

Conduction mechanisms in some graphite - polymer composites: the effect of a direct-current electric field

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 2225

(<http://iopscience.iop.org/0953-8984/9/10/011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:16

Please note that [terms and conditions apply](#).

Conduction mechanisms in some graphite–polymer composites: the effect of a direct-current electric field

A Celzard, E McRae, G Furdin and J F Marêché

Université Henri Poincaré—Nancy 1, Laboratoire de Chimie du Solide Minéral, URA CNRS 158, BP 239, 54506 Vandoeuvre les Nancy Cédex, France

Received 9 July 1996, in final form 18 December 1996

Abstract. This paper deals with the possible conduction mechanisms in highly anisotropic composites comprising 0–10 vol% graphite flakes within a polymer host. Conductivity measurements as a function of DC electric field have been made. In most cases, a non-linear behaviour of the current–voltage relationships is observed. A number of theoretical models are considered and we show that none of them is, by itself, able to explain our results. We further develop several arguments which lead us to consider the existence of a combined tunnelling effect and ionic conduction mechanism.

1. Introduction

The electrical properties of composite materials consisting of a dispersion of conducting particles in an insulating matrix have been the subject of numerous works. Two particularly studied fields are the analysis of the percolation phenomenon itself in which an insulator–conductor transition occurs when the volume fraction of conducting particles (ϕ) goes through the critical threshold value ϕ_c , and determination of the physically plausible conduction mechanisms taking place in the corresponding systems.

As far as the microscopic conduction processes in composites are concerned, Pike and Seager [1] wrote in 1977: ‘there is an incredible diversity among the models which have been proposed in the published literature’. This statement is certainly valid today with a plethora of mechanisms proposed to describe the conductivity of different materials even with chemical and structural characteristics very close to each other. To establish a classification in this large number of theories, Pike and Seager proposed placing each of these mechanisms into one of four major categories, as follows, and as schematically represented in figure 1.

(a) The uniform model (figure 1(a)): the very small conducting particles are dispersed in the insulator. An impurity-conduction-type mechanism is then expected, and is more probable in the low-particle-concentration range.

(b) The uniform channel model (figure 1(b)): the particles give uniform-composition conducting paths which span the whole sample. The particles can be sintered or randomly bonded. In this case, the conductivity variations are mainly due to tortuosity and density modifications of the channels. This model is most applicable to the case of high particle concentrations.

(c) The non-tunnelling barrier model (figure 1(c)): the conducting channels are randomly interrupted by semiconducting or weakly insulating material barriers. The major

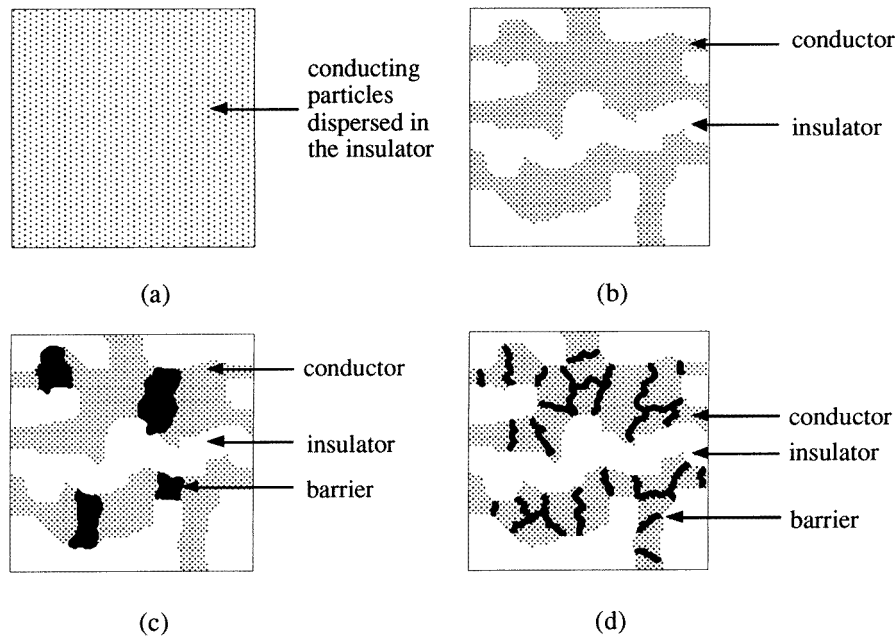


Figure 1. Major categories of conduction models in composite materials (after [1]). (a) A uniform model. (b) A uniform channel model. (c) A non-tunnelling barrier model. (d) A tunnelling barrier model.

mechanisms in this case are space-charge-limited conduction, the Poole–Frenkel effect, and Schottky emission.

(d) The tunnelling barrier model (figure 1(d)): the channels are interrupted by sufficiently thin barriers to allow a tunnelling process, either directly between particles or through one or several intermediate states within the insulator.

