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Temperature-dependent resistivity and conduction mechanism in carbon particle-filled polymers

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The filler-concentration dependence of the room temperature conductivity of epoxy resins filled with various carbon particles is reported: two carbon blacks differing by the particles size and short carbon fibres were used. The familiar insulator-to-conductor transitions are evidenced and analysed according to percolation theory predictions. The temperature variations below room temperature of the resistivity of selected samples are studied. Two distinct temperature dependences are shown, and interpreted as being due either to tunnelling of electrons among neighbouring particles, or to differential thermal expansion of the matrix and the particles when the latter touch one another. All these results are consistent with general results of colloidal stability theories when particle size and shearing (achieved during material processing) are taken into account.

1. Introduction

Intrinsically insulating polymers filled with conducting particles have many industrial applications in electricity as antistatic materials, EMI (Electromagnetic interference) shields, materials for electronics, etc. When lower conductivities are required, carbon particles (which are much cheaper and lighter than metallic particles) are widely used [1]. In most cases, they are either carbon blacks or short carbon fibres eventually coated with a metal-like nickel. As the filler concentration is varied, the conductivity exhibits a well known insulator-to-conductor transition now interpreted as a percolation threshold: the filled polymer is conducting only when an array of connected conducting particles is formed throughout the material (the "infinite cluster" in percolation theory).

conducting filled polymers exhibits several interesting features. Above room temperature a sharp, reversible drop in conductivity is sometimes observed. This effect depends on the composition of the material (filling factor, polymer, filler nature). Its origin is still not clearly accounted for, but it has led to various industrial applications as PTC (positive temperature coefficient of resistance) materials for safety devices and self-regulated heaters [2]. Below room temperature, various behaviours may be observed and, as is usually the case in solid-state physics, the temperature dependence of the resistivity provides a good means for investigating the conduction process in such heterogeneous materials.

Filled polymers frequently exhibit a semiconducting behaviour [3], especially when the filler is a carbon black whose typical particles size ranges between 0.01 and 0.1 μm. As recalled recently [4], it is frequently admitted that in these cases, conduction proceeds by hopping of carriers among neighbouring particles or aggregates of particles. Two approaches to interpreting the experimental temperature dependences of the conductivities have been proposed [4].

(i) A "local" approach in which hopping of carriers is dominated by thermal fluctuations. It predicts a temperature dependence of the form [5]

$$\rho = \rho_0 \exp \frac{T_1}{T + T_0} \tag{1}$$

in which ρ_0, T_1 and T_0 are constants which may depend essentially on the characteristics of the tunnel junctions, which are supposed to be functions of various parameters (filling factor, particle size and shape, sample processing).

(ii) A "global" approach based on the critical path method [4, 5] originally developed for granular metals. It leads to a temperature dependence of the form

$$\rho = \rho_1 \exp \frac{T_2}{T^\alpha} \tag{2}$$

in which ρ_1, T_2 and α are constants, the latter being supposed to depend on the particle-size distribution [4].

Such behaviours are then expected when conducting particles belonging to the infinite conducting cluster of percolation theory remain separated by thin

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layers of polymer. On the other hand, it has been shown in a few instances [6, 8] that conduction probably proceeds by direct contact of particles ruling out tunnelling effects and leading to different temperature dependence of the resistivities.

Experimental results obtained on three distinct series of carbon polymer composites with varying filling factors differing in the nature, size and shape of the carbon particles are reported. We will show that Equation 1 seems to be appropriate to one of the series of materials, whereas neither of the proposed equations 1 or 2 holds for the other two series. A new mechanism for the temperature dependence will be proposed, and we will show that the observed differences in temperature dependence of the resistivities are actually correlated to differences in the particle aggregation process.

