Some Investigations on Structure–Property Relationship in XNBR Vulcanizates in the Presence of Bis(diisopropyl thiophosphoryl)disulfide

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ABSTRACT: The study reveals that a new type of sulfidic crosslinks arising from the reaction between carboxylated nitrile rubber (XNBR) and bis(diisopropyl)thiophosphoryl disulfide can improve the mechanical properties of the XNBR vulcanizates. The study further reveals the fact that these sulfidic crosslinks in combination with metallocarboxylate crosslinks produce a significant effect in XNBR vulcanization. Some investigations have been carried out using a methyl iodide probe to elucidate the formation of chemical linkages during cure. Also, attempts have been made to establish the relationship between the structure and physical properties of the XNBR vulcanizates in this respect. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 2623–2630, 1997

INTRODUCTION

Carboxylated nitrile rubber (XNBR) is a high potential elastomer having a wide range of reactivity toward various compounds.[1–3] Recently, we observed that the carboxyl group of XNBR is capable of reacting with several thiophosphoryl disulfides and thus brings about the vulcanization of XNBR. In this process, an entirely new type of sulfidic crosslink (nonconventional sulfidic crosslink) is introduced into the rubber matrix.[4,5] Since the physical properties of the rubber vulcanizates are very much controlled by the various linkages present in the network, it was decided to investigate some of the structure–property relationship characteristics of XNBR vulcanizates, particularly in the light of the above-mentioned nonconventional sulfidic crosslinks. With this in mind, the present work was undertaken.

EXPERIMENTAL

Materials

Bis(diisopropyl)thiophosphoryl disulfide (DIPDIS) was prepared and purified according to the procedure reported by Pimblott et al.[6] Tetramethylthiuram disulfide (TMTD) was a commercial sample used after the necessary purification. Analytical zinc oxide and extrapure stearic acid were used as rubber additives. Methyl iodide was used after distillation. Carboxylated nitrile rubber (K 221, highly carboxylated with medium acrylonitrile content: ML-1 + 4′ at 100°C, 50; total ash content, −0.7%; bound monomer, 26.6%), was obtained from Polysar, Sarnia, Canada.

Preparation of the Vulcanizates and Measurement of Physical Properties

The procedure for the preparation of the vulcanizates was given earlier.[5] The cure data were obtained on a Monsanto rheometer (R-100) and physical properties, e.g., modulus, tensile strength, and elongation at break, were measured according to the ASTM D 412-51T procedure.[5] Shore-A hard-

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ness values were obtained by a Durometer. The procedures for the measurement of the age-resistance property and the oil-resistance property of the vulcanizates were reported earlier.[7]

Removal of Excess Zinc Oxide from XNBR Vulcanizates

To avoid postcuring of XNBR vulcanizates[1] 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 dibutyldithiocarbamate 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 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 the Vulcanizates with Methyl Iodide

Methyl iodide breaks the various sulfidic links[8–12] of XNBR vulcanizates while the ionic crosslinks remain unaffected.[13] The samples of the vulcanizates, freed from excess zinc oxide together with redistilled methyl iodide (1.90 g/g of vulcanizate), were sealed *in vacuo* ($<10^{-5}$ mm) under a nitrogen atmosphere and then heated in the dark at 80°C for 4 days. Samples of the 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 an isooctane : toluene (70 : 30) medium at 30 ± 2°C.

RESULTS AND DISCUSSION

In the pursuance of this study, several mixes (A–E) were prepared. To start with, the cure and physical data were first analyzed.

The mix formulations are given in Table I and the respective cure data are presented in Table II. Corresponding cure curves are depicted in Figure 1. The numbers on the curves correspond to those used in the mix formulations in Table I. Tetramethylthiuram disulfide (TMTD) was included in the study in order to have a clear idea about the activity of DIPDIS since both TMTD[14] and DIPDIS[5,6] actively behave as an accelerator cum sulfur donor. It can be expected that as TMTD does not react with the —COOH group[4] some differences in the nature of various crosslinkages in those two accelerated systems are bound to occur. It is evident from the foregoing study that the presence of stearic acid may interfere with the reaction between DIPDIS and XNBR during compounding as well as during the vulcanization.[4] We noticed that DIPDIS cannot liberate isopropyl alcohol from natural rubber (NR) already compounded with ZnO and stearic acid.[15] This suggests that either stearic acid has completely reacted with ZnO (to form zinc stearate) or it has somehow or other been deactivated. In the polar medium using XNBR instead of NR, stearic acid is expected to react faster with ZnO and thus it will not interfere with the reaction between XNBR and DIPDIS.