Each of these groups has mechanism-specific characteristics which, when applied to our particular case, can shed light on the processes involved in the composites of this study. The materials in which we are interested comprise single-crystal graphite particles in a polymeric matrix. These new and original composite films have been shown to be highly anisotropic [2] and we have discussed their particularly low value (of the order of 1%) of ϕ_c [3]. The present article will deal with the conductivity behaviour as a function of electric field, and following papers will treat the conduction processes as a function of temperature [4] and hydrostatic pressure [5]. We will examine these different categories of model, and compare them to our experimental results. Moreover, we will take care to keep in mind that several mechanisms can act successively or at the same time, depending on the particle concentration and the experimental conditions.

2. Experimental details

The conducting filler used in the elaboration of our composites consists of single-crystal graphite flakes, the average diameter of which is 10 μm and the thickness of which is close to 0.1 μm . Due to these geometric characteristics, these particles are called flat micronic graphite (FMG) [6]. They are dispersed in two types of thermally cured polymer, epoxy and

polyurethane, as described elsewhere [2]. The composites are obtained in the form of thick films (100 to 200 μm), in which the graphite flakes retain a preferential orientation [2]. The ambient temperature conductivity of a certain number of samples characterized by their FMG volume content has been measured both parallel and perpendicular to the films; a high anisotropy (about 50 000 at 6–8 vol% filler loadings) and an insulator–conductor transition at low particle concentrations [2] have been found. Critical volume percentages of 1.3% and 1.7% were observed in epoxy–FMG and polyurethane–FMG composites, respectively, in good agreement with excluded-volume-theory predictions [3].

To determine the current–voltage characteristics of our materials, we used two sample geometries. For in-plane measurements, rectangles of roughly 1 cm^2 surface area were cut from the composite films, and submitted to various values of a DC electric field applied at their extremities. For perpendicular measurements, discs with surface areas close to 2 cm^2 were used, each face being covered with silver paint. In the experimental set-up, the samples were put inside a shielded measurement box. The electric field E was supplied by a series of dry cells placed in an insulated box, and the current I was measured by a Keithley 610 BR electrometer. The range of electric fields was constrained for the following reasons. At very low fields, the current measured by the electrometer exhibited strong fluctuations, hence limiting the accuracy of the current determination. This was particularly the case with the highly resistant samples. In contrast, for the most conductive composites, it was still not possible to raise the field above a certain limit, which was a function of the graphite concentration. Indeed, since the material becomes increasingly conducting as the field rises, shorting of the voltage generator quickly occurs. For this reason, we studied only the composites with FMG volume percentages from 0.40 to 4.58% (volume fractions $\phi = 0.004\text{--}0.0458$) under fields varying from 0.1 to 2000 V cm^{-1} . In the following, it will be more convenient to consider the current density $j(E)$ rather than the current I .

3. Experimental results: $j(E)$ characteristics

In this section, we will examine the non-linear $j(E)$ behaviour as a function of ϕ . The experimental results can then be examined in the light of the four general classes of conduction mechanism model schematically represented in figure 1.

We briefly recall here the conclusions drawn in reference [7]. In that paper, we analysed the applicability of the dynamic random resistor network (DRRN) and the non-linear random resistor network (NLRRN) to the composites of the present study. The NLRRN model involves a network of conducting bonds, each element of which has a small non-linear contribution which manifests itself when the field rises above a critical value. On the other hand, the DRRN model is based on a network of bonds, all having ohmic characteristics, but comprising a certain number of initially insulating channels, able to become conducting above a critical value of the applied external field. While neither of these models gives any detailed information on the nature of the microscopic conduction mechanism(s), examination of the critical exponents did suggest that the latter model was more applicable and we further asserted that the interparticle conduction dominated over the intraparticle mechanism.

3.1. Evaluation of the non-linearities of FMG–polymer composites

In the electric fields and FMG concentration ranges studied ($E = 0.1\text{--}2000 \text{ V cm}^{-1}$ and $\phi = 0.004\text{--}0.0458$, respectively), after an initially linear current density–electric field, $j(E)$, relationship, nearly all of the samples exhibit non-linearities in $j(E)$. When the materials no longer follow Ohm's law, the empirical relationship $I = AV^\alpha$ ($\alpha \neq 1$) has been proposed

