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## Broadband ac conductivity of conductor-polymer composites

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The electrical conductivity of a composite model system formed by highly structured carbon black (CB) filled, within an amorphous polymer, poly(ethylene terephthalate) composite is studied. The dc conductivity as a function of CB content follows a scaling law of the type  $\sigma \propto (p - p_c)^t$  yielding for the percolation concentration,  $p_c = 0.011$  and for the exponent,  $t = 2.17$ . The analysis of the temperature dependence of the conductivity suggests that for temperatures larger than 45 K, conduction can be ascribed to thermal fluctuation induced tunneling of the charge carriers through the insulating layer of polymer separating two CB aggregates. At lower temperatures, conductivity becomes temperature independent, which is typical of conventional tunneling. The frequency dependence of the conductivity is also studied between dc and  $10^9$  Hz. By the introduction of a shift factor  $a_p$ , a procedure for the construction of a master curve based on a "time-length equivalence principle" is proposed. Finally, a model is introduced to describe the frequency dependence of the conductivity of CB-filled composites based on the behavior of charge carriers placed in a fractal object. [S0163-1829(98)06304-8]

### I. INTRODUCTION

The electrical conductivity of insulating materials can be increased by the addition of a conductive material in particulate form. It is known that for very low content of the conducting element, the direct current (dc) conductivity of the composite system remains at the level of the unfilled insulating material. As the conducting loading is increased above the percolation concentration  $p_c$ , a sharp rise of 8–10 orders of magnitude of the conductivity is observed. Kirkpatrick<sup>1</sup> and Stauffer<sup>2</sup> treated conduction of a conductor-insulator composite as a theoretical percolation problem. As the concentration of the conducting additive is raised above  $p_c$ , the number of continuous paths through the compound increases allowing conduction of charge carriers, yielding, for the conductivity, the scaling law

$$\sigma_{dc} \propto (p - p_c)^t. \quad (1)$$

Various expressions have been proposed for the conductivity exponent,  $t = 1 + 2\beta$ ,  $(5d - 6)\nu/4$ ,  $[(3d - 4)\nu - \beta]/2$ , etc.,<sup>2</sup> where  $d$  is the space dimension and  $\nu$  and  $\beta$  are the scaling law exponent of the correlation length,  $\xi \propto |p - p_c|^{-\nu}$ , and the probability of a particle to belong to the infinite cluster,  $\mathbf{P}_\infty \propto (p - p_c)^\beta$  with  $p > p_c$ , respectively. These expressions seem to agree with values of  $t = 1.6$ – $2.0$  obtained by Monte Carlo calculations in simulations of three dimensions ( $d = 3$ ). Several experimental values of  $t$  measured in real systems like carbon black (CB) filled polymers, however, disagree with this theoretical value. Indeed, when in a Monte Carlo experiment physical contact between conductive particles is needed to permit the conduction of the charge carriers through the compound, in real conductor-insulator composites the electrons are allowed to tunnel from one conductive cluster to another separated by a thin insulating polymer layer. In order to investigate the conduction mechanism and nature of the contact between conductive clusters,

the characterization of the temperature dependence of the dc conductivity is of crucial interest.

Charge transport via phonon-induced tunneling of electrons between randomly distributed localized states (variable range hopping, VRH) often follows a temperature dependence of the type

$$\sigma_{dc} \propto \exp[-(T_0/T)^\gamma], \quad (2)$$

where  $T_0$  is a parameter depending on the density of states at the Fermi level on the distance of the wave functions decay. In their respective model, Mott<sup>3</sup> and Ambegaokar, Halperin, and Langer<sup>4</sup> found  $\gamma = \frac{1}{4}$ . When Coulomb effects are important,  $\gamma \cong \frac{1}{2}$  was proposed by Efros and Shklovskii.<sup>5</sup> In order to explain the value  $\gamma \cong \frac{1}{2}$  experimentally measured in materials where Coulomb effects are believed to be negligible, Deutscher, Levy, and Souillard<sup>6</sup> included the effect of the fractal nature of conductor-insulator composites in the Mott model, yielding  $\gamma \cong \frac{3}{7}$  for CB-polymer composites. Finally, Van der Putten and co-workers<sup>7,8</sup> modified the Mott-Deutscher model for VRH by assuming Coulomb-dominated hopping between electronic states superlocalized on the fractal conducting network.

Similarly, Sheng and co-workers<sup>9,10</sup> suggested that electrical conductivity could be ascribed to tunneling through a potential barrier of varying height due to local temperature fluctuations. The thermal fluctuation induced tunneling model predicts a temperature dependence for the conductivity of the type

$$\sigma_{dc} \propto \exp[-T_1/(T + T_0)], \quad (3a)$$

where

$$T_1 = wA\varepsilon_0^2/8\pi k, \quad (3b)$$

$$T_0 = 2T_1/\pi\chi w, \quad (3c)$$

where  $\chi = \sqrt{2mV_0/\hbar^2}$  and  $\varepsilon_0 = 4V_0/ew$ , with  $m$  and  $e$  the electron mass and charge, respectively,  $V_0$  the potential bar-

TABLE I. CB content of composites.

$x_{\text{CB}}$ (%)	0.50	1.00	1.25	1.50	2.00	3.00	5.00	7.50	10.00
$w_{\text{CB}}$	0.67	1.34	1.67	2.00	2.67	3.99	6.60	9.82	12.99

rier height,  $w$  the interparticle distance (gap width), and  $A$  the area of the capacitance formed by the function.

From Eqs. (1)–(3) there is no indication that conductivity should be frequency dependent. However, as the frequency of the electric field is increased above a critical value  $f_{\xi}$ , experiments show that the conductivity increases too. This effect has been attributed to the fractal nature of the conducting network.<sup>11,12</sup> The value of the critical frequency  $f_{\xi}$  depends on the conducting concentration and on the correlation length of the system. The rise of the conductivity can be interpreted as due to the reduction of the length scanned by the charge carriers as frequency is increased. When this length is smaller or equal to the correlation length—this corresponds to a frequency  $f \geq f_{\xi}$ —the dynamics of the charge carriers is sensitive to the fractal nature of the conducting network. In this case it has been proposed that frequency and dielectric function would scale as  $\sigma \propto f^x$  and  $\varepsilon' \propto f^{-y}$ , respectively, where  $x = t/\nu(2 + \theta)$ ,  $y = s/\nu(2 + \theta)$  with  $2 + \theta = \delta_{rw}$  is the fractal dimension of the trajectory of a random walker placed on a fractal object, and  $x + y = 1$ .<sup>11,12</sup>

CB, an intrinsically semiconductor material, is widely used to modify the conductive properties of insulating polymers. The level of conductivity of the polymer-CB composite can be varied over 8–10 orders of magnitude depending on several factors. Among these we can mention CB content, specific conductive properties of the CB, surface free energy and rheological properties of the polymer, processing conditions which mainly affect the degree of CB dispersion in the polymeric matrix, etc.<sup>13</sup>

In this work, we have studied the electrical properties of a model composite system formed by a thermoplastic polymer, poly(ethyleneterephthalate) (PET), filled with different concentrations of a highly structured CB. We have determined the dc conductivity of the composites as a function of CB content and the percolation concentration  $p_c$ , and have determined the conductivity exponent  $t$ . In order to determine the conduction mechanism controlling charge transport through the compound, the temperature dependence of the conductivity has been studied and compared to existing models of the literature. Finally, we have measured the conductivity of the CB-PET composites as a function of frequency for the different CB contents. An approach is proposed to explain the frequency dependence of conductivity at high frequency, for concentrations close to the percolation concentration  $p_c$ . A procedure to construct a *master curve* based on a time-length equivalence principle is proposed to characterize the conductivity variation with frequency in conductor-insulator composites.

