Measurement and interpretation of nonuniversal critical exponents in disordered conductor–insulator composites

Michael B. Heaney

Research and Development Division, Raychem Corporation, 300 Constitution Drive, Menlo Park, California 94025-1164

The dc resistivity of carbon-black–polymer composites as a function of carbon-black concentration has been measured and fit to a power law, yielding a conductivity critical exponent $t = 2.9 \pm 0.1$. This value is in excellent agreement with the mean-field value $t = 3$. The sample-to-sample variations in resistivity at each concentration also show power-law behavior. If interpreted as due to correlation length fluctuations, these data yield a correlation-length critical exponent $\nu = 0.51 \pm 0.02$. This value is in excellent agreement with the mean-field value $\nu = \frac{1}{2}$. These results suggest that nonuniversal ($t \neq 2$) transport behavior in this and similar composites is caused by the composite being outside the universal scaling regime and in the mean-field regime.

Disordered conductor–insulator composites exhibit a variety of incompletely understood phenomena,[1] some of which have important commercial applications.[2] One such phenomenon is the transition of the bulk composite from insulator to conductor as the concentration (volume fraction) of the conductive component is increased above a threshold value. This transition is fairly sharp and is believed to be a continuum percolation phase transition.

In analogy with lattice percolation, it was suggested[3] that the resistivity of these composites would obey a power law of the form $\rho \sim (p - p_c)^{-t}$ near the transition, where ρ is the bulk resistivity of the composite, p is the concentration of the conductive component, p_c is the percolation threshold concentration, and t is a universal exponent. The currently accepted theoretical value for the universal conductivity critical exponent for three-dimensional lattices is $t = 2.0$.[4] This universal behavior is expected to occur only in a "scaling regime" sufficiently close to the transition.

Several groups[5] have measured conductivity critical exponents in good agreement with $t = 2.0$ for various disordered conductor–insulator composites. Others[6] have measured conductivity critical exponents greater than 2.0 in both similar and different types of disordered conductor–insulator composites. This seems to indicate that transport behavior in continuum percolation can be nonuniversal. The nonuniversal ($t \neq 2.0$) behavior has been interpreted as a fundamental difference between continuum percolation and lattice percolation.[7] Nonuniversal behavior has been theoretically demonstrated for an anomalous diverging distribution of resistances between the conductive elements,[8] for a quantum tunneling model of conduction between the conductive elements in a composite,[9] and for a "Swiss-cheese model," where spherical voids are introduced in a continuous conductor.[10] These continuum percolation theories predict a nonuniversal conductivity critical exponent $t \geq 2$ (Refs. 8 and 9) or $t \leq 2.5$ (Ref. 10) for three-dimensional systems.

This paper presents experimental data on carbon-black–polymer composites which show a conductivity critical exponent $t = 2.9 \pm 0.1$. This value is in excellent agreement with the expected mean-field value $t = 3$ and in clear disagreement with the expected universal scaling value $t = 2.0$. The sample-to-sample resistivity fluctuations also show power-law behavior and may be interpreted as mean-field behavior with a correlation-length critical exponent $\nu = 0.51 \pm 0.02$. This value is in excellent agreement with the expected mean-field value $\nu = \frac{1}{2}$ and in clear disagreement with the expected universal scaling value $\nu = 0.88$. However, since the fitted formula in the latter case is only a proportionality, it is not possible to say conclusively that the resistivity fluctuation data are caused by mean-field behavior. These results suggest that nonuniversal transport behavior occurs because the composite is outside the universal scaling regime and in the mean-field regime.

