

Development and Electrical Conductivity Behavior of Copper-Powder-Filled-Epoxy Graded Composites

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ABSTRACT: This article reports the development and direct-current (dc) conductivity behavior of copper-powder-filled-epoxy graded composite. Copper-powder-filled-epoxy composites with 10 wt % copper powder and epoxy resin were developed. dc conductivity measurements were performed on the graded composites with an electrometer in the temperature range of 28–146°C. The dc conductivity decreased with an increase in the distance in the direction of the centrifugal force, and this showed the formation of a graded structure. The dc conductivity increased as the

copper powder content increased. Two-phase conduction occurred in all the copper-filled-epoxy graded samples. The activation energy calculated with an Arrhenius equation for one sample was 0.88 eV, and this was mainly due to conduction electronic. Another sample had an activation energy of 1.33 eV. Three samples exhibited ionic conduction. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2384–2387, 2008

Key words: composites; fibers; epoxy; graded

INTRODUCTION

Metal-filled polymers are extensively used for electromagnetic interference shielding. They are lighter than metals and less costly and can be easily molded into components. The electrical properties of composites with metallic fillers depend on the concentration and morphology of the metal particles.¹

The physical properties and percentages of the filler materials must be optimized to achieve useful composite materials. The electrical conductivity of insulating polymers can be improved by the addition of metallic fillers. Metal-filled polymers have been used as antifouling compounds and corrosion-resistant paints and for the maintenance and repair of products and tools. The electrical and thermal conductivity of polymers can be improved by the addition of carbonaceous fillers.^{2–6} From the point of view of applications, it is necessary to understand the effects of metallic fillers on the properties of a polymer matrix.⁷

In a material, direct-current (dc) conduction occurs because of the movement of free charge carriers under an applied electric field and depends on the strength of the applied electric field. The temperature dependence of dc conductivity in the case of organic semiconducting thin films of copper-, zinc-,

and nickel-filled polymer composites was reported by Shihub and Gould.⁸ They found that at 100°C, the current of thin films of copper- and zinc-filled polymer composites increased because of the desorption of water vapor.⁸

Percolation in a conductive composite depends on the filler particle shape and spatial distribution in the polymer matrix. It has been reported in the literature that the conductivity of metal-filled polymers depends on the interlayer thickness, temperature, and strength of the external field and electron tunneling.^{9,10}

Functionally graded polymer composites exhibit variations in the chemical composition over distance. The electrical properties of such materials are important. There is no report in the literature on the dc conductivity characteristics of copper-powder-filled-epoxy graded composites.

The aim of this work was to develop graded composites of copper-powder-filled epoxy and to determine and analyze the dc conductivity behavior of those copper-powder-filled-epoxy graded composites.

EXPERIMENTAL

The copper powder used in this study was 63 μm in size and had a density of 8.92 g/cc; it was obtained from Merck India. A copper-powder-filled-epoxy gradient composite was developed with a centrifugation process. In this process, centrifugal force was applied in the X direction. Gradient samples were prepared from the copper-powder-filled mix with

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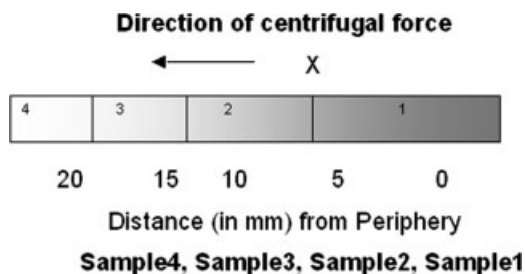


Figure 1 Schematic diagram of the copper powder distribution in four sections.

10 wt % copper powder. Copper powder was added to a mix of an epoxy resin and hardener (10 : 8). The total mix was thoroughly stirred with the help of a glass rod. The details of the setup and process of making gradient composites were the same as those reported in an earlier patent (Chand and Hashmi¹¹). The total mix was poured into the mold to make a sample. The sample-filled mold was rotated at 800 ± 50 rpm and at a radius of 130 mm. Samples were removed from the mold after postcuring at room temperature for 24 h. Slicing to make pellets from the molded pin was done according to the schematic diagram shown in Figure 1. Samples were coated with air-drying-type silver paint before the measurements. The epoxy used in this study was obtained from Hindustan Advanced Materials (India) Pvt., Ltd. (Mumbai, India). The density of the sliced test pellets was measured with a Mettler–Toledo (Columbus, OH) precision balance.

Resistivity measurements

Resistance values of copper-powder-filled-epoxy gradient samples were measured with a Keithley (Delray, FL) model 610C electrometer in the temperature range of 28–146°C. The heating rate was kept constant at $\pm 1^\circ\text{C}/\text{min}$.

The density (ρ) values were calculated with the following relation:

$$\rho = R \times A/l$$

where R is the resistance of the sample, A is the area of the electrodes (cm^2), and l is the thickness of the sample (cm).

