

Current transport in conducting particle filled epoxies

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Summary

The electrical contact resistance between isolated pairs of micron-sized gold particles has been measured as a function of their separation using apparatus constructed in house. When incorporated into a percolation model for current transport in a conducting particle filled insulator, the results of such measurements have been shown to be consistent with the observed variation of conductivity with filler content beyond the percolation threshold in gold filled epoxies. This has been tested further by using adsorbed alkanethiol monolayers to control the interparticle spacing in the composites, demonstrating the importance of the contact resistance for the macroscopic current transport properties.

Introduction

Blending of polymers with a conducting filler provides a convenient means of exploiting the ease of processing and mechanical properties of structural polymers in electrical applications requiring significant conductivity. The electrical properties of conducting filled polymers are also of specific interest, particularly since their conductivity may be very sensitive to matrix dilatation (which tends to diminish the electrical contact between the filler particles). This is certainly true of composites containing relatively large conducting elements ($\geq 1 \mu\text{m}$, say), such as those to be discussed here. It is therefore as well to distinguish at this stage between these and the so-called “nanocomposites”, which are based mainly on carbon black or precipitated particles, and whose global behaviour can often be accounted for in terms of their local microscopic properties.

Although their electrical behaviour is somewhat dependent on the presence of impurities, conventional polymer matrices may be considered to be insulators, so that in order to achieve adequate conductivity under ambient conditions, sufficient filler must be added to ensure continuous conducting paths throughout a given composite. Thus models

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for these and other systems based on insulating matrices often make use of a percolation approach, which should take into account the dispersion and geometry of the filler, and be based on appropriate assumptions regarding the nature of the contact between individual filler particles (1, 2). Nevertheless attempts at direct characterization of the electrical contact between filler particles are uncommon, and such studies as exist in the literature appear to be limited to fibres, as opposed to low aspect ratio particles (3, 4). One of our aims has therefore been to develop a means of measuring the contact resistance between pairs of individual filler particles in order to provide input to a percolation-based model for the observed macroscopic conductivity in the corresponding composites beyond the percolation threshold. Measurements on individual filler particles have clearly shown both a strong dependence of the contact resistance on the particle separation and the important role of matrix shrinkage in thermosets in pushing the particles together, thus promoting good interparticle electrical contact in practice. To demonstrate further the effect of varying minimum particle separation and hence varying contact resistance on the global conductivity in gold particle filled epoxy composites, we have used alkanethiols of various molecular weights to introduce organic (insulating) layers of well defined thickness to the surface of the particles, prior to their incorporation into the epoxy resin.

Experimental

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 hours and a final resistivity $\rho_{EP} \geq 4 \times 10^{16} \Omega\text{cm}$. 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 , as determined from scanning electron micrographs. The particles were globally spherical, but displayed pronounced surface roughening, reflecting their dendritic microstructure, as shown in Figure 1(a) (hence the need for *ad hoc* methods for characterizing their contact resistance). To remove organic contaminants from the particle surfaces, they were washed in a "Piranha solution" (5) consisting of 7 parts of concentrated sulphuric acid and 3 parts hydrogen peroxide (30%), and then rinsed three times in distilled water and dried under vacuum prior to use. For the alkanethiol coatings, a 1 mM solution of alkanethiol of the required molecular weight in absolute ethanol was prepared (by gentle heating if necessary). Washed particles were rinsed in ethanol and then immersed in the alkanethiol solution for 24 hours. They were rinsed a further 5 times in ethanol prior to blending with the epoxy resin. In the present series of experiments, n , the number of carbon atoms in the alkane chains was varied between 2 and 18 which corresponds to theoretical monolayer thicknesses of 6 to 22 Å, based on the arrangement sketched in Figure 1(b) (all trans conformation of the carbon-carbon bonds). Ellipsometric measurements of alkanethiol

layers deposited on planar gold surfaces suggest the calculated layer thicknesses to reflect reasonably well the true layer thicknesses for $n \geq 8$, but for smaller n the layer thickness given here are taken to be equal to the measured values (6).

