Electrically Conductive Composites of Poly(urea-formaldehyde) and Cellulose Filled With Aluminum

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This article addresses the preparation and characterization of composite materials obtained with compression molding of mixtures of aluminum powder and a commercial grade thermosetting resin of poly(urea-formaldehyde) filled with α-cellulose in powder form. The homogeneity of these composites was checked by the morphologies of the constituents (filler and matrix) by optical microscopy. The density of the composites was measured and compared with values calculated by assuming different void levels within the samples, to discuss the porosity effect, in connection with optical microscopy observations. Then, the dependence of electrical conductivity of the composites on volume fraction of the metal filler was investigated. The conductivity of the composites is <10^{-12} S/cm unless the metal content reaches the percolation threshold at a volume fraction of V_c = 38.6 vol%, beyond which the conductivity increases markedly by as much as nine orders of magnitude, indicating an insulator–conductor phase transition. The obtained results on electrical conductivity have been well interpreted with the statistical percolation theory. The deduced critical parameters, such as the threshold of percolation, V_c, the critical exponent, t, and the packing density coefficient, F, were in good accord with earlier studies. In addition, the hardness of samples remained almost constant with the increase of metal concentration. POLYM. COMPOS., 33:2188–2194, 2012. © 2012 Society of Plastics Engineers

INTRODUCTION

Various methods of manufacture of composites of polymers containing dispersed conductive fillers, as well as information about their properties, have been reported widely in the literature for the last years [1–4], due to their different technological applications in a variety of areas. As it is well known, most polymers are thermally and electrically insulating, but the increase of both thermal and electrical conductivities of polymers opens large new markets. For example, King et al. [5] remarked that the advantages of conductive polymer composites as compared to typically used metals includes aspects such as improved corrosion resistance, lighter weight, and the ability to adapt the conductivity properties to suit the application needs.

Common technological applications of conducting polymer composites and conductive resins are concerned with areas such as electromagnetic/radio frequency interference shielding for electronic devices (e.g., in computer and cellular housings), self-regulating heaters, overcurrent protection devices, photothermal optical recording, chemical detecting sensors used in electronic noses, bioelectronics, and more [6–9]. The used conductive fillers are usually metal particles or metal flakes, metal-coated glass fiber, carbon black, and graphite fibers, with different sizes (10 nm to some hundreds μm).

It is known that, in general, the percolation theory is used to describe the electrical conductivity of conducting polymer composites. This theory describes the conductive phase of these materials formed by a network of the filler materials at a given volume percentage. 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 by some orders of magnitude from the insulating range to values in the semiconductive or conductive range [10]. For efficiency, with the aim of decreasing the difficulty of the process and economic costs, the amount of the conductive phase for achieving materials with high conductivity should be usually as small as possible. A huge number of different models have been proposed for the estimation of the conductivity (or inverse resistivity) versus filler concentration curves [11–14].

This work deals with further developments in previous reported investigations of preparation and characterization of different electroconductive (thermoplastics and thermosets) polymer composites [1, 15–22]. We report an experimental study about the influence of filler concentration on the electrical conductivity of composites elaborated by hot compacting, i.e. compression molding of mixtures of aluminum powder and poly(urea-formaldehyde) embedded in α-cellulose powder (UFC/Al). Short fibers of α-cellulose are usually used as reinforcing filler in commercially available poly(urea-formaldehyde) molding compounds. The homogeneity of composites was controlled by morphological pictures obtained by optical microscopy. Furthermore, to check the void level within the samples, which influences remarkably the electroconductivity, the porosity rate has been calculated from densities of the composites. These data, along with the reported previously may be helpful to understand the variation of electrical properties of such kind of polymer composites.

As in our cited previous articles, to complete the characterization of these materials, we also studied the influence of filler concentration on the hardness of the composites, as an example of mechanical property.

