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Non-linear current–voltage characteristics in anisotropic epoxy resin–graphite flake composites

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The conductivity of anisotropic composite materials constituted of single-crystal graphite flakes in an epoxy resin and subjected to a variable d.c. electric field has been studied. Non-linearities in the current–voltage characteristics have been found and are discussed within the framework of two theoretical models, the non-linear random resistor network and the dynamic random resistor network. We show that our materials can be modelled by the non-linear random resistor network, which, to our knowledge, is the first time that the predictions of this model seem so well supported in a real, three-dimensional composite.

1. Introduction

Many studies have treated the phenomenon of dielectric breakdown in networks constituted of insulating and conducting bonds. They concern systems of conducting particle concentration p less than p_c, the critical threshold concentration. When the electric field applied to such a system is increased, dielectric breakdown occurs with a consequential increase in conductivity [1–9]. The case in which $p > p_c$ has also been treated but in this case, it is the conducting links which are broken and become insulating upon increasing the electric field [3, 7, 10, 11]. In both cases, the current–voltage (I–V) relationship becomes strongly non-linear when breakdown starts to occur. Studies relative to percolating systems, treating reversible non-linearity are considerably rarer. In this work, we were particularly interested in the studies of Gefen *et al.* [12–14] for systems in which the concentration, p, tends toward p_c from above. These authors considered two different phenomenological models to interpret the deviations from ohmic behaviour in their composites: the non-linear random resistor network (NLRRN) and the dynamic random resistor network (DRRN). In the present work, the applicability of these two models to epoxy graphite flake composites was tested and the implications, as concerns the conductivity mechanisms, were examined.

2. Experimental procedure

The composites were synthesized in the form of thick films (100–200 μm) constituted of an epoxy resin and a conducting charge of graphite particles. These latter are designated flat micronic graphite (FMG) [15] and have the following characteristics. They are single-crystal graphite, roughly disc-shaped, of average diameter 10 μm and thickness of the order of 0.1 μm, thus possessing an aspect ratio of about 100. The desired volume fraction, ϕ, of the flakes is incorporated into the epoxy resin which has been previously dissolved in its specific solvent. After homogenization of the resin–solvent–FMG mixture, it undergoes thermal treatment leading to evaporation of the solvent and reticulation of the resin. Using this protocol, samples of various concentrations in conducting charge were obtained with $0 < \phi \leq 0.09$.

The high aspect ratio of the FMG particles obviously confers on them the capacity to deposit in a flat manner. Thus composite materials are obtained in which the conducting charge is preferentially oriented parallel to the plane of the film. Using X-ray diffraction, an average disorientation of the graphite flakes of $\pm 20^\circ$ was observed, independent of the volume fraction of FMG present [16]. This factor, as well as the intrinsic conductivity anisotropy of graphite ($\sigma_a/\sigma_c > 10^2$), therefore motivated two types of measurement for each sample, one parallel and a second perpendicular to the plane of the film. The results show that these are three-dimensional, but strongly anisotropic, composite films with σ_a/σ_c between 10^4 and 10^5 for the highest concentrations tested, $0.05 \leq \phi \leq 0.09$ [17, 18]. Such measurements further allowed observation of an insulating to conducting transition with a percolation threshold at a critical concentration, ϕ_c, of 0.013 [16].

3. Theory

The first model which can account for current–voltage non-linearities in a composite calls upon a random resistor network of intrinsically non-linear resistors; this is commonly referred to [12–14, 19] as a non-linear random resistor network (NLRRN). Each resistance has a small, non-linear component, so that the current–voltage relationship is

$$V = rI + CI^a \tag{1}$$

where r and C are constants and a is an exponent greater than unity. For sufficiently small values of current, the behaviour is considered linear. A cross-over current is defined such that beyond it, the overall (non-linear) conductance deviates from the linear conductance by a fraction (see below) defined as ε [12]. This current I_c, is such that

