Cure Synergism in XNBR Vulcanization in Presence of Thiophosphoryl Disulfides and Amine Disulfide/Thiazole Accelerators

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SYNOPSIS

The study deals with the vulcanization of carboxylated nitrile butadiene rubber (XNBR) having synergistic combinations of accelerators comprising thiophosphoryl disulfide as one of the components. Other constituent accelerators employed in the present investigation are 2-mercaptobenzothiazole (MBT), 2-mercaptobenzothiazyl disulfide (MBTS), bis(N-oxydiethylene)disulfide (ODDS), N-oxydiethylene 2-benzothiazole sulfenamide (OBTS), etc. The binary combinations of thiophosphoryl disulfides with OBTS exhibited the highest mutual activity in the respective areas, so far as the physical properties are concerned. Structural characterization of different thiophosphoryl disulfide-accelerated XNBR vulcanizates, including those formed from the synergistic combinations with OBTS, were studied using a methyl iodide probe. It was found that the amount of sulfidic crosslinks arising from the reaction between —COOH groups of XNBR and thiophosphoryl disulfides, actually controls the network structure as well as the physical properties of the vulcanizates. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the preceding studies, it was shown that thiophosphoryl disulfides[1,2] can be used as effective curatives cum accelerators in the vulcanization of carboxylated nitrile butadiene rubber (XNBR). Earlier workers[3-11] noticed that in many cases binary combinations of accelerators provide more effective vulcanization and exhibit synergistic activity (than with either accelerator alone) that is manifested in the enhanced physical properties of the vulcanizates. The vulcanizing activity of bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) along with bis(N-oxydiethylene)disulfide (ODDS) was studied in the presence of various rubbers.[12] Some investigations were also carried out in this laboratory to study the synergistic activity of DIPDIS in the presence of thiazole or thiazole sulfenamide[13,14] in NR vulcanization. However, no work has been reported so far regarding the synergistic activity of the binary system of accelerators containing DIPDIS as one of the components, in the vulcanization of XNBR. Keeping all these in mind, the present work was undertaken to gain insight into the cure synergism, thus throwing additional light on the mechanism of vulcanization of XNBR, and to endeavor to study the structure–property relationship of the vulcanizates.

EXPERIMENTAL

Materials

The accelerators employed in the present study are given in Table I. DIPDIS, bis(diisobutyl)thiophosphoryl disulfide (DIBDIS), and bis(dicyclohexyl)-thiophosphoryl disulfide (DCHDIS) were prepared and purified according to the procedure discussed earlier.[1,2] 2-Mercaptobenzothiazole (MBT), dibenzothiazyl disulfide (MBTS), and N-oxydiethylene benzothiazole sulfenamide (OBTS) were commercial samples that were used after necessary purifications. ODDS (Monsanto Company, U.S.A.) was used as received.

Table I Compounds Used

Chemical Name	Abbreviation Used	Structure
1. Bis(diisopropyl)thiophosphoryl disulfide	DIPDIS	$(CH_3)_2CH—O$ ... $P—S—S—P$ ... $O—CH(CH_3)_2$ (with S double bonds)
2. Bis(dicyclohexyl)thiophosphoryl disulfide	DCHDIS	dicyclohexyl thiophosphoryl disulfide structure
3. Bis(diisobutyl)thiophosphoryl disulfide	DIBDIS	$(CH_3)_2CHCH_2—O$ ... $P—S—S—P$ ... $O—CH_2CH(CH_3)_2$
4. 2-Mercaptobenzothiazole	MBT	benzothiazole C—SH structure
5. 2-Mercaptobenzothiazyl disulfide	MBTS	benzothiazole C—S—S—C benzothiazole structure
6. N-Oxydiethylene-2-benzothiazole sulfenamide	OBTS	benzothiazole C—S—N(morpholine) O structure
7. Bis(N-oxydiethylene)disulfide	ODDS	O(morpholine)N—S—S—N(morpholine)O structure

XNBR (Krynac X7.50, 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%) was obtained from Polysar Ltd., France.

Preparation of Vulcanizates and Measurements of Physical Properties

The procedure for the preparation of the vulcanizates was given earlier.[2] The combinations of accelerators in various stocks are given in Table II. The cure data were obtained on a Monsanto Rheometer (R-100) and physical properties, for example, modulus, tensile strength, elongation at break, etc., were measured according to the ASTM D412-51T procedure.[2,15] Shore A hardness values were obtained by Durometer.

The procedures for the measurement of age resistance and oil resistance properties of the vulcanizates were reported earlier.[2,15]

Removal of Excess Zinc Oxide from XNBR Vulcanizate

To avoid postcuring of XNBR vulcanizates[16] during aging, the excess of zinc oxide was removed through the reaction with dibutyl amine and carbon disulfide in carbon tetrachloride solvent. The resulting zinc dibutyl dithiocarbamate was removed from the solution by repeated solvent extraction. The complete absence of zinc dibutyl dithiocarbamate was assured from a gas chromatography study, using a Hewlett-Packard (Model 5710A) gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3380A integrator. The analysis was conducted at 160°C using a UCW column (508 × 3 mm).