EXPERIMENTAL

Materials

The matrix used in our experiments was a commercial grade poly(urea-formaldehyde) resin embedded in α-cellulose supplied in the form of powder by Aicar S.A. with a density of 1.36 g/cm^3 and an electrical conductivity of around 10^{-13} S/cm. The content of α-cellulose in the resin, according to the manufacturer, is 30 wt%. A micrograph of this powder is shown in Fig. 1, where the longitudinal shape of particles can be observed.
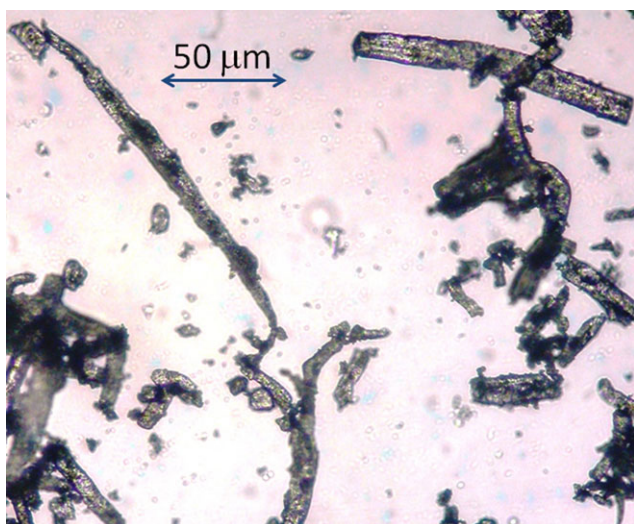

FIG. 1. Optical microscopy micrograph of the poly(urea-formaldehyde) resin embedded in cellulose powder used as matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
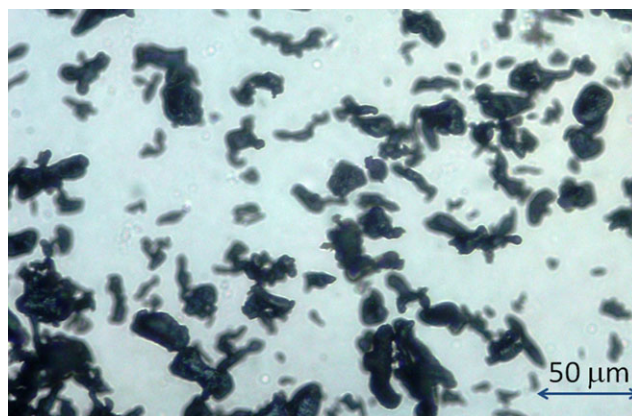

FIG. 2. Optical microscopy micrograph of the aluminum powder used as filler. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The electrical conducting filler used was aluminum, delivered by Panreac with a purity around 99.5%, average particle size of 30–70 μm, density of ∼ 2.70 g/cm^3 and electrical conductivity, taken as the tabulated value [16] of the order of 4×10^5 S/cm. The shape of the particles of filler is illustrated in Fig. 2. Both, the polymer and the metal powders were thoroughly dried before use at 60°C during 48 h.

Polymer Composite Fabrication

Composites of poly(urea-formaldehyde) embedded in α-cellulose powder filled with aluminum were fabricated via simple blending and hot pressing route, by mixing the polymer matrix and the filler powders for 2 h in a specially designed internal mixer (Fig. 3) at 60 rpm. The mixings were followed by compression molding in a specifically designed mold with three cavities of 30.0 mm diameter and 3.0 mm thickness each one, as can be seen in Fig. 4. The molding parameters were 20 MPa and 150°C for 30 min. These fabrication conditions were suggested by our previous experience with the same matrix [20–22]. Samples were cooled as much as room temperature in ∼ 30 min.

Samples with filler contents on the range 0–80 wt% (corresponding on the range 0–0.67 in volume fraction) were prepared. In order to improve the finish of the sample and ensure a better electrical contact for resistance measurements, the surfaces were polished with sandpaper. Sample thickness (necessary for the calculation of electrical conductivity) was determined using a micrometer, Schmidt Technology model J 50, to an accuracy of 0.01 mm. Thickness measurements were taken at five locations and averaged.

Polymer Composite Characterization Techniques

The microstructures of the powders used in the preparation of composites and of samples were observed by

FIG. 3. Photographs of the internal mixer designed for the mixing of poly(urea-formaldehyde) embedded in α-cellulose powder and aluminum powder. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reflection by means of a Nikon model Eclipse E200 optical microscope. The electrical conductivity was determined, at 23°C, through the electrical resistance values that were measured using a two-point arrangement as described previously [15–18]. Three specimens of each composition were tested, taking five data points on each sample. To decrease the contact resistance, the sample surfaces were coated with silver paint and dried during 24 h.

