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Scanning electron microscopy studies on mechanism of tear fracture of styrene–butadiene rubber

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Scanning electron microscopy (SEM) studies on tear fracture of styrene–buatadiene rubber (SBR) vulcanizates have been made with respect to the following parameters: (a) the nature of cross-links (flexible sulphur ($-S_x-$) type and rigid carbon–carbon (–C–C–) type); (b) the effect of addition of reinforcing filler, ISAF carbon black (N 220) in both cross-linking systems; and (c) the effect of cross-link density in the case of sulphur-cured vulcanizates. It was observed that peroxide-cured SBR (unfilled) vulcanizate undergoes brittle fracture whereas the optimum cross-linked sulphur-cured unfilled vulcanizate undergoes fracture in the shear planes and with branching of the tear path. In the case of sulphur-cured SBR (unfilled) vulcanizate with a higher cross-link density the fracture pattern is similar to that of the vulcanizate which has an optimum cross-link density. When the cross-link density is increased or the nature of cross-link is changed to the rigid C–C type, stress dissipation becomes difficult and hence the tear resistance decreases. Peroxide-cured SBR (filled) vulcanizate shows a typical stick–slip mode of fracture as well as steady tear and microfolds over the surface. Sulphur-cured SBR (filled) vulcanizates show short and curved tear lines. Fillers help to arrest crack growth and to increase stress dissipation, thereby increasing tear resistance.

1. Introduction

Recently, scanning electron microscopy (SEM) has been used to study the failure modes of rubbers [1]. In our previous reports [2–7] we reported the results of our SEM studies of fractured surfaces of natural rubber, nitrile rubber and carboxylated nitrile rubber. It was observed that the failure mechanism is very much dependent on the nature of the test, the nature of the base polymer and the formulations from which the vulcanizates were prepared. Attempts have been made to correlate the relative strength of different vulcanizates on the basis of SEM photomicrographs of the failure surface.

In order to achieve a longer service life of rubber products, resistance to various types of failure, among which tear is important, should be high. Several theories have been proposed [8–11] to describe the tear fracture of rubber vulcanizates. These authors have described tear criteria in terms of the tearing energy which is related to the loss of elastic strain energy in the test piece and equals the work done per unit volume to break the material. Medalia [12] has reviewed the reinforcing effects of carbon black which enhances the tear resistance of filled vulcanizates. Bartenev and Zuyev [13] have used SEM to study the tearing of various commercial rubbers. According to them, the tearing of the samples consists of two stages, the deformation of the crack tip followed by the growth of the cut. However, the nature of the fracture surface under tear rupture has not been fully explored in these studies. SEM studies are expected to throw more light on the understanding of the mechanism of rubber tear.

In this paper we report the results of our SEM studies on the tear fracture of styrene–butadiene rubber, which is a non-strain crystallizing rubber.

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TABLE I Formulations of the mixes

Mix	A	B	C	D	E	F
SBR*	100	100	100	100	100	100
Zinc oxide	–	5	5	–	5	5
Stearic acid	–	2	2	–	2	2
ISAF black†	–	–	–	50	50	50
Processing oil	–	–	–	5	5	5
Sulphur	–	2	4	–	2	4
CBS‡	–	0.8	1.5	–	0.8	1.5
DCP§	2	–	–	2	–	–

*Styrene–butadiene rubber (SBR-1502), supplied by Synthetics and Chemicals Ltd, Bareilley.

†Intermediate super abrasion furnace black (ISAF, N 220), supplied by Phillips Carbon Black Ltd, Calcutta.

‡N-cyclohexyl 2-benzothiazole sulphenamide (Accicure HBS) obtained from Alkali and Chemical Corporation of India Ltd, Rishra.

§Dicumyl peroxide (DCP), supplied by BDH Chemicals Ltd, UK.

We included the following factors in our studies: SBR with both a sulphur-curing system, producing flexible $-S_x-$ cross-links, and a peroxide-curing system, giving rigid –C–C– cross-links. The extent of cross-linking was varied in the case of sulphur-cured unfilled and filled SBR mixes. Reinforcing carbon black, ISAF (N 220), was used as filler in all mixes.

