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Metal oxide–polymer thermistors

DAWNE M. MOFFATT, JAMES P. RUNT, ARVIND HALLIYAL,
ROBERT E. NEWNHAM
*The Materials Research Laboratory, Pennsylvania State University, University Park,
Pennsylvania 16802, USA*

Composites consisting of semi-crystalline or amorphous polymers and a conducting metal oxide filler, V_2O_3, have been prepared. They exhibit relatively low room temperature resistivities, (PTC) of resistance effects of up to nine orders in magnitude, and an NTC transition near −100° C. A previously proposed model that describes the resistivity behaviour of metal–insulator composites as a function of both temperature and filler concentration has been applied to V_2O_3–polyethylene and V_2O_3–rigid epoxy composites. The predictions of this model are then compared with the experimental behaviour of the composites. In addition, SEM micrographs of the composites are shown to illustrate the wetting characteristics of the various polymers on V_2O_3.

1. Introduction

The study of thermistors, or temperature-dependent resistors, has spanned several branches of materials research and the temperature sensitive resistance of these materials leads to many possible applications. These include circuit protection devices, flow meters, and thermal detectors. Traditionally, thermistors have been prepared from doped $BaTiO_3$ ceramics, in which the transition from the ferroelectric to paraelectric state at the Curie temperature is utilized. The ceramic consists of conducting grains and insulating grain boundaries that form a barrier to electron flow. The structure changes from cubic to tetragonal with a decrease in temperature through the Curie point, and the polarization that is induced in the ferroelectric state results in a decrease in resistivity. These thermistors exhibit a fairly large positive temperature coefficient (PTC) of resistance at the Curie temperature and the breadth of the transition is a function of the dopants used in the $BaTiO_3$. $BaTiO_3$ compositions have been widely used for some time, although they are limited to certain applications by relatively high room temperature resistivity (40–100 Ω cm) and high manufacturing costs [1].

In a move toward lower room temperature resistivities as well as away from relatively expensive ceramic processing, thermistors have been developed that are based on metal–insulator composites. The most common of these is one composed of conducting carbon black particles dispersed in an insulating matrix of semi-crystalline polyethylene. These polymer composites show substantial PTC effects and can exhibit room temperature resistivities near 1–10 Ω cm [2–5]. In the past several years we have been explaining composite thermistors based on mixtures of transition metal oxides and polymers [6–9]. The filler materials include such oxide compounds as TiO, TiO_2, VO_2, and V_2O_3; these are dispersed in the appropriate polymer, crystalline or amorphous in nature, to form composites that exhibit acceptable room temperature resistivities, as low as 5 to 200 Ω cm, depending on the filler. In the case of crystalline matrices, the PTC effect is very sharp in comparison to the effect observed in amorphous polymer composites. For both types of polymers the location of the PTC transition is a function of the polymer matrix. Composites consisting of semi-crystalline polymers exhibit a PTC effect near the melting point of the polymer. This phenomena is believed to be a result of the separation of the conducting particles due to the thermal expansion of the polymer. As the filler particles move apart, the existing conducting pathways are broken, causing an increase in resistivity. Some composites, such as those incorporating V_2O_3, show an additional transition at lower temperatures, which is responsible for the negative temperature coefficient (NTC) of resistance that, combined with the existing PTC, results in a resistivity against temperature curve with a square-well appearance. There exists a window of temperatures within which the resistivity is quite low; beyond this window the resistivity is dramatically higher.

The behaviour of these composites, composed of either type of polymer, is dependent upon the idea of percolation [10–12]. Percolation theory allows one to describe the richness of interconnections present in a random system. In a plot of log resistivity against volume fraction filler (see, for example, Fig. 8), three regions may be distinguished. At low filler concentrations, the high resistivity of the composite is indicative of the insulating phase. The percolation threshold is defined as the volume fraction at which conducting paths begin to form. In the so-called percolation region, the resistivity begins to decrease as more conducting pathways are formed. Finally, a saturation region is reached wherein the resistivity is relatively insensitive to filler concentration due to extensive interparticle contacts. Here the resistivity value is expected to approach that of the pure conductor.