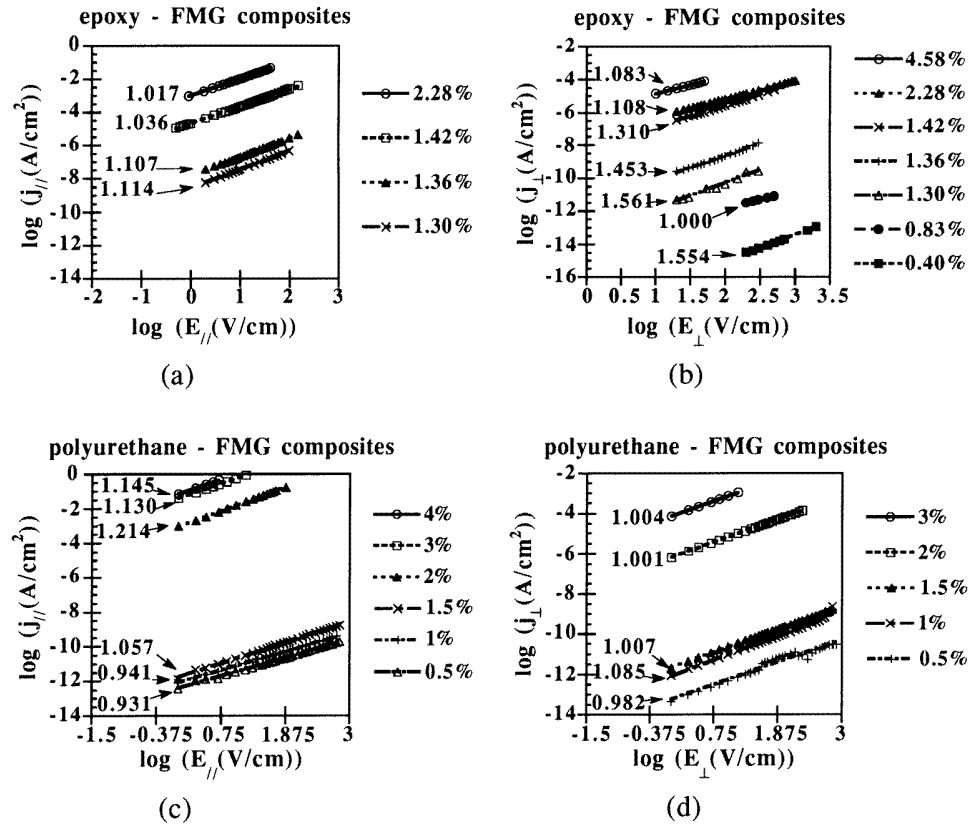


Figure 2. Use of the empirical relation $j \propto E^\alpha$ for epoxy-based ((a) and (b)) and polyurethane-based ((c) and (d)) composite samples, filled with various FMG volumic loadings as indicated to the right. The values of α are indicated within the plots. (a), (c) In-plane measurements. (b), (d) Perpendicular measurements.

and fits correctly a great number of systems. In this equation, A is a constant having the dimension of a conductance, V is the applied voltage and α is a parameter related to the non-linearity of the sample. To be able to compare our composites directly, we have plotted in figure 2 the current density j as a function of E on a logarithmic scale; we then test the following relationship:

$$j \propto E^\alpha. \quad (1)$$

As can be seen, the in-plane and perpendicular measurements for epoxy- and polyurethane-based samples follow equation (1) quite well. We recall that (1) is not related to any specific, well defined conduction mechanism.

Figure 2 furnishes some clear information on the exponent α . At low fields and with only one exception (polyurethane-based samples measured perpendicular to the plane), α increases when the FMG concentration varies down to the percolation threshold. This effect is particularly clear in epoxy-based composites, for which we studied samples with filler loadings very close to the critical concentration (1.3 vol%). This means that materials on the conducting side of the transition become increasingly non-linear as the threshold is approached from above. Below the threshold and always at low electric fields, the

materials are either ohmic or deviate from linearity, with $\alpha < 1$ in the case of polyurethane-based composites. Finally, it seems obvious from the orders of magnitude separating low- and high-concentration values of conductivity that different mechanisms are implicated. So, the results in figure 2, which show no sharp change in behaviour above and below ϕ_c , suggest that the passage from one mechanism to another is a progressive, somewhat sample-dependent process.

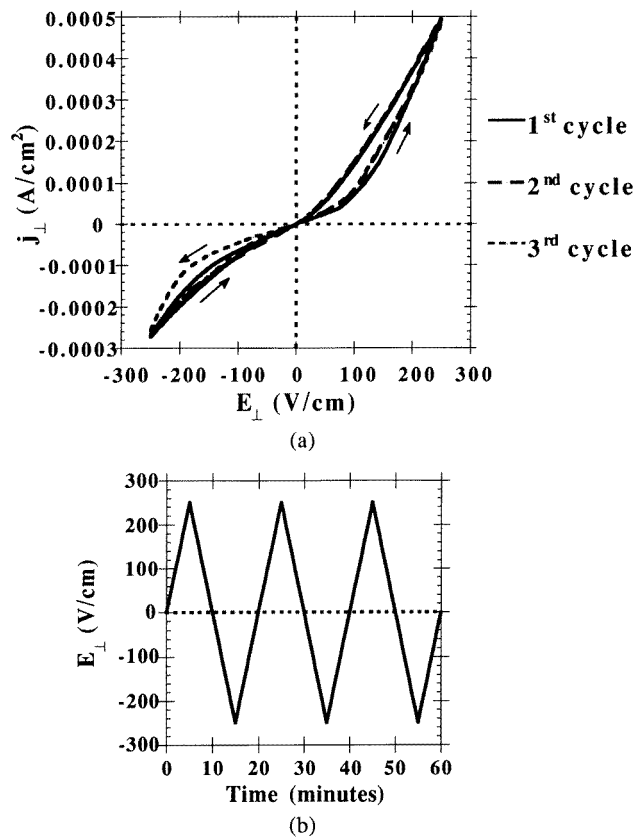


Figure 3. The perpendicular current density versus electric field characteristics (a) for an epoxy-2.28 vol% FMG composite sample subjected to three successive cycles of the time-dependent electric field shown in (b).