Treatment of Vulcanizates with Methyl Iodide

Methyl iodide breaks the various sulfidic links[17-21] of XNBR vulcanizates while the ionic crosslinks re-

main unaffected.[22] The samples of the vulcanizates, freed from excess zinc oxide together with redistilled methyl iodide (1.96 g/g of vulcanizate), were sealed *in vacuo* ($<10^{-5}$ mm) under nitrogen atmosphere and then heated in the dark at 80°C for 4 days. Samples of vulcanizates in the control experiment were similarly heated in the absence of methyl iodide. Excess methyl iodide was removed *in vacuo* at room temperature, and the degree of crosslinking was then determined by equilibrium swelling in isooctane: toluene (70 : 30) medium at $30 \pm 2°C$.

RESULTS AND DISCUSSION

DIPDIS-MBT Combinations

To start with, the synergistic effect of DIPDIS-MBT combinations, in the vulcanization of XNBR, were studied (mixes 1–5, Table II). The corresponding cure data are presented in Table II. Figure 1 depicts the cure behavior of DIPDIS and its progressive replacement by MBT keeping the total concentration of the accelerators fixed at a constant level of 9 mM phr. The numbers on the curves correspond to those used in the mix formulations presented in Table II.

It can be seen from the figure that cure curves of mixes 1 and 2 are distinctly different in nature. Curve 1 is comprised of two wavy regions (characteristic of DIPDIS cure). Here, the initial fast curing reactions are based on zinc oxide and DIPDIS, which at the second phase are taken over by sulfur vulcanization caused by sulfurating complex generated from zinc oxide, DIPDIS, and sulfur. Curve 2 is more or less S shaped in nature. Cure curves of binary combinations of DIPDIS and MBT (mixes 3–5) in different proportions also consist of two wavy regions as in curve 1. The above phenomenon becomes more and more prominent and the second portions of the respective cure curves become steeper and steeper as the proportion of DIPDIS is progressively increased. In fact, a synergistic effect with regard to R_∞ value is obtained for DIPDIS: MBT (6 : 3) accelerated stock. However, the t_2 values of all the stocks (mixes 1–5) are very close to one another and indicate pronounced scorchy behavior of the rubber mixes due to the presence of both fast curing[1,2] zinc oxide and DIPDIS.

The synergistic activity with regard to physical properties of the vulcanizates is evident from the data presented in Table II. It is apparent from the table that maximum synergism with regard to modulus, tensile strength, and hardness is provided by

mix 3 containing DIPDIS and MBT in the ratio of 6 : 3. However, the level of synergism is moderate.

It was found earlier[13] by HPLC study that when DIPDIS is heated with MBT at 140°C for 2 min, diisopropyl thiophosphoryl 2-benzothiazyl disulfide (DIBDS) (see Scheme 1) is formed as a major product of heating. This DIBDS acts as an effective sulfur donor cum accelerator that can steer the vulcanization reaction. In our case also, DIBDS is likely to be formed *in situ* and thus is responsible for the observed synergistic activity with regard to the physical properties of the vulcanizates of mixes 3–5.

DIPDIS-MBTS Combinations

The results in terms of cure data and physical properties for DIPDIS–MBTS combinations (mixes 1, 6–9) are presented in Table II and the cure curves are shown in Figure 2. It is evident from Table II that the highest synergistic effect with regard to R_∞ and modulus values is manifested in mix 7 (DIPDIS: MBTS, 6 : 3), but with regard to tensile strength is found in mix 8 containing equimolar amount of DIPDIS and MBTS. As expected, t_2 values are low for all the cases.

The level of synergism in DIPDIS-MBTS combinations is similar to that in DIPDIS–MBT combinations. Here also, DIBDS, formed *in situ* by the reaction between DIPDIS and MBTS, seems to influence the vulcanization reaction as well as the physical properties of the vulcanizates. To understand the effect of DIBDS in the vulcanization of XNBR, some work was carried out. Already mentioned is that when equimolar quantities of DIPDIS and MBTS are heated at 140°C for a few minutes, DIBDS results. The product thus obtained was incorporated in XNBR along with other ingredients such as zinc oxide, stearic acid, sulfur, etc., and the resultant mix was designated as stock 8' (Table II). If the results of mix 8 are compared with those of mix 8', having otherwise identical composition, the R_∞ value of the latter is found to be higher than that of the former indicating a higher extent of crosslinking reaction in the latter case. The vulcanizates of mix 8' possess higher modulus values than those obtained from mix 8. More or less the same trend is also observed for the tensile values of the corresponding vulcanizates.

DIPDIS-ODDS Combinations

It was shown by earlier workers that the synergistic activity of the DIPDIS–ODDS system[12] results in the vulcanization of *cis* 1,4 polyisoprene, ethylene