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For the carbon black–polyethylene composite system a large PTC transition is observed near 130° C, the melting point of polyethylene. One drawback of using a thermoplastic matrix like polyethylene is that a strong NTC effect is observed at temperatures above PTC transition. This is presumably due to movement of the conducting particles in the polymer melt and formation of new conducting pathways. In order to alleviate this problem, the composites can be crosslinked through either thermal or radiation treatment [2, 13, 14]. At sufficiently high crosslink densities, the sample has excellent stability and a fairly temperature insensitive resistivity.

In contrast to the metal–semi-crystalline polymer composites, systems composed of a conducting filler and amorphous polymers are not as easily understood. One usually expects to observe large PTC effects over a very narrow range of compositions in the critical region for all systems where a small change in interparticle distance or effective volume fraction results in a significant change of resistivity, [4]. Some metal fillers do exhibit a PTC when combined with certain amorphous polymers [6–9, 15, 16]. In these cases, the transition appears to occur beyond this narrow compositional range. Most of these PTC resistance effects are not as dramatic as those seen in semi-crystalline polymer composites.

In order to better understand the resistivity behaviour of these composite thermistors, a theoretical model developed by Sherman *et al.* [17] was examined. Other models exist [18, 19], but this one was chosen because it directly incorporated both the temperature and concentration effects on the resistivity. This model, which was originally designed for carbon black and metal-filled composite systems, incorporates three physical phenomena: percolation, thermal expansion, and quantum mechanical tunnelling. It has been previously applied to describe the behaviour of nickel particles in a polyethylene matrix and carbon black–polyethylene composites [17]. The important features of the Sherman, *et al.* model are described in the following paragraphs.

1.1. Percolation

An important consequence of including percolation behaviour in this model is that it enables one to incorporate the idea of a density threshold into the discussion. At a critical volume fraction filler, v_c^p, the overall resistance of the system decreases sharply from insulating to conducting in nature. This critical point can be described by Equation 1, where f is the maximum packing fraction and z is the lattice coordination number,

$$v_c^p = \frac{2f}{z} \qquad (1)$$

The maximum packing density is a function of particle shape and lattice packing and may range from 0.5 to 0.8 for common shapes and packing sequences.

1.2. Thermal expansion

The thermal expansion of a polymer is generally much larger than that of the conducting filler and is believed to be the primary phenomena responsible for the PTC effect in many metal–insulator composites. The changes in polymer density and effective filler volume fraction with temperature constitute an important part of this model. If the expansion of the polymer with increasing temperature and its effect on the concentration of filler particles are taken into consideration, a PTC transition can be built into the model. Implicit in this discussion is the assumption that the polymer is homogeneous.

1.3. Quantum mechanical tunnelling

While percolation is governed by the macroscopic movement of charge within the system and thermal expansion incorporates the effect of temperature dependence on the conducting filler and polymer matrix, there are several possible mechanisms that could be responsible for the conduction [20, 21]. The one that Sherman *et al.*, consider to be the most appropriate in describing the conduction in composite thermistors is quantum mechanical tunnelling. Tunnelling is concerned with the movement of electrons on a microscopic scale, from one conducting particle to another, across the gap between the particles. This causes a decrease in the resistance expected in the polymer alone.

Tunnelling theory has been described by several authors [22–25]. In the present model, the theory has been somewhat simplified. First, to describe percolation, one must define the critical volume fraction. Then, depending on whether one is considering concentrations above or below this chosen point, the resistivity is calculated from the following equations

$$\varrho = \left(\frac{l}{s_p}\right)\left(\frac{1 - zv_c}{2f}\right) \qquad v_c < v_c^p$$

$$\varrho = \left(\frac{l}{s_c}\right)\left(\frac{1 - 2/z}{v_c/f - 2/z}\right) \qquad v_c > v_c^p$$

where

$$s_p = \frac{a_{ct}}{\varrho_p l_g}$$

$$s_c = \left[\varrho_c\left(\frac{l_c}{a_c}\right) + \left(\frac{1}{a_{ct}^{1/2}}\right)\right]^{-1}$$

In these equations, s_c and s_p are the conductance of the conductor and polymer respectively, a_{ct} the effective mean cross-sectional tunnelling area, ϱ_p the resistivity of polymer, l_g, the gap length between conductor particles and ϱ_c, l_c, a_c, and v_c the resistivity, particle length, mean cross-sectional area and volume fraction of the conductor respectively. To describe the resistivity as a function of temperature, the same expressions are used. The major change is the addition of the temperature dependence of the volume fraction and gap length.

