

# Percolation and eddy currents in random close packed metal polymer composites

S. REICH

*Department of Materials Research, Weizmann Institute of Science, Rehovot, Israel*

Bare and copper-coated polystyrene (PS) beads are mixed to give various volume fractions of electrically conducting and insulating spheres. This random mixture is subsequently sintered under pressure in a hot dye. The resulting solid is a polymer body in which thin ( $\sim 0.3 \mu\text{m}$ ) copper shells form a tightly packed cellular cluster which exhibits electrical continuity. This continuity is detected by inductive coupling via eddy currents to a coil at r.f. frequency. The percolation threshold for both two- and three-dimensional systems is observed by changing the thickness of the samples in a range in which it is comparable to the size of the beads. The observed thresholds for percolation are in good agreement with the theory.

## 1. Introduction

Materials for electromagnetic shielding are often composed of a conductive phase embedded in a polymer matrix. The performance of such materials is in part dictated by the eddy current coupling to the external field. Recently we proposed a scaling theory [1] for describing the electrical conductance of rings in percolating systems. This theory was formulated in terms of universal critical exponents for the infinite percolating system. Also, computer simulations on a two-dimensional lattice were found to be in good agreement with the predictions of the theory.

In this paper measurements of eddy currents coupling to metal polymer random composites are presented. These composites were prepared by mixing bare and copper-coated  $\sim 0.5 \text{ mm}$  polystyrene (PS) beads which were subsequently sintered into a continuous body by a process similar to that presented by Narkis *et al* [2].

The metal content in the composite is 1.83% (wt/wt) so that to a very good approximation the bare and the coated beads are identical in size distribution and density. These features justify the assumptions that upon mixing a true stochastic ensemble is generated. During the sintering stage at a temperature high above the glass transition ( $T_g = 94^\circ\text{C}$ ) of the polymer this random close packed ensemble of spheres is converted into a dense polymer body in which the copper shells form a cellular structure as the copper-coated beads burst and coalesce upon sintering. When the volume fraction of the copper-coated spheres is high enough, a continuous cellular structure, the walls of which are a fraction of a micrometre thick, infiltrates the polymer continuum. The magnitude of inductive coupling at r.f. frequency via eddy currents was studied as a function of the volume fraction of copper-coated beads in the composite. Also, the inductive coupling was measured as a function of the dimensionality of the system at a constant volume fraction of the copper-coated spheres. This last experiment was made feasible by choosing a macroscopic bead diameter so

that samples of thickness comparable with the bead dimension were readily made.

## 2. Experimental details and results

### 2.1. Electroless copper plating of PS beads

The plating process involves four steps: etching, sensitizing, nucleation and electroless plating [3]. Polystyrene beads 300 to 600  $\mu\text{m}$  in diameter are immersed in sulphochromic acid for about 3 h. After filtration on a sintered glass, the beads are mixed with distilled water, neutralized by 0.1 N NaOH and rinsed again thoroughly with water. After the etching step, the PS beads become hydrophilic. Sensitizing involves rinsing with ethanol and immersion for a few minutes in:  $\text{SnCl}_2$  10 g/litre, HCl (37%) 40 ml/litre aqueous solution. In the nucleation step the beads are rinsed in water to remove excess sensitizer and treated with  $\text{PdCl}_2$  0.25 g/litre, HCl (37%) 2.5 ml/litre aqueous solution at room temperature. The beads are subsequently rinsed with distilled water. For electroless plating the following solution was used:  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  15 g/litre,  $\text{NaHCO}_3$  10 g/litre, Rochelle salt 30 g/litre, HCHO (37%) 100 ml/litre.  $\text{pH} \geq 11.5$  was controlled by addition of NaOH. For 50 g beads, a volume of 400 ml of the above solution was used. The plating time was  $\sim 10$  min. The copper-coated beads were rinsed in methanol and dried. Copper-plated spheres are shown in Fig. 1.

### 2.2. Conditions for compression moulding

The mixture of coated and bare PS spheres was moulded at  $190^\circ\text{C}$  for 25 min under a pressure of 1600 p.s.i. ( $\sim 11 \text{ N mm}^{-2}$ ). The resulting disc sample, 29 mm diameter, was cooled under pressure to room temperature. A few samples containing different volume fractions of copper-coated beads are shown in Fig. 2.

