Electrical resistivity of polymeric matrix loaded with nickel and cobalt powders

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This paper reports on the electrical properties of various polymers (epoxy resin, silicone, polyurethane) filled with metal particles (Cobalt and Nickel). The results of this study give evidence of the expected non-conducting to conducting transition as the conducting filler volume fraction V_f is increased. The location of threshold is found to depend on the features and the properties of composite's constituents: the type, the viscosity and the surface tension of the matrix as well as the nature, the size, the shape, the geometry and the surface energy of the conducting particles and the composite porosity. The morphology of the filler particles and their dispersion in the matrix have been investigated by Optical and Scanning Electron Microscopies (SEM) and density measurements.
The obtained results have been explained on the basis of the statistical percolation theory.
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1. Introduction

During last years, the utilization of electrically conducting composite materials based on filled metal organic polymers, has undergone a considerable growth. This development is generally due to their various advantages over other conductive materials owing to their processability, flexibility, ability to absorb mechanical shock, corrosion resistance, light weight and electrical conductivity control. These properties make them devoted to different applications: shielding of electromagnetic fields of devices, conductive adhesives, cold seals, switching devices, underfill for flip chips, static charges dissipating materials, devices for surge protection, intermediate layers for high voltage cables [1–9].

It is widely known that polymeric materials are typical insulators. The easiest method of producing conductive polymer composites is to fill an insulating polymer, having good mechanical properties, with highly conductive particles (metal powders or carbon black). Since the early sixties Gurland [10], Malliaris and Turner [11] have studied the electrical conductivity of metal filled polymers and have evidenced the known classical Insulating to Conducting Transition (ICT). The behavior of this property depends strongly on the filler concentration. It increases when the concentration of metal increases and the transition occurs at a fixed fraction called threshold of percolation.

Different models have been proposed to interpret the behavior of the electrical conductivity of different mixtures of insulating and conductive materials. They are nicely described by Lux [12]. These models could be summarized as follow:

(i) Several slightly different geometrical percolation models were suggested in the case of the different dry-premixed conductive and insulating powders [2, 11, 13, 14]. They suppose that during mixing process, the particles are deformed tending to form a regular geometry.

(ii) Whereas, the structure-oriented percolation models take account of the different parameters determined from the micro-level structure of the mixtures after the final processing step [15–21].

(iii) The statistical percolation models, statistically treat clusters of connected particles dispersed in matrix [22, 23].

(iv) The thermodynamic models elucidate, in some cases, the discrepancy observed between experiment data and prediction of the statistical models [24, 25].

Among all these models, the classical statistical ones are well known and occupy a great place in the literature. They are usually used to relate the electrical conductivity 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 by [22]:

$$\sigma = \sigma_o \left(V_f - V_f^* \right)^t \tag{1}$$

where σ is the electrical conductivity of the mixture, σ_o 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 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 Equation 1 and experimental values [26]; as inasmuch as the basical classical statistical theory does not take a consideration of several parameters. Whilst, 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 the filler/matrix interactions. Mamunya *et al.* [26] have developed a model in which specific parameters for each composite have been introduced in the basical theory:

$$\sigma = \sigma_o + (\sigma_m - \sigma_o)\left(\frac{V_f - V_f^*}{F - V_f^*}\right)^{t_{eff}} \tag{2}$$

where σ_m is the maximal composite reached conductivity. 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:

$$t_{eff} = t_1 + t_2 \tag{3}$$

t_1 is equivalent to the t parameter in the basic Equation 1 and t_2 depends on the specific composite. Thus, t_{eff} could have a higher values taking into account of the filler/polymer interactions.

The main goal of this paper is the preparation of various composite materials, from different polymer matrices (epoxy resin, polyurethane and silicone) and metal powders (cobalt and nickel), characterized by higher electrical conductivity limit and the investigation of the effect of matrix and fillers on the location of the percolation threshold.

