

Aging of EPDM Rubber

A. SAHA DEURI and ANIL K. BHOWMICK, *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

The effect of oxidative and thermal aging of EPDM raw rubber and rubber vulcanizate on gelation, network structure, and technical properties has been studied over a wide range of temperatures and times of aging. Three grades of EPDM having different types of diene have been considered. The kinetics of aging of both raw rubber and vulcanizates has also been reported.

Different network structures have been produced due to different reactivity of termonomers. Cross-link density, cross-link efficiency, polysulfidic linkage, zinc sulfide sulfur, combined sulfur, free sulfur, and sulfur inefficiency change with aging time and temperature. The number of polysulfidic cross-links decreases continuously with increase in time or temperature of aging. There is no definite trend in other structural features. It is quite evident that postcuring reactions as well as destruction of cross-links are taking place in the aging process. The predominance of the former or latter depends on the structure of the diene.

Tensile and tear strength of the compounds decreases or increases with time or temperature of aging. At high temperature, it always decreases with time. Changes in these properties can be approximately correlated with changes in structure only at high temperature. At lower temperature, relations between network structure and technical properties are complicated owing to the competing reactions discussed above. In general, retention of properties of ENB-EPDM vulcanizate is the best. The properties after aging do not exclusively depend on the network structure, nature of cross-link, rank of sulfur, or pendant or cyclic sulfide. The backbone structure is important in all these cases. Changes are less drastic on aging in nitrogen, but a similar trend is found. Raw EPDM rubber forms a gel, which increases with temperature of aging. The activation energy for gelation has been found to be 98 kJ/mol, similar to the oxidation of diene-containing rubbers.

The activation energy for desulfurization of various grades of EPDM vulcanizates is 60–85 kJ/mol. The activation energy for fracture calculated from aging data is, however, 30–36 kJ/mol from tensile measurement and 32–46 kJ/mol from tear strength measurement.

INTRODUCTION

The insulator compound used in solid propellant rocket motors is based on ethylene-propylene diene (EPDM) rubber. Aging of this compound, which is important in view of the mechanical and thermal stability of the rocket, has been reported in our earlier communication.¹ Rocket insulator compound consists of several fillers, such as cork, asbestos, and iron oxide (Fe_2O_3), to impart different properties. It has been observed that aging of the composite will depend on the nature of filler, amount of filler, and rubber-filler interaction. The change in base polymer could not be studied because of the complicated compounding formulation used in this study. In order to understand the mechanism of aging of the composite, based on EPDM, it is necessary and pertinent to know the aging of EPDM compounds without fillers.

Although aging of natural rubber and rubber vulcanizates has been the subject of a large number of investigations,²⁻⁴ reports on aging of synthetic rubber are few. For rubbers to be used for critical applications, these data are, however, important. Only a few investigations have been devoted to aging of EPDM rubber.⁵⁻⁹ Baldwin⁵ reported the influence of new cross-links during aging and polysulfide linkage on high-temperature compression set. The olefinic residue derived from ethylenenorbornene (ENB) has been found to be more reactive than the residue from methylenenorbornene, but the ENB residue is thermally weak. Baranwal and Lindsay⁸ systematically studied the properties of five different EPDM rubbers using ENB, 1,3-butadiene (BD), dicyclopentadiene (DCPD), methyltetrahydroindene (MTHI), and 1,4-hexadiene (HD) as termonomers. They have found HD-EPDM has the highest monosulfidic cross-link, but this does not lead to better aging properties than those of other polymers. All these rubbers are compared at one aging time at different aging temperatures.

Aging of rubber vulcanizates changes the network structure considerably, which in turn controls the technical properties. These changes are again dependent on the temperature and time of aging. It has been observed in the case of natural rubber that changes in the network structure are commensurate with those in the properties.^{10,11} For example, aging of natural rubber will reduce the number of polysulfidic cross-links, increase the main-chain modification and zinc sulfide sulfur, and so on. Hence, such properties as tensile strength, dependent on polysulfidic cross-link or main-chain modification, will deteriorate.

In the present investigation, thermal and thermoxidative aging of EPDM rubber and rubber vulcanizates have been studied over different periods of aging up to a temperature of 180°C. Three grades of EPDM having the same diene content but different types of diene (namely, ENB, DCPD, and HD) have been used. Same compounding ingredients are mixed. The kinetics of aging of both raw rubber and vulcanizates have been reported here.

TABLE I
Formulation of the Mixes

Mix no.	A ₁	A ₂	A ₃
Nordel 1040 ^a	—	—	100
Keltan 520 ^b	—	100	—
EPDM 346 ^c	100	—	—
Crystex sulfur ^d	1.5	1.5	1.5
Zinc oxide	5	5	5
Stearic acid	1	1	1
MBT ^e	1.5	1.5	1.5
TMTD ^f	1	1	1

^aHD-EPDM samples, supplied by VSSC, Trivandrum. Mooney viscosity ML 1 + 4 at 100°C, 44.

^bDCPD-EPDM samples, supplied by VSSC, Trivandrum. Mooney viscosity ML 1 + 4 at 100°C, 43.

^cENB-EPDM samples, supplied by Polysar Ltd., Canada. Mooney viscosity ML 1 + 4 at 100°C, 33.

^dSupplied by Dunlop (India), Ltd.

^eMercaptobenzothiazole, supplied by IEL, Rishra.

^fTetramethylthiuram disulfide, supplied by IEL, Rishra.

TABLE II
Curing Characteristics of the Mixes

Mix no.	Initial viscosity (dN/m)	Minimum viscosity (dN/m)	Scorch time (min)	Optimum cure time (min)	Cure rate (dN/m/min ⁻¹)
A ₁	21.0	11.0	2.5	18.0	12.0
A ₂	25.0	17.5	4.0	22.0	6.4
A ₃	25.0	16.0	4.5	24.0	3.8

EXPERIMENTAL

The formulations of mixes are given in Table I. Three varieties of EPDM having same diene content (~4%) but different types of diene, namely, ethylidene norbornene, dicyclopentadiene, and 1,4-hexadiene, were used. The viscosity-average molecular weight M_v of three grades of EPDM are 1.83×10^6 , 1.93×10^5 , and 1.90×10^5 g/g-mol, respectively. The curing characteristics of the mixes evaluated from the Rheometer R-100 are reported in Table II. The mixes were prepared on a laboratory mill. Sulfur was added after a band of EPDM had formed on the mill. Vulcanization was carried out at 150°C in an electrically heated press. Molds were quickly cooled in water at the end of the curing cycle.

