

Structure-Property Relations of Carboxylated Nitrile Rubber

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Synopsis

The technical properties and the network structure of carboxylated nitrile rubber (XNBR) having a mixed crosslink system of sulfur and metal carboxylate have been studied. XNBR of different carboxyl contents (Krynac 221, Krynac 110C), yielding different concentrations of ionic crosslinks, have been used for this purpose. The amount of ionic crosslinks was also varied by varying the amount of crosslinking agent (zinc peroxide). It has been observed that ionic crosslinks impart high tensile strength, permanent set, and hardness, while sulfur crosslinks introduce high flex crack resistance, elongation at break, and tear strength in the vulcanizate. Heat buildup and resilience could be explained with the help of stress relaxation experiments. Stress decay is more when the amount of ionic crosslinks is higher. Higher stress relaxation gives higher hysteresis. The kinetics of the crosslinking of a mixed crosslink system has also been studied. At overcure times the amount of ionic crosslinks is greater than that of sulfur crosslinks which desulfurizes in this region. The technical properties could be explained on this basis.

INTRODUCTION

Recent publications¹⁻⁶ from this laboratory report structure-property relations of natural rubber, synthetic rubbers, and rubber blends. Similar work with carboxylated nitrile rubber,⁷⁻¹¹ which lately has attracted attention of scientists and technologists due to its unique properties, is lacking. Studies on this rubber are interesting in the sense that two types of crosslinks, namely salt linkages and sulfur crosslinks, can be introduced in the XNBR vulcanizates.

In this paper, we study the effects of sulfur crosslinks and ionic crosslinks on the technical properties of vulcanizates. We have used two rubbers of different carboxyl contents, that is, Krynac 221 with high carboxyl content and Krynac 110C with low carboxyl content. The kinetics of crosslinking in mixed crosslink system and the response of metal carboxylate crosslinks with the superimposed sulfur crosslinks have also been studied.

EXPERIMENTAL

Mix formulations are given in Tables I and II and the curing characteristics are reported in Tables III and IV. Methods of mixing and preparation of the vulcanizates were the same as described earlier.² Zinc peroxide masterbatch (Krynac PA50) was added at the end of the mixing cycle. Determination of physical properties and volume fraction of rubber by swelling were described earlier.¹ Stress relaxation measurements were done in a Zwick tensile machine according to the method described by Zakharov.¹² The determination of percentage of salt crosslinks and sulfur crosslinks was done with the use of methyl iodide treatment.

TABLE I
 Formulations of Mixes

Mix no.	A	B	C	D	E
Krynac 221 ^a	100	99	95	95	100
Stearic acid	2	2	2	2	2
FEF black (N 550)	40	40	40	40	40
Sulfur	2.4	2.4	2.4	—	2.4
CBS ^b	0.8	0.8	0.8	—	0.8
Krynac PA50 ^c	—	2	10	10	—
Zinc oxide	—	—	—	—	5

^a Highly carboxylated nitrile rubber with medium acrylonitrile content, obtained from Polysar Ltd., Canada. ML 1+4 at 100°C, 50; total ash content, 0.77%, nonstaining antioxidant; specific gravity, 0.98.

^b N-Cyclohexylbenzothiazylsulfenamide obtained from Alkali and Chemical Corporation of India Ltd., Rishra.

^c 50/50 technical grade zinc peroxide/NBR curative masterbatch, obtained from Polysar Ltd., Canada.

We have observed that methyl iodide treatment works efficiently in XNBR vulcanizates as prepared by us. Vulcanized sheets were quenched in water immediately on removal from the mold and tested for chemical analysis within 48 h. The same method was applied to NBR and NR vulcanizates, and in each case methyl iodide treatment was successful.^{13,14} To avoid aging of XNBR vulcanizates, the excess of zinc salts were reacted with dimethyl amine and carbon disulfide in an alkaline medium according to the method of Brown¹⁵ before treatment with methyl iodide. Lee and Morrell,¹⁶ however, reported that sulfur crosslinks were modified to sulfone or sulfoxide in nitrile rubber if the sample