2. Experimental procedure

The formulations of the mixes are given in Table I. Mixing was carried out in a 15 cm × 33 cm two-roll laboratory mill, and vulcanization at optimum cure times, determined with a Monsanto rheometer R-100, was carried out at 150° C and 650 psi* pressure in a hydraulic press having electrically heated platens. Specimens for tensile and tear testing were punched out along the grain direction from the vulcanized sheets. Tensile testing was done as per ASTM designation D412–51T, using dumb-bell specimens. The tear strength was measured with an un-notched 90° angle test specimen (die C shown in Fig. 1a) according to ASTM method D624–54. Both tensile and tear tests were carried out in a Zwick tensile testing machine at 30° C. Samples were stretched at a rate of 500 mm min^{-1}. Fracture propagates perpendicular to the direction of applied force as shown in Fig. 1a. Fig. 1b shows the shape of two failed pieces after complete fracture had occurred. The fracture surfaces were then carefully cut out from the failed test pieces without touching the surface. These specimens were stored in a dessicator to avoid contamination from dust particles and then sputter-coated with gold within 24 h of testing.

SEM observations were then made using an ISI-60 model scanning electron microscope within 72 h of testing. From our preliminary experiments it has been found that the fracture mode did not change even after 72 h of storage of the specimen (without gold coating) after the test. There was also no change in the topography when the SEM observations were made after 7 days of gold coating. The scanning area is shown in Fig. 1c. Photomicrographs were taken along the direction (a ↔ b) as shown in Fig. 1a, which is the same as the direction of fracture propagation. The tilt was adjusted to zero degrees in all cases.

According to ASTM method D676–59T, a shore A type Durometer was used to measure the hardness of the vulcanizates. The volume fraction of the rubber in the swollen vulcanizate, V_r, was calculated using the method suggested by Ellis and Welding [14], which takes into account the correction of swelling increment with duration of immersion, after equilibrium has been attained. Benzene was used as the solvent for swelling.

TABLE II Characterization of the rubber vulcanizate

Mix	A	B	C	D	E	F
Optimum cure time (min)*	23.5	31.0	20.5	29.0	29.0	16.5
V_r, volume fraction of rubber in the swollen vulcanizate at 35° C	0.21	0.17	0.24	0.22	0.21	0.29
Hardness, Shore A	52	50	58	70	70	80
Tensile strength (MPa)	0.95	1.92	1.65	15.03	22.82	18.53
Modulus at 100% elongation (MPa)	–	0.82	1.25	2.54	2.59	5.39
Elongation at break (%)	80	400	180	280	480	240
Tear strength (kN m^{-1})	1.48	10.39	8.24	24.69	47.62	32.70

*Obtained from a Monsanto rheometer R-100 at 150° C.

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* 10^3 psi ≡ 6.89 N mm^{-2}.