It is evident from Table I that mix A contains only zinc oxide as a vulcanizing agent. Here, the low scorch time of zinc oxide-cured XNBR vulcanizate is due to early reactions of carboxyl groups. The optimum cure time value (t_{90}) of mix A is the lowest among all the mixes presented in Table II, which once again indicates that the overall reaction between zinc oxide and XNBR is very sharp[3] as also evident from curve A, Figure 1.

Mixes B and C represent, respectively, TMTD-compounded and DIPDIS-compounded stocks of XNBR, in the absence of zinc oxide. It is evident from Table II that DIPDIS-compounded stock (mix C) exhibits a higher R_∞ value (more than double) than that of TMTD-compounded stock of XNBR, which indicates a higher extent of crosslinking reaction of DIPDIS with XNBR. A higher t_2 value of mix B as compared to that of mix C is indicative of the fact that TMTD does not take part in the early part of reaction with —COOH groups of XNBR, as is usually in the case with DIPDIS.[4] The nature of cure curves (curves B and C, Fig. 1) of mixes B and C are quite different in nature. In mix C, the total cure is divided into two parts: the initial fast curing reaction between —COOH groups of XNBR and DIPDIS and the slower sulfur vulcanization at the later period exhibited by both DIPDIS and sulfur. TMTD-compounded stock (mix B), on the other hand, only exhibits rather fast sulfur vulcanization (as evidenced from lower t_{90} value of mix B) as compared to that of mix C. The marching effect indicated by the cure curve of mix C is very prominent, whereas a more or less steady cure curve is obtained for mix B.

Mixes D and E, respectively, represent TMTD-

Table I   Formulation of Mixes

	Mix No.				
	A	B	C	D	E
Krynac 221 (XNBR)	100	100	100	100	100
Stearic acid	2	2	2	2	2
Zinc oxide	5	—	—	5	5
TMTD	—	2.16[a]	—	2.16[a]	—
DIPDIS	—	—	3.834[b]	—	3.834[b]
Sulfur	—	0.5	0.5	0.5	0.5

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

accelerated and DIPDIS-accelerated stocks of XNBR in the presence of zinc oxide and sulfur. As discussed earlier,[4] for DIPDIS-accelerated XNBR vulcanizates in the presence of zinc oxide and sulfur (mix E), the total cure is distinctly divided into two regions: (i) the initial fast curing reactions based on a sulfurless cure brought about by zinc oxide and DIPDIS and (ii) the accelerated sulfur vulcanization at the later period exhibited by zinc oxide, DIPDIS, and sulfur. The cure behavior of mix D is denoted by the typical steep cure curve (characteristic of TMTD cure) and also by the higher R_α and lower t_2 values as compared to those of mix E. It can be seen from Figure 1 that the marching cure occurs with mix D, which further indicates complete absence of two different types of cure as obtained in mix E. Optimum cure time values (t_{90}) for mixes D and E are more or less similar and come next to that of mix A.

To correlate the mechanical properties of XNBR vulcanizates with the nature of crosslinkages, some of the physical properties of the mixes A–E were studied and these are presented in Table III. Different types of crosslinkages potentially present in the vulcanizates of mixes A–E and their apparent crosslink density values are presented in Table IV.

Mix A, cured by zinc oxide alone, generates solely the metallocarboxylate crosslinkages as depicted in Figure 2. These linkages are responsible for the highest modulus, tensile strength, hardness, and the low elongation at break.[3] The high tensile strength property of the metallocarboxylate crosslinks is due to crosslink exchange[16,17] under stress. The energy for such an exchange is believed to be lower than that required for complete charge separation between the two ion pairs.