## II. EXPERIMENT

### A. Materials

Composites were prepared using a high molecular weight PET (Polyclear T+6, Hoechst, Germany) with a melting point of 250 °C filled with various concentrations of carbon

black (grade XE2 from Phillips Petroleum Chemicals) composite plates were prepared in two steps: (i) mixing of the two phases in order to obtain a homogeneous compound, and (ii) compression molding of the composite plates.

The preweighed molten PET pellets and CB particles were mechanically mixed in a double spindle heated mixer specifically designed for this purpose<sup>14</sup> at a rotating velocity of 50 rpm and a temperature of 275 °C during 7 min. The homogeneous compound is then removed from the heated vessel of the mixer using a metallic spatula. Compounds of CB concentration ranging from 0.5 to 10 vol. % were manufactured (cf. Table I). The CB volume fraction  $x_{\text{CB}}$  was calculated from the weight fraction  $w_{\text{CB}}$  using for PET and for CB density values of  $\rho_{\text{PET}} = 1.34$  and  $\rho_{\text{CB}} = 1.8$ , respectively. Each compound was then compression moulded into plates of  $40 \times 40 \times 2$  mm<sup>3</sup> in a hydraulic press at a pressure of 1 MPa and a temperature of 275 °C. After 5 min compression, the plates were quenched under constant pressure at a cooling rate of  $\sim 300$  °C min<sup>-1</sup> in order to yield amorphous PET.

### B. Techniques

From each plate,  $10 \times 10 \times 1$  mm<sup>3</sup> pieces were cut and polished properly with fine-grained polishing paper to eliminate any layer of pure polymer from the surface. The four-probe as well as the two-probe technique were used to measure the dc conductivity of the samples and it was found that the resistance of the contacts, prepared with silver paint, was negligible. The samples of conductivity higher than  $10^{-5}$  S cm<sup>-1</sup> were characterized using the four-probe technique with parallel electrodes on one side of the plate and the two-probe technique with the electrodes mounted on each side of the composite were applied on the samples of lower conductivity. The resistance of each sample was measured with different voltages. It was verified that the voltage-current characteristic was Ohmic in nature.

The conductivity of the various compounds was measured as a function of the frequency between  $10^2$  and  $10^6$  Hz using an impedance analyzer (HP 4192 A LF), in the temperature range between 25 and 300 K in a closed cycle He cryostat (CTI cryogenics). Each sample was first placed under vacuum at a pressure of  $7.5 \times 10^{-9}$  Pa ( $10^{-6}$  Torr) using a diffusion pump (Edwards, England) and at a temperature of 25 K. ac conductivity was then measured every 5 K between 25 and 50 K and then every 25 K up to 300 K, once the sample temperature was stabilized.

For the  $10^6$ – $10^9$ -Hz frequency range of Novocontrol coaxial line reflectometer operating with a 4191 A Hewlett-Packard Analyzer was employed. Here rectangular samples of about  $2 \times 2$  mm<sup>2</sup> were mounted at the end of a coaxial line. The conductivity perpendicular to the free surface of the sample can be calculated by measuring the reflection coefficient.<sup>15,16</sup>

Ultras-small-angle x-ray scattering measurements were performed at the BW4 beam line at HASYLAB, Hamburg. The USAXS instrument was a pin-hole collimation. The distance between the sample and detector was 12 m. The beam path was kept in vacuum and the beam size at the sample position was about  $1 \times 2$  mm<sup>2</sup>. The wavelength selected was 0.15 nm.

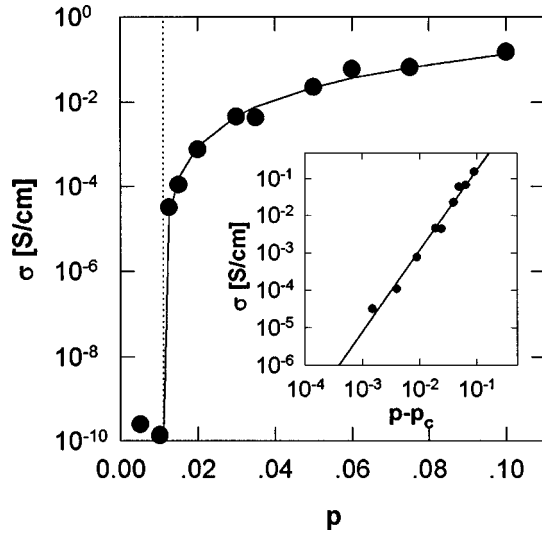


FIG. 1. Plot of  $\sigma$  as a function of carbon black volume content,  $p$  of composites; the critical concentration  $p_c$  has been determined using Eq. (1) ( $p_c = 1.1\%$ ); inset: log-log plot of  $\sigma$  as a function of  $p - p_c$ ; ( $t = 2.17$ ).

### III. RESULTS AND DISCUSSION

#### A. dc-conductivity measurements

The conductivity measured at a frequency of 1 kHz is plotted in Fig. 1 as a function of the carbon black content of the composite samples. Comparison of the conductivity measured at 1 kHz with the dc conductivity of the composite samples shows similar values. The conductivity measured at a frequency of 1 kHz will, therefore, be considered hereafter as the dc conductivity values of our samples. A stepwise increase of the conductivity from  $10^{-10}$  S  $\text{cm}^{-1}$  to values greater than  $10^{-3}$  S  $\text{cm}^{-1}$  can be observed at the critical CB volume concentration,  $p_c = 1.1\%$ . This suggests that an infinite CB percolative network has been formed through the matrix. This value for  $p_c$  is very low as compared with other types of CB-polymer systems, which are characterized by a percolation concentration ranging from 5% to over 50%.<sup>17</sup> Low values of  $p_c$  are typical of highly structured carbon black.

