Network Changes in Natural Rubber Vulcanizates under Compression

INTRODUCTION

Rubber products are subjected to various forms of mechanical and thermal strains during service life, and it is likely that their network structure undergoes changes during service. Such structural changes contribute considerably towards the deterioration of rubber products. Correlation between network structure and technical properties of rubber vulcanizates has been studied by De and co-workers.[1-5] A good knowledge about the structural changes that are likely to occur in vulcanizates under service conditions will help in understanding their failure phenomena. Nando and De[6,7] have studied changes in the network structure of natural rubber (NR) vulcanizates subjected to different physical tests, since these tests either singly or in combination simulate at least a few service conditions. Stuckey and co-workers[8] have recently reported decrease in the proportion of polysulfidic linkages in NR vulcanizates during De–Mattia flexing. Cunneen and Russel[9] reported changes in chemical structure of NR tire tread vulcanizates during simulated and actual service conditions. They found marked reduction in the concentration of polysulfidic linkages and increase in main chain modifications. Increase in crosslink density in tire treads during service was observed by Howard and Wilder.[10] But the extent of increase depends on the curative system and the nature of the base polymer. However, more extensive studies in this line are required to understand the failure phenomena in detail.

During service life, a number of rubber products are subjected to compression at elevated temperatures. In the present work we have made an attempt to study the changes occurring in NR vulcanizates under compression at elevated temperatures. The study gives an idea whether the network changes, if they occur at all, are due to compression or aging or both. For this we have chosen a conventional (conv) vulcanizing system in gum, whiting-, black-, and silica-filled mixes. The effects of using EV system and a higher test temperature were also studied in the gum mix.

It is generally known that rubber products can be protected from aging by the use of antioxidants. Hence, the effct of an antioxidant, phenyl-β-naphthylamine (PBNA), in the above compounds has also been investigated.

EXPERIMENTAL

The formulations of the various mixes are given in Table I. The details of mixing, vulcanization, and physical testing were the same as described earlier.[3-5]

Compression set of the samples was determined according to ASTM designation D 395, method B (25% strain, 22 h, 70°C). The test was done at 100°C also in the case of the gum compounds. In order to study the effect of aging alone, samples were kept simultaneously at the same temperatures without compression. V_r, the volume fraction of rubber in swollen vulcanizate, may be taken as a measure of the crosslink density. The samples were allowed to swell in benzene at 35 ± 1°C for 48 h, and V_r was determined using the relation[11]

$$V_r = \frac{(D - FT)\rho_r{}^{-1}}{(D - FT)\rho_r{}^{-1} + A_0\rho_s{}^{-1}}$$

where T is the sample weight, D is its deswollen weight, F the fraction of the insoluble components, and A_0 the weight fraction of the absorbed solvent, corrected for the swelling increment. ρ_r and ρ_s are the densities of rubber and solvent, respectively (ρ_r = 0.92 g/mL for NR and ρ_s = 0.875 g/mL for benzene). The proportion of polysulfidic linkages in the vulcanizates was found out from the difference in their V_r values before and after treatment with a solution of propane 2-thiol and piperidine (0.4M each) in n-heptane, for 2 h at room temperature under nitrogen.[12] The concentration of zinc sulfide was determined by the method used by Adams and Johnson.[13]

Samples for determining the network characteristics were taken from the inside middle sections of all the specimens. The extent of scatter in experimental results was assessed by carrying out estimations on samples taken from the surface and core of three different test pieces, selected at random. Table II gives the mean of three estimations and the standard deviation.

TABLE I
Formulations of the Mixes[a]

Mix no.	A	B	C	D	E
Natural rubber[b]	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Whiting	—	—	50	—	—
HAF black (N-330)	—	—	—	50	—
Precipitated silica	—	—	—	—	50
Naphthenic oil	—	—	—	5	5
Ethylene glycol	—	—	—	—	2
CBS[c]	0.6	3.5	0.6	0.6	0.6
Sulfur	2.5	0.5	2.5	2.5	2.5

[a] Mixes containing phenyl-β-napthylamine (1 phr) are numbered from A_1 to E_1 against the respective base mixes.