2. Experimental procedure
2.1. Manufacture of materials
The three commercially polymers we have used are an epoxy and two elastomers: epoxy D associated to HY956 hardener (CIBA–GEIGY cy), silicone RTV 148-A associated to RTV147-B hardener (RHONE–POULENC cy) and polyurethane Desmophen C200 associated to hardener Desmodur Z4470 from RHONE–POULENC cy. The fillers are metallic powders of nickel and cobalt from Aldrich Chemical cy. Some characteristics of these constituents are listed in Tables I and II. It should be noted that the viscosities given in Table I have been measured on the mixes before polymerization. The resistivities and the density of metals

TABLE I Properties of the polymers used in this study: density (d), resistivity (ρ) and viscosity (η)

	Epoxy D	Silicone	Polyurethane
d (g/cm^3)	1.17	1.30	1.08
ρ ($\Omega \cdot$ cm)	10^{13}	10^{13}	10^{11}
η (mPa $\cdot$ s) at 25°C	10000–12000	700–1600	10000

TABLE II Properties of filler particles: mean size (φ), density (d) and compressed powder resistivity (ρ)

	φ (μm)	d (g/cm^3)	ρ ($\Omega \cdot$ cm)
Cobalt	98.8	8.90	3.49
Nickel	116.4	8.90	2.67

given in Table II have been performed on the compressed metallic powders.

The volume fraction V_f of particles in the composite is given by the relation [27, 28]:

$$V_f (\%) = 100\left(\frac{V_c}{V_c + V_p}\right) \tag{4}$$

where V_c and V_p are the volume of the metallic particles and the polymer (resin and hardener) respectively.

All the samples have been prepared according to the same procedure. Adequate quantity of metallic powder was introduced in the fluid resin and dispersed manually. The formed viscous suspension was flowed in Teflon casts and placed during one hour on the rotating rollers in an oven maintained at 103°C. The mixture has been rotated during polymerization process; in order to prevent the sedimentation of the particles whose density is larger than that of polymers one (see Tables I and II). The homogeneity of the composite samples has been assessed by means of density and resistivity measurements.

2.2. Microscopy
A Nikon EPI PHOT.TME optical microscope and a Scan Electronic Microscope (SEM) were used to observe the morphology of the particles and their dispersion inside the composites (see Figs 1 and 2).
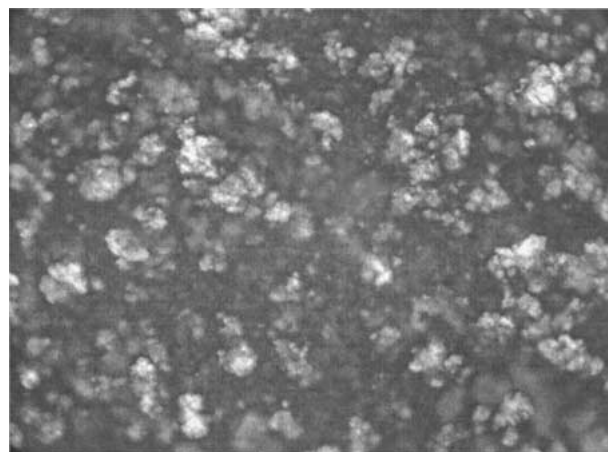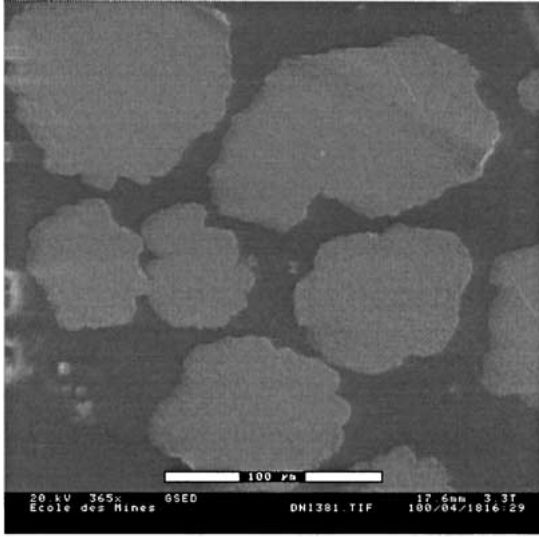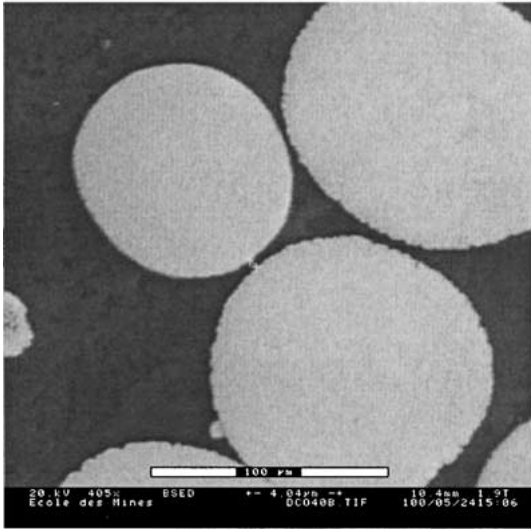

