Non-Linear Electrical Conductivity of Urea-Formaldehyde-Cellulose Loaded With Powders of Different Carbon Fillers

Abdel-Karim Maaroufi,[1] Gabriel Pinto,[2] Isabel Paz[2]

[1]Laboratory of Applied Chemistry of Solid, Department of Chemistry, Faculty of Sciences, P.B: 1014, Rabat Agdal, Morocco
[2]Departamento de Ingeniería Química Industrial y del Medio Ambiente, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28006 Madrid, Spain

ABSTRACT: This article reports on the making and characterization of composite materials prepared by compression molding of a commercial grade thermosetting resin of urea-formaldehyde filled with α-cellulose in powder form mixed successively with carbon black, synthetic graphite, and activated carbon. The morphology of the constituents and the composites has been characterized by optical microscopy. The porosity effect has been discussed from density measurements. Furthermore, it has been shown that the hardness of the samples remains almost constant with the increase of filler concentration. The electrical conductivity shows clearly a non-linear behavior. The observed values are lower than 10^{-11} S/cm, unless the filler content reaches the percolation threshold beyond which the conductivity increases markedly by as much as ten orders of magnitude, indicating insulator-conductor phase transition. The conduction threshold depends on the filler nature. The results have been interpreted by means of the statistical percolation theory. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 990–996, 2005

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

INTRODUCTION

Composites of polymers containing dispersed conductive fillers and various methods of manufacture of such materials have been reported widely in the literature for the last several years.[1–10] As is well known, most polymers are thermally and electrically insulating. Increasing the thermal and electrical conductivity of polymers opens large new markets. As pointed out by King and coworkers,[11] the advantages of conductive polymer composites as compared to metals (typically used) include improved corrosion resistance, lighter weight, and the ability to adapt the conductivity properties to suit the application needs.

The oldest and common technological applications of electrically conductive resins are concerned with a variety of areas, such as electromagnetic/radio frequency interference (EMI/RFI), shielding for electronic devices (computer and cellular phone housings, for example), self regulating heaters, over-current protection devices, photothermal optical recording, direction finding antennas, chemical detecting sensors used in electronic noses, and more.[12–17] The used fillers are metal particles, metal coated particles, or carbon particles with different sizes (10 nm to some hundreds μm).

On a fundamental level, these materials are random heterogeneous media. They have been frequently considered as experimental models on which modern theories can be tested. Among these theories, the statistical percolation theory[18–23] is usually used with success to describe the non-linear electrical conductivity of extrinsic conductive polymer composites. Hence, the electrical conductivity of polymer composites does not increase continuously with increasing electroconductive filler content. 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 range.[4,5] For efficiency and to decrease the difficulty of the processing and economic costs, the amount of the conductive phase for achieving materials with high conductivity should be usually as small as possible.

This article deals with the study of the influence of filler concentration on the electrical conductivity of the composites elaborated from urea-formaldehyde embedded in α-cellulose (UFC) filled successively by three types of carbon particles: carbon black (CB), synthetic graphite (G), and activated carbon (AC) powders. The aim of this study is, on the one hand, to

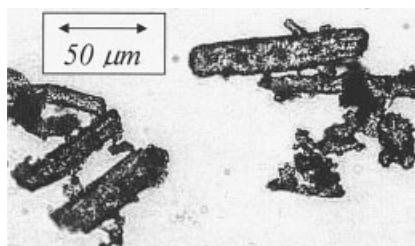**Figure 1** Optical microscopy photograph of the urea-formaldehyde resin molding compound filled with α-cellulose in powder form.

Figure 2 Optical microscopy photo of carbon black powder. The size of the aggregates is < 15 microns.

compare the effect of the filler nature on the electrical composite behavior and, on the other, to give other possibilities to obtain composites with a more or less large amount of fillers. Such possibilities are important at the industrial level in the improvement of mechanical properties, dimension stability, decrease of the price, and so forth.

