

Effect of Tensile Deformation on the Electrical Conductivity of SRF Black-Loaded SBR Blend

H. H. HASSAN,* S. A. KHAIRY, S. B. EL-GUIZIRI, and H. M. ABDEL-MONEIM

Physics Department, Faculty of Science, Cairo University, Giza, Egypt

SYNOPSIS

Styrene butadiene rubber (SBR-1502) was mixed with 100 phr superreinforcing furnace (SRF) black. The obtained rubber vulcanizate was subjected to electrical conductivity measurements at different values of tensile deformation. The $\log V$ vs. $\log I$ graphs showed two distinct linear stages, the slope of which is nearly independent of the tensile deformation in the first stage and decreases with tensile deformation in the second stage. On the other hand, the tensile deformation was found to have an appreciable effect on the electrical conductivity. It decreases sharply as the sample is suddenly strained and then increases exponentially with time. An empirical formula describing this behavior is suggested.

INTRODUCTION

Carbon black-loaded rubbers represent a great interest from both the scientific as well as the technological points of view. It has been established that the electrical conductivity of such composites depends on the type and concentration of the carbon black used.^{1,2} For heavily loaded rubber composites, the electrical conduction was attributed to hopping or tunneling of charge carriers between carbon black particles and/or aggregates.³

In addition, the electrical conductivity of these vulcanizates depends on the applied electric field⁴ and temperature.¹ The observed decrease of conductivity with temperature was explained in terms of thermal expansion of the hopping paths. Based on this fact, we thought that it is useful to study the effect of deliberate tensile deformation on electrical conductivity, which represents the aim of the present work.

EXPERIMENTAL

The rubber vulcanizate used had the following composition: SBR-1502, 100 phr; stearic acid, 2 phr; ZnO, 5 phr; SRF black, 100 phr; processing oil, 10

phr; MBTS,* 1.5 phr; PBN,[†] 1 phr; and sulfur, 2 phr.

The preparation of the rubber sample was carried out on a two-roll mill 170 mm diameter and 300 mm long; and gear ratio 1.4. After preparation, the rubber mix was left at least 24 h before vulcanization. The vulcanization process was conducted at $143 \pm 2^\circ\text{C}$ for 30 min under a pressure of 40 kg/cm². Afterwards, the test samples were cut in the form of strips 10 mm long, 3.5 mm wide, and about 0.7 mm thick.

The essential part for conductivity measurement was a Levell picoammeter type TM 9 BP (U.K.). Extension of the investigated samples was carried out using a locally made machine.

In conductivity measurements the sample was strained suddenly by 10% and the electric current was recorded against time. Experiments at higher strains were carried out by increasing the strain in successive steps of 10% in each experiment. The maximum strain attained was 120%, after which the sample was broken. The cross-sectional area of the sample for a given strain was calculated from the initial dimensions, assuming the volume to be constant.

During I - V measurements on strained samples, the current corresponding to a certain voltage was

* To whom correspondence should be addressed.

* Dibenthiazyl disulfide.

[†] Phenyl- β -naphthylamine, a possible carcinogenic compound.

recorded after it had reached its equilibrium value. The power consumed in the rubber sample did not exceed 0.1 W cm^{-3} , which justifies neglecting any Joule heating.

It is worth mentioning that the experimental runs were repeated several times on a set of samples. The obtained results proved to be reliable and reproducible.

RESULTS AND DISCUSSION

Figure 1 represents the I - V curves for 100 SRF black/SBR sample at different values of the tensile deformation ϵ (0–120%) at room temperature. As seen from the figure, the experimental curve for each deformation may be approximated by two straight lines, characterizing two different stages of current conduction (I and II). Accordingly, the I - V dependence for each strain can be described by a relation of the form:

