ELSEVIER

Polymer 41 (2000) 6589–6595

polymer

A numerical simulation of the electrical resistivity of carbon black filled rubber

G. Schwartz*, S. Cerveny, A.J. Marzocca

Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Dpto. de Física, Ciudad Universitaria, Pabellón 1, Buenos Aires 1428, Argentina

Received 17 August 1999; received in revised form 30 November 1999; accepted 1 December 1999

Abstract

A simple model is proposed and a numerical simulation is carried out to calculate the electrical resistivity of a composite of carbon black in an insulating matrix. From load of carbon black and aggregate size and distribution, it is possible to know the resistivity of the compound assuming a random lattice where the resistance between sites (aggregates) varies exponentially with the gap. A computer program was developed and several samples were prepared and measured to obtain the model parameters. Numerical results are compared with experimental data. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Numerical simulation; Electrical resistance; Composites

1. Introduction

The introduction of carbon black into polymeric materials imparts many interesting and useful properties to the filled composites. Electrically, a carbon black composite is extremely heterogeneous, consisting of a dispersion of particles of a degenerate semiconductor in an insulating matrix. The particles of carbon black range in diameter from 10 to 300 nm and are formed by burning or cracking hydrocarbon oils or gases. These particles tend to form themselves into chains, instead of being randomly dispersed, and the carbon chains give rise to the conductivity of the rubbers or plastics [1]. The values of resistivity that may be attained lie between 10^{-2} and 10^{14} Ωm.

Filled composites have been found to exhibit Ohmic or non-Ohmic behavior, different temperature dependence, critical filler concentration and particle size dispersion dependence. The development of physical models to explain all observed conductivities is a very difficult task; many models have been proposed to explain one or other effect, but not all at the same time.

It is the purpose of this paper to present a simple model that allows us to obtain the electrical resistivity of 3D composites by computer simulations. The simulation results are compared with experimental data, and it is shown that it is sensitive function of the filling fraction, temperature and particle size.

2. Background

Models of electrical resistivity (or conductivity) of composites materials have been studied for almost one hundred years. Models can be divided into three classes: (1) the continuum medium approach based on the Maxwell equation [2]; (2) the discrete medium approach based on Kirkpatrick's work [3]; (3) and the percolation approach for electrical conductivity.

All continuum medium theories such as the Brick-layer Model or the Maxwell–Wagner theory, assume that the resistivity of the medium is linear and independent of the volume fraction of the filler. This is not true to carbon black filled rubber, and it is well known that the electrical resistivity between two aggregates grows exponentially with the gap [4–6]. In earlier work, Polley and Boonstra [4], showed that

> the resistivity of carbon–rubber composites is not governed by the number of through-going particle-to-particle chains but by the width of the gaps in these chains… the probability of the electron jumping the gap decreases rapidly with increasing gap width and it is this function that actually determines the resistivity changes with loading

More recently, Kimura et al. [6], showed that the

* Corresponding author. Fax: +54-11-4576-3357.
E-mail address: schwartz@df.uba.ar (G. Schwartz).

PII: S0032-3861(99)00894-0

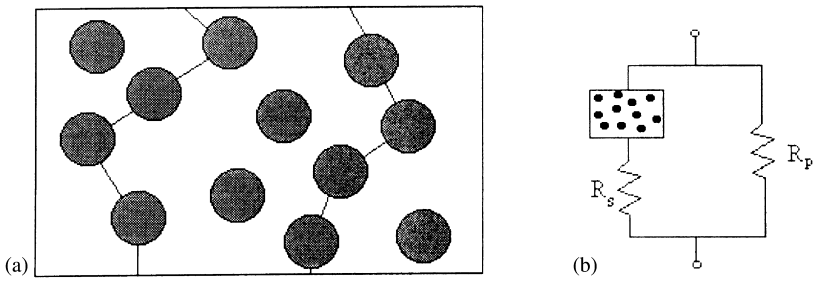

Fig. 1. (a) Aggregates dispersed in an insulating matrix. Lines show minimal paths between electrodes. (b) Complete equivalent circuit (see text).

logarithm of electrical resistance is a linear function of the elongation. This fact means that the current density is proportional to $\exp(-\omega\ C)$, where ω is the gap width and C is a constant. This shows that the logarithm of the resistivity is a linear function of the gap width.

