

# Conducting Polymer Composites of Zinc-Filled Urea–Formaldehyde

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**ABSTRACT:** This article is concerned with the preparation and characterization of composite materials prepared by the compression molding of mixtures of zinc powder and urea–formaldehyde embedded in cellulose powder. The morphologies of the constituent, filler, and matrix were investigated by optical microscopy. The elaborated composites were characterized by density, which was compared with calculated values, and the porosity rate was deduced. Further, the hardness of samples remained almost constant with increasing metal concentration. The electrical conductivity of the composites was less than  $10^{-11}$  S/cm unless the metal

content reached the percolation threshold at a volume fraction of 18.9%, beyond which the conductivity increased markedly, by as much as eight orders of magnitude. The obtained results interpreted well with the statistical percolation theory. The deduced critical parameters, such as the threshold of percolation, the critical exponent  $t$ , and the packing density coefficient were in good accord with earlier studies. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2011–2015, 2005

**Key words:** conducting polymers; composites; compression; density; fillers

## INTRODUCTION

Information about numerous existing possibilities of polymers containing dispersed conductive fillers and about the various methods of manufacture of such materials have been reported widely in the literature in recent years<sup>1–4</sup> due to their numerous technological applications in a variety of areas, including electromagnetic/radio frequency interference shielding for electronic devices (e.g., computer and cellular housings), self-regulating heaters, overcurrent protection devices, photothermal optical recording, direction-finding antennas, and chemical-detecting sensors that are used in electronic noses.<sup>5–10</sup>

It is known that in general, percolation theory is used to describe the electrical conductivity of extrinsic conductive polymer composites. Hence, the electrical conductivity for polymer composites does not increase continuously with increasing electroconductive filler content, but there is a critical composition (percolation threshold) at which the conductivity increases some orders of magnitude from the insulating range to values in the semiconductive or metallic range.<sup>11</sup> For efficiency, to decrease the difficulty of the process and the economic costs, the amount of the conductive

phase needed to achieve materials with high conductivity should be as small as possible. A huge number of different models have been proposed for the estimation of the conductivity (or inverse resistivity) versus the filler concentration curves.<sup>12–17</sup>

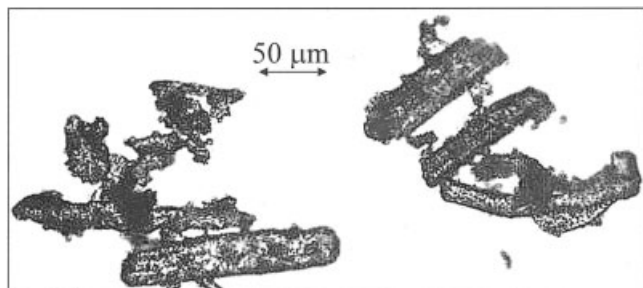
This article presents further developments to previously reported investigations of the preparation and characterization of electroconductive polymer composites.<sup>18–23</sup> We report an experimental study on the influence of filler concentration on the electrical conductivity of composites produced by hot compaction by means of the compression molding of mixtures of zinc powder and urea–formaldehyde embedded in cellulose powder. These data, along with those reported previously, may be helpful in the development of theoretical models to better understand the variation of electrical properties of such polymer composites. Furthermore, to check the void level within the samples, which remarkably influences the electroconductivity, the porosity rate was determined from the densities of the composites. Finally, to complete the characterization of these materials, we studied the influence of filler concentration on the hardness of the composites.

## EXPERIMENTAL

### Materials

The matrix polymer used in our experiments was a commercial-grade urea–formaldehyde embedded in

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**Figure 1** Photograph of urea-formaldehyde embedded in cellulose powder.

cellulose and supplied in the form of powder by Aicar S. A. (Cerdanyola del Vallès, Spain) with a density of  $1.36 \text{ g/cm}^3$  and an electrical conductivity of around  $10^{-12} \text{ S/cm}$ . The content of cellulose in the resin was 30 wt %. A micrograph of this powder is shown in Figure 1, where the longitudinal shape of particles can be observed.

The electrical conducting filler used was zinc (Pan-reac, Castellar del Vallès, Spain), with average particle size of  $15 \pm 10 \mu\text{m}$ , a density of about  $7.14 \text{ g/cm}^3$ , and an electrical conductivity taken as the tabulated value<sup>24</sup> of the order of  $1.7 \times 10^5 \text{ S/cm}$ . The shape of the particles of the filler is illustrated in Figure 2.