3.2. Hysteresis and time-dependent phenomena

Let us examine some data which further support mixed conduction. We have said so far that the current density varies as an increasing function of the field in a reversible way, without specifying that after a change in electric field, the system needs some time to settle to its new conductivity. This effect is the source of the hysteresis loops observed in figure 3(a) upon application of the voltage as a function of time as schematically represented in figure 3(b). The phenomenon is reasonably well reproducible. The feature that the loops are not symmetrical is often seen in dielectrics. It is generally interpreted in terms of the existence of an internal electric field created during the manufacturing or curing of the polymer, and

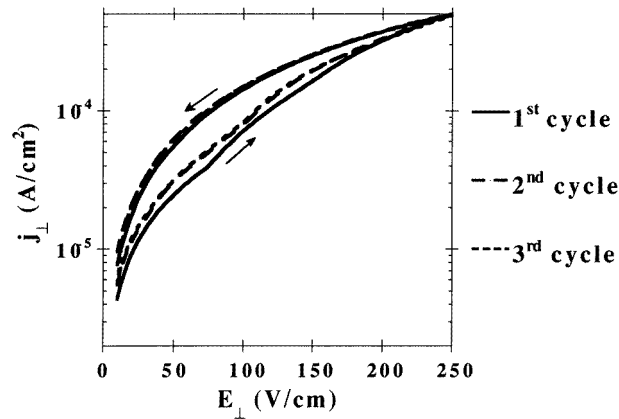


Figure 4. The data of figure 3 replotted on a semilogarithmic scale, for positive values of the current density j and electric field E . It can be seen that j increases rapidly at low fields, and then levels off. As the voltage is reversed, the current remains at a higher value.

sometimes vanishes on heating the material.

This hysteretic behaviour can be more clearly seen in figure 4, in which the data of figure 3 are plotted on a semilogarithmic scale for positive values of the electric field. The current first increases very quickly with E (by an order of magnitude for this sample), and then tends to level off. When the field is reversed, the current remains at a higher value. Samples having been exposed to very high electric fields recover their original conductivity only after several days (5 to 15) at room temperature. Such a relaxation time seems much too long for one to consider space charges generated by the field to be purely electronic in nature, and suggests the presence of ionic factors. We return to this below.

4. Discussion

4.1. General remarks

As regards the current density versus electric field behaviour, two preliminary comments should be made. First, since the sublinear $j = f(E)$ (or $I = f(V)$) behaviour is observed only when the particle concentration is below the threshold (figure 2), this effect cannot be attributed to macrobond segments within the infinite cluster in which the tortuosity involves charge carriers flowing against the field direction. Secondly, we have shown elsewhere [7], in a study dealing with the onset of non-linearities in the current–voltage characteristics, that our materials could be modelled by a non-linear random resistor network (NLRRN) but not by a dynamic random resistor network (DRRN). Thus, if indeed the NLRRN is applicable to our FMG–polymer composites, then no new conducting paths are created when the electric field increases. Knowing that the charge carriers must move across barriers, as deduced from the strong non-linearities in the neighbourhood of the threshold, let us now briefly review the mechanisms associated with figure 1 and their applicability to our experimental results—first, individually, then taken together. Further reference to the four different classes of Pike and Seager [1] will be made in the complementary studies treating the temperature and pressure dependences of our composite films [4, 5].

4.2. Analysis of the $j(E)$ curves and relationships with the conduction models

4.2.1. Uniform models. One kind of conduction process in this category is hopping between localized states. In such a process, the current density j is always exponentially dependent on some power, p , of the applied electric field E [8–12]: $j \propto \exp(E^p)$. Such processes have been studied by numerous authors who have taken account of a variety of different parameters. For instance, if the material can be seen as a random resistance network, some bonds have a field-dependent conductivity, while others do not. Correlations may be limited to nearest neighbours or extend to the n th-nearest neighbour in which case we would expect the behaviour to approach that predicted by mean-field theory. Moreover, the cluster topology may vary with the intensity of E , even further complicating the analysis. At fixed temperature, the various equations of references [8–12] manifest a considerable range of dependences on E , but none is able to fit correctly our $j(E)$ curves for the whole range of electric fields. Furthermore, our conducting particles are probably far too large to be considered as dilute impurities within the polymer. Therefore, it might be expected that such a uniform model would be more adapted to the description of a dispersion of carbon black particles (the size of which is a few nanometres) in an insulating matrix [13].

