weighed in a tared weighing bottle. After removal of the solvent in a vacuum oven, the weight of the imbibed solvent was obtained as the difference between the weight of the swollen sample and the dried sample. The swelling value, Q, defined as the grams of solvent per gram of rubber hydrocarbon, is readily calculated[3] from the expression:

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

where formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of
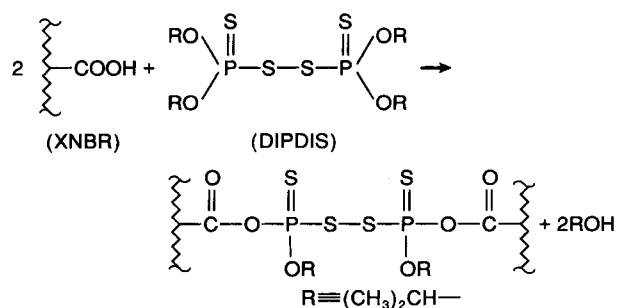
Scheme 1 Reaction of DIPDIS with XNBR.
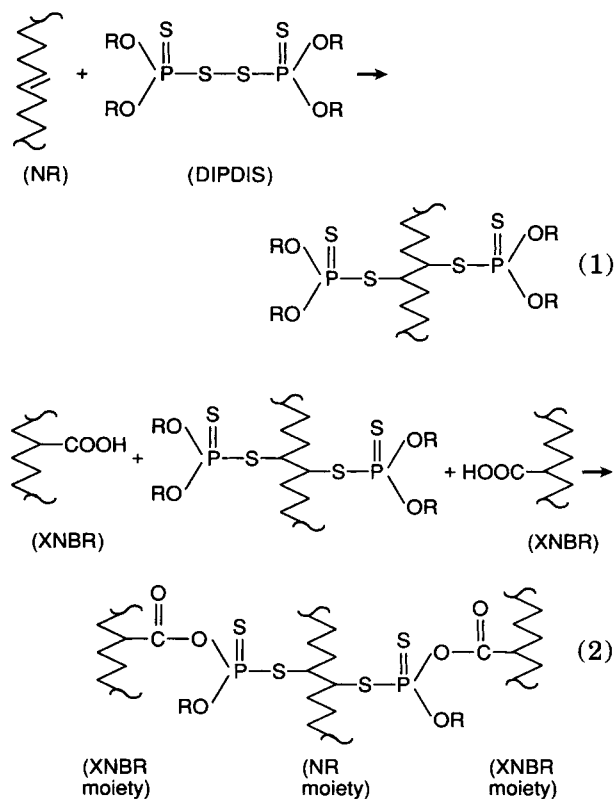
Scheme 2 Reaction of DIPDIS with NR and XNBR.

rubber. A comparison of the cross-linking values was also made from the reciprocal of swelling values.

Scanning Electron Microscopy (SEM) Studies

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

RESULTS AND DISCUSSION

It has been established[1] that DIPDIS is capable of bringing about vulcanization of XNBR even in the absence of ZnO and sulfur. The reaction is presented in Scheme 1.

From the results obtained in the vulcanization of NR in the presence of DIPDIS,[2] DIPDIS reacted with NR and formed a rubber-bound intermediate having pendent accelerator groups in the early part of vulcanization. Thus it may be reasonably expected that NR, XNBR, and DIPDIS might react in the manner as presented in Scheme 2.

Table I   Formulation of Mixes for One-Stage Vulcanization

Mix	1	2	3	4	5	6	7	8	9
NR	100	—	75	50	25	25	100	—	—
XNBR	—	100	25	50	75	75	—	100	100
ZnO	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2
DIPDIS	3.834[a]	3.834[a]	3.834[a]	3.834[a]	3.834[a]	—	—	—	—
TMTD	—	—	—	—	—	2.16[b]	2.16[b]	2.16[b]	—
S	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	—

[a] Weight corresponds to 9 mmol DIPDIS.
[b] Weight corresponds to 9 mmol TMTD.

Scheme 2 suggests that DIPDIS can form chemical links between NR and XNBR and thus establish close proximity between polar XNBR and nonpolar NR. This type of molecular arrangement is expected to influence the physical properties of these blends. Recently, it has been reported[4] that 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DBAT) can co-vulcanize vinylidenefluoride-hexafluoropropane copolymer and acrylonitrile-butadine rubber that have different reactive groups and little compatibility. Close adhesion resulting in the interface of the two polymers through DBAT also showed better physical properties.

