Critical behavior of the electrical transport properties in a tunneling-percolation system

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We report the confirmation of the tunneling-percolation model predictions by measurements on carbon black-polymer composites, in which the carbon black is of ''low structure.'' From the measurements we have determined the critical resistance exponent t, and the ratio κ/t, where κ is the critical relative resistance-noise exponent. The results found are $t=6.4$ and $\kappa/t=0.5$. It is shown that these simultaneous new t and κ/t results are consistent only with the predictions of a tunneling-percolation model. It is argued that previously reported values of t and κ/t in similar systems, which deviate from the theoretical predictions of this model, are due to nonrandom dispersion of the particles in these systems. [S0163-1829(99)02316-4]

Since the predictions of nonuniversal behaviors of the resistance[1–3] and relative resistance noise[4] in percolation systems there have been numerous experimental works in which the critical exponents that characterize these behaviors have been measured.[5,6] In particular, the critical-resistance exponent t and the ratio κ/t, where κ is the critical exponent of the relative resistance noise, have been determined. Of the systems studied there are many that can be described as made of conducting particles embedded in an insulating matrix. In one large group of systems the particles touch or overlap ''geometrically'',[6] while in the other group they only ''touch electrically''. As representatives of the first group of systems, one can consider granular metals[7] (in which the conduction, above the percolation threshold, takes place in a network made of fused-together metal particles) and various mixtures of conducting and insulating particles.[5,8] The random void (RV) and inverted random void (IRV) models have explained the nonuniversal behavior of such systems.[1,2,4,6] In the systems in which the particles do not touch ''geometrically'' but do ''touch electrically'' the measured finite macroscopic conductivity must be attributed to the existence of interparticle tunneling. In particular, in the many composites of conducting particles embedded in a continuous polymer matrix[9–22] the interparticle electrical contacts are due to tunneling[9] and the conduction network forms a well-defined percolation-like network.[3,10,12] We call such systems tunneling-percolation systems. It was found[11,12] that in some carbon black-polymer composites, the values of t are larger than the values predicted by nontunneling models[2] ($t=2.0$ or $t=2.5$) and are even larger[3,19] than the value predicted by the mean-field[11] model ($t=3$). These observations can be explained[3] by a tunneling-percolation model (hereafter, TPM) but they are also consistent with recent results[6] of the extension of the nontunneling (RV and IRV) models. Hence, another independent evidence for the validity of the TPM in the carbon black-polymer composites is called for.

A complementary transport property that can be used for testing the validity of the TPM is the relative resistance noise for which, as we show below, the TPM predictions are very different from those of the nontunneling models. In fact, quite a few results of such measurements on the above composites have been reported,[14–16,21] but no general theory to account for these results has been proposed. In particular, a recently measured[21] $\kappa/t=0.5$ value cannot be accounted for by any previous nontunneling model.[4,6] Since agreement between the measured t and κ (or κ/t) values with theoretical predictions can provide strong support for, or disprove, the applicability of the TPM,[3] and since there was no previous explanation for the diversity of already reported values of t and κ/t, it appears important to carry out the corresponding simultaneous measurements and compare their results with the theoretical predictions. Following the above considerations we have carried out such measurements on carbon black-polymer composites where the carbon black conducting particles are of ''low structure''[22] (see below). We have then extended our tunneling-percolation theory for the resistance[3] to predict the critical behavior of the relative resistance noise and we have compared the experimental results with these predictions.