$$I_c \sim \left(\frac{r}{|C|}\right)^{1/(a-1)} \tag{2}$$

In the second type of model, when the local electric field exceeds a critical value, an initially insulating (open) link may become a conducting one. In the literature, this is referred to as a dynamic random resistor network (DRRN) [12]. When the electric field to which a composite is subjected is sufficiently small, the material consequently has quasi-ohmic and ohmic behaviour for the NLRRN and DRRN models, respectively. In other words, V and I are related by

$$I = \Sigma_0 V \tag{3}$$

where Σ_0 is the linear conductance. When the current (or field) is increased, deviations from linearity arise beyond the critical values (I_c, V_c), for which the system then verifies

$$I = \Sigma V \qquad \text{with } \Sigma = \Sigma_0(1+\varepsilon) \quad \text{and } \varepsilon < 1 \tag{4}$$

Gefen *et al.* [12] showed that in this case, I_c follows a scaling relationship such that

$$I_c \sim \Sigma_0^x \tag{5}$$

x is a critical exponent, the value of which is directly linked to the spatial dimension, $\boldsymbol{d}$, and to the type of model utilized to describe the non-linearity of the percolating medium. Thus, based on Gefen *et al.*'s results [12]

$$\left.\begin{array}{lll} \text{in the NLRRN: } x \lesssim \frac{\nu}{t}(\boldsymbol{d}-1) & \text{i.e. } x \lesssim 1.05 \text{ in three dimensions} \\ \text{in the DRRN: } x \lesssim 1+\frac{\nu}{t} & \text{i.e. } x \lesssim 1.52 \text{ in three dimensions} \end{array}\right\} \tag{6a}$$

where ν is the correlation length critical exponent and t that of the conductivity, each of these exponents being applicable over a small range of volume concentrations above the percolation threshold. In three dimensions, the currently accepted values are $\nu \approx 0.89$ and $t \approx 1.7$.

Aharony [13] later established stronger bounds for the exponent x in the NLRRN

$$0.97 \lesssim x \lesssim 1.05 \qquad \text{in three dimensions} \tag{6b}$$

These limits on the values of x are valid when the exponent a of Equation 1 satisfies $1 < a < +\infty$.

4. Application to epoxy–FMG composites

For each composite sample, the electrical conductivity was measured as a function of the electric field using a number of series-connected, dry batteries which allowed a continuously variable d.c. voltage of up to 750 V to be obtained. The current flowing in the sample was measured using a Keithley 610 BR electrometer. Coaxial cables were used throughout the experimental setup for the interconnections and the measurements themselves were carried out in a shielded cell.

4.1. Search for the pertinent model

We will now see which of the two models presented above best represents our materials. To do so, the conductivity of several samples containing different volume charges of FMG (above the threshold) was measured as a function of electric field, both parallel and perpendicular to the plane of the film. For the range of electric field and FMG concentrations utilized (see numerical data below), all materials showed non-linearity in the I–V characteristics. For the lower values of electric field applied across the samples, the characteristics are linear but the behaviour becomes supralinear as the electric field rises. Furthermore, we have verified that this behaviour is reversible. Consequently, our materials lend themselves to analysis using the NLRRN and DRRN models introduced in Section 1.

Instead of using the parameters I and V, we will use j and E, the current density and electric field, respectively. The conductances Σ and Σ_0 of Equations 3–5 will then be replaced by the conductivities σ and σ_0. Because it is difficult to determine the couple (j_c, E_c) based solely on the curve $j(E)$ which deviates only slowly from linearity, we have used the following method. Different values of ε were chosen for use in Equation 4 (0.01, 0.05 and 0.10). For a sample with a given FMG charge, thus corresponding to a given conductivity, σ_0, we have extracted the critical current corresponding to the value of conductivity, σ, which verifies

$$\sigma = \sigma_0(1+\varepsilon) \tag{7}$$

where σ_0 is the conductivity of the composite in the ohmic region. σ thus being calculated, comparison with experimental $\sigma(E)$ curves allows locating the corresponding value of current density, j_c.