On the other hand, resistivity decreases exponentially with temperature; this fact would suggest that the mechanisms controlling the process are thermally activated. Resistivity ρ, can be expressed as an Arrhenius law:

$$\rho = \rho_0\ \mathrm{e}^{\Delta H/\mathrm{k}T} \tag{1}$$

where ΔH is the activation energy, T the temperature, k the Boltzmann constant and ρ_o a pre-exponential factor that depends on type and structure of carbon black.

With the development of the computers some simulation models have appeared to explain electrical conductivity of composites. An earlier report was published by Pike and Seager [7], who analyzed the problem of percolation and conductivity in a computer study; and, more recently, Han and Choi [8] proposed a computation methodology to simulate dc and ac transport properties of 2D composites. The former puts emphasis only in the percolation problem, while the latter does not explain the non-Ohmic behavior neither the temperature and particle size dependence.

3. Model

As a first approximation to the problem we can considerate the carbon black aggregates as perfectly conductive spheres immersed in an insulating polymer matrix, as can be seen in Fig. 1. Spatial distribution may be set up arbitrarily or corresponds to some measured or known distribution. The proposed model assumes the following hypothesis:

- The aggregates are disposed at random into the polymer matrix according to a uniform distribution.
- All aggregates have the same size.
- The aggregates are ideal conductors. Its real resistance is represented by a serial resistor R_s.
- The electrical resistivity between two aggregates grows exponentially with the gap. The activation energy (ΔH) is a linear function of the gap (ω).
- R_p represents other conduction mechanisms that do not take into account, as ion transport, etc.
- Each resistivity value is obtained averaging N paths and M different networks, in order to diminish the error and ensure the convergence.

The computer program was developed in C and a flow diagram is shown in Fig. 2. For the different concentrations of carbon black, the program calculates the total volume of filler (V_{CB}). Then, it begins to put aggregates (spheres) at sites chosen following a given distribution (uniform by default). The volume of each new sphere is added to the total volume until it equals V_{CB}. At this point, the evaluation of the resistivity starts up. A point, with uniform distribution, is chosen at random on the upper electrode and the nearest aggregate is looked for. The distance to the next aggregate is calculated and the corresponding resistivity is computed from a modified form of Eq. (1), and added to the R_i. Then, the nearest down neighbor is looked for, and so on until to reach the other electrode. The resistance between electrodes is computed, with the calculated values of ω_k according to the following equation:

$$R_i = \sum_k \beta\ \mathrm{e}^{\alpha\omega_k/\mathrm{k}T} \tag{2}$$

where α and β are the fit parameters.

The process repeats N times and for M different distributions of particles. For each network the resistivity R_j is computed as the parallel of the N R_i, obtaining in this way, a distribution of M calculated values that follows a gaussian distribution. The geometric mean value is taken as the resistivity value of the sample. This value is in serial with R_s and both are in parallel with R_p.

The model has then, four parameters to adjust: α, that depends essentially of polymer type; β, that depends on carbon black type and rubber filler interaction; and R_s and R_p that depends on carbon black and polymer type, respectively. These four parameters enable us to predict the electrical properties of composites for different loads, temperatures and aggregates sizes.