[b] Crumb Rubber, ISNR-5, obtained from the Rubber Research Institute of India, Kottayam.

[c] N-Cyclohexylbenzothiazyl sulfenamide, obtained from Alkali and Chemical Corporation of India Ltd., Rishra.

RESULTS AND DISCUSSION

Physical Properties of the Vulcanizates

The optimum cure times, as measured by Monsanto Rheometer R-100, and the physical properties of the mixes are given in Table III. The higher strength properties of the conventional gum mixes, in comparison to EV gum mixes, may be attributed to the higher proportion of polysulfidic linkages in the former, as shown in Table IV. For the same reason they show higher resilience and flexing resistance. Whiting is a nonreinforcing filler, and hence its addition causes reduction in strength properties. However, there is a slight improvement in modulus and hardness. The reinforcing capacity of HAF black is very much evident from the physical properties of the black-filled mixes. But the reinforcing potential of precipitated silica is not reflected in the properties of the mixes contianing it. The low crosslink density of the silica-filled mixes, caused by the adsorption of the curatives, is responsible for their poor properties. The introduction of 1 phr of phenyl-β-naphthylamine (PBNA) into the mixes causes a slight improvement in physical properties like modulus, tensile strength, tear strength, and resilience. The improvement in these properties can be correlated to the higher proportion of polysulfidic linkages, as may be seen from Tables IV and V. The marked improvement in flexing resistance resulting from the addition of antioxidant is known.[14]

TABLE II
Experimental Scatter in Determining V_r, Polysulfidic Linkage and Zinc Sulfide Sulfur

Conventional system		V_r		Polysulfide linkage, (%)		$[S^{2-}]$, (mmol/kg RH)	
		Surface	Core	Surface	Core	Surface	Core
A	Mean	0.2039	0.2071	41	43	106	117
(gum mix)	Standard deviation	0.0014	0.0025	nil	0.7	1.7	0.7
C	Mean	0.1844	0.1840	50	52	38	44
(whiting-filled mix)	Standard deviation	0.0019	0.0043	1.2	0.7	2.3	2.3
D	Mean	0.2274	0.2297	33	35	78	94
(black-filled mix)	Standard deviation	0.0049	0.0027	1.2	3.2	6.1	12.9

TABLE III
Physical Properties of the Mixes

Mix. no.	Optimum cure time, (min)	Modulus 300% (MPa)	Tensile strength, (MPa)	Elongation at break, (%)	Tear strength (kN/m)	Hardness, shore A	Resilence, (%)	Heat buildup, ΔT (°C)	Flexing resistance (kc to failure)	Compression set (%)	Abrasion loss (cm^3/1000 rev)
A	11.0	0.71	16.4	730	25.0	40	78	8.5	130	35	1.95
B	18.0	0.31	13.1	740	18.7	35	72	8.0	108	11	1.37
C	12.0	0.85	15.0	720	20.5	45	74	15.0	14	37	3.18
D	10.5	9.42	21.5	460	56.2	62	51	25.5	120	47	0.67
E	30.0	1.18	11.0	725	14.1	64	31	a	148	97	2.74
A$_1$	12.0	0.68	21.7	725	29.6	40	85	6.0	>260	41	2.59
B$_1$	17.0	0.29	18.1	700	19.6	35	75	8.0	240	18	2.02
C$_1$	11.5	0.87	19.3	700	21.1	46	77	13.0	63	51	3.02
D$_1$	12.0	9.23	23.3	530	77.3	62	51	23.5	>230	72	0.58
E$_1$	28.5	1.27	12.5	710	15.6	64	30	a	>230	96	2.17

a The dynamic set was very high and the samples slipped from the anvils.