The composites were produced by hot compaction by means of the compression molding of mixtures of one kind of powder of filler cited above and urea-formaldehyde resin molding compound embedded in powder of α-cellulose. Short fiber of α-cellulose is usually used as reinforcing fibers in urea-formaldehyde molding compounds. Furthermore, to check the void level within the samples, which influences remarkably the electroconductivity, the porosity rate has been determined from densities of the composites. Finally, to complete the characterization of these materials, the study of the influence of filler concentration on the hardness of composites has been presented. These data, along with those reported previously,[24-28] may be helpful in developing more theoretical models to better understand the variation of electrical properties of such polymer composites.

EXPERIMENTAL

Materials

The only matrix polymer used in our experiments was a commercial grade urea-formaldehyde resin filled with α-cellulose in the form of powder supplied by Aicar S.A. (Cerdanyola del Vallès, Spain), with a density of 1.36 g/cm^3 and electrical conductivity of around 10^{-12} S/cm. The content of α-cellulose in the
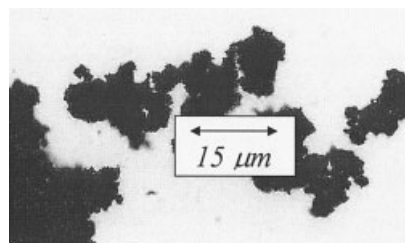
resin is 30 wt %. A micrograph of this powder is shown in Figure 1, where the longitudinal shape of particles can be observed. The electrical conducting fillers used were carbon black, synthetic graphite, and activated carbon powders. According to our experimental measurements, there is no significant difference in the electrical conductivity among the three carbon fillers used, as all of them are around 5.10^2 S/cm. Some characteristics of these fillers are listed in Table I. They were delivered by Quimipur (Arganda del Rey, Spain), with a purity of around 99.9%. The shape of the filler particles is illustrated in Figures 2, 3, and 4. Both the polymer and the filler powders were thoroughly dried before use at 60°C during 48 h.

Composite preparation

All the composites were prepared according to the same procedure, described in detail elsewhere.[25] The composites of carbon fillers 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°C for 30 min. These fabrication conditions were suggested by our previous experience. Samples with filler contents in the range of 0–25 wt % (corresponding to a 0–0.2 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
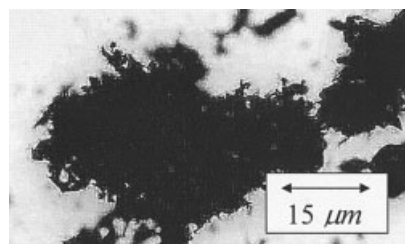
TABLE I
Properties of Filler Particles: Density and Mean Size.
(Data provided by the manufacturer.)

	Carbon black	Graphite	Active carbon
d (g/cm^3)	1.80	2.25	2.00
Size (μm)	< 15	< 40	1–3

Figure 3 Optical microscopy photo of synthetic graphite powder. The size of the aggregates is < 40 microns.
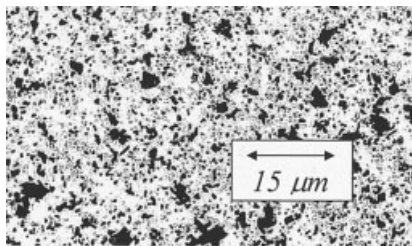
Figure 4 Optical microscopy photo of activated carbon powder. The average size of the particles is 1–3 microns.

polished with sandpaper. Sample thickness (necessary for the calculation of conductivity) was determined using a micrometer, Schmidt Technology (Cranberry Twp., PA) model J50 with an accuracy of 0.01 mm. Thickness measurements were taken at five locations and averaged. Samples were cooled to room temperature during approximately 30 min.

Composite characterization techniques

The microstructures of the samples were observed by reflection by means of a Nikon (Tokyo, Japan) model 115 optical microscope. Then, the density of the composites was measured in accordance with the ASTM D 792–91 norm, by difference of weight in the air or with the sample immersed in water as a liquid of known density at 23°C, using a Mettler Toledo (Columbus, OH) AJ 100 balance equipped with a density determination kit. Moreover, the hardness of the samples was determined at 23°C using a Durotronic Instron (Canton, MA) model 1000 Shore D hardness tester, in accord with the ASTM D 2240–68 norm. Five data points were taken on each sample, and no difference was found between hardness measurements on both faces of each specimen.

