JOURNAL OF MATERILS SCIENCE **33** (1998) 1715–1721

A microscopic investigation of conducting filled polymers

Y. ZWEIFEL, C. J. G. PLUMMER*, H.-H. KAUSCH
Laboratoire de Polymères, École Polytechnique Fédérale de Lausanne, CH-1015, Switzerland
E-mail: christopher.plummer@lp.dmx.epfl.ch

The electrical conductivity of polymer resins containing gold and silver particulate fillers has been investigated as a function of the particle content. At the same time, an apparatus constructed in-house has permitted measurement of the conductance between two isolated filler particles in the presence of an epoxy or polyester resin undergoing cure *in situ*. Numerical simulations of the conductivity of composites for filler volume fractions beyond the percolation threshold have shown these microscopic measurements to be consistent with the observed conductivities of the macroscopic samples. © *1998 Chapman & Hall*

1. Introduction

The conductivity of filled polymers is usually strongly dependent on the nature of the contact between the conductive filler elements [1, 2]. However, although the dependence of the conductivity on filler content in composite systems has been reviewed extensively in the literature [3–5], little is known about the physics of the interface between adjacent particles. This is particularly true of composites containing particles with equivalent diameters greater than or equal to about 1 μm (as in the present study), as distinct from nanocomposites, which are based mainly on carbon black or precipitated particles. The nature of electrical transport in heterogeneous materials has also been widely studied as a function of temperature [6, 7], electric field [6, 8] and using spectroscopic techniques [9], and indeed such investigations have led to reasonable descriptions of the behaviour of nanocomposites. However, the resulting models are often inapplicable to composites containing larger particles. In the latter, the intrinsic temperature dependence is masked by effects linked to differential thermal contraction and the dielectric constant is low compared with dielectric losses (measuring the field dependence of the conductivity alone does not generally provide adequate insight into the internal mechanisms of conduction along the conducting elements, particularly where the behaviour is ohmic).

Models for the conductivity in composites with insulating matrices are generally based on the percolation approach, but such models require a knowledge of the behaviour of the contacts between adjacent conducting grains or particles. Certain studies have incorporated direct measurements of the conductance between individual filler elements [6, 10]. However, these have all concerned conducting fibres, and the control of the normal contact force or separation of the conducting elements was either poor or non-existent. Our aim has been to improve the present experimental situation by developing a reliable technique for electrical measurement between individual gold and silver conducting particles with diameters of the order of 10 μm, which can be adapted to take into account the presence of an insulating matrix undergoing cure-induced shrinkage (these will be referred to as "two-particle measurements"). The results from such measurements have been combined with simulations of the conductivity of macroscopic composite samples with filler contents beyond the percolation threshold, which have, in turn, been compared with experimental measurements.

2. Experimental procedure

2.1. Materials

The polymer matrix used for the gold-filled composites was an bisphenol-A epoxy resin (DER 361, Dow Chemicals) mixed with 47 wt % isophorondiamine-based hardener (XZ 87 706.05, Dow Chemicals), with a cure time of about 24 h and a final resistivity $\rho_{EP} \geqslant 4 \times 10^{16}$ Ω cm. The silver-filled composites were prepared from a phthalic acid/glycol-based polyester resin containing styrene (Palatal™ P 4-01, Shell Aseol) and to which 10 wt % hardener was added, giving a room-temperature cure time of about 60 h and a final resistivity $\rho_{PO} \sim 7 \times 10^{14}$ Ω cm. As well as being sufficiently compatible with the filler particles for agglomeration not to be a problem during cure of the composites, both resins fulfilled two important requirements with regard to the two-particle measurements to be described in Sections 2.3 and 3.1, namely a low initial viscosity and relatively rapid room-temperature curing.

The gold particles, provided by Metalor (Switzerland), had a mean number-average diameter of 7.1 μm with a corresponding standard deviation of 2.1 μm

---

*Author to whom all correspondance should be addressed.