TABLE IV
Chemical Characterization of Vulcanizates before and after Testing.   Temperature of Testing 70°C, Conv Vulcanizing System

Mix		Set (%)	V_r	Polysulfidic linkages (%)	$[S^{2-}]$, (mmol/kg RH)
A	a		0.2109	39	95
(gum)	b		0.2083	37	131
	c	35	0.2225	39	129
A_1	a		0.1996	55	27
(gum with PBNA)	b		0.2212	43	48
	c	41	0.2228	44	73
C	a		0.1756	48	41
(whiting)	b		0.1801	35	47
	c	37	0.1866	41	81
C_1	a		0.1995	55	16
(whiting with	b		0.2139	48	30
PBNA)	c	51	0.2165	46	30
D	a		0.2425	28	52
(black)	b		0.2364	26	90
	c	47	0.2383	25	97
D_1	a		0.2462	39	24
(black with	b		0.2542	39	53
PBNA)	c	72	0.2501	38	62
E	a		0.1382	26	140
(silica)	b		0.1461	18	131
	c	97	0.1445	25	140
E_1	a		0.1424	100	47
(silica with	b		0.1680	100	54
PBNA)	c	96	0.1671	100	58

[a] Original sample.
[b] Sample kept without compression at 70°C for 22 h.
[c] Sample kept under 25% compression at 70°C for 22 h.

Changes in Network Structure of Gum Vulcanizates after Compression

The results of chemical characterization of the conventional gum vulcanizates are given in Table IV.   At 70°C these vulcanizates show either the same or higher V_r after testing.   The change is more in the case of the compressed sample.   The increase in V_r is due to the formation of new crosslinks through the unused curatives present in the samples.   The change in the proportion of polysulfidic linkages is not systematic, but the concentration of zinc sulfide increases during the testing.   As ZnS formation may occur through crosslink destruction,[15] it can be assumed that crosslink destruction occurs during the test.   However, its effect is more than compensated by crosslink formation during testing.   With the addition of antioxidant PBNA, the compression set increases, and this can be correlated to the higher proportion of polysulfidic linkages in these samples.   The lower concentration of zinc sulfide in these samples indicates that crosslink destruction reactions are minimized by the antioxidant and hence the effect of postcuring is more pronounced.   Table V gives the network characteristics of the EV gum vulcanizates.   As expected, the set is much lower.   The EV system gives rise to a more stable network, and this is evident from the minimum changes in V_r, polysulfidic linkages, and zinc sulfide concentration.   In the EV system, also, the effect of PBNA is similar to that in the case of the conventional gum mix, giving rise to a higher proportion of polysulfidic linkages and a higher set.

Table V also gives the results of chemical characterization of the gum mixes tested at 100°C.   As expected, the set value is higher than that at 70°C.   The V_r values are reduced remarkably, indicating the predominance of crosslink destruction during testing.   This is further evident from the large increase in the concentration of zinc sulfide and the reduction in polysulfidic linkages.   Here again, the changes are less in the case of the EV mix.

TABLE V
Effect of Changes in Vulcanizing System and Test Temperature on Compression Set and Network Changes[a]

Mix		Test temp (°C)	Set (%)	V_r	Polysulfidic linkages (%)	$[S^{2-}]$ (mmol/kg RH)
B	b	70		0.1715	3	15
(gum EV)	c	70		0.1742	4	20
	d	70	11	0.1791	6	30
B_1	b	70		0.1739	8	negligible
(gum EV with	c	70		0.1850	12	1
PBNA)	d	70	18	0.1871	5	2
A	b	100		0.2109	39	95
(gum conv)	c	100		0.1624	11	148
	d	100	78	0.1849	8	137
B	b	100		0.1715	3	15
(gum EV)	c	100		0.1725	3	21
	d	100	39	0.1723	1	52

[a] Results of conv gum vulcanizates at 70° C are given in Table IV.
[b] Original sample.
[c] Sample kept without compression at 70°C for 22 h.
[d] Sample kept under 25% compression at 70°C for 22 h.

Changes in Network Structure of Filled Vulcanizates after Compression

In the case of whiting-filled vulcanizates, at 70°C, the changes are similar to those in the gum mixes. The changes in V_r and in zinc sulfide concentration are slightly more in the samples under compression. In the case of the black-filled vulcanizates, the changes in V_r and polysulfidic linkages are not significant. However, the increase in zinc sulfide concentration indicates crosslink destruction during the testing. It is assumed that in black-filled vulcanizates postcuring and crosslink destruction reactions occur to the same extent, resulting in an almost constant V_r value. The increase in V_r and zinc sulfide concentration in silica-filled vulcanizates indicates that a larger number of new crosslinks are being formed than those undergoing desctruction.

