

# Resistivity Behavior of Carbon-Black-Filled Silicone Rubber in Cyclic Loading Experiments

J. KOST, M. NARKIS,\* and A. FOUX, *Departments of Biomedical and Chemical Engineering, Technion, Haifa 32000, Israel*

## Synopsis

Stress-relaxation and cyclic loading behavior of silicone/EC black vulcanizates have been measured at several strains up to 0.8. The first extension is always very different from the subsequent ones. Orientation effects of anisometric carbon particles are starting to play an important role only after a certain elongation has been exceeded. The conductive elastomers can be stabilized by mechanical preconditioning procedures involving cycling at high extensions. The stabilized specimens then behaved nearly reversibly when cycled at strains below about 50% of the previous preconditioning strain. The resistivity-extension cycle consists of a single peak or a double peak per a strain peak depending on the strain level. The transition from single to double resistivity peaks depends on whether particle orientation takes place during the stretching process, which depends upon the level of strain.

## INTRODUCTION

In a previous publication<sup>1</sup> the effects of the first axial stretching (the specimens have never been stretched before) on the resistivity of Ketjen-black EC/silicone rubber vulcanizates were reported. It was shown that such effects are carbon-black-concentration-dependent, and their significance increases by reducing the black concentration towards the threshold percolation concentration described by the insulator to conductor transition of the specific carbon black/elastomer system. The resistivity of stretched samples was also found to depend upon the rate of extension. These facts have led to the conclusion that the resistivity of carbon black/elastomer materials undergoing stretching is determined by the transient distribution of the conductive particles array. Preliminary relaxation and dynamic loading experiments in which the resistivity was monitored continuously as function of time, or strain and time, respectively, have shown very clearly the importance of the time effect on the resistivity. It is the subject of this paper to report and explain such time effects and also to demonstrate how by mechanical preconditioning it is possible to confer to such conductive elastomers nearly reversible changes of their resistivity upon mechanical cycling.

Bending or other modes of deformation can cause severe problems in conductive plastics and elastomers utilized as resistors, temperature sensitive resistors, strain measuring devices,<sup>2</sup> or heating elements.<sup>3</sup> A list of relevant publications was given in the previous article.<sup>1</sup> Relevant studies published until 1970 were summarized by Norman.<sup>2</sup> These reports distinguish between large tensile strains (above 30%) and small tensile strains,

\* To whom correspondence should be addressed at the Department of Chemical Engineering.

concluding that the recovery behavior of the resistivity of strained samples upon their release from large strains is very complicated, whereas the recovery may be complete from small strains if sufficient time of recovery is allowed.

### EXPERIMENTAL

Silicone rubber (Siloprene HV 3/5000u, Bayer), carbon black (Ketjenblack EC, Akzo Chemie), and peroxide (liquid 96% dicumyl peroxide, Hercules) were mixed on a cold two-roll mill. Sheets ( $15 \times 15 \times 0.18$  cm) from these mixes were compression-molded at  $170^{\circ}\text{C}$  and post-cured in an air oven for 6 h at  $200^{\circ}\text{C}$ .

The details of the experimental measuring setup using an Instron testing machine and a four-terminal potentiometric method for simultaneous recording of the stress-strain and resistance-strain curves were given in the previous article.<sup>1</sup>

Relaxation tests were carried out at two constant levels of strain, 0.2 and 0.8. The specimens were stretched to these levels at a constant cycling strain rate of  $2 \text{ min}^{-1}$ . The stress and resistance were measured as a function of time. Some specimens were unloaded after a 1560-s relaxation time, and their resistivity followed thereafter.

Cyclic loading was conducted with the first cycle starting at zero load on the specimen, and then the specimen was stretched at a constant strain rate of  $0.2 \text{ min}^{-1}$  to a predetermined strain level; at that point, the strain was released using the same strain rate down to 0.08 kg load. The lower load limit of the cycles was necessary due to residual elongation of the specimens after each loading cycle.