The dc conductivity above percolation can be analyzed in terms of the scaling law given by Eq. (1). The value of the conductivity exponent  $t$  has been determined from the slope of the resulting linear relation on a log-log scale (cf. inset in Fig. 1). A value of  $t = 2.17$  is obtained. This value, although higher, is in fair agreement with the value  $t = 2.0$  obtained by Monte Carlo studies in three dimensions<sup>2</sup> and with experimental values obtained on CB-polymer composite samples,  $t \approx 2.0 - 2.1$  (see Refs. 8 and 18, and references cited therein). Other authors, however, reported different values for  $t$ : 0.55 in  $p$ -doped Si bulk crystals,<sup>19</sup> 2.6 for UHWPE gel decorated with a conducting polymer,<sup>20</sup> 2.9 for CB-polymer composites,<sup>21</sup> and 6.27 for graphite-polyethylene composites.<sup>22</sup> As suggested by Carmona,<sup>23</sup> our slightly higher value for  $t$  than predicted by the percolation theory could be attributed to the difference between a perfect lattice of beads and the real polymer-carbon black composite. A correction term was needed to take into account the deviation from a spherical shape of the CB aggregates. Furthermore, the interaction be-

tween the carbon black and the polymer matrix is not considered by the theory. The degree of dispersion of CB and of interaction between the two phases will depend on a number of factors such as the matrix rheological properties,<sup>21</sup> the CB morphology,<sup>24</sup> or the flaw density at the interface, which is controlled by the surface energy of the two phases.<sup>25</sup> Finally, while in the percolation theory the formation of an infinite percolative network through the composite assumes physical contact between the conductive aggregates; in real composite systems, the charge carriers are allowed to cross from one conductive cluster to another with no need of any physical contact.

One type of evidence suggesting that physical contact is not required, is the very low value of the critical black concentration,  $p_c = 0.011$ , measured in our samples. Janzen<sup>26</sup> proposed for the critical black concentration an expression

$$p_c = \frac{1}{1 + \rho\nu(C_{\max}/c_{\text{crit}})}, \quad (4)$$

where  $\rho$  is the black density,  $\nu$  is the DBP absorption on the crushed CB expressed in  $\text{cm}^3 \text{g}^{-1}$ ,  $c_{\text{crit}}$  is the number of contacts of a particle with neighboring particles at the critical black concentration, and  $C_{\max}$  is the maximum number of contacts a particle can have with its neighbors ( $C = 6$ ). The absorptive capacity of CB for liquids increases with the complexity of its structure. The DBP absorption test (ASTM D 2414-90) consists of measuring the quantity of di(*n*-dibutyl) phthalate (DBP) needed to yield a sharp rise of the suspension viscosity, which is continuously measured. The DBP absorption test (DBPA) is one of the most widely used methods for measuring the level of aggregate absorptivity in carbon blacks. Based on a Monte Carlo simulation, Janzen obtained a value for  $c_{\text{crit}} = 1.5$ . Introducing our values in Eq. (4) [ $p_c = 0.011$ ,  $\rho = 2 \text{ g cm}^{-3}$ , and  $\nu = 3.7 \text{ cm}^3 \text{g}^{-1}$  (Ref. 15)] we obtain  $c_{\text{crit}} = 0.5$ , suggesting that a lower number of physical contacts are required to yield a conductive path than a physical network through the composite sample. Several mechanisms have been proposed to explain the conduction of electrons through barriers of insulating polymer separating two neighboring conductive clusters [cf. Eqs. (2) and (3)].

It can be seen that Eq. (3) for fluctuation-induced tunneling can be written in the form<sup>10</sup>

$$\sigma_{\text{dc}} \propto \exp(-2\chi_T w), \quad (5)$$

where  $\chi_T = \sqrt{2mV_{0T}/h^2}$  with  $V_{0T} = V_0 / (1 + 16\pi\chi kT/A\varepsilon_0^2)$  and the other parameters are defined in Eq. (3). Thus, the conductivity can be interpreted as a simple tunneling conductivity in which the barrier height decreases with increasing temperature. If the CB dispersion in the insulating matrix is homogeneous, the composite conductivity at a given temperature can be described by the behavior of a single tunnel junction, and the gap width can be assumed to be  $w \propto p^{-1/3}$ .<sup>27</sup> The expected linear relation between  $\ln\sigma$  and  $p^{-1/3}$  is shown in Fig. 2, suggesting that tunneling conduction may be present in our samples.

An elegant way to assess conclusively what mechanism controls the conduction of a conductor-insulator composite is to characterize a type of the temperature dependence of the dc conductivity.

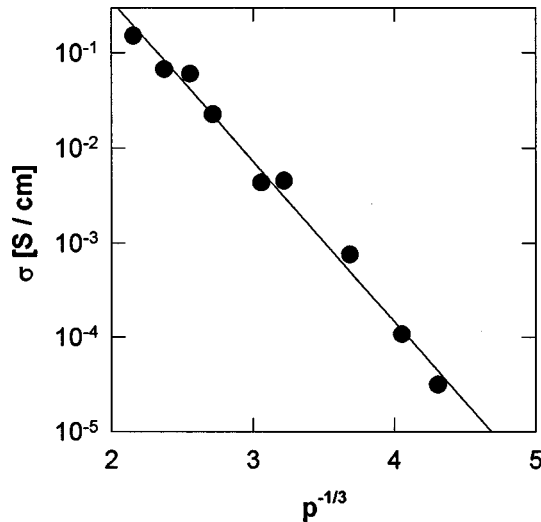


FIG. 2. Linear variation of  $\ln\sigma$  vs  $p^{-1/3}$ .

### B. Temperature dependence of conductivity

The temperature dependence of conductivity has been studied for temperatures ranging from 25 to 300 K for various CB concentrations. The resulting specific conductivity,  $\sigma/\sigma_{300\text{K}}$ , is plotted in Fig. 3 as a function of  $T^{-1}$ . To better visualize the results, each individual curve has been shifted vertically by a multiple of 0.2 unit. It can be seen that for all CB concentration, conductivity decreases with temperature down to about 45 K and then it stabilizes from 45 to 25 K. This leveling off of the conductivity at temperatures lower than 45 K, which to our knowledge is unreported in the literature, has been observed repeatedly and consistently on all the investigated samples.

The VRH model [Eq. (2)] has been compared to the experimental data for temperatures larger than 45 K yielding values for the exponent  $\gamma$  ranging from 0.1 for high CB concentrations to 0.15 for low values of  $p$ . These results are in clear disagreement with the theory that predicts values for  $\gamma$  comprised between 0.25 and 0.66 depending on the authors.<sup>4-9</sup> It can thus be concluded that the VRH mechanism

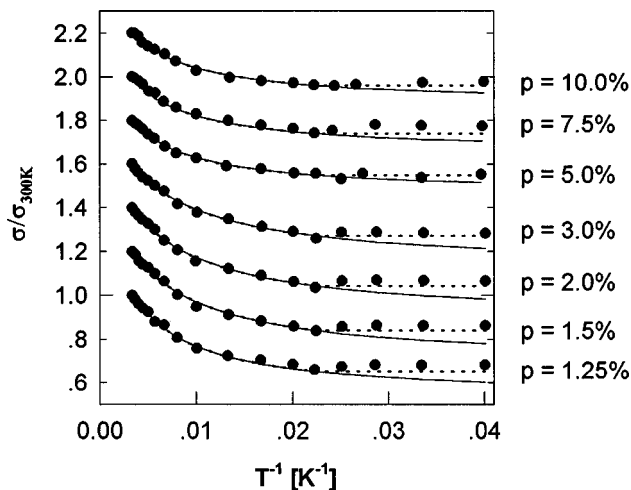


FIG. 3. Plot of  $\sigma/\sigma_{300\text{K}}$ , as a function  $T^{-1}$ . Each curve has been shifted upward by 0.2 unit from the previous one. The solid line is defined by Eq. (3) (see text).