 TABLE II
 Formulations of Mixes

Mix no.	F	G	H	I	J
Krynac 110C ^a	100	99	95	100	95
Stearic acid	2	2	2	2	2
FEF black (N 550)	40	40	40	40	40
Sulfur	2.4	2.4	2.4	2.4	—
CBS ^b	0.8	0.8	0.8	0.8	—
Krynac PA50 ^c	—	2	10	—	10
Zinc oxide	—	—	—	5	—

^a Low carboxylated nitrile rubber with medium acrylonitrile content, obtained from Polysar Ltd., Canada. ML 1 + 4 at 100°C, 50; total ash 0.7%, nonstaining antioxidant, specific gravity, 0.98.

^b N-Cyclohexylbenzothiazylsulfenamide, obtained from Alkali and Chemical Corporation of India Ltd., Rishra.

^c 50/50 technical grade zinc peroxide/NBR curative masterbatch, from Polysar Ltd., Canada.

 TABLE III
 Curing Characteristics Using Monsanto Rheometer (R-100) and Mooney Viscometer

Mix no.	A	B	C	D	E
Mooney scorch time, t_5 at 120°C (min)	34.0	15.5	7.0	9.5	2.0
Mooney No. ML (1 + 4) at 120°C	51.0	54.0	55.5	64.0	218.0
Optimum cure time at 150°C (min)	55.0	25.0	33.0	52.0	35.0
Cure rate (% min ⁻¹)	1.96	4.76	3.39	2.1	3.07

TABLE IV
Curing Characteristics Using Monsanto Rheometer (R-100) and Mooney Viscometer

Mix no	F	G	H	I
Mooney scorch time, t_5 at 120°C (min)	34.0	23.5	19.0	18.0
Mooney No. ML (1 + 4) at 120°C	56.0	60.0	70.5	79.0
Optimum cure time at 150°C (min)	36.0	10.5	10.0	9.5
Cure rate (% min ⁻¹)	3.33	19.04	21.05	22.22

was removed hot from the press, and hence solubility of the sulfur vulcanized rubber would not be achieved. We did not experience such difficulty with our method. This treatment was carried out at 80°C for 4 days under sealed nitrogen atmosphere. Sulfur crosslinks are believed to undergo complete cleavage due to methyl iodide treatment while the ionic crosslinks remain unaffected.¹⁴

RESULTS AND DISCUSSION

Technical properties and chemical characterization of vulcanizates of Krynac 221 are summarized in Table V. It has been shown that, for pure sulfur system (mix A), the flex cracking, heat buildup, resilience, tear strength, and abrasion resistance are good while the sulfur system mixed with metal carboxylate crosslinks (mix C) gives higher tensile strength and hardness and lower perma-

TABLE V
Characterization of Filled Krynac 221 Mixes

Mix no.	A	B	C	D	E
Tensile strength (MPa)	19.07	16.07	20.25	22.35	22.29
300% modulus (MPa)	15.88	—	—	—	—
Elongation at break (%)	440	245	225	230	215
Tear strength (MN/m)	5.74	5.50	4.56	4.15	5.99
Hardness, Shore A	74	77	85	78	90
Resilience (%)	42	40	35	32	40
Heat buildup ($\Delta T^\circ\text{C}$)	32	32	49	58	35
Permanent set (%)	2.2	1.9	1.9	1.0	1.7
Flex cracking upto failure, Kilo cycles	15.6	10.5	0.3	0.1	1.0
Abrasion loss (cm ³ /1000 rev)	0.29	0.31	0.36	0.39	0.38
Volume fraction of rubber (V_r)	0.217	0.244	0.266	0.257	0.267