Table II   Cure Characteristics and Physical Data of Stocks Obtained at 160°C

Mix No. and Composition (mM)	Max Rheometric Torque, R_α (N m)	Scorch Time, t_2 (min)	Optimum Cure Time, t_{90} (min)	200% Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness Shore A	Aged in Air, 72 h at 100°C				
								Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Swelling Index, Q	Crosslinking Value, $1/Q$
1. DIPDIS, 9	4.95	1.00	17.0	1.46	11.65	610	65	1.80	10.27	500	0.3295	3.0349
2. MBT, 9	4.30	0.75	16.0	1.30	8.76	590	60	1.69	7.51	470	0.3852	2.5960
3. DIPDIS, 6 / MBT, 3	5.20	1.00	16.5	1.49	14.82	580	66	1.82	13.90	520	0.3165	3.1595
4. DIPDIS, 4.5 / MBT, 4.5	4.70	1.00	15.0	1.47	14.67	600	65	1.78	13.77	500	0.3176	3.1486
5. DIPDIS, 3 / MBT, 6	4.60	1.00	14.5	1.47	14.36	610	65	1.69	13.41	520	0.3184	3.1407
6. MBTS, 9	5.35	0.50	19.0	1.38	8.50	560	59	1.88	7.10	470	0.3873	2.5819
7. DIPDIS, 6 / MBTS, 3	5.50	1.00	16.5	1.54	13.47	560	67	1.83	12.03	500	0.3259	3.0684
8. DIPDIS, 4.5 / MBTS, 4.5	5.40	1.00	17.5	1.48	14.57	600	66	1.88	13.26	500	0.3187	3.1377
8'. DIPDIS, 4.5[a] / MBTS, 4.5	5.70	1.50	18.5	1.75	14.88	590	—	2.39	15.40	480	—	—
9. DIPDIS, 3 / MBTS, 6	5.45	1.25	18.0	1.50	13.71	580	67	1.88	12.00	480	0.3244	3.0826
10. ODDS, 9	5.90	0.50	30.0	1.44	12.21	550	64	2.04	10.34	440	0.3575	2.7972
11. DIPDIS, 6 / ODDS, 3	5.20	1.00	15.5	1.54	15.63	590	67	1.88	13.76	460	0.3069	3.2583
12. DIPDIS, 4.5 / ODDS, 4.5	5.40	1.00	16.0	1.68	18.26	600	68	2.19	16.96	450	0.2914	3.4317
13. DIPDIS, 3 / ODDS, 8	5.55	1.00	19.0	1.54	16.56	600	67	2.32	14.15	470	0.3004	3.3288
14. OBTS, 9	4.40	0.75	16.0	1.61	13.02	550	67	2.24	13.22	420	0.3659	2.7329
15. DIPDIS, 6 / OBTS, 3	4.98	1.00	14.0	1.73	18.94	580	69	2.35	18.45	480	0.2866	3.4650
16. DIPDIS, 4.5 / OBTS, 4.5	4.88	1.00	14.0	1.75	18.88	580	69	2.15	18.98	480	0.2873	3.4806
16'. DIPDIS, 4.5[a] / OBTS, 4.5	5.15	1.00	12.5	1.85	20.50	570	—	2.46	19.70	460	—	—

Mix	Accelerators												
17.	DIPDIS, 3 / OBTS, 6	4.70	1.00	12.5	1.70	18.43	580	68	2.08	17.90	500	0.2898	3.4506
18.	DIBDIS, 9	4.80	1.00	20.0	1.67	15.87	560	68	2.36	14.43	470	0.3198	3.1269
19.	DIBDIS, 6 / OBTS, 3	4.80	1.50	18.5	1.73	19.74	580	69	2.32	19.04	450	0.2765	3.6166
20.	DIBDIS, 4.5 / OBTS, 4.5	4.75	1.50	20.0	1.75	19.40	570	68	2.31	19.01	450	0.2789	3.5855
21.	DIBDIS, 3 / OBTS, 6	4.50	1.50	16.5	1.70	18.47	570	68	2.28	17.77	480	0.2864	3.4916
22.	DCHDIS, 9	4.80	1.75	20.5	1.72	16.98	600	68	2.42	16.10	510	0.3113	3.2020
23.	DCHDIS, 6 / OBTS, 3	4.90	1.50	20.0	1.74	19.62	540	69	2.26	20.02	480	0.2779	3.5984
24.	DCHDIS, 4.5 / OBTS, 4.5	4.85	1.25	19.5	1.77	19.28	560	70	2.28	18.94	500	0.2763	3.6192
25.	DCHDIS, 3 / OBTS, 6	4.75	1.25	18.0	1.73	18.86	550	69	2.18	18.10	490	0.2799	3.5727

The stock contains zinc oxide 5 phr, stearic acid 2 phr, accelerator(s) 9 mM phr, and sulfur 0.5 phr.
* The mixture of accelerators was heated for 6 min at 140°C and then mixed with rubber along with other ingredients, viz., ZnO (5 phr), stearic acid (2 phr), and S (0.5 phr).

propylene diene monomer rubber (EPDM), styrene butadiene rubber (SBR), polychloroprene rubber (CR), nitrile butadiene rubber (NBR), etc. To study the effect of the DIPDIS–ODDS system upon the vulcanization of XNBR, we also carried out some investigations. The results are summarized in Table II and depicted in Figure 3 (mixes 1, 10–13). For ODDS-accelerated XNBR vulcanization, an extended sulfur crosslinking region is observed at the second phase after an initial fast curing reaction, as evident from curve 10 in Figure 3. The high t_{90} value of mix 10 also corroborates the above phenomenon. As ODDS is progressively replaced by DIPDIS, the second region becomes steeper and more wavy in nature as evident from the lowering of t_{90} values of mixes 11–13. It is evident from Table II that R_∞ value is highest for mix 10 while those for the combinations (mixes 11–13) attain some intermediate values between mixes 1 and 10. As usual, t_2 values are low for all the cases denoting scorchiness of the mixes as induced by both fast curing zinc oxide and DIPDIS.