TABLE II. Value of  $T_0$  and  $T_1$  [cf. Eq. (3)].

$p$	$T_0$ (K)	$T_1$ (K)
0.0125	196.3	210.0
0.015	131.5	134.6
0.020	125.7	127.0
0.030	122.0	109.2
0.050	249.6	187.7
0.075	221.1	161.2
0.100	216.1	155.5

cannot be used to describe the temperature dependence of the conductivity of our CB-PET composites.

Fitting of the thermal fluctuation-induced tunneling model [Eq. (3)] (cf. solid lines in Fig. 3) gives a good description of the conductivity variation with temperature for temperatures larger than 45 K. The value of the parameters  $T_0$  and  $T_1$  are listed in Table II for each curve. At lower temperatures, however, the model underestimates the actual conductivity of the samples, which becomes nearly independent of temperature. A possible explanation is that at temperatures lower than 45 K, the thermally induced barrier height fluctuations,  $\varepsilon_T = (kT/C)^{1/2}$ , where  $C$  is the capacitance formed by the junction between two CB aggregates, becomes too small. Consequently, conduction proceeds by conventional tunneling through a potential barrier.<sup>10</sup> Conventional tunneling is nearly independent of temperature<sup>28</sup> and can be described by a parabolic barrier by Eq. (5) with  $\chi_T \cong \text{const}$ . The dotted lines in Fig. 3 are defined by Eq. (3) for temperatures larger than 45 K and are constant [ $=\sigma(45\text{K})/\sigma_{300\text{K}}$ ] for lower temperatures where conventional tunneling conduction would replace fluctuation-induced tunneling.

The values for  $T_0$  and to a minor extent  $T_1$  listed in Table II are much larger than those reported by Sichel and co-workers, which are of the order of 1–5 K and 22–135 K, respectively.<sup>9,10,29</sup> These authors have studied high content (15–45 wt %) CB filled poly(vinylchloride) (PVC) of relatively poorly structured CB particles. According to Sichel, Gittelman, and Sheng,<sup>29</sup>  $T_1$  can be regarded as the energy required for an electron to cross the insulating gap between CB aggregates and  $T_0$  determines the low-temperature temperature-independent resistivity. It is clear that  $T_0$  and  $T_1$  strongly depend on the nature of the polymer, the structure of the conductive filler, and its loading. It is thus not surprising to find different values for our low filler content CB-PET composites (1.25–10 vol. %), which are characterized by a very low percolation concentration,  $p_c = 1.1$  vol. %. The high values of  $T_0$  and  $T_1$  are reflected by a lower temperature dependence of our CB-PET system than observed in the CB-PVC composites by Sichel and co-workers.

From Eqs. (3b) and (3c) one sees that the ratio  $T_1/T_0$  is proportional to the gap width  $w$ , which is approximately proportional to  $p^{-1/3}$ . If the fluctuation-induced tunneling [Eq. (3)] can be used to describe the temperature dependence of the conductivity of our CB-PET samples, then the  $T_1/T_0$  ratio as listed in Table II should be linearly related to  $p^{-1/3}$  as shown in Fig. 4.

Based on the results presented in Figs. 2–4, we can propose the following conduction mechanism for our CB-PET composites.

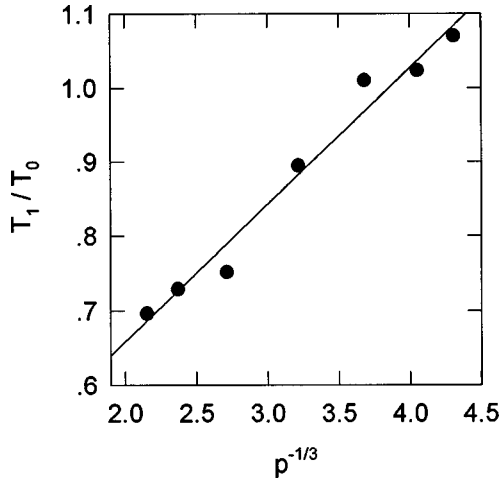


FIG. 4. Plot of  $T_1/T_0$  vs  $p^{-1/3}$ .

(i) From room temperature down to 45 K, conduction proceeds by tunneling of the charge carriers through the thermally fluctuating potential barriers,  $\varepsilon_0 \pm \varepsilon_T$ , formed by the layer of dielectric PET separating two neighboring conductive CB aggregates; this mechanism is well described by Eq. (3) with the parameters listed in Table II.

(ii) For temperatures lower than 45 K, the thermal fluctuations of the barrier height  $\varepsilon_T$  become negligible and conduction becomes temperature independent, proceeding by tunneling through a potential barrier.

### C. ac-conductivity measurements

The conductivity of CB-PET composites is plotted in Fig. 5 as a function of frequency for various CB concentrations. Two cases must be distinguished:  $p$  lower and higher than  $p_c$ , respectively. In the former case, conductivity is frequency dependent with a slope of 1.0 in a log-log scale, in agreement with the expression  $\sigma = 2\pi f \varepsilon'' \varepsilon_0$ , valid for dielectric materials, where  $\varepsilon''$  is the imaginary term of the dielectric constant of the material and  $\varepsilon_0$  is the vacuum dielectric constant. For carbon black concentrations close to and greater than  $p_c$ , conductivity is frequency independent below a critical frequency  $f_c$ —which value increases with CB content—and increases with increasing frequency above  $f_c$ , with a slope of 0.72 independent of  $p$ . It must be noted that the data measured at a frequency higher than  $10^6$  Hz (cf. Sec. II) are analytically corrected with a multiplying factor of about one order of magnitude to assure a continuity in the conductivity curves. This effect is due to the fact that there is a certain degree of anisotropy in composite materials between the value of the conductivity measured in the direction parallel ( $f < 10^6$  Hz) and perpendicular ( $f > 10^6$  Hz) to the surface of the sample.<sup>30,31</sup> The merging of the two sets of data only introduces a slight error in the value of  $f_c$ .

#### 1. Master curve

Several authors have reported experimental evidence suggesting that the  $\ln \sigma$  versus  $\ln f$  curves are parallel to each other above  $f_c$  for all CB concentration  $p$  greater and close to  $p_c$ .<sup>12,15,20</sup> Assuming that the shape of the conductivity curve is thus independent of  $p$ , and that only the value of the dc conductivity  $\sigma_{dc}$  and the critical frequency  $f_c$  depend on