4. Experimental

In order to compute the value of the resistance from the proposed model, it is necessary to know how it depends on the gap between particles of carbon black. The hypothesis d

Table 1
Resistivity values of the experimental samples (resistivity values are in Ωm)

Temperature (K)	50 phr	55 phr	60 phr	65 phr	70 phr
333	6334 ± 1176	1323 ± 26	551 ± 41	186 ± 8	97 ± 6
343	2431 ± 142	703 ± 59	297 ± 17	128 ± 10	79 ± 7
353	1420 ± 330	540 ± 49	248 ± 9	124 ± 5	78 ± 8
363	810 ± 77	366 ± 9	182 ± 12	103 ± 2	74 ± 7
373	560 ± 105	190 ± 18	140 ± 15	80 ± 9	60 ± 5

proposed in the model assumes an exponential dependence for the resistance between aggregates, with an activation energy that depends lineally with the gap. These hypotheses, in fact, are verified experimentally, and it is possible to obtain this dependence of ΔH from the experimental data. In order to do this, five compounds of SBR 1502 and carbon black N330 at different loading (50, 55, 60, 65 and 70 phr—weight parts per one hundred of rubber—see Appendix A) was prepared. Samples were mixed in a Farrel mixer of 1.5 l at 296 K, cold water running, 77 rpm and ram pressure 700 kPa. The cycle was: 0 min, elastomer; 1 min, carbon black; 3.5 min, sweep; dump at 433 K. Band on a roll mill and make three cuts from each side.

Sample resistivity was measured according to the methodology and equipment described elsewhere [9]. The measurements were made at different temperatures from 333 to 373 K on uncured samples. Five samples were measured at each temperature and each load and the results were averaged in order to lessen the experimental error. The results are shown in Table 1.

From these data, and according to Eq. (1), it is possible to obtain the activation energy of the process at each load. In fact, plotting $\log(\rho)$ vs. $1/T$ we obtain ΔH as the slope of the straight line. Fig. 3 shows experimental data with the best fit at each load.

It is clear from Fig. 3 that samples with different loads have different ΔH. Moreover, the increase of the load decreases the distance between aggregates of carbon black and consequently decreases the energy that an electron needs "to jump" from one aggregates to another. Table 2 shows the activation energies for each load.

It is possible, from simple geometry arguments, to set a relation between the distance between aggregates (ω) and its diameters (ϕ), (for an ideal distribution) for the known