The samples are composed of commercial carbon-black and polymer. The carbon-black resistivity is of order 10^{-2} Ω cm and the polymer resistivity is of order 10^{18} Ω cm. The carbon-black consists of 200 nm mean diameter aggregates composed of smaller fused semispherical particles of 80 nm mean diameter. Carbon-black aggregates are known to form larger agglomerates when melt compounded with polymer. The largest structures visible in a transmission electron micrograph which may be agglomerates are about 1 μm in diameter. The polymer is high density polyethylene with a melting point of 130 °C. The preweighed carbon-black and powdered polymer are mechanically mixed and then melt compounded in a Moriyama mixer at 150 °C. Fourteen different mixtures were made, with carbon-black concentrations ranging from about 0.18 to 0.40. Each compound is compression molded into three slabs of nominal thickness 0.025 cm and then cut into samples of nominal width 1.25 cm and nominal length 14 cm, giving a total of about 30 samples at each concentration. The concentration of carbon-black in the composite is determined by thermogravimetric analysis of four pieces near the edges of the three slabs.

Electrical contact is made with silver paint. A comparison of two- and four-point measurements showed that contact resistance can be significant, especially for composites close to the percolation threshold. Therefore, all measurements are made with a four-point technique. All measurements are made in the linear (Ohmic) range of the resistance versus

voltage characteristic and show no significant time dependence. All measurements are made at room temperature.

The dc resistivity ρ versus carbon-black concentration p is shown in Fig. 1. The resistivity error bars $\pm \delta\rho$ represent the standard deviations of the sample-to-sample fluctuations in resistivity at each concentration. The concentration error bars $\pm \delta p$ represent the standard deviations of the four thermogravimetric measurements made at each concentration. The data have been fit to the power law

$$\rho = \rho_0[(p-p_c)/(1-p_c)]^{-t}, \qquad (1)$$

where ρ_0 is the resistivity scale factor, p is the concentration of carbon-black, p_c is the percolation threshold concentration, and t is the conductivity critical exponent. The weighted nonlinear least-squares fit gives a conductivity critical exponent $t = 2.9 \pm 0.1$, a percolation threshold $p_c = 0.170 \pm 0.001$, and a resistivity scale factor $\rho_0 = 15 \pm 2$ mΩ cm. The reduced χ square for the fit is 1.3, indicating a good fit.

I fabricated and measured the dc resistivity of several additional composites with carbon-black concentrations ranging from 0 to 0.1676. The dc resistivities of these composites were all greater than 10^{15} Ω cm. This verifies the actual occurrence of a percolation threshold. Combined with the lowest concentration shown in Fig. 1 this also provides an independent determination of the range of possible values for the percolation threshold: $0.1676 < p_c < 0.1789$.

There are some possible trends in Fig. 1 suggesting the resistivity values may be starting to approach a limiting resistivity at low concentrations. Such saturation of the resistivity would occur on these axes if the estimate of p_c obtained from the fit were larger than the true p_c, and could imply a falsely low value for the fitted conductivity critical exponent. I examined this possibility by refitting the data holding $p_c = 0.1676$, the lower bound from direct measurement. This yielded a conductivity critical exponent $t = 3.07 \pm 0.05$, not significantly different than the original value. I also replotted the data using various smaller values of p_c down to values known from direct measurement to be less than the true p_c. If saturation of the resistivity were occurring, the trend in the data should disappear at some value in this range. This does not occur, suggesting the apparent trends in Fig. 1 are experimental error and are not due to saturation.

The fitted value for the conductivity critical exponent $t = 2.9 \pm 0.1$ is in excellent agreement with the theoretical mean-field value $t = 3$ and in clear disagreement with the theoretical universal scaling value $t = 2.0$.[4]

The fitted value 0.170 ± 0.001 for the percolation threshold is in good agreement with the Scher and Zallen criterion[11] of 0.16. As others have noted,[12] the physical interpretation of this agreement is not immediately obvious.

The fitted value 15 ± 2 mΩ cm for the resistivity scale factor is within an order of magnitude of the pure carbon-black resistivity.