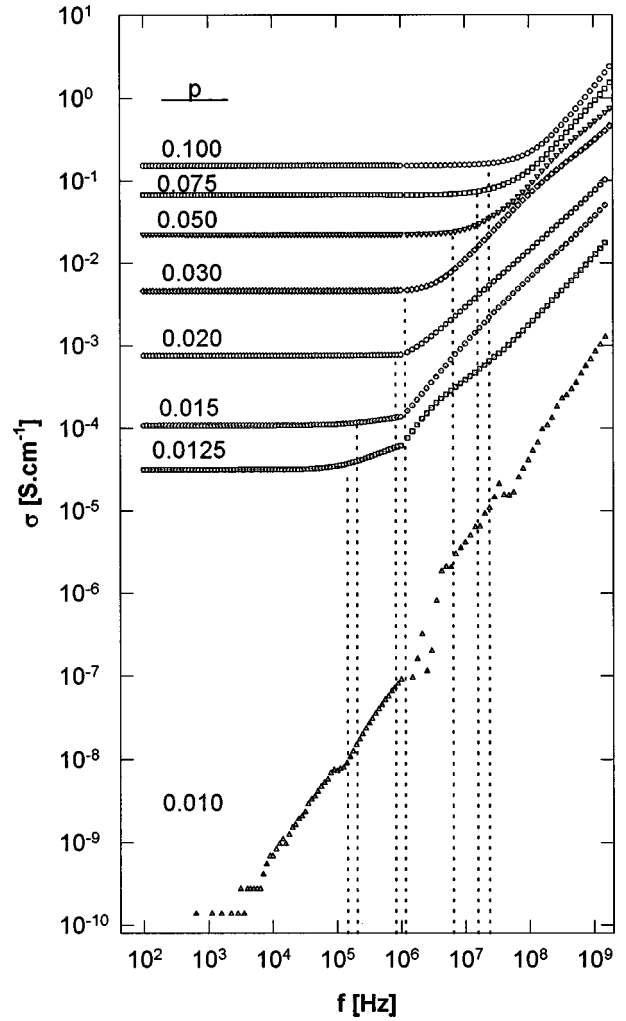


FIG. 5. Log-log plot of  $\sigma$  vs  $f$  for composites with various CB concentrations.

$p$ , it is possible to construct a master curve independent of  $p$  of the normalized conductivity,  $\sigma/\sigma_{dc}$ , as a function of  $a_p f$ , where  $a_p$  is a shift factor depending on  $p$ . This procedure consists in the superposition of the conductivity curves for different values of  $p$  on a reference curve for a CB concentration  $p_{ref}$ . The construction of a master curve is widely used to characterize the mechanical properties of viscoelastic materials such as polymers. It is based on the principle of time-temperature superposition.<sup>32</sup> Similarly, we can define a principle of time-length superposition justifying the construction of a master curve applied to the frequency dependence of the conductivity in conductor-insulator composites. The shift factor can thus be defined as

$$a_p = \frac{f_{c,ref}}{f_c}, \quad (6)$$

where  $f_{c,ref}$  is the critical frequency of the reference compound of CB concentration  $p_{ref}$ .

A  $\sigma/\sigma_{dc}$  versus  $a_p f$  master curve is plotted in Fig. 6 with our data using as a reference concentration,  $p_{ref} = 0.10$  with  $f_{c,ref} = 2.40 \times 10^7$  Hz. The value of the dc conductivity, critical frequency, and shift factor for the other curves are listed

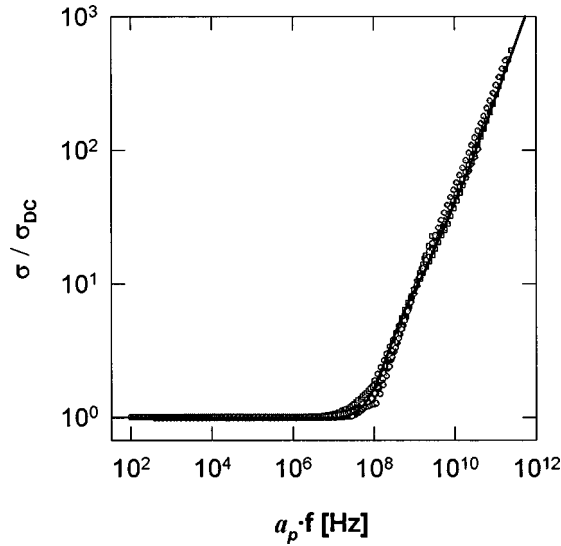


FIG. 6. Master curve,  $\sigma/\sigma_{dc}$ , as a function of  $a_p f$ . The solid line is the prediction of Eq. (9).

in Table III. The solid line is the conductivity as a function of frequency prediction of the model presented below [cf. Eq. (2)].

The interest in constructing a master curve of the type depicted in Fig. 6 lies in the fact that one can obtain the frequency-related conductivity behavior of a specific conductor-insulator composite over a frequency range much larger than the frequency range experimentally available. It also gives a clear criterion for the value of the critical frequency  $f_c$  for a CB content  $p$  relative to the value of the reference critical frequency  $f_{c,ref}$ .

Laibowitz and Gefen<sup>12</sup> used a similar approach to build up a scaling function consisting of superimposing the  $\sigma/\sigma_{dc}$  curves by multiplying the frequency by an empirically determined factor  $\xi^{2+\theta}$ . These authors found good agreement between these values and those of the correlation length  $\xi$  determined from the analysis of digitized TEM micrographs of their samples. In what follows, it will be shown that our shift factor can be expressed as  $a_p = f_{c,ref}/f_c (\xi/\xi_{ref})^{2+\theta}$ . In this way we shall show that our dimensionless shift factor is equivalent to the numerical value of their factor  $\xi^{2+\theta}$  if we state that  $\xi_{ref} \equiv 1$ .

## 2. Frequency dependence of conductivity

Various approaches have been suggested to explain the frequency dependence of conductivity at frequencies higher

TABLE III. Value of  $\sigma_{dc}$ ,  $f_c$ , and  $a_p$  for different values of  $p$ .

$p$	$\sigma_{dc}$ (S cm <sup>-1</sup> )	$f_c$ (Hz)	$a_p = f_{c,ref}/f_c$
0.0125	$3.16 \times 10^{-5}$	$1.47 \times 10^5$	163.7
0.015	$1.08 \times 10^{-4}$	$2.07 \times 10^5$	115.9
0.020	$7.60 \times 10^{-4}$	$8.25 \times 10^5$	29.1
0.030	$4.53 \times 10^{-3}$	$1.17 \times 10^6$	20.6
0.050	$2.24 \times 10^{-2}$	$6.56 \times 10^6$	3.7
0.075	$6.68 \times 10^{-2}$	$1.56 \times 10^7$	1.5
0.100 <sup>a</sup>	$1.52 \times 10^{-1}$	$2.40 \times 10^7$	1.0

<sup>a</sup> $p_{ref} = 0.10$  and  $f_{c,ref} = 2.40 \times 10^7$  Hz.