2. Experimental procedure

Two types of conducting fillers were used in this study. First, composites were prepared from vanadium (III) oxide, V_2O_3, supplied by Alfa Products. The particle size was determined with the Leeds and Northrup Microtrack to be approximately 5 μm. The

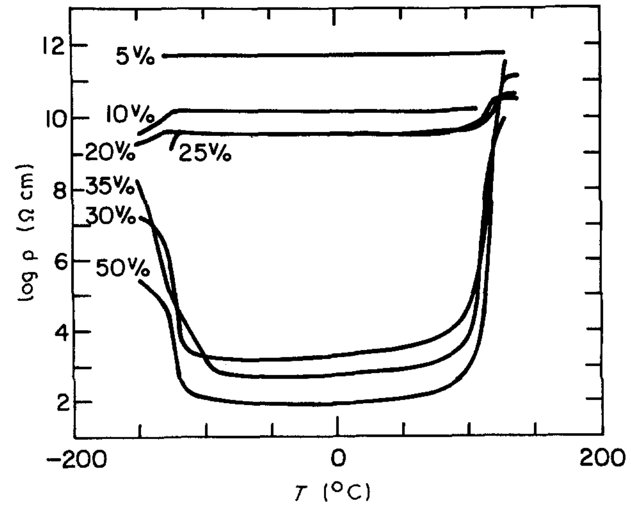

Figure 1 Resistivity plotted against temperature at 1 kHz for V_2O_3–polyethylene composites.

room temperature resistivity of single crystal V_2O_3 is approximately 10^{-2} to 10^{-3} Ωcm [26]. In addition, this material becomes semiconducting at temperatures below −100° C. The transition from semiconductor to metal is a result of the change in crystal structure and delocalization of electrons in the structure. The second filler was carbon black obtained from Cabot (Vulcan P). The nature of this conductor allows for the formation of conducting aggregates that form long, chain-like structures throughout the composite.

A variety of polymers were utilized in fabricating composites. These include semi-crystalline, high density polyethylene and several amorphous polymers: a flexible epoxy, a rigid epoxy, a polyurethane, and polymethylmethacrylate (PMMA). The polyethylene was obtained from Phillips Petroleum (Marlex EHM6001) and has a melting point of 130° C. Spurrs B, the rigid epoxy, has a T_g of 80° C and was obtained from Polysciences, Inc. The flexible epoxy, Eccogel 1365-0, was purchased from Emerson–Cuming and has a glass transition near −30° C. The polyurethane (Dexter Hysol, US0038) has a T_g near 15° C, and the PMMA, T_g = 100° C, was obtained from Rohm and Haas.

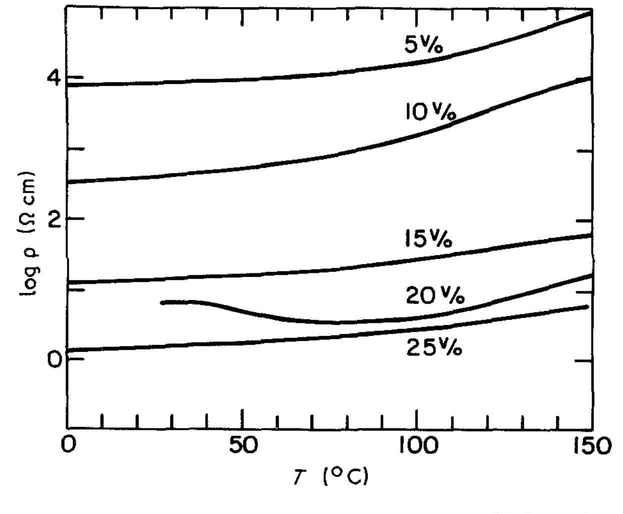

Figure 2 Resistivity plotted against temperature at 1 kHz for carbon black–rigid epoxy composites.