Determination of Technical Properties

Modulus, tensile strength, and elongation at break were measured at 22°C in an Instron model 1195 according to ASTM D412-80T. A dumbbell-shaped specimen was used. Measurement of tear strength and hardness was carried out per ASTM D624-81 method C and ASTM D2240-68, respectively. Oxidative aging of rubber samples was carried out in a Blue M aging oven at different temperatures (from 100 to 180°C). Thermal aging was carried out in nitrogen atmosphere in a Precision Scientific oven at different temperatures.

Determination of Volume Fraction of Rubber and Concentration of Chemical Cross-links

Volume fraction of rubber V_r was determined using 0.2–0.3 g (W) samples allowed to stand in excess of *n*-hexane for 48 h at 35°C. Swollen weight and deswollen weight D were noted. V_r was calculated from these measurements using the relation

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

where F is the weight fraction of the insoluble components, A_0 is the weight of the absorbed solvent, and ρ_r and ρ_s are the densities of rubber and solvent, respectively. $\rho_r(\text{EPDM}) = 0.86$ g/ml and $\rho_s(n\text{-hexane}) = 0.68$ g/ml were used.

The values of V_r were converted to cross-link density using the following relationship:

$$-\left[\ln(1 - V_r) + V_r + \chi V_r^2\right] = \frac{\rho}{M_c} v_s (V_r^{1/3} - V_r/2) \quad (2)$$

$$\chi = \chi_0 + \beta V_r \quad (3)$$

where χ is an interaction parameter and M_c is the molecular weight between cross-links. For an EPDM-*n*-hexane system,¹² $\chi_0 = 0.354$ and $\beta = 0.083$.

Determination of Concentration of Polysulfide Cross-links

Vulcanizate samples of about 0.2–0.3 g were treated with a solution of propane-2-thiol ($\sim 0.4M$) and piperidine ($\sim 0.4M$) in *n*-heptane for 2 h at room temperature, according to a procedure reported earlier.^{10,13} The samples were then washed four times with petroleum ether (40–60°C) and dried in vacuum. The polysulfide cross-link was found using the difference between the cross-link density of the untreated samples and that of the treated samples.

Gel Analysis of Raw Rubber

Gel percentage of raw rubber (HD-EPDM) was determined using 0.2–0.3 g samples, *A* (~ 0.5 mm thick), allowed to stand in measured cyclohexane at 35°C for 16 h. The solution was then filtered, and the residue was dried in an oven to a constant weight *B*. The gel percentage was calculated using the formula

$$\text{Gel}(\%) = \frac{B}{A} \times 100$$

Determination of Free Sulfur and Zinc Sulfide Sulfur and Cross-linking Efficiency

Free sulfur was determined iodometrically by converting it to sodium thiosulfate according to ASTM D297-81A. Sulfide sulfur was determined iodometrically from the formation of cadmium sulfide as described in B.S. 920 Pt 1310, 1958.

Microscope Studies

Fracture surfaces of a few samples were observed with the help of a scanning electron microscope (SEM). The samples were sputter coated with gold and were examined within 48 h after fracture.

RESULTS AND DISCUSSION

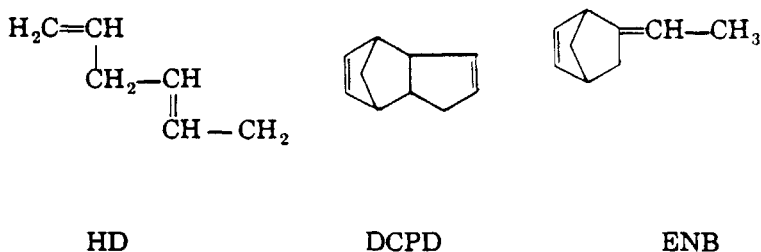
Gum vulcanizates of EPDM with three different types of diene, HD, ENB, and DCPD, were used (Table I). The same amount of compounding ingredients was incorporated in the mixes. Curing characteristics of the mixes are reported in Table II. As shown, EPDM containing 1,4-hexadiene has the

TABLE III
Physical Properties of Unaged EPDM Gum Vulcanizates

Mix no.	Hardness (Shore-A)	Tensile strength (MPa)	Elongation at break (%)	Modulus at 300% elongation (MPa)	Tear strength (kN/m)	E_b ($J/m^3 \times 10^{-5}$) ^a
A ₁	59	1.70	210	—	7.42	9.3
A ₂	52	1.93	355	0.58	8.44	15.3
A ₃	53	2.59	380	0.64	8.80	19.4

^a E_b , energy at break per unit volume.

maximum initial viscosity, scorch time, optimum cure time, and lowest cure rate. This shows the different activity of the same accelerator combination in three different EPDM. The structure of three different dienes is as shown below:



It is easily understandable from the structure that the presence of two active,

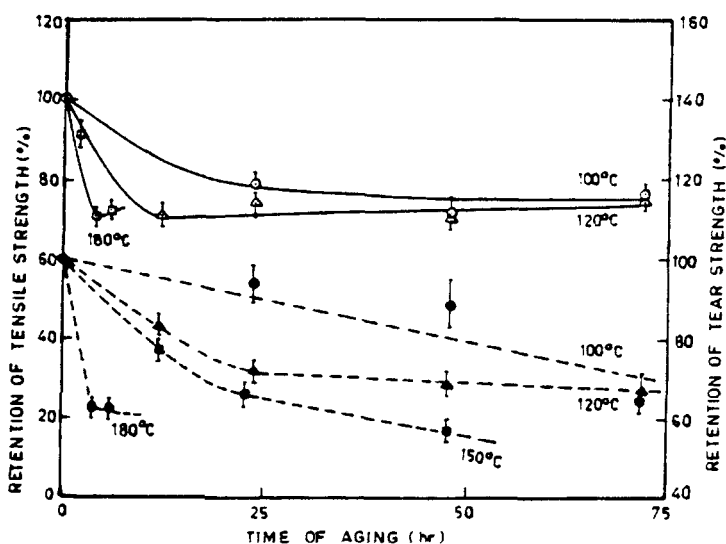


Fig. 1. Variation of percentage retention of tensile and tear strength with time of aging in air for HD-EPDM gum vulcanizate at different temperatures. For tensile strength: (○) 100°C; (△) 150°C; (□) 180°C. For tear strength: (●) 100°C; (▲) 120°C; (■) 150°C; (○) 180°C.