4.2.2. Uniform channel models. In such a representation, conduction takes place in a uniform-composition material, where the constituting chains are tortuous and extremely variable in diameter. The conducting chains in our composites may indeed be such, but purely graphitic conducting chains would be ohmic so this representation cannot account for the rise of the conductivity as a function of the electric field, for composites above the percolation threshold. Furthermore, the conductivity at high filler loadings, where the $\sigma(\phi)$ curve has started to saturate, is orders of magnitude lower than the conductivity of graphite both parallel and perpendicular to the film plane. Thus, this model does not seem suitable for our materials.

4.2.3. Non-tunnelling barrier models. In this representation, the conducting component forms channels which are inhomogeneous in composition, because they are interrupted by semiconducting or weakly insulating regions. If the conduction process is not a tunnelling effect, the mechanisms most frequently encountered are Schottky emission, the Poole-Frenkel effect and space-charge-limited conduction. These three effects rely upon the possibility for an electrode to inject charge carriers into a dielectric in a way analogous to thermionic emission, in which a hot metallic cathode emits electrons into the vacuum. It has been shown that the potential barrier at a metal-insulator contact can be much lower than that of a metal-vacuum interface [14], and consequently, there occurs electronic injection from the conductor into the insulator at ambient temperature and even below.

In the Schottky emission process, the electric field lowers the interfacial energy between conducting and insulating materials, in such a way that the current density-electric field characteristics are given by

$$j = j_0 \exp\left[\frac{e}{kT}(\beta\sqrt{E} - \Delta)\right] \quad \text{with } \beta = \sqrt{\frac{e}{a\pi\epsilon_0\epsilon}} \quad (\text{in CGS units}). \quad (2)$$

j_0 is a constant, Δ is the contact barrier height (a function of the metal constituting the electrode), $\epsilon_0\epsilon$ is the high-frequency value of the dielectric permittivity, and $a = 4$ in the β -term. Developing the exponential term as a series, for small E , this equation gives a sublinear conductivity dependence on the field, with $j \propto \sqrt{E}$; thus it cannot be used to explain the behaviour observed in figure 2. This result is perhaps not unexpected if we recall

that Schottky emission is said to take place in the field range 10 to 1000 kV cm⁻¹ [15], values well above those of figure 2 (although perhaps attainable between FMG particles within the film).

The Poole–Frenkel effect is similar, but it occurs around the impurities within the insulator which are ionized either by the electric field or thermally. The charge carriers thus created may jump from one localized centre to another by crossing the potential barriers, the heights of which are lowered by application of the field. When the density of sites is sufficiently low, the current density versus electric field response is very similar to that of Schottky emission, the only change being that $a = 1$ in equation (2). We can draw the same conclusions as above: if this effect is present in our composites, some other contribution is also required because in no case were we able to obtain a straight line by plotting $\log(j)$ versus \sqrt{E} .

In the case of space-charge-limited conduction, the charge carriers emitted by conducting particles constitute a volumic space charge around them. So the electric field between sites is reduced, and the conductivity is thus limited by the generation and recombination of charge carriers. The general relationship between current and voltage is often of the type [16]

$$j = j_0 \frac{E^{n+1}}{r^{2n+1}} \quad (3)$$

where n is an integer (generally 1 or 2) and r the average distance between particles. This kind of law yields $\log(j)$ versus $\log(E)$ curves with greater slopes than observed in figure 2. However, results have been published [17] showing that such a relationship does not necessarily hold for conduction in amorphous materials. The hypothesis of a mechanism involving space charges cannot, for the moment, be eliminated.

4.2.4. The tunnelling barrier model. The basic equation for tunnelling through a junction is given by

$$j(\varepsilon) = j_0 \exp \left[-\frac{\pi \chi w}{2} \left(\frac{|E_j|}{E_0} - 1 \right)^2 \right] \quad \text{for } |E_j| < E_0 \quad (4a)$$

where E_j is the electric field across the junction, j_0 the pre-exponential factor (constant at constant temperature and fixed field), and w the width of the barrier. E_0 and the tunnelling constant χ are defined as

$$\chi = \sqrt{\frac{2mV_0}{\hbar^2}} \quad \text{with} \quad \begin{cases} \hbar = \frac{h}{2\pi}, h \text{ being Planck's constant} \\ V_0 = \text{potential of the barrier} \\ m = \text{electron mass} \end{cases} \quad (4b)$$

$$E_0 = \frac{4V_0}{ew} \quad \text{where } e \text{ is the electron charge.}$$

Starting from this basic equation, Sheng *et al* [18] developed a special kind of tunnelling effect, in which thermal fluctuations induce voltage fluctuations, making the conductivity increase when the temperature rises. These authors showed that the behaviour of a bond network within a composite material can be well described by that of a single junction, and gave the following relationship between the current density and applied electric field E :

$$j \approx j_0 \exp \left[-a(T) \left(\frac{E}{E_0} - 1 \right)^2 \right] \quad \text{with } a(T) = \frac{T_1}{T + T_0}. \quad (5a)$$

T is the absolute temperature, and T_0 and T_1 are parameters of the model, such that

$$\begin{cases} T_0 = \frac{u\varepsilon_0^2}{k} \\ T_1 = \frac{2u\varepsilon_0^2}{\pi\chi wk} \end{cases} \quad \text{with } u = wA/8\pi \quad (5b)$$

where u is the junction volume, and A the area of its cross section. The physical significance of these parameters is the following. T_0 represents the temperature above which the fluctuation effect becomes significant. So, at $T < T_0$, the $j(E)$ relationship reduces to that of a simple tunnelling effect. T_1 can be seen as the energy necessary for an electron to cross the potential barrier, and corresponds to the height of this latter. When the temperature increases, j becomes a simple exponential function of T and hence, at room temperature, it is no longer possible to distinguish this particular tunnelling process from any other. It was found at room temperature that relation (5a) is not able to fit our $j(E)$ curves over the range of electric fields investigated.

