

Direct current electrical conductivity of silver-thermosetting polyester composites

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The electrical conduction of composites made from unsaturated polyester with silver powder and silver-coated glass spheres is investigated. The samples are generally non-ohmic and exhibit switching effects. There is a noted difference in the threshold concentrations for the two types of samples. It is also found that electrical current is conducted via discrete paths.

1. Introduction

The d.c. electrical conduction behaviour of composites made from conducting powders dispersed in polymeric materials has been the subject of many previous investigations. In many of these studies [1-3], carbon black is employed as the conducting phase because it is chemically inert and readily available, and because such composites have wide industrial applications.

In other investigations, metal powder fillers are used. Matsushita *et al.* [4] studied the resistivity of compressed silver powder and polystyrene. For copper-polyvinylchloride composites after prolonged annealing, Bhattacharyya *et al.* [5] found ohmic relations between current and voltage. De Araujo and Rosenberg [6] reported switching effects in a number of metal-epoxy composites, which, according to Littlewood and Briggs [7], are due to particle separation resulting from differential thermal expansion.

Various formulas [8-11] have been proposed for calculating the dependence of resistivity on the volume per cent of conducting particles in ohmic composites. Scarisbrick [12] suggested formulas for bulk and surface conductivity which incorporate a geometrical factor. Coutts [13], in a review paper, demonstrated that electrical conductivity of several mixed phase systems can be predicted on the basis of percolation conduction. In non-ohmic composites, the current-voltage behaviour was found to obey a power relationship (Sodolski *et al.* [14]), but no definite conclusion on the conduction mechanism was reached.

In this work, the electrical conduction of composites made from unsaturated polyester with silver powder (SP) and silver-coated glass spheres (SCGS) as fillers has been investigated. The electrical behaviour of composites formed with the latter filler material has not been reported in the literature. Both types of samples, when freshly prepared, exhibited switching effects and are generally non-ohmic.

It has been noted by several authors [1, 9, 12, 15] that the degree of dispersion of the filler is an important parameter influencing the threshold concentration at which a sharp drop in resistivity occurs. With our sample preparation procedure, high uniformity in particle distribution is achieved in samples with silver-coated glass spheres as filler. There is a noted difference between the threshold concentrations for SP and SCGS composites.

The results of this work indicate that electric current is conducted via discrete paths in the non-ohmic samples investigated and that several different mechanisms may be responsible for electrical conduction at different stages.

2. Sample preparation and measuring circuit

The samples are prepared from an unsaturated polyester resin, PolyLite 499 (DIC, Japan) with 5% by weight MEKP hardener. Samples set at room temperature (20°C) are transparent and soft and will not harden for a few days. When formed with silver powder or silver-coated glass

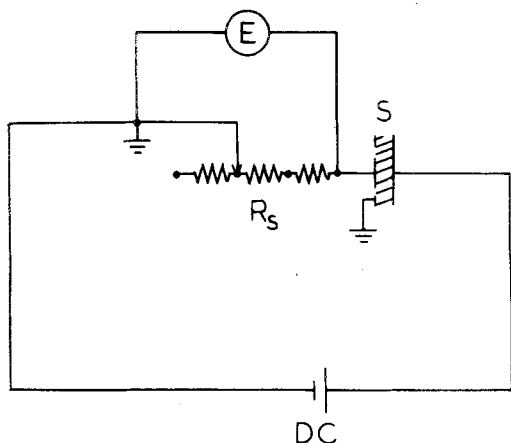


Figure 1 Circuit for high resistance measurement: E—electrometer, R_s —standard resistors, S—sample and DC—regulated power supply.

spheres as filler, they are brown and opaque. Hardness may be achieved by heat-curing.

The sample preparation procedure is as follows. First, Polylite and hardener are thoroughly mixed and then a known amount of filler is stirred into the mixture. After degassing, the mixture is transferred to a sample moulder mounted on a rotor in an oven. The rotor is set to run at 5 rev min^{-1} (to prevent sedimentation of the filler) with the oven temperature kept at 60°C for 16 h. The baked specimen is hard and has dimensions of 6.4 cm diameter and 2 mm thickness. Silver epoxy with an area of 10 cm^2 is pasted onto both surfaces after polishing, and subsequent curing at 60°C for 2 h is required.

