Conducting Polymer Composites of Zinc-Filled Nylon 6

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ABSTRACT: The present work is concerned with the effect of processing variables and filler concentration on the electrical conductivity, hardness, and density of composite materials prepared by compression molding of a mixture of zinc powder and nylon 6 powder. The electrical conductivity of the composites is $<10^{-12}$ S/cm, unless the metal content reaches the percolation threshold at a volume fraction of about 0.18, beyond which the conductivity increases markedly by as much as 10 orders of magnitude. The density of the composites was measured and compared with values calculated by assuming different void levels within the samples. Furthermore, it is shown that the hardness increases with the increase of metal concentration, but for values of filler volume fraction higher than about 0.30 the hardness of samples remains almost constant. Two parameters of molding process, temperature and time, were shown to have a notable effect on the conductivity of composites, whereas pressure has no influence on this property in the pressure range considered. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1449–1454, 2001

Key words: percolation; electrical properties; conducting polymer composites; nylon 6; zinc powder filler

INTRODUCTION

Information about numerous existing possibilities of polymers containing dispersed conductive fillers and various methods of manufacture of such materials has been reported widely in the literature for the past 20 years[1–7] because of their numerous technological applications in a variety of areas such as electromagnetic/radio frequency interference (EMI/RFI) shielding in electronic devices (computer and cellular housings, for example), self-regulating heaters, overcurrent protection devices, photothermal optical recording, direction-finding antennas, chemical detecting sensors used in electronic noses, and more.[8–20]

It is known that, in general, the 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, although 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.[8] For efficiency, to decrease the difficulty of the process and economic costs, the amount of the

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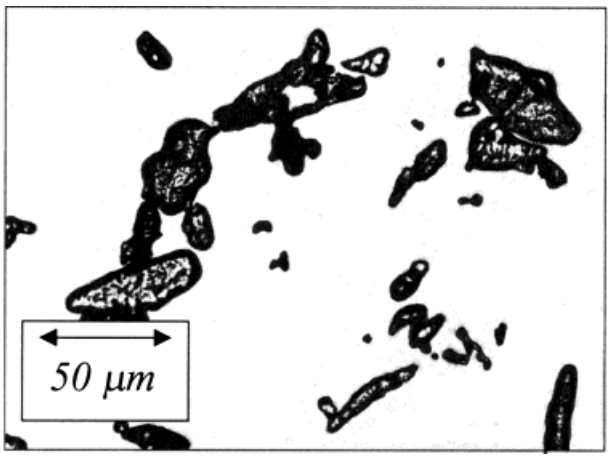

Figure 1 Micrograph of nylon 6 powder.

conductive phase for achieving materials with high conductivity should usually be as small as possible. A great number of different models have been proposed for the estimation of the conductivity (or inverse resistivity) versus filler concentration curves.[21–27]

This study presents further developments in previously reported investigations of properties and influence of processing parameters of composites made of copper powder, carbon black, and aluminum powder also embedded in nylon 6.[28–31] We report an experimental study about the influence of filler concentration on the electrical conductivity of composites produced by hot compaction by means of the compression molding of a mixture of zinc powder and nylon 6 powder. The effects of temperature, pressure, and time of processing on the conductivity of the composites will also be discussed. Along with other previously reported data, these data may be helpful in developing theoretical models to better understand the variation of electrical properties of such polymer composites.

Void levels within the samples, which significantly influence electroconductivity, were calculated from the density of the composites.

As cited in the previous investigations, to complete the characterization of these materials, we present a study about the influence of filler concentration on the hardness of the composites as an example of mechanical property.

EXPERIMENTAL

Materials

The matrix polymer used in our experiments was a commercial-grade nylon 6 supplied in the form of powder by Poliseda (Alcalá de Henares, Spain), with a weight-average molecular weight (M_w) of 24,500, a density of 1.13 g/cm^3, a glass-transition temperature of about 50°C, a melting temperature of about 225°C, and electrical conductivity of around 10^{-13} S/cm. The cumulative size distribution of the polyamide 6 powder was reported in previous works.[28,29] 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, delivered by Panreac (Castellar del Vallés, Spain), with an average particle size of 15 ± 10 μm, density of about 7.14 g/cm^3, and electrical conductivity taken as the tabulated value[32] of the order of 1.7×10^5 S/cm. The shape of the particles of filler is illustrated in Figure 2.