It is evident from the data, presented in Table II, that the highest synergistic activity with regard to modulus, tensile strength, hardness, etc., can be achieved for mix 12 comprising an equimolar amount of DIPDIS and ODDS.

It was shown by earlier workers[23] that ODDS transforms into polysulfides in accordance with the following reactions (Scheme 2). Obviously, there occurs some delay in sulfur curing and this is manifested in the t_{90} value for mix 10 as stated earlier. Evidently sulfur radicals, which are also formed from the polysulfides, take part in the crosslinking reaction. The reaction scheme indicates the generation of amines (morpholine) that also activates[24] the ring opening of sulfur and thus promotes further curing as evinced by the system.

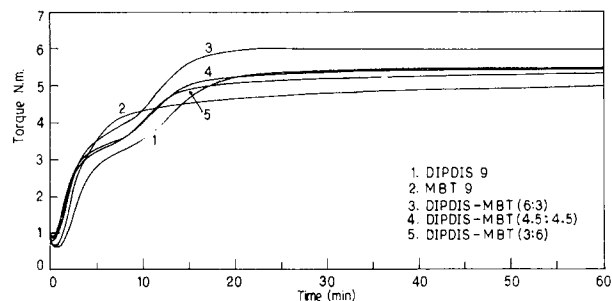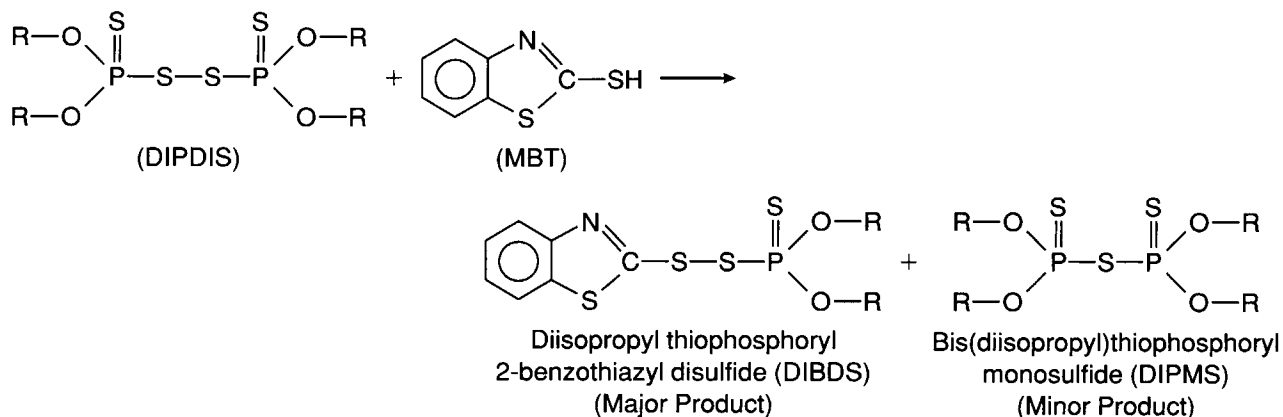It is now an established fact that DIPDIS acts as a sulfur donor at 160°C.[1,2,25] Additional sulfur, apart

1. DIPDIS 9
2. MBT 9
3. DIPDIS-MBT (6:3)
4. DIPDIS-MBT (4.5:4.5)
5. DIPDIS-MBT (3:6)

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

Scheme 1 Various products formed from the reaction between DIPDIS and MBT at 140°C for 2 min.

from that present in the recipe, also comes from ODDS as mentioned above. So, in the ODDS-DIP-DIS system additional crosslinks are likely to be formed. This is reflected in the modulus and hardness values of the vulcanizates. It appears from the nature of the vulcanization reactions that simultaneously two types of polysulfidic linkages are formed[2]: (i) —COOP(S)—S—S_n—S—P(S)OOC—, nonconventional polysulfidic linkage and (ii) —C—S_x—C—, conventional polysulfidic linkage. The nonconventional polysulfidic crosslinks of type (i), as mentioned above, are flexible[2,15] enough to facilitate crosslink slippage. The resultant effect is the enhancement of tensile strength values for all the combinations belonging to this system (mixes 11–13).

Binary Systems Consisting of Thiophosphoryl Disulfides and OBTS

To begin with, the dual system of accelerators comprising DIPDIS and OBTS was studied. The relevant cure and physical data are presented in Table

II (mixes 1, 14–17). The course of vulcanization is recorded in the corresponding cure curves as shown in Figure 4.

It is evident from Figure 4 that the nature of the cure curve of mix 14, that is, OBTS-accelerated XNBR mix, is very similar in nature to that of mix 1, that is, DIPDIS-accelerated XNBR mix; the difference lies only in the extent of cure. The R_∞ value of mix 1 is higher than that of mix 14. However, R_∞ values of mixes 15–17 are very close to that of mix 1, and t_{90} values of mixes 15–17 are also very close to each other. But these values of t_{90} are somewhat lower as compared to those of mix 1 and mix 14. However, the physical data of the corresponding vulcanizates (mixes 1, 14–17; Table II) signify marked synergism for all the combinations of DIP-DIS and OBTS.