For resistance measurements on high resistance

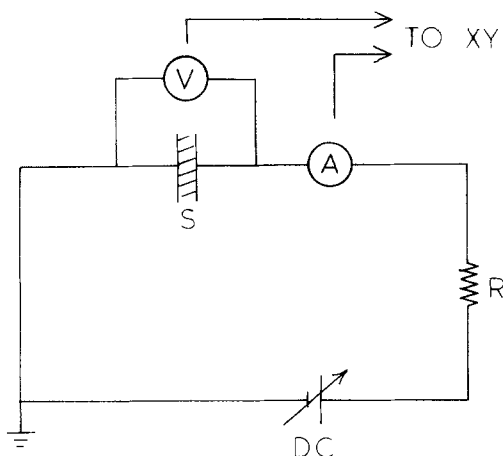


Figure 2 Circuit for low resistance measurement: XY—XY-plotter.

samples, the circuit shown in Fig. 1 is used. An additional ring of silver epoxy is pasted onto such samples for use as a guard ring to eliminate the effects of surface currents.

For low resistance samples, the circuit shown in Fig. 2 is used. In studying current–voltage characteristics, the voltage is allowed to vary with the outputs recorded on an XY plotter.

It has been noted that the resulting I – V plot is non-linear and moreover depends on the history of the voltage applied, i.e. there is a conditioning effect. This will be described in Section 4. The rate of increase of the applied voltage was standardized to 4.5 V min^{-1} .

The study of the I – V relationship for SCGS samples consists first of applying a gradually increasing voltage at a rate of 4.5 V min^{-1} , starting from zero, across the sample until its switch-on voltage is reached, i.e. until a sudden jump in current is observed. This has been called the first run. Then a second run, again starting from zero, brings the applied voltage to about the switch-on voltage.

3. Results

3.1. Switch-on voltage and subsequent conditioning

Investigated samples made with silver powder (average size $\sim 1 \mu\text{m}$) have filler volume concentration from 0 to 6% whilst those made with silver-coated glass spheres (average diameter $\sim 10 \mu\text{m}$) have a concentration in the range 0 to 30%. Photomicrographs of both types of samples are shown in Fig. 3. SCGS samples show reasonably even particle distribution with no cluster formation.

All freshly prepared samples studied have negligible conductivity when a small voltage is applied across them. Considerable current is observed only after a certain “switch-on” voltage is reached. The upper limit of the conductivity below the switching threshold is about $10^{-12} \text{ ohm}^{-1} \text{ m}^{-1}$. The switch-on voltage is found to depend to a great extent on the concentration of the filler. Figs 4 and 5 exhibit the threshold (switch-on) voltage for SP samples and SCGS samples, respectively, as a function of the filler concentration. In comparison it is noted that a much higher concentration of SCGS filler is required to obtain a switch-on at a particular voltage and that the switch-on voltage in the SCGS samples is higher than in the SP samples for the same concentration. The difference may be due to

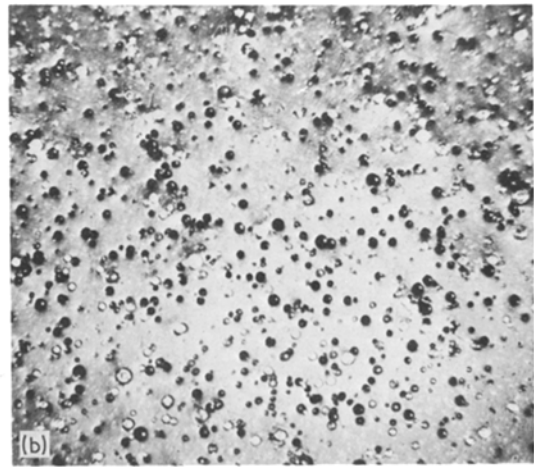
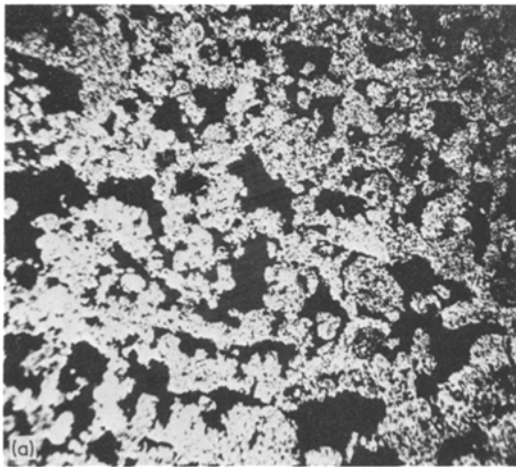