One-Stage Vulcanization

To start with the cure behavior of compounded NR (mixes 1 and 7), XNBR (mixes 2 and 8), and their blends (mixes 3–6), in accordance with the recipes presented in Table I, was studied. The data for the cure characteristics, obtained from Monsanto Rheometer (R-100), are presented in Table II and the course of vulcanization reaction is depicted in Figures 1 and 2. The numbers shown on the curves correspond to those used for the formulations recorded in Table I. DIPDIS, apart from its reaction with NR and XNBR,[1] is recognised as a sulfur donor[2] in the vulcanization of NR. TMTD like DIPDIS also functions as a sulfur donor but it does not react with the —COOH group of XNBR.[1] It was thus thought that in this study the inclusion of

TMTD would help to explain the function of DIPDIS in the vulcanization of blends. It can be seen from the cure data (Table II) that both DIPDIS and TMTD are capable of raising the R_∞ values of XNBR and NR. The intermediate formulations (mixes 3–6), however, show a decrease in R_∞. The reaction of XNBR both with DIPDIS and TMTD under the experimental conditions is very fast and thus the recipes exhibit low values of t_2 for XNBR and XNBR–NR combinations (except for mix 3). The optimum cure time values (t_{90}) for DIPDIS- and TMTD-accelerated compositions of XNBR seem to be unexpectedly high (mixes 2 and 8) in the light of the fastness of cure. It is seen from Figure 1 that marching cure occurs in TMTD accelerated stock (mix 8) with two different types of cure (evident from the cure curve) resulting for DIPDIS-accelerated vulcanization.[1] This is also true for the intermediate compositions (mixes 4 and 5). Here an initial onset of cure proportional to the concentration of XNBR was observed. Mere absence of two types of reaction in mix 3 (containing the lowest amount of XNBR) corroborates this fact and a typical S-shaped cure curve was obtained in this case. However, the situation was quite different in the presence of TMTD. The cure behaviour of mix 6, where the composition resembles that of mix 5, showed the typical steep cure curve (characteristic of TMTD cure) and complete absence of two types of reactions as seen in the vulcanization of mix 5.

The physical data obtained in one stage vulcan-

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

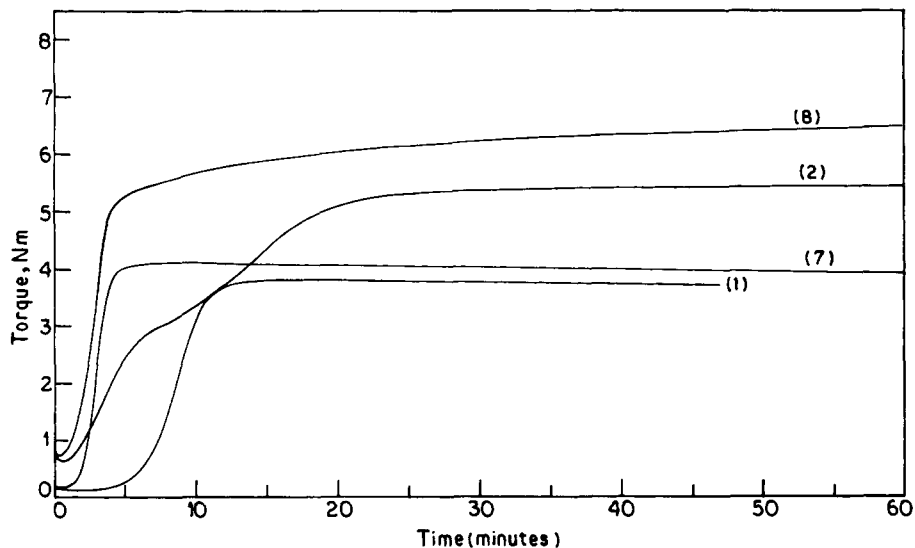| Mix	1	2	3	4	5	6	7	8
Maximum rheometric torque, R_∞, (Nm)	3.70	4.95	3.30	3.20	3.20	2.70	3.95	5.80
Scorch time t_2 (min)	4.5	1.0	5.0	1.0	1.0	1.0	1.5	1.0
Optimum cure time, t_{90} (min)	10.5	19.0	13.0	15.0	17.0	4.5	4.0	16.5

Figure 1 Rheographs of mixes 1, 2, 7, and 8 (Table I) cured at 160°C.

ization are presented in Table III. The results indicate that modulus values of NR vulcanizates (mixes 1 and 7) obtained either with DIPDIS or with TMTD are more or less the same but are considerably lower than that obtained with XNBR vulcanizates under similar conditions (mixes 2 and 8). Note that the modulus values of the vulcanizates of mixes 2 and 8 are also more or less similar. The intermediate compositions (mixes 3–5) exhibited significantly high modulus. Like the torque values, the modulus of TMTD-accelerated vulcanizates of mix 6 were very close to that of DIPDIS-accelerated vulcani-

zates (mix 5) having otherwise identical amounts of rubber additives.