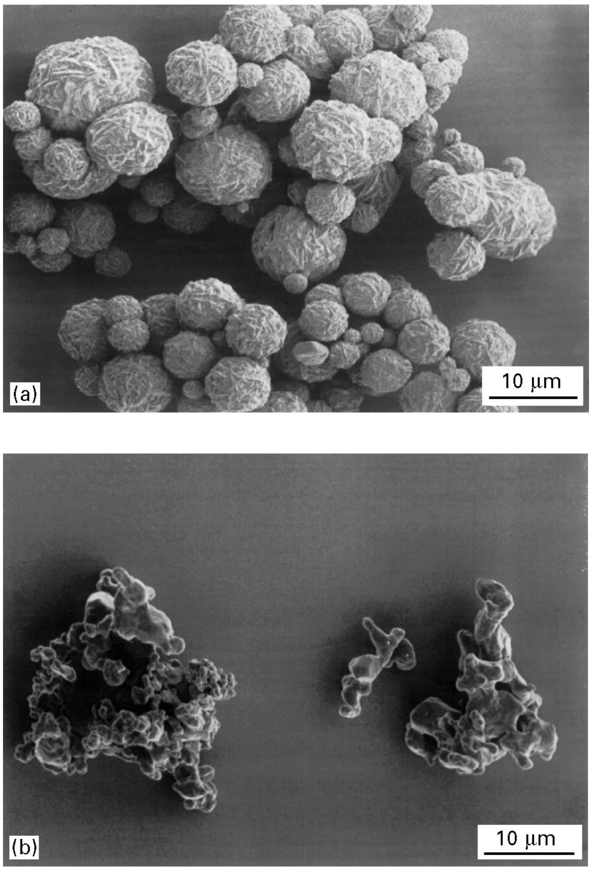

Figure 1 Scanning electron micrographs of (a) the gold powder, and (b) the silver powder, used in this study.

(as determined from scanning electron micrographs). The particles were globally spherical, but displayed pronounced surface roughening, reflecting their dendritic microstructure, as shown in Fig. 1a. In order to remove all organic contaminants from the particle surfaces, the powder was washed in a "Piranha solution" [11] consisting of 7 parts of concentrated sulfuric acid and 3 parts of hydrogen peroxide (30%), and then rinsed three times in distilled water and dried under vacuum prior to use.

The silver powder was provided by Johnson Matthey Gmbh (Germany). The particle geometry was irregular (Fig. 1b), and the equivalent particle diameter was therefore defined as the diameter of a circle having the same area as the projected area of the particle in scanning electron micrographs. This gave a number-average diameter and standard deviation of 11 and 6.2 μm, respectively. The powder was rinsed twice in absolute ethanol and dried under vacuum prior to use.

2.2. Preparation and characterization of the composites

Small cuboid composite samples were prepared for macroscopic conductivity measurements using a four-probe test. This test consists of passing a fixed current through the sample via two electrodes, and measuring the potential drop between two additional electrodes placed along the current path. The resin and the powder were mixed together by hand for 1 min and then poured into a mould with a rectangular base of $5 \times 10\ \mathrm{mm}^2$. The total amount of resin and powder was calculated to give a mean sample thickness of about 2 mm. After curing, and machining to eliminate any surface roughness, the sample ends were coated with conducting silver paint, which provided electrodes for current transport into the composite.

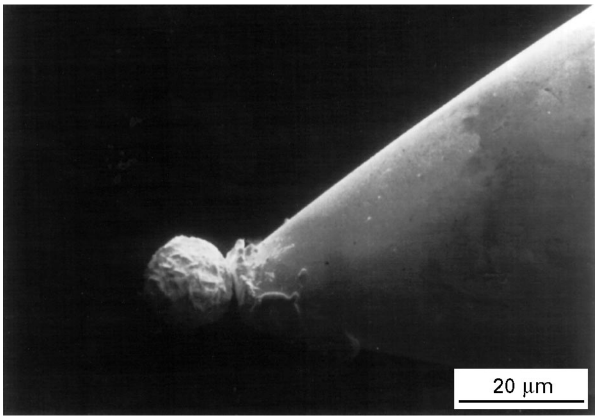

Figure 2 A single gold particle welded to the tip of a sharpened tungsten wire.

