Fractal analysis of the percolation network in epoxy-polypyrrole composites

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The macroscopic dc conductivity and structure of epoxy-polypyrrole composites are studied as a function of the polypyrrole amount and interpreted with percolation concepts. The fractal dimension D of the infinite cluster is found to increase substantially from 1.25 to 1.88 with the conducting filler concentration. An original representation of the conducting backbone is obtained using image analysis techniques and suggests a finitely ramified structure. The Minkowski dimension of the backbone is determined to be an excellent approximation of the fractal dimension D_B and it is seen to increase as the polypyrrole concentration increases while the fractal dimension of the elastic backbone is found to keep the constant value $D_E = 1.13$. These results are compared to scaling percolation theory. [S0163-1829(97)00933-8]

I. INTRODUCTION

In recent years, considerable interest on conducting polymer composites has developed[1–3] due to many potential applications in technology and especially due to the process ability and the electrical and mechanical properties of this class of materials. Theoretical and applied research has been carried out in order to understand and to improve (i) the synthesis of conducting polymers or conducting polymer composites, (ii) the morphology of these materials and the structure of the conducting polymer network in the composites, and finally (iii) the electrical transport mechanisms in such materials. Basically much of the recent investigations can be summarized as the study of three key parameters, which are the nature, structure, and conductivity of conducting polymers or composites. The nature of the conducting polymer and the matrix influences the metallic state formation, the structure of the conducting network, and the conduction mechanisms in the composite. The morphology[4] plays an important role in the electrical properties as it has been observed that quantum-mechanical tunneling occurs more or less efficiently as a function of the geometrical parameters. While the structure or property relationships of such a class of material are not fully understood, it seems important to characterize clearly their morphology before investigating their optical or electrical behavior. The real morphology of conducting polymers or composites appears to be a very complex arrangement[5] of aggregates with different size and shape distributions. In many cases the aggregates are extremely irregular and exhibit a self-similarity when the observation scale is changed. These features correspond basically to the fractal concepts[6] and the conducting materials may be characterized by a fractal dimension D. The fractal geometry as well as the mathematical or experimental methods used to determine the corresponding fractal dimension have to be examined carefully as the irregular structure of the polymer or the conducting composite would strongly affect its properties.

In this paper, the topological one-dimensional cluster boundaries are characterized by a fractal dimension D in epoxy-polypyrrole composites. As the conducting filler amount increases and leads to changes in the finite and infinite cluster morphology, we discuss the evolution of D, which intuitively quantifies the irregularities and the degree to which the boundaries ''fill the planes'' with $2 \geqslant D \geqslant 1$. We also propose an original representation of the backbone at different filler concentrations in the vicinity of the percolation threshold, extracted from direct microscopy imaging of the conducting network. These representations of the real backbone in the composites allow us to have a better comprehension of the network structure and to determine D_B.

II. THEORY

The static and dynamic properties of the percolation network have been the object of many studies in the past ten years.[7] Much of the current interest in the properties of disordered conductor-insulator composites such as carbon-black–polymer composites,[8,9] blends of polyaniline nanoparticles with conventional polymers,[2] as well as Monte Carlo simulations[10] indicate that the infinite cluster acquires a fractal geometry[6] over a wide range of length scales above a microscopic lattice distance a and below the percolation correlation length ξ. The morphology of the primary filler aggregates,[11] which influences the shape of the infinite cluster at the percolation threshold, presents, in general, a complex irregular geometry that cannot be described by Euclidean geometry concepts. Therefore the incipient infinite cluster, whose formation in the host matrix depends on many parameters,[12] e.g., the nature of the filler, the filler shape, the filler-matrix interactions, the mixing and the processing techniques, has an internal self-similar fractal geometry, quantified by D.

The infinite cluster may be decomposed into different categories, that do not present the same properties. The dead-end branches or ''danglings'' represent the most important part of the percolation cluster. They can be detached from the infinite cluster by cutting a single bond and do not carry any current. The effective part of the infinite cluster which carries the current is known as the backbone.[13] In disordered conductor-insulator composites just above the percolation threshold, the vast majority of the conducting filler is situ-

ated in finite-size clusters that coexist with the percolation network and in the dangling bonds that are attached to the infinite cluster. Only a small part of the conducting filler, which forms the backbone, contributes to the conduction of the current through the composite.

