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Study of the volume fraction, temperature, and pressure dependence of the resistivity in a ceramic–polymer composite using a general effective media theory equation

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A quantitative general effective media (GEM) equation is used to describe quantitatively the resistivity of an Fe_3O_4–epoxy composite system over a large range of volume fractions in terms of the resistivities of each component and two percolation morphology parameters. One parameter is the critical (percolation) volume fraction, ϕ_c, and the other is an exponent, t. Preliminary models, also based on the GEM equation, are used to describe the positive temperature coefficient of resistivity (PTC) and the piezoresistivity (uniaxial pressure) of the composite when the composition is near the percolation threshold.

1. Introduction

Ceramic fillers can be incorporated into polymer matrices to produce composite materials having properties different from those of the two separate components. The properties of the composite material vary as a function of the volume fraction of each component. For example, the resistivity of a conducting ceramic-filled polymer composite gives a percolation-type curve as shown in Fig. 1 for an Fe_3O_4–polymer composite. At low volume fractions of the conducting material (filler), the resistivity is close to that of the polymer (matrix). As the volume fraction of the filler increases, the resistivity slowly decreases until the percolation threshold is reached. At this point on the curve, a small increase in the filler volume fraction will produce a large decrease in the resistivity. Finally, at volume fractions above the percolation threshold, the resistivity approaches that of the conducting component.

Composite materials with volume fractions near the percolation threshold (or critical volume fraction) which can exhibit a measurable change in resistivity with temperature are known as thermistors. Likewise, composites which show a strong pressure-dependent resistivity are known as piezoresistors or pressure sensors. In this article an equation which combines aspects of both percolation theory and effective media theories is used to describe the volume fraction, the temperature, and the pressure dependence of the resistivity of the Fe_3O_4–epoxy composite system.

2. The general effective media (GEM) equation

Much experimental and theoretical work has been done to examine and to explain how the volume fractions and the morphology of the components affect the electrical behaviour of the composite materials (see, for example, [1]). Previous theoretical work has been based on both percolation and effective media theories. Percolation theory [2, 3] is limited in that the percolation equations are valid near the percolation threshold only when the ratio of the resistivities of the two components is infinite [4]. This can be a problem when dealing with real systems where all the components have finite resistivities. However, percolation theory does become valid in cases of finite resistivities near the percolation threshold by the use of scaling factors [4].

Effective media theories [3] are used to try to predict the effective, or large-volume average, of the electrical resistivity, dielectric constant, thermal conductivity, gaseous diffusion, and magnetic permeability of composites. There are two special cases for which effective media theories exist, the symmetric and the asymmetric cases [3]. The symmetric case assumes that a random mixture of spherical (oriented ellipsoidal) particles of two (or more) components completely fill all space. In the asymmetric case the surfaces of the particles of one component (the filler) are always completely covered by the other component (the matrix). The volume ratio of the coating to the interior is the same for all filler particles. In the derivation of both theories, the particle sizes are assumed to have an infinite size range in order to fill all space. When one component is a perfect insulator, the symmetric media theory contains a conductor–insulator transition at a specific conductor volume fraction, whereas the asymmetric theory does not [3]. In practice,

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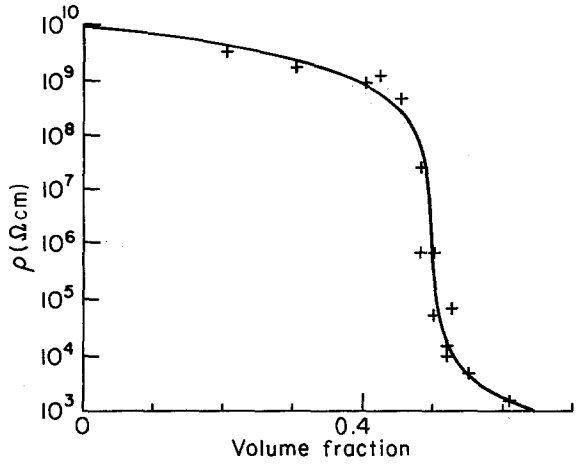

Figure 1 The resistivity versus volume fraction of filler material for Fe_3O_4 composites. (——) Generated using the GEM equation. The parameters used are given in the text.

