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Investigation on the dependence of the electrical conductivity of FEF/SBR vulcanizates on the cyclic strain

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Summary

The constant deformation fatigue test was found to affect the electrical properties of 70 FEF/SBR vulcanizates. The conductivity of 70 FEF/SBR sample is so sensitive to the value of strain amplitude and the number of cycles. When the specimens were subjected to a large number of rapidly repeating strain cycles, the transverse conductivity, σ_T, shows an initial rapid fall with increasing number of cycles, probably due to carbon structure breakdown. This is followed by dynamic equilibrium, where the conductivity remains almost constant over the temperature range 30 - 85 °C.

The equilibrium state between destruction and reconstruction of carbon black aggregates has been detected for all strains of certain values of strain cycles (1.2×10^5, 4.7×10^4, 4.7×10^4, and 1.7×10^4 cycles for 50%, 75%, 100%, and 130% strains, respectively).

1. Introduction

If an electrically conducting polymer is to find technical application in electronic devices[1], it should have good mechanical properties such as flexibility, film forming ability, and normal moldability. A summary of the technology and physics of electrically conducting elastomers and plastic containing carbon blacks and carbon fibers can be found in some recent books[2-6].

Previous publications[7-12] describe the effect of pre-extension and compression on the electrical properties of carbon-black-loaded rubbers. They present methodology, details of the experiments, and conclusions.

As a continuation to the previous work, this paper describes the influence of cyclic strains on the electrical behaviour of Styrene Butadiene Rubber (SBR) loaded with Fast Extrusion Furnace (FEF) carbon balck vulcanizates. In this respect two factors are varied: 1) The strain amplitude and 2) The number of cycles.

2. Experimental Work

A 70 phr (phr: Parts per hundred parts by weight of rubber), of Fast-Extrusion Furnace black (FEF) was introduced into Styrene-Butadiene Rubber (SBR) according to the recipe illustrated in Table (1).

The choice of FEF black is governed by its low tendency-as compared to other furnace blacks - to aggregates, as well as its relatively high elasicity. The test specimens were prepared on a two-roll mill with 170 mm diameter, working distance 300 mm, speed of slow roll 24 revolution/min, and gear ratio 1.4.

Table (1).

Ingredients (phr)	Sample
SBR	100
Stearic acid	2
FEF black	70
Processing oil	10
MBTs[a)]	2
PBN[b)]	1
Zinc oxide	5
Sulphur	2

a) Dibenzthiazyl disulphide
b) Methyl-β-naphthylamin

The compounded rubber was left for at least 24 hours before vulcanization, which was conducted at 143 ± 2 °C under a pressure of about 40 kg/cm^2 for 20 minutes.

The rubber specimens with dimensions of 3 cm in length, 0.6 cm in width, and 0.19 cm in thickness were clamped from both ends in a constant deformation fatigue tester (see Fig. 1) and subjected to a given number of cycles

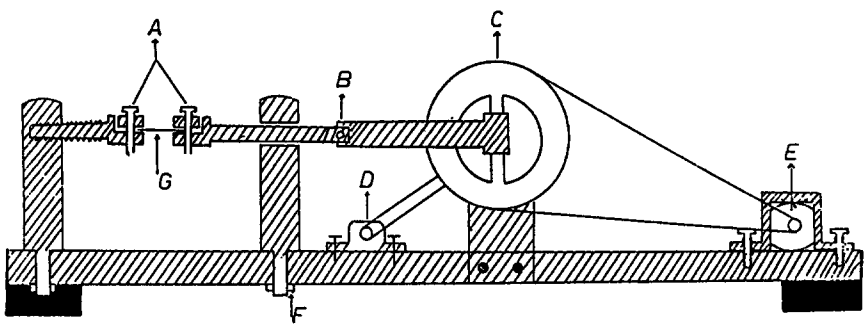

Fig. (1): Schematic representation of the constant strain fatigue tester. A. Clamps. B. Joint. C. Wheel. D. Counter. E. Motor. F. Nut. G. Specimen.

at a constant strain. The specimen was left to rest for 15 minutes after cycling and the temperature dependence of its transverse electrical conductivity, σ_T (measured in a direction normal to the direction of strain) were measured using a simple device as was described in previous works. The electrical conductivity was calculated using the original dimensions. The same steps were repeated under different numbers of cycles, and under different strain amplitudes.