2. Materials and experimental results

This study is concerned with three series of carbon–polymer composites with varying carbon particle volume concentrations. They are labelled MO/AF; ST/LY and F/AF, respectively, and their main characteristics are reported in Table I. In all cases the matrix is an epoxy: it is either an Araldite LY or an Araldite F with convenient hardeners as provided by Ciba-Geigy. Two of the fillers are carbon blacks: Monarch 1100 (MO/AF materials) with 14-nm particle diameter, and Sterling FT (ST/LY materials) with 300-nm particle diameter from Cabot Cy. The third filler is made of carbon fibres AGT by Serofim, of 8-μm diameter, which are cut to 1 mm length. Some results on ST/LY materials have been reported previously [6], as well as the concentration dependence of the room temperature conductivities of MO/AF materials [7]. Materials of F/AF series are analogous to short carbon fibre-filled polymers, as described in earlier studies [8].

In every case, an adequate amount of filler is added to the viscous resin and dispersed. The obtained suspension is outgassed, then heated either at 45 °C (ST/LY materials) or at 140 °C (MO/AF and F/AF materials) for several hours. d.c resistivity measurements were performed using a standard four-wire method. Results obtained at room temperature are plotted in Figs 1–3, respectively, as function of the volume fraction ϕ of the respective filler. The sharp drops in resistivity associated with the familiar insulator-to-conductor percolation transitions are clearly seen. The values of the critical concentrations ϕ^* at

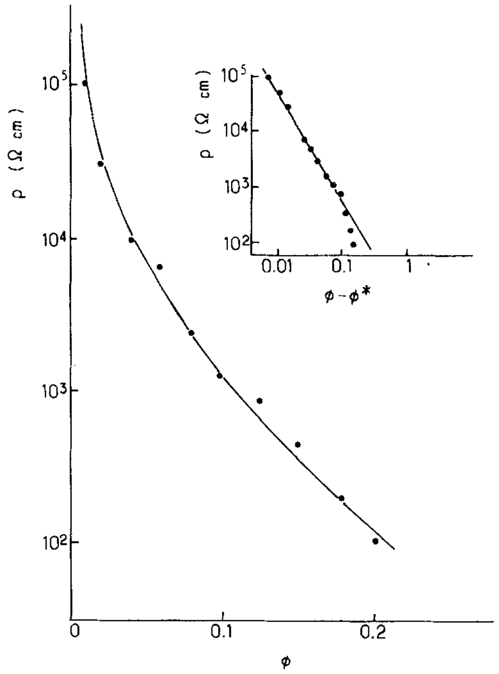

Figure 1 Concentration dependence of the room temperature resistance of MO/AF materials. Log–log plot of the resistivity against ϕ–ϕ^* with $\phi^* = 0.005$ showing the power law dependence (Equation 3) is given in inset: straight has slope $t = 2.0$.

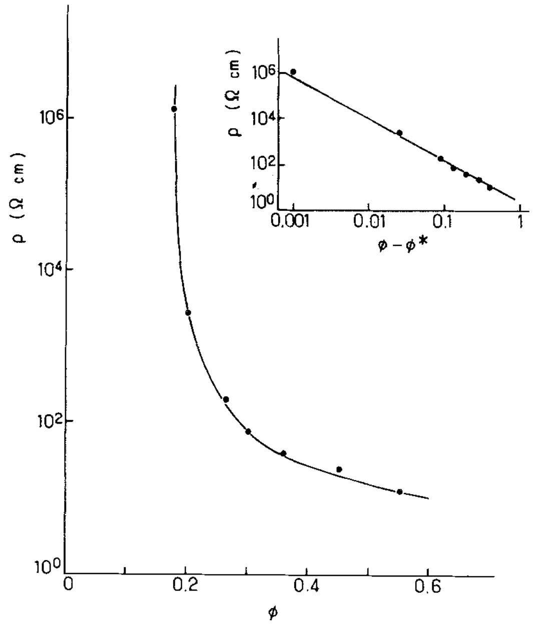

Figure 2 As Fig. 1 for ST/LY materials with $\phi^* = 0.175$ and $t = 1.85$.

TABLE I Labelling and characteristics of the three series of carbon-particle polymer composites used in this study. ϕ^* and t are the respective critical volume fraction and critical exponent, as deduced from the fits of Equation 3 to the data (See Figs 1–3).