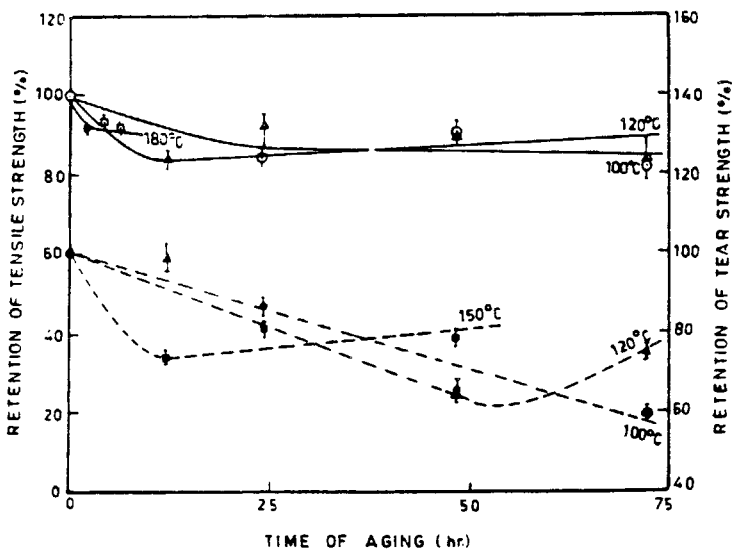


Fig. 2. Variation of percentage retention of tensile strength and tear strength with time of aging in air at different temperatures for DCPD-EPDM gum vulcanizate. For tensile strength: (○) 100°C; (△) 120°C; (□) 180°C. For tear strength: (●) 100°C; (▲) 120°C; (■) 150°C.

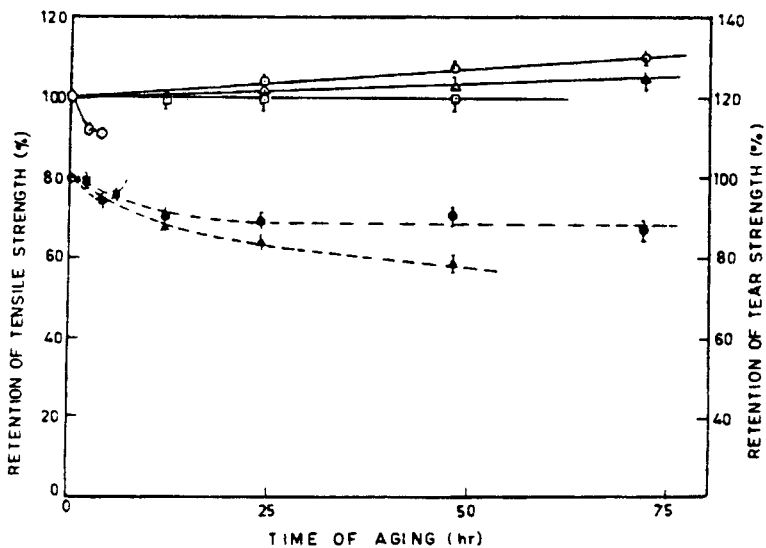


Fig. 3. Variation of percentage retention of tensile strength and tear strength with time of aging in air for ENB-EPDM gum vulcanizate at different temperatures. For tensile strength, (○) 100°C; (△) 120°C; (□) 150°C; (◇) 180°C. For tear strength, (●) 120°C; (▲) 150°C; (■) 180°C.

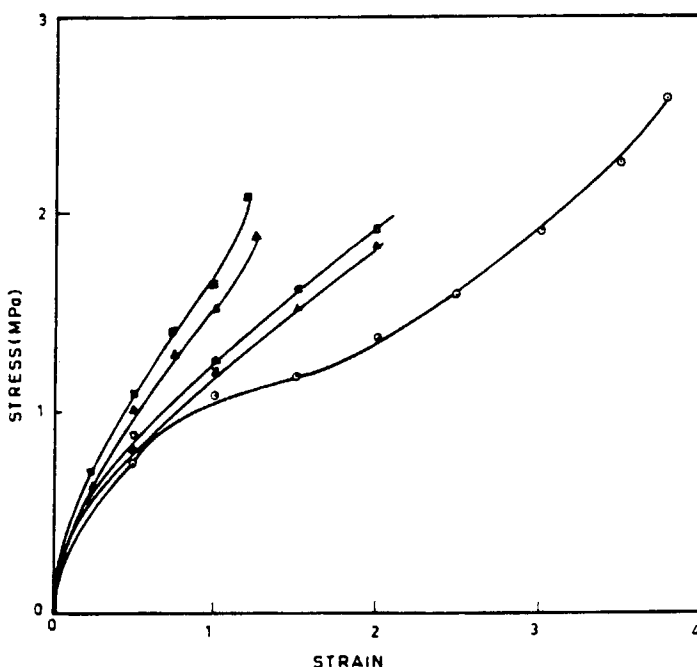


Fig. 4. Stress-strain curve for HD-EPDM gum vulcanizate: (○) unaged; (△) aged at 120°C for 12 h; (□) aged at 120°C for 24 h; (▲) aged at 150°C for 12 h; (■) aged at 150°C for 48 h.

allylic hydrogen-bearing carbon atoms in ENB, compared with the others, results in fastest curing, highest cure rate, lowest scorch time, and lowest optimum cure time of the three. Baldwin et al. suggested that the internal olefin generally lead to faster curing.¹⁴

The physical properties of the unaged gum vulcanizates are reported in Table III. EPDM containing HD has the highest tensile strength, elongation at break, modulus, and tear strength.

Aging properties of the various mixes were determined at different temperatures at various times of aging, both in nitrogen and in air. Figure 1 shows the retention of tensile strength and tear strength at various times of aging in air for the HD-EPDM mix. Both the strength properties drop sharply at the initial stage. The drop is less afterward. For other mixes there are no definite trends. There is a stiffening effect, and the increase of tensile and tear strength after the initial drop is observed for other mixes (Fig. 2). Similar observations have been made for oxidative aging of natural rubber at higher aging times.¹⁵ The tensile strength of the ENB-EPDM mix, however, decreases or increases steadily with time of aging depending on the temperature of aging (Fig. 3). Hardness for all three grades of EPDM decreases slowly with aging time at high temperature (e.g., at 180°C), but at lower temperature it shows a marginal increase. Stress-strain properties of the mixes have been plotted in Figure 4. It has been shown that the modulus increases with aging