Comparing the physical data of mixes B and C (Table III), it is found that the mechanical properties in respect of modulus, tensile strength, hardness, etc., for the vulcanizates obtained from mix C are superior to the corresponding values obtained from the vulcanizates of mix B. By virtue of the reaction between DIPDIS and —COOH groups of XNBR, a new type of nonconventional disulfidic crosslinks [—COOP(S)—S—S—(S)POOC—] are formed in mix C in addition to the conventional sulfidic crosslinks (Fig. 3). These new nonconventional sulfidic crosslinks are flexible[5,7,18] enough to facilitate crosslink slippage and thereby enhance the tensile strength of the vulcanizates of mix C. A probable mechanism of crosslink slippage of nonconventional sulfidic crosslinks may be proposed as shown in Figure 4. Obviously, this type of crosslink is

Table II   Cure Characteristics of the Stocks Obtained at 160°C

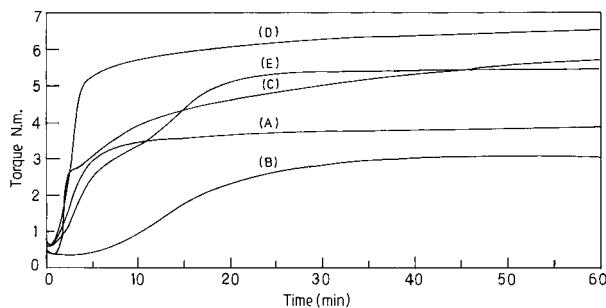|	Mix No.				
	A	B	C	D	E
Maximum Rheometric torque, R_∞ (N-m)	3.20	2.70	5.70	5.80	4.95
Scorch time T_2 (min)	0.75	5.0	1.75	0.50	1.00
Optimum cure time t_{90} (min)	12.0	28.0	49.0	16.5	17.0

Figure 1 Rheographs of mixes A–E (Table I) cured at 160°C.

absent in the vulcanizates of mix B containing TMTD and thus only conventional sulfur crosslinks $(-C-S_x-C-)$ are obtained in this case.

From a comparison of the physical data obtained from mixes D and E, it appears that although modulus values of the vulcanizates are nearly the same, the tensile strength and elongation at break values vary widely. In the present investigation, a high-accelerator-to-low-sulfur ratio was used. Therefore, primarily, monosulfidic crosslinks are likely to be formed in the vulcanizate network which evidently exhibit poor tensile strength. On the other hand, good mechanical properties of mix E arise from the conjoint effect of flexible metallocarboxylate crosslinks and nonconventional sulfidic crosslinks of the type $-COOP(S)-S-S_n-S-(S)POOC-$ generated from the reaction between DIPDIS and $-COOH$ groups of XNBR.[5,7,18] The crosslinkages present in the vulcanizates of mix E are presented in Figure 5. The poor tensile strength of TMTD-accelerated vulcanizates of mix D can be accounted for by the absence of this type of flexible nonconventional sulfidic crosslinks, which is again due to the incapability of TMTD to react with the $-COOH$ groups of XNBR.[4] Moreover, fast-curing TMTD forms monosulfidic links which perhaps obstruct

the free movement of metallocarboxylate crosslinks, thereby hampering, to a large extent, crosslink slippage and causing further decline in the tensile values. The above proposition can also be corroborated by comparing the physical data of mixes A and D. The vulcanizates of mix A can form only metallocarboxylate crosslinks. From Table III, it is evident that the vulcanizates obtained from mix A possess modulus and tensile values significantly higher than those obtained with TMTD-accelerated stock (mix D).