$$I = CV^n \quad (1)$$

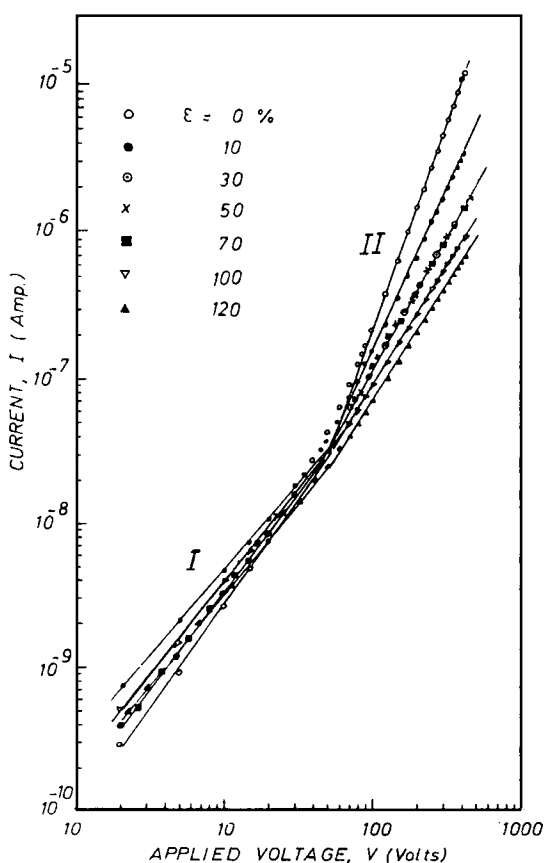


Figure 1 The I - V characteristics of 100 SRF black/SBR vulcanizate at different tensile deformations.

Table I Values of n in the Relation $I = CV^n$ for Different Tensile Deformations ϵ in Stages I and II of Current Conduction

ϵ (%)	n	
	Stage I	Stage II
0	1.45	2.61
10	1.06	2.45
30	1.13	1.71
50	1.06	1.71
70	1.13	1.71
100	1.10	1.67
120	1.09	1.43

where C and n are constants; meanwhile, the exponent n characterizes the mechanism of conduction in each stage. Calculations using eq. (1) yielded Table I, representing the dependence of n on ϵ in stages I and II.

Current conduction in polymers is a quite complicated process. However, it is acceptable at the present time⁵ that electric conduction in rubber could be explained by three mechanisms, namely, the ohmic conduction, space charge limited conduction (SCLC), and trap field limited conduction (TFLC). The values of n in eq. (1) characterizing these mechanisms are 1, 2, and 3, respectively.⁶

It may be seen from Table I that n has its highest values at $\epsilon = 0\%$ in both stages I and II; moreover, n is higher in stage II than in I. This may be interpreted as follows: In both stages I and II, the electrical conduction is explained by the above mentioned three mechanisms. But in stage I the applied electric field is small, and hence the TFLC may be neglected. Taking the injection of charge carriers from electrodes into the sample under consideration, the contribution of SCLC, for which $n = 2$, to the measured current is appreciable. This, in turn, explains why n is considerably greater than unity at $\epsilon = 0\%$ in this stage. On the other hand, the electric field through the sample is high enough in stage II such that the contributions of both SCLC and TFLC are comparable, giving rise to a value of n considerably greater than 2 at $\epsilon = 0\%$ in this stage.

As the tensile deformation increases, n decreases to a value close to 1 in stage I and 1.7 in stage II. As shown in the literature,⁷ the carbon-carbon contacts in the rubber matrix are responsible for the ohmic conduction, while nonohmic conduction is closely related to the carbon-rubber contacts. Moreover, it was shown that the rubber-carbon adhesion approaches in strength the adhesion of

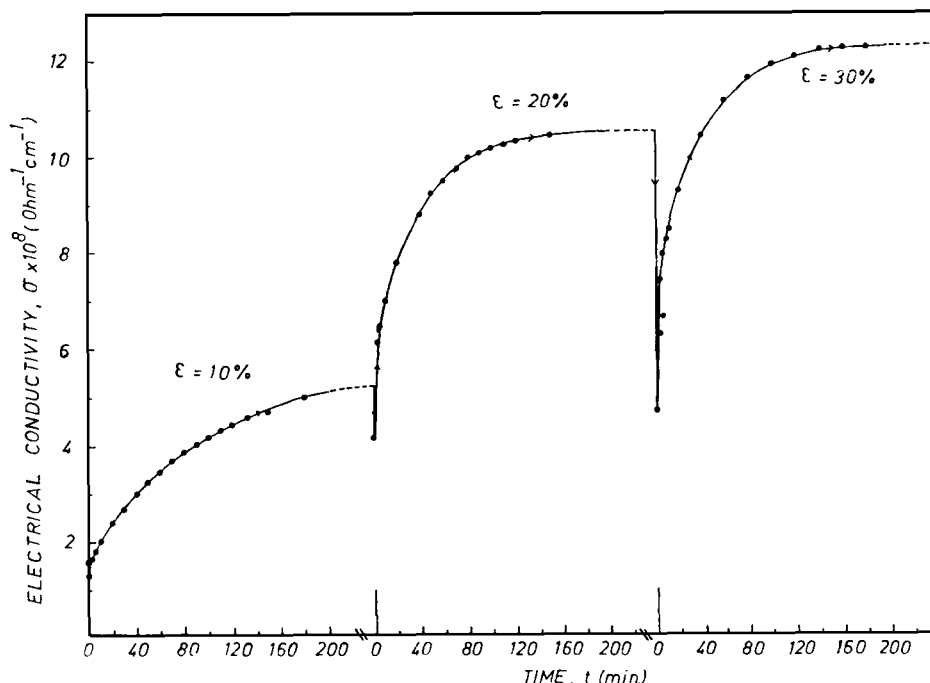


Figure 2 Variation of the electrical conductivity σ of 100 SRF black/SBR vulcanizate with time at different tensile deformations.