This method was applied to several samples of concentration near the percolation threshold. In order to apply Equation 5, we then plotted the values of j_c as a function of σ_0 on a log–log plot for different measurements carried out parallel and perpendicular to the plane of the films. These curves are given in Fig. 1. It is observed that the results are relatively insensitive to the three values of ε chosen above. The exponent x of Equation 5 is then taken as the average slope of the three curves.

As observed on this figure, the values of x obtained are in excellent agreement with those predicted using the NLRRN approach. This leads to the belief that the microscopic resistances in the resin–FMG system are intrinsically non-linear and that it is not necessary to

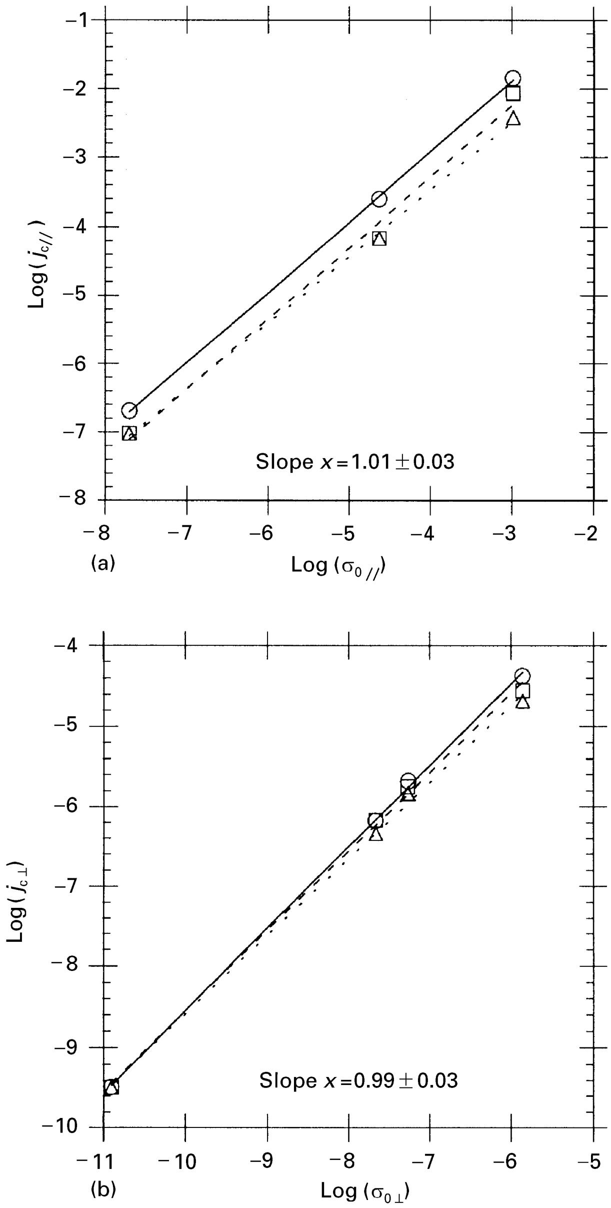

Figure 1 Log(j_c) versus log(σ_0), above the threshold, (a) within the plane of the composite films and (b) perpendicular using three values of ε: (○) 0.1, (□) 0.05, and (△) 0.01. The value of the critical exponent, x, defined by Equation 5 is taken as the average of the three slopes in each of the two cases.

call upon the creation of supplementary percolation paths when the electric field is increased. Because graphite is generally ohmic, it must thus be the interparticle resistances which dominate the macroscopic conductivity behaviour. However, the expression for x in the DRNN model is only given as a simple inequality, contrary to the case of the NLRRN (Equation 6b). Consequently, a lower limit to the possible values remains unknown. Thus, the fact that a value $x \approx 1$ is found does not unambiguously and exclusively prove that we are in the presence of a NLRRN. This is the reason for which it was necessary to supplement our analysis with the following arguments, which show that the DRRN is not pertinent in the case of our materials.