For the sample preparation, we have utilized our previously described procedure[23] except that, in the present paper we also compared results obtained for four different types of carbon black (CB) powders. Briefly, the samples are composed of a mixture of a commercial CB and a polymer. The CB resistivity is of the order of $10^{-2}\,\Omega$cm while that of the polymer is of the order of $10^{18}\,\Omega$cm. Many different mixtures were prepared with a wide range of CB volume %, denoted here by v. Each compound was compression molded into thin slabs. The composition of the composite was determined by thermogravimetric analysis.[22] To retest our suggestion[3] that the ''lower'' the ''structure'' of the carbon black (i.e., the closer the structure of the carbon black particles to compact spheres[22]) the better the description of

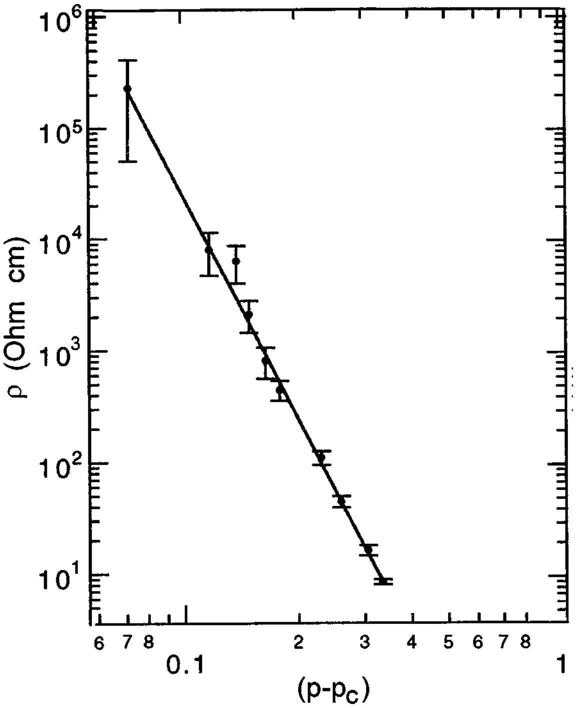

FIG. 1. The measured dependence of the resistivity on the proximity to the percolation threshold, in our (low structure) CB-polymer composite.

the system by the TPM (Ref. 3) (in which the particles are assumed to be randomly dispersed and well removed from each other), we have checked the degree of the ''structure'' [22] using the well-known dibutylphtholate (DBP) test.[22] This common semiquantitative measure of the structure consists of finding the ratio of the DBP-oil volume that can be adsorbed to 100 g of CB particles. The larger this value the larger the deviation from spherical-compact particles, i.e., the ''higher'' the ''structure'' of the CB. For the four types of carbon blacks studied, the lowest ''structure'' was found to have a DBP of 43 cm^3/100 g while the highest had a DBP of 180 cm^3/100 g.

The four-probe measurements of the resistivity ρ have confirmed the trend we found[3] previously on another series of composites (made with different types of carbon black), i.e., that the lower the ''structure,'' the higher the percolation threshold (i.e., the critical CB volume %, v_c) and the larger the value of t. Following our suggestion[3] that the higher these values the better the description of the system by the TPM, we concentrate in this letter on the composites of the ''lowest structure,'' i.e., on those of a DBP value of 43 cm^3/100 g and an average primary particle size of 320 nm.[22] The resistivity of the corresponding composites as a function of the proximity to the percolation threshold p-p_c is shown in Fig. 1. In this paper, we define the experimental p and p_c as $v/(1-v_c)$ and $v_c/(1-v_c)$, respectively. The best fit to that data, shown in Fig. 1, yields a v_c of 39±2% and a t value of 6.4±0.7. For completeness and in agreement with the above-mentioned suggestion,[3,24] let us mention that for all other composites $v_c \leqslant 20.3\%$ and $t \leqslant 3.1$. As far as we know, the present $t=6.4$ value is the largest ever reported on CB-polymer composites and thus (according to the above argument of Ref. 3), this composite is the best available system for testing the predictions of our TPM.

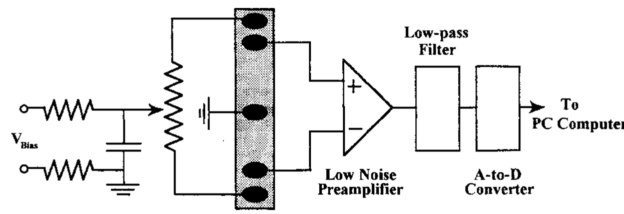

FIG. 2. A schematic of the sample configuration and the experimental setup used for the present noise-power measurements.