The backbone exhibits a fractal character and provides an acceptable idea of the general structure of the percolation network. The study of the infinite cluster geometry and especially the backbone geometry is clearly the first step to understanding the properties of composites such as the macroscopic conductivity. The elastic backbone, introduced by Herrmann *et al.*[14] as a fractal object, can be extracted from the backbone by the so-called burning method. The fractal dimension of the backbone and the elastic backbone give valuable information on the structure and irregularities of the effective conducting network and the main paths that are responsible for conduction in disordered media.

Near the percolation threshold, the network can be characterized by many percolation parameters which obey scaling laws, independently of the network structure and its microscopic details. Hence the fraction of bonds in the infinite cluster $P(p)$, the backbone fraction $P_b(p)$, the correlation length $\xi(p)$, or the macroscopic conductivity $\sigma(p)$ can be described by different statistical power laws with the corresponding universal exponents β, β_B, ν, and t, respectively, whose values depend only on the topological dimension of the system. The geometrical exponents β, β_B, and ν have been determined[7] as exact results or through numerical estimations for different dimensionalities ($d=2,3,\ldots,6$) of the system, and they were found to be dependent[10] on the fractal dimensions of the network as shown in Eqs. (1a) and (1b), where D is the fractal dimension of the infinite cluster, D_B is the fractal dimension of the backbone, and d is the topological dimension of the system:

$$D=d-\frac{\beta}{\nu}, \tag{1a}$$

$$D_B=d-\frac{\beta_B}{\nu}. \tag{1b}$$

In an ordinary lattice, the transport exponent t can also be related[7] to the critical geometric exponents and the conductivity exponent ξ as follows:

$$t=(d-2)\nu+\zeta, \tag{2}$$

where ζ satisfies the scaling law $\sigma \propto L^{-\zeta}$ between the conductivity σ and the size of the network L. With the introduction of the fractal model and the Einstein diffusion equation,[15] a relation has been established between t, the geometric exponents β and ν, and D_w, the fractal dimension of the random walk (or ''diffusion'' exponent):

$$t=(D_w-2)\nu+\beta. \tag{3}$$

Alexander and Orbach[15] proposed a simplified equation based on the assumption that the spectral dimension $D_s=2D/D_w$ equals the constant value $\frac{4}{3}$. They then obtained the ''super-universality'' relation

$$t=\frac{1}{2}[\nu(3d-4)-\beta]. \tag{4}$$

In a more general manner and for a large number of composite samples the exponent t can be easily determined through conductivity measurements and its values given in the literature seem to vary considerably as was recently summarized and discussed by Heaney.[16] It was found to be either in good agreement with the percolation theory prediction $t\approx 2$, obtained from Monte Carlo simulations as a critical result, or much higher than this theoretical value ($t>2$) leading to a nonuniversal behavior of the electrical conductivity.

It is rather difficult to determine experimentally such quantities as $P(p)$, $P_B(p)$, or $\xi(p)$ in order to discuss their evolution when p increases and to compare their values with the statistical concept of the percolation. The conductivity and the fractal dimension of the real percolating network are the two main experimental parameters which can be determined from conducting composites. Microscopy imaging (transmission electronic microscopy, transmission optical microscopy) and scattering techniques (small-angle neutrons, x-ray, light) allow the direct determination of the fractal dimension of clusters or percolating networks. However, the fractal dimension of the backbone cannot easily be characterized through experimental techniques. The different values[14] of D_B proposed in the literature are generally calculated using Eq. (1b) or deduced from Monte Carlo,[10] random, or nonrandom[17] fractal models as it is rather difficult to observe the backbone in real disordered systems. We should notice that geometrical feature of discontinuous films,[18] including the infinite cluster as well as the backbone, have been analyzed through transmission electron micrograph. This work which analyzed the structure of the percolation network and the backbone in real materials led to the conclusion that the metal-insulator transition in such films belongs to the same universality class as the idealized percolation problem.