Both, the polymer and the metal powders were thoroughly dried before use (48 h at  $60^\circ\text{C}$ ).

### Composite preparation

Composites of zinc with urea-formaldehyde embedded in cellulose powder were fabricated by the mixture of the polymer and the filler powders for 2 h in an internal mixer, followed by compression molding in a specially designed mold with three cavities, each 30.0 mm in diameter and 3.0 mm thick. The molding parameters were 20 MPa and  $150^\circ\text{C}$  for 30 min. These fabrication conditions were suggested by our previous experience. Samples with filler contents in the range 0–75 wt % (corresponding to a 0–0.45 range in volume fraction) were prepared. To improve the finish of the sample and ensure a better electrical contact for resistance measurements, the surfaces were polished with sandpaper. The sample thickness (necessary for the calculation of conductivity) was determined with a micrometer (Schmidt Technology, Cranberry Twp., PA; model J 50) to an accuracy of 0.01 mm. Thickness measurements were taken at five locations and averaged. Samples were cooled to as much as room temperature in approximately 30 min.

### Composite characterization techniques

The electrical conductivity was determined with the resistance values, which were measured with a two-

point arrangement. Three specimens of each composition were tested, taking four data points on each sample. To decrease the contact resistance, the sample surfaces were coated with silver paint.

Measurements of volume electrical resistance higher than  $10^3 \text{ ohm}$  were made with a programmable megohmmeter (Quadtech, Maynard, MA; model 1865). Measurements of low resistance were made with a digital multimeter (Leader, Melrose, MA; model 856). A constant voltage of 100 V was supplied to the samples, and the resistance of the samples was measured after 1 min, with a test cycle consisting of a 20-s charge, a 20-s dwell, a 20-s measure, and a 20-s discharge. Before a new test was started, the electrodes were short-circuited for 5 min to eliminate any effect of the previous electrification. The procedure used to estimate the conductivity from resistance in this study was similar to one reported earlier.<sup>21</sup>

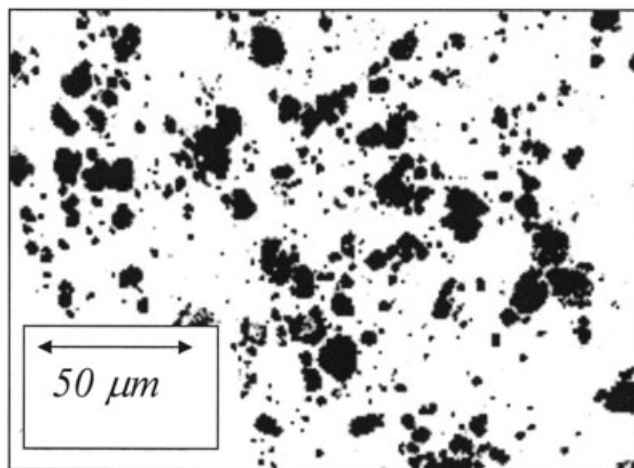
The density of the composites was measured in accordance with ASTM D 792-91 by the difference of weight in the air or with the sample immersed in water, as the liquid of known density, at  $23^\circ\text{C}$  with a Mettler Toledo (Columbus, OH) AJ 100 balance equipped with a density-determination kit.

The hardness of the samples was determined at  $23^\circ\text{C}$  with a Durotronic (Canton, MA) model 1000 Shore D hardness tester in accordance with ASTM D 2240-68. Five data points were taken on each sample, and no difference was found between the hardness measurements on both faces of each specimen.

The microstructures of the samples were observed by reflection with a Nikon (Tokyo, Japan) model 115 optical microscope.

## RESULTS AND DISCUSSION

The theoretical density of the composite ( $d_t$ ) was calculated from the relation<sup>23</sup>



**Figure 2** Photograph of zinc powder.

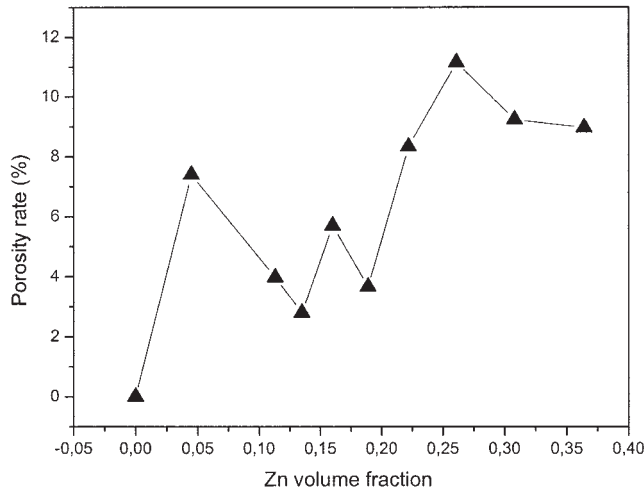


Figure 3 Porosity rate versus Zn volume fraction.

$$d_t = (1 - V_f)d_m + V_f d_f \quad (1)$$

where  $V$  is the volume fraction,  $d$  is the density, and  $m$  and  $f$  stand for the matrix and filler, respectively.