The electrical conductivity was determined from the resistance values that were measured using a two-point arrangement as described elsewhere.[26,29] 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 with a programmable megohmeter Quadtech (Maynard, MA) model 1865. Measurements of low electrical resistance were made with a digital multimeter Leader (Melrose, MA) model 856.

RESULTS AND DISCUSSION

Microscopy

Figures 1 to 4 present optical micrographs of the constituents. It is clearly seen that the urea-formaldehyde-cellulose, carbon black, and graphite have aggregate

morphology, in spite of the difference of their particle sizes. However, the morphology concerning these aggregates remains similar. On the other hand, the activated carbon one (Fig. 4) is different and has a granular aspect. This morphology appearance could influence the composite electrical behavior.

Figures 5 to 7 represent micrographs with the structure of composite samples before (a) and after (b) the percolation thresholds. These photos show a distinction in the contrast, relating to the different color of the fillers (black) and matrix (white). On the basis of these optical micrographs, it can be appreciated that large aggregates were formed during the process. However, the morphology concerning these aggregates remains similar and uniformly dispersed, indicating homogeneous composites.

Porosity

The homogeneity of composites could also be verified by density measurements. Indeed, the morphology is in part influenced by the porosity rate in such materials. The porosity rate should be determined from comparison between the calculated and measured densities.

The theoretical composite density of the two constituents is given by the relation:[28]

$$d_t = (1 - V_f) \cdot d_m + V_f \cdot d_f \tag{1}$$

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

Then, the composites' porosity τ has been deduced from the formula:[28]

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

where d_e represents the experimental density.
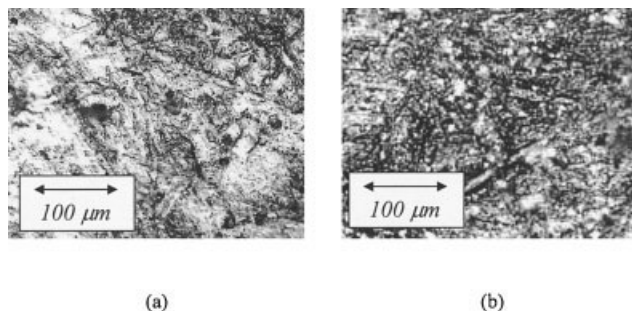

(a)   (b)

Figure 5 Optical microscopy micrographs of the carbon black filled composites containing (a) 5 wt % of filler and (b) 25 wt % of filler.
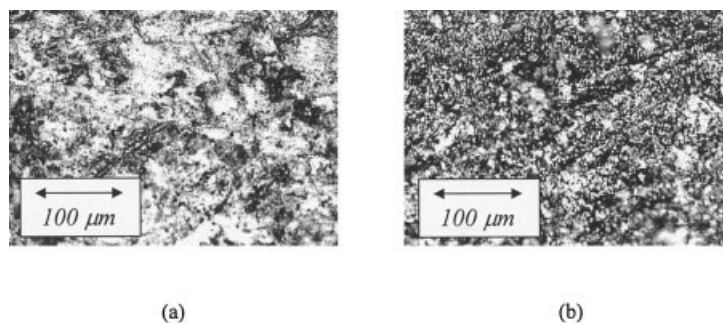
Figure 6 Optical microscopy micrographs of the synthetic graphite filled composites containing (a) 5 wt % of filler and (b) 25 wt % of filler.

The fit of the experimental density data with eq. (1) is good. This constitutes a confirmation of microscopic observations, that the produced composites are almost homogeneous. Consequently, the presence of air is negligible. The small deviation between d_e and d_t corresponds to the porosity. The rate of this porosity is given by eq. (2). Figure 8 shows the porosity rate of the prepared composites as a function of the filler volume fraction. It is to be noted that, in the case of carbon black and graphite, the porosity rate increases with volume fraction and becomes almost constant (1–3 vol %) from a value around 0.06, corresponding to the conduction threshold (see below). The graphite composites show a value slightly higher than CB-composites. Such behavior is coherent. It is well known that graphite has an appreciable porosity, more so than carbon black, which is used in some industrial applications. The porosity rate of active carbon composites is larger than the other fillers and increases linearly versus AC-volume fraction, but does not exceed 6 vol %. A high value of τ will decrease electrical conduction. The change in slope around 0.13 corresponds to the conduction threshold. Similar behavior was observed by Wessling on thermoplastic polymers filled with CB.[30] Elsewhere, it is also known that AC has a large porosity and specific area, which are used in the clarification of water, for example. These results are therefore consistent with microscopic indications.

