Conductive Copper-PMMA Nanocomposites: Microstructure, Electrical Behavior, and Percolation Threshold as a Function of Metal Filler Concentration

V.H. Poblete,[1] **M.P. Álvarez,**[1,2] **V.M. Fuenzalida**[3]

[1]*Facultad de Ciencias de la Construcción, Universidad Tecnológica Metropolitana, Dieciocho 390, Santiago-Chile*

[2]*Instituto de Física, Facultad de Ciencias Básicas y Matemáticas, Pontificia Universidad Católica de Valparaíso, Av. Brasil 2950, Valparaíso, Chile*

[3]*Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Av. Blanco Encalada 2008, Santiago, Chile*

The copper-PMMA conductive composites were manufactured using different copper concentrations dispersed into the polymeric matrix by hot compression molding in inert atmosphere. The PMMA matrix was analyzed using dilute solution viscosimetry analysis and it did not evidence degradation in its molecular weight. The microstructure was examined by means of SEM and the electric conductivity was measured as a function of the concentration of copper particles in the polymer matrix. The 10 vol% copper composite presented conductivity between 11 and 13 orders of magnitude higher than that of pure PMMA. The experimental results are in agreement with the theoretical model considering the percolation path theory for a segregated structure. POLYM. COMPOS., 30:328–333, 2009. © 2008 Society of Plastics Engineers

INTRODUCTION

The research effort on electrically conducting polymer composites filled with metallic powders has had a great development in the last two decades. The central concept consists in infiltrating (mixing) the conducting particles into an electrically insulating polymeric matrix, thus preserving the mechanical properties of the polymer while exploiting the electrical conduction properties of the metal. These polymer-based electrically conducting composites have several advantages over their pure metal counterparts, including lower cost, ease of manufacture, high flexibility, reduced weight, mechanical shock absorption ability, corrosion resistance, and conductivity control [1–3] for specific applications. Metal-filled conducting polymer composites have found uses in electromagnetic shielding of computers and electronic equipment [4, 5], as conducting adhesives in electronics packaging, underfill for flip chips, cold solders, switching devices, static charge dissipating materials, and devices for surge protection [6, 7].

The literature shows a considerable amount of experimental and theoretical data regarding the preparation methods of metal-filled composite materials that can increase dramatically the conductivity of the polymer. The electrical conductivity of polymers can be increased by several orders of magnitude by incorporating metallic fillers made of fibers, powders of conducting materials [8–11], or intrinsically conducting polymers [12, 13]. In applications that require high-conductivity materials, a value of practical use is achieved when the volume fraction of the filler material exceeds that of the percolation threshold of the specific filling material in the polymer. The percolation threshold is typically ~15–30 vol% for dense spherical micron-size particles [14–17]. However, the desirable mechanical properties of a pure polymer, such as ductility and toughness, are lost at such volume fraction loading, showing an elevated fragility because of the high metal concentration required to achieve practical conduction through percolation of the metallic particles. A practical need that arises when fabricating these types of composites at the industrial level is to determine how
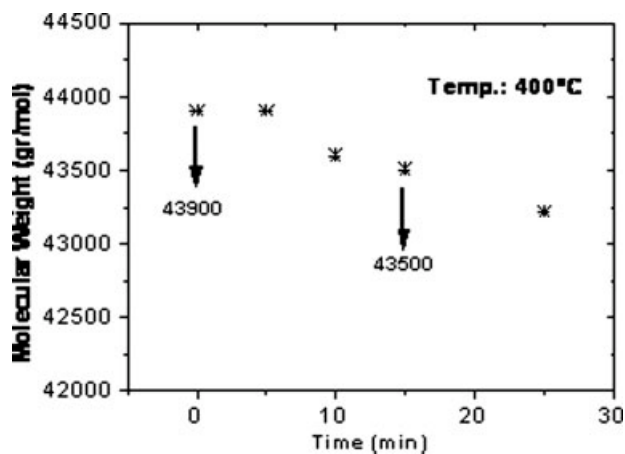
FIG. 1. Dilute viscosimetry analysis for PMMA matrix before and after the molding process.

much metal filler is to be put in to achieve the desired conductivity and whether the mixing process is adequate.

To explain how low percolation limits can be achieved, that is, below the theoretical limit established using structureless particles, theoretical work has succeeded in characterizing the percolation transition in disordered systems [18, 19]. Many mechanisms have been proposed to explain this transition and they range from simple tunneling, thermal induced tunneling, and simple physical contact. This indicates that to understand the physical properties of the composite it is necessary to elucidate the main parameters that describe the system, such as the volume fraction, the morphology of the particles or particle aggregates, and the conductivity ratio between the conducting and insulating phases.