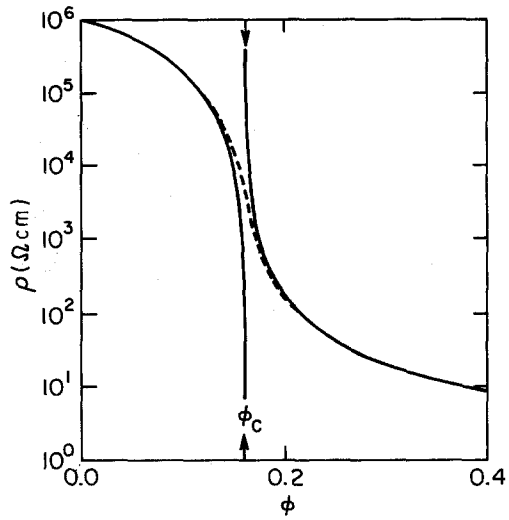

Figure 2 Equations 1, 2 and 3 are plotted for $\sigma_l = 10^{-6}\,\Omega\text{cm}^{-1}$ ($\rho_h = 10^6\,\Omega$cm), $\sigma_h = 1\,\Omega\text{cm}^{-1}$ ($\rho_l = 1\,\Omega$cm), $\phi_c = 0.16$ ($f_c = 0.84$), and $t = 1.7$ as a function of ϕ.

conductor–insulator transitions occur over a wide range of volume (or area in two dimensions) fractions (see, for instance, [5–10]).

A generalized effective media (GEM) equation with two morphology parameters, ϕ_c and t, has been proposed by McLachlan [5]. It was derived as an interpolation between the symmetric and asymmetric effective media theories. The GEM equation written in terms of electrical conductivity is

$$\frac{1-\phi(\sigma_l^{1/t}-\sigma_m^{1/t})}{\sigma_l^{1/t}+[(1-\phi_c)/\phi_c]\sigma_m^{1/t}} + \frac{\phi(\sigma_h^{1/t}-\sigma_m^{1/t})}{\sigma_h^{1/t}+[(1-\phi_c)/\phi_c]\sigma_m^{1/t}} = 0 \qquad (1)$$

where ϕ is the volume fraction of the high conductivity component, and ϕ_c is the critical volume fraction of the high conductivity component at which a percolation path is formed through the media by the high conductivity component. Here, σ_l is the conductivity of the low conductivity component, σ_h is the conductivity of the high conductivity component, σ_m is the conductivity of the medium itself, and t is an exponent. Equation 1 reduces to the symmetric and asymmetric theories and has the mathematical form of the percolation equation in the appropriate limits [5].

The GEM equation can also be viewed as a matched asymptotic expression as it interpolates between the two percolation equations given below. When $\sigma_l = 0$, the GEM equation, with $f = 1 - \phi$ and $f_c = 1 - f_c$, reduces to

$$\sigma_m = \sigma_h(1 - f/f_c)^t \qquad (2)$$

and when $\sigma_h = \infty$, $\rho_h = 1/\sigma_l$, $\rho_l = 1/\sigma_h$ it becomes

$$\rho_m = \rho_h(1 - \phi/\phi_c)^t \qquad (3)$$

This is illustrated in Fig. 2 where Equations 1, 2 and 3 are plotted for the typical three-dimensional morphology parameters $\phi_c = 0.16$ and $t = 1.7$ with $\sigma_h = 1\,\Omega\text{cm}^{-1}$ or $\rho_l = 1\,\Omega$cm and $\sigma_l = 10^{-6}\,\Omega\text{cm}^{-1}$ or $\rho_h = 10^6\,\Omega$cm. This figure clearly indicates where the percolation equations will not suffice and the GEM equation must be used.

When $f_c = 1$ or $\phi_c = 1$, Equations 2 and 3 are both forms of the Bruggeman asymmetric equation [3] which allows values for L_f, L_ϕ, m_f, and m_ϕ to be calculated from the corresponding exponent in the asymmetric media theory [5, 11, 12], which gives

$$L_f = 1 - f_c/t \qquad (4a)$$

$$L_\phi = \phi_c/t \qquad (4b)$$

$$m_f = t/f_c \qquad (4c)$$

$$m_\phi = t/\phi_c \qquad (4d)$$

Values of m_f and m_ϕ as functions of the demagnetization coefficient $L_c \neq (L_b = L_a)$ calculated for $\sigma_l = 0$ and $\sigma_h = \infty$, respectively, from Equation 23 in [12], are plotted in [5].

The GEM equation has been used to fit accurately a vast amount of conductivity data [5–10]. It has also been used to fit the electrical and thermal conductivities, and experimental permeability data from a series of sintered nickel samples (0.14–0.95 volume fraction of nickel) while using the same two morphology parameters, f_c and t [6].

In Section 4, the GEM equation is used to fit quantitatively the resistivity versus volume fraction data for Fe_3O_4–epoxy composites. In Section 5 the temperature coefficient of resistivity and the pressure dependent resistivity for a 47 vol% Fe_3O_4 sample is modelled using the GEM equation.