Figure 1 Optical microscope image of cobalt (35 vol%) in epoxy D (40×).

(a)

(b)

Figure 2 Electron images: (a) 38.1 vol% of nickel in epoxy *D* taken at 20 kv and 365×, (b) 40 vol% of cobalt in epoxy *D* taken at 40 kv and 405×.

2.3. Porosity
In order to determine the porosity rate of the composites, the density has been measured by means of a helium pycnometer Micromeritis Accupyc 1330.

The theoretical density of the composite has been calculated from the relation:

$$d_t = (1 - V_f)d_m + V_f d_f \qquad (5)$$

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

The composites' porosity τ has been determined from the formula:

$$\tau = \left(\frac{d_t - d_e}{d_t}\right)100 \qquad (6)$$

where d_e represents the experimental density.

2.4. Resistivity
The electrical resistance has been performed according to the method described in detail elsewhere [28, 29]. The resistance of poorly conducting materials, corresponding to the composites with low filler loading, has been measured using the known sandwich method (two-points). The composite have a disk-like geometry of 3–4 mm of thickness and 10 mm of diameter; two copper electrodes were attached to it by means of a silver conductive colloidal suspension (Acheson-MIBK). To allow for the complete evaporation of the solvent, the electrical measurements has been carried out at least 24 h later. The current passed through the electrodes using a KEITHLEY 617 electrometer. The voltage drop across the disk has been measured by a Hewlett-Packard 3490A digital multimeter. The resistivity ρ has been calculated using the relation:

$$\rho = \frac{1}{\sigma} = R \cdot \frac{S}{a} \qquad (7)$$

where ρ is the resistivity, σ is the conductivity and R is the resistance of the sample, S is the section and a is the thickness of the disk.

However, the resistivity of high filler loading has been measured using a four-points method [28, 29] using a KEITHLEY 617 electrometer as the current source and a KEITHLEY 191 digital multimeter has been used for the voltage drop measurement. Care has been taken for performing the measurements inside the ohmic region (low current). The results are given in Figs 4b and 5.

3. Results and discussions
3.1. Microscopy
Fig. 1 represents a typical optical micrograph of cobalt charged epoxy *D*, which shows an uniform repartition of filler particles.

In order to visualize the nickel and cobalt particles' respective shapes, SEM pictures of thin slices of composites are illustrated in Fig. 2. These pictures show clearly a smooth and almost spherical-like shape in the case of cobalt particles and rough and irregular shape in the case of the nickel particles.
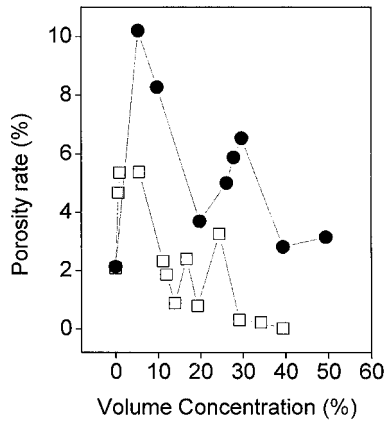
3.2. Porosity
The porosity rates of various composites are reported as function of the filler volume fraction on Figs 3 and 4a. It is to be noted that in all cases, before any loading and at low filler content, the porosity is large. It decreases sharply as the filler content increases and reaches very weak values. This decrease depends strongly on both the matrix and the filler nature (see Figs 3 and 4a). This behavior could be related to the packing process of the fillers inside the matrix leading to an inter-connection between clusters [26, 30].