It was reported[13] that when a mixture of DIPDIS and OBTS is heated for 2 min at 140°C, MBT, DIBDS, bis(diisopropyl)thiophosphoryl monosulfide (DIPMS), ODDS, and diisopropyl thiophosphoryl N-oxydiethylene sulfenamide (DIPTOS) are
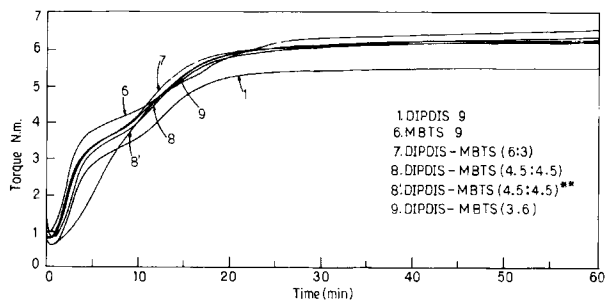

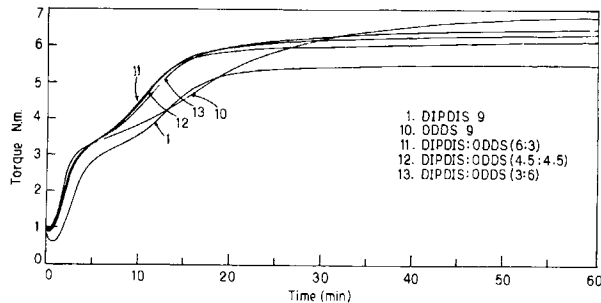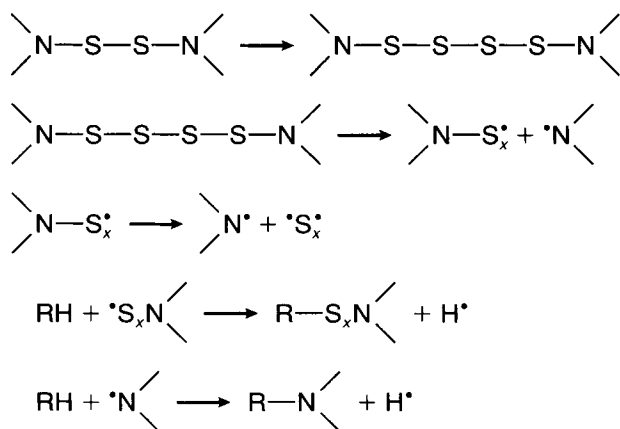**Figure 2** Rheographs of mixes 1 and 6–9 (Table II) cured at 160°C.

Figure 3 Rheographs of mixes 1 and 10–13 (Table II) cured at 160°C.

$$\text{>N—S—S—N<} \longrightarrow \text{>N—S—S—S—S—N<}$$

$$\text{>N—S—S—S—S—N<} \longrightarrow \text{>N—S}_x^\bullet + {}^\bullet\text{N<}$$

$$\text{>N—S}_x^\bullet \longrightarrow \text{>N}^\bullet + {}^\bullet\text{S}_x^\bullet$$

$$\text{RH} + {}^\bullet\text{S}_x\text{N<} \longrightarrow \text{R—S}_x\text{N<} + \text{H}^\bullet$$

$$\text{RH} + {}^\bullet\text{N<} \longrightarrow \text{R—N<} + \text{H}^\bullet$$

RH = rubber.

Scheme 2 ODDS transformation into polysulfides.

generated (see Scheme 3). All of these compounds are effective rubber additives. Some of them function as accelerators and the others as sulfur donors that take part in the vulcanization of rubber. The net effect is thus the enhancement of cure by effective utilization of the curatives that eventually bring about notable synergism. In the vulcanization reaction accelerated by the DIPDIS + OBTS system, the nonconventional sulfidic crosslinks of type (i) (as mentioned previously), owing to their flexible nature, also play a significant role that is manifested in enhanced physical properties. To justify the above proposition, an equimolar amount of DIPDIS and OBTS (based on the proportion actually present in mix 16) were heated at 140°C for 6 min. The reaction product was then added to XNBR (following the usual procedure) along with zinc oxide, stearic acid, and sulfur. The above composition was designated as mix 16'. From the cure data of mix 16' as presented in Table II, it is evident that R_∞ value is higher than that of the corresponding stock of mix 16. It can be seen that the t_{90} value of mix 16' is much lower than that of mix 16. This indicates, once again, the occurrence of a very sharp reaction at the second stage of the cure of mix 16' that is also evident from its steeper second wavy region (compare cure curve of mix 16 with that of mix 16' in Fig. 4). The modulus and tensile strength values of the vulcanizates of mix 16', as expected, are higher than the corresponding values of mix 16. The higher activity in respect to physical properties of the vulcanizates of mix 16' as compared to that of mix 16 can be explained in the following way. It was mentioned earlier (Scheme 3) that in the early part of the reaction between DIPDIS and OBTS, several intermediate

rubber accelerators are formed of which DIBDS and ODDS need special mention for their significant activity in enhancing the physical properties. It was also shown[13] that in the rubber medium DIPDIS and OBTS rapidly generate MBT, while in the absence of rubber the proportion of MBT was found to be very small. So, when a mixture of DIPDIS and OBTS are preheated first and then added to the rubber medium (mix 16'), it may be reasonably expected that a higher amount of DIBDS compared to that in mix 16 is probably present in the early part of vulcanization. As a result, the physical properties are bound to increase.