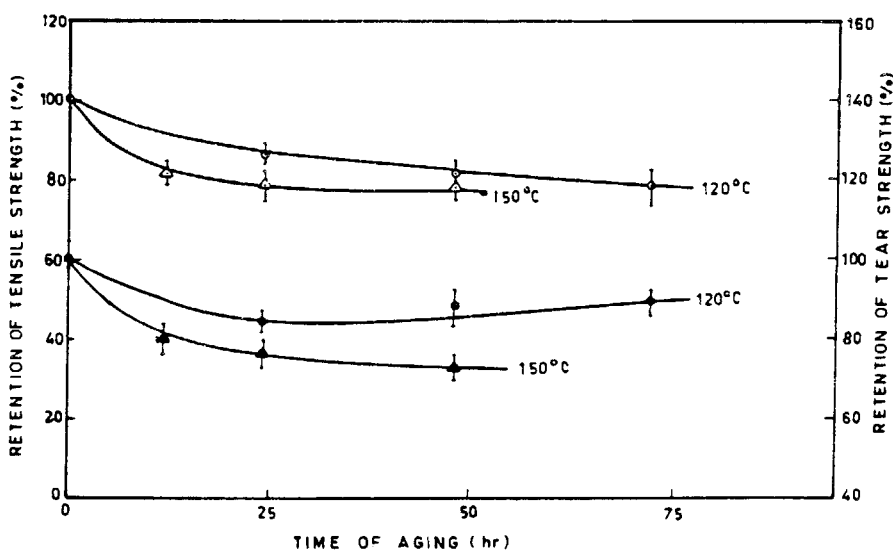


Fig. 5. Variation of percentage retention of tensile strength and tear strength with time of aging in nitrogen atmosphere for HD-EPDM gum vulcanizate at different temperatures. For tensile strength: (○) 120°C; (△) 150°C. For tear strength: (●) 120°C; (▲) 150°C.

time and temperature. The changes in properties in nitrogen atmosphere are somewhat less, but the trends are very similar to those in air (Fig. 5).

The changes in these properties may be best understood from the changes in network structure and the structure of the backbone. The network structure of various mixes with and without aging is reported in Tables IV through

TABLE IV
Chemical Characterization of ENB-EPDM Vulcanizate on Aging in Air

Aging temperature (°C)	Aging time (h)	I^a	Free sulfur (g per 100 g RH)	Zinc sulfide sulfur (g per 100 g RH)	Cross-linking density, ($1/2 M_c$) (mmol/kg RH)	Polysulfide linkage (%)	$[S_n]$ (mol per 100 g RH)	E (atoms per chemical cross-link)	Z^b
Unaged	0	1.633	0.330	0.033	119.5	68.9	0.0396	3.3	7.29
	24	1.633	—	0.110	143.4	42.1	0.0476	3.3	8.78
100	48	1.633	—	0.176	153.1	34.2	0.0454	3.0	9.37
	72	1.633	—	0.209	153.0	31.2	0.0445	2.9	9.37
120	24	1.633	—	0.132	125.5	59.7	0.0468	3.7	7.68
	48	1.633	—	0.165	135.7	38.2	0.0458	3.4	8.31
120	72	1.633	—	0.242	135.7	22.6	0.0434	3.2	8.31
	12	1.633	—	0.132	118.0	13.5	0.0468	4.0	7.22
150	24	1.633	—	0.220	118.0	13.4	0.0440	3.7	7.25
	48	1.633	—	0.165	118.7	5.8	0.0458	3.9	7.27
180	2	1.633	—	0.319	86.4	1.3	0.0409	4.7	5.20
	4	1.633	—	0.264	91.7	0	0.0427	4.6	5.61
180	6	1.633	—	0.254	92.1	0	0.0430	4.7	5.64

^a Compounded sulfur available for cross-linking (g per 100 g RH).

^b $Z = \frac{\text{cross-link density}}{I \times 10^3}$ per gram of available sulfur.

TABLE V
Chemical Characterization of HD-EPDM Vulcanizate on Aging in Air

Aging temperature (°C)	Aging time (h)	I^a	Free sulfur (g per 100 g RH)	Zinc sulfide sulfur (g per 100 g RH)	Cross-linking density, $1/2 M_c$ (mmol/kg RH)	Polysulfide linkage (%)	$[S_n]$ (mol per 100 g RH)	E (atoms per chemical cross-link)	Z^b
Unaged	0	1.633	0.550	0.088	88.5	53.8	0.0310	3.5	5.41
	24	1.633	—	0.132	110.4	46.0	0.0469	4.3	6.76
100	48	1.633	—	0.179	126.1	33.8	0.0465	3.6	7.72
	72	1.633	—	0.209	126.5	34.3	0.0446	3.5	7.75
	24	1.633	—	0.165	115.3	32.1	0.0458	3.9	7.04
120	48	1.633	—	0.209	117.1	11.3	0.0445	3.8	7.17
	72	1.633	—	0.231	125.7	4.8	0.0438	3.5	7.69
	12	1.633	—	0.154	107.2	9.0	0.0462	4.3	6.56
150	24	1.633	—	0.209	112.7	6.8	0.0445	3.9	6.90
	48	1.633	—	0.110	126.4	0	0.0476	3.8	7.74
	2	1.633	—	0.154	83.9	0	0.0462	5.5	5.14
180	4	1.633	—	0.132	97.5	0	0.0469	4.8	5.97
	6	1.633	—	0.121	110.2	0	0.0472	4.3	6.74

^a Compounded sulfur available for cross-linking (g per 100 g RH).

^b $Z = \frac{\text{cross-link density}}{I \times 10^3}$ per gram of available sulfur.

TABLE VI
Chemical Characterization of DCPD-EPDM Vulcanizate on Aging in Air

Aging temperature (°C)	Aging time (h)	I^a	Free sulfur (g per 100 g RH)	Zinc sulfide sulfur (g per 100 g RH)	Cross-linking density, $1/2 M_c$ (mmol/kg RH)	Polysulfide cross-link (%)	$[S_n]$ (mol per 100 g RH)	E (atoms per chemical cross-link)	Z^b
Unaged	0	1.633	0.660	0.077	75.4	55.4	0.0282	3.7	4.61
	24	1.633	—	0.132	101.4	25.7	0.0469	4.6	6.21
100	48	1.633	—	0.198	108.9	30.9	0.0448	4.1	6.67
	72	1.633	—	0.231	110.2	23.9	0.0438	4.0	6.75
	24	1.633	—	0.154	84.6	17.7	0.0462	5.5	5.18
120	48	1.633	—	0.209	85.1	7.7	0.0445	5.2	5.21
	72	1.633	—	0.253	85.3	10.7	0.0431	5.0	5.22
	12	1.633	—	0.088	55.0	0	0.0483	8.8	3.37
150	24	1.633	—	0.220	55.2	0	0.0441	8.0	3.38
	48	1.633	—	0.154	61.9	0	0.0462	7.5	3.79
	2	1.633	—	0.385	36.2	0.05	0.0390	10.8	2.21
180	4	1.633	—	0.319	36.2	0	0.0410	11.2	2.23
	6	1.633	—	0.253	35.6	0	0.0431	12.1	2.18

^a Compounded sulfur available for cross-linking (g per 100 g RH).

