

Non-ohmic I – V behaviour of random metal–insulator composites near their percolation threshold

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A large increase in electrical conductivity has been observed when a direct current voltage is applied to random metal–insulator composites near their percolation threshold. This reversible non-ohmic I – V behaviour, which is similar to that observed in zinc oxide varistors, has been studied in three metal/insulator systems including silver particles in a matrix of potassium chloride, and two different systems of nickel particles in a matrix of polypropylene. These composites have all been prepared by mechanically mixing metal particles with an insulator host in predetermined volume fractions. A physical model with a semi-phenomenological equation has been proposed to describe this non-ohmic I – V behaviour. The non-ohmic effect is postulated to arise from a localized reversible dielectric breakdown between narrowly separated metal clusters in the metal/insulator composite.

1. Introduction

The phenomenon of a large increase in electrical conductivity from a mixture of metal particles (filings) within a non-conducting medium under an external field was first observed by Branly in 1890 [1, 2]. He found that by applying a radio frequency (r.f.) field or an electric spark at some distance from metallic filings randomly dispersed in a vessel, new conducting paths could be created where there were none initially. This effect was applied by Marconi in his early wireless telegraph device as an electromagnetic wave detector [3]. However, the physical mechanisms are still not entirely understood.

A system very similar to that which Branly studied is the so-called random metal–insulator composite, where metal particles are randomly dispersed in an insulator matrix. At low metal volume fractions, no infinite conducting paths exist in the sample and the bulk sample behaves like an insulator. Increasing the metal volume fraction creates continuous connections between metal particles, and the resistivity of the sample decreases significantly. The critical volume fraction where the transition from insulator to conductor occurs is usually called the percolation threshold, P_c . Further increases in metal volume fraction create more metal particle networks, however, these networks decrease the bulk resistivity only slightly.

The effect of an external applied electrical field on the electrical conductivities of metal–insulator random composite has not been fully studied. For metal/insulator composites with metal volume fractions slightly above P_c (i.e. a conducting sample), thin films

made by co-sputtering from a nickel and an SiO_2 target on to fused quartz substrates have been studied by Sheng and co-workers [4, 5]. These two-dimensional random composites have very fine metal particles (average diameter about 6 nm) and very thin insulating barriers between adjacent metal grains (average separation distance about 1 nm). At low temperature, 1.25 K, the d.c. conductivity, G , shows an exponential dependence on electric field, E , in the form of $G \sim \exp(-E_0/E)$, where E_0 is a constant related to the metal grain size and the separation of the insulating barrier. This effect has been attributed to the field-induced electronic tunnelling between adjacent metal particles separated by one or more insulating barriers. However, this effect diminishes gradually as the temperature increases due to the increasing density of thermally excited charges. Near room temperature, G becomes field independent with a temperature dependence of $\exp(-1/kT)$.

For samples with the metal volume fraction below P_c , the effect of applied field on the conductivity has not been systematically studied. It had been reported that non-ohmic I – V behaviour at room temperature has been observed in some metal–polymer or carbon–polymer random composite systems [6–9]. Sodolski *et al.* [8] suggested that the I – V curves generally follow a power-law expression, $I = AV^n$, where A is a constant, and the exponent n ranges from 1–1.85.

Similar non-ohmic I – V behaviour have been reported by Kwan *et al.* [7] on silver-coated glass sphere (SCGS)–thermosetting polyester composites and,

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further, that a switching effect (i.e. a dramatic increase in conductivity when the applied voltage is beyond a certain value) can be observed. However, the conductivity was highly unstable after the composite had switched-on. Further, this composite exhibited more stable electrical conductivity if it had been previously "conditioned" at a high voltage for a long period of time. The switch-on voltage decreased as the SCGS volume fraction increased. The switching effect was verified experimentally by using an electrochemical technique that found newly created conducting paths arising from strong local electric fields. The creation of the new conducting path was proposed to be initiated by electron hopping between conducting particles, followed subsequently by high-energy electrons bombarding metal atoms into the ionic state and causing ionic transport through the insulating layer. Finally, a metallic filament across the plastic barrier may be created [10, 11].