than a critical value  $f_c$  (Ref. 15 and references cited therein). An interpretation based on the theory of percolation in a fractal structure is presented here. It has been reported that, at length scales smaller than a given value defined as the *correlation length*  $\xi$ , CB-polymer composites exhibit a *fractal* structure, while the structure is defined as *Euclidian* at larger length scales.<sup>33-35</sup> The correlation length  $\xi$  is defined as the size of the largest finite-size cluster, i.e., excluding the infinite network. If we assume that a charge carrier scans a distance  $\xi$  at the frequency  $f_\xi$ , it follows that the mean distance it covers at frequencies smaller than  $f_\xi$  will be larger than  $\xi$ . Conversely, the mean distance will be smaller than  $\xi$  for frequencies larger than  $f_\xi$ . In the former case,  $f < f_\xi$ , the electrons displace themselves in an Euclidian structure over a mean distance  $L \propto f^{-1/2}$ , and only the charge carriers present in the infinite cluster contribute to the conductivity of the composite (since the largest finite-size cluster is smaller than  $L$ ). In the latter case,  $f > f_\xi$ , the electrons belonging to the infinite cluster behave similarly than at lower frequencies, while the electrons belonging to finite-size clusters, which are self-similar fractal,<sup>35-37</sup> cover a mean distance  $L \propto f^{-1/\delta_{rw}} < \xi$ , where  $\delta_{rw} = 2 + \theta$  is the fractal dimension of the trajectory of a random walker placed on a fractal object.<sup>2,11</sup> Note that the incipient infinite cluster, i.e., the infinite cluster at  $p = p_c$ , is a fractal of same dimension as the large finite clusters at the threshold. Above  $p_c$ , however, the infinite cluster is Euclidian of dimension  $d$  (see Ref. 2, p. 68). At high frequencies, an increasing number of electrons—the ones belonging to the infinite cluster and those belonging to the clusters larger than  $L \propto f^{-1/(2+\theta)}$ —contribute to conductivity which, therefore, as a result increases with increasing frequency for  $f > f_\xi$ .

The largest length scale at which the system is a self-similar fractal is the correlation length, which is related to the critical frequency as  $\xi \propto f_c^{-1/\delta_{rw}}$ . Since  $\xi \propto |p - p_c|^{-\nu}$ , the frequency  $f_\xi$  can be expressed as

$$f_\xi \propto \xi^{-\delta_{rw}} \propto |p - p_c|^{\nu \delta_{rw}}. \quad (7)$$

Introducing known values of  $\nu = 0.88$  and  $\delta_{rw} = 2 + \theta = 3.5$  for a lattice space dimension,  $d = 3$ ,<sup>11</sup> into Eq. (7) yields for the critical frequency exponent the value,  $\nu \delta_{rw} = 3.1$ .

The question arises as whether the critical frequency  $f_c$  can be associated to the correlation frequency  $f_\xi$  and follows the scaling law (7). The critical frequency  $f_c$ , measured on samples containing 1.25–10.0 vol. % CB, is plotted as a function of  $p$  in Fig. 7 and of  $p - p_c$  in a log-log scale in the inset of Fig. 7. The white circles are the values of the frequency corresponding to 5.0% increase in conductivity compared to  $\sigma_{dc}$ , i.e.,  $\sigma = (1 + \varepsilon)\sigma_{dc}$ , with  $\varepsilon = 0.05$ . The black circles are the values of  $f_c$  calculated from the shift factor  $a_p$  [Eq. (6)], used for the construction of the master curve with  $f_{c,ref}$  corresponding to 5.0 % increase in conductivity of the sample of CB content,  $p_{ref} = 0.1$ . It can be seen that the two sets of data are comparable and that they follow the scaling law (7). The value of the exponent, given by the slope of the straight line in the log-log plot, is however, equal to 1.5, i.e., considerably different from the expected value of  $\nu \delta_{rw} = 3.1$  predicted by the theory. Consequently, although closely related, the critical frequency  $f_c$  and the correlation

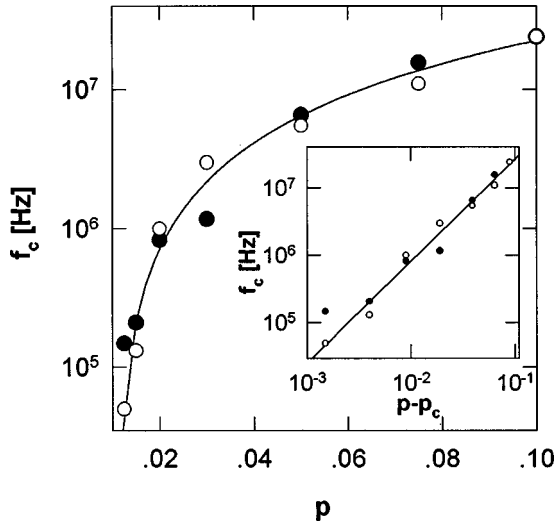


FIG. 7. Critical frequency  $f_c$  plotted as a function of CB concentration; inset: log-log plot of  $f_c$  vs  $p - p_c$ . Solid line, Eq. (7); open circles, frequency at which the conductivity is 5% higher than  $\sigma_{dc}$ ; black circles, values of  $f_c$  using Eq. (6).

frequency  $f_\xi$  cannot be conclusively amalgamated. For the system studied here,  $f_\xi \propto f_c^m$  with  $m = \nu \delta_{rw} / 1.5 \approx 2$ .

### 3. Modeling of the frequency dependence of the conductivity above $f_\xi$

In order to fully understand the rise of the conductivity with increasing frequency, the behavior of a charge carrier placed in a fractal object should be described. At length scales larger than the correlation length, the system is Euclidian and the filling density of carbon black,  $M/L^d$  [ $M$  is the mass of CB contained in a volume  $L^d$ , with  $d$  the lattice space dimension ( $d=3$ )], is independent of length scale. However, at length scales lower than  $\xi$ , the system becomes fractal and the CB filling density varies with  $L$  as  $M/L^d \propto L^{-\delta}$ , where  $\delta$  is the fractal dimension of the structure of the lattice.<sup>36-38</sup> It can be shown easily that the CB concentration  $p \propto M/L^d$ . It follows that, if an electron is located in a noninfinite cluster of a composite of CB volume fraction  $p$  under an alternative electric field of frequency  $f > f_\xi$ , it will "see" the cluster it belongs to as a fractal object of CB concentration,  $p_f \propto L^{-\delta} > p$ . Since the mean distance scanned by the electron follows a scaling law of the type  $L \propto f_{rw}^{-1/\delta}$ , the CB concentration  $p_f$  actually perceived by the charge carrier will vary with frequency as

$$p_f \propto f^{\delta/\delta_{rw}}. \quad (8)$$

Theory predicts  $\delta_{rw} = 3.5$  and that the fractal dimension  $\delta$  is given by  $\delta = d - \beta/\nu \approx 2.53$  for  $d = 3$ .<sup>38</sup> In order to verify this value we have carried ultrasmall-angle x-ray scattering experiments in the samples as a function of CB content. Figure 8 illustrates the plot of  $\ln I$  versus  $\ln S$ ,  $S$  being the scattering vector, for typical values below and above the percolation limit. The experimental data for pure PET were taken from Ref. 39. From the slope of the scattering curves we estimate a fractal dimension  $\delta \approx 2.5 \pm 0.2$  in good agreement with the above theoretical predictions.<sup>34</sup> Viswanathan and Heaney<sup>37</sup>

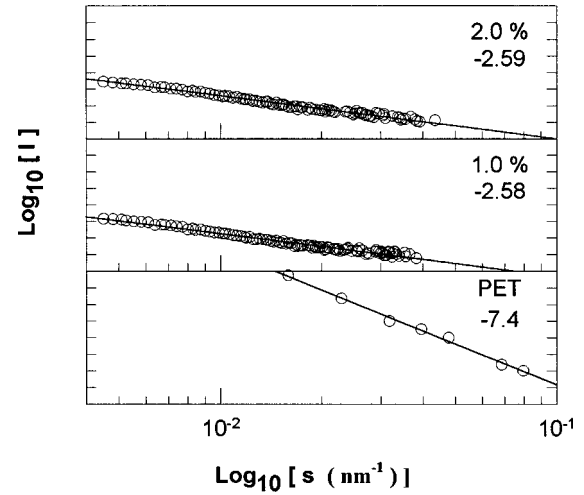


FIG. 8. Double logarithmic plot of x-ray scattered intensity of CB-PET composites vs scattering vector.

characterized experimentally the fractal dimension of percolation networks and reported the values  $\delta = 1.9 \pm 0.4$  at small length scales and  $2.6 \pm 0.6$ , yielding  $\delta/\delta_{rw} \approx 0.7 \pm 0.3$ .