Figure 3 (a) Section of a 6% SP sample, (X 250); (b) Section of a 6% SCGS sample, (X 250). No cluster formation is observed.

large particle size and a more even particle distribution in the case of the SCGS filler. Furthermore, it should also be noted that silver-coated glass spheres are spherical while silver powder particles are quite irregular in shape. The sharp edges of the silver powder particles may create very high local electric fields between adjacent particles, thus resulting in a lower switch-on voltage. Fig. 6 shows an $I-V$ plot of an SCGS sample on the first run,

with the applied voltage going beyond the threshold. It is noted that the current is highly unstable after the switch-on.

Typical second runs from zero to about the switch-on voltage for both types of samples are shown in Figs 7 and 8. An SP sample does not behave quite as steadily as an SCGS sample with respect to voltage-current characteristics. The instability in electrical behaviour of SP samples is

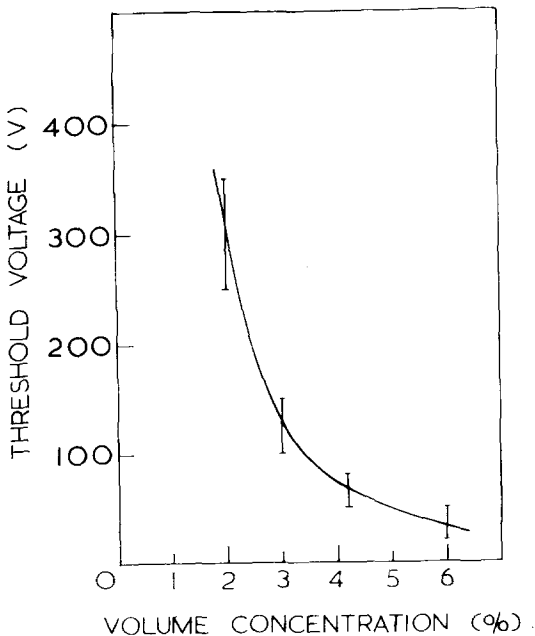


Figure 4 Threshold voltage plotted against concentration of silver powder.

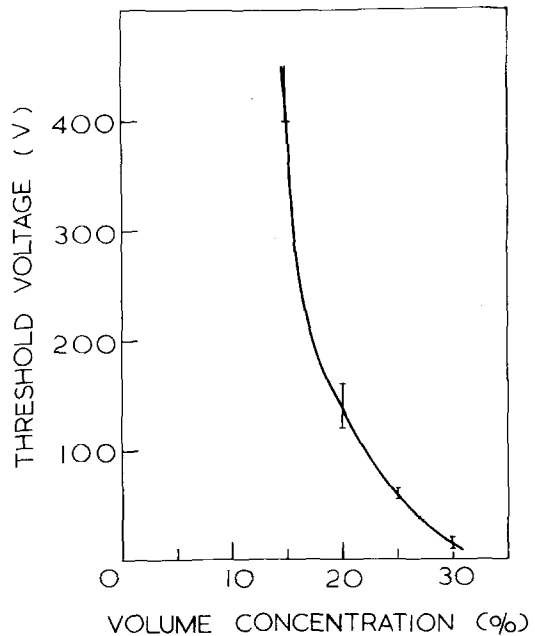


Figure 5 Threshold voltage plotted against concentration of silver-coated glass spheres.

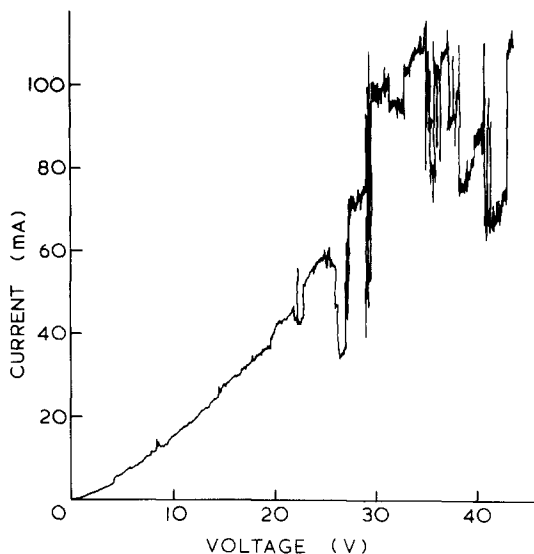


Figure 6 I - V plot of an SCGS sample on the first run, with the applied voltage going beyond the threshold.