### RESULTS AND DISCUSSION

Carbon black aggregates consist of small carbon black particles fused together due to particle coalescence during the formation process. The preparation conditions can be varied to control the degree of coalescence and therefore the size and anisometry of the aggregates formed. Aggregated particles form a persistent, irreversible structure while transient reversible structures characterize agglomerated particles. Reversible agglomeration-deagglomeration processes may take place in systems undergoing mechanical stressing or thermal changes while irreversible deaggregation (or breakdown) processes occur possibly in compounding and fabrication processes where high shear fields are developed. Thus, deaggregation processes may be ignored in conductive elastomers, moderately loaded, in stretching, flexing, relaxation or cyclic experiments, using the later described mechanically preconditioned specimens. The transition from one transient structure of the carbon network to another is thus mainly caused by translation and rotation movements of the anisometric aggregates and by destruction and buildup of agglomerates.

"Structure" in carbon black aggregates is a terminology used to describe the number of carbon black particles fused together to form an aggregate. "High structure" in carbon black aggregates means a large number of particles per aggregate. In this respect EC black is considered as a low

structure black.<sup>4</sup> Its superior conductivity is attributed to an extremely low apparent particle density caused by the presence of a large number of hollow-shell particles. Repeated crushing of EC black particles has caused very small changes in the structure of this black, which explains the relatively low sensitivity of the resistivity of compression-molded plaques to prior compounding conditions of EC black compounds. Different fabrication methods, however, of EC black compounds may give products having different resistivities due to differences in the distribution details of the anisometric conducting particles.<sup>5</sup>

Electron conduction in carbon-black-filled polymers occurs along particles contacting each other or separated by very small gaps. These interaggregate gaps may be considered as potential barriers for electrons to hop by tunneling. Reduction of the interaggregate gaps enhances the flow of electrons and decreases the macroscopic resistivity. The average interaggregate distance is affected by many parameters including concentration, structure, size and shape of the aggregates, size distribution, mixing efficiency, temperature, and stressing. Conductor-insulator composites become conductive only after a certain threshold concentration of the conductive filler has been added. This critical percolation threshold represents a system where continuous conductive chains have been first formed. The conducting elements of these chains are either making contacts between themselves or separated by very small distances across which electrons can hop by tunneling. The experimental volumetric percolation concentrations representing good electrically conductive carbon blacks are usually far-below theoretical predictions or experimental data for spherical conducting elements (MT black, for example) dispersed in polymers. The main reason for this "discrepancy" is attributed to the unique aggregate structure, rather than individual spherical particles of carbon blacks. This aggregate structure leads to a "filamentary" conducting network requiring significantly lower concentrations to reach the critical percolation concentration. Thus, only 6% w/w EC-black are required to convert the nonconductive silicone elastomer into a conductive rubber.<sup>1</sup> Similar critical concentrations were found for other conductive carbon blacks in crosslinked polyethylene,<sup>6</sup> while about 35% w/w MT black were needed to convert polyethylene into a conductive material.<sup>7</sup>

Figures 1 and 2 represent stress and relative electrical resistivity relaxation experiments using virgin, previously unstretched, samples. The stress decay after 1500 s is 30% [Fig. 1(a)] independent of the strain level, at least up to 0.8 strain. Contrary to this result, the decay in electrical resistivity [Fig. 1(b)] is 60% for a strain level of 0.2 and 34% for the higher strain level of 0.8. Figure 2 demonstrates a recovery experiment following 1560 s of relaxation under a constant strain of 0.8. Upon complete retraction of the sample the stress drops to zero in a normal fashion [Fig. 2(a)] while the resistivity initially responds by a very sharp increase and decrease of its level followed by an apparently irreversible plateau value [Fig. 2(b)]. The retracted unstrained sample, thus, has a resistivity about 65% higher than its original value, which characterizes the unstrained virgin sample. Many researchers have studied mechanical irreversible phenomena in unfilled and filled elastomers, whereas only a very few publications describe irre-