More recently, Ag-KCl random composite specimens below (i.e. on the insulating side), but very close to the percolation threshold, were studied. This system also showed a switching effect on conductivity as the external direct current (d.c.) potential field was increased [12]. In the present study, the previous work [12] is extended to three systems of random metal/insulator composites slightly below their percolation threshold. These three systems are silver particles in the matrix of potassium chloride (Ag-KCl) and two systems of nickel particles in the matrix of polypropylene (PP). In the latter two systems, the polypropylene matrix was the same but the morphology of the nickel was varied, using filamentary nickel particles in one (Ni/F) and nodular particles in the other (Ni/N) [13]. These composites have all been prepared by mechanically mixing metal and insulator particles in predetermined volume fractions. Filamentary-shaped nickel particles show a spiky surface geometry and tend to form long chain-like agglomerates, while nodular-shaped nickel particles have much less tendency to form clusters. This geometric difference in metal particles has been used to study the influence of metal phase geometrical shape on the electrical properties. The Ag-KCl system is a metal-ionic salt composite, and the relative size of the metal particles is much smaller than in the Ni-PP systems which are metal-polymer composites. Thus, the effect of matrix phase on the electrical properties has been examined. The repeatability of the non-ohmic effect has also been investigated.

2. Experimental procedure

2.1. Sample preparation

The Ag-KCl specimens were prepared previously [14] using several pressing/grinding cycles of silver (average particle size 20 nm) and KCl powder. The final pressed pellets were coated with either gold (by sputtering) or silver (with silver paste) to ensure good electrical contact on the surface of the specimen.

For Ni/F-PP and Ni/N-PP specimens, pre-weighed metal and insulator powders in appropriate ratios were thoroughly mixed using a vortex mixer

and metal ball milling. X-ray energy dispersive spectrum (EDS) analysis of the mixed powder was performed and showed no detectable level of contamination from metal ball milling. The mixed powder was then pressed into a pellet using a hydrostatic press with a maximum pressure of 900 MPa. During the pressing process, the die was slowly heated to 95–100 °C, which is above the heat deflection temperature of polypropylene (PP). Filament shaped nickel (Ni/F) particles with a spiky surface are formed into chain-like structures resembling strings of small nickel beads with an aspect ratio about 5–10. The nickel beads have an average bead size about 1.2 µm. Nodular-shaped nickel particles have a rough surface with an average particle size about 9.2 µm. The PP particles have a rough surface and irregular shape with an average particle size about 1.6 µm. Both PP and metal particles show a log-normal distribution [15]. Density measurements of Ni/F-PP and Ni/N-PP specimens have been performed using Archimedes' method. No, or very low, porosity in the samples was observed after compaction.

2.2. Electrical properties measurement

For the Ag-KCl specimens, the electrical properties were measured by superimposing a small alternating current (a.c.) signal on to a d.c. field through a HP4192A LF impedance analyser. The amplitude of the small a.c. signal was 10 mV. Sample response for frequencies between 5 Hz and 13 MHz were recorded at various d.c. potentials. Each of these reported impedances is an average value of five consecutive measurements.

Conductivity measurements and I - V curves were performed using a HP4140b pA meter/d.c. voltage source. All the resistance data shown here have a correlation coefficient of 0.90 and above for the slope calculation from the I - V curve. Measured data were recorded using an IBM-PC through IEEE-488 interfacing system.

3. Results and discussion

The effect of an external electric field on the electrical properties of the random composite specimen has been measured by superimposing a small a.c. signal on a d.c. field. Fig. 1 shows the impedance response of a specimen which has a silver volume fraction equal to 0.213 under different external d.c. fields. This sample is very close to the percolation threshold in this Ag/KCl system (insert, Fig. 1). For low external d.c. fields, (0–1 V), the complex conductivity or admittance of the specimen is relatively independent of the external d.c. potential. At about 1 V d.c., an increase in the real part of the conductivity is observed. The d.c. conductivity, G , can be estimated from the impedance data by determining the real part of the admittance as the frequency approaches zero. The d.c. conductivities, G , of four samples in the neighbourhood of the percolation threshold are plotted as a function of d.c. field potential, $V_{d.c.}$, in Fig. 2. The capacitance, C , and