The tensile strength of NR vulcanizates obtained either with DIPDIS or with TMTD (compare the values of mix 1 with mix 7) is almost the same, but differences appear in the presence of XNBR (compare the values of mix 2 with that of mix 8). The tensile strength values of intermediate compositions (mixes 3–5), accelerated by DIPDIS are significantly high. Unlike modulus, TMTD-accelerated vulcanizate of mix 6 showed very poor tensile strength as compared to that of DIPDIS-accelerated
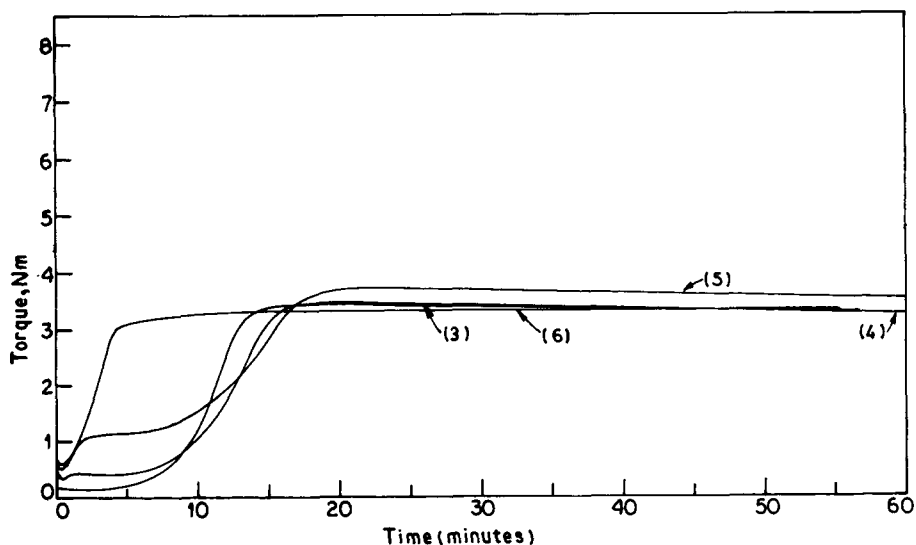

Figure 2 Rheographs of mixes 3–6 (Table I) cured at 160°C.

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

| Mix | 200% Modulus (MPa) | Tensile Strength (MPa) | Elongation at Break (%) | Aged in Air, 72 h at 100°C | | | | |
				Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Swelling Index (Q)	Cross-linking Value (1/Q)
1	0.59	14.90	720	0.87	7.26	520	3.00	0.33
2	1.49	11.11	610	1.83	7.96	495	0.32	3.08
3	1.01	13.14	650	1.06	10.03	500	2.04	0.49
4	1.09	15.07	600	1.62	10.64	470	1.04	0.96
5	1.37	17.94	620	1.68	16.42	520	0.54	1.86
6	1.38	7.80	450	1.99	7.84	390	1.95	0.51
7	0.53	14.51	730	0.56	7.05	600	2.61	0.38
8	1.53	4.11	430	2.76	6.77	350	0.35	2.82
9	1.84	12.67	570	—	—	—	—	—

vulcanizate of mix 5. Table III also records the data of elongation at break that showed nonuniformity in the results.

In order to understand clearly the underlying principles of the above facts, let us consider the different types of cross-links potentially present in different vulcanizates: metallocarboxylate cross-link arising between the reaction of XNBR and ZnO; nonconventional disulfidic cross-link formed in the reaction of XNBR and DIPDIS (Scheme 1); conventional sulfur crosslink; and interrubber linking through DIPDIS (Scheme 2).

It is well known that metallocarboxylate cross-links are highly flexible and thus are capable of imparting high tensile strength and modulus.[5]

The last two cross-links, arising from the reactions according to Schemes 1 and 2, facilitate crosslink slippage,[6] thereby enhancing modulus and tensile strength of the vulcanizates.