4.2. Confirmation of model

Gefen *et al.* [14] showed that their curves $I(V)$ could be very well fitted by the relationship

$$I = \Sigma V + \Sigma V^b \tag{8a}$$

where Σ and b are adjustable parameters, and with b such that the exponent x verifies, in the DRRN

$$x = \frac{b}{b-1} \tag{8b}$$

Equation 8a between I and V can fit our data very well, but the relationship established between x and b in Equation 8b is not verified at all. This result therefore would suggest that the DRRN is not applicable.

Chakrabarty *et al.* [19] went further, supposing a supplementary scaling law. These authors postulated that their curves $I(V)$ could be perfectly fitted

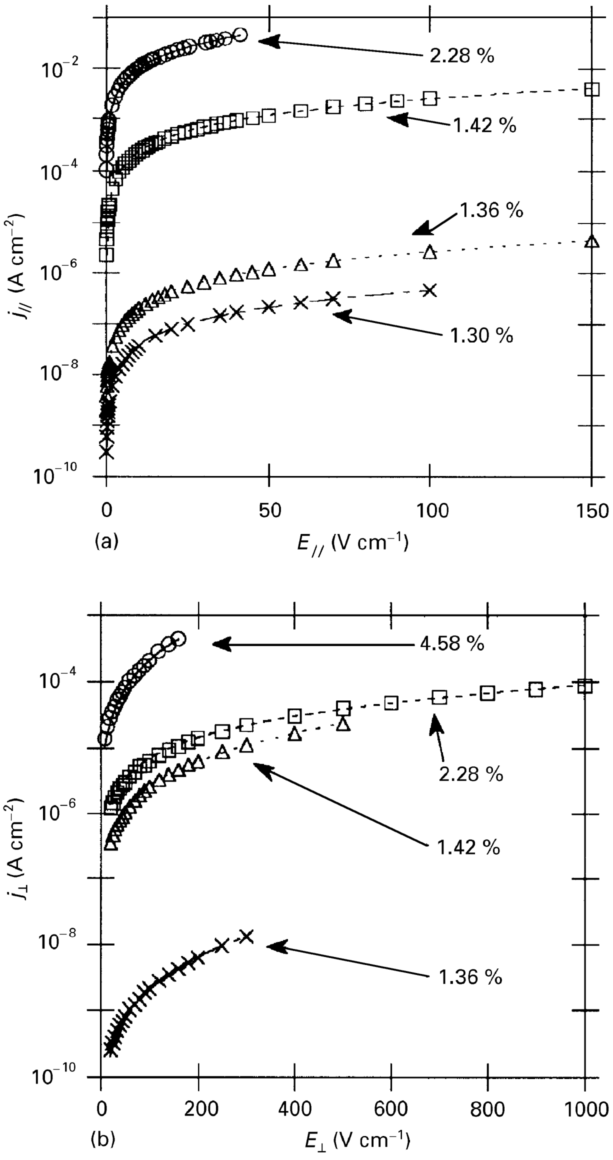

Figure 2 Fit of current density, j, as a function of electric field, E, to the expression $j = \sigma_1 E + \sigma_2 E^2$. The volume percentages of FMG incorporated in each sample are indicated on the right-hand side of each figure. Replacing the quadratic term with a cubic term gives results which are visually indistinguishable. (a) Basal plane measurements, (b) transverse measurements.