^b $Z = \frac{\text{cross-linking density}}{I \times 10^3}$ per gram of available sulfur.

VII. As shown in Figures 6 and 7, the cross-link density of samples aged in air increases or decreases with aging time, depending on the temperature of aging. In general, at a particular aging time, cross-link density decreases with the increase in temperature of aging. Polysulfidic cross-link, however, systematically decreases with aging time or temperature for all the mixes (Fig. 8). Hence, desulfurization of polysulfidic cross-links to monosulfidic and disulfidic cross-links takes place with a longer aging time. Since the variation in

TABLE VII
Chemical Characterization of HD-EPDM Vulcanizate on Aging in Nitrogen Atmosphere

Aging temperature (°C)	Aging time (h)	I^a	Free sulfur (g per 100 g RH)	Zinc sulfide sulfur (g per 100 g RH)	Cross-linking density $1/2 M_c$ (mmol/kg RH)	Polysulfide cross-link (%)	$[S_c]$ (mol per 100 g RH)	E (atoms per chemical cross-link)	Z^b
Unaged	0	1.633	0.550	0.088	86.5	53.8	0.0310	3.5	5.41
	24	1.633	—	0.145	107.0	38.1	0.0465	4.3	6.55
120	46	1.633	—	0.222	112.3	25.1	0.0441	3.9	6.87
	72	1.633	—	0.229	112.5	24.5	0.0438	3.9	6.89
	12	1.633	—	0.133	135.5	33.3	0.0468	3.4	8.29
150	24	1.633	—	0.215	140.1	27.2	0.0443	3.2	8.57
	48	1.633	—	0.155	140.3	23.5	0.0462	3.3	8.59

^a Compounded sulfur available for cross-linking (g per 100 g RH).

^b $Z = \frac{\text{cross-link density}}{I \times 10^{-4}}$ per gram of available sulfur.

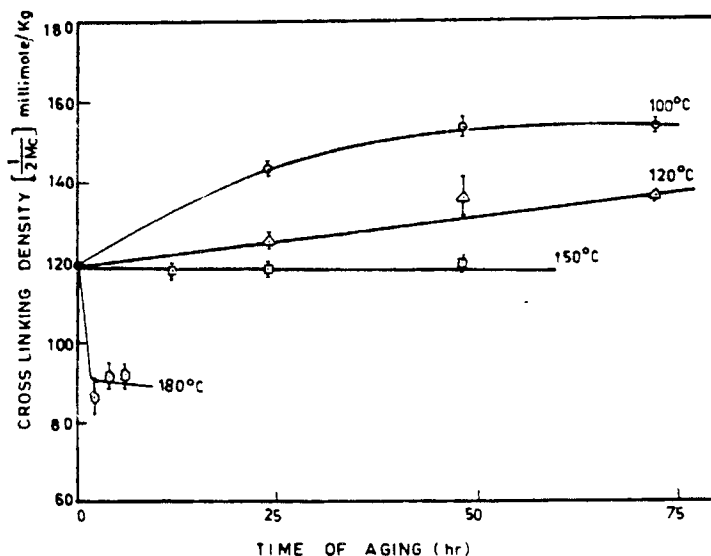


Fig. 6. Variation of cross-link density with time of aging for ENB-EPDM gum vulcanizate aged in air.

cross-link density with aging time is not systematic, the possibility of destruction of some cross-links along with the formation of a sulfidic cross-link is quite evident. The increase or decrease in cross-link density will depend very much on these two factors. This is also reflected in the amount of zinc sulfide sulfur (Tables IV through VI), which is a measure of cross-link formation in the initial stage and cross-link destruction in the later stage of aging. In fact, at a very high temperature of aging (180°C), mostly cross-link destruction is taking place, as evident from the decreased values of ZnS with aging time. Cross-linking efficiency Z follows the same trend as the cross-link density versus aging time and is maximum in the case of the ENB-EPDM mix (Fig. 9) owing to the greater reactivity of the diene. Combined sulfur increased with

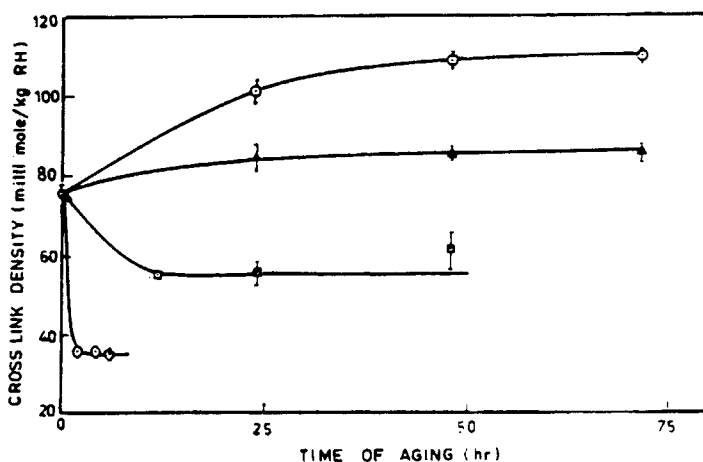


Fig. 7. Variation of cross-link density with time of aging for DCPD-EPDM gum vulcanizate aged in air: (○) 100°C; (△) 120°C; (◻) 150°C; (◇) 180°C.

aging initially due to the slow reaction of the EPDM and then decreased owing to the destruction of the less stable polysulfidic cross-link (Fig. 10). This is directly related to the formation of zinc sulfide sulfur.

The scheme for the aging of rubber vulcanizate may be summarized as follows:

		Original rubber network ($R-S_x-R/R-S_2-R/R-S_1-R$)			
Aging path length depends on time and temperature	↑	Cross-link shortening with additional cross-linking	Cross-link destruction along with main-chain modification and cyclic sulfide formation	S-S bond interchange, main-chain modification	Degradation of rubber backbone (at very high temperature)
	↓				
		Aged rubber network			

The changes in network structure for samples aged in nitrogen atmosphere are almost similar to those in air. The only differences are (1) a steady increase in total cross-link density with aging time or aging temperature, and (2) less reduction in the polysulfidic linkage (Table VII).