TABLE VI
Characterization of Filled Krynac 110C Mixes

Mix no.	F	G	H	I
Tensile strength (MPa)	18.33	19.89	17.59	17.47
300% modulus (MPa)	7.21	11.54	12.15	12.30
Elongation at break (%)	573	470	400	393
Tear strength (MN/m)	7.33	6.68	5.65	4.91
Hardness, Shore A	67	72	74	75
Resilience (%)	48	49	53	51
Heat buildup ($\Delta T^\circ\text{C}$)	41	33	32	32
Permanent set (%)	7.08	2.63	3.73	2.2
Flex cracking upto failure (kcycles)	315.7	286.5	276.7	149.7
Abrasion loss (cm ³ /1000 rev)	0.39	0.45	0.51	0.54
Volume fraction of rubber (V_r)	0.147	0.181	0.178	0.182

nent set. Mix B, containing the smaller proportion of zinc peroxide, gives the desired set of properties. Mix D, which comprises of only metal carboxylate linkages, gives the highest tensile strength, lowest flex resistance, and highest heat buildup. Mix E, containing zinc oxide (instead of peroxide), gives similar properties as mix C, but the scorch time, as expected, is very low and the Mooney number is very high (Table III). For metal carboxylate crosslinks, low scorch time is due to early reaction of carboxyl group. The slower cure rate of XNBR compounds is attributed to the restriction of freedom of motion by steric hindrance and molecular interaction.¹⁷ The high strength property of rubber containing metal carboxylate crosslinks is due to crosslink exchange under stress, as shown in Figure 1. The energy for such an exchange is believed to be lower than that required for complete charge separation between the two ion pairs. Poor flex cracking properties of these systems might be due to high heat buildup and high crack growth rate owing to the high strain energy. The high hardness of mixes C, D, and E is due to higher crosslink density as represented by V_r , the volume fraction of rubber in swollen vulcanizate (Table V). V_r values are higher in the case of mixes C and E which are comprised of mixed crosslink system. It is evident that sulfur vulcanization is retarded in the mixed sulfur-metal carboxylate system. Assuming that the carboxylic groups are fully utilized, the V_r value is not increased to the extent expected. The V_r value of mix E is almost the same as mix C (Table V). The optimum cure time is also comparable. This indicates that activation by ZnO_2 and ZnO in these formulations follow similar paths for vulcanization reaction.

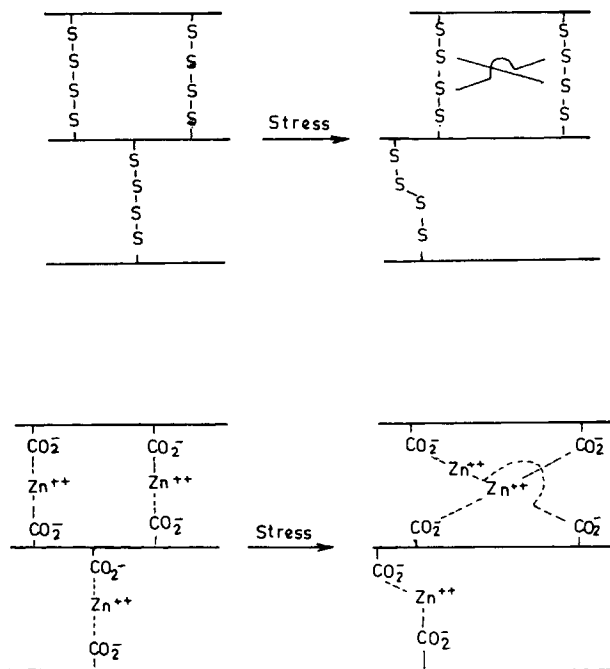


Fig. 1. Crosslink exchange under stress.