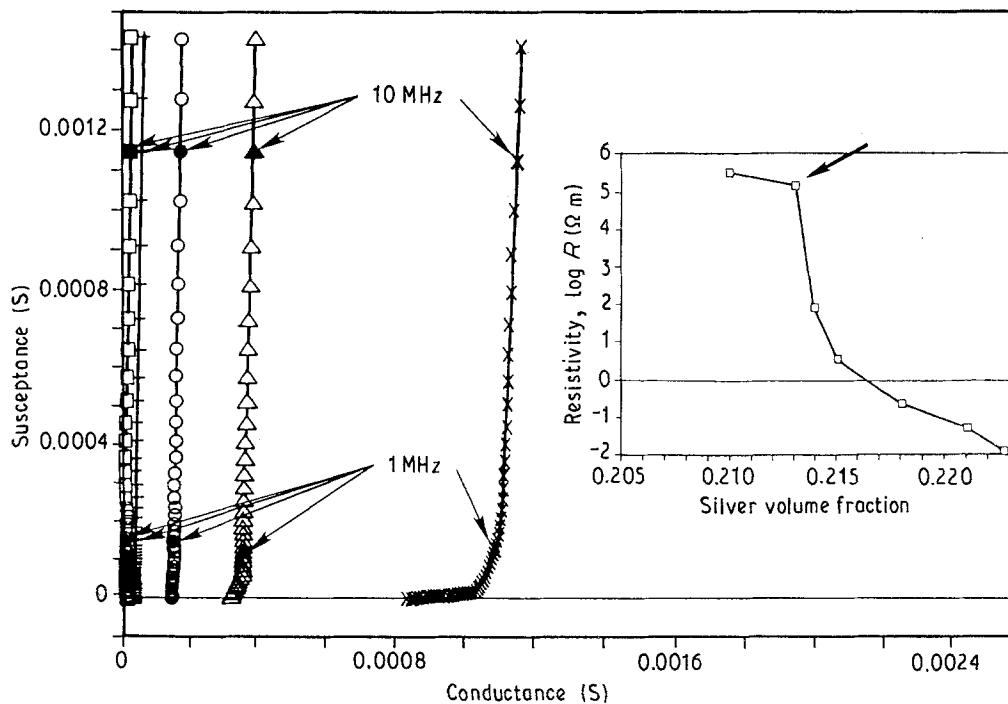


Figure 1 The a.c. response in the complex admittance plane of one specimen (volume fraction of silver = 0.213) under different external d.c. potential: (\square) 0–0.8 V, (+) 0.9 V, (\circ) 1.3 V, (\triangle) 2.0 V, (\times) 3.0 V. Insert shows the sample's relative location in the metal-to-insulation transition region.

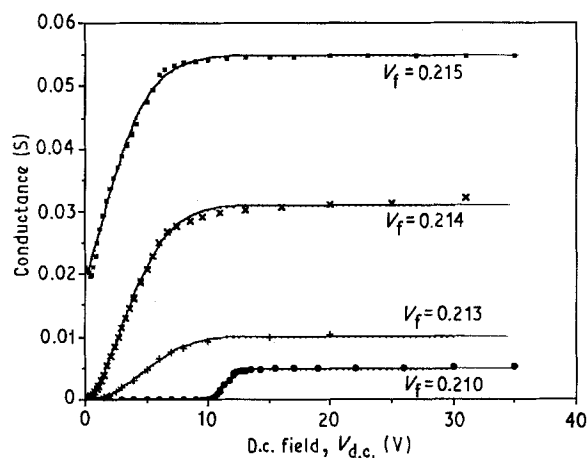


Figure 2 The effect of an external d.c. potential field, $V_{d.c.}$, on the d.c. conductance, G . Points correspond to the experimental data and the solid line corresponds to the best fit of Equation 1.

dielectric loss tangent, $\tan \alpha$, do not show significant variation as the d.c. potential field is increased.

The admittance increase in Fig. 1 observed along the horizontal axis in the admittance plane at high d.c. external potentials as frequency is increased is believed to result from a time-dependent process which will be discussed later. When the a.c. measurements were made in the reverse direction (from high frequency to low) immediately after the forward scan at the same d.c. potential, the horizontal region was not observed. Thus, this material requires time both to become conducting (switch-on) and time to return to its original state (switch-off). The data shown in Figs 1 and 2 are reproducible as long as the material is given sufficient time to relax back to its initial state. For example, the data shown in Fig. 2 for the sample with 0.213 silver volume fraction were obtained from two

separate measurements separated by about 6 months. Although the exact time constant, i.e. the time required to return to e^{-1} of the saturated conductance, for this "healing" process has not been measured, it appears to be on the order of minutes at room temperature. The time required to return to the original state is, of course, much longer.