according to the expression

$$I = \Sigma_1 V + \Sigma_2 V^2 \tag{9}$$

where Σ_1 is the linear conductance (i.e. in the ohmic region corresponding to the quantity Σ_0 in Equation 3) and where Σ_2 is the second-order conductance. Thus Σ_2 would follow a scaling law such that

$$\Sigma_2 \sim \Sigma_1^y \tag{10}$$

Because the non-linearities are considered to become significant only when $\Sigma_2 V^2$ attains a certain fraction of $\Sigma_1 V$ as discussed above for Equation 2, then

$$I_c \sim \frac{\Sigma_1^2}{\Sigma_2} \tag{11a}$$

and because, from Equation 5, $I_c \sim \Sigma_1^x$, one has

$$x + y = 2 \tag{11b}$$

We have verified that a scaling law exists calling upon an exponent y. To do so, we fitted our data with a non-linear term varying as V^2, but we also note that an expression $I = \Sigma_1 V + \Sigma_2 V^3$ would also have been valid. In general

$$I = \Sigma_1 V + \Sigma_2 V^c \tag{12a}$$

The critical current would then vary as

$$I_c \sim \Sigma_1^{c/(c-1)} \Sigma_2^{1/(1-c)} \tag{12b}$$

and consequently

$$(c-1)x + y = c \tag{12c}$$

Fig. 2 presents, on a logarithmic scale, j as a function of E for our epoxy–FMG composites (for concentrations above the threshold) fitted by the relationship

$$j = \sigma_1 E + \sigma_2 E^2 \tag{13}$$

The agreement is excellent, and the correlation coefficient R is greater than 0.9995. If the fit is carried out using a non-linear term proportional to E^3, the fit obtained is also very good, with R only slightly smaller. The agreement decreases slowly for higher order terms of E. It might also be noted that, as expected, σ_1 is found identical to the quantity σ_0 of Equation 7, used above to determine j_c.