For the relative resistance noise measurements we have cut $14\times5\times0.25\,mm^3$ strips of the composites. The samples and the experimental setup used for these measurements are illustrated in Fig. 2. Five contacts were attached by first scribing the surface of the sample and then applying a layer of a silver paste. The noise measurements were carried out then in a standard five-probe configuration. Such a setup reduces bias and contact noise. Assuming a single bulk $1/f$ noise in the resistivity fluctuations the noise power of the voltage fluctuations of the 10–100 Hz range is given by $N = \tau\int_{10}^{100}[S_V(f)/V^2]df$, where τ is the volume of one arm of the sample, V is the voltage across one arm, f[Hz] is the frequency, and $S_V(f)$ is the power spectral density of the voltage noise. As noted in previous works,[5,21] the determination of κ/t is much more accurate than the determination of κ since no derivation of, or an assumption on, the value of the percolation threshold is necessary. Hence, we present our results in Fig. 3 in terms of the resistivity dependence of N. The best fit of the data to a power law dependence is found to yield a value of $\kappa/t=0.5\pm0.1$. We will show below that while the latter value *cannot* be explained by the nontunneling models[2,4,6] *it is* in excellent agreement with the predictions of the following TPM.

Let us assume then that we have a random distribution of spheres (of radius b) the average distance between which is a $[=2(3n/4\pi)^{1/3}]$, where n is the volume density of the spheres. Under these conditions the distribution function of the distances between two adjacent particles r is expected

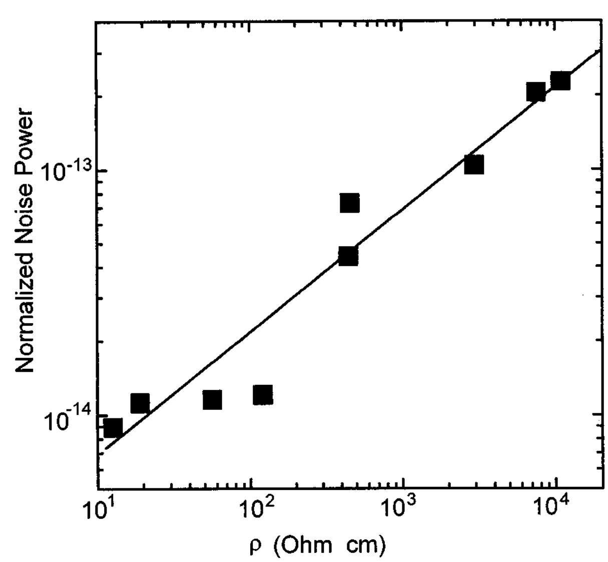

FIG. 3. The measured dependence of the relative resistance-noise power on the resistivity in our (low structure) CB-polymer composites.

to be peaked around $r=a$. This distribution function, known[25] as the Hertz distribution, is given by: $(3r^2/a^3)\exp[-(r/a)^3]$. Since for the present purpose of the tunneling between relatively far-apart spheres, the important feature of the distribution is its exponential decrease with r, and *since we would like to use as a simple analytic function as possible, which still retains this feature, we adopt*[3] *a ''simplified Hertz distribution''* of the form $(1/a)\exp(-r/a)$. For this distribution the probability that r is larger than some r_0, is simply $\exp(-r_0/a)$. Applying the nodes-links-blobs (NLB) approach,[25,26] as in all previous theories,[2–6] we now use the fact that in a link of the NLB model there are L_1 singly connected resistors. Hence, the probability that in the link there will be no resistor for which $r>r_0$, is $[1-\exp(-r_0/a)]^{L_1}=\exp[-L_1\exp(-r_0/a)]$. The typical largest distance between two particles in the link r_0 is given then by: $L_1\exp(-r_0/a)\approx 1$.