### 2.3. Characterization of the copper thin-film shells and structures in the PS bulk

The thickness of the copper shells was determined by

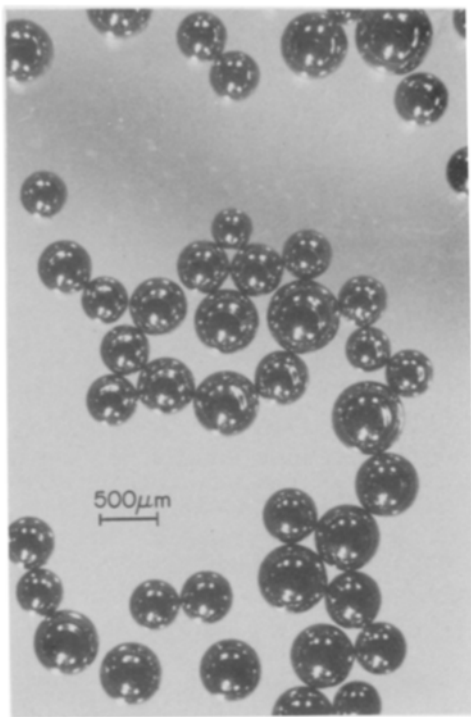


Figure 1 Macrograph of copper-coated PS spheres.

two independent methods. In Fig. 3, a transmission electron micrograph of a thin section through a copper-plated bead is presented. The average thickness of the metal film as determined from many micrographs is  $d = 0.3 \pm 0.05 \mu\text{m}$ . In another experiment, a known number of copper-plated spheres was immersed in methylene chloride under stirring for 6 days — the solvent was exchanged a few times so that practically all PS was dissolved. On weighing the copper shells after this extraction process the thickness of the shells was calculated to be  $d = 0.32 \mu\text{m}$ .

The three-dimensional structure of the copper cells in the sintered polymer body is a tightly packed structure shown in Fig. 4. This cellular structure was revealed by a freeze fracture preparation.

#### 2.4. Measurement of inductive coupling

A schematic illustration of the measuring apparatus is shown in Fig. 5. A HP4815 A r.f. vector impedance meter was operated at 99 MHz. In the experimental apparatus the spatial relation of the sample to the flat coil is fixed in space and reproducible. The impedance,

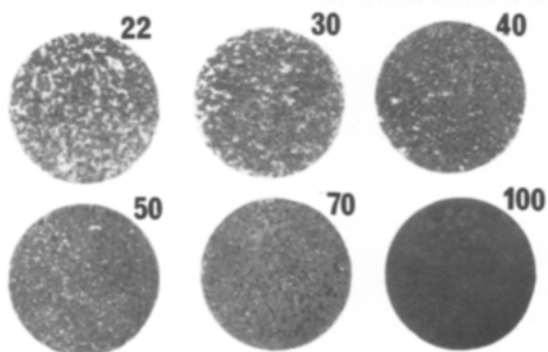


Figure 2 Copper-polymer composites, 1.2 mm thick samples were illuminated from below, numbers show the volume fraction (%) of the copper-coated spheres.

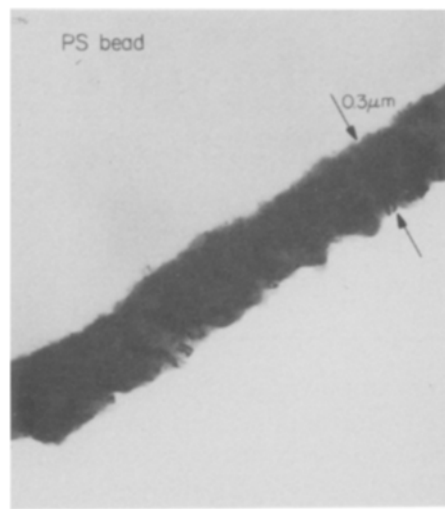


Figure 3 Transmission electron micrograph of a copper-coated bead.

$L_0$ , of the coil probe at 99 MHz is  $923 \Omega$  and its d.c. resistance is  $2.3 \times 10^{-2} \Omega$ . The experimental results, where  $(L - L_0)/L_0$  is plotted against volume fraction of copper-coated beads, are shown in Fig. 6. Two sets of experiments were made, one for thin discs 1.2 mm, and one for 5.8 mm thick discs.

