

Submicron Copper-Low-Density Polyethylene Conducting Composites: Structural, Electrical, and Percolation Threshold

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ABSTRACT: Copper-embedded low-density polyethylene (LDPE) composites were fabricated using different copper concentrations in the polymer matrix. The copper particles were spherical with a mean particle size between 200 and 300 nm. All the samples were compacted under pressure and melted. The LDPE matrix was analyzed using gel permeation chromatography (GPC) and it did not evidence degradation of the LDPE matrix. The microstructure of the composites was examined with scanning electron microscopy. The electrical conductivity was measured as a function

of the copper content, and the composite fabricated with a 10 vol % copper presented a conductivity 15 orders of magnitude higher than that of pure LDPE. The enhancement in conductivity can be explained by means of segregated percolation path theory and the experimental results are in agreement with the theoretical law.

Key words: polymer; composites; microstructure; electrical properties; percolation

INTRODUCTION

Composites made of polymers with a conducting filler phase allow the combination of the mechanical properties of polymers and its ease of processing with electrical applications requiring significant conductivity. Polymer-based electrically conducting materials have several advantages over their pure metal counterparts, which include cost, flexibility, reduced weight, ability to absorb mechanical shock, corrosion resistance, ability to form complex parts, and conductivity control.¹⁻³ Filled conducting polymer composites are used for electromagnetic shielding of computers and electronic equipments.⁴ In addition, they are used as conducting adhesives in electronics packaging, flip-chips, cold solders, switching devices, static charge dissipating materials, and devices for surge protection.⁵⁻⁷ Low cost, lightweight, and flexible conducting polymer wires can be used for signal transmission in aviation as well as in land-based electronics, having a lower cost and being a better alternative to pure metal-conducting wires. Metalized polymer

fibers are also being investigated for use as lead wires in intrafascicular microelectrodes.⁸ Despite a growing number of potential applications, these composites are plagued by a serious drawback: to achieve a conductivity that is of practical value ($>1 \times 10^1$ S/cm), the volume fraction of the filler material has to exceed the percolation threshold, i.e., the continuity of the filler phase is reached to maintain electrical contact of the filling material. The percolation threshold is typically ~15–30 vol % for dense spherical micron size particles,⁹⁻¹² the lowest value for segregated percolation. At such volume fraction loading, the desirable mechanical properties of a polymer, such as ductility and toughness, are lost.¹³⁻¹⁴ Also, a dramatic increase in strain-to-failure and a drop in the glass transition temperature are observed when the filler particles are nano-sized instead of micron-sized.¹⁵

The need for highly conductive polymer-based materials has been the motivation to develop a new class of filler material composed of copper micropowders, which enable the retention of the desirable polymer characteristics, including ease of processing ability, in combination with high conductivity and low cost. Our strategy was to manipulate the morphology of the filler phase so that a high electrical conductivity could be achieved at a low percolation threshold.

EXPERIMENTAL

The composites were synthesized using spherical copper particles (Alfa Aesar #43978, mean particle size:

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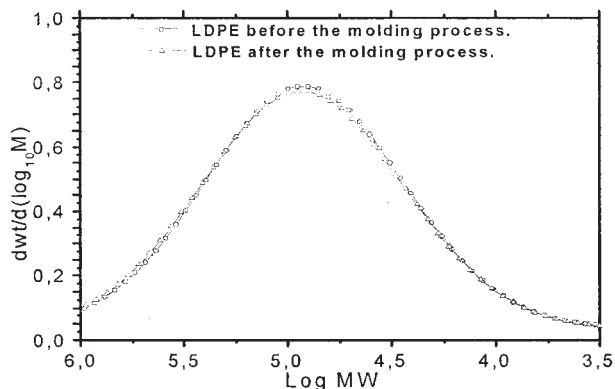


Figure 1 GPC molecular weight analysis for LDPE matrix before and after the molding process.

200–300 nm) embedded in a polyethylene low-density matrix (LDPE, Goodfellow #ET316050, mean particle size: 1000 μm), using different volume concentrations of filler metal. All the samples were homogenized using a SPEX/MIXER 81057 at 1400 rpm for 15 min. The homogenized mixture was compacted in a mold at a pressure of 40 MPa and a temperature of 400°C under nitrogen atmosphere for 10 min. To verify that the LDPE matrix did not present changes in its molecular weight, a gel permeation chromatography (GPC) analysis was carried out using an Alliance 2000 Waters equipment (flux: 1 mL/min, analysis temperature: 135°C). The microstructure was investigated by means of optical microscopy using a Leica reflection microscope and scanning electron microscopy with a JEOL 5600 LV SEM with a resolution of 5 nm, under a pressure of 20 Pa. The room temperature conductivity was measured using the two-probe technique with parallel silver contacts. The ohmic behavior was confirmed performing current–voltage (I–V) measurements on each sample.

RESULTS AND DISCUSSION

Figure 1 shows the GPC analysis for the LDPE matrix before and after the molding process. In both cases, the results are close to 168,000 g/mol, indicating that no degradation occurred after processing at 400°C. These experimental conditions were applied to all the experiments reported in this work.