These are due to postcuring phenomena in which free sulfur is used up in forming new cross-links, compensating for the destruction of the weakest polysulfidic linkage. For EPDM vulcanizates, it was reported⁷ that a polysulfidic cross-link (S_x , where $x \geq 2$) can act as an inhibitor in oxidative degradation by depleting R' or RO' (where RH is the rubber) concentration, which is thought to arise from the interaction of oxygen with rubber, as shown

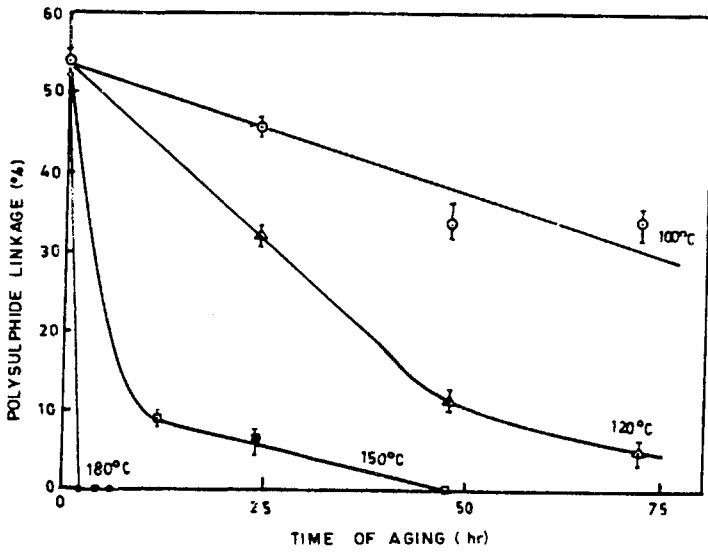


Fig. 8. Variation of polysulfidic cross-linkage with time of aging in air for HD-EPDM gum vulcanizate.

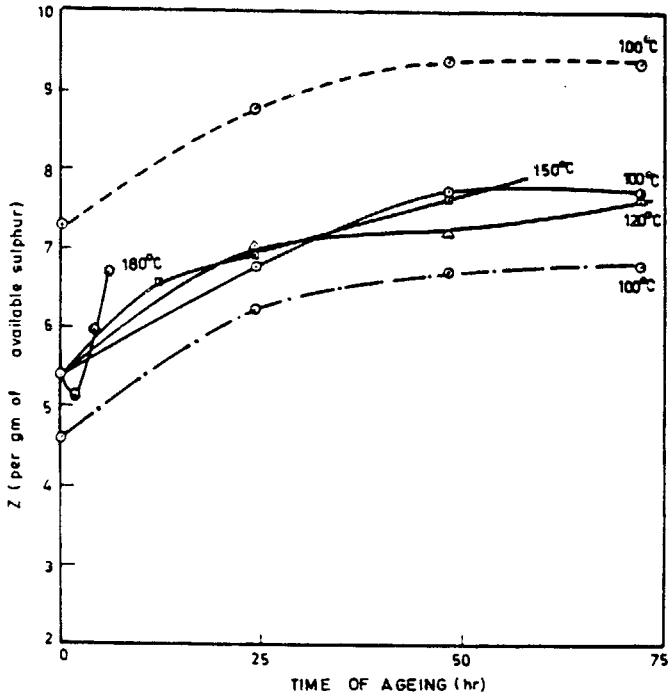


Fig. 9. Variation of cross-linking efficiency with time of aging of EPDM gum vulcanizates: (---) ENB-EPDM vulcanizate; (—) HD-EPDM vulcanizate; (-·-) DCPD-EPDM vulcanizate. Aged at (○), 100°C; (△), 120°C; (□), 150°C; (◇), 180°C.

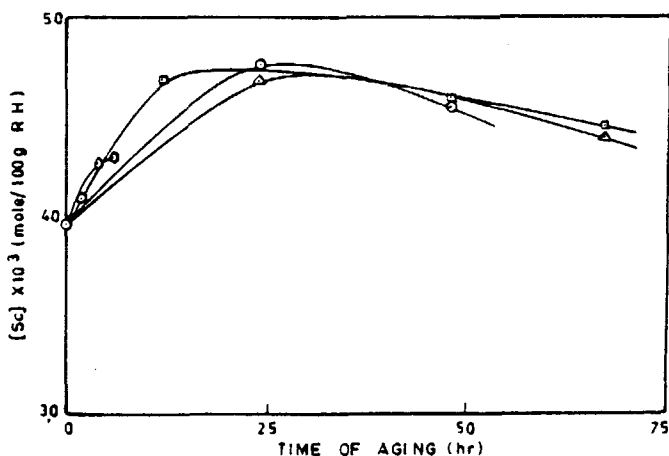
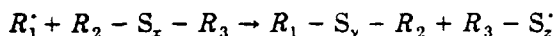
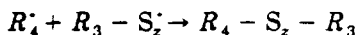


Fig. 10. Plot of sulfur combined with time of aging in air for ENB-EPDM gum vulcanizate at: (○) 100°C; (△) 120°C; (□) 150°C; (◇) 180°C.

below:



where $x = y + z$ and



This scheme explains the shortening of the polysulfidic cross-link and the generation of additional cross-links.

It is interesting to note that the most reactive ENB compound gives the maximum amount of cross-linking and polysulfidic cross-link (68%). ENB compound also shows the highest value of combined sulfur $[S_c]$. In this respect, the DCPD compound is least reactive (minimum values for cross-link density and combined sulfur, Tables IV through VI). ENB compound, with the highest polysulfidic linkage, becomes more susceptible to oxidative aging. In fact, at 100°C for 72 h aging, the decrease in polysulfidic cross-link for ENB-EPDM is about 55%, but in HD-EPDM it is only 36% for the same time of aging at the same temperature. Moreover, the properties do not exclusively depend on the nature of the cross-link, or the rank of the sulfur, pendant sulfur, or cyclic sulfur. The physical properties in the case of HD-EPDM are much better. This is quite contrary to the behavior of natural rubber. Similar observations have been made by Baranwal and Lindsay³ on EPDM rubber and on polybutadiene rubber (BR) by Bhowmick and De.¹⁶ Hence, the properties measured here depend mainly on the backbone structure and its modification.