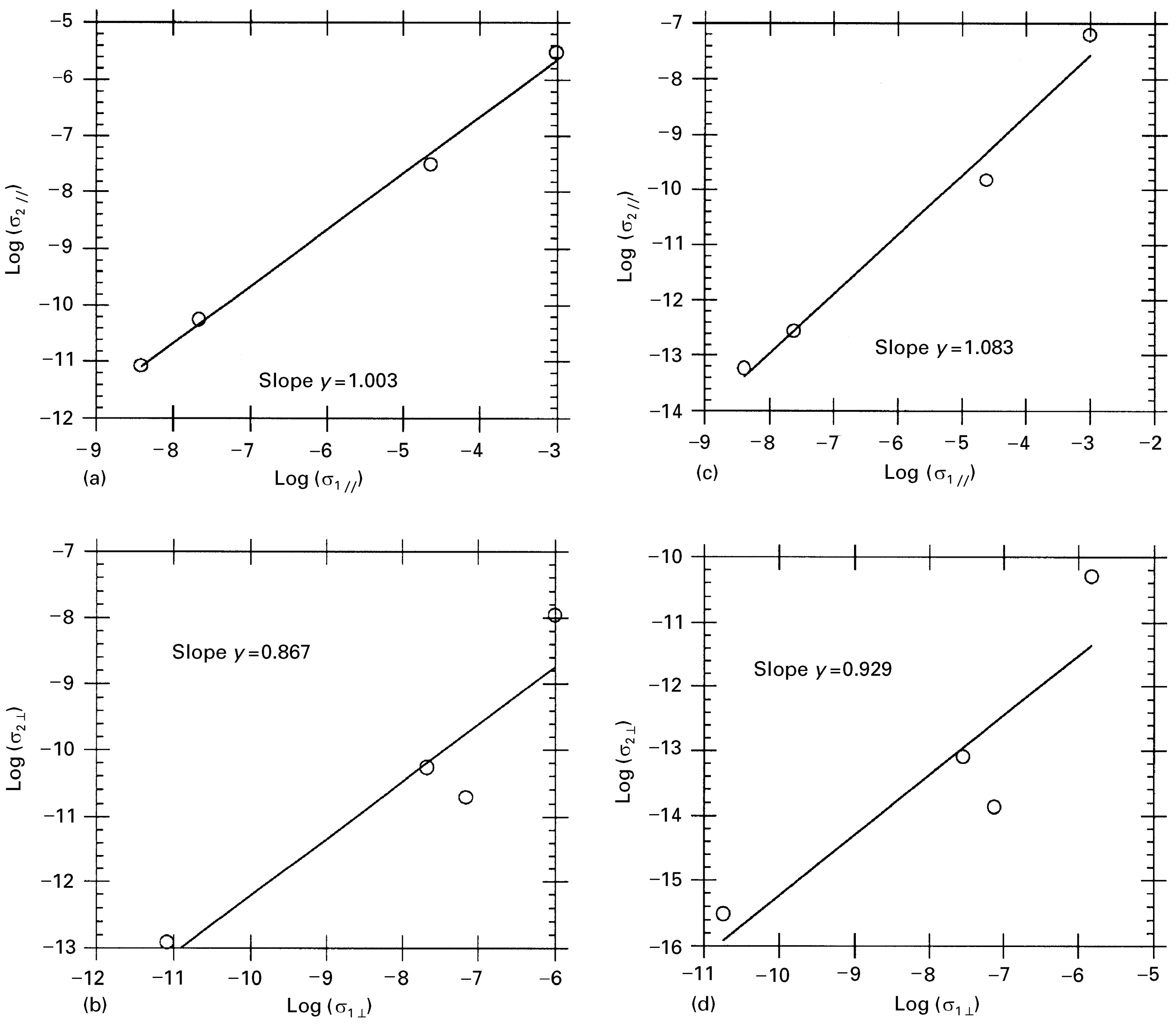

Figure 3 Test of relationship $\sigma_2 \sim \sigma_1^y$ for concentrations above the threshold. The values of y are the slopes of the indicated lines. The values of σ_1 and σ_2 were found based on the $j(E)$ data of Fig. 2 fitted to $j = \sigma_1 E + \sigma_2 E^2$ in (a) the basal plane and (b) perpendicular, and to $j = \sigma_1 E + \sigma_2 E^3$ (c) in and (d) across the basal plane.

We have used the values of σ_1 and σ_2 for each FMG concentration for the two types of fit (E^2 and E^3) in order to determine the exponent y. So as to apply Equation 10, the results are presented on a log–log plot in Fig. 3.

The results of this figure show that all the curves yield a value of y close to unity. The basal plane values are higher than the transverse values, and passing from a quadratic fit to a cubic fit increases the value of y by about 0.07 in both directions. This is in very good agreement with what was predicted by Chakrabarty *et al.* [19] who, based on the nodes, links and blobs image of the infinite cluster [20], showed that

$$y \gtrsim 2 - \frac{\nu}{t}(\boldsymbol{d} - 1) \tag{14}$$

i.e. $y \gtrsim 0.95$ in three dimensions in the NLRRN. It can thus be noted that the expression $(c-1)x + y = c$ given in Equation 12c is verified, with $x = y = 1$, whether c be equal to 2 or 3.

5. Conclusion

By measuring the electrical behaviour of epoxy–graphite flake composites under the effect of a d.c. electric field, it has been shown that the current–voltage characteristics are reversibly non-linear beyond a certain critical field. The magnitude of this field is linked to the concentration in conducting particles which allowed the existence of scaling relations to be shown. The corresponding critical exponents were demonstrated to be compatible with the NLRRN model, whereas the DRNN model had to be rejected. To our knowledge, this is the first time that the NLRRN has been encountered in a real, three-dimensional composite. From the point of view of conduction mechanisms, the implications of the NLRRN are the following. Because the microscopic resistances of the model system are non-linear and the graphite particles themselves in the real composite are ohmic, the non-linear I–V characteristics must originate from the interfacial contacts between the graphite particles. In other words, it is these contacts which govern the overall macroscopic electrical behaviour of the composite material. Such a conclusion is well known in other composites and explains why the resistivity of heavily loaded composites is always significantly greater than that of the conducting particles themselves [21, 22]. A tunnelling mechanism between particles might explain these non-linear I–V characteristics, and this will be treated elsewhere.

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