The need for highly conductive polymer-based materials has been the motivation to develop a new class of composites conformed by polymethylmethacrylate (PMMA) and copper filler particles of micrometric and nanometric size, not reported in the literature, which enable the retention of the desirable polymer characteristics, including ease of processing, in combination with high conductivity and low cost. Our strategy consisted in manipulating the morphology of the filler so that high conductivity could be achieved at a low percolation threshold.

This work shows the results of the fabrication of PMMA filled with copper particles of micron and nanometer size, not reported in the literature. The electrical properties of the polymers were studied as a function of the copper concentration achieving a percolation threshold for each system.

EXPERIMENTAL

The Cu-PMMA composites were prepared by mixing copper powders of micron size (0.2–0.3 μm, Alfa-Aesar, no. 43978; 3.25–4.75 μm, Alfa-Aesar, no. 42455) and nanometer size (78 nm, Nanostructured and Amorphous Materials, no. 0293WF) with PMMA (Goodfellow, 600 μm, no. ME306010) using the hot compression molding

method and different volume concentrations of filler metal. All the samples were homogenized using a SPEX/MIXER 81057 at 1,400 rpm for 15 min. The homogenized mixture was compacted in a mold at a pressure of 40 MPa and at 400°C, under nitrogen atmosphere for 15 min.

To verify that the PMMA matrix did not present changes in its molecular weight, a dilute solution viscosimetry analysis was carried out. The actual composite density was measured using ASTM D 792, a standard test that measures the density of plastics by water displacement. The microstructure was investigated by means of scanning electron microscopy (SEM) 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.

For all samples with a conductivity greater than 10^{-4} S/cm, the four electrical resistivity test was applied using a Keithley 224 programmable current source and Keithley 182 digital sensitivity voltmeter. For samples with a conductivity less than 10^{-4} S/cm, it was necessary to run the transverse resistivity test and it was measured according to ASTM D 257 using a Keithley 6517A electrometer.

From a theoretical point of view the statistical percolation theory was used to describe the insulator-to-conductor transition of the samples and the experimental data were fitted.

RESULTS AND DISCUSSION

Figure 1 shows the dilute viscosimetry analysis for the PMMA before and after the molding process. In both cases, the results are close to 43,000 g/mol, indicating that no degradation after processing at 400°C was observed. These experimental conditions were applied to all the experiments reported in this work.

The density results are shown in Table 1. In this table, the residual density or the difference between the measured density and the theoretical density is shown as a function of volume percent of conductive filler. These results show that differences between the actual and theoretical densities are negligible. Actual densities close to the expected values provide confidence that the actual composition of the samples is close to the target value.

TABLE 1. Density results for Cu-PMMA composites.

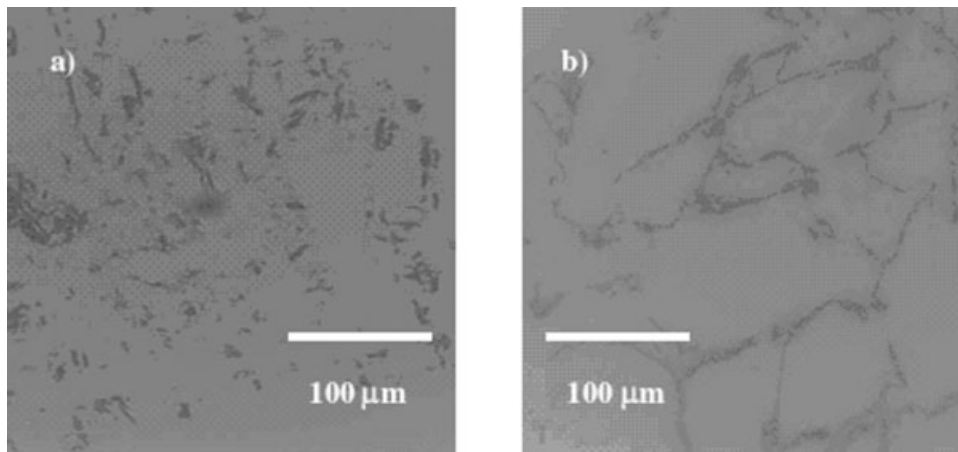| Cu (%, v/v)	δ_c, Theoretical	δ_c, Residual	Number of samples	Standard deviation
2.5	1.385	−0.0025	3	0.0035
5	1.579	−0.0268	3	0.0423
10	1.967	−0.0198	3	0.0389
15	2.356	−0.0188	3	0.0443
20	2.744	0.0356	3	0.0979
25	3.133	−0.0015	3	0.0047
30	3.521	0.0035	3	0.0123
35	3.909	−0.0031	3	0.0122

FIG. 2.   Optical micrograph of Cu-PMMA composites (78 nm): (a) 1 vol% Cu, (b) 10 vol% Cu.