Once again, it is interesting to note that the mechanical properties like modulus, tensile strength, hardness, etc., of the vulcanizates derived from DIPDIS-compounded stocks, in the absence of zinc oxide, are inferior to those of the vulcanizates derived from DIPDIS-compounded stocks, in the presence of zinc oxide (compare physical data of mix C with those of mix E). This once again proves the necessity of zinc oxide for the vulcanization reaction in the presence of DIPDIS. Earlier workers[6] described that zinc oxide is an integral part in the DIPDIS (sulfur donor) vulcanization of rubber. In the preceding study,[4] we discussed the effect of zinc oxide variation on the nature of vulcanization of XNBR accelerated by DIPDIS. From the physical data, presented in Table III, it is apparent that the presence of zinc oxide is necessary in the vulcanization of XNBR, accelerated by DIPDIS, not only as a curative but also as an activator of DIPDIS. The role of zinc oxide here is analogous to that in the TMTD-accelerated[14] vulcanization of rubber, since in both cases, zinc oxide, in combination with DIPDIS or TMTD, forms a highly effective sulfurating complex which acts as a precursor of an ultimate matured network. So, the ultimate strength property of such a network very much depends upon the initial vulcanization reactions.

Table III Nature of Crosslink and Apparent Crosslink Density of Different XNBR Vulcanizates

Mix No.	Modulus at 200% Elongation (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Hardness Shore-A	Aged in Air, 72 h at 100°C		
					Moulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
A	1.84	12.67	570	73	2.40	24.01	350
B	0.54	1.7	550	51	0.68	1.34	350
C	1.01	3.6	600	57	1.10	2.81	400
D	1.53	4.11	670	67	2.76	6.77	400
E	1.46	11.65	610	65	1.80	10.27	500

Table IV Physical Data of XNBR Vulcanizates Obtained at 160°C

| Mix No. | Type of Crosslinks | | | Apparent Crosslink Density ($1/Q$) |
	Metallocarboxylate	Nonconventional Sulfidic	Conventional Sulfidic	
A	Present	—	—	3.48
B	—	—	Present	2.12
C	—	Present	Present	2.47
D	Present	—	Present	2.85
E	Present	Present	Present	3.08

Thus, the observed wide variation in the mechanical properties of mixes C and E can be explained in this way.

Age-resistance behavior of the vulcanizates derived from mixes A–E are presented in Table III. Vulcanizates obtained from XNBR seem to be resistant to heat and oxidation under the experimental condition presumably due to the presence of metallocarboxylate crosslinkages.[3,7,13,18] For the vulcanizates, derived from mix A containing metallocarboxylate crosslinks only, the tensile strength becomes almost double the original value, obtained after aging for 72 h at 100°C. This has been ascribed to the occurrence of the postvulcanization reaction between —COOH groups of XNBR and excess zinc oxide present in the mix.

Although it appears from the data presented in the table that the original tensile values of TMTD-accelerated XNBR vulcanizates are extremely poor (see physical properties of mixes B and D); however, the age-resistance behavior of these vulcanizates appears to be good. This is due to the presence of a high extent of monosulfidic crosslinks that are believed to possess very good age-resistance property.[14]

DIPDIS-accelerated rubber vulcanizates possess high thermal and thermal oxidative stability due to the formation of zinc diisopropyl dithiophosphate (ZDP) *in situ*.[6] XNBR vulcanizates, as mentioned above, are resistant to heat and oxidation due to the presence of metallocarboxylate crosslinks. So, it is expected that XNBR vulcanizates in the presence of DIPDIS will exhibit prominent age-resistance behavior. Actually, this is observed from the tensile values (Table III) of the vulcanizates of mixes C and E. The extent of retention of the original tensile values of the vulcanizates is evidently good in both the cases.