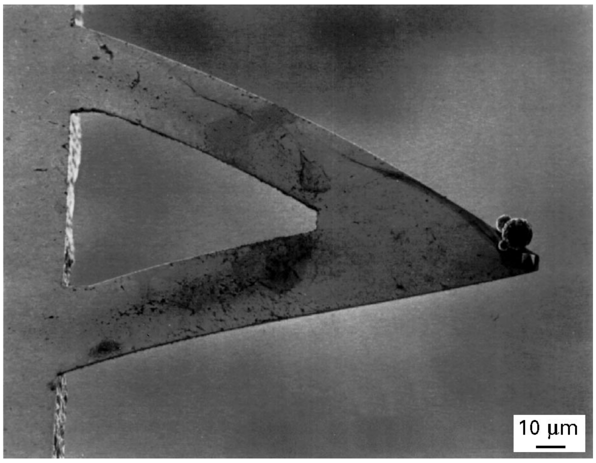

Figure 3 An atomic force microscope cantilever coated with titanium and platinum. A gold particle has been welded to the tip using the electrical discharge technique.

2.3. Two-particle measurements

For electrical measurements on contacts between pairs of individual particles, these latter needed to be fixed to a substrate, both for manipulation and in order to establish electrical contact with the measuring circuit. For each measurement, one particle was fixed to the tip of an electrochemically sharpened tungsten wire (Fig. 2), and the other, to the end of an atomic force microscopy microcantilever (Fig. 3). Analogous set-ups have been used for surface force measurements using silicone microspheres [12]. In the present work, in order to ensure good electrical contact, an electric-arc welding technique was used to mount the particles on their supports, as shown schematically in Fig. 4a. Each particle was slightly compressed between the tungsten and an aluminium

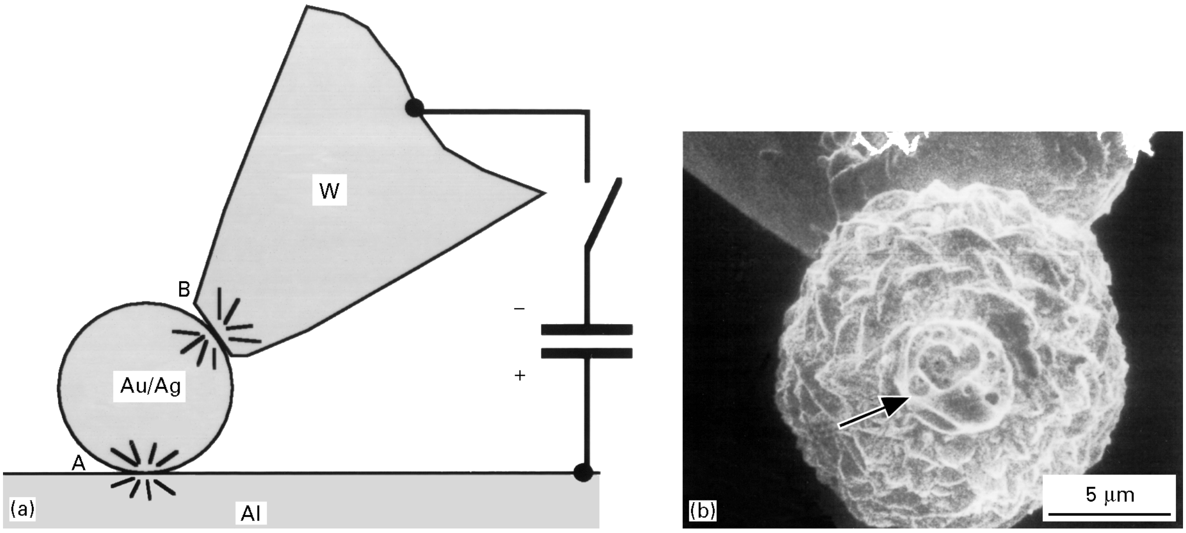

Figure 4 (a) Diagram of the set-up used to weld a gold particle to the tip of a tungsten wire. During welding, the axis of the tungsten tip was tilted with respect to the aluminium plate so that the surface in contact with a second particle during subsequent measurements was not affected by the discharge current between the particle and the aluminium (A). (b) The result of the discharge can be seen.

surface. A capacitor (0.1–2 μF), connected to the aluminium plate, was charged to 5–10 V. When the capacitor was subsequently discharged by closing the circuit sketched in Fig. 4a, ohmic heating induced fusion of the gold (or silver) at the points of contact A and B indicated in the figure, and effectively welded the particle to the tungsten (but not to the aluminium). The microcantilevers, made from 0.6 μm thick silicon nitride wafers, were provided by Park Scientific Instruments. In order to render their surfaces conductive, they were sputter coated with a 0.2 μm thick layer of titanium, followed by a 0.4 μm thick layer of platinum. The titanium promoted adhesion with the cantilever and the platinum essentially carried the current and facilitated welding of the particles to the cantilever tip using the same technique as for the tungsten wire. The estimated compliance of the resulting multilayer system was 0.55 $\mathrm{N\,m^{-1}}$.