To illustrate the magnitude of the change in conductivity as the field is applied, the conductivity is plotted semi-logarithmically in Fig. 3 for the sample with a silver volume fraction equal to 0.210. The conductivity changes by over four orders of magnitude in a 1 V region between 9 and 10 V. There is also good agreement between the open squares, obtained from the a.c. impedance analyser by the method described above, and the closed circles, taken by applying a d.c. voltage and measuring the current. Thus, the

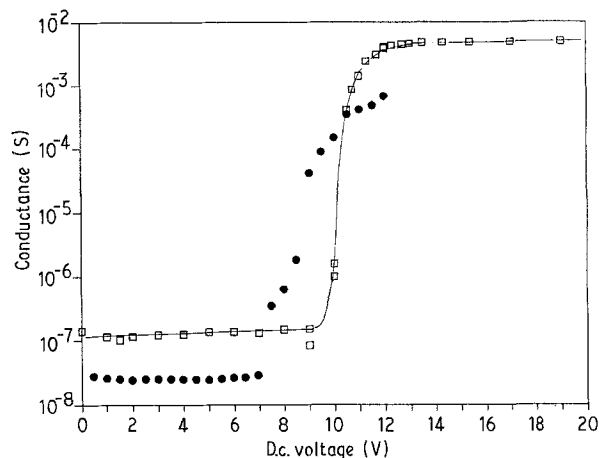


Figure 3 The effect of an external d.c. potential field, $V_{d.c.}$, on the d.c. conductance, G , from two different measurements. (\square) Data obtained from a.c. impedance analysis, (\bullet) data obtained from d.c. I - V measurements.

applied a.c. potential is not overly influencing the system as expected. The differences between the two measurement methods in the low-voltage d.c. region are an artefact of the low-input impedance of the a.c. impedance analyser. However, only a slight change is observed in the voltage where the conductivity increases: the switching voltage, V_{do} . The lower V_{do} in the d.c. I - V measurement may be due to some small fraction of unrecoverable dielectric breakdown in some of the newly created conducting paths which occurred during the first runs of the a.c. impedance measurements. The limitation of maximum current allowed using the pico-ammeter prohibits reaching the saturation stage. These results also indicate the relative reproducibility of the switching effect.

The large increase in conductivity which occurs in a narrow range of applied potential indicates that there must be new conducting paths being created by the electric field. The mechanism of the creation of these new paths is not known, but may be related to the strong inhomogeneity of the field inside the composite. Below the percolation threshold there are numerous metal clusters each of which is isolated from, but closely spaced to the others. Assuming that the local electric field intensity between the clusters in the sample is inversely proportional to the distance between them, the conductivity will be a strong function of the applied d.c. potential because new conducting paths can be created as the local electric field increases above the dielectric breakdown field of the insulator. The number of new paths created will depend on the applied potential. At low d.c. fields, there are no local regions with fields high enough to cause conduction. Thus the conductivity does not change significantly. As the bias is increased, regions with the smallest inter-cluster spacing would conduct first, then more and more regions would become conducting with increasing bias. If the inter-cluster spacing follows a normal distribution, the rise in conductivity would be given by the cumulative distribution function for the normal probability density function [16]. Finally, nearly all of the inter-cluster regions would be conducting so that a linear relationship between conductance and d.c. bias would arise from simple ohmic behaviour.