The two effects responsible for the frequency related conductivity behavior described above can be summarized as follows.

(i) Below the critical frequency  $f_\xi$ , only the electrons belonging to the infinite network contribute to conductivity, which is independent of frequency and is described by Eq. (1).

(ii) Above the critical frequency  $f_\xi$ , conductivity increases with frequency due to the additional contribution of the electrons belonging to the clusters of finite-size  $R$  larger than the distance  $L \propto f^{-1/\delta_{rw}}$  scanned by the electrons, i.e.,  $L \leq R \leq \xi$ ; these perceive a carbon black concentration  $p_f > p$  [cf. Eq. (8)], due to the fractal nature of the finite-size clusters.

The additional contribution to conductivity of the electrons belonging to finite-size fractal clusters can be accounted for by expressing Eq. (1) as

$$\sigma \propto [p + p_f \mathbf{P}_L (1 - \mathbf{P}_\infty) - p_c]^t, \quad (9a)$$

$$\sigma \propto [p \times g(f) - p_c]^t, \quad (9b)$$

with

$$g(f) = 1 + \mathbf{P}_L (1 - \mathbf{P}_\infty) \frac{C}{p} f^{\delta/\delta_{rw}}, \quad (9c)$$

where  $C$  is a proportionality constant for Eq. (8), and  $\mathbf{P}_\infty \propto (p - p_c)^\beta$  and  $\mathbf{P}_L$  are the probability that a CB particle belongs to the infinite cluster and the probability that a CB particle belongs to a cluster larger than  $L$ , respectively. The product  $\mathbf{P}_L (1 - \mathbf{P}_\infty)$  is thus the probability that a CB particle belongs to a cluster of size  $R$ , comprised between  $L$  and  $\xi$ . It can be interpreted as the cumulative size distribution of the noninfinite CB aggregates as a function of the frequency; it is null below  $f_\xi$  ( $R > \xi$ , is the infinite cluster) and increases with the frequency above  $f_\xi$ , tending asymptotically towards



$(1 - \mathbf{P}_\infty)$  at high frequencies ( $R \rightarrow 0$ ). At this stage no reference giving an expression for  $\mathbf{P}_L$  is known to the authors. Assuming an exponential aggregate size distribution as a function of the frequency of the type  $F(f) = \alpha \exp[-\alpha(f - f_\xi)]$ , the cumulative size distribution function can be written as  $\mathbf{P}_L = 1 - \exp[-\alpha(f - f_\xi)]$ , which fulfills the requirements stated above. By introducing this expression for  $\mathbf{P}_L$  in Eq. (9) we obtain an expression describing the frequency-related behavior of the composite conductivity using two fitting parameters,  $C$  and  $\alpha$ . All the other parameters in Eq. (9) can either be measured independently on the samples ( $p, p_c, t, f_\xi$ ), or can be predicted by the percolation theory ( $\delta_{rw}, \delta, \nu, \beta, \mathbf{P}_\infty$ ). It must be kept in mind, however, that the latter values are valid for an ideal fractal system only while the behavior of a real system may deviate considerably from theory.

Figure 9 shows the prediction of the frequency dependence of  $p_f$  [Eq. (8)],  $\mathbf{P}_L$ ,  $g(f)$  [Eq. (9c)], and  $\sigma$  [Eq. (9)] for  $p = 0.0125$ ; the latter plot is compared to the experimental conductivity data (open circles) showing excellent fit. The model prediction is also presented in the master curve in Fig. 6 (solid line). The value of the constant  $C$  in Eq. (9c) and  $\alpha$  defining  $\mathbf{P}_L$  is  $(5.6/f_c) \times 10^{-4}$  and  $8.0 \times 10^{-7}$ , respectively, and the exponent  $\delta/\delta_{rw} = 0.42$  is within the error band obtained with the values of  $\delta$  proposed by Viswanathan and Heaney.<sup>37</sup>

#### IV. CONCLUSIONS

The highly structured CB-filled PET composite system presented in this work is characterized by a very low percolation threshold  $p_c = 0.011$  and a conductivity exponent  $t = 2.17$ . The analysis of the temperature dependence of the electrical conductivity of our sample suggests that for temperatures dependence of the electrical conductivity of our samples suggests that for temperatures larger than 45 K conduction proceeds by the tunneling of the charge carriers through the thermally induced fluctuating potential barrier formed by the thin polymer layer separating two neighboring CB aggregates. At lower temperatures, conductivity becomes temperature independent as expected from conventional tunneling.

An approach has been proposed for the description of the frequency dependence of the CB-polymer composites. It is based on the growing number of CB clusters contributing to conductivity with increasing frequency, together with the description of the evolution of the CB concentration with frequency in a fractal structure. The model has shown to fit very well our experimental data, which have been presented in the form of a master curve. The construction of a master curve to describe the frequency-dependent conductivity of a composite is based on the principle of time-length superposition. The master curve allows one to derive the frequency-related

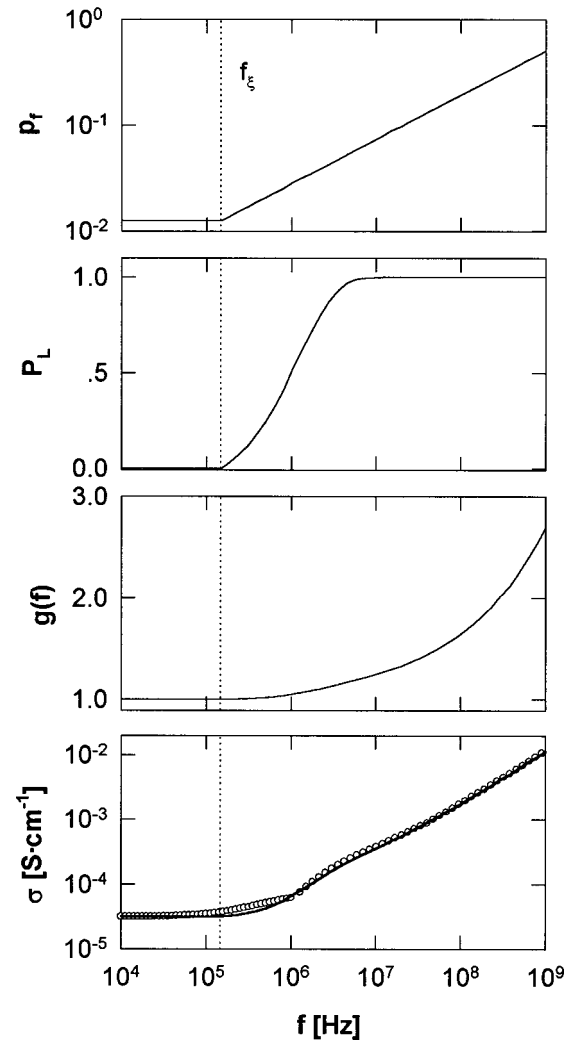


FIG. 9. Frequency dependence for the 0.0125 CB filled composite of  $p_f$  [Eq. (8)],  $\mathbf{P}_L$ ,  $g(f)$  [Eq. (9c)], and conductivity [Eq. (9)]. Solid line, model prediction; open circles, experimental data.