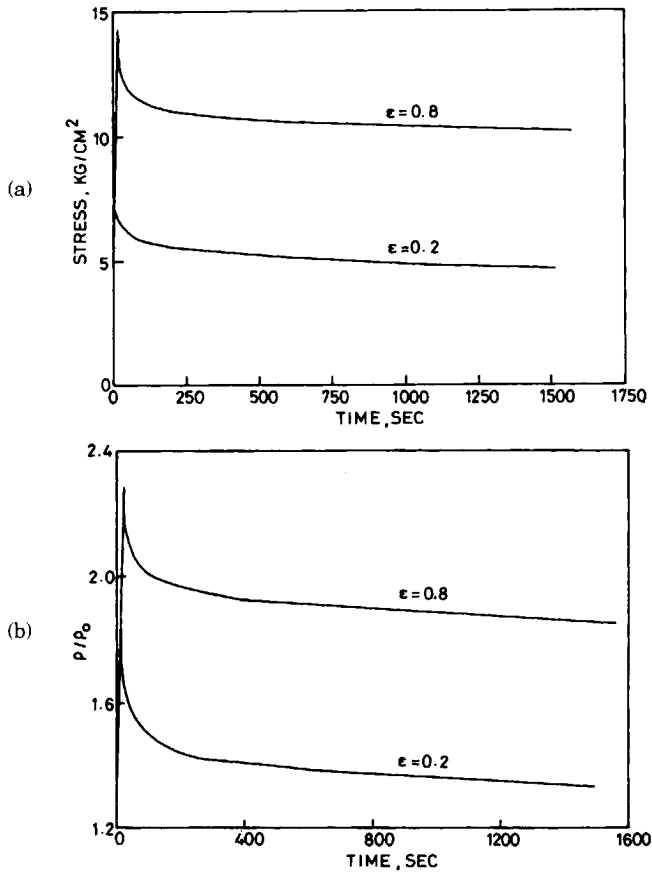


Fig. 1. Relaxation experiments of virgin conductive silicone samples containing 10% w/w EC black. Relaxation of (a) stress and (b) relative resistivity.

versible phenomena associated with the electrical resistivity of such materials.<sup>8-10</sup> The various phenomena can generally be explained in terms of formation and destruction of the carbon network, orientation of carbon anisometric aggregates, and rupture of carbon black elastomer bonds. The latter effect becomes important only at high extensions and does not apply to the present work where strains are always below 0.8. The orientation effect is unimportant at low extensions (less than about 25%) where the formation and destruction of the carbon network is the dominant process. In a stress-relaxation experiment at time intervals where the rate of stress decay is small the transient carbon network structure is in a quasiequilibrium state. Any slight perturbation (such as the beginning of the recovery step) will cause an instantaneous destruction-reformation process of the very loose contacts between the conducting particles as shown by the sharp peak in Fig. 2(b). This sharp and short response of the resistivity of a strained conductive rubber can be utilized for monitoring perturbations in practical applications. As shown, the resistivity of relaxed, strain-released specimens differs from the resistivity of the original unstrained samples and depends upon the previous strain during relaxation. This certainly complicates the

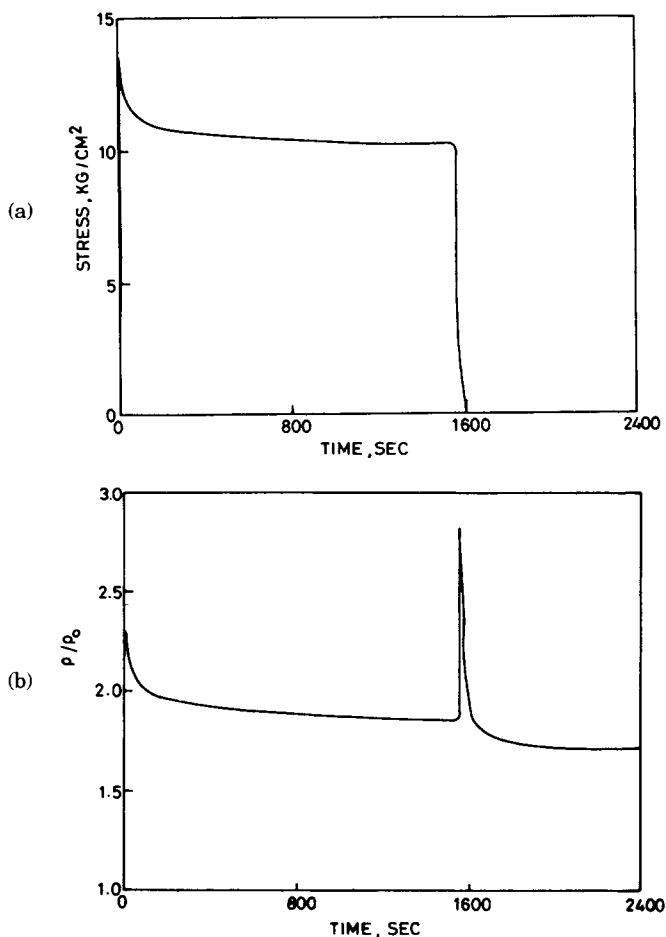


Fig. 2. Relaxation recovery experiments of virgin conductive silicone samples containing 10% w/w black. Relaxation recovery of (a) stress and (b) relative resistivity.