In other systems such as granular metals, a certain number of other equations have been obtained [19], depending on the intensity of the applied electric field and the type of distribution of the site energies but none of them was found suitable to fit our results over a range of electric fields.

At this level of our study, we conclude that the models *individually examined* are unable to explain our results. Thus, either we have several effects playing a role simultaneously or there is indeed a single mechanism, but a certain number of parameters are to be modified to account for the particularities of our composites. For example, tunnelling and hopping processes can lead to very different behaviours (several conductivity versus temperature laws), depending on the kind of material in which these mechanisms take place. This will be dealt with in the following section.

4.3. Combinations of mechanisms

The analyses of section 4.2 lead us to the conclusion that we must consider processes taking place simultaneously, the relative contributions of which are functions of the FMG concentration and the electric field intensity. We will consider two plausible contributions.

4.3.1. Internal field emission and modified tunnelling combination. In the past, numerous authors have noted that the standard tunnelling effect theory is not suitable for correctly describing real materials—sometimes not even qualitatively. One means of overcoming this has been to slightly modify the theory in such a way that the charge carriers going from one particle to another pass via one or several intermediate states localized in the barrier. Field emission is then considered.

Internal field emission is a general term referring to a number of processes involving electron transfers across forbidden zones [20]. The tunnelling effect is then a particular case of field emission [21]. The relationship between the current I and the voltage V is often given by the equation

$$I = AV^n \exp\left(-\frac{B}{V}\right) \quad (6)$$

in which A , B , and n are constants ($1 \leq n \leq 3$); the particular case where $n = 2$ is designated 'Fowler-Nordheim tunnelling'. A is a function of the tunnelling frequency,

i.e., the number of attempts per second made by the carrier to cross the barrier. The factor $\exp(-B/V)$ represents the probability of transition from one site to another. Thus, this transmission coefficient increases with the field if $B > 0$. If these parameters are not constrained, then such a law fits our data relatively well for most of the FMG concentrations, with values of n between 1 and 2: however, a negative value of B is always found. This would imply that the transparency of the barrier is lowered with increasing field, contrary to what would be expected for the tunnelling process. We must then conclude that in the range of fields used, the apparent agreement between experimental values and relationship (6) has no physical meaning.

A particularly interesting tunnelling effect model is that developed by Pike and Seager [1]: the barriers between conducting particles contain a certain number of impurities or dispersed defects, with an energy level accessible to charge carriers. These localized states are attractive potential wells for electrons, and enhance the probability of tunnelling. Furthermore, since these defects or impurities can themselves move slightly under the influence of the field, this too may influence the conductivity. Finally, a great number of charge carriers can be created by the effect of the field itself [22]. Such intermediate states as mentioned above, with a spread in position and energy, can thus be traps for or sources of carriers subjected to an electric field, and give rise to non-linear effects which can be modelled using the NLRRN approach. However, we have no firm footing on which to establish the j - E relationship, and thus are not able to reach a conclusion as to whether a field emission process is really applicable.

4.3.2. Ionic–electronic mixed conduction. The intervention of ionic processes has been suggested in studies on other composite materials, and some of our own results also suggest this. For the ranges of electric field and filler concentration studied here, α (cf. figure 2) lies in the range $0.93 < \alpha < 1.6$, comparable to that found by Sodolski *et al* [23] in carbon black–polyester composites ($1 \leq \alpha \leq 1.85$). However, these authors neither found exponent values lower than 1 nor found correlation with the conducting particle concentrations, except for filler loadings much higher or much lower than the critical point. Indeed, their materials were non-ohmic only close to the percolation threshold. Their interpretation of these phenomena was the following. At low concentrations and fields, the composite behaviour was ohmic due to an ionic diffusion process, while when the concentration was high, linear I - V behaviour was obtained due to real physical contact between individually ohmic particles. At intermediate filler loadings, an electron tunnelling effect would then lead to an electric field-dependent conductivity, close to the percolation threshold.