Recent work [17] shows that the inter-particle spacing does not actually follow a normal distribution, but rather has a distribution which depends on the fractal dimension, d_f , of the metal clusters. Functionally, this leads to a conductance, G , given by

$$G = (G_s - G_o)[1 - \exp(-V_{d.c.}/V_{do})^{n(d_f)}] + G_o \quad (1)$$

where G_o and G_s are the d.c. conductance at initial and saturation state respectively, $V_{d.c.}$ is the applied d.c. field to the composite, V_{do} is the voltage required to cause the metal clusters with the most probable separation distance to conduct, and $n(d_f)$ is the breakdown exponent related to the fractal nature of the cluster. A simplex non-linear fitting scheme has been used to obtain the parameters described above [18]. An excellent fit between Equation 1 (solid lines in Fig. 2) and experimental results (symbols) indicates that the model described above is adequate to account

for the switching effect. A clear switching effect on G is observed as the d.c. electric field ($V_{d.c.}$) approaches V_{do} . The magnitude of the conductance change during switching is dependent on the metal volume fraction, varying from nearly five orders of magnitude at silver volume fraction of 0.213 to less than one order of magnitude at a silver volume fraction of 0.215 (Fig. 4). The closer a sample is to the percolation threshold, P_c , the smaller the change in conductivity during switching.

To quantify better the changes that occur in the conductivity when a d.c. field is applied to various different samples, the fitting parameters, $n(d_f)$ and V_{do} of Equation 1, are plotted as a function of silver metal fraction in Fig. 5. The switching voltage, V_{do} , and the breakdown exponent, $n(d_f)$, both decrease when approaching the percolation threshold. This is consistent with the description above where the voltage required

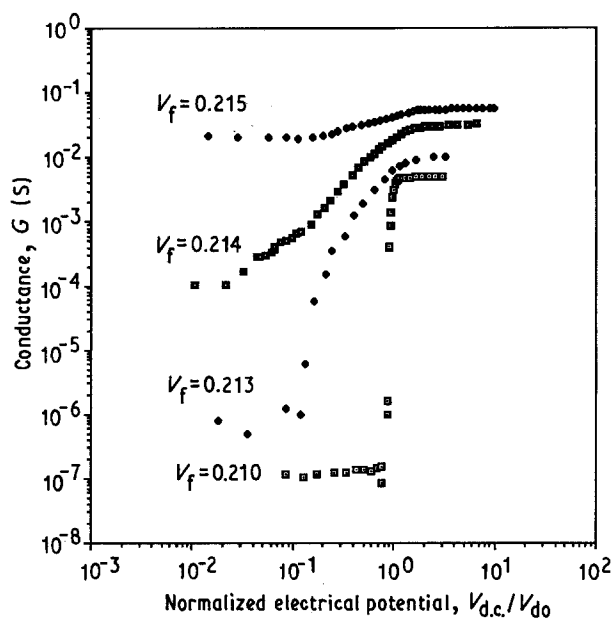


Figure 4 A log-log plot of the d.c. conductivity, G , versus normalized potential ($V_{d.c.}/V_{do}$) of the data shown in Fig. 2.

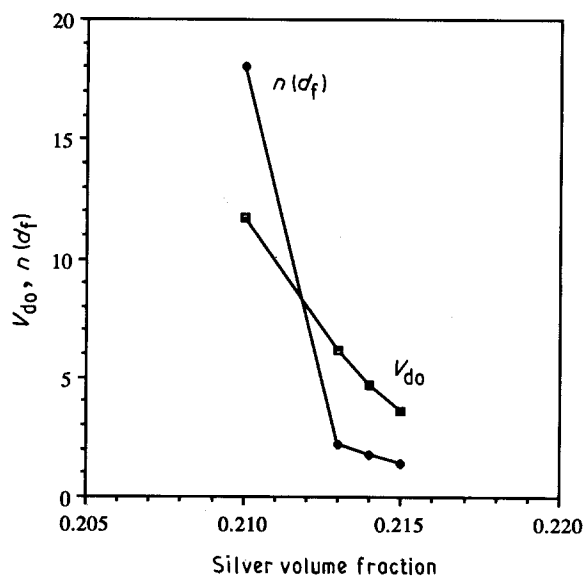


Figure 5 The parameters V_{do} and $n(d_f)$ as a function of silver volume fraction. The data are obtained from the best fit of Equation 1.

to initiate dielectric breakdown locally should decrease as the number and size of clusters increases when nearing percolation. The exponent, $n(d_r)$, which can be measured from the slope of transition region in Fig. 4, should also decrease for the same reason.