Figure 2 shows optical reflection micrographs of a composite with 1 vol % copper [Fig. 2(a)] and 10 vol % copper [Fig. 2(b)]. The particles appear inhomogeneously distributed, exhibiting dendritic aggregates corresponding to the so-called segregated particulate distribution.¹⁶ There is no evidence of continuous conducting paths along the complete micrograph, but this is not required for percolation, since the system is three-dimensional. The size of the voids between the metallic paths is around 100 μm , one order of magnitude lower than the size of the polymer grains before melting.

Figure 3(a) is a scanning electron micrograph of an aggregate from a 1 vol % Cu sample (nonconducting), exhibiting a similar particle distribution as the 10 vol % Cu sample [Fig. 3(b)]. The latter micrograph, recorded from the inside of one of the continuous paths in a 10 vol % copper sample, reveals that the copper particles are randomly distributed and form a cluster that seems to touch and thus, percolate and conduct.

The results suggest that the benefits of a favorable segregated geometry can be obtained using the method of heated compression molding.¹⁶ The formation of a dispersed filler segregated structure in the polymer matrix may be achieved by pressing the mixture of thermoplastic polymer powder having a mean particle size D , and the conductive filler having particle size d , provided that $D \gg d$. Similar results were obtained by Mamunya et al. in the nickel–polymer powder system,¹⁷ but they did not report on the mo-

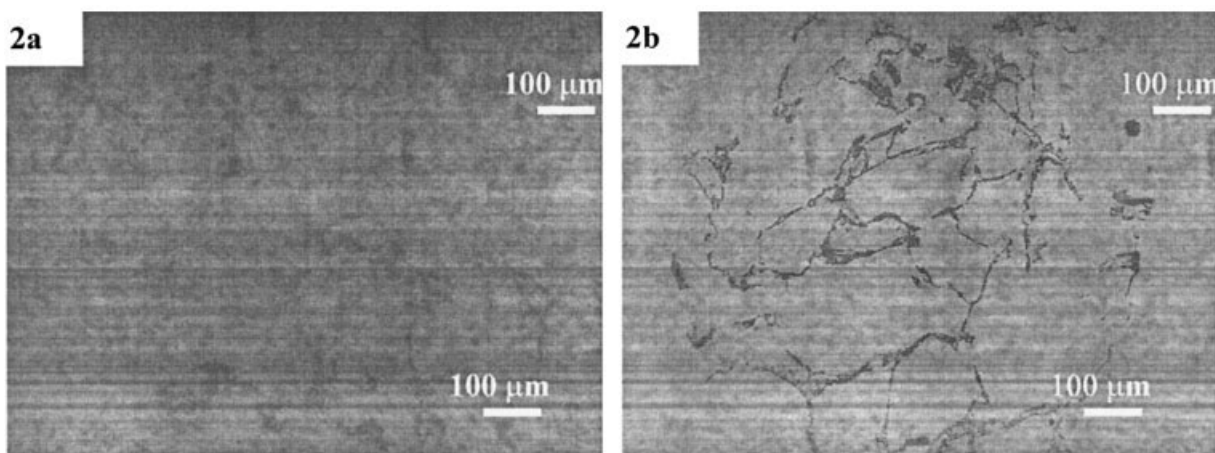


Figure 2 Photomicrography of copper-LDPE composite with (a) 1 vol % Cu and (b) 10 vol % Cu.

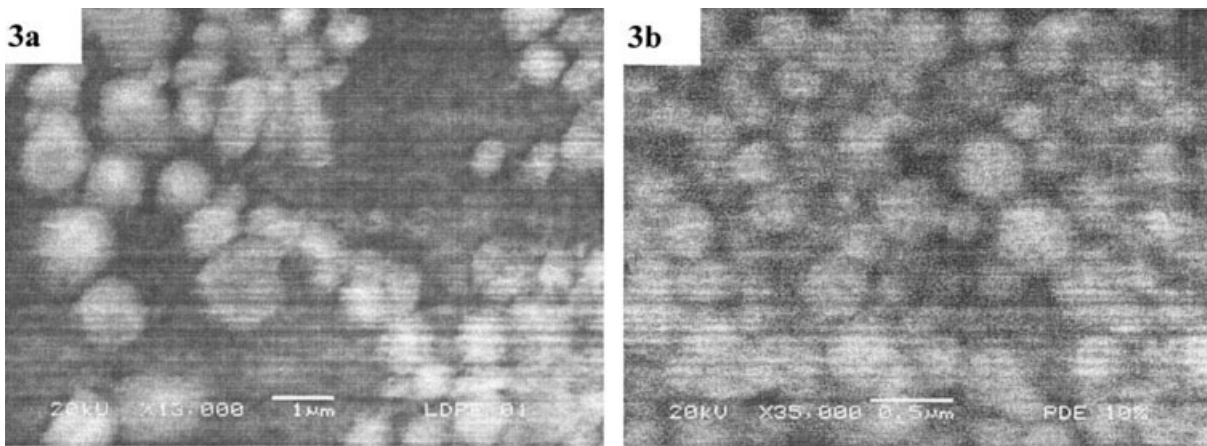


Figure 3 SEM of copper-LDPE composite with (a) 1 vol % Cu and (b) 10 vol % Cu. (The cut specimen position corresponds to the center of each sample. Perpendicular cuts.)

lecular weight analysis to verify if the polymer was degraded or not.