The structures of the vulcanizates are very much dependent upon the nature and number of crosslinkages introduced during cure. Thus, some investigations were carried out to determine the crosslink density of the vulcanizates derived from mixes A–E (Table IV). It was found that the vulcanizates of mix A comprising solely metallocarboxylate crosslinks exhibit the highest crosslink density, whereas the vulcanizates obtained from mix E containing three types of crosslinks, namely, metallocarboxylate crosslinks and non-
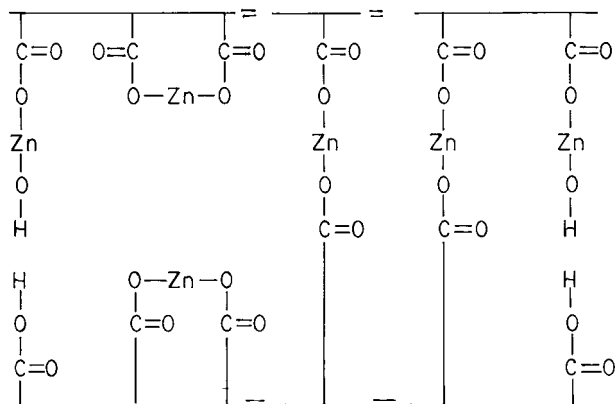
Figure 2 Crosslinkages potentially present in metallocarboxylate vulcanizates (mix A, Table I).
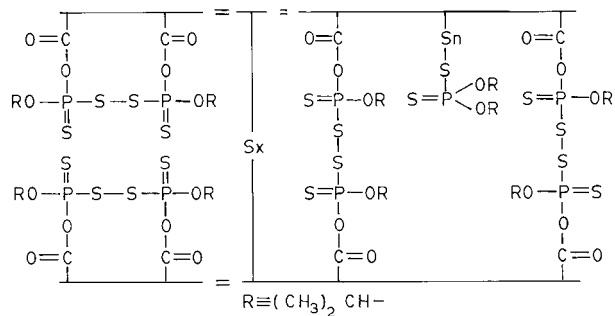
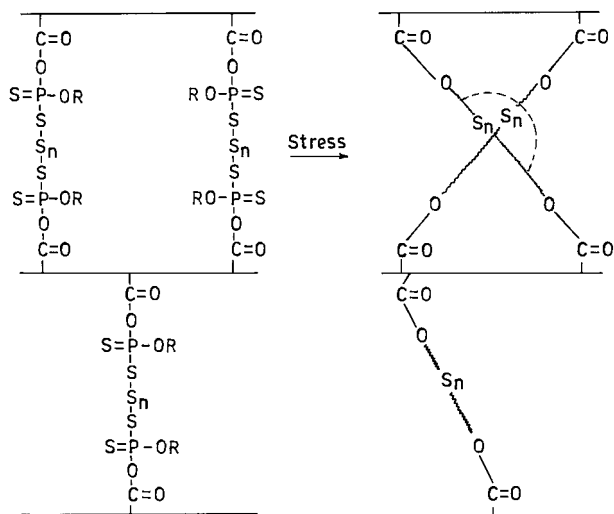**Figure 3** Crosslinkages potentially present in mix C (Table I).

Figure 4 Crosslink exchange under stress.

conventional sulfidic and conventional sulfur crosslinks, rank second in terms of apparent crosslink density value. Apart from its intermolecular reaction with the —COOH groups of XNBR leading to the formation of nonconventional sulfidic crosslinkages, DIPDIS might also generate intramolecular links (see Figs. 3 and 5). But this type of link is virtually small in case of the vulcanizates obtained with ZnO (mix A).[3] It may be assumed that a significant amount of DIPDIS might be consumed in the process of intramolecular bond formation. So, there occurs significant depletion of —COOH groups and, thus, intermolecular crosslinks. The net result is thus decreased in the $1/Q$ values of mixes C and E than in mix A. TMTD-accelerated XNBR vulcanizates in the presence of zinc oxide and sulfur (vulcanizates derived from mix D) which contain conventional sulfidic and metallocarboxylate crosslinks give a $1/Q$ value, somewhat lower than that of mix E. Comparing the apparent crosslinking values of the vulcanizates of mixes B and C, it can be seen that DIPDIS-compounded vulcanizates (i.e., mix C) exhibit higher crosslink density than those obtained with mix B. It is revealed from the study that the nonconventional sulfidic crosslinks resulting from the reaction between —COOH groups of XNBR and DIPDIS increase the apparent crosslink density, and, consequently, the oil-resistance property of the vulcanizates obtained from mixes C and E (compare the $1/Q$ values for mixes C and E with those of mixes B and D).