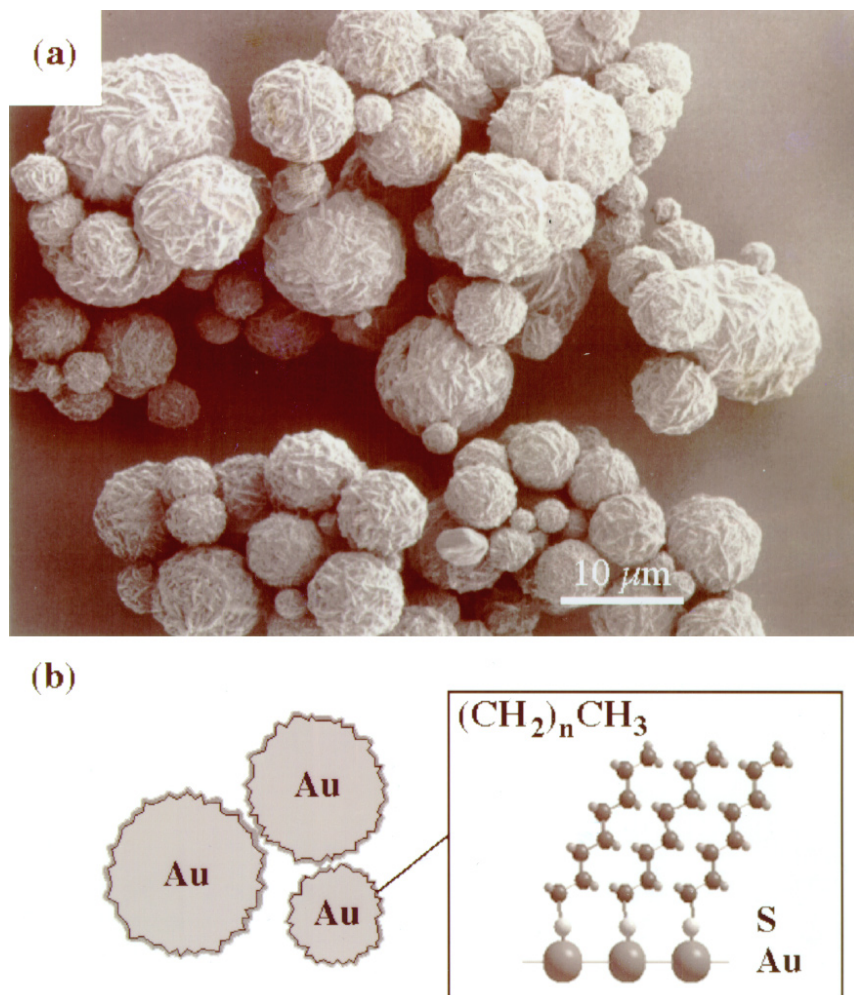


Figure 1. (a) Scanning electron micrograph of the gold powder as received; (b) schematic representation of adjacent metallic particles separated by an adsorbed organic alkanethiol monolayer, and the arrangement of the alkanethiol on the gold surface.

The electrical measurements on contacts between pairs of individual particles have been described in detail elsewhere (7, 8). Essentially one particle was welded to a rigid support, and the other to a 0.6 μm thick silicon nitride AFM cantilever (to avoid excessive

contact forces). The two particles were then brought together using a piezoelectric crystal, allowing relative displacements with an accuracy of about 5 Å, and the current between the particles was monitored as a function of their displacement at constant tension (typically 1 mV). In order to observe the effect of the matrix shrinkage on the electrical contact, a drop of resin was placed on one of the particles 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, and the current was monitored as a function of cure time, again at constant tension. It has not so far been possible to carry out successful measurements of this type on the alkanethiol coated particles, since the alkanethiol treatment must be carried out *in situ*, necessitating a compliant support capable of resisting the cleaning agent. Efforts have been made to construct miniature gold springs for this purpose, but as yet the contact forces remain relative large, apparently resulting in destruction of the alkanethiol layer once contact is made (the spring constants were of the order of 1500 Nm⁻¹ which compares with about 0.4 Nm⁻¹ for the AFM cantilevers (7)).

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 one minute and then poured into a mould with a rectangular base of 5 x 10 mm². The total amount of resin and powder were 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.

Results and discussion

Microscopic measurements Figure 2 shows the evolution of the conductance of the contact between two gold particles as they are brought together in air (i.e. as the particle separation is decreased). There is an initial exponential increase in conductance with decreasing particle separation, and then a sharp rise to a plateau, which is assumed to correspond to physical contact between the particles. Establishment of physical contact is given as the zero nominal particle separation in Figure 2. However it is more likely that the discontinuity in the curve is associated with attractive forces between the particles, via the formation of a meniscus of adsorbed water, for example, bringing them abruptly into contact below some critical value of the particle separation, and maintaining a roughly constant normal contact force (cf. AFM, for which “stickiness” of the point places a lower limit on the contact force in air of around 0.1 nN). Thus although the behaviour is reversible up to the establishment of contact, negative displacements of up to 100 nm are needed to break the contact, suggesting a contact force of about 30 nN (7). To the left of

In the presence of an epoxy meniscus, the initial contact resistance was comparable with that measured in air, that is again about 100Ω . As curing proceeded, a compressive stress was assumed to develop at the interface owing to shrinkage (a total of 0.5 % for the resin used here), leading to an increase in the effective contact force and a consequent increase in conductance. The final resistance of the interface between two gold particles after seven days of curing was about 4Ω .

Macroscopic measurements Figure 3 shows the evolution of the conductance of a macroscopic gold filled composite with filler content, showing a steep initial increase from a threshold of about 20 volume %, which is identified with the percolation threshold in this material. Well above this threshold, such curves have been successfully modelled using a numerical approach (7, 8), which incorporates the measured contact resistance between individual particles in the presence of the matrix of about 4Ω (see the previous section), and in which the increase in conductivity with filler content is due to increased degeneracy of continuous conducting paths through the material. The position of the percolation threshold itself is determined by the geometry (size and dispersion) of the filler and is independent of the contact resistance, but at high particle volume fractions, a variation in contact resistance will result in a corresponding vertical displacement in the model curves. Thus if this approach is valid, such shifts should be reflected in systems where the contact resistance has been varied systematically.