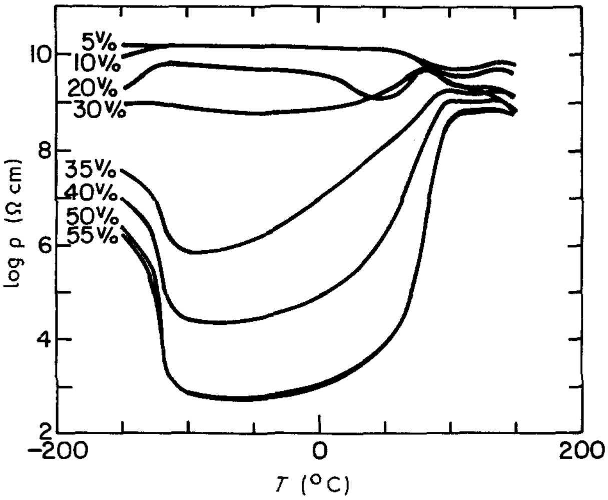

Figure 3 Resistivity plotted against temperature at 1 kHz for V_2O_3–rigid epoxy composites.

V_2O_3 composites with polyethylene and PMMA were prepared in a high temperature shear mixer (Brabender, Inc.) at 150° C for 20 to 30 minutes. The resulting mixture was pressed into pellets at 200° C for polyethylene (180° C for PMMA). Composites prepared from the remaining polymers were mixed at room temperature, cast, and cured according to the prescribed directions: Spurrs B, 80° C for 24 h; Eccogel 1365-0, 70° C for 24 h and the polyurethane, 80° C for 2 h. The resulting pellets were polished and electroded with air-dry silver paint. Resistivity as a function of temperature measurements were performed at 1 kHz using an Hewlett Packard 4274A Multi-Frequency LCR Meter over a temperature range of −150 to 200° C. In addition, d.c. resistivity measurements were made at room temperature with the Hewlett Packard 16055A Picoammeter. This was done so that a direct comparison between the experimental data and the theoretical model could be made.

The microstructure of the composites was analysed using the ISI-DS130 Dual Stage Scanning Electron Microscope. The samples were fractured at liquid nitrogen temperatures to avoid significant plastic deformation of the polymer and then gold coated to eliminate charging.

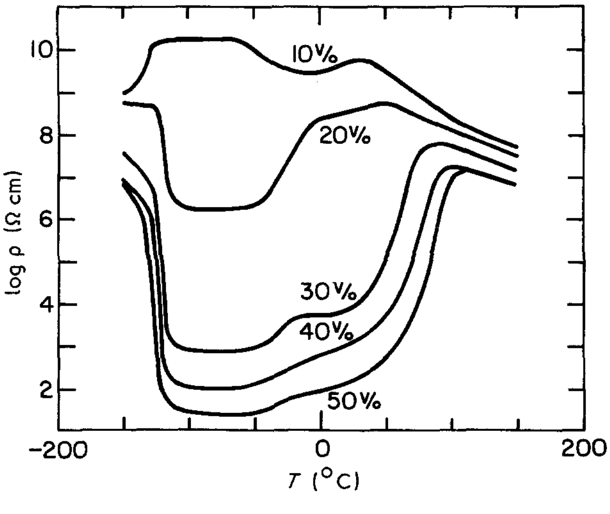

Figure 4 Resistivity plotted against temperature at 1 kHz for V_2O_3–flexible epoxy composites.

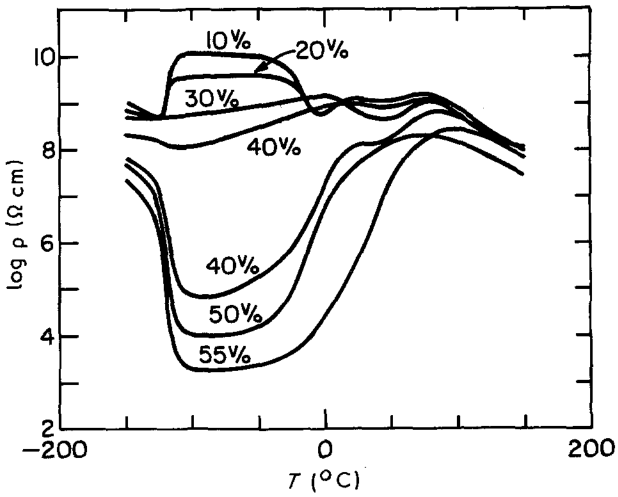

Figure 5 Resistivity plotted against temperature at 1 kHz for V_2O_3–polyurethane composites.