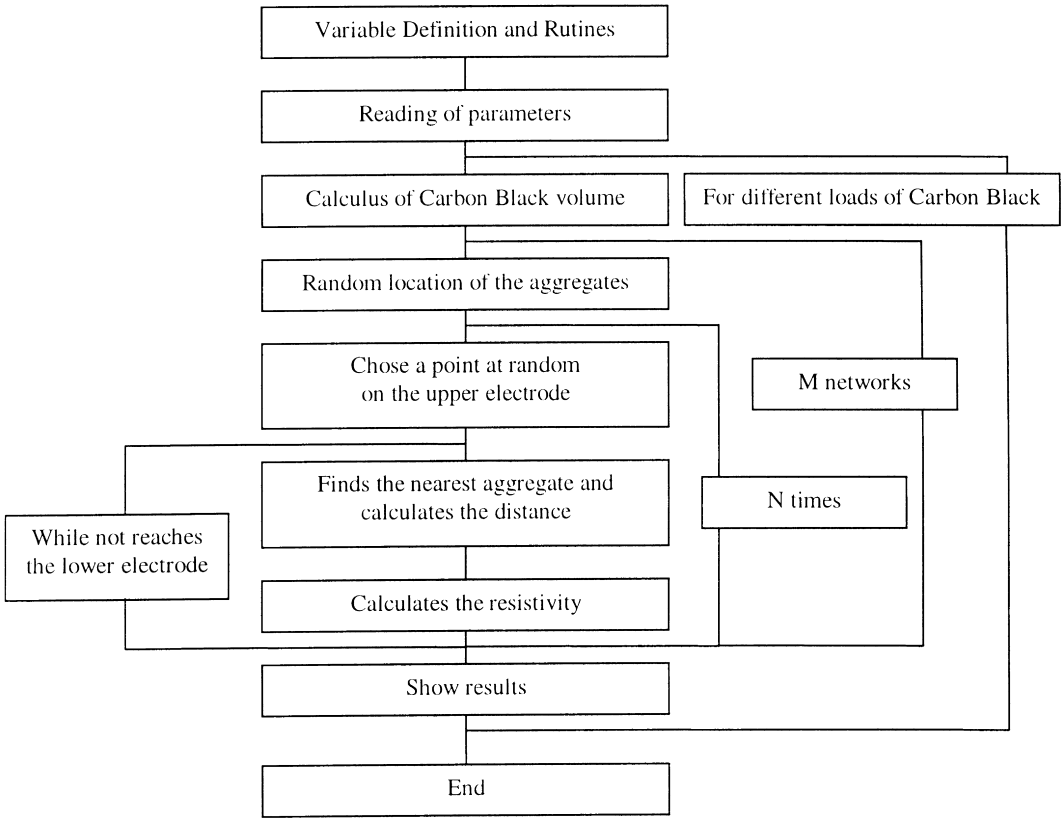

Fig. 2. Flow diagram of the computational program.

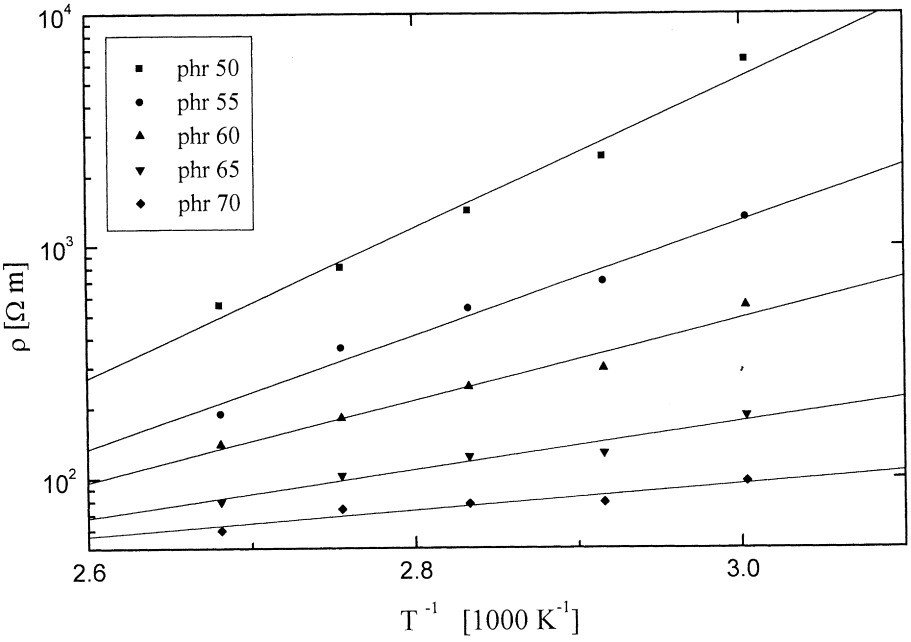

Fig. 3. Arrhenius resistivity plot for measured samples. Lines are the best fit to experimental data.

load of carbon black [8].

$$\omega = \phi\left[\left(\frac{200 + L}{1.91L}\right)^{1/3} - 1\right] \tag{3}$$

where L is the carbon black load in phr and suppose that the density of the carbon black is twice that of the polymer. As it was pointed out by Medalia [5], this equation was derived on what appears to be a highly unrealistic model, but remarkably, it predicts, for example, the correct loading of equal resistivity for two blacks of quite different particle size [heat-treated MPC (S301) and FT (N880)].

From these considerations, and calculated values of ΔH, it is possible to express the activation energy as a function of ω and ϕ. Fig. 4 shows this dependence and least squares fit.