3.3. Resistivity
The results of the electrical measurements are reported in Figs 4b and 5. As expected from the published
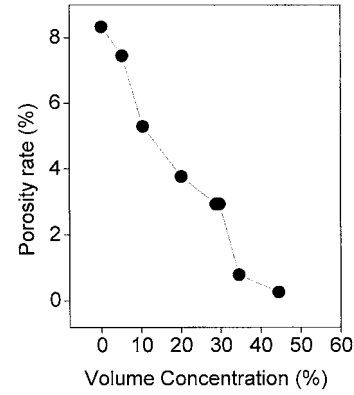
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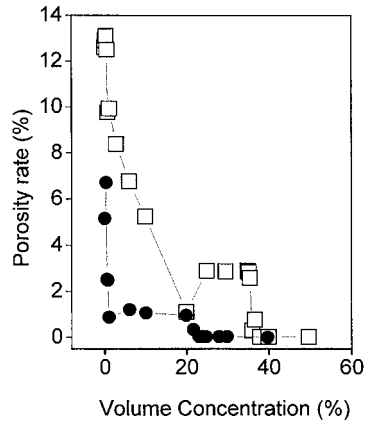
(a)

(b)

Figure 3 (a) Porosity rate τ of epoxy *D* loaded with nickel or cobalt as function of volume fraction of nickel (-□-) and cobalt (-•-). (b) Porosity rate of silicone loaded with cobalt or nickel as function of volume fraction of nickel (-□-) and cobalt (-•-).

(a)

(b)

Figure 4 Porosity rate (a) and electrical resistivity (b) of polyurethane loaded with cobalt versus volume fraction of cobalt.

literature [9, 31–34], all resistivity versus concentration curves exhibit a sharp decrease in the neighborhood of a critical filler volume concentration, V_f^*, which depends on both the matrix and the filler nature. The corresponding values of the five studied series of composites are given in Table III. It can be observed that the resistivity of the most concentrated composite is quite close to the limiting value of the corresponding metallic powder.
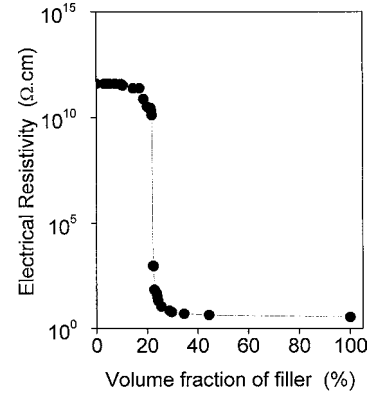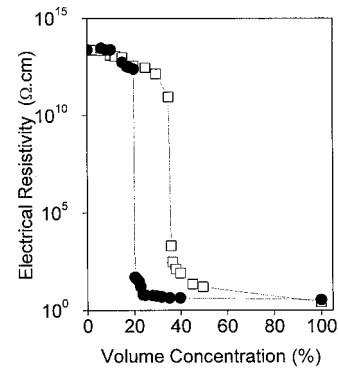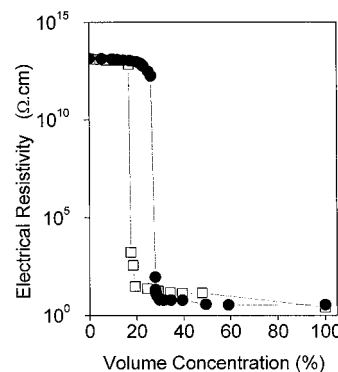
Above the critical threshold, Equation 2 fits the electrical conductivity variation versus the filler volume fraction. The data are depicted in Figs 6, 7 and 8. It should be noted that, in most of the cases, the agreement between the experiment and the theory is fairly

(a)

(b)

Figure 5 (a) Electrical resistivity of epoxy *D* loaded with nickel or cobalt as function of volume fraction of nickel (-□-) and cobalt (-•-). (b) Electrical resistivity of silicone loaded with nickel or cobalt versus volume fraction of nickel (-□-) and cobalt (-•-).