It is well known that pure rubber without compounding ingredients also forms a gel on aging in air or nitrogen by a branching or cross-linking mechanism. The gel content is plotted at different temperatures in Figure 11. As expected, the gel content is higher at higher temperatures. It is, however, assumed in the present study that cross-link shortening reactions are much

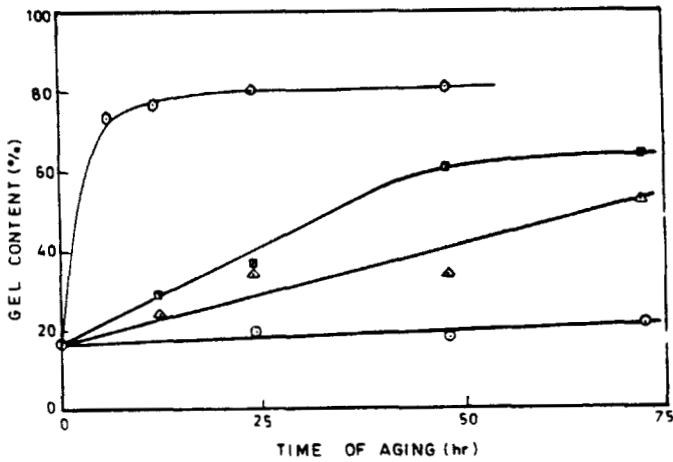


Fig. 11. Variation of gel percentage with time of aging in air for HD-EPDM raw rubber at (○) 70°C; (△) 100°C; (◻) 120°C; (⊙) 150°C.

faster than gelation and hence gelation for pure rubber in the network in the presence of compounding ingredients is negligible.

SEM Study

Figures 12 and 13 show the tensile fracture surfaces of unaged and aged HD-EPDM gum vulcanizates. These samples were aged in air at 150°C for 48 h.

The fracture surface of unaged samples shows few tear lines and small rubber particles lying at an angle to the tear lines. Similar lines were found on the tensile fracture surface of natural rubber.¹⁷ The number of tear lines drastically reduces on aging, and the fracture surface tends to become smooth. Cracks that act as flaws appear on the surface. The tear lines are on the average of 50 μm apart on an unaged sample surface. However, on aging, these



Fig. 12. SEM photograph of tensile fracture surface. Unaged HD-EPDM gum vulcanizate.

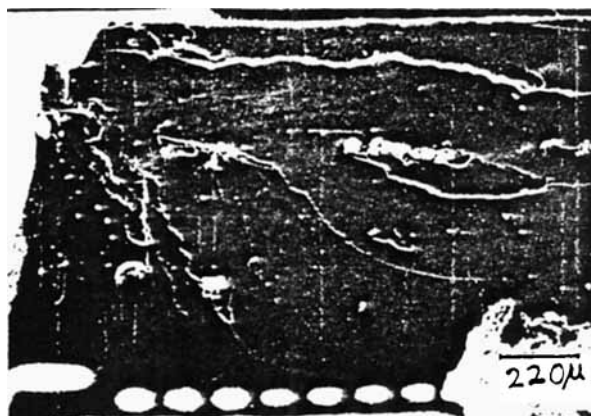


Fig. 13. SEM photograph of tensile fracture surface. HD-EPDM gum vulcanizate aged for 48 h at 150°C in air.

lines are found randomly on the surface. The relation between tear lines and crack lines has recently been demonstrated.¹⁸

Kinetics of Aging of EPDM Gum Vulcanizate and Gel Formation

Initial slopes from Figure 11 are calculated for samples aged at four different temperatures. The slope, which is the rate constant for gelation, can be inserted in the Arrhenius equation to calculate the activation energy for gelation,

$$k = Ae^{-\Delta E/RT} \quad (4)$$

where:

ΔE = activation energy

A = frequency factor

R = gas constant

T = absolute temperature

A similar method was used to calculate the activation energy of degradation from a stress-relaxation experiment at different temperatures.¹⁹ The activation energy for gelation was found to be 98 kJ/mol from the plot of $\ln k_0$ versus $1/T$ (Fig. 14), which is very close to the activation energy for oxidation of diene-containing rubber.²⁰

Kinetics of Aging of Cross-linked Network

It is apparent from the preceding discussion that the aging of cross-linked gum EPDM compound causes the desulfurization of polysulfide cross-links. The sulfur, along with the residual free sulfur, helps the formation of extra cross-link and main-chain modification. Hence, the kinetics of desulfurization both in air and in nitrogen have been studied here. Assuming a zero-order rate

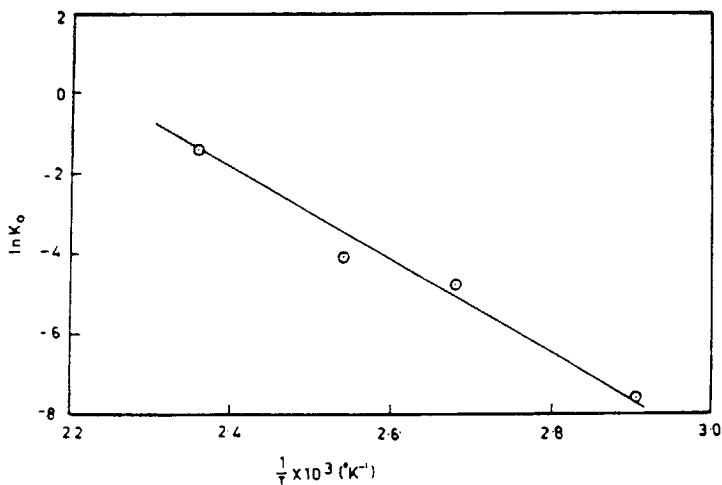


Fig. 14. Plot of rate of gelation (k_0) with reciprocal of temperature.

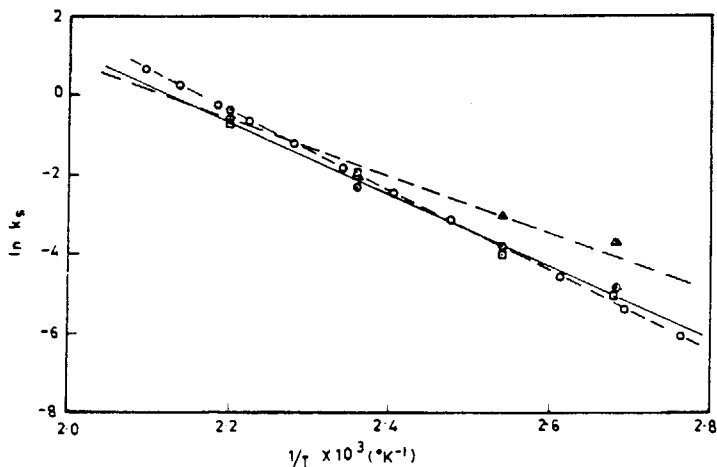


Fig. 15. Kinetic plot of degradation of polysulfidic linkage on aging in air: (\odot), ENB-EPDM vulcanizate; (Δ), DCPD-EPDM vulcanizate; (\square), HD-EPDM vulcanizate.

constant in the initial stages (Fig. 8), the rate constant for desulfurization was calculated at different temperatures. Using the Arrhenius equation (4) and plotting $\ln k_s$ versus $1/T$, the activation energy in air for desulfurization was found to vary from 60 to 85 kJ/mol for different grades of EPDM (Fig. 15). It can be concluded that desulfurization will occur first in these two competing reactions. A similar value of activation energy from zinc sulfide sulfur formation has been obtained.