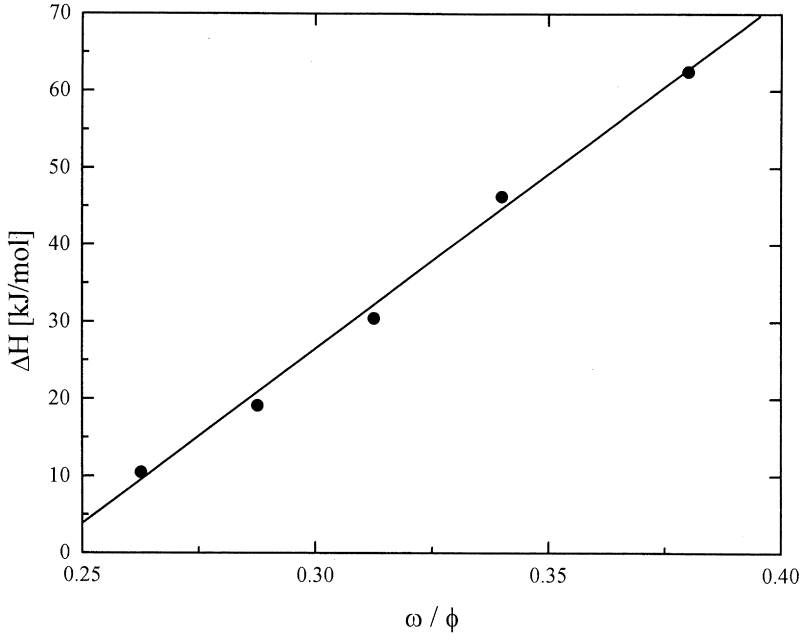

Fig. 4. Activation energy vs. gap (in diameters) between aggregates.

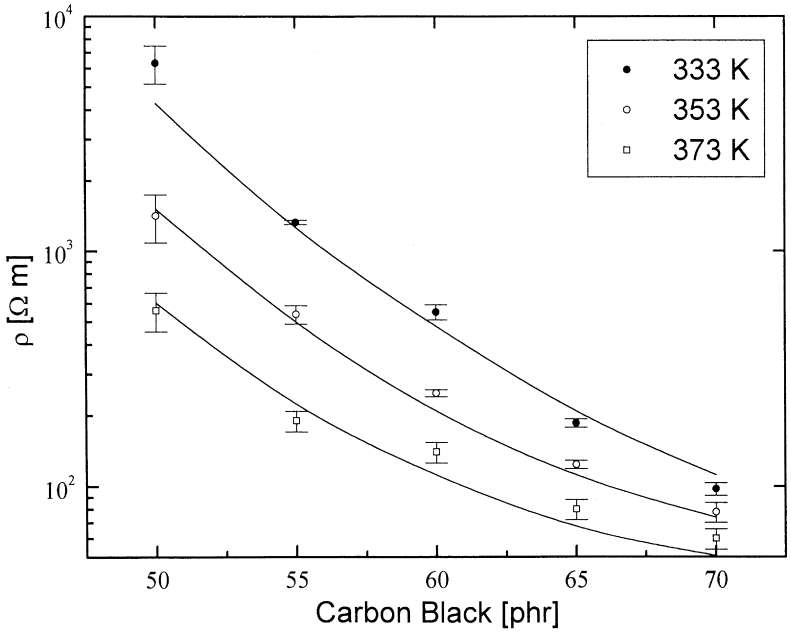

Fig. 5. Resistivity vs. load: experimental data (points) and simulated values (lines). There are only three temperatures for clarity.

5. Results and discussion

5.1. Simulation

We have carried out numerical simulations for systems of approximately 1000 particles. For each load and temperature the program realizes ten paths from one electrode to the other and repeats this process for 5000 different networks. For these values of N and M, the calculated resistivity in two different running did not vary significantly, this means that the solution had converged. In these conditions, the program takes about 15 min to compute each point, running in a 300 MHz Pentium II Personal Computer.