Both the polymer and the metal powders were thoroughly dried before use (48 h at 60°C).

Composite Preparation

Zinc-filled nylon 6 composites were fabricated by mixing 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 of 30.0 mm diameter and 3.0 mm thickness. The composite molding press used in this study was PL-15 model from IQAP-E (Manlleu, Spain). The three more important molding parameters were varied. Pressures ranging from 10.0 to 24.0 MPa and temperatures ranging from 205 to 225°C were used, for a time of molding ranging from 5 to 45 min. Samples with filler contents in the range 0 to 84 wt % (corresponding to the range 0 to 0.45 in volume fraction) were prepared. To improve the finish of the sample and

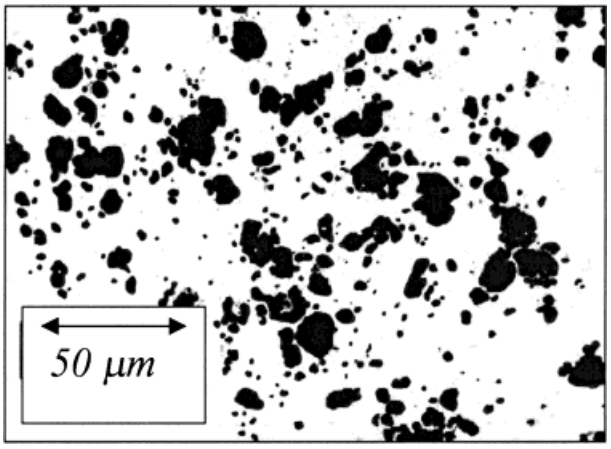

Figure 2 Micrograph of zinc powder.

ensure a better electrical contact for resistance measurements the surfaces were polished with sandpaper. Sample thickness (necessary for the calculation of conductivity) was determined using a micrometer (Shirley Developments Ltd. model J 50, Manchester, England) to an accuracy of 0.01 mm. Thickness measurements were taken at five locations and averaged. Samples were cooled to ambient room temperature in approximately 30 min.

Composite Characterization Techniques

Electrical conductivity was determined because the resistance values were measured using 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 ohm were made using a programmable megohmeter (Quadtech, Maynard, MA, USA) model 1865). Measurements of low resistance were made using a digital multimeter (Leader Model 856, Yokohama, Japan) model 856). A constant voltage of 100 V was supplied to the samples and the resistance of the samples was measured after 1 min, using a test cycle consisting of 20-s charge, 20-s dwell, 20-s measure, and 20-s discharge. Before starting a new test, the electrodes were short-circuited for 5 min to eliminate any effect of the previous electrification. The procedure used to estimate conductivity σ from resistance, in the present study, was similar to that reported earlier.[31]

The densities of the composites were measured in accordance with ASTM D 792-91, by difference of weight in the air or with the sample immersed in water as the liquid of known density, at 23°C, using a Mettler AJ 100 balance (Zurich, Switzerland) equipped with a density determination kit.

The hardness of the samples was determined at 23°C using a Durotronic (Akron OH, USA) 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 hardness measurements on both faces of each specimen.

The microstructures of the samples were observed by reflection by means of a Nikon model 115 optical microscope (Kingston upon Thames, England). Sections (100 μm) were cut by a microtome.

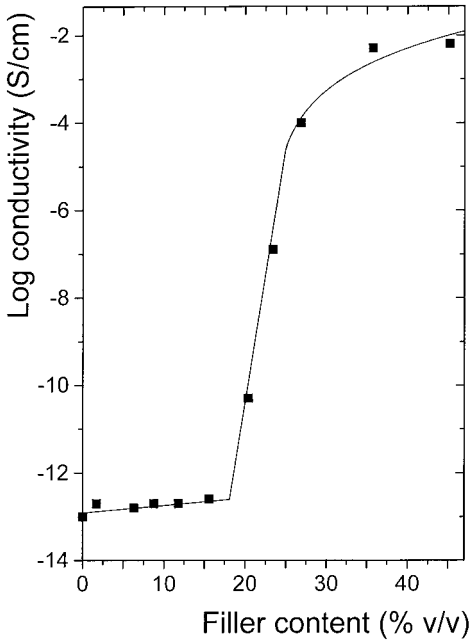

Figure 3 Variation of the electrical conductivity of nylon 6/Zn composites with filler content. The processing conditions were 215°C, 20.0 MPa, and 15 min.