3. Results and discussion

3.1. Resistivity characteristics

The presence of a PTC transition is a key to the importance of these composites. The location of the PTC effect is closely related to the chosen polymer. Fig. 1 illustrates the resistivity as a function of temperature at 1 kHz for several compositions in the V_2O_3–polyethylene system. In samples with low volume fractions of filler, the resistivity is relatively high and there is no evidence of a significant PTC transition at the melting point. As the filler concentration is increased, a PTC effect is observed and it increases in magnitude somewhat as the V_2O_3 concentration increases, primarily due to the decrease in room temperature resistivity. This is important because the room temperature resistivity, as well as the magnitude of the PTC, serves as a figure of merit for the composite.

Fig. 2 illustrates the resistivity against temperature behaviour for carbon black-Spurrs B composites. No significant PTC transition is present in this system over a concentration range of 5 to 25 vol. % carbon black. As mentioned previously, it is generally considered that amorphous polymer–conductor composites would not exhibit a PTC effect over a wide range of filler concentrations. However, as seen in Figs 3 to 6, there is, in fact, a PTC transition present when using V_2O_3 as a filler material. Fig. 3 shows the behaviour of V_2O_3–rigid epoxy composites, where a PTC effect is observed over a wide range of filler concentrations. This is consistent with results reported in a number of studies conducted on metal oxide–filled systems [6–9]. Furthermore, samples prepared from other amorphous polymers showed similar behaviour. Fig. 4 illustrates the behaviour for V_2O_3–flexible epoxy composites while Fig. 5 shows the response for V_2O_3–polyurethane composites. Finally, the resistivity–temperature behaviour of the V_2O_3–PMMA system is shown in Fig. 6. It should be noted that the temperature of the PTC transition varies from one system to another, indicative of the polymer type. There may be a correlation between the PTC transition temperature and the polymer glass transition temperature, although the composites incorporating the flexible epoxy do not fit this proposal; their transition occurs at a higher temperature.

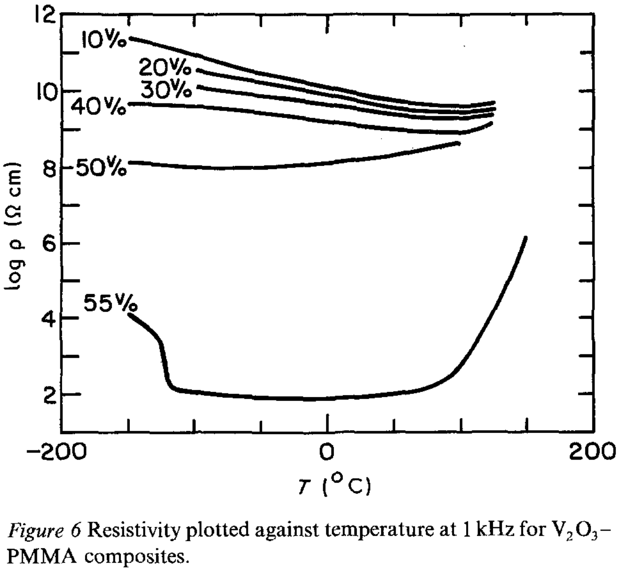

Figure 6 Resistivity plotted against temperature at 1 kHz for V_2O_3–PMMA composites.

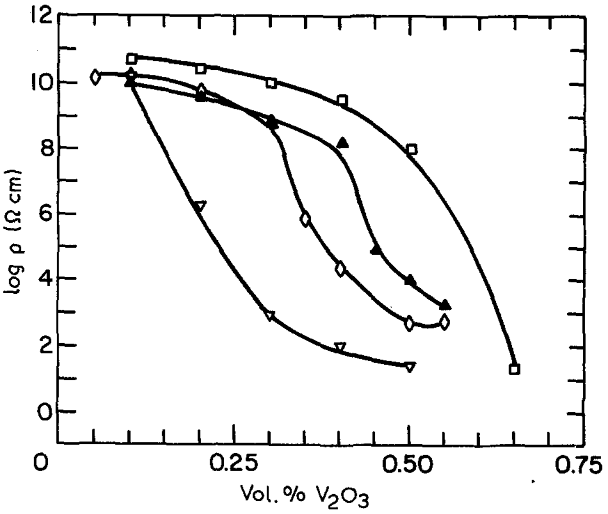

Figure 7 a.c. resistivity plotted against filler volume fraction in amorphous polymer–V_2O_3 composites at 1 kHz and −75° C. (□ PMMA, ◇ SPURR B, ▲ polyurethane, ▽ Eccogel O).