The tungsten wire was fixed to a piezoelectric actuator, and the microcantilever beam was mounted on a three-dimensional micrometer stage as shown in Fig. 5. The particles were aligned so that their common axis was vertical, and brought to within a few micrometres of each other with the micrometer screws. The final approach and the establishment of mechanical contact between the particles made use of the piezo-actuator, which permitted vertical displacements with an accuracy of 0.5 nm. In order to observe the effect of the resin on the electrical contact, a drop of resin was placed on a particle attached to the tungsten wire (which pointed upwards in the present set-up) prior to making the approach. The thin film of resin at the particle surface transformed into a meniscus once mechanical contact was established with the second particle.

For the measurements themselves, an electrical potential (usually 1 mV) was applied between the two particles, and a Keithley 487 picoammeter was used to measure the conductance of the contact. To prevent electromagnetic perturbations during the measurements, the whole apparatus was inserted in a Faraday cage, and thermal drift was minimized by (i) matching the thermal expansion coefficients of the various components, and (ii) careful thermal isolation.

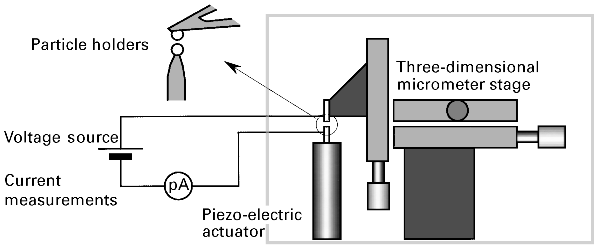

Figure 5 Schematic representation of the experimental set-up used for the measurements of the conductances between pairs of isolated particles.

3. Results and discussion

3.1. Results from the two-particle measurements

When two gold particles were brought together in air the conductance initially increased exponentially with diminishing interparticle separation (Fig. 6). At this stage, the metallic surfaces were assumed not to be in physical contact and the current to tunnel across the insulating gap between them. There followed a sharp increase in the measured current (indicated by the arrow in Fig. 6). This was assumed to occur when the particles were close enough for the naturally adsorbed film of water present on their surface to form a meniscus (this phenomenon is well known from atomic force microscopy, where adsorbed water may cause the probe to adhere to surfaces scanned in air).

Beyond this point, there was a plateau, assumed to correspond to physical contact between the two particles, and compression of the particle–particle interface owing to the capillary force of any meniscus present. The current initially increased somewhat with

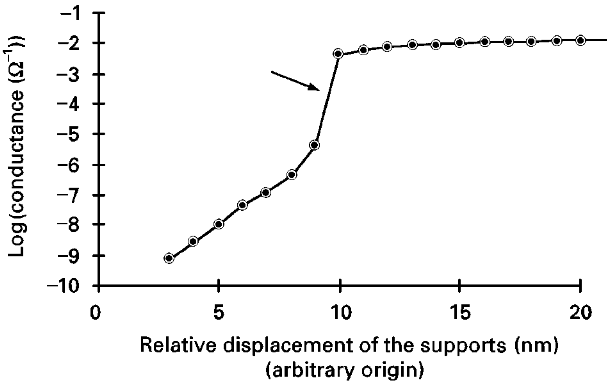

Figure 6 Electrical conductance between two gold particles (diameter $\sim 10\ \mu m$) in air brought together at a speed of $1\ nm\ s^{-1}$. The large jump in conductance indicated by the arrow is thought to correspond to the establishment of a physical contact between the conducting surfaces. The final resistance in this case, measured at an applied voltage of 1 mV, was $105\ \Omega$.

time in this regime, apparently reaching a maximum after a few minutes when the relative displacement of the supports was held constant. The corresponding interfacial resistances were found to be about $100\ \Omega$ and the contact was ohmic for applied voltages between 1 and 100 mV, with no significant hysteresis during voltage cycles.