We found earlier[2] that the vulcanizates of XNBR, derived from bis(dicyclohexyl)thiophosphoryl disulfide (DCHDIS) and DIBDIS provide notable mechanical properties among the various thiophosphoryl disulfides studied so far. Therefore, it was decided to investigate the effect of the binary systems comprising DIBDIS + OBTS and DCHDIS + OBTS on the vulcanization of XNBR. The compositions of the mixes employed in the present investigation for the DIBDIS + OBTS and DCHDIS + OBTS systems are shown in Table II (mixes 14, 18–25). Relevant cure and physical data are also given in Table II. Figures 5 and 6 depict the cure curves of different DIBDIS + OBTS and DCHDIS + OBTS combinations, respectively.

It is interesting to note that although there exist some differences among DIPDIS-, DIBDIS-, and DCHDIS-accelerated stocks of XNBR in terms of modulus, tensile strength, hardness, etc., these values, however, come very close to one another when each of the above mentioned thiophosphoryl disulfides is combined separately with OBTS.

Age Resistance Behavior of Vulcanizates

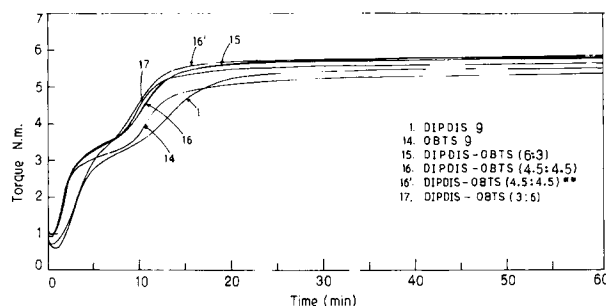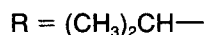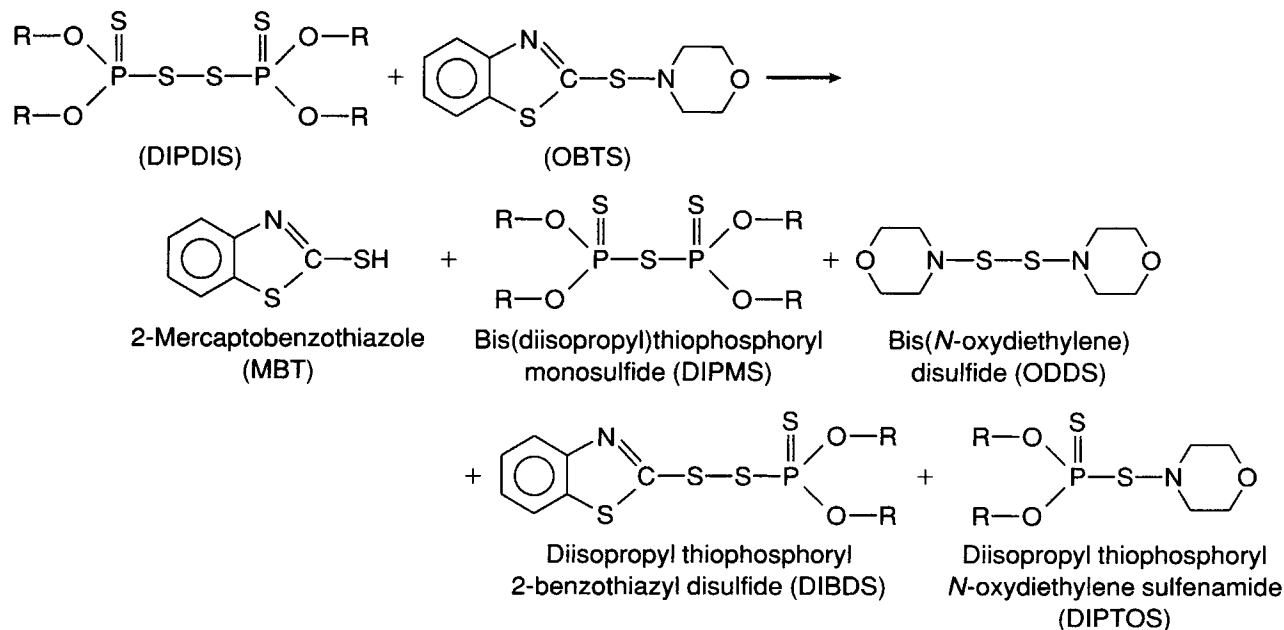Vulcanizates obtained from XNBR are resistant to heat and oxidation due to the presence of metallo-

Figure 4 Rheographs of mixes 1 and 14–17 (Table II) cured at 160°C.

R = $(CH_3)_2CH—$

Scheme 3   Various products formed from the reaction between DIPDIS and OBTS at 140°C for 2 min.

carboxylate linkages.[15,22,26] High thermal and thermal oxidative stability of rubber vulcanizates containing thiophosphoryl disulfide (DIPDIS, etc.) also arise from the formation of zinc dithiophosphate (ZDP) *in situ*.[25] ZDP, thus acting as an antioxidant,[27] is likely to add to the stability of the XNBR vulcanizates already fortified by the stable metallocarboxylate linkages. So, the vulcanizates of XNBR containing thiosphosphoryl disulfide either alone or as a component of binary combinations are expected to exhibit notable age resistance behavior and thus some investigations were made in this regard.