Material	Polymer	Filler	Particle size	ϕ^*	t
MO/AF	Araldite F	Carbon black Monarch 1100	14 nm	0.005	2.0
ST/LY	Araldite LY	Carbon black Sterling FT	300 nm	0.175	1.85
F/AF	Araldite F	Carbon fibres	length 1 mm diameter 8 μm	0.0093	3.0

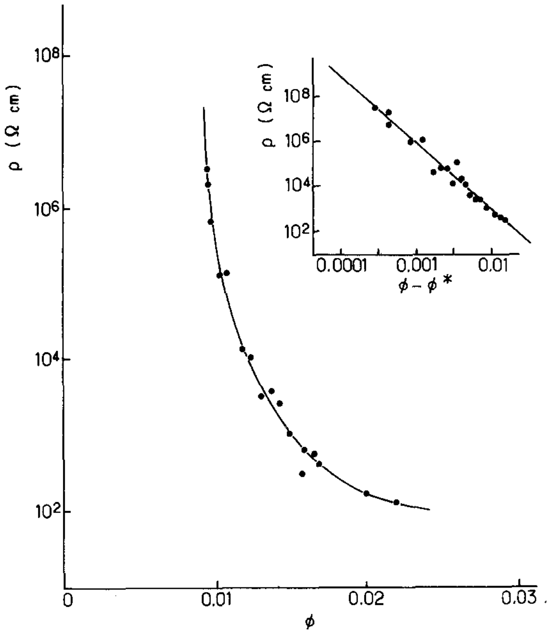

Figure 3 As Fig. 1 for F/AF materials with $\phi^* = 0.0093$ and $t = 3.0$

thresholds have been deduced from fits of the usual scaling law

$$\rho = \rho_0(\phi - \phi^*)^{-t} \qquad (3)$$

to the data. Insets of the Figs 1–3 show the log–log plots of ρ against $\phi - \phi^*$. Notice that for large values of $\phi - \phi^*$, experimental data of the MO/AF series depart from the power law dependence of Equation 3: this is in agreement with the theoretical prediction of the validity of Equation 3 restricted to the neighbourhood of the transition. The best values for ϕ^* and t are reported in Table I. The t values obtained in carbon black-filled materials are in good agreement with the value $t \simeq 2$ predicted by percolation theory [9]. In short carbon-filled polymers (F/AF), the value found for t is much larger than 2; this result, still not very well understood, is in agreement with previous findings in such materials [8].

Measurement at low temperatures of the resistivities was performed on samples selected from the three series down to either liquid helium or liquid nitrogen temperatures. The results are plotted in the Figs 4–6 as the relative variations of the conductivities against temperature for every given filler concentration.

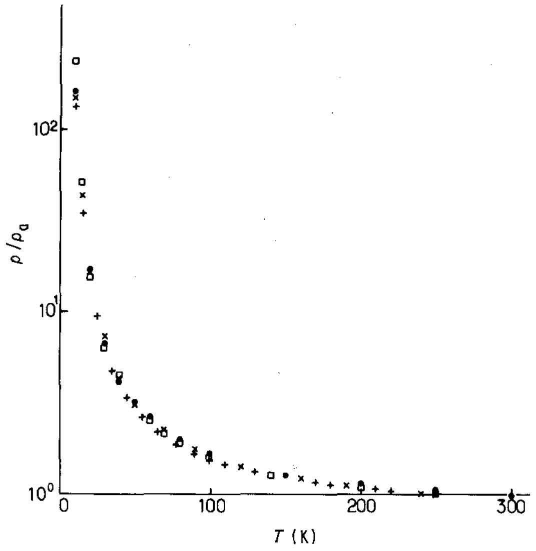

Figure 4 Plots of the relative changes of the resistivities of four MO/AF samples with values of carbon-black concentration, ϕ = ●, 0.02; □, 0.06; ×, 0.125; +, 0.20.