RESULTS AND DISCUSSION

The electrical conductivity of the composites as a function of filler content for the samples shows the typical S-shaped dependency with three regions (dielectric, transition, and conductive) (Fig. 3). As expected, samples with low filler content were almost nonconductive. However, the electrical conductivity of the composites increases dramatically as the zinc content reaches the percolation threshold with about 18% (v/v) filler. According to Flandin et al.[7] values of 20–40% (v/v) are typical for spherical particles of filler. Conductivity of the composite increases by as much as 10 orders of magnitude.

Figure 4 shows the micrographs of different composites, where the structures of composite samples before (a) and after (b) reaching the conductive character are shown. The absence or existence, respectively, of conductive channels formed by particles of filler can be observed.

Our results about the influence of processing parameters on conductivity of samples coincide in general with those reported by Chan et al.,[33] who studied the electrical properties of polymer composites prepared by sintering mixtures of carbon black and ultrahigh molecular weight polyethylene powder, and with those reported by us for

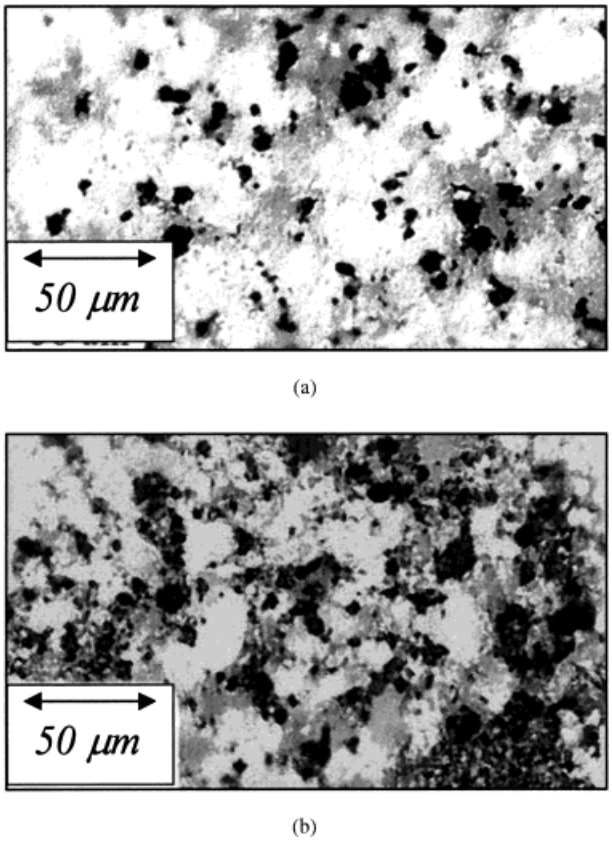

Figure 4 Optical micrographs of the zinc-filled nylon 6 composites containing (a) 16% (v/v) of filler and (b) 36% (v/v) of filler.

carbon black–filled nylon 6 composites.[30] In this way, the processing pressure has no significant effect on the conductivity in the pressure range considered (from 10.0 to 24.0 MPa). However, temperature and time processing were identified as parameters that have a significant effect on the conductivity.

Figure 5 shows the comparison between the calculated and measured density/filler concentration curves for the system under investigation. These curves were calculated assuming different extents of void fraction in the samples, as explained in previous works,[28,29] where more detail was included. The average fraction voids in volume for the samples was 5 ± 2%.