The mechanism for the PTC anomaly in crystalline polymers is generally attributed to the relatively large change in specific volume of the polymer at its melting temperature. On the other hand, the exact nature of the PTC phenomena in amorphous polymer composites is yet unknown. It could be due to polymer thermal expansion, which is, in general, greater than that of the electroceramic filler. There is, however, no discontinuity in the specific volume for amorphous polymers as there is in crystalline matrices, a fact which leads one to believe that there may be other important factors responsible for, or contributing to, the PTC transition.

Another important property of these composites is their ability to withstand repeated thermal cycling. For a 50 vol. % V_2O_3–polyethylene composite repeatedly cycled from 0 to 140° C, the room temperature resistivity increases by about 50 Ω cm from the first to the second heating run, but remains constant thereafter. The overall character of the resistivity–temperature curve changes slightly on the second heating run but the second and several subsequent

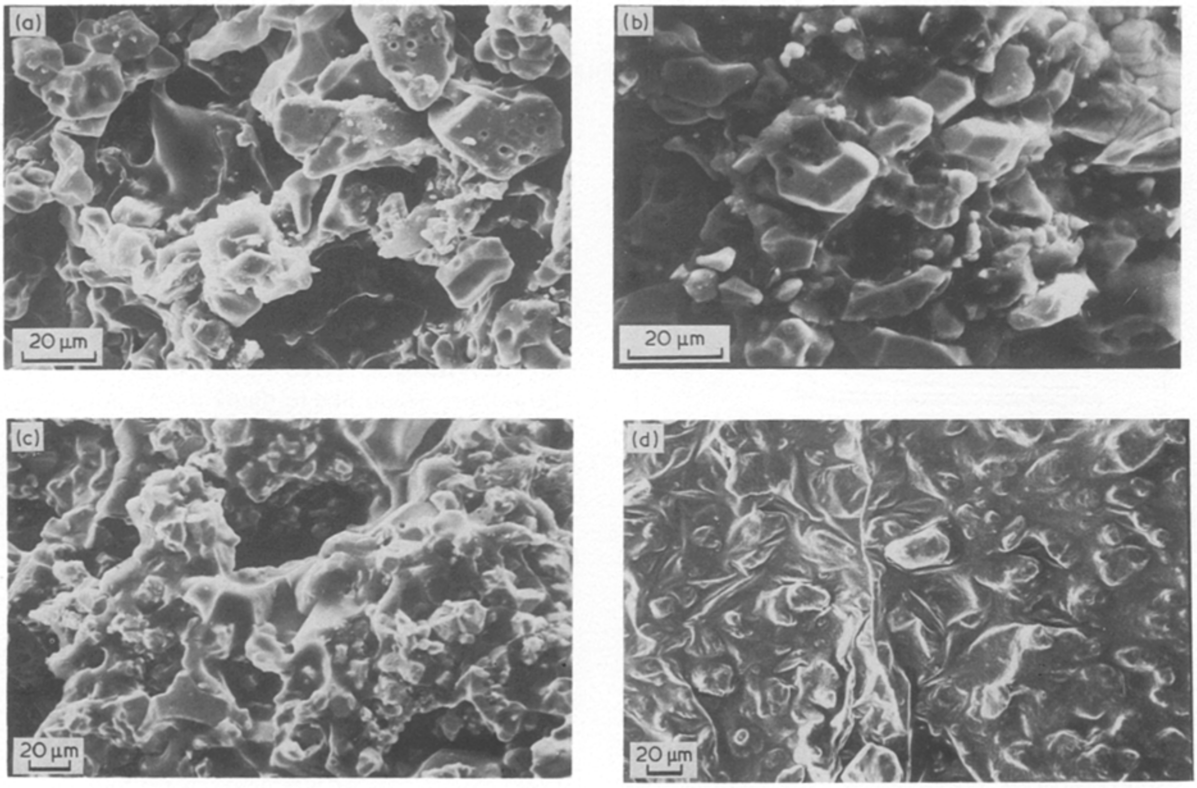

Figure 8 Scanning electron micrographs of V_2O_3-polymer composites: (a) flexible epoxy, (b) rigid epoxy, (c) polyurethane, and (d) PMMA.

runs exhibit identical behaviour, illustrating that after the initial heat-up, the thermistor maintains a constant resistivity profile. Similar behaviour is observed on thermal cycling of the 50 vol. % V_2O_3-rigid epoxy composite.