In the case of low voltage conductivity measurements a Tesla Picoammeter, type BM 483 was employed. The temperature was controlled by means of a doubly wound electric oven in the range of 30 - 140 °C.

3. Results and Discussion

During the compounding-fabrication step breakdown of carbon aggregates may take place, affecting the electrical performance and reproducibility of the conductive products[13]. High structure blacks have naturally special tendency to breakdown. Agglomeration-deagglomeration processes may also occur by mechanical deformation and thermal expansion processes.

It has already been seen that the resistivity - filler concentration curves fall sharply above a certain range of concentration[14]. Materials in this region are much more sensitive to strain than are more conductive compounds and than this is the reason behind our choice to study the effect of dynamic strain on the electrical properties of 70 FEF/SBR vulcanizates.

3.1. Effect of strain amplitude on the electrical conductivity:

The effect of strain greater than 30% on the properties of conducting elastomers are different from those of smaller strains[2].

The test sample was exposed to different strain amplitudes at constant number of cycles (1.5×10^2 and 1.7×10^4 at a constant rate of 150 cycle/min). The test specimen was allowed to rest for 15 min before subjecting to repeated measurements of the temperature dependence of its electrical conductivity. Six virgin samples from a master batch of 70 FEF/SBR were exposed to different strains from 25% up to 200% at constant number of strain cycles (1.5×10^2 and 1.7×10^4) respectively.

It is obvious from Fig. (2) that, the observed minimum conductivity value for the untreated specimen (70 FEF/SBR) can be ascribed as was done before[15], to the competition between two conduction mechanisms. The first one is due to the attenuation of conductivity (σ_T) with thermal expansion of the hopping paths between carbon black particles or aggregates, and the other is due to the thermally activated carriers. The agglomeration/de-agglomeration processes are clearly manifested in the behaviour of the temperature dependence of σ_T of 70 FEF/SBR.

At low strain (25%) the construction and/or agglomeration of carbon particles is predominating which is responsible for the observed increase in σ_T. For larger strain values the de-agglomeration (destruction) of carbon particles takes place leading to a decrease in the value of σ_T. It was also noticed that the strain amplitude values have a great influence on the hopping paths between the carbon black particles with respect to the thermally activated part. This suggestion was confirmed by the calculation of the activation energy of the activated part (see Table 2).

Figure (3) illustrates the great effect of increasing the number of cycles (1.7×10^4). The variation of the number of cycles has no appreciable effect in the case of low strain amplitude (< 50%). However, for 130% strain the conductivity σ_T seems to be temperature independent in the range 30 - 80 °C owing to both the balance between the agglomeration and de-agglomeration processes and the direct contact between the carbon particles.

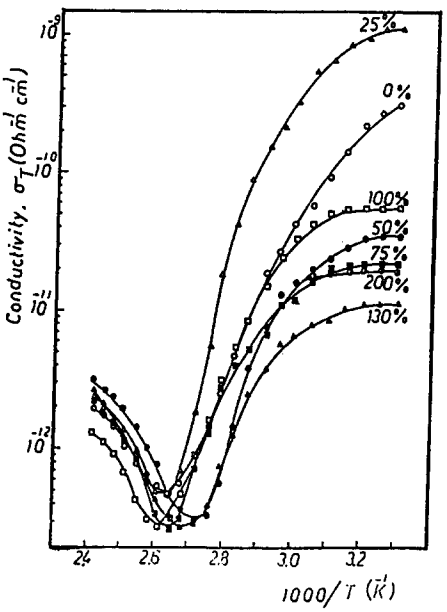

Fig. (2): Represents the temperature dependence of the transverse electrical conductivity σ_T of 70 FEF/SBR sample at different strain amplitude (at constant number of cycles 1.5×10^2).