In the present investation high accelerator to low sulfur ratio was used. Therefore primarily monosulfidic cross-links are formed in the network which exhibit poor modulus and tensile strength.[7]

The physical properties of vulcanizates obtained from blends (mixes 3–5) in the presence of DIPDIS can be explained from the consideration of viscosities of NR and XNBR. The viscosity of NR is lower than that of XNBR. So during vulcanization[8] it is likely that NR would flow first and encapsulate XNBR. In the process, the fragments of DIPDIS linked with NR backbone happen to combine with the pendent —COOH groups dispersed along the XNBR chain. This chemical union brings the two polar and nonpolar rubbers closer for the further reaction to take place.

The conjoint effect of metallocarboxylate crosslink and that due to the reaction between the —COOH group of XNBR and DIPDIS fragments pendent to NR, explains the high values of modulus and tensile strength in blends (mixes 3–5; Table III).

Table IV   Formulation of Mixes for Two-Stage Vulcanization

Mix	3'	4'	5'
First stage			
NR	75	50	25
ZnO	5	5	5
Stearic acid	2	2	2
DIPDIS	3.834[a]	3.834[a]	3.834[a]
S	0.5	0.5	0.5
Second stage (after preheating[b] compounded NR at first stage)			
XNBR	25	50	75

[a] Weight corresponds to 9 mmol DIPDIS
[b] Preheating times (t) for mixes 3', 4', and 5' at 160°C are 2.5, 4.0,, and 4.5 min, respectively.
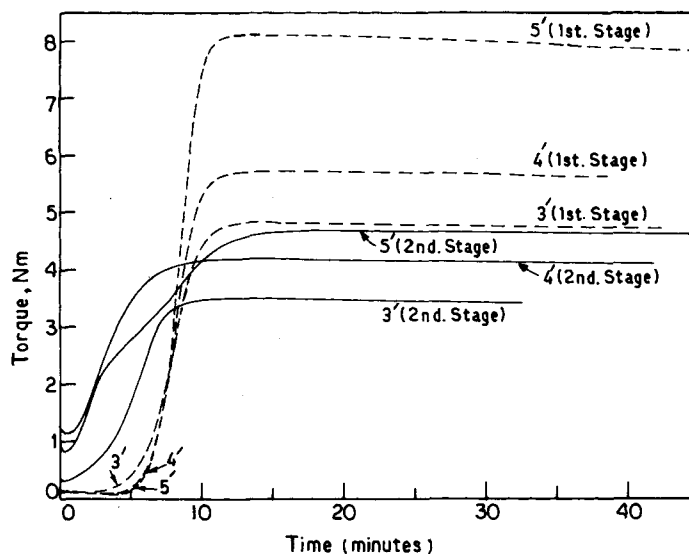
Figure 3 Rheographs of mixes 3'-5' (Table IV) cured at 160°C. (- - - -) first stage, (———) second stage.

It seems from the results that the most favorable condition for these reactions persists in the case of mix 5 (containing NR and XNBR in the ratio of 25 : 75), which evidently generates vulcanizates of highest modulus and tensile strength.

From a comparison of the physical data obtained from mixes 5 and 6, it appears that although the modulus values of the vulcanizates are nearly the same, the tensile strength and elongation at break values vary widely. This is due to the incapability of TMTD to react with the —COOH group of XNBR, resulting in the absence of interrubber linking (Scheme 2). Moreover, fast curing TMTD forms monosulfidic links that perhaps block the pendent —COOH groups of XNBR, thereby debarring these to a large extent from the formation of flexible metallocarboxylate cross-links causing further decline in the tensile values. The above proposition is also corroborated by comparing the physical data of

mixes 8 and 9. The vulcanizate of mix 9 can form only the metallocarboxylate cross-links. From Table III it is evident that this vulcanizate possesses modulus and tensile values significantly higher than those obtained with TMTD (mix 8).

Vulcanizates obtained from XNBR are resistant to heat and oxidation due to the presence of metallocarboxylate linkages.[9] DIPDIS-accelerated NR vulcanizates possess high thermal and thermal oxidative stability due to the formation of zinc diisopropyldithio phosphate (ZDP) *in situ*.[2] So it was expected that the blends would also exhibit this phenomenon. Actually this was observed from the modulus and tensile values (Table III) of vulcanizates obtained after aging for 72 h at 100°C. As expected, modulus values of all the vulcanizates increased. The tensile strength of most of the vulcanizates decreased (except those for mixes 6 and 8). The results indicate that DIPDIS-accelerated NR–

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

				Aged in Air, 72 h at 100°C				
Mix	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Swelling Index (Q)	Cross-linking Value (1/Q)
3'	1.10	15.18	660	1.66	12.08	460	0.98	1.02
4'	1.37	16.26	610	1.84	13.82	520	0.58	1.73
5'	1.63	21.94	620	2.24	20.18	530	0.34	2.94

XNBR blends (mixes 3–5) are resistant to aging. However, the vulcanizate of mix 5 exhibited the best heat resistance property as far as tensile strength is concerned (91% retention of original value). As expected the values for elongation at break also fell.