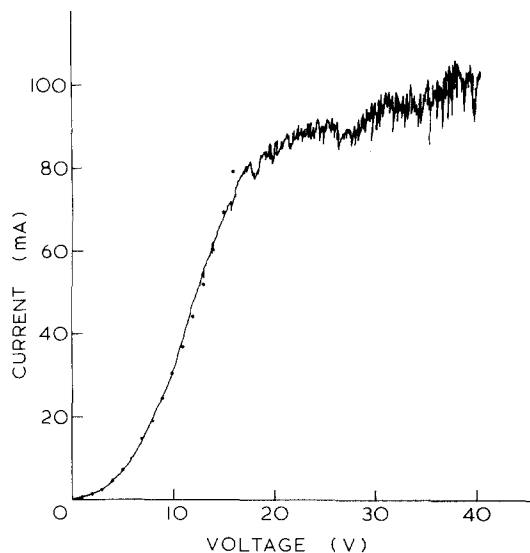


Figure 8 Typical second run for an SCGS sample. The dotted line shows the theoretical fitting $I = 0.28 V^{2.9}$.

especially severe when the applied voltage is beyond its switch-on voltage. Thus, SCGS samples are used for studying electrical behaviour under higher fields. They show noted non-ohmic characteristics.

It is also found that both types of samples with higher concentrations of filler show switching effects similar to those reported by de Araujo and Rosenberg [6], though the switching voltages are not quite reproducible.

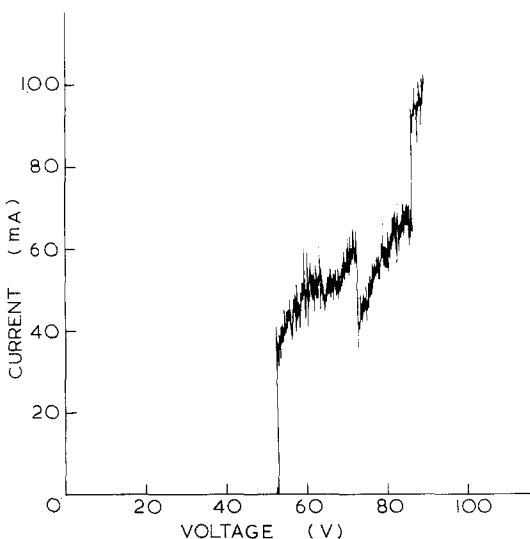


Figure 7 Typical second run for an SP sample. Instability in current beyond 25 V (its switch-on voltage) is quite severe.

3.2. Concentration threshold for SP and SCGS samples

The SP samples, after conditioning at 150 V for several hours, exhibit more stable electrical behaviour at lower voltages. Fig. 9 shows successive current-voltage plots for a typically conditioned SP sample. Resistivities of the samples of various concentrations are then measured by using a voltage of 20 V, yielding a typical resistivity-concentration plot with a sharp drop of about 10 orders of magnitude occurring between 2 and 3% as shown in Fig. 10. On comparing this threshold concentration with the data reported in other experiments [6, 9, 11, 15] and with predictions based on percolation theory [13, 16], its value appears to be quite low. On examining the photomicrographs of sections of two 3% specimens, no "conduction chains" formed from direct contact of silver particles are observed. This it seems that the appearance of the threshold concentration observed in this work has no obvious connection with percolation conduction.

Similar results are obtained from the SCGS samples with the same applied voltage of 20 V, but the threshold concentration occurs between 18 and 25%, as shown in Fig. 11. Typical successive current-voltage plots for an SCGS sample after conditioning are shown in Fig. 12.