Figures 2 and 3 show the optical reflection micrograph of the Cu-PMMA (78 nm) and Cu-PMMA (3.25–4.75 μm), respectively. The particles appear inhomogeneously distributed, exhibiting dendritic aggregates corresponding to the so-called segregated particulate distribution [7]. There is no evidence of continuous conducting paths along the complete micrography, but this is not required for percolation because the system is three-dimensional. The voids size between the metallic paths is around 100 μm, an order of magnitude lower than the size of the polymer grains before melting.

Figures 4 and 5 show the SEM micrograph of the Cu-PMMA (78 nm) and Cu-PMMA (3.25–4.75 μm), respectively. At microscopic level, a homogeneous filler particle distribution was found for all concentrations, with a particle density proportional to the metallic filler concentration. Figure 4 shows the nanometric Cu filler samples for similar concentrations like those for the micrometric filler composites. In this case, the nanometric filler also shows a homogeneous distribution of particles throughout the sample. The copper particles are randomly distributed and

form clusters that seems to touch and thus percolate and conduct.

The relationship of the metallic filler content in the composite toward electrical properties determination was investigated. Figure 6 shows the room temperature conductivity of the composite samples as a function of the concentration of the conducting phase and particle size. At no filler loading, the neat PMMA has an electrical conductivity of $\sim 1 \times 10^{-14}$ S/m.

At highest filler volume fractions (35 vol%), the composite conductivity increases approximately to 1.5×10^{-2} S/m and 1.2×10^{-1} S/m in Cu-PMMA (78 nm) and Cu-PMMA (3.25–4.75 μm), respectively. The conductivity jump around the percolation threshold zone is ~ 10 orders of magnitude at ~ 10 vol% copper. This conductivity jump is higher than other composites reported in the literature [20–23], but this behavior is similar to the Cu-LDPE system reported in a previous work [24]. For instance, the Zn-Nylon-6 system shows a percolation limit near to 18 vol%, but the Zn particle size was around of 15 ± 10 μm [17].
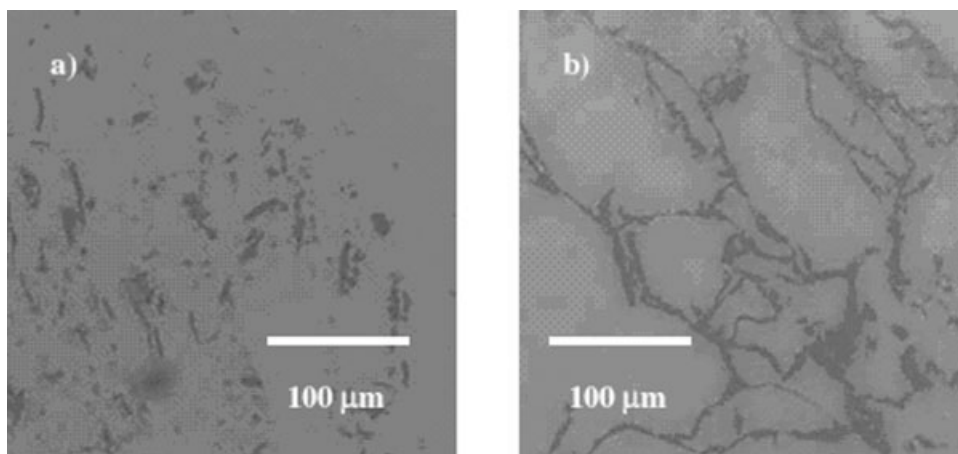