The modulus, tensile strength, and elongation at break values for all the vulcanizates (mixes 1–25), after aging for 72 h at 100°C, are presented in Table

II. As expected modulus values of all the vulcanizates increased and the values of elongation at break decreased.[24,28,29] DIPDIS-accelerated XNBR vulcanizate shows over 88% retention of its original tensile value (mix 1). The vulcanizates derived from the DIPDIS: MBT system exhibit very good age resistance behavior retaining almost 94% of their original values (mixes 3–5). The conjoint effect of DIPDIS and MBTS (mixes 7–9), however, is manifested in 88–91% retention of tensile strength values for the vulcanizates. The DIPDIS-ODDS system (mixes 11–13) also provide very good age resistant vulcanizates as compared to the DIPDIS- or ODDS-accelerated system individually. It needs mentioning here that earlier workers[12] confirmed the presence of a large
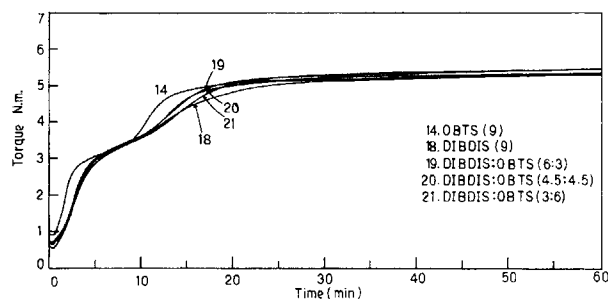

Figure 5   Rheographs of mixes 14 and 18–21 (Table II) cured at 160°C.
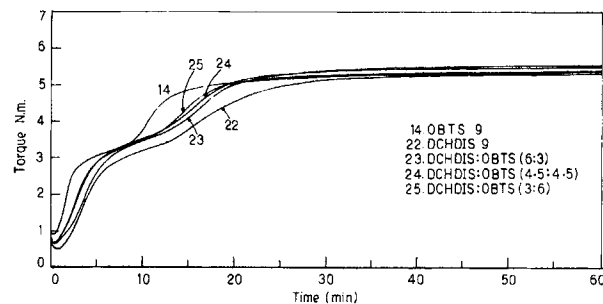

Figure 6   Rheographs of mixes 14 and 22–25 (Table II) cured at 160°C.

number of mono- or disulfidic crosslinks in the vulcanizates of diene elastomers containing DIPDIS and ODDS. The combined effect of ZDP as antioxidant and the thermally stable mono- or disulfidic crosslinks along with metallocarboxylate crosslinks is probably responsible for the observed heat and age resistance behavior of the resulting vulcanizates.

From the data presented in Table II it is evident that significant activity with respect to age resistance is exhibited by the synergistic combinations of accelerators comprising thiophosphoryl disulfides (DIPDIS, DIBDIS, DCHDIS, etc.) with OBTS. Like DIPDIS-accelerated vulcanizates of XNBR, DIB-DIS-, and DCHDIS-accelerated vulcanizates also provide notable age-resistance phenomenon as can be seen from the age resistance data presented in Table II. It is apparent from the table that tensile strength values remain practically unaffected for all the vulcanizates derived from DIPDIS-OBTS combinations (mixes 15–17), DIBDIS-OBTS combinations (mixes 19–21), and DCHDIS–OBTS combinations (mixes 23–25). It appears from the results that the compounds like DIBDS formed in the early part of vulcanization in these synergistic combinations play a significant role in boosting the age resistance property of the vulcanizates; the age resistance data for the vulcanizates of mix 16′ corroborate this fact.

Oil Resistance Behavior of Vulcanizates

The combined effect of polar acrylonitrile groups and the various crosslinks, particularly the metallocarboxylate crosslinks, are responsible for the excellent oil resistance behavior of XNBR vulcanizates.[15] Because binary combinations of accelerators are likely to enhance the crosslink density of rubber vulcanizates, the variation in the concentration of various accelerators thus seems to have a profound effect upon the oil resistance property. The results were obtained through the swelling index and are given in Table II. It is evident from the results that DIPDIS-accelerated XNBR vulcanizate exhibits a lower swelling index than that obtained with any one of MBT-, MBTS-, ODDS-, or OBTS-accelerated vulcanizates. The synergistic combinations of DIPDIS with MBT, MBTS, ODDS, or OBTS give even lower swelling indices. DIBDIS- and DCHDIS-accelerated vulcanizates of XNBR possess lower swelling indices, that is, higher crosslinking values, than those of DIPDIS-accelerated vulcanizates. It is evident from the study that binary combinations of thiophosphoryl disulfides (namely, DIPDIS, DIBDIS, and DCHDIS) with OBTS give the highest

activity regarding the oil resistance property of the vulcanizates. It is also evident from the results presented in Table II that the synergistic systems cause an increase in the crosslinking values of the vulcanizates. This is consistent with the higher modulus and tensile strength values of the vulcanizates obtained with the dual system of accelerators. The results thus additionally give testimony to the established fact that synergistic activity is associated with the enhancement of crosslink density.[11,13]

Structural Characterization of XNBR Vulcanizates

The foregoing studies point out that significant synergism with respect to physical properties is associated with the various combinations of thiophosphoryl disulfides and OBTS: namely, DIPDIS + OBTS, DIBDIS + OBTS, and DCHDIS + OBTS. As synergism involves the interaction of the accelerators that actively take part in the vulcanization of rubber, it may be reasonably expected that the mutual activity between various thiophosphoryl disulfides and OBTS is closely associated with the building of the fine structure of the XNBR vulcanizates. The mutual activity of the binary system of accelerators is manifested in the enhancement of the physical properties (modulus, tensile strength, hardness, age resistance, as well as oil resistance behavior) of XNBR vulcanizates. These properties are again governed by the nature and amount of the fine structure of rubber vulcanizates. So, this necessitates some studies on the elucidation of the network structure with regard to various crosslinkages present in XNBR vulcanizates. In this study of network characterization, stocks 1, 14, 16, 18, 20, 22, and 24, that is, DIPDIS-, OBTS-, DIBDIS-, DCHDIS-accelerated vulcanizates of XNBR as well as those containing equimolar amount of DIPDIS/DIBDIS/DCHDIS and OBTS were chosen and the results are presented in Table III.