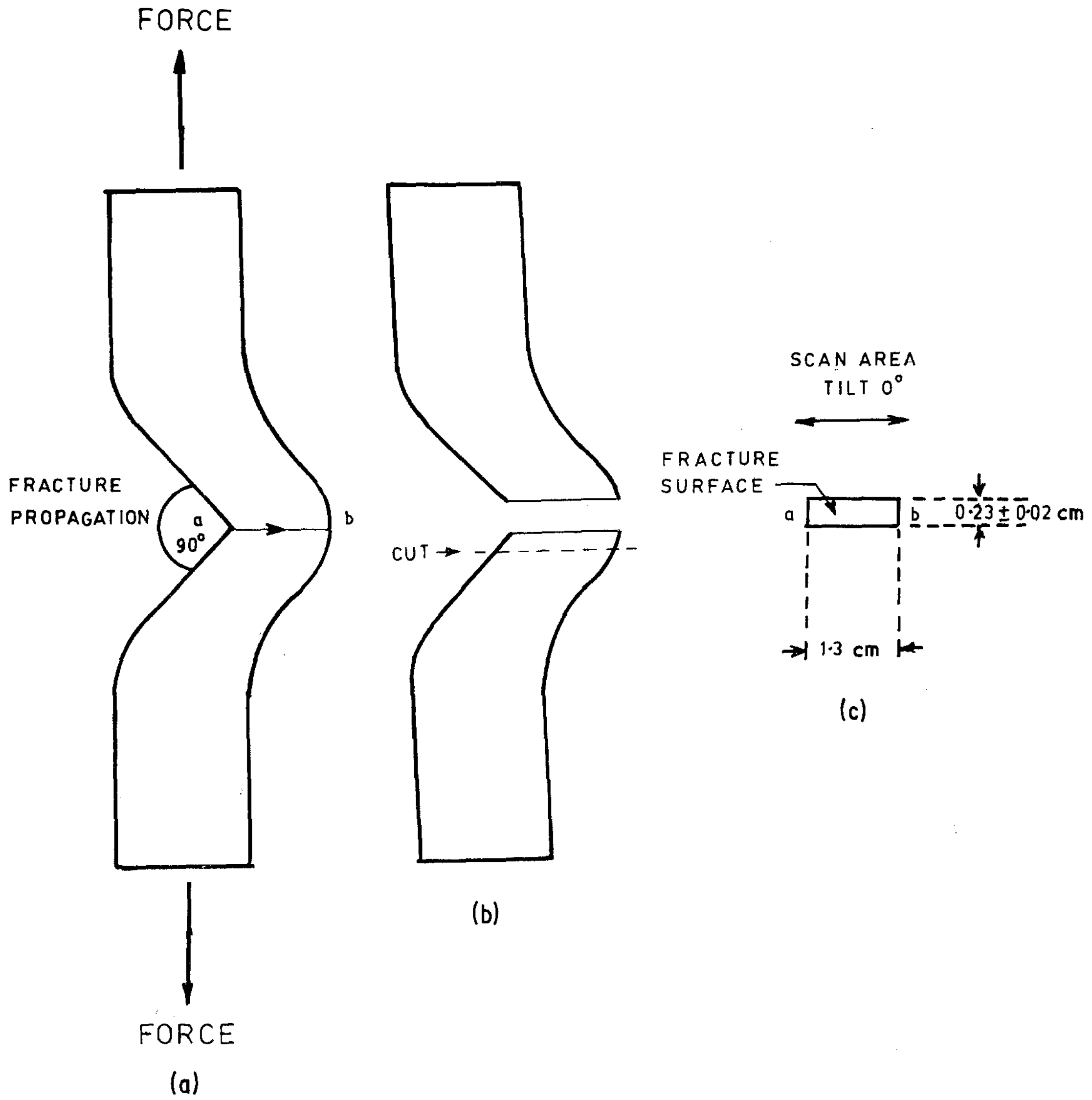

Figure 1 (a) Original test specimen (thickness 0.23 ± 0.02 cm). a, the point at which tear starts; b, the point at which tear ends. (b) Failed specimen. (c) Scan area of the fracture surface.

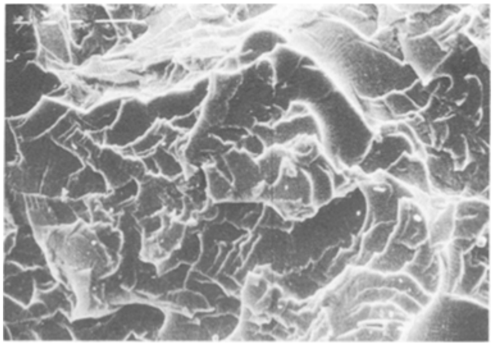

Figure 2 SEM of the tear fracture surface of peroxide-cured SBR (unfilled) vulcanizate (mix A) consisting of "slip lines" characteristic of brittle fracture, × 55.

3. Results and discussion

The V_r values of mixes C and F are higher than those of mixes B and E, respectively (Table II), indicating that the former mixes produce vulcanizates of higher cross-link density.

It is also observed from Table II that the tear strength of styrene–butadiene rubber vulcanizates is very much dependent on the type of cross-linking. As expected, the peroxide-cured SBR (unfilled) vulcanizate (mix A) shows very low tear resistance and the sulphur-cured vulcanizates (mixes B and C) show better tear properties compared to the peroxide-cured vulcanizate. The addition of reinforcing ISAF black, as in mixes D,