It is evident from the foregoing studies that the physical properties of the XNBR vulcanizates, obtained in the presence of ZnO, DIPDIS, and sul-

fur, are quite significant. As physical properties (modulus, tensile strength, hardness, age resistance, oil resistance behavior, etc.) of the vulcanizates are influenced by the different crosslink types present in vulcanizate network, it necessitates the elucidation of network structure with regard to various crosslinkages present in the XNBR vulcanizate. In this study of network characterization, vulcanizates of DIPDIS-accelerated stocks (mix E) were compared with those of TMTD-accelerated stocks (mix D) with respect to different types of crosslinkages present both in the undercured and overcured regions. The results are recorded in Table V.

It has been suggested in the preceding studies that three types of crosslinkages might be 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 sulfur 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$_n$S(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 along with the conventional sulfidic crosslinks [type (ii)], leaving only salt crosslinks [type (i)] and thus providing an idea about the network structure of XNBR. So, in the presence of thiophosphoryl disulfide, zinc oxide, and sulfur, two types of crosslinks, namely, metallocarboxylate and sulfidic crosslinks, can be determined using the methyl iodide probe. For the present investigation, we used an efficient vulcanization system (i.e., more accelerator and less sulfur). Again, as discussed earlier, a significant amount of nonconventional sulfidic crosslinks of type (iii) is gen-
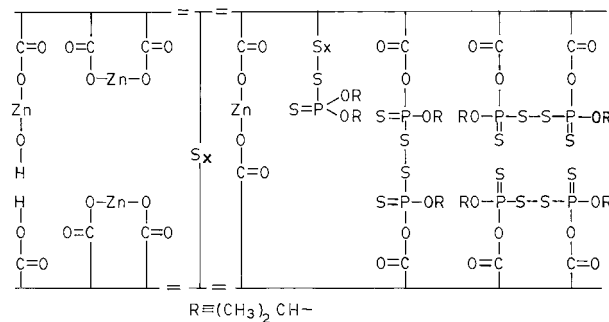

Figure 5 Crosslinkages potentially present in mix E (Table I).

Table V   Chemical Characterization of the Vulcanizate Networks

System	TMTD–XNBR (Mix D)					DIPDIS–XNBR (Mix E)				
Cure time, min at 160°C	5	10	16.5[a]	25	35	5	10	19[a]	25	35
Apparent crosslink density ($1/Q$)	1.8	2.3	2.8	3.0	3.1	1.9	2.4	3.0	3.1	3.1
Salt-type crosslink (%)	89	78	61	75	74	73	68	66	71	70
Sulfur-type crosslink (%)	11	22	39	25	26	27	32	34	29	30

[a] Optimum cure time of the respective mixes.

erated when DIPDIS reacts with XNBR. So, it may be reasonably expected that for the present vulcanization system using a significant amount of DIPDIS the linkages of type (iii) will predominate over those of type (ii). Therefore, it will be justified to say that the crosslinks in the XNBR vulcanizate network, in the presence of DIPDIS, would be mainly the salt type [type (i)] and nonconventional sulfidic type [type (iii)]. Likewise, TMTD-accelerated vulcanizates of XNBR (mix D) will be rich in the salt-type and conventional sulfidic-type crosslinks.

It is evident from Table V and Figure 6 that for mix D (curve D of Fig. 6) the amount of metallocarboxylate crosslinks becomes highest (89%) in the beginning, it then falls rapidly near the optimum cure, and, thereafter, an increase is observed. This is quite expected, since the reaction between zinc oxide and XNBR is very sharp and there also occurs a time delay for the formation of sulfur crosslinks via the sulfurating complexes. But as soon as the formation of sulfur crosslinks
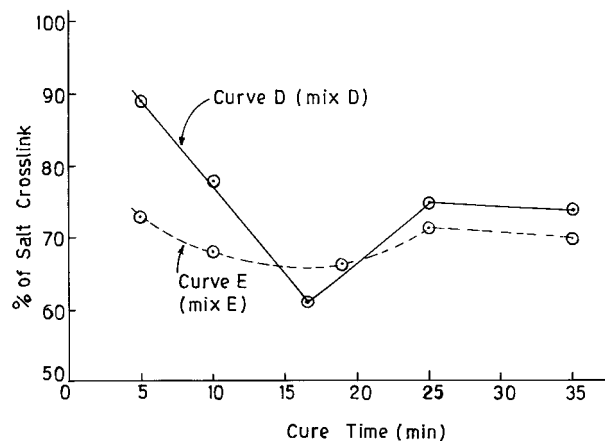