Figure 6 shows a plot of the conductivity of the material prepared at a pressure of 20.0 MPa with a processing time of 15 min and a zinc concentration of 66 wt % (0.23 in fraction volume) as a function of processing temperature. As can be observed in this figure, the conductivity of the composite materials decreases with the increase

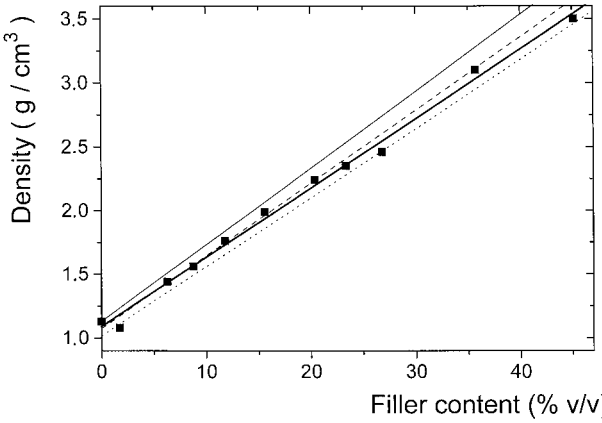

Figure 5 Measured density and calculated density/filler concentration curves for an overall volume of voids accounts for 0% (—); 5% (– – –); 10% (- - - -). The processing conditions were 215°C, 20.0 MPa, and 15 min.

of temperature processing. According to Chan et al.,[33] this is believed to be caused by the high degree of intermixing between the conductive filler and polymer particles in the interfacial regions as the result of the lower viscosity of the polymer at the higher temperatures and thus conductive clusters formed by particles of filler break up.

Figure 7 shows the effect of processing temperature on the density of materials. As found previously for carbon black–filled nylon 6 composites,[30] the increase of temperature promotes an increase in density because of the higher accessibility of molten polymer to the surface of filler particles. This increase of density and thus the decrease of

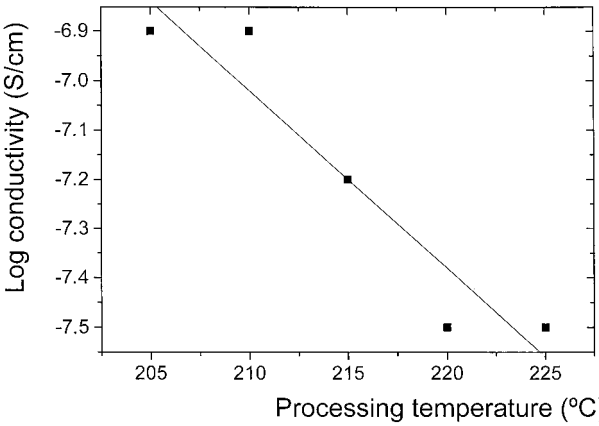

Figure 6 Plot of conductivity as a function of processing temperature at a processing time of 15 min and a zinc concentration of 23% (v/v).

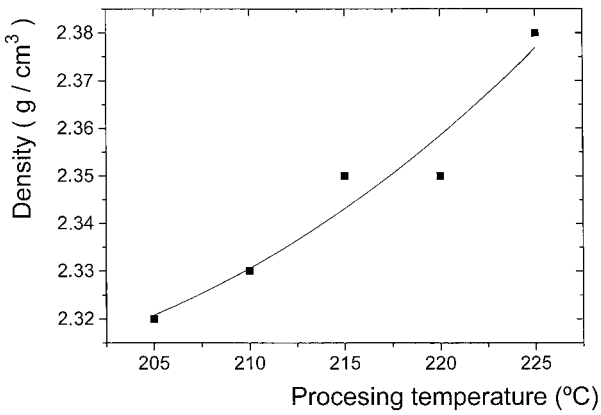

Figure 7 Plot of density as a function of processing temperature at a processing time of 15 min and a zinc concentration of 23% (v/v).

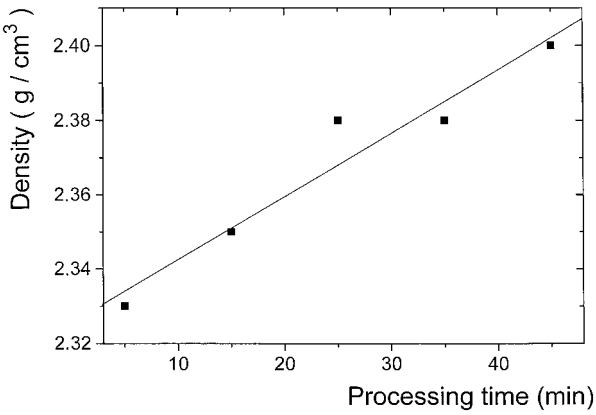

Figure 9 Plot of density as a function of processing time at a processing temperature of 215°C and a zinc concentration of 23% (v/v).

the fraction voids seem not to influence electrical conductivity because of the higher influence of dimensions of filler channels.