A similar non-ohmic $I-V$ behaviour has been observed in both types of Ni/F-PP and Ni/N-PP composite specimens near the percolation threshold, as shown in the $I-V$ response of a sample with 6.00 vol % Ni/F (Fig. 6). Two voltage levels with different magnitudes have been applied to the specimen consecutively as shown in the insert of Fig. 6. For the low level output, a relatively linear current response is observed. For an applied voltage level five times larger, a non-linear current response is observed as shown. Because linear portions of an $I-V$ curve represent a constant conductance, both the initial region shown in Fig. 6 and the region at higher potentials have a constant G . A reverse in the potential shows a relatively symmetrical non-linear behaviour.

The switching effect shown in Fig. 6 is very similar to that observed in the Ag-KCl composite specimens. In both cases, the materials show two different conducting states as the potential is increased. Further, the magnitude of the change in conductivity after switching is also similar in the two sets of samples.

The $I-V$ response shown in Fig. 6 is quite reproducible as shown in Fig. 7 where the response of three consecutive cycles of equal voltage level for a Ni/F-PP sample with 7.00 vol % Ni/F is shown. As in the Ag-KCl system, the Ni/F system also does not return immediately to its original state. This manifests itself by the presence of a hysteresis loop in the $I-V$ response between the upward and downward sweep of voltage. To show this hysteresis phenomenon better, the data of Fig. 7 are replotted on a semi-log scale of log current versus applied voltage in Fig. 8. The current changes several orders of magnitude at a critical voltage. A further increase in voltage does not change the current significantly. Subsequent decreases in voltage do not decrease the current significantly until a

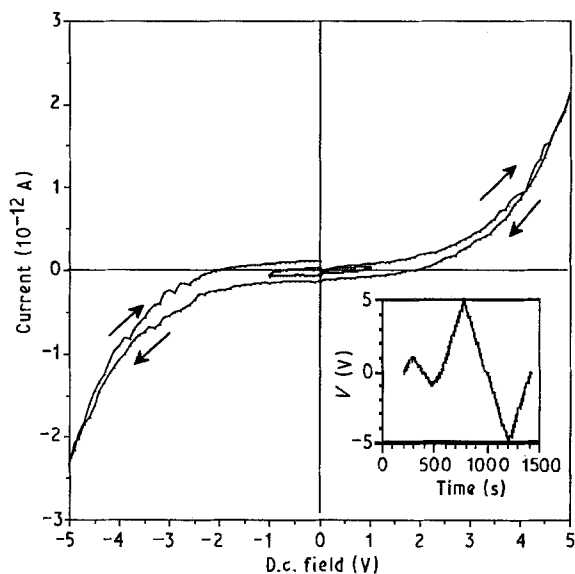


Figure 6 The $I-V$ curve of an Ni/F-PP sample with 6.00 vol % Ni/F. The insert shows the d.c. output waveform.

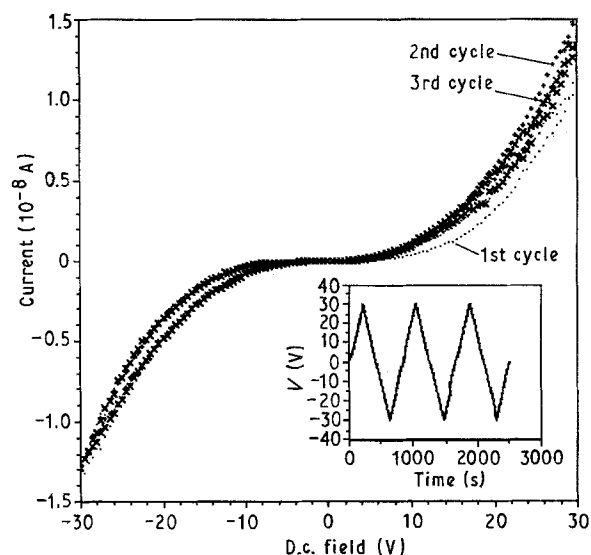


Figure 7 The $I-V$ curve of three consecutive cycles of equal voltage level for a cylindrical shaped Ni/F-PP sample with 7.0 vol % Ni/F.

relatively low voltage level. This hysteresis phenomenon suggests that the conduction mechanism is associated with some kind of excitation/relaxation process of the charge carriers. An accurate time constant of this relaxation process has not been performed.