conductivity behavior of a specific conductor-insulator composite over a frequency range much larger than the frequency range experimentally available.

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<sup>1</sup>S. Kirkpatrick, *Rev. Mod. Phys.* **45**, 574 (1973).

<sup>2</sup>D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1987), p. 89.

<sup>3</sup>N. F. Mott, *Philos. Mag.* **19**, 835 (1969).

<sup>4</sup>V. Ambegaokar, B. I. Halperin, and J. S. Langer, *Phys. Rev. B* **4**, 2612 (1971).

<sup>5</sup>A. L. Efros and B. I. Shklovskii, *J. Phys. C* **8**, 49 (1975).

- <sup>6</sup>G. Deutscher, Y. Lévy, and B. Souillard, *Europhys. Lett.* **4**, 577 (1987).
- <sup>7</sup>D. Van der Putten, J. T. Moonen, H. B. Brom, J. C. M. Brokken-Zijp, and M. A. J. Michels, *Phys. Rev. Lett.* **69**, 494 (1992).
- <sup>8</sup>D. Van der Putten, J. C. M. Brokken-Zijp, and M. A. J. Michels, *Synth. Met.* **55-57**, 5057 (1993).
- <sup>9</sup>P. Sheng, E. K. Sichel, and J. I. Gittleman, *Phys. Rev. Lett.* **40**, 1197 (1978).
- <sup>10</sup>E. K. Sichel, J. I. Gittleman, and P. Sheng, in *Carbon Black Polymer Composites*, edited by E. K. Sichel (Dekker, New York, 1982), Chap. 2, p. 51.
- <sup>11</sup>Y. Gefen, A. Aharony, and S. Alexander, *Phys. Rev. Lett.* **50**, 77 (1983).
- <sup>12</sup>R. B. Laibowitz and Y. Gefen, *Phys. Rev. Lett.* **53**, 380 (1984).
- <sup>13</sup>J. M. Funt, W. L. Sifleet, and M. Tommé, in *Carbon Black, Science and Technology*, edited by J.-B. Donnet, R. C. Bansal, and M.-J. Wang (Dekker, New York, 1993), Chap. 12, p. 3889.
- <sup>14</sup>M. Connor, Spanish Patent No. ES 9600752 (1996).
- <sup>15</sup>T. A. Ezquerra, F. Kremer, and G. Wegner, in *Dielectric Properties of Heterogeneous Materials PIER 6*, edited by A. Priou (Elsevier, New York, 1992), Chap. 7, p. 273.
- <sup>16</sup>F. Kremer, D. Boese, G. Meier, and E. W. Fisher, *Prog. Colloid Polym. Sci.* **80**, 129 (1989).
- <sup>17</sup>XE2 Extra Conductive Carbon Black, Phillips Petroleum Chemicals (1985), p. 51.
- <sup>18</sup>M. A. J. Michels, J. C. M. Brokken-Zijp, W. M. Groenewoud, and A. Knoester, *Physica A* **157**, 529 (1989).
- <sup>19</sup>T. F. Rosenbaum, K. Andres, G. A. Thomas, and R. N. Bhatt, *Phys. Rev. Lett.* **45**, 1723 (1980).
- <sup>20</sup>A. Fizazi, J. Moulton, K. Pakbaz, S. D. D. V. Rughooputh, P. Smith, and A. J. Heeger, *Phys. Rev. Lett.* **64**, 2180 (1990).
- <sup>21</sup>M. Heaney, *Phys. Rev. B* **52**, 12 477 (1995).
- <sup>22</sup>T. A. Ezquerra, M. Kulescza, C. Santa Cruz, and F. J. Baltá Calleja, *Adv. Mater.* **2**, 597 (1990).
- <sup>23</sup>F. Carmona, *Ann. Chim. (Paris)* **13**, 395 (1988).
- <sup>24</sup>N. Probst, in *Carbon Black, Science and Technology* (Ref. 13), Chap. 8, p. 271.
- <sup>25</sup>M. Connor, S. Toll, and J.-A. E. Månson, *Composites Manufacturing* **6**, 289 (1995).
- <sup>26</sup>J. Janzen, *J. Appl. Phys.* **46**, 966 (1975).
- <sup>27</sup>T. A. Ezquerra, M. Kulescza, and F. J. Baltá Calleja, *Synth. Met.* **41-43**, 915 (1991).
- <sup>28</sup>L. Solymar and D. Walsh, *Lectures on the Electrical Properties of Materials*, 3rd ed. (Oxford University, London, 1984), p. 112.
- <sup>29</sup>E. K. Sichel, J. I. Gittleman, and P. Sheng, *Phys. Rev. B* **18**, 5712 (1978).
- <sup>30</sup>F. J. Baltá Calleja, T. A. Ezquerra, D. R. Rueda, and J. Alonso-López, *J. Mater. Sci. Lett.* **3**, 165 (1984).
- <sup>31</sup>T. A. Ezquerra, F. J. Baltá Calleja, and J. Plans, *J. Mater. Res.* **1**, 510 (1986).
- <sup>32</sup>C. Oudet, *Polymères: Structure et Propriétés* (Masson, Paris, 1993), p. 170.
- <sup>33</sup>B. Mandelbrot, *Les Fractals* (Flammarion, Paris, 1975).
- <sup>34</sup>J. E. Martin and A. J. Hurd, *J. Appl. Crystallogr.* **20**, 61 (1987).
- <sup>35</sup>A. Le Méhauté, M. Gerspacher, and C. Tricot, in *Carbon Black, Science and Technology* (Ref. 13), Chap. 7, p. 245.
- <sup>36</sup>B. H. Kaye, *A Random Walk through Fractals* (VCH, Weinheim, 1989).
- <sup>37</sup>R. Viswanathan and M. B. Heaney, *Phys. Rev. Lett.* **75**, 4433 (1995).
- <sup>38</sup>A. Kapitulnik, A. Aharony, G. Deutscher, and D. Stauffer, *J. Phys. A* **16**, L269 (1983).
- <sup>39</sup>M. Imai, K. Mori, T. Mizukami, K. Kaji, and T. Kanaya, *Polymer* **33**, 4451 (1992).