rubber itself, so that when rubber is deformed, the carbon black particles move with and not through the rubber. Thus, the decrease of n with ϵ might be attributed to the increase of the number of carbon-carbon contacts, which is true for both stages I and II. This causes n to approach unity at high deformations in stage I. In addition, the increase of ϵ may cause rupture of the side groups, which act as traps in stage II. Such a process reduces the role of TFLC, so that the SCLC conduction will predominate over the ohmic conduction. Thus, the value of n will approach a constant value close to that characterizing SCLC. The decrease of n with ϵ above $\epsilon = 100\%$ in stage II is suggested to be a result of the large increase of the number of carbon-carbon contacts characterizing a tendency to ohmic conduction.

Variation of the electrical conductivity σ with time t has been studied under different conditions of tensile deformation ϵ (0–120%). As an example, the $\sigma(t)$ dependence for three values of ϵ is illustrated in Figure 2.

The observed inconsistency of the current-voltage and conductivity data may be attributed to the fact that the I - V measurements were carried out without taking changes of the sample dimensions into account.

As seen from Figure 2, the electrical conductivity of the strained sample suffers an abrupt drop at $t = 0$, followed by a gradual increase with time to reach

its equilibrium value σ_e after a sufficiently long time. Such $\sigma(t)$ dependence might be interpreted in terms of the stress-relaxation theory of polymers.⁸ The

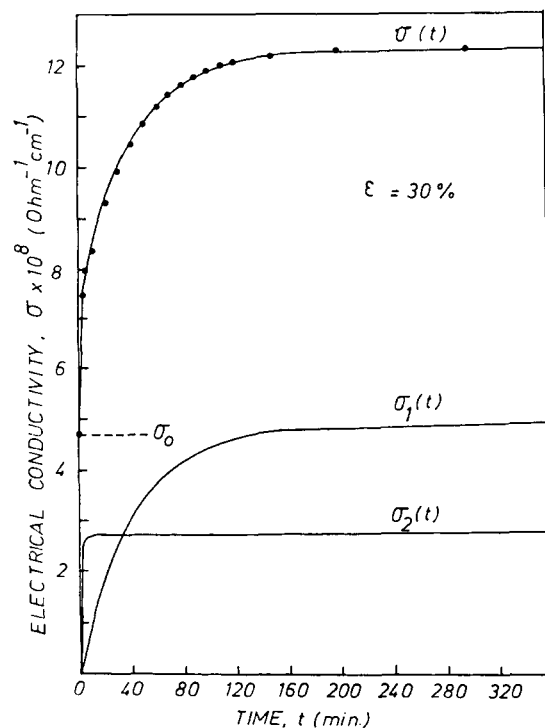


Figure 3 Curve analysis of the $\sigma(t)$ dependence [eq. (2)] for 100 SRF black/SBR vulcanizate.

Table II Fitting Parameters σ_0 , σ_1 , and σ_2 and Relaxation Times τ_1 and τ_2 in Eq. (2) for Different Tensile Deformations ϵ

ϵ (%)	$\sigma_0 \times 10^8$ ($\Omega^{-1} \text{ cm}^{-1}$)	$\sigma_1 \times 10^8$ ($\Omega^{-1} \text{ cm}^{-1}$)	$\sigma_2 \times 10^8$ ($\Omega^{-1} \text{ cm}^{-1}$)	τ_1 (min)	τ_2 (min)
10	1.33	0.28	3.74	1.25	86.20
20	3.99	2.01	4.56	0.60	40.00
30	4.70	2.72	4.90	0.78	41.66
40	3.84	2.30	6.30	1.89	125.00
50	5.37	3.06	7.26	3.14	76.92
60	6.03	3.40	8.38	3.13	142.80
70	9.06	5.61	6.34	2.53	43.47
80	11.44	3.55	6.90	1.30	25.00
90	12.90	3.24	6.78	0.90	19.20
100	12.55	3.86	9.42	0.81	37.03
110	20.70	5.29	13.08	1.06	21.27
120	21.26	9.77	8.14	3.57	41.66

SRF black/SBR sample may be represented by a three-element mechanical model consisting of spring S_1 in parallel with a non-Newtonian Maxwell unit with spring S_2 . In this model S_1 represents the rubber chains, while the Maxwell unit represents the carbon black particles in the viscous rubber matrix. When the strain is suddenly applied, the dashpot starts to slip under the effect of the applied stress and two springs are extended, which means an uncoiling of the rubber chains, and thus the sample acquires its maximum strain. This results in an increase in the average distance between carbon particles or aggregates or even temporal breakdown of the carbon black structure, which explains the abrupt drop of σ at the moment the strain is applied. After straining is stopped instantaneously, stress-relaxation at constant strain begins. Because the extension is kept constant during stress-relaxation, the elongation of the open spring S_1 is also constant, and consequently the stress acting on it remains unchanged. As the dashpot slips, the stress acting on spring S_2 decreases. The time-dependent flow, which occurs in the Maxwell unit, decreases the total stress in function of time.