III. EXPERIMENT

In this study, the samples are composed of conducting polypyrrole (PPy) and epoxy resin. PPy was synthesized[19] chemically in an aqueous solution of $FeCl_3$ (Aldrich) with an initial molar ratio iron III/pyrrole of 2.2 and 1.Naphtalene sulfonic acid (Aldrich) was used as a codopant. The grapelike structure PPy macromolecules were mixed with the epoxy polymer diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow Chemicals) with isophorone diamine (IPD, Hüls) and 3,3,5-trimethylcyclohexylamine (TMCA, Janssen Chemica). Different mixtures were prepared with PPy volume fractions ranging from 0 to 0.10. The compounds were degassed and cured for 2 h at 80 °C and 4 h at 140 °C. Square samples of nominal length 40 nm and thickness 1.7 mm were obtained at each concentration. Both sides of the sample were metallized with a 75 nm aluminum coating. The contact resistance was determined by complex impedance spectroscopy over a large frequency range [30 MHz;0.1 Hz] and was found to be negligible ($\rho<10\ \Omega$ cm) compared to the bulk resistivity of the sample ($\rho>10^4\ \Omega$ cm). Due to the relatively high level of the sample resistivity, the perpendicular conductivity measurement was made using two parallel

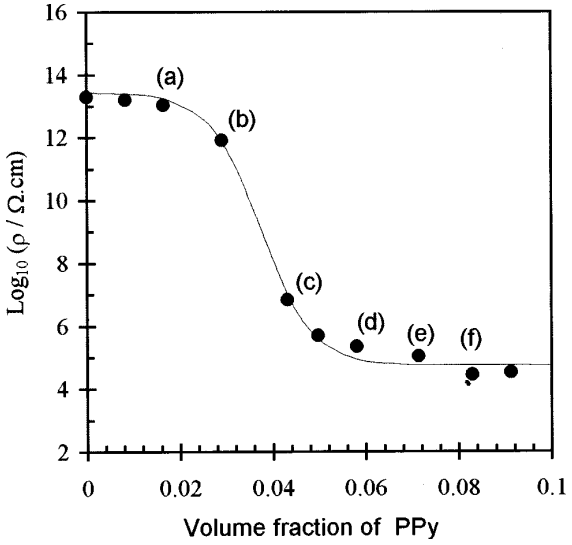

FIG. 1. Evolution of the dc resistivity ρ versus volume fraction of polypyrrole in epoxy-PPy composites. The labels near six of the experimental plots correspond to the samples whose conducting network is presented in Fig. 2.

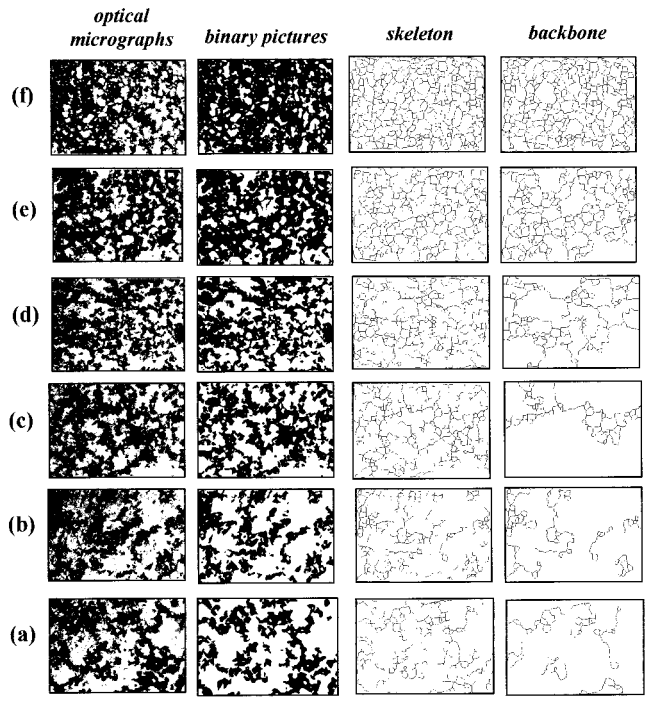

FIG. 2. General image analysis of the PPy-epoxy composites including optical micrographs, binary PPy network pictures, and the skeleton and backbone of epoxy-PPy composites with volume fractions of polypyrrole (a) $p=0.017$, (b) $p=0.029$, (c) $p=0.043$, (d) $p=0.058$, (e) $p=0.071$, and (f) $p=0.083$, respectively.

electrodes. Transmission optical micrographs were obtained from about ten 20 μm thick samples at each filler concentration, giving a good view of the macroscopic network in two dimensions. The thickness is assumed to be negligible with regards to the analyzed surface (720×480 $\mu\mathrm{m}^2$), an aspect which will be discussed in the next section.