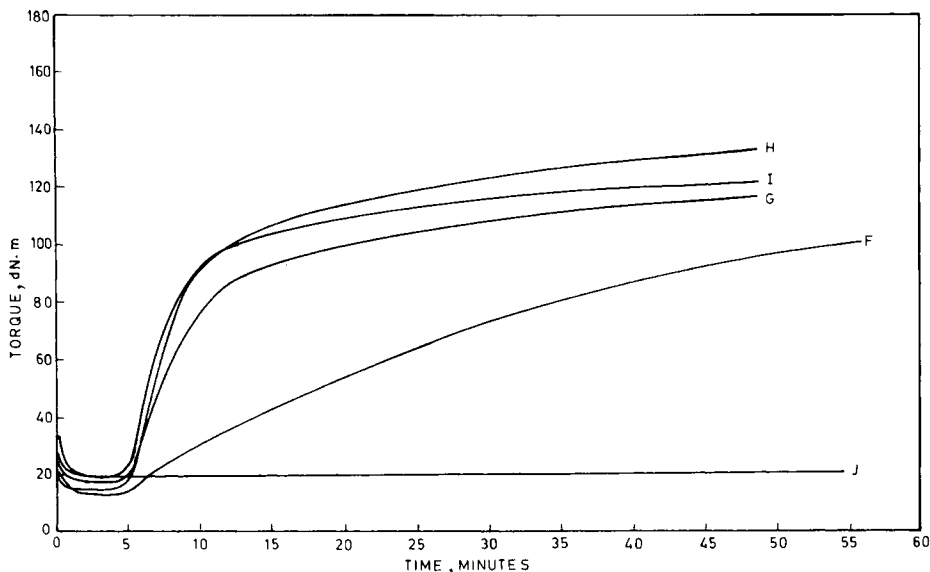


Fig. 2. Rheographs of mixes F—J at 150°C.

Aging studies are reported in Table VII. It is shown that, as the proportion of carboxylate crosslink is increased, the aging resistance is enhanced, which is due to better heat stability of the metal carboxylate crosslinks. V_r values are increased in all cases due to postvulcanization reaction.

In order to show the effect of carboxylic group on the vulcanization reaction and properties, we have also studied another series (mixes F–I). In this system, the amount of carboxylic group is so low that without the addition of sulfur no cure occurs even at prolonged time as shown in the rheograph (Fig. 2). From Tables III and IV, it has been shown that high carboxyl content increases the

TABLE VII
Percentage Retention of Properties^a

Mix no.	A	B	C	D	E
Tensile strength (%)	29	35	56	90	87
Elongation (%)	18	30	38	58	54
Tear strength (%)	21	40	50	103	77
Hardness (%)	108	106	100	120	105
Volume fraction of rubber (%)	129	118	112	110	109

^a 24-hr heat aging at 100°C.

TABLE VIII
Percentage Retention of Properties^a

Mix no.	F	G	H	I
Tensile strength (%)	19	22	44	40
Elongation (%)	10	17	32	25
Tear strength (%)	12	17	40	30
Hardness (%)	116	111	110	109
Volume fraction of rubber, V_r (%)	147	132	133	130

^a 24-h heat aging at 100°C.

optimum cure time and lowers the scorch time. It means that, though the carboxyl group in highly carboxylated rubber forms metal carboxylate crosslink at an early stage, but sulfur vulcanization occurs at a later stage and it takes more time to complete the vulcanization process. This is due to consumption of ZnO_2 in the early stage of the reaction by the carboxyl group. The Zn^{++} forms complexes with accelerators and accelerator polysulfides to increase the rate of the early reactions. This chelated form of the accelerators is believed to be more reactive than the free accelerator-sulfur complex in the early reaction. This is the reason why the mixes without ZnO or ZnO_2 (mixes A and F) are having slower cure rate. Mix I with ZnO has, as expected, low scorch time and optimum cure time. But the curing characteristics show that some of the ZnO is involved in the sulfurization process, which is further evident from the properties.

The technical properties of mixes F-I have been reported in Table VI. The effect of systems (either single or mixed crosslink type) on the technical properties is almost same as in the previous mixes (mixes A-E) except in the case of heat buildup and resilience. In Krynac 221 we observed lower heat buildup and higher resilience in the —S— crosslinking system as compared to the mixed (—S—) and (—COO—Zn⁺⁺—COO—) systems, while in the case of Krynac 110C, we have observed higher heat buildup and lower resilience in the sulfur crosslinking system. The V_r values are in line with the trends obtained from the mixes having high carboxyl content. The high heat buildup and low resilience in mixes containing carboxylate linkage or mixed crosslink system have been explained later in this paper.