Analysis of the $\sigma(t)$ dependence suggests that the time growth of conductivity is superposition of two relaxation processes (Fig. 3). This behavior is best fitted by the following empirical formula:

$$\sigma(t) - \sigma_0 = \sigma_1(t) + \sigma_2(t) \quad (2)$$

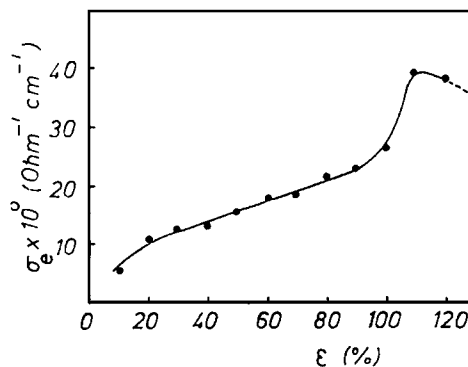
where

$$\sigma_1(t) = \sigma_1[1 - \exp(-t/\tau_1)] \quad (3)$$

$$\sigma_2(t) = \sigma_2[1 - \exp(-t/\tau_2)] \quad (4)$$

with σ_0 , σ_1 , and σ_2 fitting parameters and τ_1 and τ_2 the relaxation times for the two suggested processes (see Table II).

According to the above-mentioned concepts of the stress-relaxation theory, the shorter relaxation time τ_1 in eq. (3) might characterize a process of partial recoiling of rubber chain. This process causes the carbon particles adhering strongly to the rubber chains to come closer to each other, which results in an increase of conductivity. Such contribution to the sample conductivity is described by the term $\sigma_1(t)$ in eq. (2). The longer relaxation time τ_2 , which characterizes slipping of the dashpot, is believed to be related to the recovery of the carbon black structure. Such process gives rise to the observable increase of sample conductivity with time, which is represented by the term $\sigma_2(t)$ in eq. (2).

**Figure 4** Dependence of the equilibrium conductivity σ_e upon tensile deformation ϵ for 100 SRF black/SBR vulcanizate.

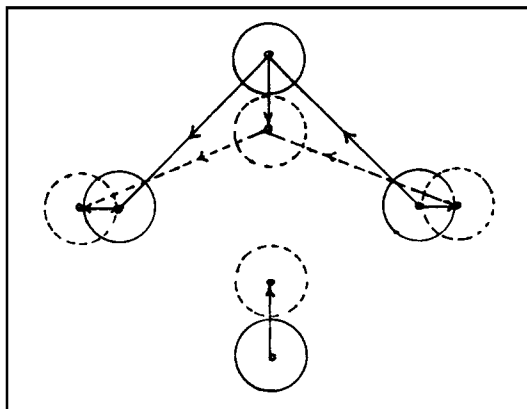


Figure 5 Schematic diagram illustrating the dependence of the hopping distance upon tensile deformation. Dashed circles represent the displaced carbon particles or aggregates.

Bartenev et al.⁹ investigated relaxation in filled and unfilled SBR vulcanizates. They concluded that the same process with a relaxation time less than 10^4 s occurs in both filled and unfilled vulcanizates and could be attributed to the movement of the polymer chain segments. In the filled vulcanizates there existed in addition a process with a relaxation time 10^5 – 10^6 s, which could be attributed to recovery of the filler structure, which is in agreement with the present data.

It may be observed from Figure 4 that the equilibrium value of the electrical conductivity σ_e increases with the tensile deformation ϵ up to $\epsilon = 110\%$. Meanwhile, it may be thought useful to note the linear proportionality in the deformation range 20–90%. This makes it possible to think of a practical strain gauge in this strain range.

The observed increase of σ_e with ϵ might be interpreted in terms of lateral contraction of the sample, as illustrated by the simple model shown in Figure 5. At small and moderate values of ϵ (below

110%), the lateral contraction results in a decrease of the average hopping distance between carbon particles or aggregates. Accordingly, the electrical conductivity will increase with tensile deformation. At $\epsilon = 110\%$, practically all carbon black particles or aggregates become aligned in the direction of tensile deformation. Further increase of ϵ may cause the rupture of carbon black chains and, hence, the conductivity to decrease.

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