The contact resistance between two conductive elements is well known to be highly dependent on the surrounding medium [1, 13]. If the elements are embedded in a polymer matrix which experiences significant shrinkage during processing, one anticipates a relatively large normal force at the interparticle interface, which may improve the conduction. In our experimental set-up, if one of the two particles was wetted with the uncured epoxy resin, a meniscus formed when the particles were brought together, as described earlier, and the contact resistance (at time Δt_1 in Fig. 7) was comparable with that measured in air. As curing proceeded, a compressive stress was assumed to develop at the interface, leading to an increase in the contact surface and a consequent increase in conductance (Δt_2 to Δt_3 in Fig. 7). The final resistance of the interface between two gold particles after 7 days curing was about $4\ \Omega$.

The total shrinkage of the epoxy resin at room temperature subsequent to gelation was 0.5%. This is a low value for a thermoset, but was apparently sufficient to improve the contact between the gold particles. However, in similar tests on silver particles using the same resin, there was no significant increase in conductance. This was true both of the measurements on pairs of isolated particles and of composites. We therefore replaced the epoxy with the polyester resin described in Section 2.1, which had a measured shrinkage of 7 % and which did make it possible to obtain silver-filled samples with improved conductivity (Fig. 8). The silver surface was thought to be partially oxidized and possibly contaminated by organic or non-organic impurities, which were not completely removed during the ethanol treatment. A larger contact force was therefore presumably necessary to overcome this insulating layer (the data obtained from the two-particle measurements were also found to be considerably noisier than for the gold particles).

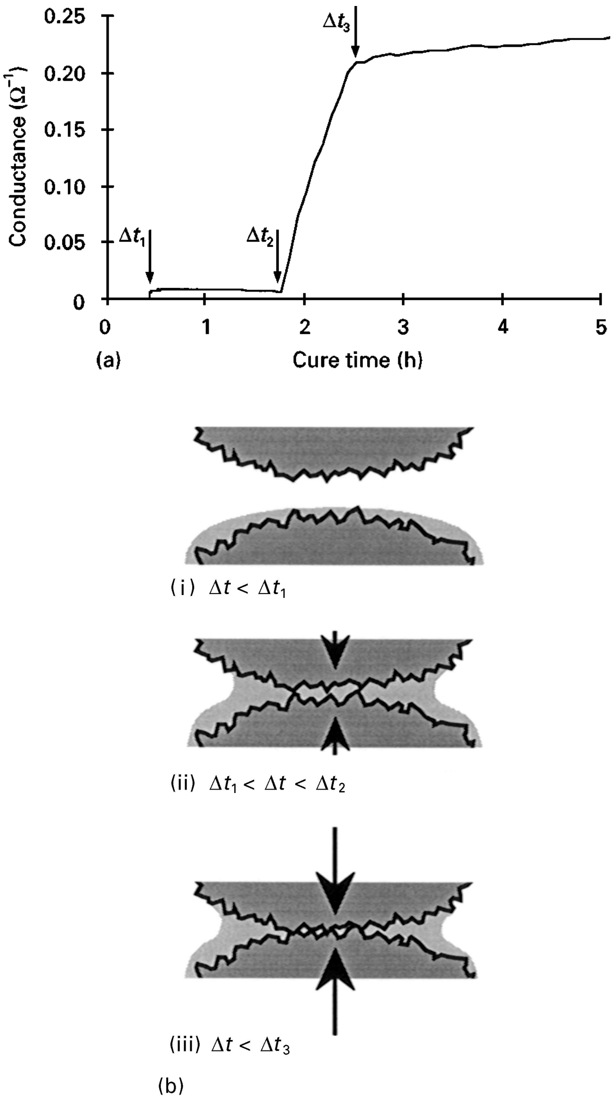

Figure 7 (a) Evolution of the conductance between two gold particles (diameter $\sim 10\ \mu m$) in contact in the presence of a meniscus of epoxy resin undergoing cure. (b) The corresponding stages in the establishment of the contact between the particles: (i) no contact; (ii) initial contact with a relatively weak compressive force at the particle–particle interface owing to the presence of the meniscus; (iii) improved contact owing to resin shrinkage. The surface roughness of the gold particles is thought to result in an effective mean contact diameter of the order of a few nanometres.