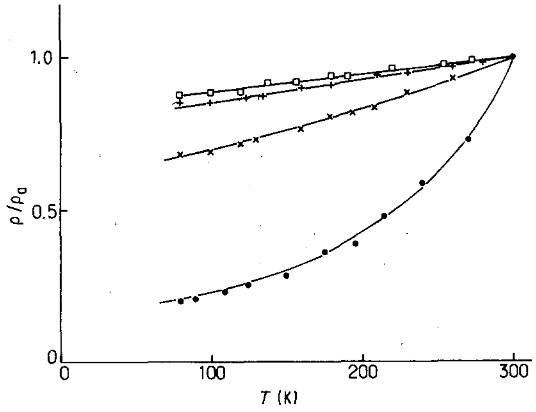

Figure 5 Plots of relative changes with temperature of the resistivities of four ST/AL samples with values of carbon-black concentration, ϕ = ●, 0.18; ×, 0.203; +, 0.266; □, 0.305. Lines are calculated with Equations 6 and 7.

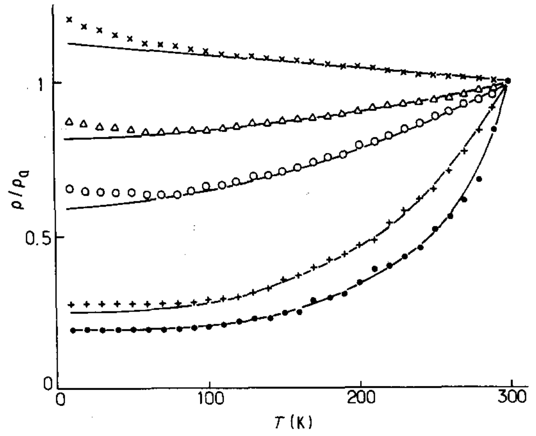

Figure 6 Plots of relative changes with temperature of the resistivities of five F/AF samples with given values of short fibre concentration, ϕ = ×, 0.025; △, 0.015; ○, 0.012; +, 0.01; ●, 0.0095. Lines are calculated with Equations 6 and 7.

Two different kinds of behaviour are clearly exhibited. Carbon black-filled MO/AF materials exhibit a semiconducting character, in agreement with many previously reported results for carbon–black–polymer composites [4, 10]. We notice however that, contrary to previous findings, the relative resistivity temperature dependence is independent of carbon-black-concentration. Contrary to this behaviour, the resistivities of samples of the other two series ST/LY and F/AF generally start to decrease as the temperature is lowered from room temperature. In the F/AF series, the resistivity against temperature curves exhibit a minimum situated near 100 K for the least-loaded materials up to $\phi = 0.015$. The behaviour is completely different for the most-loaded sample ($\phi = 0.024$) in this series. Furthermore, the relative thermal variations of the resistivities appear to be, in both series, strongly dependent on the filler concentration.

3. Discussion

As recalled in the introduction, the semiconducting behaviour of carbon-black polymer composites has been attributed to thermal fluctuation-induced tunnelling of electrons among particles, the temperature dependence of the resistivity being described by Equation 1. This equation has been fitted to the results obtained on the only samples exhibiting a semiconducting behaviour namely the MO/AF materials. ρ_0, T_0 and T_1 were considered as adjustable parameters. As noticed above, the temperature dependence of the relative conductivity being independent of the carbon-black concentration, a single set of values for T_0 and T_1 has been found for every carbon-black concentration

$$T_0 = 2.5\ \mathrm{K};\ T_1 = 66\ \mathrm{K}$$

These values are of the same order of magnitude as those previously reported for similar materials [5, 10]. Fig. 7 is a plot of the relative changes in conductivity with $(T + T_0)^{-1}$, and shows a good agreement between calculated and experimental values for all samples. This result demonstrates that, in this case, conduction actually proceeds by tunnelling of electrons among neighbouring particles. An important conclusion is that, as T_0 and T_1 are the same for all samples, the tunnelling junction characteristics (width, potential barrier and shape) remain independent of filler concentration. This means that the distance between particles involved in the macroscopic resistivity is independent of particle concentration. This important conclusion will be analysed below.