TABLE I
Densities of Gradient Composites at Different Distances

Sample	Distance from the periphery (mm)	Density (g/cc)
1	0	1.12209
2	5	1.06695
3	10	1.05925
4	15	1.03961

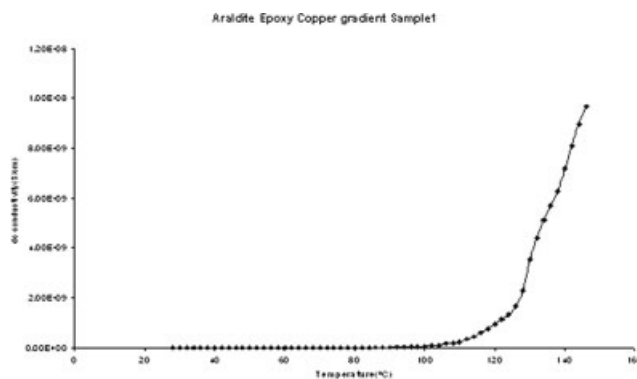


Figure 2 Variation of the dc conductivity with the temperature for copper-powder-filled epoxy sample 1.

The dc conductivity (σ_{dc}) was calculated with the following formula:

$$\sigma_{dc} = 1/\rho$$

RESULTS AND DISCUSSION

Figure 1 shows a schematic view of the gradient composite prepared with a mix of copper powder and epoxy. This schematic diagram shows the distribution of the copper powder in the composite.

Table I lists the densities of the copper-powder-filled-epoxy gradient composites. An increase in the distance from the periphery decreases the density of the composites. This is due to the decrease in the copper content. Figure 2 shows the variation of the dc conductivity with the temperature for copper-powder-filled epoxy sample 1. There is a sudden increase in the dc conductivity after 124°C. This plot shows a sharp increase in the dc conductivity from 96°C, and it continues increasing up to 146°C.

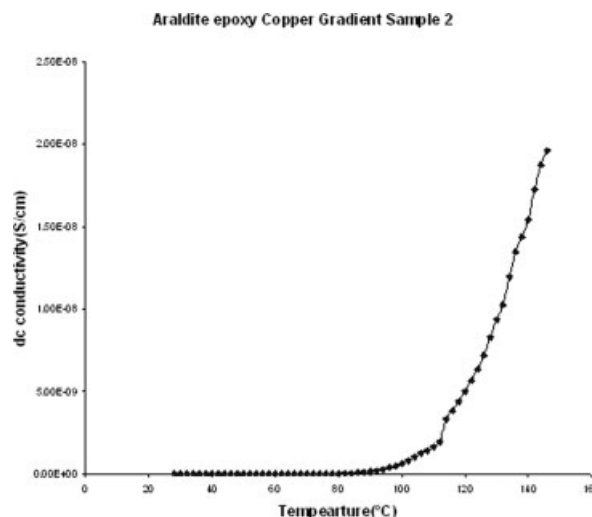


Figure 3 Variation of the dc conductivity with the temperature for copper-powder-filled epoxy sample 2.

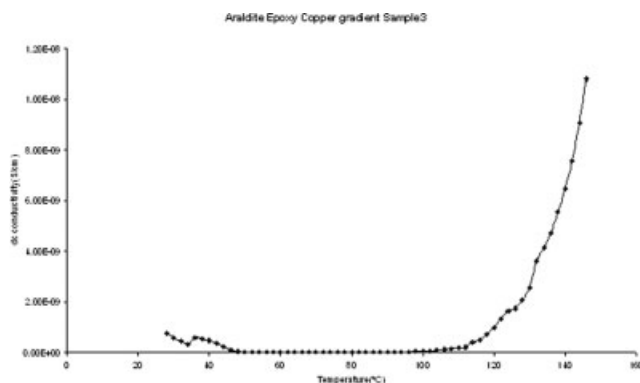


Figure 4 Variation of the dc conductivity with the temperature for copper-powder-filled epoxy sample 3.

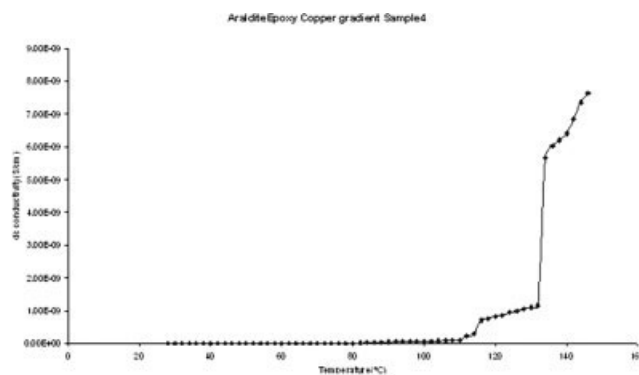


Figure 5 Variation of the dc conductivity with the temperature for copper-powder-filled epoxy sample 4.