The resistance of a resistor controlled by tunneling is $R_1\exp[(r-2b)/d]$, where R_1 is a constant (or, at most, a very weak function of r), and d is the characteristic tunneling distance of the system. Hence, the average resistance of a resistor in the link is: $\langle R\rangle_{L_1}=R_1\exp(-2b/d)\{\int_{2b}^{r_0}\exp[(-r/a)(1-a/d)]dr\}$. Considering the above relation between r_0 and L_1 we see that $\langle R\rangle_{L_1}$ diverges as $L_1^{-(1-a/d)}$. Since the links' resistance R_ξ in the NLB model is given by $L_1\langle R\rangle_{L_1}$, the additional term to that of the universal behavior (i.e., to that of an L_1 independent $\langle R\rangle_{L_1}$), in the present NLB-TPM, is simply $L_1^{(a/d-1)}$. Using the well-known[25,26] relation $L_1\propto(p-p_c)^{-1}$, we have that the resistivity critical exponent t which is defined by $\rho\propto(p-p_c)^{-t}$, will be given by

$$t=t_{\mathrm{un}}+(a/d-1), \tag{1}$$

where t_{un} is the critical exponent in the universal case.

We note in passing that in the case where the CB particles have a ''high structure,'' i.e., when the particles are elongated and/or of irregular shapes (such as in composites, where the interparticle distance is determined by interparticle friction, or entanglement) one can assume[3] a constant distance r_m-2b between the surfaces of two adjacent particles and thus a universal behavior. Hence, the expectation (fulfilled by previous[3] and present results, see above) that the ''higher'' the ''structure'' of the CB the closer the value of t to that of t_{un}. Correspondingly for composites such as the one investigated here, where $a>2b\gg d$, the larger the t, the closer the expected particle distribution to that of the Hertz distribution.

Turning to the behavior of the electrical noise in our TPM we consider, as in the theory of the nontunneling systems,[4,6] the single resistor that has the resistance R_ξ. For this ''link resistor'' we have to find the corresponding distance r_1, i.e., the distance r_1 such that $R_\xi=R_1\exp[(r_1-2b)/d]$. Since we found above that for our ''simplified'' Hertz distribution $R_\xi\propto L_1\langle R\rangle_{L_1}=L_1^{(a/d)}$, we can conclude now that r_1 is simply determined by the relation: $L_1\propto\exp[(r_1-2b)/a]$. Now, for the relative resistance noise $\delta R^2/R^2$ of a resistor element of resistance R we know[27] that the ratio of the squared fluctuations to the squared resistance is inversely proportional to the number of elements in the resistor. Hence, $\delta R^2/R^2\propto 1/\phi$, where ϕ is the volume of the resistor. The corresponding average of δR^2 over the L_1 resistors is given then by $\langle\delta R^2\rangle_{L_1}\propto\int_0^{r_1}(R^2/\phi)\exp(-r/a)dr$. In the present case, since the interparticle volume ϕ has, at most, a power law dependence on r, this dependence can be neglected. Considering the above relation between r_1 and L_1 we find then that the nonuniversal part of the fluctuations is well approximated by $\langle\delta R^2\rangle_{L_1}\propto L_1^{(2a/d-1)}$. Using this result and the above nonuniversal part of $\langle R\rangle_{L_1}$, i.e., $L_1^{(a/d-1)}$, we find that the nonuniversal contribution to $\langle\delta R^2\rangle_{L_1}/\langle R\rangle_{L_1}^2$ *is simply* L_1. Hence, we conclude that the critical exponent of the relative resistance noise [defined by $S_R\propto(p-p_c)^{-\kappa}$] is $\kappa=\kappa_{\mathrm{un}}+1$, where κ_{un} is its universal value. Numerically, this means that since in three dimensional systems[4,25] $t_{\mathrm{un}}=2$ and $\kappa_{\mathrm{un}}=1.56$, our predicted κ/t ratio for the TPM is given by

$$\kappa/t=(\kappa_{\mathrm{un}}+1)/[t_{\mathrm{un}}+(a/d)-1]=2.56/(1+a/d). \tag{2}$$