On comparison of mixes having high carboxyl content (mixes A, B, C, D, and E) with those of low carboxyl content mixes F, G, H, and I), it has been observed that in the former mixes the properties are guided by metal carboxylate linkage while those in the later mixes are controlled by sulfur linkages. For example, the high flex resistance, high permanent set, good tear strength, and high elongation at break of the later mixes can thus be explained. The higher percentage retention of physical properties (Tables VII and VIII) in the case of mixes A-E is also understood.

V_r values are higher, as expected, for mixes B and C as compared to mixes G and H. Mix F has a lower crosslink density than mix A, which varies only in carboxyl content. It is observed that mixes F and A do not vulcanize without sulfur even at long cure times, because the vulcanizates dissolved in chloroform. Therefore, there is no indication of formation of ether linkage. The reason behind mix A having higher crosslink density is like this: the sulfur and accelerator forms a complex in the initial stage of the reaction. Probably, this complex is ionic in nature and is more soluble in a mix containing a high carboxyl group. The better utilization of sulfur in mixes A-C would also be concluded from the aging studies which reflect the fact that the same aging times enhance the crosslink density of mixes F-H more than the other mixes (A-E).

TABLE IX
Values of n^a

Mix	A	B	C	D	E	F	G	H	I
n	2.68	1.62	7.25	7.85	9.29	—	—	—	—

^a From eq. (1) at 100% strain.

To understand more about the nature of crosslink and their behavior, we have studied stress-relaxation properties of these systems. It has been shown from Figures 3 and 4 that stress relaxation is maximum with maximum proportions of ionic crosslinks and it decreases as the sulfur crosslinks are introduced in the system. Rate of stress relaxation which is directly proportional to n (Table IX), was obtained from the plot of $\log f_t$ vs. $\log t$ according to the equation derived by Cotten and Boonstra,¹⁸

$$\log f_t = \log f_0 - n \log t \quad (1)$$

where f_t = force at time t , f_0 = force after 1 min of relaxation, and n = relaxation rate of material.