In our case, a displacement of ions under the influence of an electric field seems necessary to explain the time-dependent phenomena present in figures 3 and 4. The more resistive samples, with particle concentrations around the threshold value, have all shown dielectric polarization effects. The applied field may induce ion diffusion, the consequence of which is the creation of a volumic density of space charges in the neighbourhood (within a few millimetres) of the electrodes. This phenomenon was clearly shown by Reboul and Moussali [24] in samples having yet higher graphite concentration (25 vol%) and larger dimensions (16 mm) than ours. As the sign of these charges is opposite to that of the adjacent electrodes, one speaks of heterocharges. These are dragged in the material under the influence of the macroscopic field, and screen its local values because ions tend to gather near the electrodes and perhaps even the FMG particles. Given the small dimensions of our samples (roughly 10 mm in the plane and 0.1 mm perpendicular to it), one can expect these

effects to be very significant, and hence the equilibrium current (i.e. after the electrification time of the material) will be governed by the neutralization of the ions by electrons or holes coming from the electrodes [25].

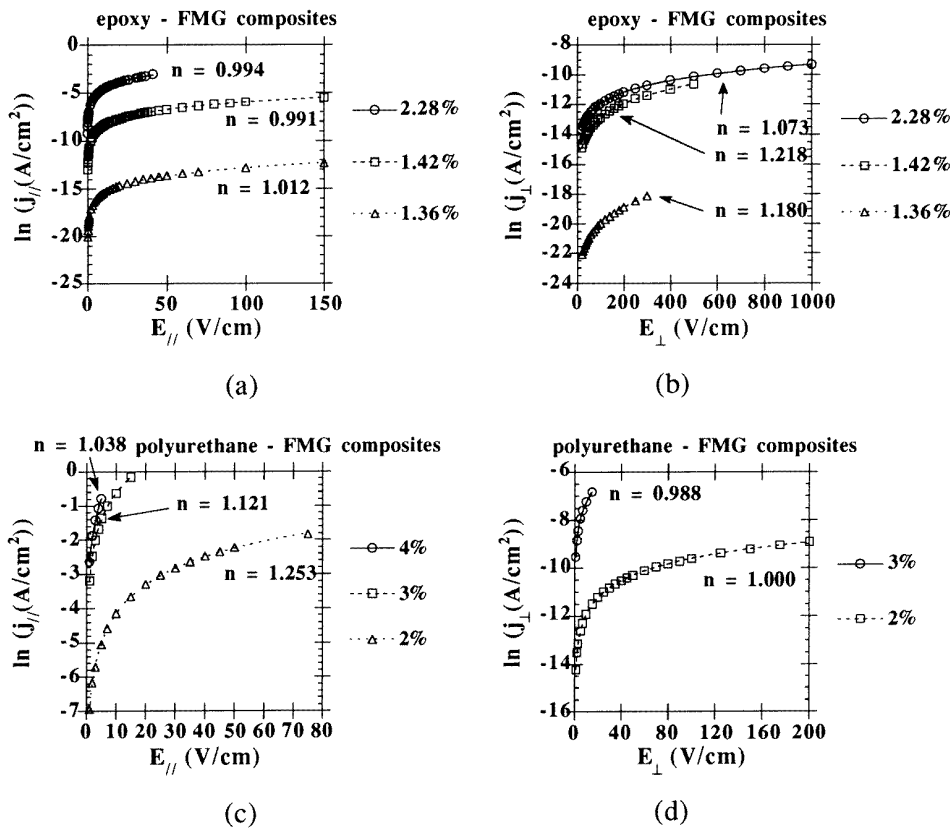


Figure 5. Fits to the equation $j = A'E^n \exp(B'E)$ for epoxy-based ((a) and (b)) and polyurethane-based ((c) and (d)) composite samples, with filler concentrations above the threshold. (a), (c) In-plane measurements. (b), (d) Perpendicular measurements.

As suggested by Cashell *et al* [25], indirect evidence of the space-charge density can be given by the following observation. As soon as the external field is turned off, there exists for a few seconds a small transient reverse current. We were able to observe this phenomenon for materials of any concentration, using a sufficiently high sensitivity range of the electrometer for the detection, this current remaining low as compared with the experimental measurement current. These authors proposed that in the case of mixed electronic-ionic conduction, the current and voltage can be linked by the phenomenological relationship

$$I = A'V \exp(B'V) \tag{7}$$

where A' and B' are constants. This kind of relationship is able to represent the neutralization of ions by electron or hole injection, either from the electrodes as discussed above, or—in our case—from the graphite flakes. In the latter case, the conduction would be electronic

inside the particles and ionic between them. Figure 5 shows the fits for the relationship

$$j = A'E^n \exp(B'E) \quad (8)$$

for various materials with concentrations above the threshold. It is noted that the exponent n , indicated on each curve of figure 5, is in most cases close to 1, which is consistent with the interpretations given by Cashell *et al.*

Finally, the saturation and hysteresis noted in figure 4 may be associated with an excitation-relaxation process of charge carriers, which could correspond to the neutralization of a limited number of ions thus leading to the saturation of j . It has been supposed elsewhere [26] that space charges, electrons and holes, are emitted by the conducting particles into the dielectric, and that the conductivity saturation occurs when the rates of generation and recombination of charge carriers become equal; this would also be a time-dependent process. Samples that have been exposed to very high electric fields recover their original conductivity only after several days (5 to 15) at room temperature. Such a relaxation time seems much too long for one to consider space charges generated by the field to be purely electronic in nature, so here again, ionic processes seem plausible.