We performed several running under different conditions varying load, temperature and particle size. Fig. 5 shows the best fit to our experimental data, while Table 3 shows the corresponding parameters. These parameters adjust the resistivity values for all temperatures analyzed. For this fitting, we use a particle size of 170 nm according with Sichel [10] for N330 carbon black. The obtained activation energies are in concordance with those calculated experimentally.

Fig. 6 shows the temperature dependence of the electrical resistivity for simulated and measure data. Again, a good agreement is obtained for $\log(\rho)$ vs. $1/T$ representation.

Varying only the particle size we can see the tendency of the electrical resistivity for samples with different carbon black type. We made running for carbon black N110, N220, N339, N550 and N660 with the same parameters given in Table 3 and using particles sizes according with Sichel [10]; Fig. 7 shows that the results follow the same tendency that those measured by O'Farrell et al. [11].

5.2. Fractal dimension of carbon black network

The carbon black filled rubbers are in fact, from the point of view of the electrical conduction, a particular case of mixtures of conductive materials (or semiconductors) with insulating materials. In general, the electrical conductivity of these mixtures increases drastically for a given concentration of the conductive component, called percolation concentration. This percolation threshold depends on the size and distribution of the loads, its form and structure, the interaction load-matrix and the mixing process.

An interesting property of the percolation phenomenon is associated with the geometric characteristics of the resulting structure. When increasing carbon black level, putting particles at random on the matrix of insulating material, the structure that is formed due to the network of loads has the characteristics of a statistical fractal. The fractal dimension is possible to calculate and it will depend on the concentration of loads in the mixture.

The fractal dimension was calculated for different concentrations of the load and was related with the

Table 2
Activation energies of measure samples

	50 phr	55 phr	60 phr	65 phr	70 phr
ΔH [kJ/mol]	62.49	46.26	30.46	19.13	10.52

Table 3
Best fit parameters to experimental data

α (kJ/mol/μm)	β (Ωm)	ρ_s (Ωm)	ρ_p (Ωm)
462	150×10^{-6}	35	10^{12}

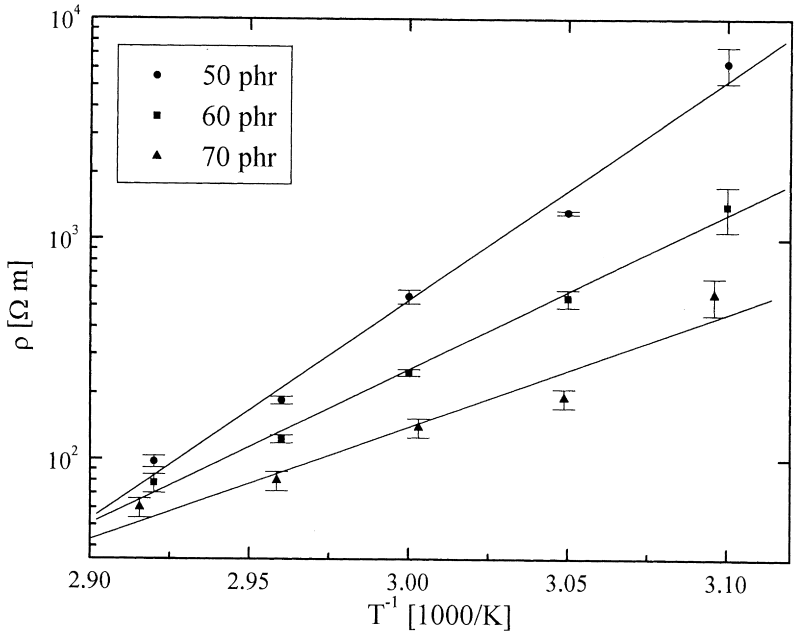

Fig. 6. Resistivity vs. 1/*T* for experimental data (points) and calculated values by numerical simulation (lines). Only three temperatures are shown for clarity.

percolation threshold and the electric characteristics of the mixture. Fig. 8 shows this dimension (D) as a function of the quantity of carbon black for particles of 300 nm diameter.