The values for the critical volume fraction,  $\phi_c$ , for both two- and three-dimensional percolation thresholds are also shown in Fig. 6. In another experiment  $(L - L_0)/L_0$  was measured against thickness of sample at 30% volume fraction of copper-coated PS spheres, the result of this experiment is shown in Fig. 7.

### 3. Discussion

The procedure for the preparation of the sintered solid from the random mixture of bare and metal-coated PS spheres seems to follow the prescription for random packing, i.e. a packing containing no statistically significant short- or long-range order. This is the case when the packing is so dense that any increase in density can be achieved only by a statistically significant increase in short-range order; and any decrease in density from the random close-packed density leads to an ensemble of particles which need not be close packed, i.e. a given particle is not necessarily in contact with other particles [4]. This definition of random close packing is very well satisfied in the pre-sintering stage, when the random ensemble of beads is closely packed. We believe that upon sintering the random clusters of the copper-coated spheres are frozen into

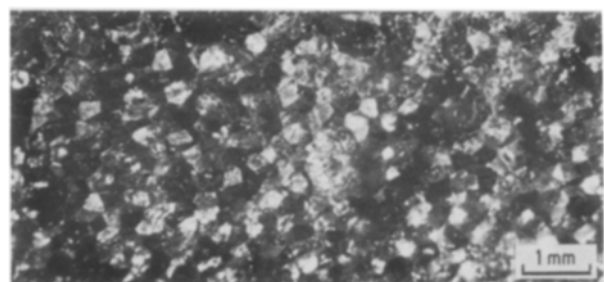


Figure 4 Macrograph of a freeze-fractured copper-polymer composite revealing a cellular structure.

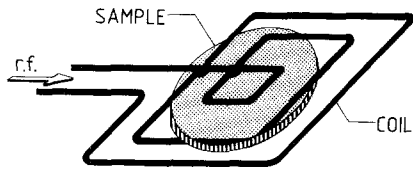


Figure 5 Schematic illustration of the r.f. measuring probe and sample configuration.

the polymer continuum. To probe the continuity of the thin copper film cellular structure in the composite, a method has been designed which integrates the electromagnetic coupling over the whole volume of the polymer-metal composite. At the same time the frequency of the experiment had to be chosen so that the probe could “see through” the sample. Having a copper wall thickness of  $d = 0.3 \mu\text{m}$  the frequency is set to have a skin depth  $\delta \gg d$ . For copper at  $\nu = 99 \text{ MHz}$ ,  $\delta = 6.64 \mu\text{m}$  so that indeed this experimental requirement is well satisfied. On the other hand, the r.f. frequency has to be as high as possible to maximize the eddy current coupling.

When a coil is brought into the vicinity of a non-ferromagnetic material, its input resistance tends to increase whereas its input inductance tends to decrease in comparison with the input values of the coil with material absent. The change in the coil impedance depends on the azimuthal component of the magnetic vector potential [5] which is found to be dependent on a number of factors: the shape and size of the coil; the spacing between the coil and the material; the thickness, conductivity and composition of the material, etc. For a vanishing thin coil of radius  $a$  in the proximity of semi-infinite conducting medium characterized by permittivity  $\epsilon_1$ , conductivity  $\sigma_1$ , and permeability  $\mu_1$ , the reflected impedance is given by [5]

$$Z_r = i\omega\mu_0\pi a^2 \int_0^\infty |J_1(\xi a)|^2 \times \exp(-2h\lambda_0) [(\mu_1\lambda_0 - \mu_0\lambda_1)/(\mu_1\lambda_0 + \mu_0\lambda_1)] (1/\lambda_0) \xi d\xi$$