3. Fitting procedure

The experimental resistivity versus volume fraction data for the Fe_3O_4–eccogel (1365-0) epoxy systems [13] were fitted to the GEM equation using the free parameters ϕ_c, t, ρ_h (the resistivity of the polymer) $= 1/\sigma_l$, and ρ_l (the resistivity of the conductive filler) $= 1/\sigma_h$. The computer program, which utilizes an IMSL non-linear regression fitting program, uses the experimental conductivity (volume fraction) to calculate a volume fraction (conductivity) called "Calc" from Equation 1. Calc is then compared with the actual volume fraction (conductivity) called "Expt".

The sum of the squares of the residuals, called "SSQ"

$$\text{SSQ} = \sum_n [(\text{Calc} - \text{Expt})]^2 \quad (5)$$

is minimized by the computer program for the n data points.

4. Volume fraction results

Fig. 1 shows the experimental data for the resistivities measured at 25 °C for varying volume fractions of Fe_3O_4 in epoxy and the theoretical fit using the GEM equation.

The parameters used to generate the theoretical curves are: $\rho_{Fe_3O_4} = 1.62 \times 10^2\ \Omega\text{cm}$, $\rho_{poly} = 8.91 \times 10^9\ \Omega\text{cm}$, $\phi_c = 0.496$ and $t = 1.50$. The extrapolated resistivity of Fe_3O_4 given by the GEM equation is in reasonable agreement with the measured resistivity of the powder (2.00–$3.00 \times 10^2\ \Omega\text{cm}$) [13]. The resistivity of the polymer (eccogel 1365-0) given by the GEM equation is in reasonable agreement with the values calculated using the GEM equation for graphite- and carbon black–epoxy composites (1.30×10^{10} and $8.3 \times 10^9\ \Omega\text{cm}$) [14], respectively. The value of the exponent, t, is similar to the universal value of 1.65 for three dimensions given in percolation theory [2]. ϕ_c and t for the Fe_3O_4–epoxy system are similar to those of the graphite–epoxy system which has been shown to exhibit the behaviour of a random distribution of filler particles in a polymer matrix [14]. A random distribution occurs in systems in which the filler particle size is approximately the same size as the polymer particle size [15, 16]. Segregated distributions, with lower values of ϕ_c, occur in systems in which the particle size of the filler material is much smaller than that of the polymer [15, 16]. Segregated-type behaviour has been shown to occur in carbon black–epoxy composites [14]. The value of the demagnetization coefficient, L_ϕ (Equation 4), for the Fe_3O_4 system is 0.331, which corresponds to a c/a ratio of approximately 1 ($c/a = 1$ for spheres). These values suggest that the Fe_3O_4 particles can be approximated as isolated spheres in a random configuration. The critical volume fractions of the segregated and random distributions are dependent upon the number of contacts per filler particle which is about 1.5 at the percolation threshold [2, 17].

In studies where conducting hard spheres are placed at random on a regular lattice or conducting hard spheres are randomly packed together with equally or near equally sized insulating spheres, the ϕ_c value is about 0.16–0.18 [2]. For systems such as Fe_3O_4–epoxy in which $\phi_c (= 0.496)$ is greater than the usual value of about 0.17, some of the filler particles do not make contact with their nearest neighbour particles, due to the partial wetting of the particles by the polymer. Hence, not only will the probability of a site being occupied by a conducting particle be less than 1 ($P_s < 1$), but so too will the probability of a bond between nearest neighbour sites ($P_b < 1$). Therefore (as illustrated in Fig. 4.18 in [2] or Fig. 7 in [18]), if the medium is to remain conducting when P_b is decreased, P_{cs} (the critical site probability) must be increased. Therefore, as $\phi_c = vP_{cs}$ (where v is the volume filling factor per site, e.g. 0.637 for randomly packed spheres) an inverse relationship exists between ϕ_c and P_b (or P_{cb} if one is exactly at the site–bond percolation threshold). In the present case the partial wetting of the conducting particles has presumably decreased the bond probability by an amount such that $\phi_c = 0.496$. Note that if the particles were completely wetted by the polymer the situation would be that of a Bruggeman asymmetric system with $\phi_c = 1$.

5. Modelling of the independent variables, temperature and pressure

The GEM equation can also be used to model the positive temperature coefficient of resistivity (PTC) and the piezoresistivity (uniaxial pressure) of a 47 vol % Fe_3O_4–epoxy composite.

In these preliminary attempts to model the positive temperature coefficient of resistivity and piezoresistivity, the following assumptions are made.