IV. RESULTS AND DISCUSSION

The resistivity behavior of the epoxy-PPy composites is shown in a decimal logarithmic scale in Fig. 1 as a function of the filler volume fraction. The electrical resistivity presents a sharp insulator-to-conductor transition at $p_c\approx0.035$ that obviously corresponds to the formation of the infinite cluster in the three-dimensional (3D) composite. The conductivity critical exponent value was found to be $t=3.0$, which is in perfect agreement with the theoretical mean-field value,[16] but this will not be discussed here. For six composites that contain different volume concentrations of PPy below and above the percolation threshold, we propose to study the geometry of the macroscopic conducting network. Each gray-leveled image corresponding to a transmission optical micrograph was converted into a binary picture through a careful thresholding transformation. The skeleton of the conducting network was extracted from the binary picture using series of erosion transformations with a C^8 square structuring element. A representation of the backbone was drawn by smoothing out the danglings and the finite clusters in the skeleton of the filler network. This image analysis was repeated for about ten different samples at each filler concentration. As the samples exhibit a rather similar fractal structure, only part of the results are shown in Fig. 2 as a representative example. It should be noticed that the backbone which is obtained with such a process cannot be considered as the real backbone of the percolating network, as it may change slightly depending on the thresholding level of the experimental picture or the structural element used in the skeleton determination. Nevertheless this image analysis technique provides valuable information on the structure and the geometry of the backbone in the experimental conductor-insulator composite. Below the percolation threshold, at $p=0.017$ [Fig. 2(a)] and $p=0.029$ [Fig. 2(b)], the binary pictures of the epoxy-PPy composite in Fig. 2 exhibit a large distribution of finite clusters characterized by fractal outlines. In the vicinity of the percolation transition as seen in Fig. 2(c), a conducting path occurs whose length of 720 μm is much greater than the correlation length ξ that was calculated to be around 100 μm. The backbone representation near p_c presents a finitely ramified structure with internal quasi-one-dimensional links as was earlier suggested.[17] The backbone structure can be more or less reflected by the schematic ''link-nodes-blobs'' models[20] in which dense regions called blobs of diameter in the order of ξ are linked by quasi-one-dimensional chains of length $L\approx\xi$. However, the quasi-one-dimensional links that play an important role in the elastic backbone geometry, seem not to extend self-similarity over a wide length scale range. The order of ramification R of the backbone satisfies $2<R<\infty$ reflecting a finitely ramified structure. R was determined as the smallest number of interactions that must be cut to isolate a point P randomly chosen from the structure. The average order of ramification $\overline{R}$, which was calculated for 200 random points chosen from ten different samples at each concentration, was found to increase from 3.10 to 9.5 as the filler concentration increases from 0.043 to 0.083.

In order to quantify the structure of the polypyrrole network and its backbone, we determine the fractal dimension of the composite binary pictures and the Minkowski dimension of the skeleton and the backbone. In the first case, the

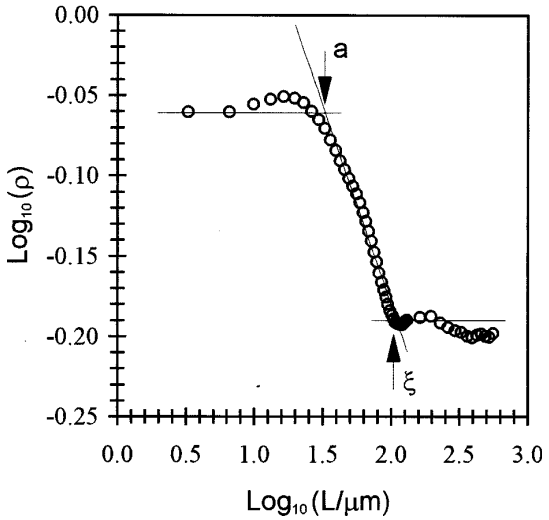

FIG. 3. A typical example of the decimal log-log average density plot $\rho(L)=M(L)/L^2$ versus the length scale L for the conducting network of the epoxy-PPy composite at the filler volume concentration $p=0.058$.