For $D = 1$ the first conduction "paths" begins to appear and we could hope that the transition of the resistivity curve is in coincidence with that point. It is observed in Fig. 8 that the transition appears for values bigger than D (or of the load L). This is consequence of that those first "paths" that appear have a high probability to have lost ends, surrounded of polymer, and that they do not touch any electrode. The transition appears for $D = 1.5$ ($L = 55$ phr) that corresponds to a critical volume of carbon black $v_c = 0.22$ that coincides approximately with the one calculated by Kirkpatrick [3] for conducting spheres in an insulating media.

6. Conclusions

A numerical simulation method was presented to model the dependence of the resistivity as a function of load, particle size and temperature for a carbon black filled rubber.

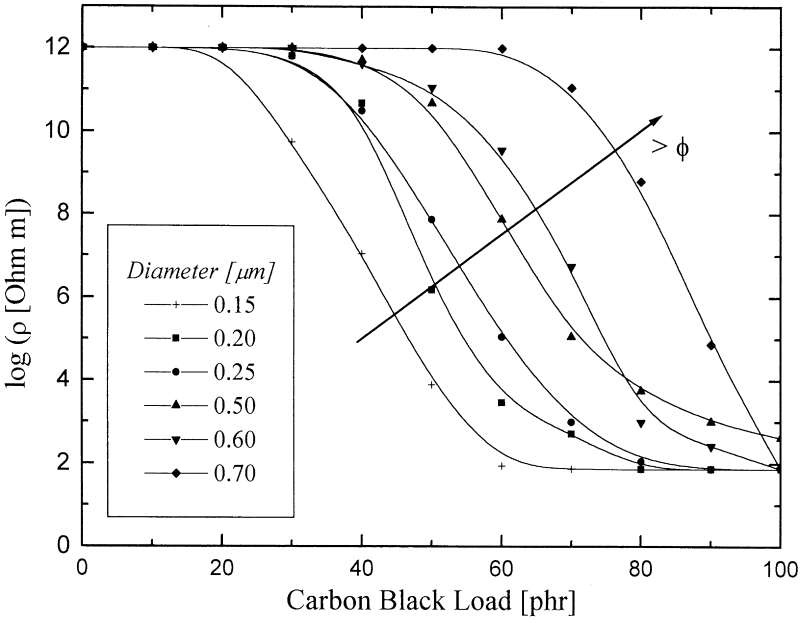

Fig. 7. Log(ρ) vs. load for different carbon black type.