3.3. Current-voltage characteristics

While studying rubber-black composites, van Beek

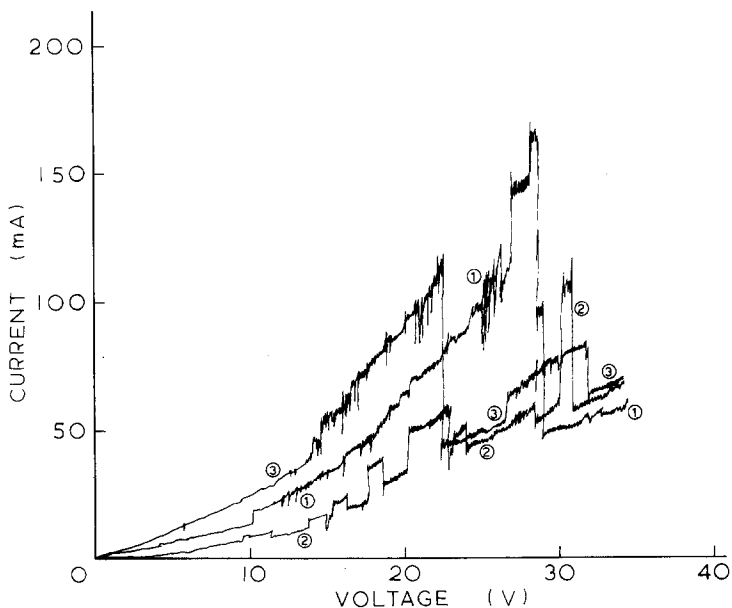


Figure 9 Successive I - V plots for a typical conditioned SP sample. (1), (2) and (3) are the first, second and third plots, respectively.

and van Pul [17] suggested that an expression of the type

$$I = AV^n e^{-B/V} \quad (1)$$

is satisfactory in relating the current I passing

through a sample with the applied voltage V , where A , B and n are constants for a given sample with n normally between 1 and 3. Equation 1 is connected to electrical conduction by internal field emission

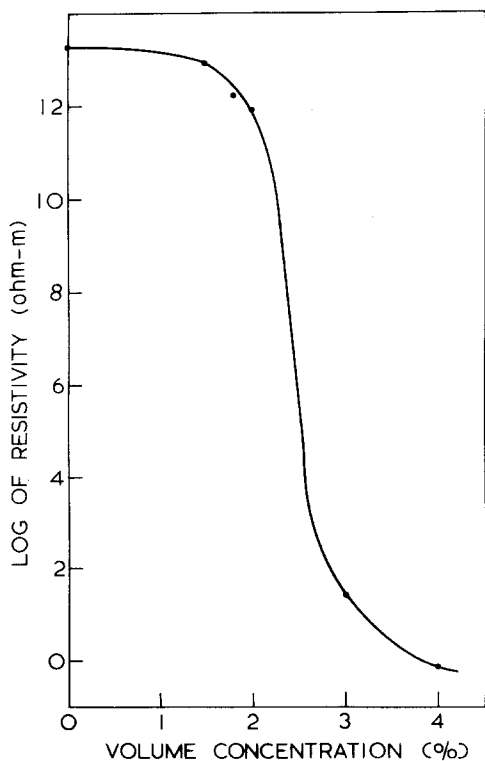


Figure 10 Resistivity-concentration plot for SP samples showing a drop of about 10 orders of magnitude between 2 and 3%.

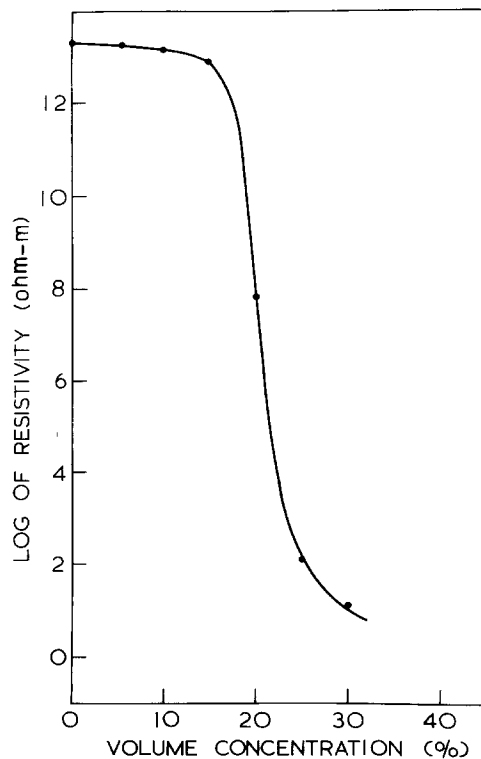


Figure 11 Resistivity-concentration plot for SCGS samples showing a drop of about 10 orders of magnitude between 18 and 25%.