In order to account for the results obtained on the other two series of materials, we make the assumption that there is no tunnelling between particles which actually forms real electrical contacts. Moreover, we assume that the contact resistance is negligible, so the overall macroscopic resistivity is dominated by conduction through the particles. This assumption is not crucial for the model we are going to develop below: a weaker assumption could be that these resistances have slight temperature dependence.

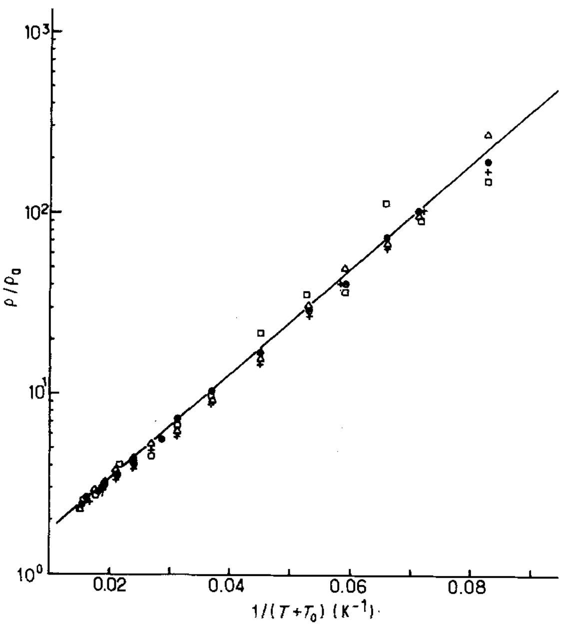

Figure 7 Relative resistivity changes of the MO/AF samples of Fig. 4 plotted as function of $(T + T_0)^{-1}$ with $T_0 = 2.5$ K, showing agreement with the predictions of Equation (1): straight line has slope $T_1 = 66$ K. ϕ = ●, 0.02; □, 0.06; △, 0.125; +, 0.20.

The only mechanisms for the temperature dependence of the conductivity are thus (i) eventual 'intrinsic' temperature dependence of the particle resistivity $\rho_c(T)$; and (ii) changes with temperature of the particle volume concentration as a result of different thermal expansion (or shrinking) coefficients of the matrix and of the particles.

We can thus develop an analysis which has already been used for temperature [6] and pressure [11, 12] dependences of random insulator–conductor composite.

$$\phi = \frac{V_c}{V_m + V_c} \tag{4}$$

in which $V_{c,m}$ are the respective volumes occupied in a sample by the carbon particles and the matrix.

$$\frac{1}{\phi}\frac{d\phi}{dT} = (1 - \phi)(\alpha_c - \alpha_m) \tag{5}$$

$\alpha_{c,m}$ being the respective volume thermal expansion coefficients for the particles and the matrix. Integration leads to the temperature dependence of the volume concentration.

$$\phi(T) = \frac{1}{1 + \dfrac{1 - \phi_a}{\phi_a}\exp(\alpha_m - \alpha_c)(T - T_a)} \tag{6}$$

in which ϕ_a is the particle volume concentration at ambient temperature T_a. For those samples close enough to threshold for which the scaling law in Equation 3 holds, the relative resistivity change is

$$\frac{\rho}{\rho_a} = \frac{\rho_c(T)}{\rho_{ca}(T)}\left(\frac{\phi(T) - \phi^*}{\phi_a - \phi^*}\right)^{-t} \tag{7}$$

subscript a referring to quantities measured at ambient temperature. $\rho_c(T)$ can be found by measuring the temperature dependence of the resistivity of pressed carbon particles. The resistivities of both carbon blacks are very weakly temperature dependent, and we will neglect $\rho_c(T)$ for the carbon-black Sterling. The resistivity of carbon fibres decreases almost linearly as the temperature increases

$$\frac{\rho_c}{\rho_{ca}} = 1 + a(T - T_a) \quad a \simeq 10^{-3}\ \mathrm{K}^{-1}$$

$\phi(T)$ depends primarily on the difference $\alpha_m - \alpha_c$. We have measured α_m of the two epoxies around room temperature below their respective phase-transition temperatures (for the Araldite LY, $T_g \simeq 40$ °C, for the Araldite F, $T_g \simeq 110$ °C). We found $\alpha_m \simeq 210^{-4}\ \mathrm{K}^{-1}$. The value of $\alpha_c \simeq -10^{-6}\ \mathrm{K}^{-1}$ around room temperature [13]. It is strongly temperature dependent, but as it is two orders of magnitude smaller than α_m, it will be neglected.