Figure 3 shows the variation of the dc conductivity with the temperature for sample 2. Up to 112°C, there is no increase in the dc conductivity. After 112°C, there is a sudden increase in the dc conductivity with an increase in the temperature at 114°C. An important observation is that the point of the sudden increase in the dc conductivity shifts toward the higher temperature side. Figure 4 shows the variation of the dc conductivity with the temperature for sample 3.

The dc conductivity suddenly increases after 116°C, and a sharp increase in the dc conductivity starts from 126°C. A peak has been found at 124°C. Figure 5 shows the variation of the dc conductivity with the temperature for sample 4. The dc conductivity increases from 110°C, and at 132°C, there is a sudden increase in the dc conductivity. A switching effect can be observed between 132 and 134°C. All the copper-filled-epoxy gradient composites show two phases of conduction, the first related to a low temperature and the second related to a high temperature. This is because copper starts participating in the conduction process along with the increase in defects.

Table II lists the dc conductivity values of samples 1–4 at different temperatures. This shows that sample 1 has the maximum dc conductivity value because of the presence of the maximum amount of copper powder, and sample 4 has the minimum value because of the presence of the minimum amount of copper powder in this region.

In the case of a carbon-black-filled polymer, Narkis and Vaxman¹² reported that the resistivity decreased because of the reagglomeration of carbon black aggregates. Kohler¹³ found that the positive temperature coefficient (PTC) effect is due to thermal expansion. He proposed that conductive particles that are spread throughout a polymer form a network of conducting chains. When the material is heated, the conductive particles are separated and increase the resistance. He assumed that the sudden expansion of the polymer at the crystalline melting point is the cause of the transition to the highly resistive state. Thermodynamically, it has been proved that at low temperatures, defects in polymers are independent of the temperature. An increase in the temperature increases the defects in the polymeric composite, and ionic conduction takes place when an ion moves from an occupied site to an unoccupied site. At 0°K, all the trapped electrons in the polymers are in deep traps. At a specific temperature and on the application of the applied electric field, some of the electrons can excite into shallow traps or to the conduction level, and these electrons take part in conduction. The increase in the temperature does not alter the total amount of the space charge but increases the portion of this space charge in the conduction band, which increases exponentially with the temperature increasing.¹⁴

Singh and Gupta,¹⁴ in the case of polypropylene, found that an electron occupying an isolated donor

TABLE II
dc Conductivity Values of Samples 1–4 at Different Temperatures

Temperature (°C)	dc conductivity (S/cm)			
	Sample 1	Sample 2	Sample 3	Sample 4
30	3.59×10^{-13}	3.48×10^{-13}	3.42×10^{-13}	3.31×10^{-13}
50	4.65×10^{-13}	3.66×10^{-13}	3.36×10^{-13}	3.32×10^{-13}
60	5.23×10^{-13}	4.32×10^{-13}	3.46×10^{-13}	3.38×10^{-13}

TABLE III
Activation Energies (eV) of Samples 1–4

Sample	Activation Energy (eV)
1	0.0885714
2	1.315112
3	1.325432
4	1.33515

has a wave function near the impurity. There is a little overlap of the wave function of an electron of the donor with those of neighboring donors. Because of this, a conduction process is possible in some circumstances when electrons move between the centers by a tunneling effect without activation. Defect conduction in the case of polypropylene was reported by Singh and Gupta. They reported that thermal agitation gives rise to defects in the material and that conduction takes place by the movement of ions from an occupied position to a unoccupied position.

On the basis of $\ln \sigma$ versus T^{-1} plot [where σ is the conductivity and T is the temperature (K)] for copper-powder-filled epoxy, the activation energy was calculated with the following Arrhenius equation:

$$\sigma = A \exp^{-W_E/kT} \quad (1)$$

where W_E is the activation energy of conduction, k is Boltzmann's constant, and A is a constant.

Table III lists the activation energies of copper-powder-filled-epoxy gradient composites. The activation energy, calculated with eq. (1), in the case of sample 1 is 0.88 eV, which is the minimum. This shows that sample 1 has predominantly electronic conduction because the maximum copper powder content is present in sample 1. An increase in the activation energy value from 0.88 to 1.33 eV has been found for sample 4. The increase in the activation energy is due to the decrease in the copper powder

content. This increase in the activation energy signifies an increase in the binding forces, which oppose dipole orientation and increase the activation energy.

CONCLUSIONS

1. The dc conductivity value increases from sample 4 to sample 1. This shows the existence of a graded structure.
2. An increase in the copper powder content increases the dc conductivity.
3. Different transition points have been observed in dc conductivity plots for different samples. The transition temperature shifts to the lower side with an increase in the copper content.
4. The activation energy decreases with an increase in the copper powder content in the samples.

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