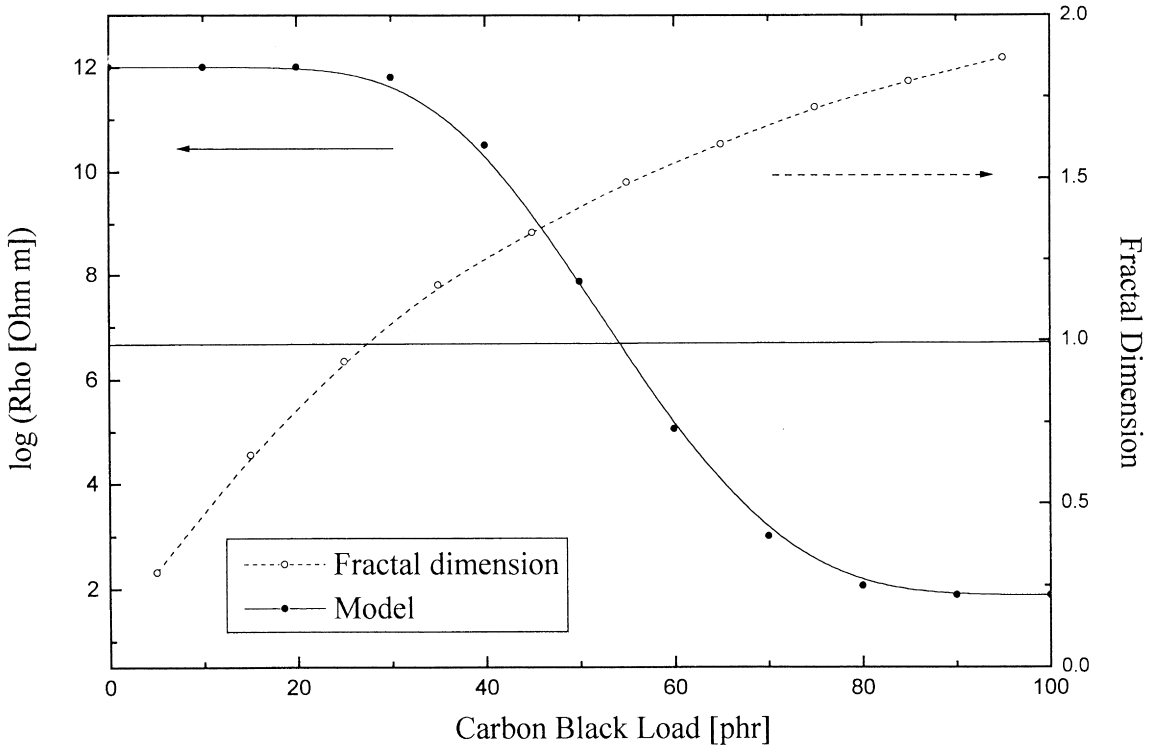

Fig. 8. Log(ρ) and fractal dimension vs. load for a typical composite.

Although the simplifications introduced in the model such as that all particles have the same size or that overlapping are allowed, it adjusts very well the experimental data and it allows predicting the resistivity curve for other particle sizes.

This method enables us to investigate the effects of different parameters on the electrical properties of carbon black filled rubber. These compounds are too much complicated to try to apply first principles to explain the electrical resistivity. In this sense, numerical simulation showed to be a useful method to study the electrical properties of these materials.

It is for a future work to introduce in the model the interaction between the loads and the polymer; this interaction depends strongly on the structure of the particles of carbon black.

Appendix A

The weight *p*arts per one *h*undred of *r*ubber (phr) is a common unit used in rubber industry and means that for each 100 g of rubber, the compound contains L grams of carbon black. The following equation relates the *phr* (L) with the volume fraction (f) for a compound that only contain rubber and carbon black:

$$f = \frac{L\rho_r}{100\rho_{cb} + L\rho_r}$$

where ρ_r and ρ_{cb} is the rubber and carbon black density, respectively.

References

[1] Norman RH. Conductive rubbers and plastics. Amsterdam: Elsevier, 1970.
[2] Maxwell JC. A treatise on electricity and magnetism, vol. 1. Oxford: Clarendon Press, 1881. p. 403.
[3] Kirkpatrick S. Rev Mod Phys 1973;45(4):574.
[4] Poley MH, Boonstra BBST. Rubber Chem Technol 1957;30:170.
[5] Medalia AI. Rubber Chem Technol 1986;59:432.
[6] Kimura T, et al. Polymer 1999;40:4149.
[7] Pike GE, Seager CH. Phys Rev B 1974;10(4):1421.
[8] Han DG, Choi GM. Solid State Ionics 1998;106:71.
[9] Roig Fernandez D, Marzocca AJ. Rubber Chem Technol 1991;64:501.
[10] Sichel EK. Carbon black-polymer composites. New York: Dekker, 1982. p. 23.
[11] O'Farrell CP, Gerspacher M, Nikiel L. International Tire exhibition and conference 1998, Akron, Paper 27B, 1998.