Then, the composite's porosity ( $\tau$ ) was determined from the formula:<sup>23</sup>

$$\tau = \left( \frac{d_t - d_e}{d_t} \right) \times 100 \quad (2)$$

where  $d_e$  represents the experimental density.

Figure 3 represents the porosity rate of various composites as function of the filler volume fraction. In all cases, the porosity was almost constant as function of Zn volume fraction, with a small change around the percolation threshold. This change was probably due to the packing effect. Nevertheless, the upper value was around 10%. Therefore, the quality of the obtained composites was good. Moreover, the hardness remained approximately constant, as  $82 \pm 4$  shore D values, independent of the filler composition.

The electrical conductivity of the composites as a function of filler content for the samples showed typical S-shaped dependency with three regions (dielectric, transition, and conductive; Fig. 4). As expected, samples with low filler content were almost nonconductive. However, the electrical conductivity of the composites increased dramatically as the zinc content reached the percolation threshold at 18.9% (v/v) filler. The value of the percolation threshold was obtained from the maximum of the derivative of the conductivity as a function of filler volume fraction (Fig. 4). According to Flandin et al.,<sup>4</sup> values of 20–40% (v/v) are typical for spherical particles of filler. Above the percolation threshold, the conductivity of composite increased by much eight orders of magnitude.

As indicated, this behavior could be explained with the statistical percolation theory. Such theory is usually used to relate the electrical conductivity of the composite to the existence of clusters of connected particles, which give rise to the so-called conducting infinite cluster above the threshold. For this theory, the relationship between the electrical conductivity of the mixture and the volume fraction of the conductive filler was given by Kirkpatrick:<sup>12</sup>

$$\sigma = \sigma_o(V_f - V_f^*)^t \quad (3)$$

where  $\sigma$  is the electrical conductivity of the mixture,  $\sigma_o$  is the electrical conductivity of the filler's particles,  $V_f$  is the volume fraction of the filler,  $V_f^*$  is the critical volume concentration at the threshold of percolation, and  $t$  is an exponent that determines the increase in the conductivity above  $V_f^*$ . This theory provided a good description of the experimental results near the transition point. Nevertheless, discrepancies were observed between the critical parameters ( $V_f^*$ ,  $t$ ) resulting from eq. (3) and the experimental values:<sup>16</sup> inasmuch as the basic classical statistical theory does not consider several parameters. Although the experimental results show that the electrical conductivity depended strongly on the viscosity and the surface tension of the filled polymers, it also depended on the filler particles geometrical parameters and the filler–matrix interactions. Mamunya et al.<sup>15,16</sup> developed a model in which specific parameters for each composite were introduced in the basic theory:

$$\sigma = \sigma_o + (\sigma_m - \sigma_o) \left( \frac{V_f - V_f^*}{F - V_f^*} \right)^{t_{\text{eff}}} \quad (4)$$

where  $\sigma_m$  is the maximal conductivity of composites,  $F$  is the filler packing density coefficient (equivalent to