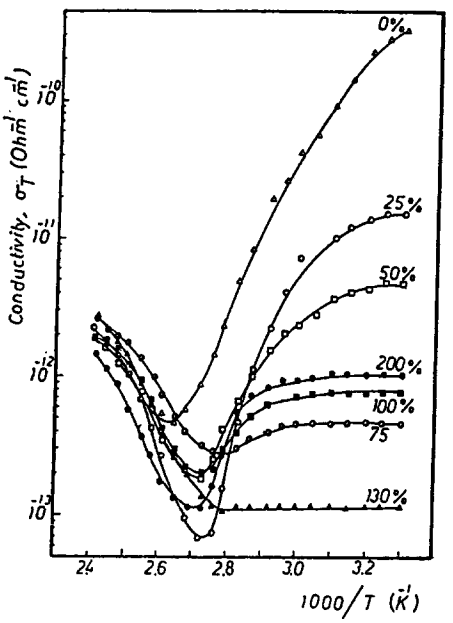

Fig. (3): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different strain amplitude (at constant number of cycles 1.7×10^4).

Table (2): The activation energy is approximately constant.

Strain (%)	1.5×10^2 cycles E (eV)	1.7×10^4 cycles E (eV)
0	0.152	0.152
25	0.137	0.105
50	0.144	0.132
75	0.141	0.177
100	0.120	0.136
130	0.103	0.052
200	0.064	0.064

3.2. Effect of the number of strain cycles on the electrical conductivity:

It is known that fatigue is the failure of mechanical properties of a given material due to oscillatory deformation or stress.

Fatigue tests are especially important for the so-called engineering plastics and composite materials which are used in load bearing structures subjected to varying loads[16].

Figures (4-9) represent the effect of the number of cycles for different strain amplitudes. The common feature of these figures may be summarized as follows:

a) An initial rapid breakdown of structure (for strain more than 25%) owing to the fact that the energy dissipated per second in the specimen is proportional to the frequency and the square of maximum deformation or stress[16] (Fig. 4).

b) An equilibrium between structure breakdown and reformation is established after about thousands of cycles depending on the amount of strain 1.2×10^5, 4.7×10^4, 4.7×10^4, and 1.7×10^4 cycles corresponding to 50%. 75%, 100%, and 130% strains respectively which was detected by the appearance of the temperature independent part of conductivity in the range 30 - 85 °C (Figs. 5,6 and 8).

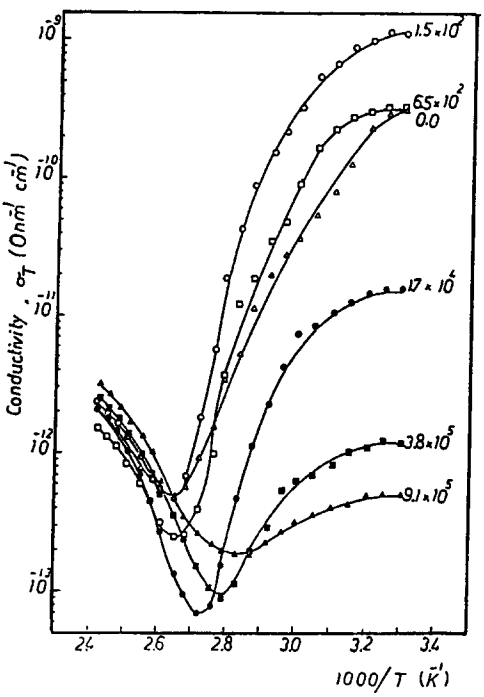

Fig. (4): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 25%).

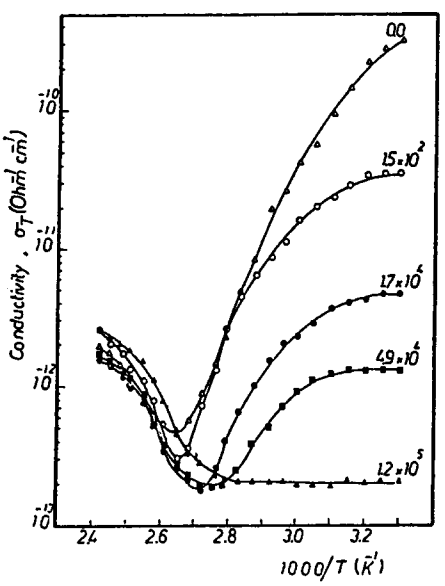

Fig. (5): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 50%).

c) An appreciable shift of the temperature (T_m) corresponding to minimum conductivity toward lower temperatures owing to the smaller role of carbon black with increasing number of cycles (Figs. 4-9).