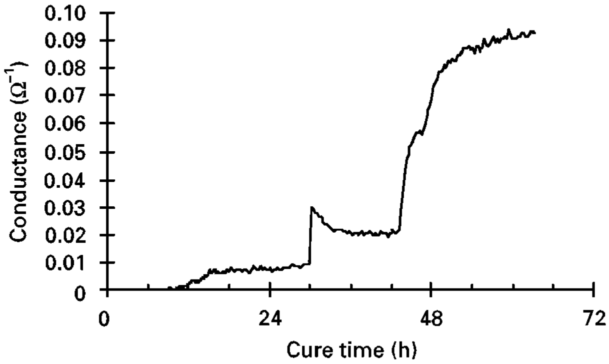

Figure 8 Increase of the conductance between two contacting silver particles in the presence of a polyester meniscus undergoing cure.

The initial conductance between two silver particles embedded in a liquid polyester was about $2 \times 10^{-6}\ \Omega^{-1}$. After the onset of gelation and shrinkage in the resin, the conductance increased with time, reaching about $10^{-1}\ \Omega^{-1}$ after 7 days (Fig. 8). Most of this increase took place over the first 2 days of the experiment, which compares with typical times to reach maximum conductance of a few hours for gold particles in epoxy resin. This reflects the relatively rapid curing kinetics of the epoxy resin.

3.2. Modelling of composite conductivities

The conductivity of a composite depends both on the conductance of the contacts between the conducting elements and their volume fraction. Here, a simple numerical percolation model has been used to link the microscopic measurements of the resistance between pairs of individual particles ($4\ \Omega$ for the gold grains and $10\ \Omega$ for the silver grains) and the effective conductivity of composite samples containing large numbers of particles.

This model was based on that proposed by Wang and Ogale [14] for the study of percolation thresholds, with modifications in order to take into consideration filler fractions much higher than the percolation threshold. Spheres were homogeneously dispersed in and around a cube. The volume fractions of spheres corresponded to the range of volume filler contents in the experimental composites, and the size distribution of the spheres was chosen to reflect that of the real powder (Fig. 9). The centres of successive spheres were placed at random positions within unoccupied regions of the cube. The restriction on overlap of adjacent spheres was relaxed somewhat at high volume fractions ($\geqslant 30\%$ for gold particles and $\geqslant 20\%$ for silver loaded composites). If ϕ_1 is the diameter of a sphere already present in the cube, ϕ_2 is the diameter of a sphere being placed in the cube and Δ_{12} is the distance separating the centres of the two spheres, the current attempt to locate the second sphere was rejected if the condition

$$\frac{1}{2}(\phi_1 + \phi_2)\left(\frac{A-n}{A}\right)^{1/2} < \Delta_{12} \quad (1)$$

was not respected, where n is the number of previous attempts to locate the sphere and A is a constant. A value of $A = 3 \times 10^4$, which defines the maximum number of attempts per particle, gave a reasonable compromise between the extent of overlap and the overall computing time.

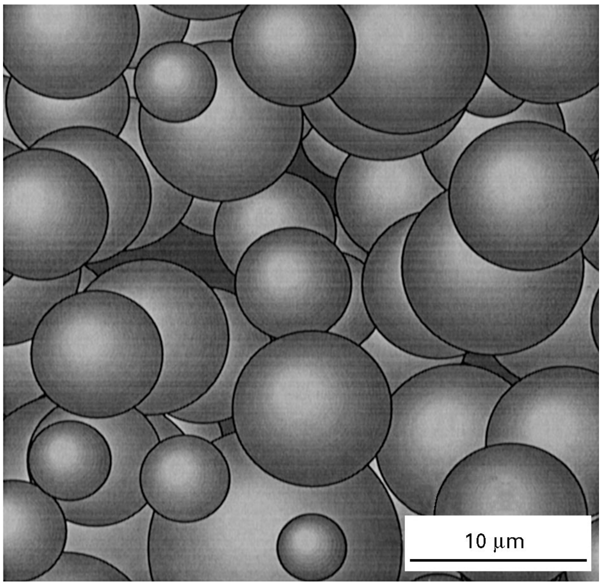

Figure 9 Example of modelling of a gold–epoxy composite sample (35% filler). The spheres, corresponding to the gold particles, are randomly positioned within the cube representing the sample.