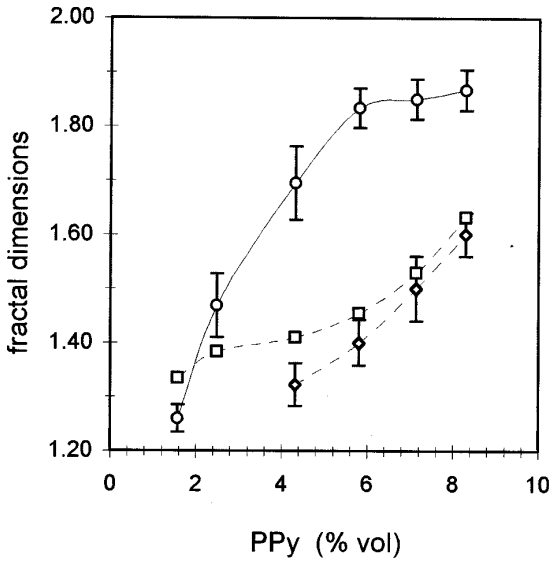

FIG. 4. Evolution of the fractal dimension of the conducting network (○) as a function of the filler volume and the Minkowski-fractal dimensions of the skeleton (□) and the backbone (◇) versus the PPy concentration.

successive squares method[8–10] was applied at 100 different initial sites of three samples at each filler concentration. The density of the conductive network $\rho(L)=M(L)/L^2$ was averaged and plotted as a function of the square size L at each PPy volume fraction. In Fig. 3, the plot of $\rho(L)$ at $p=0.058$ presents three typical regions separated by two characteristic quantities, i.e., the microscopic length a that is close to the image analysis resolution, and the correlation length ξ over which the network becomes macroscopically homogeneous at $p>p_c$. For $a<L<\xi$ the density of the network was found to fit a fractal behavior characterized by the power law $\rho(L)\propto L^{D-d}$.

It should be noticed that the thickness of our samples (20 μm) is slightly lower than the microscopic length a and much lower than the correlation length ξ for all the filler amounts. Therefore the calculation of the fractal dimension is assumed not to be significantly influenced by the thickness of the sample (below a certain value a), which is close to the image analysis resolution. A larger thickness would obviously influence the fitted value of the slope presented in Fig. 3 for $a<L<\xi$, but no reference exists in this field that clearly analyzes the influence of the sample thickness or the projected area for the two-dimensional characterization of the three-dimensional structures. Below the microscopic value a the contribution of the sample thickness on the fractal dimension calculation is believed to be negligible as is the contribution of the thresholding procedure.[8]

The fractal dimension D of the network was determined at each PPy concentration in Fig. 4 and is seen not to keep a constant value with the PPy amount. D increases from 1.25 to 1.70 in the vicinity of the percolation threshold, then it reaches a constant value about 1.88. At a microscopic length scale a constant value of the fractal dimension $D\approx 1.80$ was calculated from transmission electron micrographs in different areas of the infinite cluster of epoxy-PPy composites. One of the transmission electron micrographs is given in Fig. 5 as an example and the fractal structure of the PPy network can be clearly seen. At this microscopic length scale, the fractal dimension of the PPy infinite cluster does not change significantly when the filler volume concentration increases. Hence the fractal aspect of the infinite cluster has to be reconsidered as different values of D can be determined depending on the observation length scale and filler amount. When the infinite cluster mass increases, from a macroscopic point of view, its geometry changes slightly, becoming more irregular and leading to an increase of its fractal dimension although its microscopic structure seems to stay more or less

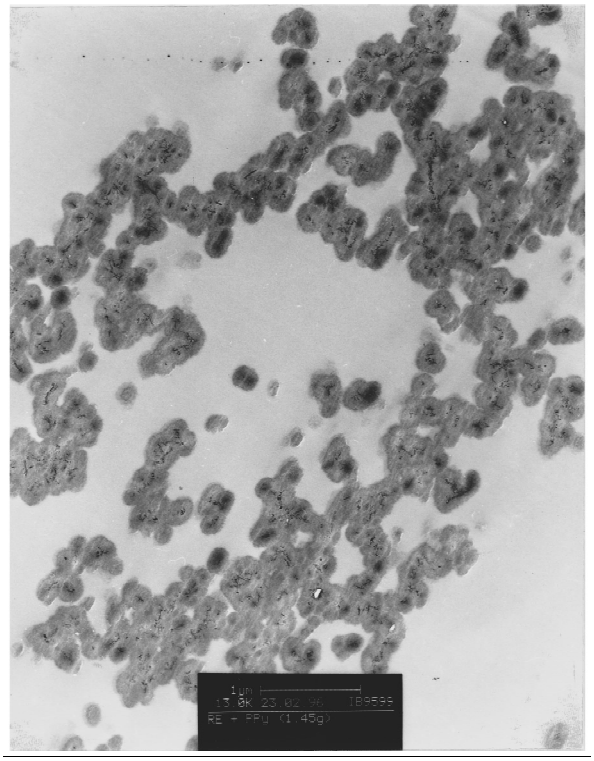

FIG. 5. Transmission electron micrograph of a part of the infinite cluster in an epoxy-PPy composite ($p=0.058$).