XNBR possesses a prominent oil resistance property; NR exhibits very poor solvent resistance. The chemical linkages between XNBR and NR is likely to influence this property. The swelling index Q (see experimental), was expected to shed some light on this. The results are given in Table III. It is evident from the table that DIPDIS-accelerated XNBR vulcanizate (mix 2) exhibited the best oil resistance property. It is followed by TMTD, accelerated vulcanizate of XNBR (mix 8). DIPDIS-accelerated blends (mixes 3–5) show significant oil resistance values that depend very much upon the concentration of XNBR in the blend. TMTD-accelerated NR-XNBR blend (mix 6) exhibits poor resistance to swelling. Although the NR to XNBR ratio (25 : 75) for this blend is exactly the same as in mix 5, an abnormally high value of Q was noticed in the former case due to the formation of noncoherent domains of NR and XNBR lacking in interrubber linking (Scheme 2). A significantly low value for Q was noticed in the latter case owing to the formation of chemical linking between NR and XNBR.

DIPDIS thus plays a significant role in the NR-XNBR blend, the vulcanizates of which could be effectively used in the areas where thermal and age resistance, oil resistance, modulus, tensile strength etc. of the rubber vulcanizates are needed most.

Two-Stage Vulcanization

DIPDIS reacts with NR in the initial part of vulcanization to form rubber-bound intermediates that ultimately take part in the interrubber cross-linking reaction (Scheme 2).

It was our objective to increase the concentration of the rubber bound intermediates through the incorporation of adequate amount of DIPDIS in NR and to preheat this resulting NR compound to obtain the maximum concentration of this intermediate. Keeping this in mind, it was decided to switch over from one-stage vulcanization to two-stage vulcanization where the vulcanization of blends were carried out in two stages. The grossly undercured material obtained in the first stage (see Experimental) is likely to contain a higher amount of reactive fragments compared to that obtained in one stage. The intermediates thus formed are expected to combine

with the —COOH groups of XNBR in the second stage of this procedure, the resultant effect being the generation of more interrubber linkages and formation of novel rubber blends of notable physical properties.

(a)

(b)

(c)
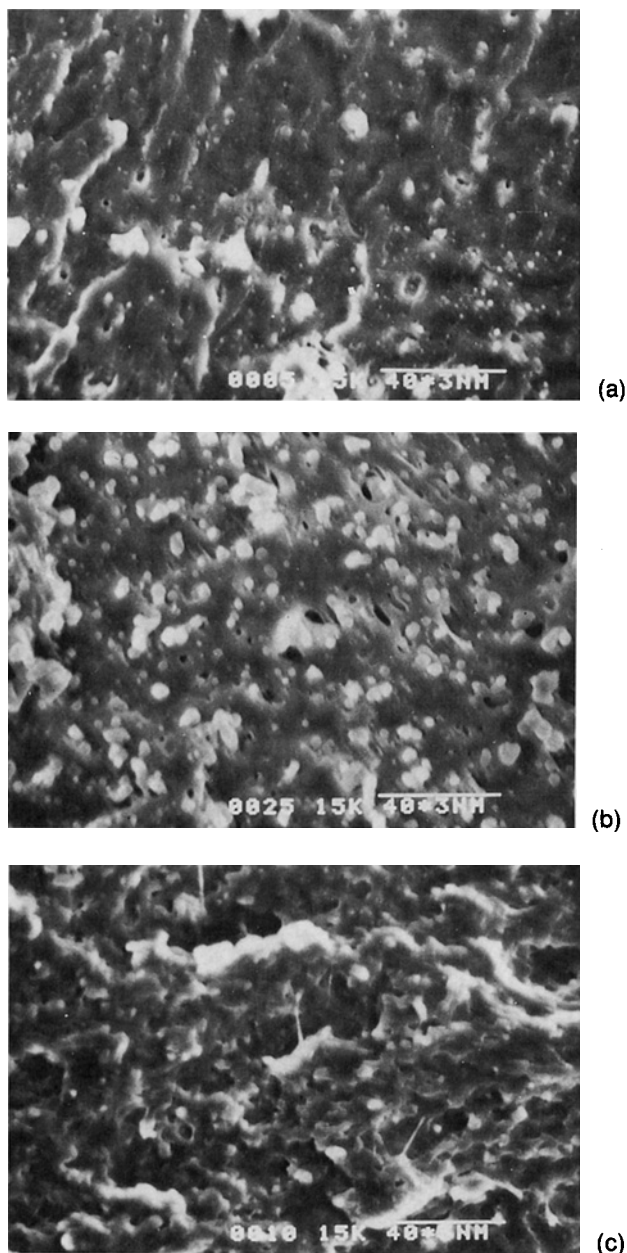
Figure 4 SEM micrographs of tensile fractured surfaces of the vulcanizates cured at 160°C; (a) 25 : 75 NR : XNBR blend containing DIPDIS (one stage) at 750×; (b) 25 : 75 NR : XNBR blend containing TMTD (one stage) at 750×; (c) 25 : 75 NR : XNBR blend containing DIPDIS (two stage) at 750×.