It was shown in the preceding studies[2,19] that three types of crosslinkages are actually present in XNBR vulcanizates obtained in the presence of zinc oxide, thiophosphoryl disulfide, and sulfur, viz., (i) metallocarboxylate crosslinkages of the type $-COOZnOOC-$, (ii) conventional sulfidic crosslinks of the type $-C-S_x-C-$, and (iii) nonconventional sulfidic crosslinks (derived from the reaction between $-COOH$ functionality of XNBR and thiophosphoryl disulfide) of the type $-COOP(S)SS_nS(S)POOC-$. The third type of crosslinkage is basically a sulfidic crosslinkage. So, on treatment with methyl iodide, these nonconventional sulfidic crosslinks [type (iii)] will also break

Table III   Distribution of Crosslink Types in Vulcanizate Network

Mix No. and Composition	Crosslink Type (%)	
	Salt	Sulfur
1. DIPDIS, 9	69	31
14. OBTS, 9	81	19
16. DIPDIS, 4.5 OBTS, 4.5	46	54
18. DIBDIS, 9	54	46
20. DIBDIS, 4.5 OBTS, 4.5	43	57
22. DCHDIS, 9	51	49
24. DCHDIS, 4.5 OBTS, 4.5	42	58

along with the conventional sulfidic crosslinks [type (ii)] leaving only salt crosslinks [type (i)], and thus in elucidating the network structure of XNBR in the presence of thiophosphoryl disulfide, zinc oxide, and sulfur, two types of crosslinks (metallocarboxylate and sulfidic crosslinks) can be determined. For the present investigation, we used an efficient vulcanization system (i.e., more accelerator and less sulfur). As mentioned earlier, thiophosphoryl disulfides react with the —COOH groups of XNBR. This reaction produces a considerable amount of nonconventional sulfidic crosslinks of type (iii). So, it may be reasonably expected that for an efficient vulcanization system with thiophosphoryl disulfide, the contribution of conventional sulfidic crosslinks of type (ii) will be very small and thus the concentration of the linkages of type (iii) will predominate over that of type (ii). Therefore, it is justifiable to say that the distribution of total crosslinks in the XNBR vulcanizate network would be mainly the salt type crosslink [type (i)] and nonconventional sulfidic crosslink [type (iii)].

It is evident from Table III that OBTS-accelerated vulcanizates of XNBR contain the highest amount (81%) of salt type crosslinks. Thus the metallocarboxylate crosslinks here control the vulcanizate structure as well as the mechanical properties. The above fact is also corroborated by the physical properties of OBTS-accelerated XNBR vulcanizates (mix 14, Table II) that are close to those of metallocarboxylate vulcanizates[15] of XNBR [modulus 1.84 MPa, tensile strength 12.67 MPa, and elongation at break (570%)]. The situation, however, becomes quite different in the presence of thiophosphoryl disulfides owing to some facile reaction of the —COOH groups of the XNBR with the thiophos-

phoryl disulfides. As a result, the concentration of metallocarboxylate crosslinks is bound to fall. The results presented in Table III reveal that the concentration of salt type crosslinks gradually decreases from DIPDIS-accelerated vulcanizate to DCHDIS-accelerated vulcanizate via the DIBDIS-accelerated vulcanizate of XNBR. In DIBDIS- and DCHDIS-accelerated vulcanizates the total number of crosslinks are more or less evenly distributed between the salt type and the sulfur type. Thus it is evident from Table III that DIBDIS and DCHDIS give rise to a higher extent of formation of nonconventional sulfidic crosslinks of type (iii) as compared to that obtained in DIPDIS-accelerated vulcanizates. The influence of these nonconventional sulfidic crosslinks, particularly in DIBDIS- and DCHDIS-compounded stocks, is well reflected in enhanced mechanical properties of the vulcanizates derived from the above stocks (Table II).

The situation becomes even more interesting in the presence of synergistic combinations of accelerators. In each of the synergistic combinations comprising DIPDIS–OBTS, DIBDIS–OBTS, or DCHDIS–OBTS, there is a sharp increase in the percentage of sulfidic crosslinks that surpass the concentration of salt type crosslinks. These synergistic combinations are likely to in situ give rise to the compounds (sulfur donors) that steer the vulcanization of XNBR through the formation of significant amount of nonconventional polysulfidic crosslinks [type (iii)]. This is manifested in the physical properties of the vulcanizates (Table II). The results thus indicate that in the synergistic combinations, the nonconventional sulfidic crosslinks have a profound effect upon the vulcanizate structure as well as the mechanical properties of the vulcanizates.

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