Figure 6   Variation of salt crosslinks with cure time for mixes D and E.

commences, the concentration of salt crosslinks apparently falls when the total number of crosslinks are considered. This is also reflected in the data from the swelling experiment ($1/Q$ values). It is evident also that at optimum cure time the amount of sulfur crosslinks is maximum, and beyond this, there occurs a decrease in the total number of sulfur crosslinks again. It has been observed by earlier workers[14] that on extended cure, especially in the presence of zinc dithiocarbamate (ZDC), some of the sulfur crosslinks are destroyed. The fall in the concentration of sulfur crosslinks as seen from these data suggests that desulfuration might occur in this case also. It is evident from the $1/Q$ values that the total number of crosslinks was not affected beyond optimum cure and, in fact, a small increase in their concentration is noticed. The reason might be due to an increase in the proportion of salt crosslinks in this region. This proposition is also corroborated by the rheograph of mix D (curve D, Fig. 1). Thus, the vacuum caused by the depletion of sulfur crosslinks is filled by the generation of salt bridges. It is evident from Table V and curve E of Figure 6 that the metallocarboxylate crosslinking formed initially is lower for the vulcanizates containing DIPDIS than that comprising TMTD. These crosslinkages also continue decreasing, comparatively at a slower rate, up to an optimum cure time and then increase as the cure proceeds. Evidently, the reverse is true for sulfidic linkages. It was shown earlier that like ZnO DIPDIS also reacts sharply with XNBR, as a result of which nonconventional sulfur crosslinks are generated. These crosslinks thus account for the higher number of sulfur crosslinks for mix E at the initial stage than those obtained from the vulcanizates of mix D. In this case, as the reaction between DIPDIS and —COOH groups occurs prior to that

arising from the sulfurating complex (generated from ZnO, DIPDIS, and sulfur), the contribution made by the conventional sulfur crosslinks toward the total number of crosslinks in the initial part of vulcanization is not much. However, as the cure progresses, the —COOH groups become sparse in the rubber matrix and ZDP formation obviously gains prominence and this ZDP is then transformed into the sulfurating complex which ultimately produces sulfur crosslinkages. The increase in the concentration of sulfidic linkages for the vulcanizates of mix E may thus be explained (Table V). This is also true for the vulcanizates of mix D where ZDC[14] (obtained from ZnO and TMTD) generates the sulfurating complex. It needs mentioning here that in the overcured region the decrease in the concentration of sulfidic crosslinks for the vulcanizates of mix E is comparatively less than that observed with the vulcanizates of mix D. This phenomenon is suggestive of the protective action of DIPDIS over the degeneration of sulfidic linkages.

So far, we have observed the influence of nonconventional sulfidic crosslinks in XNBR vulcanizates, their mode of generation and degeneration, and their role in the ultimate matured network formation. The effect of these nonconventional sulfidic crosslinks is strongly manifested in the physical properties of the vulcanizates. Although the nonconventional sulfidic crosslinks alone impart moderate mechanical properties in vulcanizates, their combinations with metallocarboxylate crosslinks produce a significant effect as reflected in the enhanced mechanical properties of the vulcanizates. Thus, for nonconventional sulfidic crosslinks, the characteristics like crosslink flexibility and rapid stress relaxation seem to be very much similar to those of metallocarboxylate crosslinks. The flexibility as well as crosslink slippage obviously arises from the presence of oxygen and polysulfur ($-O-S_n-O-$) as depicted previously in Figure 5. However, further investigations in this regard need to be carried out in order to have more precise knowledge about the physicochemical character of the nonconventional sulfidic crosslinks in the presence of various network structures of rubber vulcanizates.

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