Hardness

The hardness was also measured on each sample. It remains approximately constant, as 82 ± 4 shore D values, independent of the filler composition. The fact that the shore D hardness has no appreciable differences among the five data points on each sample on both faces for each composition is a proof of the material homogeneity. These results seem to confirm the optical microscopic observations and the density deductions. Therefore, all these characterizations indicate that the elaborated composites are homogenous.

Electrical conductivity

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. 9). As expected, samples with low filler content were almost nonconductive. However, the electrical conductivity of the composites increases dramatically as the filler content reaches the percolation threshold, which depends on
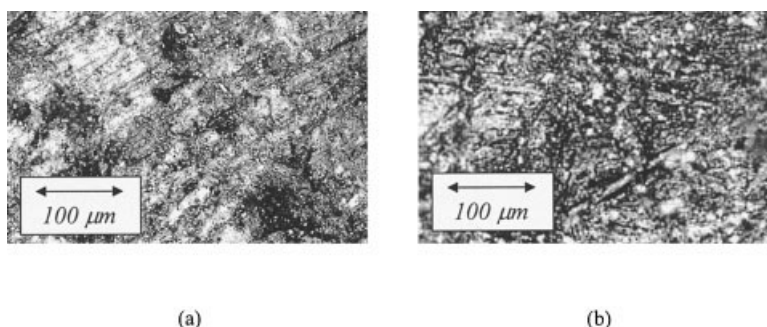

Figure 7 Optical microscopy micrographs of the activated carbon filled composites containing (a) 5 wt % of filler and (b) 25 wt % of filler.
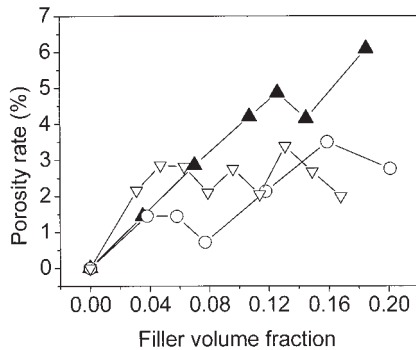
Figure 8 Porosity rate in the urea-formaldehyde and cellulose composites filled with: (○) carbon black powder, (▽) synthetic graphite powder, and (▲) activated carbon powder; versus filler volume fraction.

TABLE II
Critical Conduction Threshold from Experimental Data: Percolation Threshold, Critical Exponents, and Filler Packing Density Coefficient F for the Three Series of Composites from Eq. (4).

Samples	V_f^* (vol %) experiment	V_f^* (vol %) eq. (4)	t_{eff}	F
CB/UFC	5.8	5.7	2.8	1
G/UFC	6.3	6.2	3.7	1
AC/UFC	12.6	12.6	3.1	1

the filler nature. The corresponding values of the three studied series of composites are given in Table II. Then, the conductivity of composites increases by much as 11 orders of magnitude.

As indicated above, this behavior could be interpreted with the statistical percolation theory. Such a theory is usually used to relate the electrical conductivity of a 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 by:[18]

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

where σ is the electrical conductivity of the mixture, σ_0 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 determining the increase of the
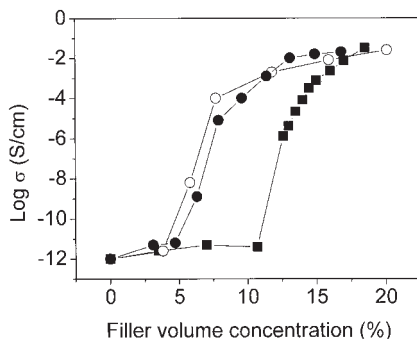

Figure 9 Variation of the electrical conductivity of urea-formaldehyde embedded in cellulose composites filled successively with: (○) carbon black powder, (●) synthetic graphite powder, and (■) activated carbon powder as a function of these filler contents.