Preliminary experimental work shows no direct relationship between metal volume fraction and the switch-on voltage as was observed in the Ag-KCl composites (Fig. 4). The wide spread in d.c. resistivity near the percolation threshold may mask this relationship [15]. A modification of the preparation procedure with repeated grind/compact processes, such as that for Ag-KCl specimens, may yield a better random distribution of metal particles and reduce the experimental scatter.

The Ni/N-PP specimens behave very similar to that of Ni/F-PP specimens, except that a relatively higher switching voltage (about 70 V) is observed [15]. The higher switching voltage associated with Ni/N-PP samples is postulated to arise from two effects, the difference in particle sizes between the Ni/N particles (mean diameter = 9.2 μm) and the Ni/F particles (mean diameter = 1.2 μm), and the difference in nickel particle morphology (spiky versus smooth). Both these features would tend to increase the local electric field between clusters in the Ni/F-based composites compared to that for the Ni/N materials. Such an increase would then lead to lower switching voltages for the former material compared with the latter, as observed.

Three effects must be considered to elucidate this non-ohmic switching effect. First, new conducting paths must be created in the narrow insulating barrier at a certain critical potential field. Second, a conduction mechanism capable of predicting the relationship between the current and the external electrical field must be developed. Third, the conduction mechanism must be able to explain the relaxation process which returns the sample to its original state after the d.c. electric field has been turned off.

The initiation of new conducting paths is probably related to the high local electric field at narrowly

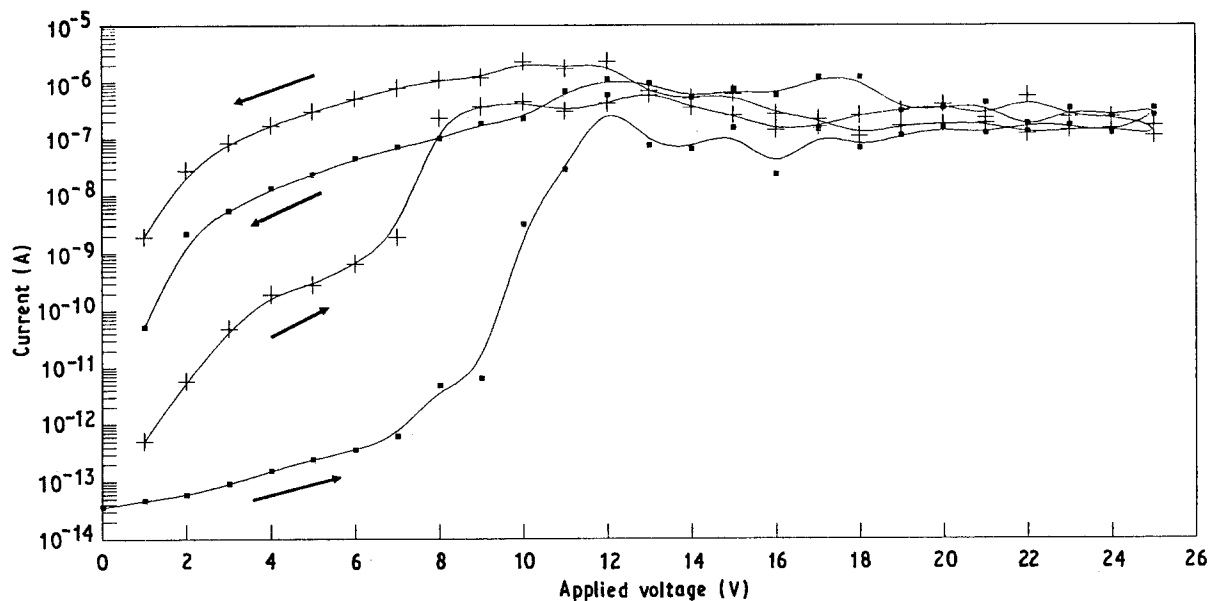


Figure 8 The semi-log scale I - V curve of the sample discussed in Fig. 7. (■) Run 1, $dt = 10$ s; (+) run 2, $dt = 10$ s.