Figure 4(a) shows results from composites with alkanethiol coated particles with various n compared with the model curve for uncoated particles (cf. Figure 3), and Figure 4(b) shows the same data plotted against twice the estimated monolayer thickness (i.e. the effective particle separation) for different filler contents. Although there is considerable scatter close to the percolation threshold there was no evidence for any systematic changes in this threshold (for filler contents less than 20 volume % the conductance was not measurable for the majority of the samples). For the thinnest coating ($n = 2$) the behaviour was comparable with that of the uncoated particles, which suggests surface contamination of these latter, in spite of the cleaning procedure. However there was a clear decrease in conductance with the estimated layer thickness for higher n . Indeed, the magnitude of the decreases in conductance was consistent with the rate of exponential decay in conductance with particle separation observed in the two particle measurements (Figure 2), although the trend was less marked for the highest filler contents and layer thicknesses. This is encouraging in terms of the model, although the results should be viewed with caution. First, the approach is phenomenological, since no attempt is made to model the details of the contact, taking into account for example the local radius of curvature on the effective layer thickness (it is implicit in the discussion that the thioalkanes form a planar layer with uniform coverage). Second, for the thicker layers the composite conductance has been

observed to increase steadily with time over periods of up to 100 days (7), which is well beyond the cure time of the matrix, suggesting progressive degradation of the layers, which may also account for the deviations from expected behaviour for $n = 18$. Third, we have not verified the extent of monolayer coverage of the particles quantitatively, although the presence of the thiol groups at the particle surfaces has been confirmed by ESCA.

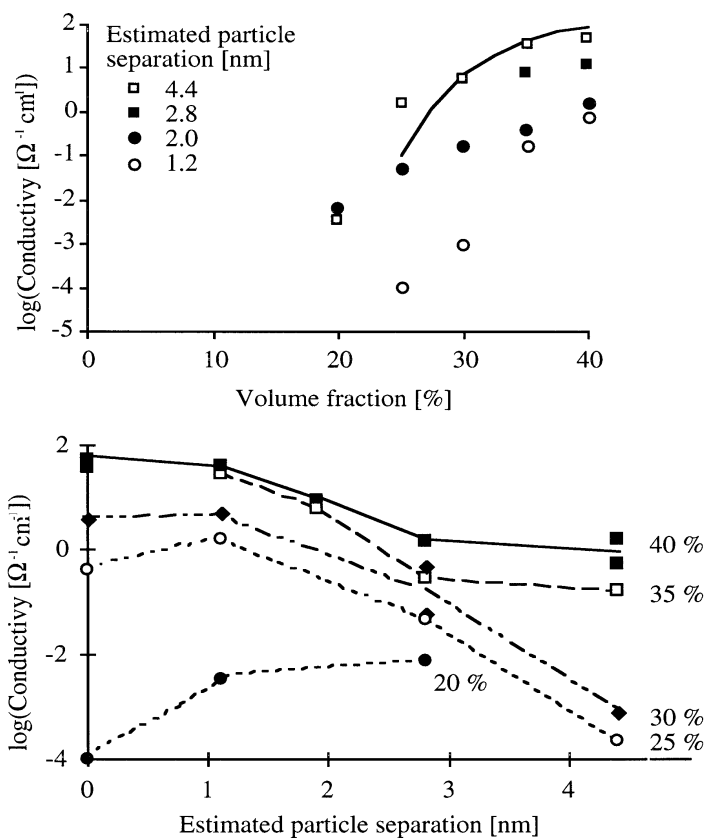


Figure 4. Effect of an alkanethiol monolayer coating the surface of particles on the mean conductivity of a polymer charged with the coated particles: (a) as a function of filler content for different layer estimated layer thicknesses, along with the model curve for uncoated particles; (b) as a function of layer thickness for the different filler volume fractions indicated.

The vulnerability of the interparticle contacts has been demonstrated not only by the two particle measurements referred to earlier, but also by electrical measurements made on

coated particle composites cooled to liquid nitrogen temperature. Decreasing the temperature invariably resulted in an increase in conductivity by about one order of magnitude (the opposite behaviour is expected for current transport through an insulating layer), which was ascribed to further matrix shrinkage. Moreover this effect was substantially irreversible. When the composites were brought back to room temperature, there was a substantial degradation in conductance compared with the initial values, which was attributed to cavitation at the particle-particle interfaces (another manifestation of the role of the contact resistance).

Conclusions

The results demonstrate the importance of particle-particle contacts for the overall conductivity of conducting particle filled epoxies, the decrease in conductance of composites in which the particle separation has been varied by use of alkanethiol coatings being consistent with the exponential decay in conductance between isolated pairs of gold particles with separation in the non-contact regime. The dependence of the conductance on alkanethiol layer thickness has nevertheless yet to be confirmed by direct measurement owing to difficulties in controlling the contact forces, excessive forces tending to destroy the layer at the point of contact. The apparent exponential decay in conductance with layer thickness is suggestive of a tunnelling mechanism, but initial attempts to test this by varying the test temperature have lead to results dominated by matrix shrinkage effects.

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