Stress relaxation experiments involve the measurements of the force required

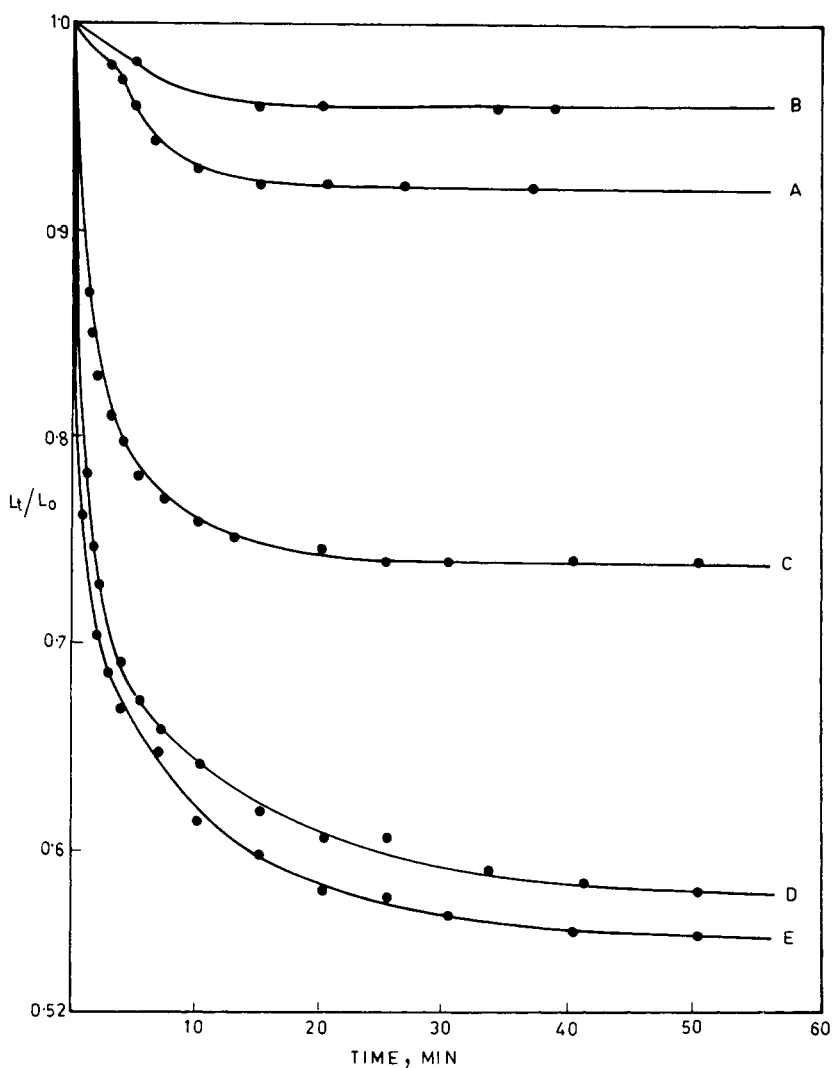


Fig. 3. Stress relaxation at 100% strain of the vulcanizates at room temperature.

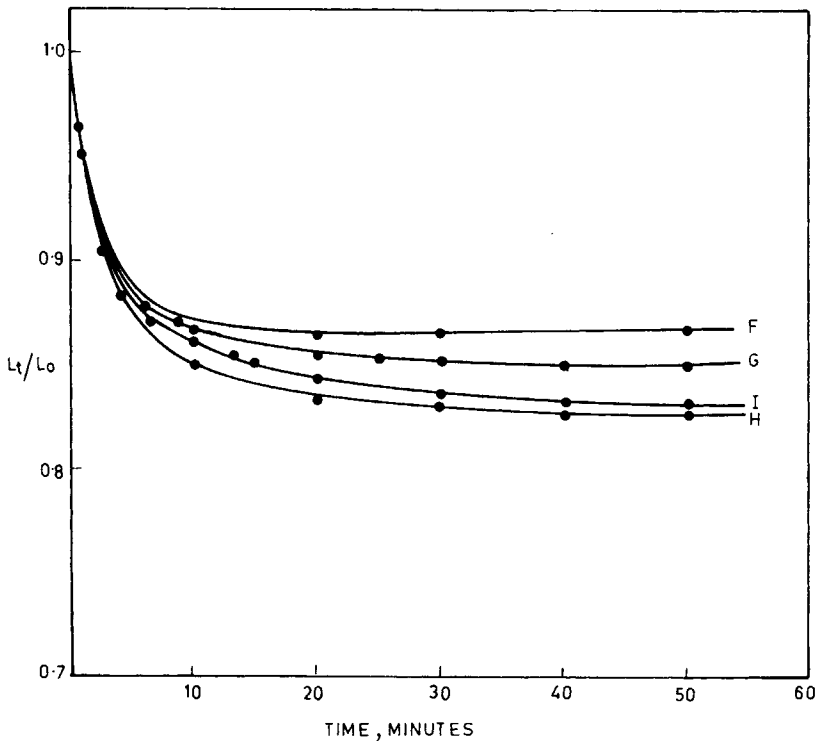


Fig. 4. Stress relaxation at 200% strain of the vulcanizates at room temperature.

to maintain the deformation produced initially by an applied stress as a function of time. Stress decay in our system could occur from the following chemical mechanisms:

(a) Polysulfide links undergo cleavage at the crosslink or along the main chain.

TABLE X
Values of n^a

Mix	A	B	C	D	E	F	G	H	I
n	—	—	—	—	—	2.36	2.91	2.91	2.84

^a From eq. (1) at 200% strain.