Measurements of volume electrical resistance higher than 10^3 Ω were made, at 23°C, using a programmable megohmeter (Quadtech model 1865). Measurements of low resistance (lower than 10^3 Ω) were made using a digital multimeter (Leader 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 in the present study to estimate the electrical conductivity, σ, from electrical resistance, in the present study was similar to that reported earlier [18, 19].

The density 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 Toledo AJ 100 balance equipped with a density determination kit. For each formulation, we evaluated three tests.

The hardness of the samples was determined at 23°C using a Durotronic Instron model 1000 Shore D hardness tester, in accord with ASTM D 2240-68. Five data points were taken on each samples and no difference was found between hardness measurements on both faces of each specimen.

RESULTS AND DISCUSSION

Table 1 lists samples of composites of poly(urea-formaldehyde) embedded in α-cellulose powder filled with aluminum, the concentration of filler for them, corresponding density, and corresponding values of decimal logarithm of electrical conductivity.

Figure 5 represents a micrograph with the structure of a composite sample after the percolation threshold (38.6 vol%), which corresponds to the insulating-conductive phase transition. The photo shows a distinction in contrast, related to the different color of the filler and matrix. The morphology of samples remains similar and the filler is uniformly dispersed, indicating homogeneous composites.

The homogeneity of composites also was verified by density measurements. The variation of the density of composites with volume fraction of aluminum is represented in Fig. 6. It behaves linearly when the amount of metallic filler increases, like binary compound. This

FIG. 4. Photograph of the mold designed for the fabrication of composites studied in this work. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1. List of samples of composites of poly(urea-formaldehyde) embedded in α-cellulose powder filled with aluminum, concentration of filler, corresponding density and corresponding values of decimal logarithm of electrical conductivity.

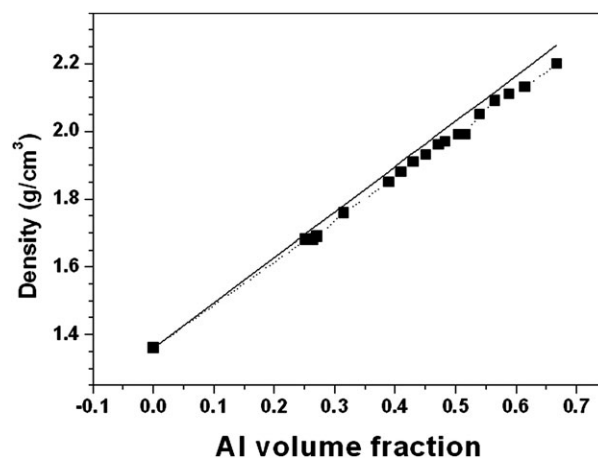| Samples	Al volume fraction	Density (g/cm^3)	Log σ (S/cm)
1	0.000 ± 0.000	1.360 ± 0.002	-13.00 ± 0.20
2	0.252 ± 0.001	1.676 ± 0.004	-13.00 ± 0.20
3	0.265 ± 0.001	1.681 ± 0.003	-13.04 ± 0.30
4	0.271 ± 0.001	1.688 ± 0.004	-12.52 ± 0.20
5	0.315 ± 0.001	1.758 ± 0.003	-12.22 ± 0.40
6	0.390 ± 0.001	1.852 ± 0.003	-12.30 ± 0.60
7	0.410 ± 0.001	1.883 ± 0.004	-8.69 ± 0.70
8	0.430 ± 0.001	1.908 ± 0.003	-6.74 ± 0.80
9	0.451 ± 0.002	1.929 ± 0.004	-5.64 ± 0.80
10	0.472 ± 0.002	1.958 ± 0.004	-3.66 ± 0.50
11	0.483 ± 0.002	1.971 ± 0.003	-3.52 ± 0.15
12	0.505 ± 0.002	1.987 ± 0.006	-3.18 ± 0.05
13	0.516 ± 0.002	1.993 ± 0.006	-3.00 ± 0.04
14	0.540 ± 0.002	2.051 ± 0.005	-2.70 ± 0.05
15	0.565 ± 0.002	2.092 ± 0.004	-3.00 ± 0.03
16	0.589 ± 0.002	2.107 ± 0.003	-2.74 ± 0.03
17	0.615 ± 0.002	2.126 ± 0.005	-2.75 ± 0.04
18	0.668 ± 0.002	2.198 ± 0.006	-2.68 ± 0.03