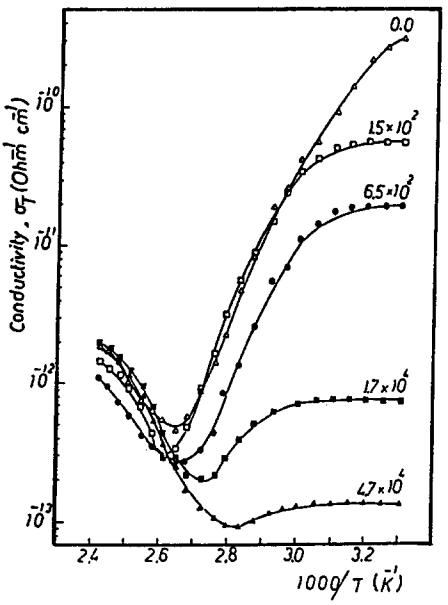

Fig. (6): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 75%).

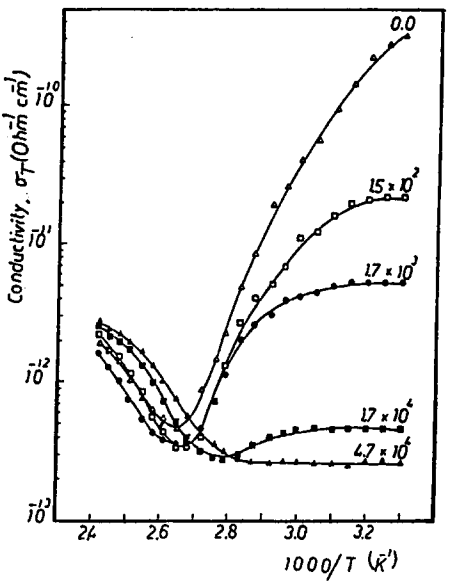

Fig. (7): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 100%).

d) There is a slight change in the activation energy depending on both the strain amplitude and the number of cycles as was shown in table (3).

Table (3):

25% strain		100% strain	
n cycles	E (eV)	n cycles	E (eV)
0	0.152	0	0.152
1.5×10^2	0.137	1.5×10^2	0.120
6.5×10^2	0.125	6.5×10^2	0.136
1.7×10^4	0.105	1.7×10^4	0.136
3.8×10^5	0.147	4.7×10^4	0.137
9.1×10^5	0.156	-	-

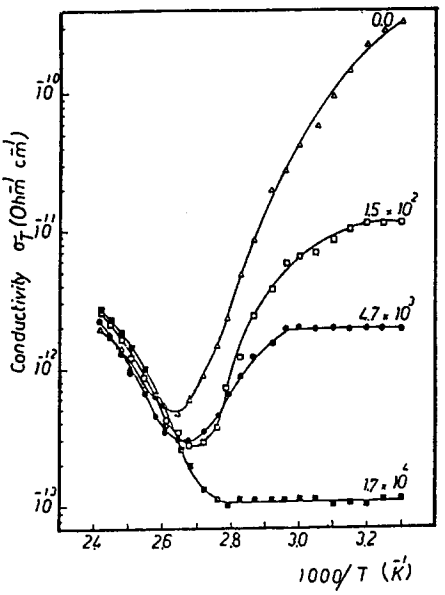

Fig. (8): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 100%).