Leaving aside particle overlap, because the model particles were spherical shells of zero thickness, the probability of their touching was negligible. It has been suggested that this problem can be overcome by use of a capture radius $R + \delta$ where R is the radius of each particle [14]. If two adjacent spheres defined by the capture radius of the corresponding particles overlap, the particles are assumed to be in electrical contact. Percolation then occurs when a continuous path of particles in contact connect two opposite faces of the model composite. The mean percolation threshold, p_{av}, for a finite system is higher then the infinite percolation threshold, p_{c}. Using many simulations with different sized models, it was possible to extrapolate the value of the percolation threshold in order to estimate p_{c} using

$$p_{\mathrm{av}}(N) - p_{\mathrm{c}} = CN^{-\beta} \quad (2)$$

where N is the average number of particles in the model at the percolation threshold, C is an empirical constant and the exponent β is approximately -0.375 for a regular network [5].

The thickness, δ, of the virtual shell around the particles was chosen so that the estimated percolation concentration corresponded to the experimental measurements on real composites. Wang and Ogale found that the shell thickness, δ, for the simulation should be 0.7 μm in order to obtain a calculated threshold comparable to that of a nickel powder–polyethylene composite [14]. With our gold–epoxy system, the experimental threshold occurred at a particle volume fraction of about 20%. A shell thickness, δ, of 0.75 μm was necessary to give a threshold at the same particle volume fraction in the model. The size of δ reflects the tendency of the particles to come into contact with each other in a given composite sample, but it should be emphasized that it has nothing to do with the maximum conduction gap in an insulating matrix, which is usually orders of magnitude smaller.

The behaviour of the model composites was investigated for a range of spherical conducting particle volume fractions extending from the threshold value up to 40%. Each sphere was considered to be equivalent to a node in a resistor network. Pairs of nodes corresponding to contacting spheres were connected with resistors whose value was taken to be equal to the measured resistances between isolated particles as described in Section 3.1. Because of the statistical character of the results, many simulations were carried out for each condition (model size and particle volume

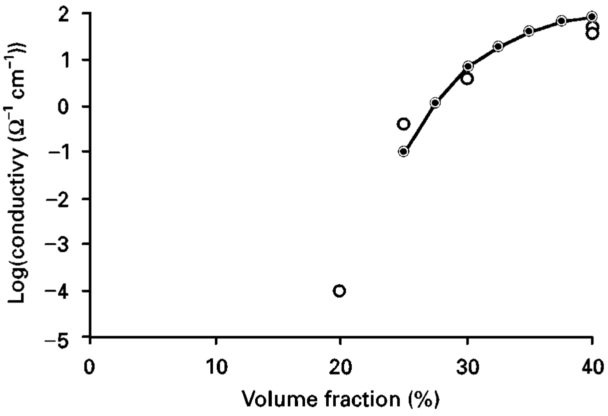

Figure 10 Conductivity versus volume fraction of filler for (○) gold–epoxy composites compared with (●) the predictions of the model.

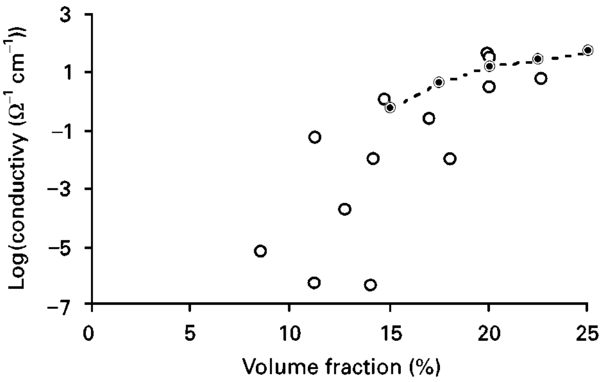

Figure 11 Conductivity versus volume fraction of filler for (○) silver–polyester composites compared with (●) the predictions of the model.

fraction). The smaller the model, the higher the required number of calculations (up to one thousand for a 30 μm cube).

Results for the conductivity $\sigma(N)$ of finite models containing N particles were then extrapolated in order to estimate the conductivity, σ_∞, of the corresponding system containing an infinite number of particles, as was done for the percolation threshold (although this approach is not adapted to the estimation of the conductivity very close to the percolation threshold). Fig. 10 shows the measured conductivities of gold–epoxy composite samples compared with the simulated conductivity (for volume fractions between 25% and 40%). The good fit of the experimental results to those obtained from the model suggests the contact resistances estimated from the two-particle measurements to be realistic, and representative of those in the interior of the composite samples.