analysis and utilization of conductive rubbers and requires exploration of stabilization methods to produce nearly reversible electrically conductive elastomers.

Cyclic loading tests were carried out on specimens containing 12% EC carbon black. The strain rate in the loading and unloading parts of the cycle was  $0.2 \text{ min}^{-1}$ . Samples were stretched to a given strain and then released to a low load limit as explained in Experimental. Figures 3 and 4 demonstrate selected cycles with upper strain limits of 0.08 and 0.8, respectively. Two different types of behavior are clearly seen for the two levels of strain. At the low strain (Fig. 3) the general trend of the resistivity peak is similar to the strain peak, and the maxima in strain and resistivity occur simultaneously; however, the resistivity is slightly lagging behind the strain during the unloading step, and the resistivity minimum occurs only shortly after the minimum strain has occurred. During the stretching step carbon network destruction dominates all other processes and an "extra" net destruction after the strain maximum does not occur. During the un-

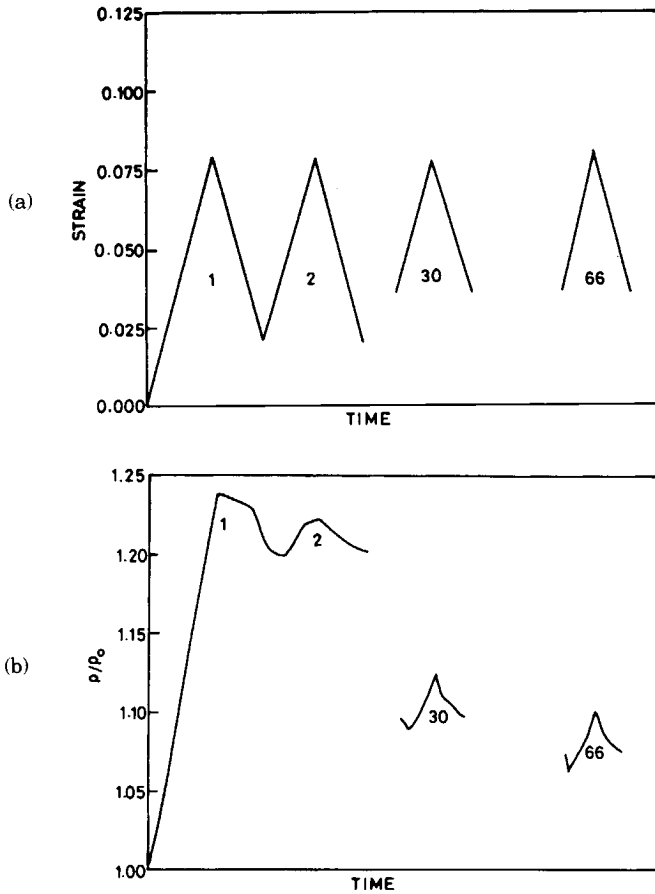


Fig. 3. Cycling experiments of virgin conductive silicone samples containing 12% w/w EC black. Maximum strain limit 0.08. Periodic change of (a) strain and (b) relative resistivity.

loading part of the cycle the macroscopic contraction and internal relaxations dominate. At the point of minimum strain (the load is 0.08 kg), where the strain direction reverses, an additional resistivity decrease occurs [see the initial very rapid and significant resistivity drop in a relaxations experiment, Fig. 1(b)] causing the resistivity lag behind strain. A much more complicated behavior is shown in the higher 0.8 strain cycling experiments. The general trend of the resistivity, as shown in Figure 4, is to increase with time (number of cycles) and apparently to reach a state of reversible cycles (an opposite trend of the resistivity change with time is shown in Fig. 3 for the low strain cycling experiment). Additionally, during a single strain cycle (see cycle 15) a double resistivity peak is obtained. Numerous cycling experiments have shown that the resistivity response is either a single or a double peak per a single strain peak depending upon the maximum strain limit used in the experiment and the previous mechanical history of the specimen. The latter is very important and can be eliminated, as will be shown later, by high-strain mechanical preconditioning operations.