FIG. 3.   Optical micrograph of Cu-PMMA composites (3.25–4.75 μm): (a) 1 vol% Cu, (b) 10 vol% Cu.
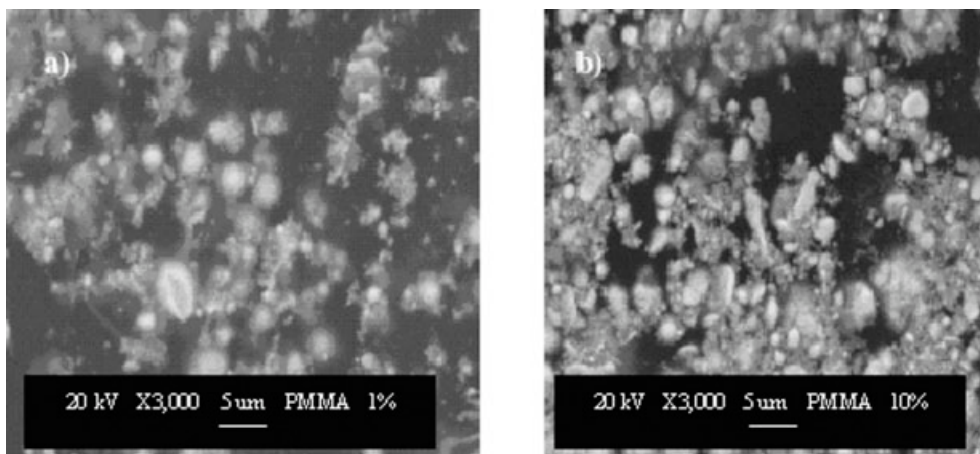
FIG. 4.   SEM micrograph of Cu-PMMA composites (78 nm): (a) 1 vol% Cu, (b) 10 vol% Cu.

In both the micrometric and nanometric Cu-PMMA composites, the resistivities decreased markedly at the percolation threshold for each particle size. In addition, the copper concentration above the percolation threshold produces a slow decreasing in the resistivity. The highest conductivity value can be obtained with highest particle size.

The stage of decrease and increase in the resistivity can be explained by inspection of the Figures 2 and 3. They show the microstructural changes in the composite, when the volume fraction is increased. Very near to the critical volume fraction ($\sim$10 vol% copper), percolation is prevalent but not complete; there is a number of incomplete chains which do not contribute to the resistivity. With a small increase in filler content, the incomplete chains can be completed. At this stage, the maximum number of particles contributed to the conductivity, and a true conductive skeleton was formed. Further loading, without the aid of pressure forcing the particles into open areas, results in a complete skeleton, but between the skeletal particles, there was no longer a sufficient volume of polymer to occupy the open areas. It was a crosslinked,

shrinking polymer which provided the force for good electrical contact between the particles. As a result, the resistivity increases with increasing volume fraction after the minimum resistivity was reached.

To determine the percolation threshold, the fitted data are shown in Figure 7, according to the percolation theory, as follows:

$$\sigma_C = A(f - f_C)^t \qquad (1)$$

where A is a constant, t is a critical exponent, f is the volume fraction of the conductive phase, and f_C is the volume fraction at the percolation threshold. The fit of the experimental data using *Eq. 1* is shown in Figure 7. The calculated parameters of *Eq. 1* are listed in Table 2.

In this study, we get an excellent fit according to the percolation law. The critical exponent $t = 2.0$ is in agreement with the theoretical value predicted by the theory and attributable to thermally induced hopping between disconnected or weakly connected path (part) of the percolating network. The particle size increases, producing both a lower f_c value and high conductivity values. The percolation threshold value depends on many factors such
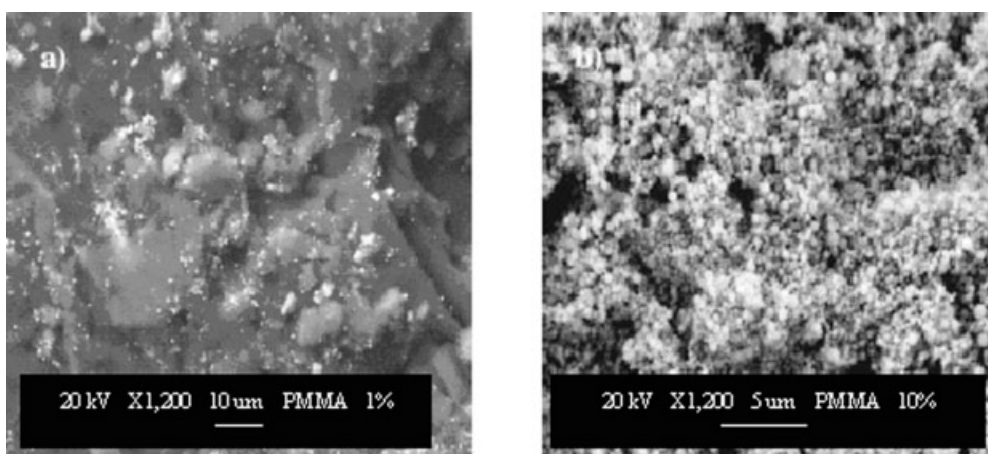