where  $\mu_0$ ,  $\epsilon_0$  are air permeability and permittivity,

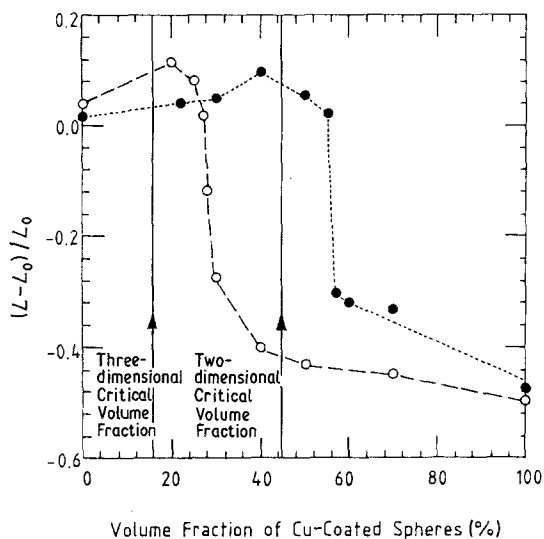


Figure 6 The inductive coupling plotted against volume fraction of copper-coated spheres. (O) 5.8 mm thick discs, (●) 1.2 mm thick discs. The threshold values for the critical volume fraction,  $\phi_c$ , are also shown for both two- and three-dimensional systems.

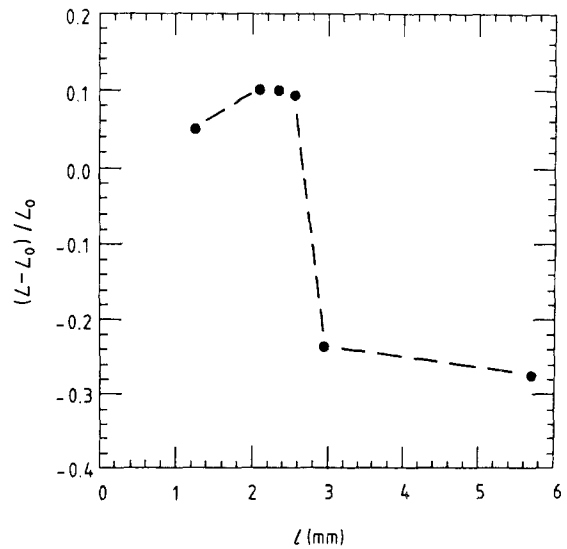


Figure 7 The inductive coupling as function of sample thickness for 30% volume fraction of copper-coated spheres.

$J_1(\xi a)$  is a Bessel function of the first kind (and first order),  $h$  is the distance between the coil and the medium,  $\lambda_0 = (\xi^2 - k_0^2)^{1/2}$ ;  $\lambda_1 = (\xi^2 - k_1^2)^{1/2}$ ;  $k_0 = \omega^2\mu_0\epsilon_0$ ;  $k_1 = \omega^2\mu_1\epsilon_1 - i\omega\mu_1\sigma_1$ . To a first approximation the measured quantity  $(L - L_0)/L_0$  is the normalized reflected reactance of the coil.

The contactless method implemented in this experiment circumvents some of the difficulties common to d.c. methods where the contacts to the sample are sometimes a source of artefacts. Also, this method integrates very well over the whole body of the sample which is characteristically composed of  $\sim 10^4$  conducting elements.

The experimental results are presented as functions of volume fractions of copper-coated spheres. This was done so that the percolation threshold,  $\phi_c$ , is insensitive to the lattice structure of the composite [6]. To within a few per cent, the critical volume fraction,  $\phi_c$ , is 0.45 in two-dimensional and 0.16 in three-dimensional structures [7] so that the critical volume fraction constitutes an approximate dimensional invariant for the threshold in a site-percolation process. The experimental results are in sound agreement with the above  $\phi_c$  values. Note, a rising trend for the experimental data points in the vicinity of  $\phi_c$  for  $\phi < \phi_c$ , Fig. 6. This phenomenon is probably due to a marked increase in the dielectric constant of the polymer-metal composite around the percolation threshold [8]. The dependence of the inductive coupling on thickness at constant volume fractions of copper-coated spheres (Fig. 7) is sharp and quite remarkable. The observed phenomenon may provide an additional handle for the design of polymer-metal composites for electro-magnetic shielding. This feature is important in a system in which for a given r.f. frequency the thickness of the composite is comparable to the size of the conducting element which at the same time possesses a skin depth value much larger than the thickness of the thin film metal component.

## Acknowledgements

I wish to thank J. Cohen for his valuable assistance in

the electroless plating process, and also S. Vega from the Isotope Department, for important comments and suggestions.

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*Received 14 November 1986  
and accepted 29 January 1987*