The ranking of activation energies of desulfurization of polysulfidic linkage for three different grades of EPDM is found to be ENB > 1,4-HD > DCPD. The activation energy for the degradation of HD-EPDM in nitrogen is found to be more than that in air (95 compared to 70 kJ/mol).

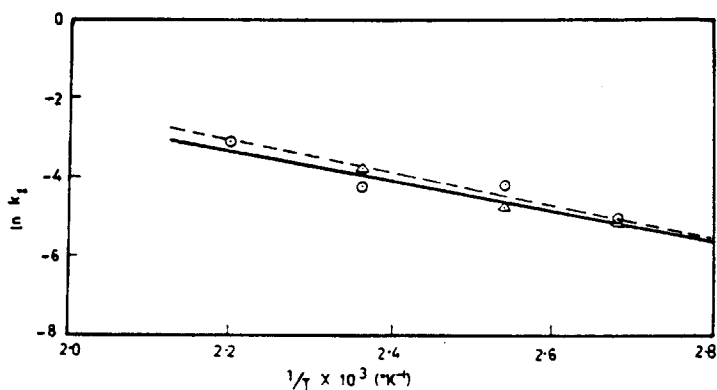


Fig. 16. Plot of rate of degradation of physical properties on aging in air versus reciprocal of temperature for DCPD-EPDM gum vulcanizate: (O), from tensile strength measurement; (Δ), from tear strength measurement.

The apparent rates of property degradation were also calculated from the initial linear region for EPDM gum compounds (Figs. 1 and 2). An apparent zero-order reaction rate was assumed, which is valid when the loss of strength property is proportional to the number of molecular changes associated with degradation. Using eq. (4), the activation energy for property degradation was calculated (Fig. 16). This is about 30–36 kJ/mol from tensile strength measurement and 32–46 kJ/mol from tear strength measurement. However, in nitrogen atmosphere, it is 45 kJ/mol from tensile strength data and 55 kJ/mol from tear strength data. Pett and Tabor¹⁵ reported excellent agreement of activation energy for the oxidation of cross-linked natural rubber with activation energies calculated using the above method. Our results are, however, not in agreement. The reason is that the fracture of an elastomer starts from a flaw and it is controlled by the flaw size and depth as guided by Griffith's law.²¹ The activation energy of the oxidation of rubber is calculated from the degradation of the chain, whereas in the fracture process, only a few chains in front of the propagating crack path on the fracture plane are involved. In this context, the results of Pett and Tabor are merely a coincidence. Our results show that the activation energy of degradation calculated from the loss in properties is always lower than the activation energy of oxidation of rubber or activation energy for a gelation or desulfurization reaction. Presumably, if an equilibrium modulus were measured, it could be directly related to real M_c . In that case, the chemical activation energy and physical property data would have coincided. The comparative results, however, give an understanding of the amount of energy for the energy barrier or ideas about the least resistance to the crack path. Similar thought was given by Zhurkov using the values for time to fracture.²²

The authors gratefully acknowledge the support of the Indian Space Research Organisation for funding and the help of Prof. S. K. De, Rubber Technology Centre, and Dr. R. Ghosh, Chemistry Department, I.I.T., Kharagpur. The authors also thank Dr. A. K. Bhattacharya and Dr. P. P. De for experimental assistance.

References

1. A. S. Deuri and A. K. Bhowmick, presented at the 128th Rubber Div., A.C.S. meeting, Cleveland, October 1985.
2. E. M. Bevilacqua, in *Thermal Stability of Polymers*, R. J. Conley, Ed., Marcel Dekker, New York, 1970.
3. J. R. Shelton, in *Stabilization and Degradation of Polymers*, D. L. Allara and W. L. Hawkins, Eds., Adv. Chem. Ser. 169, American Chemical Society, Washington, D.C., 1978.
4. A. K. Bhowmick, S. Rampalli, and D. McIntyre, *J. Appl. Polym. Sci.*, **30**, 2367 (1985).
5. F. P. Baldwin, *Rubber Chem. Technol.*, **43**, 1040 (1970).
6. M. Imota, Y. Minoura, K. Goto, H. Harada, K. Nishihira, H. Fujita, K. Fujimoto, T. Izuta, K. Kono, K. Fujioka, A. Shiota, M. Oba, H. Oshita, and T. Usamoto, *Rubber Chem. Technol.*, **43**, 431 (1970).
7. F. P. Baldwin and G. Ver Strate, *Rubber Chem. Technol.*, **45**, 709 (1972).
8. K. C. Baranwal and G. A. Lindsay, *Rubber Chem. Technol.*, **45**, 1334 (1972).
9. M. L. Studebaker and J. R. Beatty, *Rubber Chem. Technol.*, **47**, 803 (1974).
10. A. K. Bhowmick and S. K. De, *Rubber Chem. Technol.*, **52**, 985 (1979).
11. C. M. Blow and C. T. Loo, *J. Inst. Rubber Ind.*, **7**, 205 (1973).
12. F. P. Baldwin, P. Borzel, and H. S. Makowski, *Rubber Chem. Technol.*, **42**, 1167 (1969).
13. B. Saville and A. A. Watson, *Rubber Chem. Technol.*, **40**, 100 (1967).
14. F. P. Baldwin, P. Borzel, C. A. Cohen, H. S. Makowski, and J. F. Van de Castle, *Rubber Chem. Technol.*, **43**, 522 (1970).
15. R. A. Pett and R. J. Tabor, *Rubber Chem. Technol.*, **51**, 1 (1978).
16. A. K. Bhowmick and S. K. De, *J. Appl. Polym. Sci.*, **26**, 529 (1980).
17. A. K. Bhowmick, G. B. Nando, S. Basu, and S. K. De, *Rubber Chem. Technol.*, **53**, 327 (1980).
18. A. Saha Deuri and Anil K. Bhowmick, *J. Mat. Sci.*, in press.
19. S. Tamura and K. Murakami, *Rubber Chem. Technol.*, **48**, 141 (1975).
20. J. R. Shelton, *Rubber Chem. Technol.*, **45**, 359 (1972).
21. A. A. Griffith, *Philos. Trans. R. Soc., London, Ser. A221*, 163 (1921).
22. S. N. Zhurkov and S. A. Abasov, *Viysokomol. Soed. in.*, **3**, 441, 450 (1960).

Received January 23, 1986

Accepted July 31, 1986