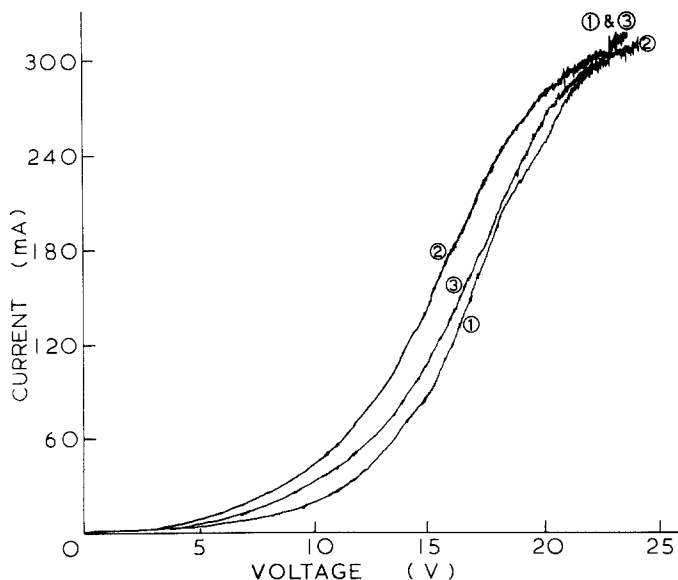


Figure 12 Successive I - V plots for a typical conditioned SCGS sample. (1), (2) and (3) are the first, second and third plots, respectively.

between adjacent carbon black particles. Sodolski *et al.* [14], however, found that the expression

$$I = AV^n \quad (2)$$

is satisfactory for describing samples with carbon black concentration in the range 0.4 to 1 phr*; they found that n ranges from 1 to 1.85 and that there is no obvious correlation between n and the concentration of the filler.

The current-voltage characteristics of the well conditioned SCGS samples investigated show non-ohmic characteristics which can be described by Equation 2 at low voltage, with n ranging from 2 to 3.

4. Discussion on possible conduction mechanisms

By removing the conducting paint on one face of the conditioned sample and electroplating in dilute copper sulphate solution, it is established by visual observation that electrical conduction in the sample is through selected conduction paths, rather than by bulk conduction. In fact, the number of spots of copper deposition ("conduction paths") on a sample depends on its filler concentration. The total number of visible spots on SCGS samples of varying concentrations are listed in Table I. When some of the spots are then insulated from the solution, deposition is found to occur on other new spots. This would mean new "conduction paths" are formed.

* phr: parts per hundred parts of resin.

We believe the mechanism for the first onset of conduction at the threshold voltage is by electrons hopping through the gaps left open in the more or less random distribution of the conducting filler material.

Once a current is flowing, the following may then happen. In the first stage, the electrons bombarding a silver particle may be energetic enough to break some metallic bonds, thus setting free some silver ions which are then driven by the local field in a direction opposite to the electron flow. The net result is that silver is sputtered along some path forming a "filament", which is the "conduction path" mentioned earlier. The formation of a metallic filament is reported by Zarabi and Satyam [18] and has been identified as the switching agent for the switching effect observed in copper oxide. The samples investigated here also exhibit switching effects though with quite irregular switch-on and switch-off voltages.

The stage after switching-on is believed to be a conditioning stage in which permanent changes in the sample occur. A typical current-voltage plot corresponding to the second run (as detailed in

TABLE I

Concentration of silver-coated glass spheres (%)	Number of spots
20	0
25	10-20
30	40-50
40	over 300

Section 2) is shown in Figs 7 and 8. Sudden finite jumps (up or down) and spikes in the current are characteristic of conditioning. It is noted that the current tends to increase in between jumps though spikes occur everywhere. Since conduction is due to discrete conduction paths, a finite jump may be associated with the formation of a new path or the destruction of an existing path. The formation or destruction of a path may be brought about by (i) the formation or burning-out of a silver "filament" discussed above, by (ii) a rearrangement of silver particle sites due to stress relaxation in the polymer made possible by local softening of the polymer due to the heating effect of the current, or by (iii) a rearrangement of silver particle sites due to intense local electric fields.

It has been noted that a much higher concentration of SCGS filler is required to obtain a switch-on at a particular voltage than is required for SP samples of the same concentration. This may be due to better dispersion, but, of course, the larger particle size and the spherical shape of the SCGS samples may be the cause.

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