FIG. 6. Variation of the density of composites with volume fraction of aluminium. The squares are the experiments points and the line is calculated density as explained in the text.

indicates that the obtained composites are homogenous, in good accord with previous studies using the same matrix [18–20] and microscopic observations. The theoretical density of the composites was calculated with binary *Eq. 1*:

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

where d_t is the theoretical density of composite and V is the volume fraction; m and f indices stand for the matrix and filler respectively.

This figure shows that the theoretical density is higher than the experimental one. This means that there is a loss mater in prepared composites. This loss is occupied by the hole or porosity. Then, the composites' porosity τ has been deduced from the formula:

$$\tau = \left(\frac{d_t - de}{d_t} \right) \cdot 100 \qquad (2)$$

where d_e represents the experimental density.

The composites' porosity, as a function of the filler volume fraction, is shown in Fig. 7. It is to be noted that the average fraction voids in volume for the samples is almost constant with a value of $2 \pm 1\%$. Therefore, the quality of the obtained composites was good.
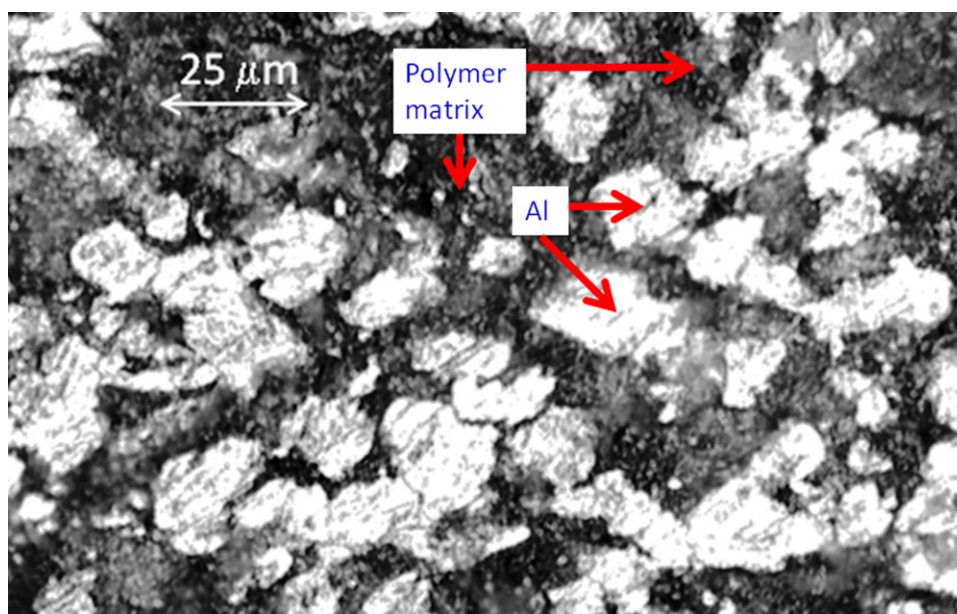

FIG. 5. Optical microscopy micrograph of the aluminum-filled urea-formaldehyde and cellulose composites containing 66.8 vol% of aluminum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
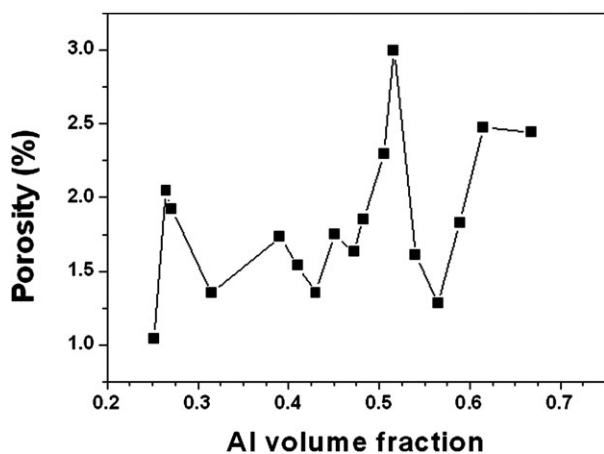
FIG. 7.   Porosity rate of composites versus aluminum volume fraction.