3.2. Percolation and microstructure

In addition to examining the temperature response in these systems, we also evaluated the percolation behaviour. Fig. 7 compares the percolation curves at −75° C for all of the V_2O_3-amorphous polymer systems examined here. This temperature was chosen because the resistivity of the composites is at its minimum here; most of the PTC transitions either begin in the vicinity of room temperature or at lower temperatures. The width of the percolation region for these systems varies from one polymer to another and the location of the threshold is also a function of the polymer type. The Eccogel 1365-0 composite has a percolation threshold near 10 vol.% V_2O_3, while the PMMA composites do not reach the threshold until close to 40 vol. % V_2O_3. A more comprehensive discussion of the percolation behaviour of these composites will appear in a subsequent publication.

A possible explanation for the difference in the percolation behaviour of the composites could involve

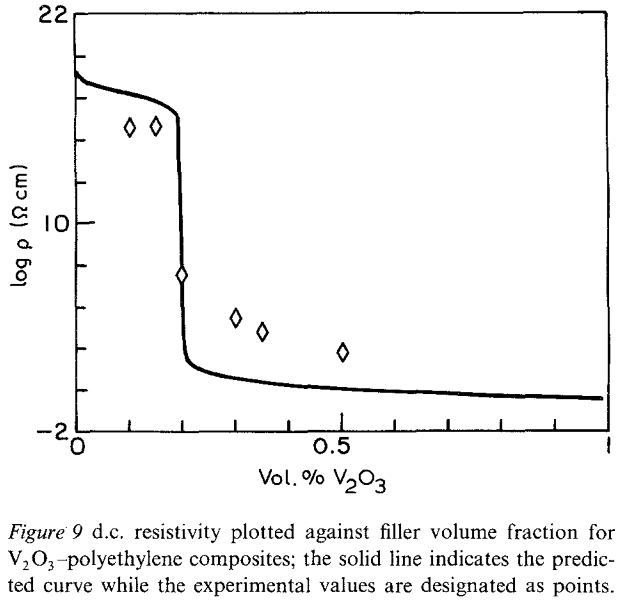

Figure 9 d.c. resistivity plotted against filler volume fraction for V_2O_3-polyethylene composites; the solid line indicates the predicted curve while the experimental values are designated as points.

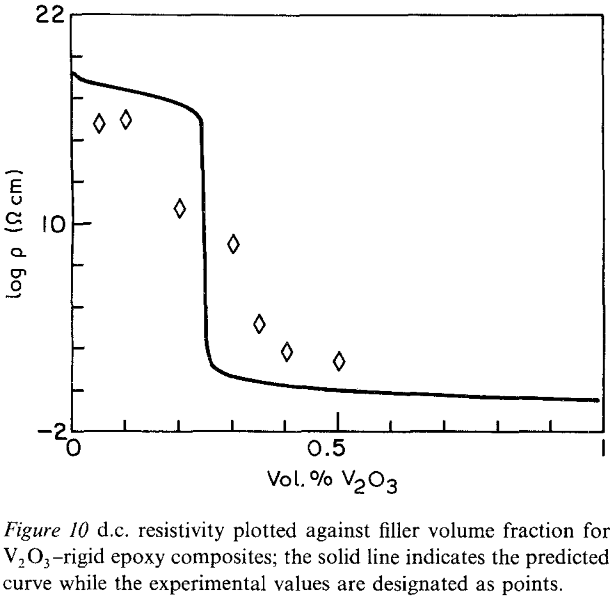

Figure 10 d.c. resistivity plotted against filler volume fraction for V_2O_3-rigid epoxy composites; the solid line indicates the predicted curve while the experimental values are designated as points.