TABLE XI
Technical Properties of the Mix C at Different Cure Times

Cure time (min)	10	20	33	45	60
Tensile strength (MPa)	8.45	15.86	18.31	19.64	19.07
Elongation at break (%)	836	416	316	223	220
Tear strength (MN/m)	4.39	5.31	5.96	5.64	5.65
Resilience (%)	35	35	37	37	37
Hardness, Shore A	65	74	80	84	85
Abrasion loss (cm ³ /1000 rev)	0.35	0.35	0.35	0.36	0.35
Heat build up ($\Delta T^\circ\text{C}$) after 20 min at 50°C	49.5	47.5	46.5	46.5	46.5
Compression set (%)	40	25	25	25	25
Flex cracking up to failure (kcycles)	8.3×10^2	8×10^2	1.19×10^2	0.8	0.3

(b) Metal carboxylate bonds undergo cleavage at the crosslink or along the main chain.

(c) Since the compound is black filled, there might be lowering of the polymer-filler interactions.

Since the carbon black is same in all the mixes (provided rubber-filler interaction is unaffected by difference in curing systems adopted), the difference in stress relaxation will obviously arise due to (a) and (b). The difference in stress decay also explains the flexing properties (mixes A–E and mixes F–I). The higher the stress decay (as indicated by the higher value of n), lower is the flex resistance. This trend also explains the results of heat buildup and resilience of mixes A–E. The higher the amount of ionic crosslink, the higher is the stress relaxation and hence the higher is the heat buildup. This is in accordance to the observation made by Gent,¹⁹ who observed a direct relation between rate of relaxation and hysteresis. The constancy of resilience in mixes F–I is due to the constancy in stress decay. The above experiment was done at 100% strain. When the same experiment was done at 200% strain, mixes D, E, and A fail and mixes F–I show some minute difference in stress decay which cannot explain the results of heat buildup and resilience of mixes F–I. One reason might be that stress-induced crystallization might occur around 100% extension in the case of carboxylated nitrile rubber.

It has been shown above how the metal carboxylate crosslink with the superimposed sulfur crosslinks control the technical properties. Hence it would be interesting to know the change in structure and properties of mixed crosslink network with the progress of the cure. For this we have chosen mix C. Technical properties and the chemical characterization of the same mix above and below the optimum cure time have been reported in Tables XI and XII, respectively.

It has been observed that, as the cure progresses, tensile strength, hardness, and resilience increase while compression set, heat buildup, and elongation at break decrease. The abrasion loss remains constant at all cure times. The flex cracking and tear strength decrease at long cure times after passing through an optimum.

The crosslink density as measured by the volume fraction of rubber (V_r) increases with cure time. As shown in Table XI, the amount of metal carboxylate crosslinks increases while that of sulfur crosslinks decreases at longer cure times. It implies that the increase in crosslink density at overcure times is due to the increase in metalcarboxylate crosslinks. The destruction of sulfur crosslinks in this region is evident from the high value of zinc sulfide sulfur content and low value of network combined sulfur [S_c]. It seems from [S_c] values that sulfur crosslinks are formed up to about optimum cure time and then desulfurization of the combined sulfur takes place.

TABLE XII
Chemical Characterization of the Vulcanizate Network

Cure time (min)	10	20	33	45	60
Volume fraction of rubber (V_r)	0.136	0.190	0.230	0.250	0.255
Network combined sulfur, $S_c \times 10^4$ (g-atom/g-RH)	5.07	7.35	7.08	6.94	6.85
Sulfide sulfur (g-ion/g-RH $\times 10^4$)	—	0.09	0.15	0.29	0.38
Salt-type crosslink (%)	87	76	74	81	80
Sulfur type crosslink (%)	13	24	26	19	20

The technical properties can be correlated to the network structure. Increased tensile strength and hardness are due to increased crosslink density and higher amount of salt linkages, which helps in better stress relaxation. Decreased elongation at break, compression set, and flex cracking as cure proceeds are also due to increased ionic crosslinks in the system. It is apparent that, in the mixed crosslink system comprised of sulfur crosslinks and the metal carboxylate crosslink in XNBR vulcanizates, the properties are guided more by the ionic crosslinks, especially at overcure times. This observation is similar to that reported earlier by Bhowmick and De.¹⁰ The destruction in sulfur crosslinks is counterbalanced by the formation of ionic crosslinks in the systems.

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