The relative fluctuations in resistivity $\delta\rho/\rho$ versus carbon-black concentration p are shown in Fig. 2. The data have been fit to the power law

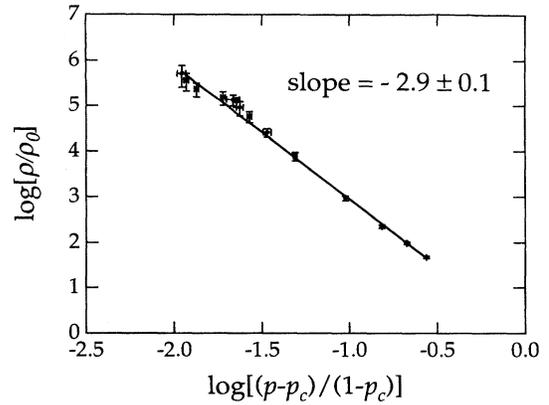$$\delta\rho/\rho = a[(p-p_c)/(1-p_c)]^{-b}, \qquad (2)$$

FIG. 1. The dc resistivity ρ versus concentration p of carbon-black for 14 different concentrations. The solid line is a fit to a power law [Eq. (1)]. On these axes the slope of the fitted line is equal to the negative of the conductivity critical exponent t.

where a is the scale factor, p is the concentration of carbon-black, p_c is the percolation threshold concentration, and b is the exponent. The critical concentration p_c is taken as the value found from the resistivity versus concentration fit, since this gives a more reliable value and reduces the number of free parameters. The weighted nonlinear least-squares fit gives an exponent $b = 0.77 \pm 0.03$ and a scale factor $a = 0.016 \pm 0.002$. The reduced χ square for the fit is 1.0, indicating a good fit.

The resistivity fluctuation data appear to show power-law behavior. However, the interpretation of this behavior is not completely clear. Four different models will be discussed, involving fluctuations in the structure of the conductive backbone, the carbon-black concentration, the percolation threshold, and the carbon-black resistivity.

The first model was initially proposed by Carmona, Prudhon, and Barreau,[6] who interpreted the relative resistivity fluctuations in similar composites in terms of the correlation length. This interpretation assumes that sample-to-sample
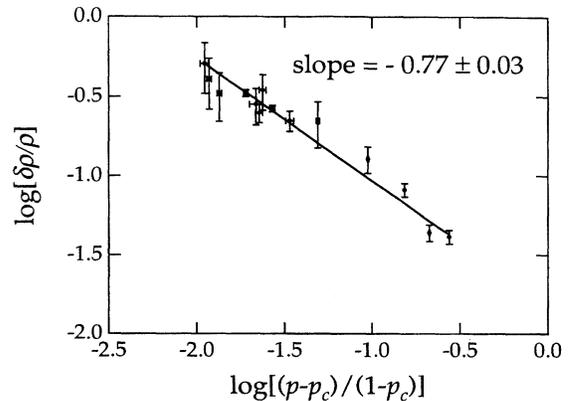

FIG. 2. The relative fluctuations in dc resistivity versus concentration p of the carbon-black for 14 different concentrations. The solid line is a fit to a power law [Eq. (2)]. On these axes the slope of the fitted line is equal to the negative of the exponent b.

fluctuations in resistivity are caused by sample-to-sample fluctuations in the structure of the conductive backbone. Straley[13] derived an equation relating these quantities,

$$(\delta\rho/\rho)^2 \sim \xi^3/V,$$ (3)

where $\delta\rho$ is the standard deviation of the sample-to-sample fluctuations in the resistivity and ρ is the mean resistivity at a given concentration, ξ is the correlation length, and V is the sample volume. The correlation length ξ is expected to obey the power law

$$\xi = \xi_0[(p-p_c)/(1-p_c)]^{-\nu},$$ (4)

where ξ_0 is the correlation-length scale factor, p is the concentration of carbon-black, p_c is the percolation threshold concentration, and ν is the correlation-length critical exponent. The correlation-length scale factor is expected to be roughly the same order of magnitude as the minimum building block of the network. Combining Eqs. (3) and (4) gives

$$\delta\rho/\rho \sim (\xi_0^3/V)^{1/2}[(p-p_c)/(1-p_c)]^{-3\nu/2}.$$ (5)