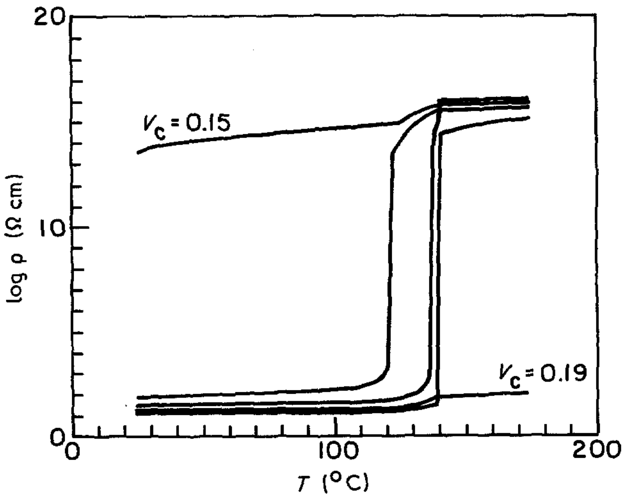

Figure 11 d.c. resistivity plotted against temperature for V_2O_3–polyethylene composites as predicted by the model.

the correlation between the percolation threshold and the polymer–powder wetting characteristics. Fig. 8 contains an SEM micrograph of a 50 vol. % filled composite of each amorphous polymer type. It can be seen that the V_2O_3–flexible epoxy composite, which has its threshold at the lowest filler concentration, appears to exhibit the worst particle wetting. The PMMA samples appear to exhibit excellent wetting characteristics and have a much higher V_2O_3 concentration at the threshold. Miyasaka *et al.* [27] suggest that the critical concentration in the percolation description may be related to the surface tension of the polymer matrix. For composites of carbon black and various amorphous and crystalline polymers, Miyasaka has shown that the larger the surface tension of the polymer, the larger the critical concentration for percolation. The behaviour of the composites examined in this study may follow their argument, but further measurements must be made and will be discussed at a later time.

3.3. Theoretical model

Fig. 9 illustrates the predicted percolation curve, as well as the experimental data, for the V_2O_3–polyethylene system. The parameters used in the model are as follows $f = 0.80$, $z = 8$, $\varrho_c = 5 \times 10^{-2}\,\Omega\,\text{cm}$, $\varrho_p = 8.99 \times 10^{16}\,\Omega\,\text{cm}$, $L_0 = 4.11 \times 10^{-4}\,\text{cm}$, $L_g = 1 \times 10^{-6}\,\text{cm}$, $L_c = 4.1 \times 10^{-4}\,\text{cm}$, $A_c = 1.32 \times 10^{-8}\,\text{cm}$, $A_{ct} = 2.3 \times 10^{-9}\,\text{cm}^2$. The values for f and z were chosen so that the calculated critical volume fraction corresponded to the experimental value; ϱ_p(d.c.) was determined by direct measurement; L_0 and A_{ct} were estimated from Sherman, *et al.*, L_g was assumed to be 10 nm; and A_c and L_c were determined from SEM micrographs. It is obvious that the model does not fit the data quantitatively, although it follows the same basic trend. A similar calculation was performed for the V_2O_3–rigid epoxy composites, as shown in Fig. 10. Once again, the model fits the experimental data reasonably well from a qualitative point of view. The parameters are $f = 0.75$, $z = 6$, $\varrho_c = 5 \times 10^{-2}\,\Omega\,\text{cm}$, $\varrho_p = 1.03 \times 10^{16}\,\Omega\,\text{cm}$, $L_0 = 4.11 \times 10^{-4}\,\text{cm}$, $L_g = 1 \times 10^{-6}\,\text{cm}$, $L_c = 4.1 \times 10^{-4}\,\text{cm}$, $A_c = 1.32 \times 10^{-8}\,\text{cm}$, $A_{ct} = 2.3 \times 10^{-9}\,\text{cm}^2$.

This particular model falls short when predicting the temperature dependence of the resistivity for V_2O_3–polyethylene, illustrated in Fig. 11. In the curve calculated with the model, a PTC effect is predicted over a range of 3–5 vol. % conducting filler. This disagrees with the experimental findings illustrated earlier where a PTC effect was observed over a concentration range of 30 vol. % filler. Clearly, an alternative model is required to provide a more quantitative representation of the experimental data.

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