In all the filled vulcanizates, as in the case of the gum mixes, the antioxidant causes an increase in the proportion of polysulfidic linkages and, consequently, in a higher set. The increase in polysulfidic linkages is abnormally large in the silica-filled mix. But as the set values are very high in these mixes, the effect of the antioxidant is not noticeable. It is known that zinc forms a sulfurating complex[15] as shown below:

$$\text{Ac}-\text{S}_x-\overset{\displaystyle \text{L}}{\underset{\displaystyle \text{L}}{\text{Zn}}}-\text{S}_x-\text{Ac}$$
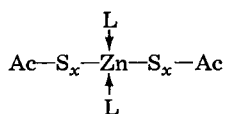
where L is a basic group, Ac is the accelerator moiety, and x is the number of sulfur atoms. The effectiveness of this complex is enhanced by the addition of PBNA, especially in the conventional mixes. It is known that this complex forms initially unstable polysulfidic crosslinks which then breaks into mono-, and disulfidic links. Since the conversion of polysulfides into mono- and disulfides is minimized by PBNA, the mixes containing it show a higher proportion of polysulfidic crosslinks and less crosslink destruction during the test.

CONCLUSIONS

When vulcanizates are kept under compression at elevated temperature, two types of changes occur: postcuring and crosslink destruction. At 70°C the former is predominent, while at 100°C crosslink destruction occurs to a larger extent. These changes are minimum in the EV mixes. The addition of antioxidant (PBNA) increases the proportion of polysulfidic linkages in the vulcanizates and consequently increases the compression set. Antioxidant minimizes crosslink destruction re-

actions as well.   The changes in network structure are mainly the effect of aging, although in many cases compressive strain accelerates the changes occurring due to temperature.

References

1. A. K. Bhowmick and S. K. De, *Rubber Chem. Technol.*, **52,** 985 (1979).
2. A. K. Bhowmick and S. K. De, *Rubber Chem. Technol.*, **53,** 960 (1980).
3. R. Mukhopadhyay, S. K. De, and S. N. Chakraborty, *Polymer*, **18,** 1243 (1977).
4. R. Mukhopadhyay and S. K. De, *Rubber Chem. Technol.*, **51,** 704 (1978).
5. R. Mukhopadhyay, A. K. Bhowmick, and S. K. De, *Polymer*, **19,** 1176 (1978).
6. G. B. Nando and S. K. De, *Polymer*, **21,** 10 (1980).
7. G. B. Nando and S. K. De, *J. Polym. Sci., Polym. Lett. Ed.*, **19,** 5 (1981).
8. R. Bakshandeh, A. J. Gregory, A. J. Rigby, and J. E. Stuckey, paper presented at the International Conference on Structure—Property Relations of Rubber, Kharagpur, India, December 29–31, 1980.
9. J. I. Cunneen and R. M. Russel, *J. Rubber Res. Inst. Malaya*, **22,** 300 (1969); *Rubber Chem. Technol.*, **43,** 1215 (1970).
10. W. S. Howard and C. R. Wilder, paper presented at a Meeting of the Division of Rubber Chemistry, American Chemical Society, Philadelphia, October 15–18, 1974.
11. B. Ellis and G. N. Welding, *Techniques of Polymer Science*, Soc. Chem. Ind., London, 1964, p. 46.
12. B. Saville and A. A. Watson, *Rubber Chem. Technol.*, **40,** 100 (1967).
13. H. E. Adams and B. L. Johnson, *Rubber Chem. Technol.*, **26,** 741 (1953).
14. N. M. Mathew, A. K. Bhowmick, and S. K. De, *Rubber Chem. Technol.*, to appear.
15. L. Bateman, C. G. Moore, M. Porter, and B. Saville, in *The Chemistry and Physics of Rubber Like Substances*, L. Bateman, Ed., Maclaren, London, 1963, Chap. 15.

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