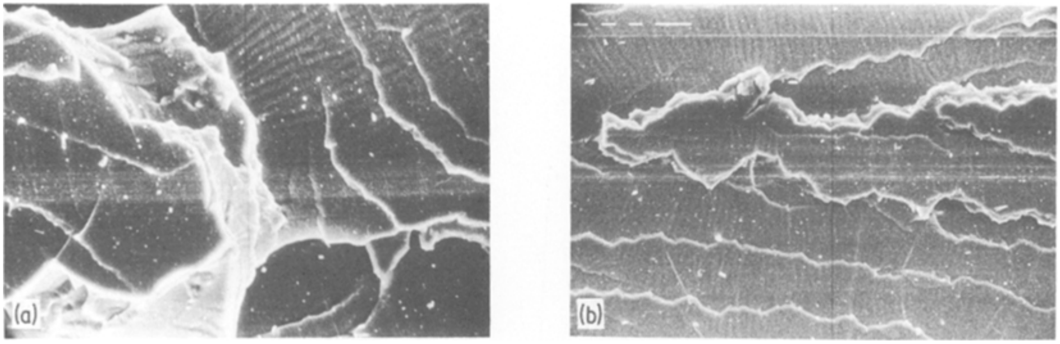

Figure 3 SEMs of tear fracture surfaces of optimum cross-linked sulphur-cured SBR (unfilled) vulcanizate (mix B). (a) Tear path starts from one end and proceeds towards the other side, ×70. (b) Shear plane fracture and branching of tear path, ×47.

E and F, enhances their tear resistance remarkably. Near the tip of a growing crack, stress dissipation by viscoelastic mechanism is essential for the development of high strength. In the case of sulphur-cured vulcanizates, stress dissipation is possible through cross-link slippage, whereas a rigid carbon–carbon type of cross-links, as in peroxide-cured vulcanizate, hinders this type of slippage thereby preventing stress dissipation. The addition of reinforcing carbon black registers additional mechanisms through which dissipation of strain energy can take place. In addition to increasing the strain energy dissipation, dispersed particles also serve to deflect or arrest growing cracks, thereby giving further resistance to failure. The SEM observations discussed below are in good agreement to these proposed explanations.

Fig. 2 shows a scanning electron micrograph of the fracture surface of peroxide-cured SBR (unfilled) vulcanizate (mix A). From the micrograph it is apparent that the vulcanizate undergoes brittle fracture with a very low tear strength and elongation at break. The fracture surface shows many "slip lines" characteristic of typical brittle fracture.

Optimum cross-linked sulphur-cured SBR (unfilled) vulcanizate (mix B) shows a different type of fracture. The tear path starts from side "a" and moves towards the other side (Fig. 3a). Fracture in shear planes and branching have been observed (Fig. 3b).

Fig. 4 shows a scanning electron micrograph of the fracture surface of sulphur-cured unfilled-SBR vulcanizate (mix C) with a higher cross-link density. The fracture pattern is similar to that of the optimum cross-linked system. The lower tear strength in mix C than in mix B is due to restriction of the slippage of cross-links owing to a higher cross-link density. Thus stress dissipation is minimized.

With the addition of ISAF black to the peroxide-cured vulcanizate of SBR (mix D) the tear strength increases remarkably. This improvement in strength is also reflected in the nature of the fracture surface. Brittle-type failure, as observed in unfilled vulcanizate (Fig. 2), is not observed here. The tear propagates in a stick–slip way (Fig. 5a). Fig. 5b is a magnified image of the surface which shows microfolding on a portion of one of the tear paths. Some tear lines are, however, steady in nature (Fig. 5c).

Figs. 6a and b are SEMs of the fracture surfaces of optimum cross-linked sulphur-cured SBR (filled) system (mix E). Fig. 6a shows several short tear lines starting from "a". The middle of the fracture surface is rough and consists of several curved tear lines. Fillers help to arrest crack growth and to enhance stress dissipation thus increasing tear

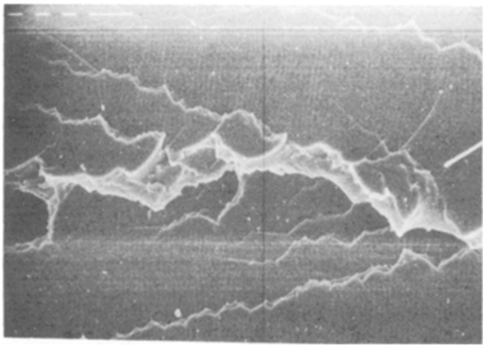

Figure 4 SEM of the tear fracture surface of sulphur-cured SBR (unfilled) vulcanize (mix C) with a higher cross-link density showing branched and broken tear path, × 55.