Table IV shows the composition and preparation of the blends in two-stage vulcanization. It can be seen from Table IV that DIPDIS:NR ratio in mixes 3', 4', and 5' is progressively increased to obtain the desired results. Figure 3 represents the cure curves at first stage and second stage.

The physical properties of the vulcanizates derived from mixes 3', 4', and 5' in two-stage vulcanization are shown in Table V. In all the cases there was significant improvement in modulus and tensile strength values than those obtained in one-stage vulcanization of blends. As expected, the vulcanizates of mix 5' exhibit highest modulus and tensile strength. This trend was also observed in the age resistance and solvent resistance behaviour of the vulcanizates.

Scanning Electron Microscopy

The chemical bonding between NR and XNBR in the presence of DIPDIS is apt to form compact rubber matrix. SEM studies were considered to throw some light in this regard.

From the preceding studies, it is clear that DIPDIS-accelerated vulcanizates derived from mix 5 (Table I) give the best result as far as modulus and tensile strength are concerned (Table III). Hence mix 5 was selected for the SEM study. Mix 6 was also included in the investigation in order to visualize the effect of TMTD for the same NR-XNBR ratio (25 : 75) where poor mechanical properties were obtained.

Figures 4(a,b) represent the SEM micrographs of DIPDIS- and TMTD-accelerated NR-XNBR (25 : 75) vulcanizates obtained in one-stage vulcanization, respectively. Figure 4(c) depicts the SEM micrograph of vulcanizate of mix 5'.

From Figures 4(a,b), it is evident that the vulcanizate of mix 6 contains large number of vacuoles but that obtained in mix 5 is comparatively very low. This is suggestive of the inhomogenity of NR-XNBR blend consequent upon the absence of chemical bonding in the presence of TMTD. This phenomenon also explains the poor mechanical

properties of the vulcanizates of mix 6. On the other hand, the coherency as indicated in micrograph 4(a) for mix 5 accounts for its good physical properties. The effect of two-stage vulcanization can be visualized from the comparison of the 4(a,c) micrographs. It is evident that the two-stage vulcanization further reduces the number of vacuoles thereby rendering vulcanized rubber matrix more compact. This phenomenon may further explain the enhancement in modulus and tensile values of the vulcanizates of mix 5 to mix 5'.

REFERENCES

1. T. Biswas, N. Naskar, and D. K. Basu, *Kautschuk Gummi Kunststoffe,* **46,** 125 (1993).
2. J. G. Pimblott, G. Scott, and J. E. Stuckey, *J. Appl. Polym. Sci.,* **19,** 865 (1975).
3. C. R. Parks and R. J. Brown, *Rubber Chem. & Technol.,* **49,** 233 (1976).
4. Kunio Mori, *Rubber Chem. & Technol.,* **60,** 822 (1987).
5. H. P. Brown, *Rubber Chem. & Technol.,* **36,** 931 (1963).
6. 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.
7. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *The Chemistry and Physics of Rubber-like Substances,* L. Bateman, Ed., Maclaren and Sons Ltd., London, 1963, Chap. 15, p. 449.
8. D. R. Paul and J. W. Barlow, *J. Macromol. Sci., Rev. Macromol. Chem.,* **C18**(1), 109–168 (1980).
9. S. K. Chakraborty, A. K. Bhowmick, and S. K. De, *J. Appl. Polym. Sci.,* **26,** 4011–4020 (1981).