Comparison with Eq. (2) suggests the correlation-length critical exponent $\nu = 2b/3$. Using the fitted value of b, this gives $\nu = 0.51 \pm 0.02$, which is in excellent agreement with the theoretical[4] mean-field value $\nu = \frac{1}{2}$. The comparison with Eq. (2) also implies the correlation-length scale factor ξ_0 is

$$\xi_0 \sim V^{1/3} a^{2/3}.$$ (6)

Using the mean sample volume and the fitted value for a gives a correlation-length scale factor $\xi_0 \sim 360 \pm 30$ μm. This is over two orders of magnitude larger than the largest potential carbon-black agglomerate visible in a transmission electron micrograph and larger even than the sample thickness. Carmona, Prudhon, and Barreau[6] also obtained a very large correlation-length scale factor. This may cast doubt on the interpretation of resistivity fluctuations as due to fluctuations in the structure of the conductive backbone. However, there are two reasons why the fitted correlation-length scale factor might be larger than expected in this interpretation. First, power laws such as Eq. (4) are only asymptotic relations, and are known to contain nonuniversal prefactors. Second, since Eq. (6) is only a proportionality, the correlation-length scale factor is just *proportional* to 360 μm. In the absence of knowledge of the nonuniversal prefactor in Eq. (4) and the constant that should multiply the right-hand side of Eq. (6), it is not possible to determine conclusively if this model is correct or not.

A second interpretation of the relative resistivity fluctuations is that they are due to sample-to-sample fluctuations in the carbon-black concentration. This effect can be estimated by differentiating Eq. (1) with respect to the concentration p and simplifying to obtain

$$|\delta\rho/\rho| = [t\delta p/(1-p_c)][(p-p_c)/(1-p_c)]^{-1}.$$ (7)

Comparison with Eq. (2) suggests the exponent $b = 1$. This is not in good agreement with the fitted value $b = 0.77 \pm 0.03$. The comparison with Eq. (2) also implies the scale factor a is

$$a \approx t\delta p/(1-p_c).$$ (8)

The sample-to-sample variation in carbon-black concentration δp can be estimated from the four thermogravimetric measurements made at each concentration. The value of δp shows no trends versus concentration, and has an average value for all concentrations of $(7 \pm 5) \times 10^{-4}$. Using this value for δp and the fitted values for t and p_c gives $a \approx 0.003 \pm 0.002$. This is about a factor of 5 less than the fitted value.

The concentration was measured on small pieces of the slabs near but outside the actual sample area. One might argue that the concentration fluctuations may be much greater over the actual sample areas. To test this possibility, I prepared a series of six samples at the same nominal carbon-black concentration with nominal dimensions $0.7 \times 0.7 \times 0.03$ cm^3. The resistivity of each sample was measured with a four-point technique. The carbon-black concentration in the *entire* sample for each sample was then measured thermogravimetrically. The data show no correlation between carbon-black concentration and resistivity. The measured sample-to-sample fluctuations in carbon-black concentration are about a factor of 5 too small to explain the measured sample-to-sample fluctuations in resistivity. This confirms the original experimental estimate of the magnitude of the effect. It appears that a model based on sample-to-sample fluctuations in concentration cannot by itself satisfactorily explain the resistivity fluctuation data. Neither the exponent nor the magnitude of the effect are in good agreement with the data.

A third interpretation of the relative resistivity fluctuations is that they are due to sample-to-sample fluctuations in the percolation threshold. This effect can be estimated by differentiating Eq. (1) with respect to the percolation threshold p_c and simplifying to obtain

$$\delta\rho/\rho = t\delta p_c[(1-p)/(1-p_c)^2][(p-p_c)/(1-p_c)]^{-1}.$$ (9)

Since the concentration p appears in the prefactor, a comparison with Eq. (2) is not immediately obvious. Attempts were made to fit the resistivity fluctuation data to Eq. (9), using the values of t and p_c found from the resistivity versus concentration fit and allowing δp_c to vary. The reduced χ square for the fit was 7, indicating a poor fit. Setting p_c to various values spanning the range determined by direct measurement of the percolation threshold while fitting yielded similarly poor fits. The fitted value for δp_c in both cases was about 0.0021 ± 0.0001. This suggests a model based on sample-to-sample fluctuations in the percolation threshold cannot by itself satisfactorily explain the resistivity fluctuation data.