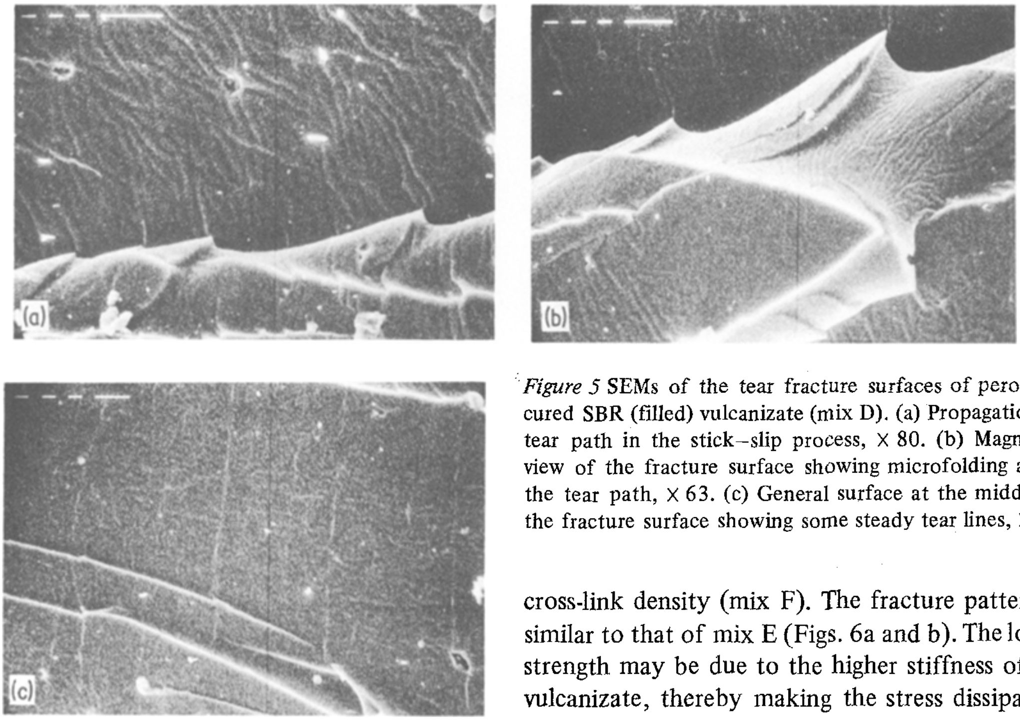

Figure 5 SEMs of the tear fracture surfaces of peroxide-cured SBR (filled) vulcanizate (mix D). (a) Propagation of tear path in the stick–slip process, X 80. (b) Magnified view of the fracture surface showing microfolding along the tear path, X 63. (c) General surface at the middle of the fracture surface showing some steady tear lines, X 44.

resistance [15, 16]. Fig. 6b shows an SEM of the middle of the fracture surface. The presence of a rough surface with a larger number of short tear lines and the absence of any major tear path covering the whole surface is the cause of the higher tear strength of this vulcanizate compared to the peroxide-cured SBR (filled) system (mix D). It was reported earlier for carboxylated nitrile rubber, that the nature of cross-linking changes the tear mechanism [6].

Fig. 7 is an SEMs of the fracture surface of sulphur-cured SBR (filled) system with higher cross-link density (mix F). The fracture pattern is similar to that of mix E (Figs. 6a and b). The lower strength may be due to the higher stiffness of the vulcanizate, thereby making the stress dissipation process difficult.

Styrene–butadiene rubber is a non-strain crystallizing rubber. There is some difference in the fracture pattern between this rubber and natural rubber (NR), which is strain crystallizing. Peroxide-cured unfilled NR vulcanizates do not show brittle failure. Instead they exhibit tearing by a stick–slip process [5]. Crystallites in NR formed at a high strain play the role of filler particles. Therefore, the effect of reinforcing carbon black filler is more prominent in SBR than in NR in both sulphur-curing and peroxide-curing systems, but the general principles of reinforcement are the same in both cases.