conductivity above V_f^*. This theory gives a good description of experimental results near the transition point. Nevertheless, discrepancies were observed between critical parameters (V_f^*, t) resulting from eq. (3) and experimental values[22] inasmuch as the basic classical statistical theory does not take into consideration several parameters. 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 filler particles' geometrical parameters, as well as on filler/matrix interactions. Mamunya and coworkers[21,22] have developed a model in which specific parameters for each composite have been introduced in the basic theory:

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

where σ_m is the maximal conductivity reached by the composite. F is the filler packing density coefficient (equivalent to the maximal value of the filler volume fraction), and t_{eff} is given by the relation:

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

t_1 is equivalent to the t parameter in the basic eq. (3), which usually takes a value around 1.7, and t_2 depends on the specific composite. Thus, t_{eff} could have higher values taking into account filler/polymer interactions.

The classic percolation theory (eq. (3)) was tested in our case without success. Equation (4), on the other hand, was used with success in earlier similar studies to interpret the experimental results,[26,28,29,31] and it provides a good result here. Therefore, the fit, above the percolation threshold of electrical conductivity, as a function of volume fraction of fillers is given in Figure 10. It should be noted that the agreement between the experiment and the theory is good. The obtained parameters are given in Table II.

The determined packing density coefficient F value is higher than obtained in metallic fillers.[26,28,29,31] In all studied carbon fillers, the packing coefficient is maxi-
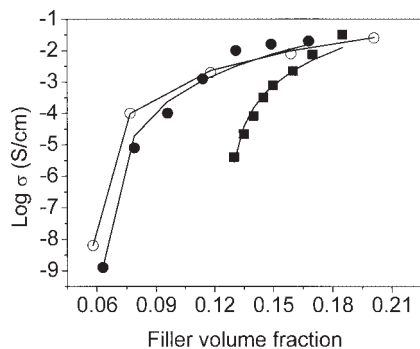
Figure 10 Electrical conductivity above the percolation threshold of urea-formaldehyde and cellulose composites filled with: (○) carbon black powder, (●) synthetic graphite powder, and (■) activated carbon powder. Solid line is the fit with eq. (4).

CONCLUSIONS

In this experimental work, we have described the effects of the carbon charged content filled urea-formaldehyde embedded in cellulose on electrical conductivity. The obtained results show clearly the great dependence of the conduction threshold on several parameters associated with the filler particles' nature. Indeed, the porosity seems to play an important role in the location of the conduction threshold. The percolation threshold obtained values seem to be coherent. The determined values of critical exponents appear non universal. Besides, the electrical conductivity behavior as a function of filler content is reasonably fitted, above the percolation threshold, with extended basic statistical percolation theory. The obtained critical parameters are realistic and coherent with experimental values and earlier studies.

mal. The F higher value seems due to the fact that in the present case the fillers and matrix are the same chemical species. This chemical affinity could enhance F. The matrix is not saturated by filler packing. Elsewhere, similar dependences were observed previously for polymers filled with carbon black.[4]

The t_{eff} obtained values are around 3. Similar values have been obtained in epoxy filled successively with carbon black and polypyrrole.[32,33] According to the Heany theory,[34] the exponent t could take a value higher than 2, predicted for three dimensional lattices, in mean-field theory.[35,36] The t value is independent of the exact composition of the random composites.[35]

The experimental values of the percolation threshold obtained from the maximum of the conductivity derivative as a function of filler volume fraction and these deduced from fit with eq. (4) are listed in Table II. They are in good agreement.

Indeed, the random composite electrical conductivity has already been shown to depend on several parameters,[24–28,37,38] such as: the viscosity and the polymers surface tension, especially in the case of the mixes 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. In this study, the dispersion procedure has been maintained uniform. The particle shapes of CB and graphite are similar, involving close percolation threshold values. The slight difference should be due to the small porosity disparity. In the case of activated carbon, the conduction threshold is higher. This effect should be connected to the distinction in the shape and porosity. It is already shown that the porosity effect plays an important role on the conductivity behavior.[28] This behavior appears to be coherent. It is well known that electrical conductivity is very sensitive to compound impurities.