A plot of the conductivity as a function of processing time at a pressure of 20.0 MPa, a processing temperature of 215°C, and a zinc concentration of 66% wt % (0.23 in fraction volume) is shown in Figure 8. The conductivity increases in the beginning and decreases after approximately 30 to 35 min of compaction. According to Chan et al.,[33] this result can be explained by the nature of the compaction process. In the beginning, when the material is being compacted, solid conductive channels start to form; hence the conductivity increases. The maximum conductivity is reached when the compaction process is completed. Further increases in processing time will promote the interfacial mixing of the zinc particles and the polymer and this intermixing will reduce the dimension of the zinc channels and, consequently, conductivity decreases.

Figure 9 shows the effect of processing temperature on the density materials. An increase of the processing temperature parameter promotes an increase in density as a result of the higher facility of molten nylon to access the surface of zinc particles. As for the processing temperature, the difference of density and thus the fraction of voids seem to exert only a low influence on electrical conductivity variation.

Figure 10 shows the dependence of Shore D hardness of the different specimens on the filler content. The hardness/filler concentration data reveal that, after a sharp increase in hardness with increase of filler fraction, the hardness is

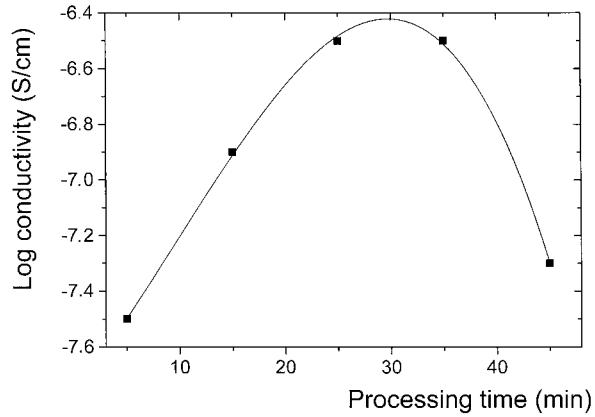

Figure 8 Plot of conductivity as a function of processing time at a processing temperature of 215°C and a zinc concentration of 23% (v/v).

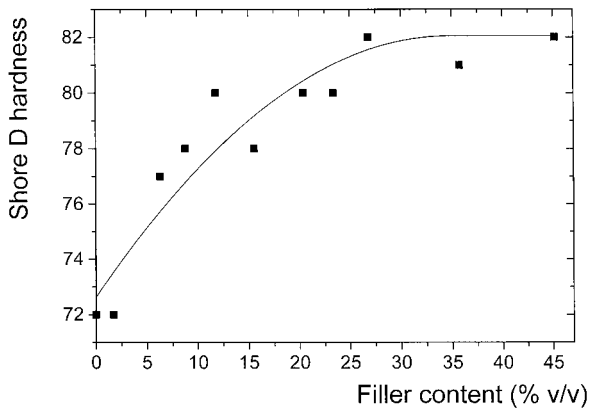

Figure 10 Variation of Shore D hardness for composites with filler content.

approximately constant as the filler composition exceeds a value of about 30% (v/v).

CONCLUSIONS

In this investigation we have described an experimental study about the effects of the filler content and processing parameters on the electrical conductivity, density, and Shore D hardness of composites of zinc powder embedded in nylon 6 prepared by compression molding. From the results obtained, the following conclusions can be shown:

1. The electrical conductivity of composites increases as much as 10 orders of magnitude for a given range of filler concentration, showing the typical percolation transition from dielectric to conductive region of such polymer composite materials.
2. The percolation threshold concentration corresponds to a volume fraction of zinc of about 0.18.
3. Time and temperature are two processing parameters that have a significant effect on the conductivity of materials, whereas the processing pressure has been shown to be an unimportant parameter in the range considered (10.0 to 24.0 MPa).
4. Increases of both processing temperature and time processing promote an increase in density, and subsequently a decrease in volume voids, although this phenomenon does not seem to highly influence the electrical conductivity.
5. The Shore D hardness increases with the increase of filler concentration and it remains approximately constant for values of filler volume fraction higher than about 0.30.

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