A fourth interpretation of the relative resistivity fluctuations is that they are due to intrinsic fluctuations in the resistivity of the carbon-black. This model predicts

$$\delta\rho/\rho = \delta\rho_0/\rho_0.$$ (10)

This would give a constant value of resistivity fluctuations, which is clearly not seen. The resistivity fluctuation data suggest an upper limit on intrinsic fluctuations in the carbon-black resistivity $\delta\rho_0/\rho_0$ of about 5%.

One may ask if any combination of these four models could explain the data. Combining the fourth model with any of the first three models predicts the resistivity fluctuations

will reach a limiting asymptotic value at higher concentrations, in clear disagreement with the data. Combining the second and third models predicts a resistivity fluctuation exponent of 1, in clear disagreement with the data. Combining the first model with the second or third model might possibly explain the data with a smaller correlation-length scale factor.

It appears that the resistivity data can be explained very well by mean-field theory. The resistivity fluctuation data might be explained by mean-field theory as well, but it is not possible to say so conclusively.

The results suggest a reinterpretation of earlier experimental results: the nonuniversal *width* of the scaling regime causes some continuum systems[5] to exhibit universal transport behavior and other continuum systems[6] to exhibit mean-field transport behavior over the same range of reduced concentrations. Note that there are currently no rigorous theoretical bounds on the width of the scaling regime for disordered conductor–insulator composites. In thermodynamic systems the presence of long-range interactions is known to cause a narrowing of the critical regime, resulting in mean-field behavior. If each particle interacts with many particles in its neighborhood, it effectively sees an average, or mean-field, environment. Carbon-black aggregates are known to bind together to form extended, ramified agglomerates. The carbon-black agglomerates have the possibility of interacting with many nearby neighbors. These longer-range interactions may cause a narrowing of the critical regime and give rise to mean-field behavior.

This interpretation would explain why Lee *et al.*[6] obtained a conductivity critical exponent $t = 3.1 \pm 0.3$ rather than the expected $t \leqslant 2.5$ in an experimental approximation of the "Swiss-cheese model," and why most of the other experimental work showing nonuniversal conductivity critical exponents[6] obtained values in good agreement with $t = 3$ and not any arbitrary values $t \geqslant 2$ as predicted by more general nonuniversal behavior models.[8,9] The possibility that nonuniversal transport exponents in a continuum system are due to mean-field behavior has been proposed before by Carmona and El Amarti.[14]

In summary, the transport critical exponent of these carbon-black–polymer composites is in excellent agreement with the mean-field value and in clear disagreement with the universal value. Sample-to-sample variations in resistivity, when interpreted as due to correlation-length fluctuations, give a correlation-length critical exponent in excellent agreement with the mean-field value and in clear disagreement with the universal value. However, the fitted correlation-length scale factor is very large. Since Eq. (4) contains nonuniversal prefactors and Eq. (6) is only a proportionality, it is not possible to determine conclusively if the sample-to-sample fluctuations are due to mean-field behavior. Several alternative models have been examined, none of which satisfactorily explains the resistivity fluctuation data. These results suggest a reinterpretation of earlier experimental results on conductor-insulator composites. The most plausible explanation is that the width of the scaling regime varies in different conductor-insulator composites, as it is known to vary in different thermodynamic systems. Observation of $t \neq 2.0$ in some conductor-insulator composites occurs because the scaling regime width is narrow and only the mean-field regime has been probed. This would explain why most of the experimental observations of $t \neq 2.0$ gave values in good agreement with the mean-field value $t = 3$. This reinterpretation also renews the possibility that transport in continuum percolation is universal: counterexamples to universality are caused by the particular conductor-insulator composite systems being probed outside the scaling regime and in the mean-field regime. An alternative and more speculative reinterpretation is that there is no scaling regime and mean-field theory is valid all the way to $p = p_c$ in some conductor-insulator composites.

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