5. Conclusions

In this paper we have presented current density versus electric field data (j versus E) close to the percolation threshold on composite films comprising graphite flakes as the conducting filler. We have illustrated the non-linear relationship between the two as well as some time-dependent $j(E)$ results. Analysis leads to the conclusion that several mechanisms must be called upon to explain the observed $j(E)$ behaviour in these composites, depending on the conducting particle concentration, applied external electric field, and time; however, the complex effects render it difficult to draw any final conclusion as to a given process.

We can, nevertheless, stress the following points. It has been shown that no *single* conduction mechanism accounts for the experimental $j(E)$ data. If we consider combinations of the different mechanisms, only the uniform channel model, relating to a filamentary conduction, seems unadapted for the samples studied here with filler loadings less than 5 vol%. Combinations of the other mechanisms discussed above cannot be ruled out in a definitive way. The time- and field-dependent effects argue for some ionic contribution; the proposition of combined tunnelling and ionic conduction mechanisms seems plausible. Nevertheless, it is necessary to verify this hypothesis through study of the conductivity as a function of temperature and pressure, and these results will be forthcoming.

Acknowledgments

The authors thank the Centre du Ripault for financial support, and Drs M Dufort and C Deleuze for fruitful discussions on parts of this work.

References

- [1] Pike O E and Seager C H 1977 *J. Appl. Phys.* **48** 5152
- [2] Celzard A, McRae E, Maréché J F, Furdin G, Dufort M and Deleuze C 1996 *J. Phys. Chem. Solids* **57** 715
- [3] Celzard A, McRae E, Dufort M, Deleuze C, Furdin G and Maréché J F 1996 *Phys. Rev. B* **53** 6209
- [4] McRae E, Celzard A, Maréché J F and Furdin G 1997 *J. Phys.: Condens. Matter* submitted
- [5] Celzard A, McRae E and Sundqvist B 1997 *J. Phys.: Condens. Matter* submitted
- [6] *French Patent, CNRS No PCT/EP 92/02317*
- [7] Celzard A, Furdin G, Maréché J F and McRae E 1996 *J. Mater. Sci.* **31** at press

- [8] Hill R M 1971 *Phil. Mag.* **24** 1307
- [9] Pollak M and Riess I 1976 *J. Phys. C: Solid State. Phys.* **9** 2339
- [10] Shklovskii B I 1976 *Sov. Phys.-Semicond.* **10** 855
- [11] Talamantes J, Pollak M and Baron R 1987 *J. Non-Cryst. Solids* **97-98** 555
- [12] Apsley N and Hughes H P 1975 *Phil. Mag.* **31** 1327
- [13] Mehbod M, Wyder P, Deltour R, Pierre C and Geuskens G 1987 *Phys. Rev. B* **36** 7627
van der Putten D, Moonen J T, Brom H B, Brokken-Zijp J C M and Michels M A J 1993 *Synth. Met.* **55-57** 5057
van der Putten D, Moonen J T, Brom H B, Brokken-Zijp J C M and Michels M A J 1992 *Phys. Rev. Lett.* **69** 494
Aharony A, Harris A B and Entin-Wohlman O 1993 *Phys. Rev. Lett.* **70** 4060
- [14] Lampert M A and Mark P 1970 *Current Injection in Solids* (New York: Academic)
- [15] Morant M J 1960 *J. Electrochem. Soc.* **107** 671
- [16] Radhakrishnan S, Chakne S and Shelke P N 1994 *Mater. Lett.* **18** 358
- [17] Jonscher A K 1969 *J. Electrochem. Soc.* **116** 217C
- [18] Sheng P, Sichel E K and Gittleman J L 1978 *Phys. Rev. Lett.* **40** 1197
Sichel E K, Gittleman J L and Sheng P 1978 *Phys. Rev. B* **18** 5712
Sheng P 1980 *Phys. Rev. B* **21** 2180
- [19] Bourbie D, Olivier G and Mostefa M 1989 *Physica A* **157** 198
- [20] van Beek L K H and van Pul B I C F 1962 *J. Appl. Polym. Sci.* **6** 651
van Beek L K H and van Pul B I C F 1964 *Carbon* **2** 121
- [21] Chynoweth A G 1960 *Prog. Semicond.* **4** 95
- [22] Neugebauer C A and Webb M B 1962 *J. Appl. Phys.* **33** 74
Abeles B 1975 *RCA Rev.* **36** 594
- [23] Sodolski H, Zielinski R, Slupkowski T and Jachym B 1975 *Phys. Status Solidi a* **32** 603
- [24] Reboul J P and Moussali G 1976 *Int. J. Polym. Mater.* **5** 133
- [25] Cashell E M, Cohey J M D, Wardell G E, McBrierty V J and Douglass D C 1981 *J. Appl. Phys.* **52** 1542
- [26] Chen I G and Johnson W B 1992 *J. Mater. Sci.* **27** 5497