The hardness of samples remains approximately constant, as 85 ± 5 Shore D values, independently of the filler composition, as found for other composites prepared with the same matrix [18–20, 22].

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. 8). Samples with low filler content are almost nonconductive, but the electrical conductivity of the composites increases dramatically as the aluminum content reaches the percolation threshold at 38.6 vol% of metal filler. The value of the percolation threshold is obtained from of the maximum of the derivative of the conductivity as a function of filler volume fraction. According to Flandin et al. [2] values of 20–40 vol% are typical for spherical particles of filler. Above the percolation threshold, the conductivity of composite has increased by much nine orders of magnitude.

This behavior could be explained with the statistical percolation theory. Such theory is usually used to relate the electrical conduct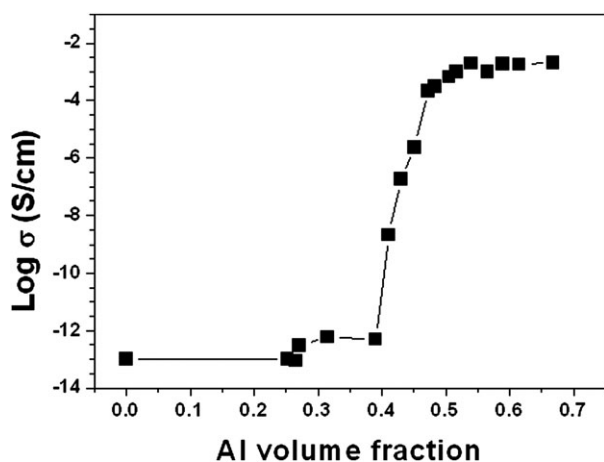ivity of composite to the existence of clusters of connected particles; which give rise to the so-called conducting infinite cluster above the threshold. In this theory, the relationship between the electrical conductivity of the mixture and the volume fraction of the conductive filler is given above the percolation threshold by a power-law relationship as developed by Kirkpatrick [23]:

$$\sigma = \sigma_o (V - V_c)^t \tag{4}$$

where σ is the electrical conductivity of the mixture, σ_0 is the electrical conductivity of the filler's particles, V is the volume fraction of the filler, V_c is the critical volume concentration at the threshold of percolation, and t is an exponent determining the increase of the conductivity above V_c. As shown in Fig. 9, this theory gives a good description of experimental results near the transition point. The parameters for this equation were $V_c \approx 0.39$, $t \approx 5.78$, with a factor of correlation of $r^2 \approx 97.5\%$.

Nevertheless, usually discrepancies were observed between critical parameters (V_c, t) resulting from *Eq. 4* and experimental values [13]: in as much as the basic classical statistical theory does not take into consideration of several parameters, while the experimental results show that the electrical conductivity depends strongly on the viscosity and the surface tension of the filled polymers. It depends also on the geometrical parameters of the filler particles as well as on the filler/matrix interactions.

Mamunya et al. [13, 14] have developed a model in which specific parameters for each composite have been introduced in the basic theory:

$$\sigma = \sigma_o + (\sigma_m - \sigma_o) \cdot \left(\frac{V - Vc}{F - Vc} \right)^{t_{\text{eff}}} \tag{5}$$

where σ_m is the maximal conductivity of composite, F is the filler packing density coefficient (equivalent to the