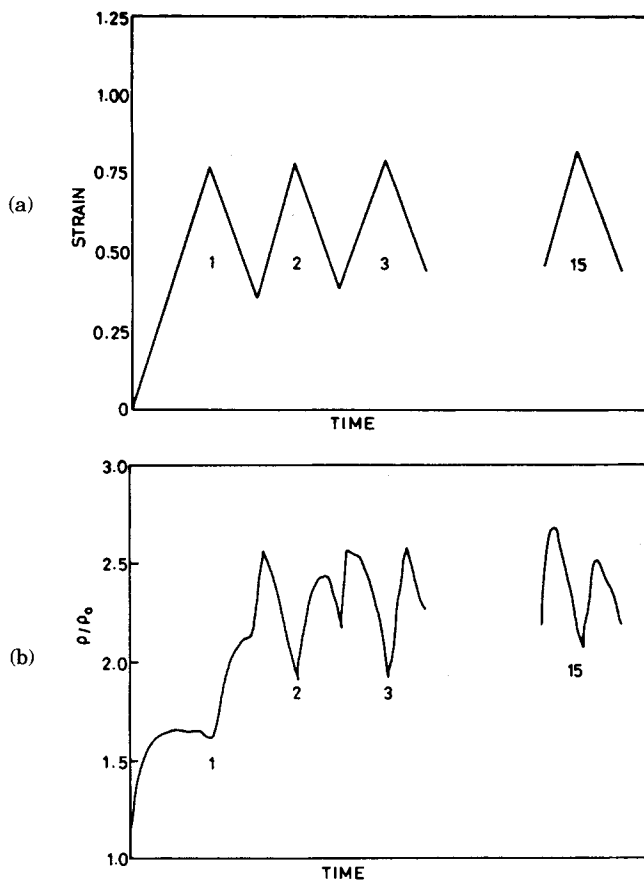


Fig. 4. Cycling experiments of virgin conductive silicone samples containing 12% w/w EC black. Maximum strain limit 0.8. Periodic change of (a) strain and (b) relative resistivity.

The foregoing stress-relaxation and cycling experiments have shown that a reproducible and characteristic electrical resistivity behavior can only be obtained after many repeated cycles. This, naturally, leads to the idea that some mechanical preconditioning methods should be searched for stabilization of the resistivity of the rubbery conductive materials.

A typical stabilization procedure consisted of 15 cycles at a rate of  $0.2 \text{ min}^{-1}$  and maximum strain 0.8 followed by storing the specimens at rest for 10 h. These preconditioned samples were found to perform mechanically and electrically as reproducible elements up to a maximum strain limit of 0.4. A summary of cyclic tests done on the stabilized preconditioned specimens is given in Table I. The resistivity of all the specimens after the cyclic tests returns to the original values of the preconditioned samples. Thus, the conductive elastomers function electrically in a reversible manner. Characterization and utilization of electrically conductive elastomers should be done on properly mechanically preconditioned materials.

Figures 5 and 6 show the stress, relative resistivity, relative resistance, and strain as function of time in cyclic stretching of the stabilized precon-

TABLE I  
Resistivity of Stabilized<sup>a</sup> Samples Before and After Periodic Loading Tests

Carbon black concentration (% w/w)	Periodic loading test, rate 0.2 min <sup>-1</sup> (no. of cycles)	Strain limit	Resistivity <sup>b</sup>	
			Before loading test ( $\Omega$ cm)	After periodic loading test ( $\Omega$ cm)
8	70	0.05	115	116
8	34	0.10	114	119
8	7	0.20	117	118
8	9	0.30	118	120
12	95	0.05	24.5	24
12	101	0.10	24.0	24.5
12	17	0.25	24.6	24.7
12	10	0.40	23.4	23.4

<sup>a</sup> 15 cycles at a rate of 0.2 min<sup>-1</sup> and maximum strain 0.8.