TABLE III Filler critical volume fraction at conduction threshold and critical exponents from Equations 1 and 2 and filler packing density coefficient *F* for the five series of composites

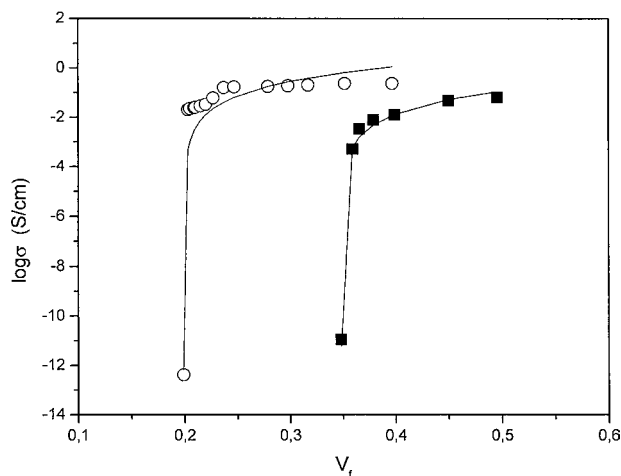| Samples	V_f^* (vol%) Equation 1	V_f^* (vol%) Equation 2	*t*	t_{eff}	*F*
Epoxy *D*/Cobalt	19	19.90	1.72	2.52	0.47
Epoxy *D*/Nickel	35	34.85	1.64	2	0.77
Silicone/Cobalt	27	29	1.68	1.75	0.64
Silicone/Nickel	17	17.50	1.71	1.70	0.46
Polyurethane/Cobalt	22	21.90	1.62	1.70	0.37

Figure 6 Electrical conductivity versus filler volume fraction above the conduction threshold of epoxy D/cobalt ($\circ$), epoxy D/nickel ($\blacksquare$) and fit (—) with Equation 2.
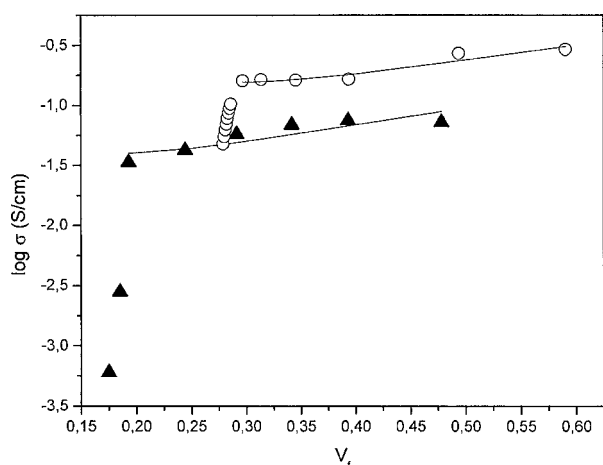

Figure 7 Electrical conductivity versus filler volume fraction above the conduction threshold of silicone/cobalt ($\circ$), silicone/nickel ($\blacktriangle$) and fit (—) with Equation 2.
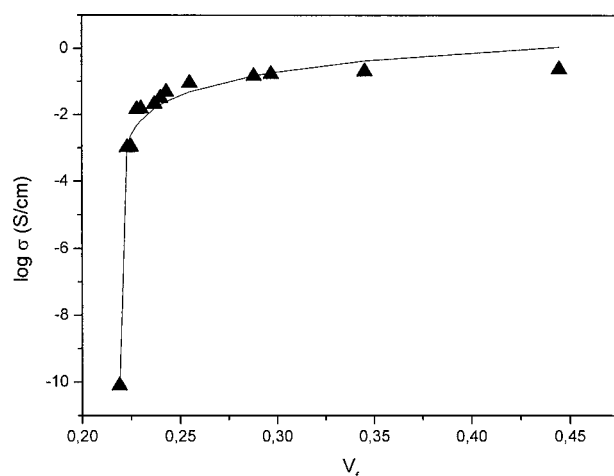

Figure 8 Electrical conductivity versus filler volume fraction above the conduction threshold of polyurethane/cobalt ($\blacktriangle$) and fit (—) with Equation 2.

good. The deduced parameters are given in Table III and compared with those obtained from Equation 1.