the same. These results show the limit of the self-similarity in real random fractal materials. They also suggest a continuous increase of the fractal dimension with the filler concentration. That is not in contradiction with the theoretical studies[7,10] which generally predict three distinct values corresponding to the three percolation regimes, i.e., $D=1.56$ below p_c, $D=1.89$ at $p=p_c$, and $D=2$ above p_c. However, the results in Fig. 4 suggest a significative evolution of D as the material is filled with the conducting polymer. Wiswanathan and Heaney[8] proposed that $D=2.6\pm0.6$ in three-dimensional disordered carbon-black–polyethylene composites at intermediate length scales. It seems very difficult to compare this result to the scaling theory prediction $D=2.53$ ($d=3$) as the experimental value can vary from 2 to 3.2 (we note that $D>3$ would not be consistent for a dimensionality $d=3$). We could analyze the experimental results in Fig. 4 from a statistical point of view, and propose a mean value $D=1.67\pm0.26$ as the fractal dimension of the epoxy-PPy composites for different percolation regimes. However, our observations and calculations seem to indicate that the fractal dimension of the system does not keep a constant value as the infinite cluster grows. Andrade *et al.*[3] recently proposed a percolation model for a conducting polymer in terms of a random resistor network. The plot of the conducting backbone which is extracted from the network at the percolation threshold, is very similar to our representation in real conducting polymer composites, exhibiting a finitely ramified structure with quasi-one-dimensional internal links. The critical exponent for the conductivity ζ was studied, corresponding to the scaling law $\sigma\propto L^{-\zeta}$, where σ and L are the conductivity and the size of the system, respectively. Andrade *et al.* showed that ζ can change significantly as a function of the specified polymer length chain and the conductivity mode in the polymer. Quantitatively a deviation of 13% between a calculated value $\zeta=1.10\pm0.02$ and the theoretical prediction $\zeta=0.9745$ can be observed. The variation in the critical exponent and the fact that the fractal dimensions of the conducting network do not equal the discrete values predicted by the percolation theory suggest that all conducting polymer materials cannot be fully described by the percolation scaling theory.

In the case of the skeleton and backbone picture, we calculated the Minkowski dimension[21] which can be considered as a morphological parameter and gives a good estimation of the fractal dimension. An excellent correlation was found between the Minkowski dimension D' and the fractal dimension D for many deterministic fractal curves. For example, we calculated $D'=1.49$ for the well-known Von Koch curve[6] whose fractal dimension is $D=1.5$. The Minkowski dimension $D'(X)$ of a set of lines X can be calculated using successive dilations of the set with balls of fixed radius d. The area of the dilated set is labeled (X_d) and the Minkowski dimension is given by

$$D'(X)=\lim_{d\to 0}\left[2-\frac{\ln[\mathcal{A}(X_d)]}{\ln(d)}\right]. \tag{5}$$