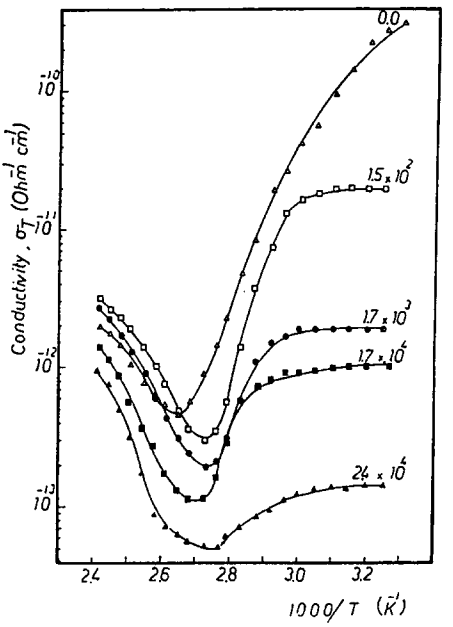

Fig. (9): Represents the temperature dependence of σ_T of 70 FEF/SBR sample at different number of strain cycles (at constant strain amplitude 130%).

Beside the above mentioned feature we may underline two extreme cases:

a) In the case of 25%, deformation, i.e. small strain, the reconstruction process of carbon black particles takes place during the early few cycles after which destruction proceeds by increasing the number of cycles. The variation of σ_T with the number of cycles for such a low strain is rather detectable than for greater strains. This could be explained qualitatively on the basis of Marshall's[17] geometrical model of the carbon black configuration, which implies that the carbon black particles move with and not through the rubber. Hence it is to be expected that some of the rubber (SBR) will diffuse over some of the carbon-carbon contacts and prevent them from approaching each other sufficiently closely to remake an electrical contact.

b) In the case of 200% strain the de-agglomeration process predominates and there is no equilibrium between reformation and destruction of carbon particles owing to the large deformation.

4. References

[1] Y. Kishimoto and W. Shimotsuma, J. of Polymer Science Polym. Phys. Ed. 20, 845 (1982).

[2] R.H. Norman, "Conductive Rubbers and Plastics", North-Holland, Amsterdam (1970), p. 129.

[3] J.B. Donnet and A. Voet, "Carbon Black", Marcel Dekker, New York (1976).

[4] A.I. Medalia and D. Rivin, "Carbon Blacks", in Characterization of Rubber surfaces, G.D. Parfitt and K.S.W. Sing (eds.), Academic, London (1976).

[5] E.K. Sichel, "Carbon Black-Polymer Composites", Marcel Dekker, New York (1981).

[6] J. Delmonte, "Technology of Carbon and Graphite Fiber Composites", Van Nostrand Reinhold, New York (1981).

[7] M. Amin, H.H. Hassan and G.M. Nasr, Die. Angew. Makromol. Chemi. 119, 47 (1983) & 119, 39 (1983).

[8] M. Amin, G.M. Nasr, S.A. Khairy and E. Ateia, Die. Angew. Makromol. Chemi. 141, 19 (1986).

[9] H.H. Hassan and G.M. Nasr, Die. Makromol. Sci. Chemi. A18, 14, 535 (1982).

[10] G.M. Nasr, M. Amin, H.M. Osman and M.M. Badawy, Die. Angew. Makromol. Chemi. 150, 2408, 21 (1987).

[11] G.M. Nasr, M. Amin, H.M. Osman and M.M. Badawy, Accepted for Publication in J. Appl. Polym. Sci. (1988).

[12] G.M. Nasr, M. Amin, H.M. Osman and M.M. Badawy, to be Published in J. Polym. Mat. (1988).

[13] M. Narkis and A. Vaxman, J. Appl. Polym. Sci. 29, 1639 (1984).

[14] E.M. Abd-El Bary, M. Amin and H.H. Hassan, J. of Polymer Science, Polymer Chemistry Edition, 17, 2163 (1979).

[15] E.M. Abd-El Bary, M. Amin and H.H. Hassan, J. of Polymer Science, Polymer Chemistry Edition, 15, 197 (1977).

[16] L.E. Nielsen, "Mechanical Properties of Polymer and Composites", (1972), p. 349.

[17] D.G. Marshall, Proc. of the third Rubber Technology Conference, pp. 483-495 (1954) (from R.H. Norman, "Conductive Rubber and Plastics", Applied Science Publisher LTD, London, 1970).

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