1. For site–bond percolation ($P_{cs} - P_{cb}$), as P_{cb} decreases, P_{cs} increases, where P_{cb} and P_{cs} are defined as the values of P_s and P_b along the locus of points defining the boundary between the percolating (conducting) and non-percolating (insulating) regions. ($P_{cs} - P_{cb}$ phase boundaries are illustrated in Fig. 4.18 of [2] and Fig. 7 of [18].)

2. The relationship [2] $vP_s = \phi$ is valid everywhere in the site–bond space defined in the aforementioned figures. Only on the P_{cs}–P_{cb} boundary is the equation $vP_{cs} = \phi_c$ valid.

3. For values of P_b and P_s close to the P_{cs}–P_{cb} boundary ($P_b \approx P_{cb}, P_s \approx P_{cs}$, and $\phi \approx \phi_c$) and for small changes along the P_{cs}–P_{cb} boundary, assumptions 1 and 2 are assumed to be good approximations. Therefore, as a first approximation, $P_b (\approx P_{cb}) \propto 1/\phi (\approx 1/\phi_c)$. A linear dependence of the bond probability between nearest neighbour particles on the temperature and pressure is assumed. However, it should be noted that for large changes along the P_{cs}–P_{cb} boundary and for values of P_b and P_s far from the boundary, these relations may not be valid and/or the inverse relation may not be a linear one.

Based on these assumptions, the equation used to model the PTC effect assumes that at some critical temperature, T_c, the critical volume fraction, ϕ_c, becomes equal to the actual volume fraction, ϕ

$$\phi_c(T) = \phi/[1 - m(T - T_c)] \quad (6)$$

where m is a multiplier and ϕ is the volume fraction of the Fe_3O_4. The experimental data are fitted by substituting Equation 6 for ϕ_c in the GEM equation (Equation 1). The five variable parameters for the fit are t^*, σ_l, σ_h, T_c, and m with ϕ being fixed, where t^* describes the temperature-dependent conductivity. t^* should not be compared with t, which describes the volume fraction-dependent conductivity, as they do not describe the same physical processes. The following equation was also used to fit the data

$$\phi(T) = \phi_c[1 - m(T - T_c)] \quad (7)$$

This equation assumes that at some temperature, T_c,

the volume fraction at room temperature, ϕ, which is a function of temperature, would become equal to the critical volume fraction, ϕ_c. Equation 7 was found not to fit the data as satisfactorily as Equation 6.

Similarly, it is assumed for the piezoresistivity that the number of contacts changes as a linear function of pressure

$$\phi_c(P) = \phi_c(0)/(1 + mP) \quad (8)$$

The experimental resistivity versus pressure data are fitted using the GEM equation, Equation 8 substituted for ϕ_c and now only four parameters (t^*, ρ_l, ρ_h, and m) are variables as $\phi_c(0)$ is assumed to have the value obtained from fitting the resistivity versus volume fraction data (Fig. 1).

6. Positive temperature coefficient of resistivity results

Fig. 3 shows the experimental data and two theoretical fits for the resistivity versus temperature of a 47 vol % Fe_3O_4–epoxy composite. The data are only shown over the temperature range where the resistivity changes rapidly because of the simplistic linear model being used.

The parameters used to generate the solid line in Fig. 3 are $\rho_{Fe_3O_4} = 9.94\,\Omega\,cm$, $\rho_{poly} = 10^{12}\,\Omega\,cm$, $t^* = 1.49$, $T_c = 40.8\,^\circ C$, and $m = 2.73 \times 10^{-5}$. These parameters are obtained using the starting values of $\rho_{Fe_3O_4}$, ρ_{poly}, and t from the resistivity–volume fraction data, a T_c in the mid-temperature range, and an appropriately small value of m. The resistivities of the Fe_3O_4 and the polymer given by the temperature-dependent results are not consistent with the values given by the volume fraction results. The $\rho_{Fe_3O_4}$ is two orders of magnitude lower and the ρ_{poly} is two orders of magnitude higher than the volume fraction resistivities. To force self-consistency between the resistivities of the temperature dependent and the volume fraction results, the resistivities of the Fe_3O_4 and polymer were fixed to the values given by the volume fraction results. The results of this three-parameter fit to the data