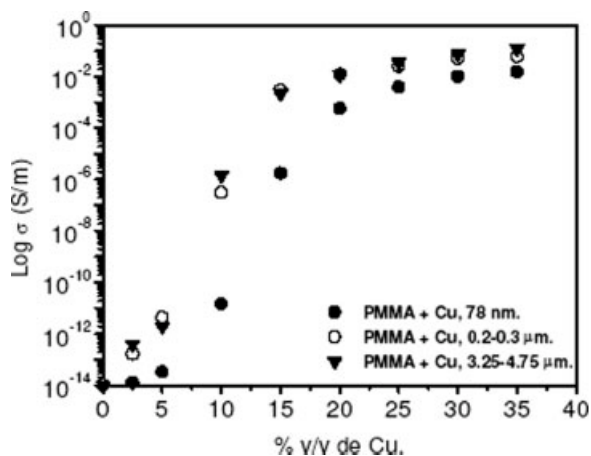FIG. 5.   SEM micrograph of Cu-PMMA composites (3.25–4.75 μm): (a) 1 vol% Cu, (b) 10 vol% Cu.

FIG. 6.   Electrical conductivity of Copper-PMMA composites.

TABLE 2.   Scaling parameters calculated for Cu-PMMA composites containing different particle size.

Composite	f_C	t	R (correlation coefficient)
Cu-PMMA (78 nm)	13.95	2.0 ± 0.097	0.997
Cu-PMMA (0.2–0.3 μm)	11.00	2.0 ± 0.100	0.996
Cu-PMMA (3.25–4.75 μm)	9.28	2.0 ± 0.100	0.997

as the size, the shape, and the spatial distribution of the filler particles within the host polymer matrix, the adhesion and the possible interactions between two phases, and finally, the processing method. Considering the particle size, the nano-sized particles tend to pack less dense than the micro-sized particles to the highest f_C value obtained.

CONCLUSIONS

In this investigation, we have described an experimental study, not reported in the literature, about the effect of the filler content on the electrical conductivity, percolation threshold, and structural distribution of the copper powder particles of different size embedded into PMMA, prepared by compression molding. From the results the following conclusions can be shown:

The SEM analysis shows that the filled particles are distributed randomly inside the PMMA matrix displaying continuous contact between themselves, thus forming the conducting paths within the polymeric matrix. This behavior increase as a function of the concentration of the
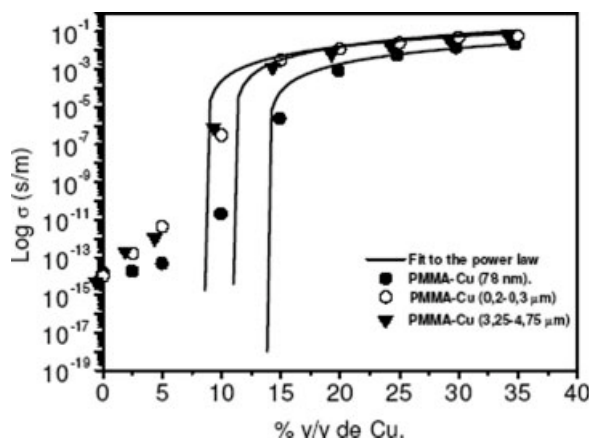
filler metal. At a macroscopic level the composite shows a typical segregated structure in agreement with the preparation method. Here the formation of a segregated structure is a consequence of this fabrication method that allows the control of those properties that are susceptible to the spatial filler particle distribution. On the other hands, the use of short exposure times at temperatures higher than the melting point of the polymer is crucial to obtaining Cu-PMMA composites without degradation of the polymer matrix.

The addition of copper powder particles of different size to PMMA induces an increase in the electrical conductivity value. The electrical conductivity of composites increases as much as 12 orders of magnitude, showing the typical percolation transition from dielectric to conductive region of such polymer composite materials. The electrical conductivity evidenced a dependence on the particle size of the filler material.

The percolation threshold concentration corresponds to a volume fraction of copper of 13.99 vol% and 9.28 vol% for Cu-PMMA (78 nm) and Cu-PMMA (3.25–4.75 μm) composites, respectively, lower than 15–30% reported in the literature. The percolation threshold value increases as a function of the mean size particle and decreases with the f_C obtained value. The obtained results are in agreement with our initial hypothesis that to obtain a controlled percolation limit at low concentrations of metal filler, retaining the desirable characteristics of the polymer, with conductivities in typical ranges, is required in some technological applications. In addition, this controlled electrical conducting behavior in the composites, which can be produced using the same generic technology, can be used in an array including electromagnetic interference and electrostatic discharge applications.

FIG. 7.   Fit of electrical conductivity data to the power law. Cu-PMMA (78 nm), Cu-PMMA (0.2–0.3 μm), Cu-PMMA (3.25–4.75 μm).

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