Taking Equation 6 into Equation 7, and recalling that values for ϕ^* and t have been determined experimentally (see Table 1), we can then calculate the predicted temperature dependence of the resistivities of materials ST/LY and F/AF as a function of filler concentration. Calculated values of ρ/ρ_a are plotted in Figs 5 and 6, respectively. We notice that the agreement with experimental values is better for ST/LY materials than for F/AF ones. In this case, whereas the overall concentration dependence of the thermal variations is well accounted for at temperatures higher than 100 K, (notice that it accounts nicely for the resistivity increase when T decreases for the sample filled with $\phi = 0.024$) our model fails to reproduce correctly the resistivity minimum, especially for intermediate values for ϕ. This discrepancy could be attributed to either a change of α_m with temperature, or to a third contribution to the resistivity changes. As our experimental set-up for measuring α_m does not allow measurements at very low temperatures, the first effect cannot be ruled out. We have also analysed the differences between calculated and experimental values of ρ/ρ_a: no definite temperature and concentration dependences of this difference have been clearly evidenced. We may however point out that, as the deviation between experimental to calculated values increase with ϕ_a, its origin can hardly be attributed to tunnelling effects.

We may however conclude that in carbon particle-filled polymers, two different resistivity temperature dependences associated to distinct conduction mechanism can be found. It remains to explain why either one can be present in those materials. We have noticed that throughout this study and other published studies, tunnelling conduction has been found when particles are small (less than a tenth of a micrometre). On the other hand, conduction dominated by direct particle–particle contact has been found in this and previous studies [6, 8, 12] when the materials are filled with large particles (carbon blacks with particle diameter larger than 0.1 μm, short carbon fibres). It results that, depending on their size, particles involved in conducting aggregates or clusters either make direct contact or remain at finite distances from one another. As aggregation of the particles in the course of material processing is eventually achieved while introducing the filler into a viscous fluid and dispersing it, it can be viewed as a floculation phenomenon [14] governed by interactions among the particles when they are immersed in a fluid. The D.L.V.O. [15] theory of colloidal stability can then apply, provided that the effect of shearing of the suspension is taken into account [16]. This approach, which correctly accounts for the polymer properties' dependence on the critical volume fractions ϕ^* [17], actually predicts that large particles will experience 'primary coagulation' (at very short distances) while small particles will experience 'secondary coagulation' (at finite distances). Furthermore, the equilibrium distance between small coagulated particles depends mostly on the fluid and the particle properties (surface tension, surface energy, particles size and shape) and should depend weakly on particles concentration. All these predictions agree with the conclusions that we have drawn from the observed resistivity temperature dependences.

4. Conclusions

We have shown that carbon particle-filled polymers may exhibit two distinct conductivity temperature dependences. The first, due to tunnelling of electrons among particles, is generally found in carbon-black-filled polymers. The second is found when carbon particles are large, and comes from differential thermal expansions of the matrix and the filler. A combination of these two mechanisms (change of tunnel junction width induced by thermal expansion) has been proposed to interpret a minimum in the resistivity against temperature curve in a polyethylene filled with a carbon black [10]. In this study, we have shown that in the non-semiconducting series (ST/LY and F/AF) results are not consistent with tunnelling conduction, but rather with direct contact of particles. We have shown that the two behaviours may be understood within the framework of the general theories for colloidal stability. This conclusion underlines the importance of the processing conditions of the composites on their electrical properties. This aspect will be further developed in a forthcoming paper.

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