The t and t_{eff} obtained values (Table III) are slightly different but close to 2, which represents the accepted

theoretical value for three dimensional lattices [35, 36]. This theoretical value is independent of the exact composition of the random composites [35]. However, Equation 2 seems to induce certain ameliorations with respect to the Equation 1 data. On the other hand, the critical threshold percolation values obtained from the Equations 1 and 2 are approximately the same. The influence of both polymer matrix and filler particles characteristics on these values is clearly shown (see Figs 4b and 5).

Indeed, the random composites electrical conductivity has already been shown to depend on several parameters [9, 31–34]; such as:

(i) the viscosity and the polymers surface tension, especially in the case of the mixes in which the conductive powder is dispersed;

(ii) the size, the shape and the surface energy of the filling particles and

(iii) the powder dispersion procedure, i.e., type, duration and strength of shear.

In this study the particle sizes are almost the same and the dispersion procedure has been maintained uniform. The analysis of the obtained results seems to show the effect of the viscosity on percolation threshold. Indeed, in the case of cobalt filled polymers, the location of percolation threshold corresponding to the Insulating Conductor Transition (ICT) can be correlated to the polymer viscosity: a large volume fraction at percolation threshold is found in the case of the least viscous matrix, namely the silicone elastomer (see Table I). The other two polymers have similar viscosities and exhibit a close critical volume fractions. Such a viscosity dependence on the critical volume fraction, for large filler particles, has already been found in analogous composites [9]. However, in the case of nickel filled polymers, the relationship between critical volume fraction and viscosity is simply reversed. It is believed that in the later case, other parameters like the shape (see Fig. 2), the surface energy of the particles and the polymers surface tension might be at origin of this behavior. It has been indicated that the surface tension of inorganic fillers, such as alumina, copper dioxide, silica or titanium dioxide, can be affected by the addition of a polymer, inducing changes in the particle surface energy [37–39]. Besides, the adhesion strength of polymeric chains on surfaces of filler depends on the nature and precisely on the polymer formulation [40], which may induce changes in the conduction threshold.

In addition, these results show an apparent correlation between the porosity rate and the resistivity (see Figs 3, 4 and 5). When the volume fraction of the filler increases, both the porosity rate and resistivity decrease. The more the porosity of unfilled polymer is large, the more the conduction threshold value is important. This porosity-critical volume fraction relationship is given in Fig. 9, from which it could be seen that the critical threshold increases rapidly with the porosity rate. This phenomenon seems to be related to the packing process of the filler inside the polymer matrix,
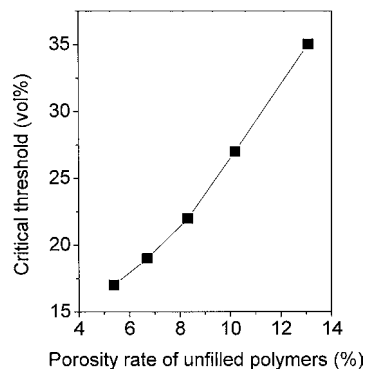
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Figure 9 Conduction thresholds as function of the porosity of the un-filled polymers.

as pointed out by E. P. Mamunya *et al.* [26] and Yu. N. Anisimov *et al.* [30]. The obtained packing density coefficient values (Table III) are in good agreement with the prediction of Equation 2. A such behavior appears to be coherent. It is known that the electrical conductivity is very sensitive to the compound defaults. The packing process reduces these defaults and therefore the electrical conduction is enhanced.

4. Conclusion

In this experimental electrical study of random composites, various combinations of metallic fillers and polymers matrix have been used. The parameters deduced from the classical and extended statistical percolation theories are comparable, although the latter shows a better fit of experimental data above the percolation threshold. The obtained results show clearly the great dependence of the conduction threshold on several parameters associated with both the filler particles and the polymer matrix nature. Indeed, the viscosity and the porosity seem to play an important role in the location of conduction threshold. The percolation threshold obtained values seem to be coherent. The determined critical exponents are in keeping with the three- dimensional lattices universal value. The relation between the electrical conductivity and the porosity seems to be established. But no clear and straightforward relationship between porosity and viscosity of the unfilled polymers appears to exist, as one might have expected. Such ambiguous correlation is not easy to interpret. However, the most interesting output of this study is the possibility of obtaining a highly conductive composites with low metallic powder content.

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