<sup>b</sup> Resistivity measurements were always taken after 30 min at rest following the periodic loading test.

ditioned specimens. These figures represent two levels of maximum strain in the cyclic experiments—0.15 and 0.4. A satisfactory reproducibility of the resistivity cycle has been achieved for the mechanically stabilized specimens. A double resistivity peak per single strain peak appears at the higher strain (Fig. 6) whereas a single resistivity peak per single strain peak is found for the lower strain (Fig. 5). At the lower strain (Fig. 5,  $\epsilon = 0.15$ )

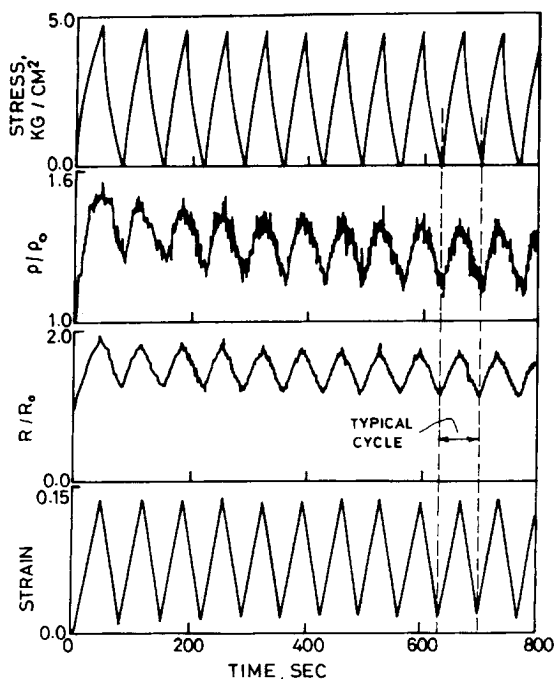


Fig. 5. Cycling experiments of mechanically stabilized preconditioned samples containing 12% EC black. Maximum strain limit 0.15.



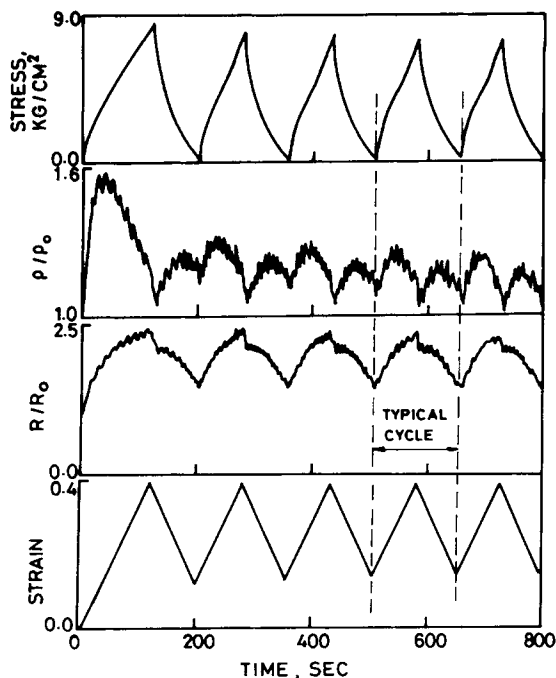


Fig. 6. Cycling experiments of mechanically stabilized preconditioned samples containing 12% EC black. Maximum strain limit 0.4.

orientation effects of the anisometric particles are insignificant and only destruction-formation processes of the carbon network are important. The resistivity peak thus follows the strain peak. At the higher strain (Fig. 6,  $\epsilon = 0.4$ ) orientation effects become important, causing a resistivity reduction until the end of the stretching part. During the contraction part the resistivity initially increases due to gradual randomization of the aligned anisometric particles and then decreases to roughly its original value due to rebuilding of the carbon network previously destroyed by stretching (the first half of the cycle). The transition from single to double resistivity peaks for the mechanically stabilized samples was found to be independent of the sample history (critical strains of 0.15–0.25 and about 0.3 were found for the samples containing 12% and 8% w/w EC black, respectively).

In a future article quantitative resistivity (or resistance)–strain–time relationships will be derived and compared to typical experimental results representing the mechanically stabilized preconditioned materials.

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