separated metal clusters. Dielectric breakdown is usually thought of as permanent damage to an insulating material by high electric fields. The permanent damage is the consequence of destruction of material by heating in a localized current path. The initiation of dielectric breakdown has been studied by Anderson and Kurtz [19] by using a method to measure the distribution of electrical charge (space charge) within dielectric films. The results show that the onset of dielectric breakdown may be caused by tunnelling of electronic carriers into higher energy states by the build-up of local high electric fields. This process generates large current densities as well as heat which leads to dielectric breakdown. It has also been suggested [20] that the high local electric fields may be strong enough to bend the electron bands near the metal-insulator interface so that thermally activated electrons can move through the insulator. Direct measurement of the Ag-particle agglomerates of Ag-KCl specimen in TEM shows the spacing in the range of tens of nanometers between agglomerates [12]. Thus, the local electric field intensity is on the order of 10^8 V m⁻¹, which could very well cause local dielectric breakdown in such regions.

The mechanism operating here is clearly not traditional dielectric breakdown because it is reversible. We propose a mechanism for the materials studied here which explains the entire reversible electrical switching phenomenon as follows: excess space charges are created in the dielectric material surrounding the conducting particles as an external field is applied due to the strong local electrical field, as discussed above [19]. The newly created excess charge carriers are capable of hopping [10, 21] under a strong local electrical field and thereby carry a limited amount of current. As the external electric field is increased, the local electrical field also increases giving rise to even larger numbers of charge carriers. The conductivity thus continues to increase. The conductivity will saturate when the rate of generation and recombina-

tion of the charge carriers becomes equal. This effect can explain the time-dependent conductivity increase in Fig. 1. When the external field is removed, the excess space charge as well as any material defects caused by the strong electrical current start to recover to their stable stage. This recombination procedure is a time-dependent relaxation process. Because these newly created conductive paths are randomly distributed in space throughout the composite, joule heat generated by the increased current can be released to the matrix without overheating any localized points. Thus, permanent damage from overheating can be avoided.

The bulk d.c. conductivity is the sum of the current through all the narrowly spaced metal clusters, and can be expressed empirically by Equation 1, as discussed previously. Because the number of metal clusters which are susceptible to the formation of conducting paths increases as the metal volume fraction approaches the percolation threshold [7], a large number of potential conducting sites are available to the composite near the percolation threshold. Thus, the switching voltage will decrease rapidly as the metal volume approaches P_c .

Functionally, this non-ohmic switching phenomenon is very similar to that of commercial varistors, which are made of sintered zinc oxide (ZnO) particles with small amount of trace metals such as bismuth, cobalt, manganese, etc, which form electrically insulating barriers at the ZnO grain boundaries. An empirical power-law relation identical to Equation 1 can be used to describe the current transition region for a varistor. The critical exponent, n , is equal to $d(\ln I)/d(\ln V)$ of the transition region, with typical values of n for ZnO varistors of 25–50 [22]. The highly non-linear I - V behaviour of the varistor has been attributed to electron tunnelling effect across the high resistivity boundary layer [23]. Although there are fundamental differences in the electrical properties of ZnO, which is a semiconductor, and the metallic

particles used in this study, the geometric effect of the random composite creates similar functionality among these two classes of materials.

4. Conclusion

A reversible switching effect of electrical conductivity with increasing external d.c. potential has been observed in three systems of random metal-insulator composites, Ag-KCl, Ni/N-PP, and Ni/F-PP. The effect is believed to be initiated by strong local electric fields and the creation of space charges in narrowly separated insulating barriers between conducting clusters near percolation. Subsequent hopping conduction of these charge carriers forms a new conducting path and causes the large increase in conductivity.

A phenomenological equation has been proposed to describe the relationship between conductance and external potential. The breakdown exponent associated with the switching is believed to arise from a distribution of inter-cluster spacings which follows a distribution related to the fractal dimension of the near-percolating clusters. A very good fit is shown by the Ag-KCl composite system to this expression.

The magnitude of the conductivity change for this phenomenon is dependent on the metal volume fraction, i.e. the distance from the percolation threshold, P_c . The switching field, V_{do} , is a strong function of the local electric field intensity. It thus depends on the metal particle shape and size, with larger more rounded particles leading to higher switching potentials. The functional similarity between this switching effect and that of ZnO varistors indicates the possible application of the random metal/insulator composite as varistors.

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