The electrical conductivity was measured as a function of the volume concentration of the filler metal in the polymeric matrix (LDPE). In Figure 4, the room temperature conductivity of the Cu-LDPE composite is shown as a function of volume concentration of copper in LDPE, which exhibits that the filler metal increases the conductivity of the composite ~ 15 orders of magnitude, compared to the conductivity of the pure LDPE. The conductivity jump around the percolation threshold zone is around 11 orders of magnitude at ~ 10 vol % copper. This conductivity jump is higher than that in other composites reported in the literature.^{11,12,14,18,19}

The conductivity of pure LDPE was measured to be $\sim 10^{-13}$ S/m. In samples with copper content between 2.5 and 5 vol %, the conductivity is slightly increased to $\sim 10^{-11}$ S/m. Between 5 and 15 vol %, the composite

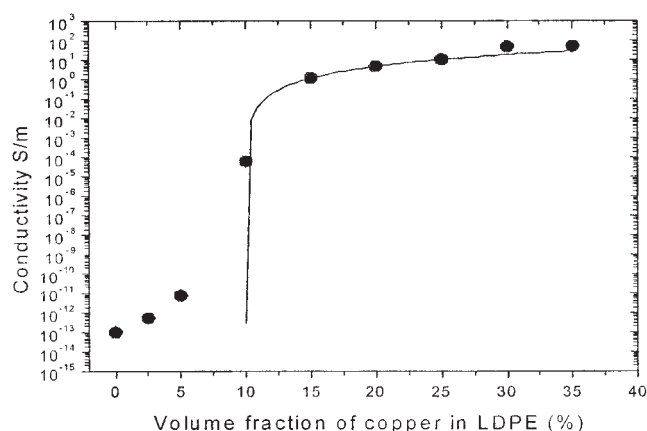


Figure 4 Electrical conductivity of copper-LDPE composites. The percolation threshold is around 10 vol % Cu. The solid line is a fit to the power law [eq. (1)], with $t = 2$.

displays a dramatic increase by 11 orders of magnitude. Finally between 15 and 35 vol %, the conductivity increases by two orders of magnitude. The conductivity of the 35 vol % sample was measured to be $\sim 10^2$ S/m, whereas the conductivity of pure copper is 5.98×10^7 S/m (Alfa Aesar #43978, mean particle size: 200–300 nm).

The electrical response of the composite can be described by percolation theory,²⁰ which states that the conductivity is given by:

$$\sigma_c = A(f - f_c)^t \quad (1)$$

where σ_c is the composite conductivity, A is a constant, f is the volume percent of the metal filler in the composite, t is the power-law exponent (typically 1.6–2.0 in 3D) and f_c is the percolation threshold, near 0.15 for random 3D systems.²¹ The fit of the experimental data using eq. (1) is shown superimposed on Figure 4, where the results are in qualitative agreement with the theoretical law. The critical exponent $t = 2$ is in excellent agreement with the theoretical universal scaling value predicted by the theory. The percolation threshold around $f_c = 10$ is far below the 15 vol % for a random distribution, but corresponds well to a segregated percolation in which the conducting phase forms paths on the surface of the larger insulating particles.

CONCLUSIONS

In this work, we have described an experimental study of the structural, electrical, and percolation threshold of composites, using copper powder embedded in LDPE matrix prepared by hot compression molding.

At a macroscopic level, the composite shows a segregated structure, but at the microscopic level, the

metallic particles are distributed randomly in the polymeric matrix, displaying continuous contact between themselves, thus, forming the conducting paths within the polymer matrix. This behavior was observed in all the studied concentrations and it increases as a function of the concentration of the filler metal.

The addition of copper submicrometric particles into the LDPE matrix increased the conductivity by 15 orders of magnitude because of the introduction of conducting filler paths in the polymer.

The reduction of the percolation threshold from 15–30 vol % to 10 vol % could be due to the fabrication process of hot compression molding that produces a favorable penetration of the metal into the polymer (particle size $D \gg d$). In this case, the formation of a segregated structure obtained as a consequence of this fabrication method allows the control of those properties that are susceptible to the spatial filler particle distribution. In addition, the use of short exposure times at temperatures higher than the melting point of the polymer is crucial for obtaining Cu–LDPE composites without degradation of the polymer matrix.

Studies in progress in our laboratories will allow to establish a comparison of the electric and mechanical properties of the polymeric conducting composites formed by metallic submicron particles of Cu, Ag, and Al, in LDPE and poly(methyl methacrylate) polymeric matrix, using the method described in this work.

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