The silver particles were non-spherical and possessed a large surface to volume ratio, which explains the relatively low percolation threshold of 11%. The calculations were thus slightly modified to take this into account. In spite of the irregular shape of the silver particles, spheres were used in the models, with the equivalent particle diameter again being defined as described in Section 2.1. However, because the volume fraction of conducting particles in the real composites was estimated from the total mass of filler added to the resin, it was not be equated to the total volume of the spheres in the models. To correct for this, three-dimensional model particles were constructed from modelling clay, based on the SEM observations at different tilts. These were used to estimate the dependence of the diameter of a spherical particle having the same volume as the real (non-spherical) particle, ϕ_{Ag}, on the equivalent particle diameter, ϕ_{Sph}. This lead to the empirical expression

$$\frac{\phi_{\mathrm{Ag}}}{\phi_0} = 1.61\left(\frac{\phi_{\mathrm{Sph}}}{\phi_0}\right)^{0.75} \qquad (3)$$

where $\phi_0 = 1$ μm is a scaling factor. Equation 3 was used to estimate the true particle volume fraction corresponding to each model. In spite of the crudeness of these adjustments, the conductivity calculated by combining the model with the microscopic measurements was again consistent with the experimental results (Fig. 11). However, in this case it was more difficult to verify the accuracy of the model owing to the large scatter in the experimental data, with at least an order of magnitude variation in the composite conductivity being observed in samples with identical filler contents – this would correspond to an order of magnitude variation in the contact resistance.

4. Conclusion

The results presented here have shown that a microscopic approach to the study of composite conductors or semiconductors may help in understanding the main factors which influence their global conductivity. A continuous percolation model, requiring as input (i) the contact resistance between two particles, and (ii) the percolation threshold, was found to be suitable for the description or prediction of electrical conductivity in materials filled with particles whose size is of the order of a few micrometres. Using experimental measurements of the contact resistance and percolation threshold, the model was found to give results consistent with experimentally measured conductivities in composites containing different filler contents.

Acknowledgements

This research was financed by the Swiss Priority Program for Materials. We also acknowledge the contributions of R. Strümpler (ABB), P. Bujard (Ciba Speciality Chemicals), Professor L. Zuppiroli, S. Paschen and O. Chauvet (IGA, EPEL).

References

1. G. R. RUSCHAU, S. YOSHIKAWA and R. E. NEWNHAM, *J. Appl. Phys.* **72** (1992) 953.
2. M. BLASZKIEWICZ, D. S. MCLACHLAN and R. E. NEWNHAM, *J. Mater. Sci.* **26** (1991) 5899.
3. J. JANSEN, *J. Appl. Phys.* **46** (1975) 966.
4. D. S. MCLACHLAN, *J. Phys. C Solid State Phys.* **20** (1987) 865.
5. D. STAUFFER, *Phys. Reports* **54** (1979) 1.

6. S. PASCHEN, M. N. BUSSAC, L. ZUPPIROLI, E. MINDER and B. HILTI, *J. Appl. Phys.* **78** (1995) 3230.
7. P. SHENG, *Phys. Rev. Lett.* **31** (1973) 44.
8. S. K. RADHAKRISHNAN, *Polym. Commum.* **26** (1985) 153.
9. D. M. GRANNAN, J. C. GARLAND and D. B. TANNER, *Phys. Rev. Lett.* **46** (1981) 375.
10. B. BRIDGE, M. J. FOLKES and H. JAHANKHANI, *J. Mater. Sci.* **25** (1990) 3061.
11. C. D. BAIN, J. EVALL and G. M. WHITESIDES, *J. Amer. Chem. Soc.* **111** (1989) 7155.
12. W. A. DUCKER, T. J. SENDEN and R.M. PASHLEY, *Nature* **352** (1991) 239.
13. F. CARMONA, *Ann. Chim. Fr.* **13** (1988) 395.
14. S. F. WANG and A. A. OGALE, *Compos. Sci. Technol.* **46** (1993) 93.

Received 25 July
and accepted 5 December 1997