In the other extreme case of a constant r_m-2b, both $\langle\delta R^2\rangle_{L_1}$ and $\langle R\rangle_{L_1}^2$ are constants and thus both t and κ have their universal values so that $\kappa/t=\kappa_{\mathrm{un}}/t_{\mathrm{un}}=0.78$. This case of a single-value resistors in the system, cannot be distinguished from the nontunneling universal case. Hence, in composites where the CB is of ''high structure'' a percolation independent evidence (such as in Refs. 9 or 18) for the existence of interparticle tunneling is necessary. If the extended RV and IRV models are considered,[6] our measured $t=6.4$ value would imply that κ/t is 1.86, if the RV model applies, and 3.0, if the IRV model applies. In no case of these models can the value of κ/t be less than 0.78. We see then that the present experimental results of, $t=6.4\gg t_{\mathrm{un}}$ and $\kappa/t=0.5$ are consistent *only* with our TPM predictions [Eqs. (1) and (2)].

The above reconfirmation of the trend that the lower CB structure yields a higher p_c and a larger t, indicates that the particle distribution in our system is relatively close to that of the randomlike Hertz distribution. We note of course that in view of the simplifications used in the model and the significant deviation of the experimental system from that of the ideal Hertz distribution, the a/d values that can be deduced from the measurement of t may be quite different from the actual a/d values in the experimental system. For example, for the composite at hand, one would expect[22] a priori an a/d value of the order of 130 ($2b/d\approx 6500/50$) rather than 5.4 that can be deduced from the measured value of $t=6.4$. This large deviation can be explained, however, within the framework of the above model since apparently the present, experimentally studied system is far from having an ideal Hertz distribution. We may view then the present experimental system as an ''intermediate case'' between that of a constant distance between the surfaces of two adjacent particles, and that of the ideal Hertz distribution. Hence, our experimental system is too far from the ideal Hertz case, to yield the ''actual'' high-t values, but is close enough to the ideal case, to yield κ/t values that are lower than the universal values. *Hence, the a/d value that one may deduce from the measured t is more of a measure of the proximity to the Hertz distribution than the actual a/d ratio.* We have to stress then that the experimental system under study, while being still far from the ideal ''Hertz system'' is the best approximation to such a system, among the available carbon-black polymer composites. *The important point is, however, that the value we measure for κ/t is beyond the expectation from all other available nonuniversal percolation theories*.[6] This makes the present TPM the only available explanation of the experimental results presented here. We further note that the TPM is based on two well-established features of the system, i.e., the tunneling between the carbon black particles[9] and the larger dispersion with the lower structure of these particles,[22] as manifested by the higher p_c found here and pointed out previously.[3] The approximation we made here is not designed then to yield exact values for the exponents but rather the values of their limits. Indeed, the experimental results are accounted for by these limits and are clearly distinguishable from those of previous theories.[6] We can conclude then that the t values, which lie in the interval between the universal value (as measured in some works[13,18,20]), and the previous[3,11,12,14,19] and present, high nonuniversal values, are consistent with our[3] explanation of the deviation of the measured system from the random-uniform Hertz distribution. In particular, suppose that during the molding process the particles are pushed against each other so that there is no polymer layer between them. In that case, there is a percolation network that consists of particles that in practice ''touch geometrically''[24] so that it is better described by the IRV models[2,6] than by our TPM. This seems to be the case in Refs. 14 and 15. In another study,[21] it was found that by increasing the applied voltage, a transition from a $\kappa/t=1.7$ value (which is consistent with the extended IRV model[6]) to a $\kappa/t=0.5$ value (which is in agreement only with the present TPM) has been observed. This observation suggests that the effect of increasing the voltage is to switch the conduction from that of a voltage-independent IRV-like network to that of a voltage-dependent tunnelinglike network.

In conclusion, combined measurements of the resistance and relative resistance noise and the corresponding theoretical analysis of the tunneling-percolation network indicate clearly the existence of the tunneling-percolation scenario. Comparison with other data and other models suggested in the literature makes us conclude that for some systems the above scenario applies while in others the extended inverted random void model is a better description.

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