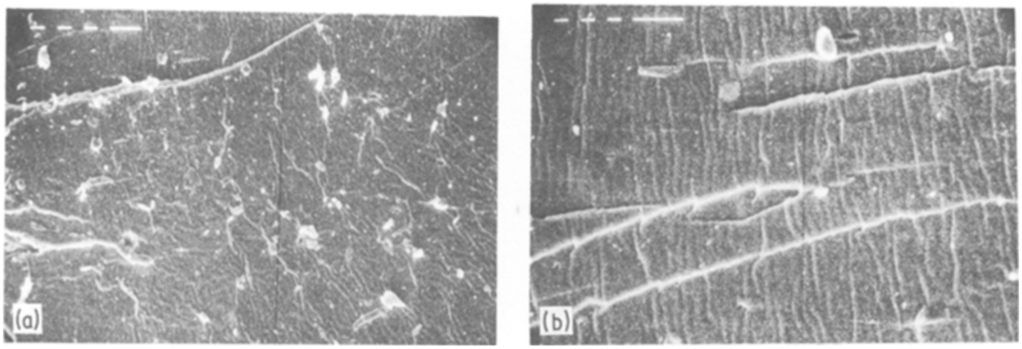

Figure 6 SEMs of the tear fracture surfaces of optimum cross-linked sulphur-cured SBR (filled) vulcanizate (mix E). (a) General surface at side "a" of the fracture surface showing several short tear lines, X 40, (b) general surface at the middle of the fracture surface showing a larger number of short tear lines, X 67.

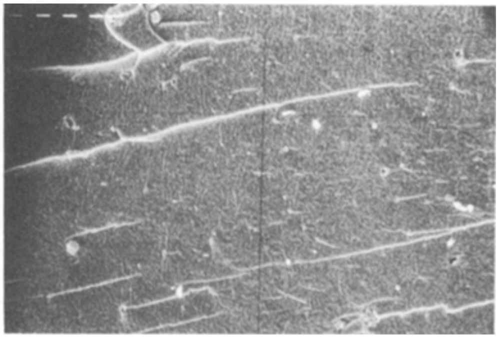

Figure 7 SEM of the tear fracture surface of a sulphur-cured SBR (filled) system (mix F) with a higher cross-link density, showing the presence of many tear lines, × 40.

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References

1. W. D. BASCOM, *Rubber Chem. Technol.* **50** (1977) 875.
2. D. K. SETUA, S. K. CHAKRABORTY, S. K. DE and B. K. DHINDAW, *J. Scanning Electron Microsc.* in press.
3. A. K. BHOWMICK, G. B. NANDO, S. BASU and S. K. DE, *Rubber Chem. Technol.* 53 (1980) 327.
4. A. K. BHOWMICK, S. BASU and S. K. DE, *ibid.* 53 (1980) 321.
5. N. M. MATHEW and S. K. DE, *Polymer* **23** (1982) 632.
6. S. K. CHAKRABORTY, A K. BHOWMICK, S. K. DE and B. K. DHINDAW, *Rubber Chem. Technol.* 55 (1982) 41.
7. A. K. BHOWMICK, S. BASU and S. K. DE, *J. Mater. Sci* 16 (1981) 1654.
8. R. S. RIVLIN and A. G. THOMAS, *J. Polymer Sci.* **10** (1953) 291.
9. H. W. GREENSMITH, *ibid.* **21** (1956) 175.
10. H. W. GREENSMITH and A. G. THOMAS, *ibid.* **18** (1955) 189.
11. A. N. GENT, in "Science and Technology of Rubber", edited by F. R. Eirich (Academic Press, New York, 1978) Chap. 10.
12. A. I. MEDALIA, paper presented at the International Conference on the "Structure Property Relations of Rubber" (Indian Institute of Technology, Kharagpur, India, 1980).
13. G. M. BARTENEV and Yu. S. ZUYEV, in "Strength and Failure of Viscoelastic Materials" (Pergamon Press, London, 1968) p. 96.
14. B. ELLIS and G. N. WELDING, "Techniques of Polymer Science" (Soc. Chem. Ind. London, 1964) p. 46; *Rubber Chem. Technol.* 37 (1964) 571.
15. J. R. M RADOK and C. L. TAI, *J. Appl. Polymer Sci.* 6 (1962) 518.
16. G. KRAUS, in "Science and Technology of Rubber", edited by F. R. Eirich (Academic Press, New York, 1978) Ch. 8.

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