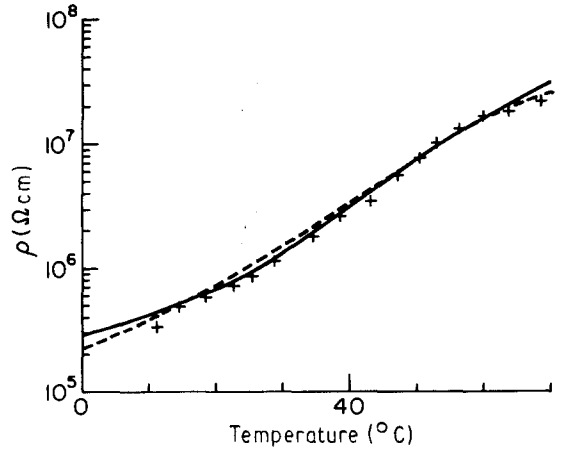

Figure 3 The resistivity versus temperature for a 47 vol % Fe_3O_4–epoxy composite. (——) Generated using the GEM equation and a five-parameter fit, (– – –) generated using the GEM equation and a three-parameter fit to the data. The model and the parameters are given in the text.

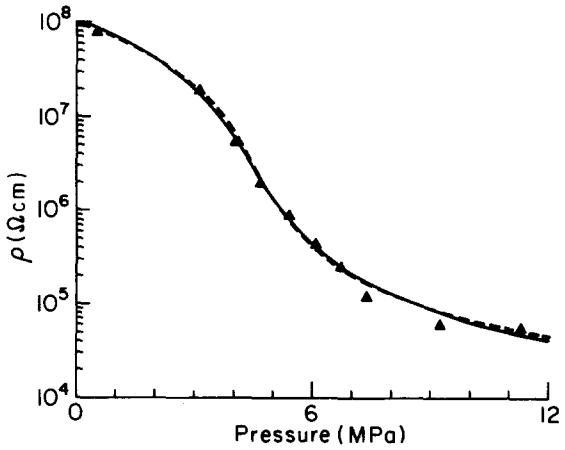

Figure 4 The resistivity versus uniaxial pressure for a 47 vol % Fe_3O_4–epoxy composite. (——) Generated using the GEM equation and a four-parameter fit, (– – –) the three-parameter fit. The details are given in the text.

give the dashed line in Fig. 3. The parameters are: $t^* = 3.44$, $T_c = 29.3\,^\circ C$ and $m = 4.19 \times 10^{-3}$. Given the crudeness of the model (i.e. a linear approximation and not accounting for the temperature-dependent resistivity of the separate components of the composite), the theoretical fits to the experimental data are reasonable.

7. Uniaxial piezoresistivity results

Fig. 4 shows the experimental data and a theoretical three-parameter ($\rho_{Fe_3O_4}$, t^*, m) fit for the resistivity versus uniaxial pressure of a 47 vol % Fe_3O_4–epoxy composite. The resistivities given in the actual paper [13] were normalized using the resistivity at zero pressure. To get quantitative data, the resistivity at zero pressure is taken to be $\rho(0) = 1.10 \times 10^8\,\Omega\,cm$, which corresponds to the resistivity of a 47 vol % sample given by the GEM equation in Fig. 1.

Initially, a four-parameter fit to the data was attempted and produced the parameters: $\rho_{Fe_3O_4} = 4.0 \times 10^2\,\Omega\,cm$, $\rho_{poly} = 1.55 \times 10^{10}\,\Omega\,cm$, $t^* = 1.69$ and $m = 0.0122$, which is shown as a solid line in Fig. 4. A three-parameter fit, shown as the dashed line in Fig. 4, which used a fixed value of $\rho_{poly} = 8.91 \times 10^9\,\Omega\,cm$ (Section 4) gives: $\rho_{Fe_3O_4} = 6.58 \times 10^2\,\Omega\,cm$, $t^* = 1.54$, and $m = 0.0121$. The theoretical curve can be seen to be at least semi-quantitatively correct. Because the changing geometric factor is not taken into account, the data points are also only semi-quantitative.

9. Conclusion

The general effective media (GEM) equation has been used to quantitatively fit the resistivity–volume fraction data for a ceramic–polymer composite (Fe_3O_4–epoxy). The value of ϕ_c and the demagnetization coefficient, L_ϕ and m_ϕ, suggest a random distribution of filler particles for the composite system in which the filler particles are partially wetted by the polymer, i.e. $P_b < 1.0$.

A more detailed account of effective media and percolation theories as well as the derivation and

properties of the GEM equation are given in a review article [18].

A preliminary attempt to model the positive temperature coefficient (PTC) of resistivity and the piezoresistivity (uniaxial pressure) of a ceramic–polymer composite near the critical volume fraction, ϕ_c, using simplistic linear models, produced reasonable fits to the experimental data. The model assumed that the number of contacts per particle changed linearly with the temperature and pressure. Considerably better theoretical models for $\phi_c(T)$ and $\phi_c(P)$ and more experimental work are needed to elucidate fully these effects.

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