FIG. 8.   Variation of the electrical conductivity of poly(urea-formaldehyde) resin embedded in cellulose powder/Al composites with Al content.
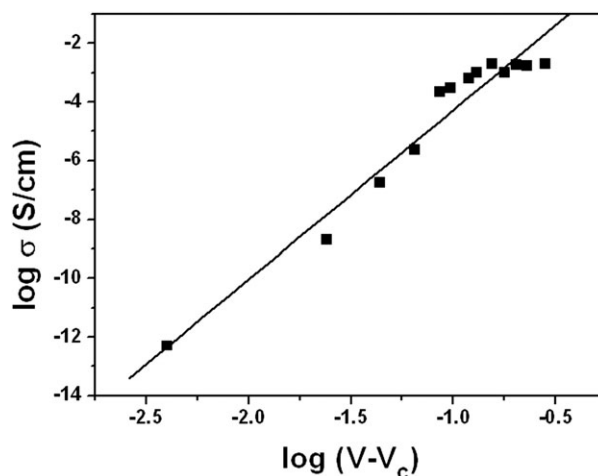

FIG. 9.   Comparison between experiment above percolation threshold (square points) and the *Eq. 4* (solid line) of the electrical conductivity of the UFC/Al composites.
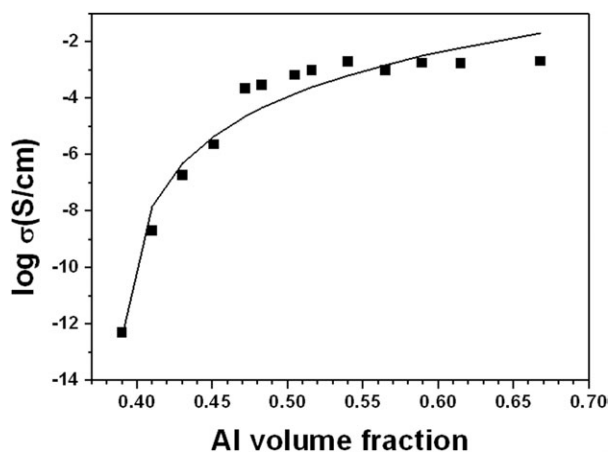
FIG. 10. Comparison between experiment above percolation threshold (square points) and the *Eq. 5* (solid line) of the electrical conductivity of the UFC/Al composites.

maximal value of the filler volume fraction) and t_{eff} is an effective critical exponent, which can takes values upper than 2 (mean three dimensional value).

Hence, to find out which model is the most appropriate for describing the electrical conductivity of UFC/Al composites, the experimental data have been fitted to *Eq. 5*. The equation was used with success in earlier studies to interpret the experimental results [1, 20, 22].

The plot of $\log(\sigma)$ as function of Al volume fraction is presented in Fig. 10. The deduced parameters are $V_c \approx$ 0.39, $t_{eff} \approx 5.7$ and $F \approx 0.59$. These parameters are obtained with factor correlation $r^2 \approx 95\%$. It should be noted that the agreement between the experiment and the theory is good.

The determined packing density coefficient F value is in good agreement with the prediction of *Eq. 5* [24]. On the other hand, the critical threshold percolation value obtained is in good agreement with that determined by derivation by experience (see Fig. 8). Elsewhere, this result is also close to 0.34 found for a similar (in size and in shape) filler but with another polymer (nylon-6) as matrix [16].

Indeed, the electrical conductivity of random composites has already been shown to depend on several parameters [25], such as the viscosity and the surface tension of the polymers, especially in the case of the mixtures in which the conductive powder is dispersed; the size, the shape, and the surface energy of the filling particles and the powder dispersion procedure, that is, type, duration and strength of shear.

CONCLUSIONS

In the last two decades, significant progress has been made in manufacture and applications of electroconductive polymer composites by blending conductive fillers with polymer matrices. In summary, an experimental study about the effects of the aluminum content on the electrical conductivity of composites of a poly(urea-formaldehyde) resin embedded on α-cellulose filled with that metal has been discussed in this article. From the obtained results, the following conclusions could be made:

1. The electrical conductivity of composites increases as much as nine 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 aluminum of 0.39, in good agreement with previous experiments.
3. The relation between filler content and electrical conductivity is fairly fitted with the extended basic statistical percolation theory. The deduced critical parameters are reasonable and coherent with experimental values and the earlier predictions.
4. The average fraction voids in volume is almost constant, with a value of $2 \pm 1\%$.
5. The shore D hardness remains approximately constant (85 ± 5 Shore D values) with the increase of filler concentration.

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