Each digitalized picture can be considered as a square grid of pixels, so we choose the square C^8 as the structuring element rather than the ball, which is very convenient for our calculation and fairly acceptable from a mathematical point of view.[21] The square side can be written $d=\delta n$ where δ is the pixel width and n is an entire number corresponding to the dilation step. The plots of $\{\ln[\mathcal{A}(X_n)]-\ln(n)\}$ as a function of $\ln(n)$ present a linear section of slope α for every backbone and skeleton which allows the Minkowski dimension to be calculated as $D'=2-\alpha$ and plotted in Fig. 4 versus the PPy filler amount. D' is seen to increase above p_c from about 1.30 to 1.55–1.6. This behavior of the Minkowski-fractal dimension corresponds to the decrease of the quasi-linear paths in the backbone structure as the PPy concentration increases. This result depends obviously on the methods used to obtain the skeleton and the backbone representation, however, it must be pointed out that it describes an experimental material structure, whereas most of the previous results are calculated from Eq. (1b) or arise from mathematical simulations. Herrmann *et al.*[14] have summarized the different values proposed in the literature for the backbone fractal dimension that was found to vary from 1.55 in the case of Monte Carlo simulations or PSGR to 1.80 in the case of Serie's expansion for the dimensionality $d=2$. The mean value $D_B=1.6$ is commonly accepted for the backbone at the percolation threshold. However, it has not been established that D_B should keep a constant value when the filler concentration increases and we attempt to demonstrate that this is not the case. Indeed the Minkowski dimension of the backbone increases slightly in the range [1.32–1.6] as a function of the PPy amount, above the percolation threshold. This result may be related to the evolution of the backbone which becomes more and more ramified as the mass of the infinite cluster increases, as seen in Fig. 2. On the other hand, the Minkowski or fractal dimension of the backbone increases with an increase of the order of ramification, resulting from the formation of new blobs and nodes in the percolating cluster. Hence, we have to reexamine the definition of the backbone which seems not to exhibit a constant structure but whose arrangement changes with the filler concentration, becoming more and more irregular. In such physical fractals it should be noticed that the self-similarity seems limited or very difficult to investigate.

The elastic backbone which is defined as the most direct path for the current through the network, may be easily determined and extracted from the backbone representations using a very simple algorithm. We calculated the fractal dimension of many elastic backbones that were obtained as mentioned above and we found a constant value $D_E=1.127\pm0.006$. This value is in good agreement with the theory[7,14] which proposes $D_E=1.10$–1.13. Therefore, we may consider that the structure of the shortest path in the infinite cluster does not change significantly when the filler amount is increased. At the percolation threshold p_c, a set of conducting paths occurs in the materials, in which one or many shortest paths called the elastic backbone can be found. As the infinite cluster grows for $p>p_c$, its external structure and its backbone change, becoming more irregular and complicated, but the shortest path keeps roughly the same geometry that can be represented by an irregular line whose fractal dimension is about 1.13. One possible interpretation is that the fractal dimension of the finite-size clusters does not equal the fractal dimension of the percolating infinite cluster. Hence, during the aggregation process, finite-size clusters contribute to the formation of the infinite cluster

leading to a change in the fractal dimension of the latter and that of the backbone, however, the elastic backbone geometry is not affected. Wiswanathan and Heaney[8] have explicitly shown the presence of two fractal structures in conducting polymers composites. Recently Andriaanse *et al.*[22] have demonstrated the existence of two scaling regimes in similar materials, dominated by the infinite percolating cluster and the finite-size cluster, respectively. Another possible interpretation is the universal feature of the elastic backbone in such conducting polymer composites. This would suggest that the fractal dimension of the elastic backbone would be a critical value although the geometric or the transport properties of the percolating network are not fully described by the percolation models.

V. CONCLUSION

In this article we have shown a fundamental difference in the properties of the percolation networks resulting from theoretical models or Monte Carlo simulations and the percolation networks observed in random heterogeneous materials such as the epoxy-polypyrrole composites of this study. In the standard discrete lattice percolation model, an increase of p above the percolation threshold does not lead to an increase of the irregularity of the network, which is composed of elementary defined objects, such as squares, cubes, and balls. In this case, the infinite cluster and the backbone exhibit a fractal structure quantified by a constant fractal dimension and characterized by a self-similarity over a wide range of length scales. This behavior has been frequently observed in various experimental samples[2,8,17] whose electrical or geometrical properties, such as the correlation length or the fractal dimension, are perfectly described with percolation models and critical exponents. In our conducting polymer composites, the fractal dimensions of the network and the backbone were found to increase with the conducting filler amount. The conducting network arrangement depends upon many experimental parameters that are usually not considered in theoretical models and the infinite cluster structure is clearly seen to change when the filler concentration increases. It seems that a continuous change in the fractal dimension value of the infinite cluster results from the continuous change in its structure as the filler amount is increased. This behavior suggests that the fractal dimension of the infinite cluster D and the fractal dimension of the backbone D_B may not be considered as universal values as minor changes in the filler concentration p around the percolation threshold p_c would lead to major changes in the fractal dimension value. However the fractal dimension of the elastic backbone seems to keep a constant value $D_E = 1.13$ in good agreement with the scaling percolation theory.

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