References

1. Norman, R. H. Conductive Rubbers and Plastics; Elsevier: New York, 1970.
2. Bueche, F. J Polym Sci 1973, 11, 1319.
3. Carmona, F.; Delhaes, P.; Barreau, F.; Ordiera, D.; Canet, R.; Lafeychine, L. Rev Chim Min 1981, 18, 498.
4. Miyasaka, K.; Watanabe, K.; Jojima, E.; Aida, H.; Sumita, M.; Ishikawa, K. J Mater Sci 1982, 17, 1610.
5. Sihel, E. Carbon-Black Polymer Composites; Dekker: New York, 1982.
6. Thakur, M. Macromolecules 1988, 21, 661.
7. Celzard, A.; Mcrae, E.; Mareche, J. F.; Furdin, G.; Dufort, M.; Deleuze, C. J Phys Chem Solids 1996, 57, 715.
8. Son, S. H.; Lee, H. J.; Park, Y. J.; Kim, J. H. Polym Int 1998, 46, 308.
9. Bouchet, J.; Carrot, C.; Guillet, J. Polym Eng Sci 2000, 40, 36.
10. Flandin, L.; Chang, A.; Nazarenko, S.; Hiltner, A.; Baer, E. J Appl Polym Sci 2000, 76, 894.
11. King, J. A.; Tucker, K. W.; Meyers, J. D.; Weber, E. H.; Clingerman, M. L.; Ambrosius, K. R. Polym Compos 2001, 22, 142.
12. Delmonte, J. In Metal/Polymer Composites; Van Nostrand Reinhold: New York, 1990.
13. Lafuente, P.; Fontecha, A.; Díaz, J. M.; Muñoz-Escalona, A. Rev Plást Modern 1993, 447, 257.
14. Gul, V. E. In Structure and Properties of Conducting Polymer Composites; VSP: New York, 1996.
15. Yi, X. S.; Wu, G.; Pan, Y. Polym Int 1997, 44, 117.
16. Muñoz, B. C.; Steinthal, G.; Sunshine, S. Sensor Review 1999, 19, 300.
17. Mottahed, B. D. Polym Eng Sci 2000, 40, 61.
18. Kirkpatrick, S. Rev Mod Phys 1973, 45, 574.
19. Lux, F. J Mater Sci 1993, 28, 285.
20. Chen, X. B.; Devaux, J.; Issi, J. P.; Billaud, D. Polym Eng Sci 1995, 35, 637.
21. Mamunya, E. P.; Davidenko, V. V.; Lebedev, E. V. Comp Interfaces 1997, 4, 169.

22. Mamunya, E. P.; Davidenko, V. V.; Lebedev, E.V. Polym Compos 1995, 16, 319.
23. De Bondt, S.; Froyen, L.; Deruyttere, A. J Mater Sci 1995, 27, 319.
24. Larena, A; Pinto, G. Polym Compos 1995, 16, 536.
25. Pinto, G.; López-González, C.; Jiménez-Martín, A. Polym Compos 1999, 20, 804.
26. Pinto, G.; Jiménez-Martín, A. Polym Compos 2001, 22, 65.
27. Pinto, G.; Maidana, M. B. J Appl Polym Sci 2001, 82, 1449.
28. Maaroufi, A.; Haboubi, K.; El Amarti, A.; Carmona, F. J Mater Sci 2004, 39, 265.
29. Pinto, G.; Maaroufi, A. J Appl Polym Sci 2005, 96, 2011.
30. Wessling, B. Synth Met 1988, 27, A83.

31. Pinto, G.; Maaroufi, A. Polym Compos 2005, 26, 401.
32. Carmona, F.; Prudhon, P.; Barreau, F. Solid State Commun 1983, 51, 225.
33. Fournier, J.; Boiteux, G.; Seytre, G.; Marichy, G. Synth Met 1997, 84, 839.
34. Heaney, M. B. Phys Rev B 1995, 52, 12477.
35. Stauffer, D. Introduction to the Percolation Theory; Taylor and Francis: London, 1985.
36. Berezina, N. P.; Karpenko, L. V. Colloid J 2000, 62, 676.
37. Carmona, F. Ann Chim Fr 1988, 13, 395.
38. Genetti, W. B.; Yuan, W. L.; Grady, B. P.; O'rear, E. A.; Lai, C. L.; Glatzhofer, D. T. J Mater Sci 1998, 33, 3085.