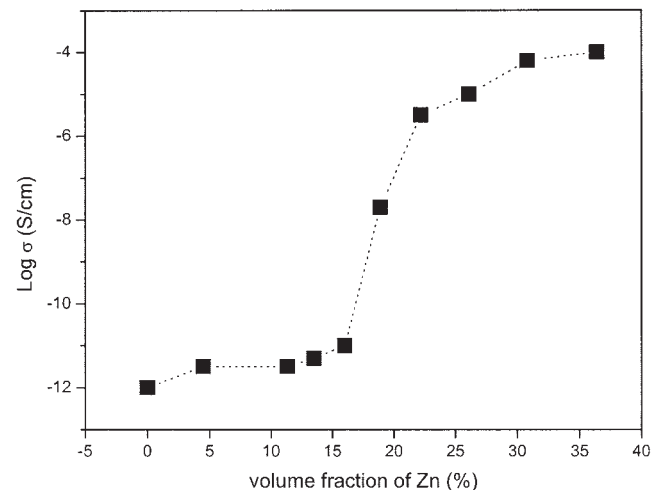
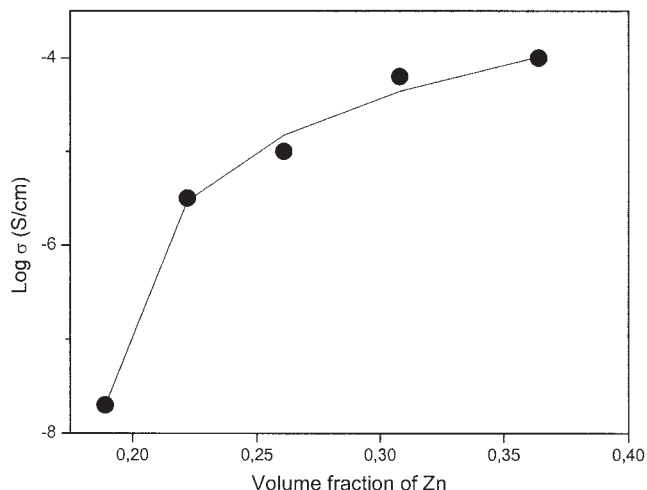


Figure 4 Variation of the electrical conductivity of urea-formaldehyde embedded in cellulose powder/Zn composites with Zn content.



**Figure 5** Electrical conductivity versus volume fraction of Zn-filled urea–formaldehyde embedded in cellulose powder above the percolation threshold. The solid line is the fit with eq. (4).

the maximal value of the filler volume fraction), and  $t_{\text{eff}}$  is given by the relation

$$t_{\text{eff}} = t_1 + t_2 \quad (5)$$

where  $t_1$  is equivalent to the  $t$  parameter in the basic eq. (3), which usually has a value around 1.7, and  $t_2$  depends on the specific composite. Thus,  $t_{\text{eff}}$  could have higher values depending on the filler–polymer interactions.

Equation (4) was used with success in earlier studies to interpret experimental results.<sup>21,23</sup> The fit, above the percolation threshold, of the electrical conductivity as function of the volume fraction of Zn filled in urea–formaldehyde embedded in cellulose powder is given in Figure 5. The agreement between the experiment and the theory was fairly good. The deduced parameters were  $V_f^* \approx 18.5\%$ ,  $t_{\text{eff}} \approx 2.25$ , and  $F \approx 0.45$ .

The determined packing density coefficient was in good agreement with the prediction of eq. (4).<sup>25</sup> The  $t_{\text{eff}}$  obtained value was close to 2, which represented the accepted theoretical value for three-dimensional lattices.<sup>26,27</sup> This theoretical value was independent of the exact composition of the random composites.<sup>26</sup> On the other hand, the critical threshold percolation value obtained was in good agreement with that determined by experience,  $V_f^* \approx 18.9\%$ . Elsewhere, this result was also close to the 18% found in Zn-filled nylon 6.<sup>22</sup> Indeed, the random composite's electrical conductivity was already shown to depend on several parameters,<sup>18–23,28,29</sup> such as the viscosity and the polymer's surface tension, especially in the case of mixes in which the conductive powder is dispersed; the size, shape, and surface energy of the filling particles; and the powder dispersion procedure, that is, the type,

duration, and strength of shear. In this study, the particle sizes and shape of Zn filled in nylon 6 and urea–formaldehyde were the same, and the dispersion procedure was maintained uniformly. Consequently, the small difference in threshold values observed between nylon–Zn and urea–formaldehyde/Zn composites was probably due to the specific matrix–filler interaction and viscosity effects.

## CONCLUSIONS

In this article, we described an experimental study on the effects of the content of zinc-filled urea–formaldehyde embedded in cellulose on the electrical conductivity. From the obtained results, we conclude that

1. The density measurement showed that the void fraction in all samples was low.
2. The Shore D hardness remained approximately constant with increasing filler concentration.
3. The electrical conductivity of the composites increased as much as eight orders of magnitude for a given range of filler concentration, showing the typical percolation transition from the dielectric to the conductive region of such polymer composite materials.
4. The percolation threshold concentration corresponded to a volume fraction of zinc of  $V_f^* \approx 18.9\%$ , which was in good agreement with previous experiments.
5. The electrical conductivity behavior function of the filler content was fairly fitted with extended basic statistical percolation theory. The deduced critical parameters were reasonable and coherent with experimental values and the earlier predictions.

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