Experimental observation of nonuniversal behavior of the conductivity exponent for three-dimensional continuum percolation systems

Sung-Ik Lee, Yi Song, Tae Won Noh, Xiao-Dong Chen, and James R. Gaines
Department of Physics, Ohio State University, Columbus, Ohio 43210-1106
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We measured the conductivity of both silver-coated-glass—Teflon composites and indium-glass composites made with use of standard mixing and pressing techniques. In the conducting-sphere—insulator composites, the silver-coated glass spheres were randomly distributed inside the Teflon host, with the conduction occurring only through the contact point between spheres. For this composite, we found $t=2.0\pm0.2$ and $p_c=0.170\pm0.002$, in agreement with the conventionally accepted values of t and p_c for a three-dimensional (3D) random composite. In the insulating-sphere—conductor composites, the hard glass spheres were randomly distributed inside the indium. For these composites, we found the percolation threshold to be strongly dependent upon the pressure used to make the sample, with p_c usually falling between 0.04 and 0.1, well below the expected value for a 3D random composite. Scanning-electron-microscope pictures show that narrow necks of the conducting paths do exist. The conductivity exponent was independent of the pressure used to make the sample and equal to $t=3.1\pm0.3$. The difference between the above two exponents shows that the conductivity exponent for continuum percolation systems in 3D is not universal.

Until recently, it was believed that the conductivity exponent t in percolation problems was universal.[1] In the standard theory[1] of a metal-insulator composite with component volume fraction p and $1-p$, respectively, there is a critical metallic volume fraction p_c, above which conduction through the composite takes place. For ideal metal-insulator composites, the effective conductivity of the composite σ_{eff} can be expressed as

$$\sigma_{\text{eff}}=\sigma_0(p-p_c)^t \quad \text{for } p>p_c \ . \tag{1}$$

The conductivity exponent t in this equation should depend only on the dimensionality of the system if it is "universal." In other words, if the local microstructure is isotropic and contains only short-range correlations, t should be independent of this microstructure. However, Kogut and Straley[2] showed that t would be greater than its universal value of 1.3 in two dimensions and 1.9 in three dimensions, if the composite had a conductivity distribution of the form $P(\sigma)=(1-p)\delta(\sigma)+Ap\sigma^{-\alpha}$ where A is a constant and $0<\alpha<1$. Thus opened the door for nonuniversality tests of t.

Several studies[3,4] have since shown that t does depend on the value of α in the above distribution. If we define t_{latt} as the universal value of t, as found in a lattice system where all of the metal components have the same conductivity, the effective medium approximation[2] gives $t(\alpha)=t_{\text{latt}}+\alpha/(1-\alpha)$. Straley[4] further showed, using the concept of renormalization, that $t(\alpha)$ should be given by

$$t(\alpha)=t_{\text{latt}}-\zeta+1/(1-\alpha) \quad (1<\zeta<1.35) \ ,$$

where ζ is the exponent for the chain resistance in a percolating cluster.

Recently, Halperin, Feng, and Sen[6] studied some critical exponents of a continuum system consisting of randomly distributed spherical holes in a uniform transport medium (also called the "Swiss-cheese continuum model") or the random-void continuum model). For this system, they found that the critical exponents have different values from those of the lattice systems. This result was based on the variety of the neck sizes that exist (allowing a distribution of bond strength) in the continuous media near p_c. Except for the conductivity exponent in the two-dimensional 2D case, the exponents of the transport properties (such as electrical conductivity, elastic constant, and fluid permeability) for this model were shown to be larger than those of a discrete lattice system. Thus for real systems, the percolation exponents could deviate from the classical percolation theory values.

To test the predictions of Halperin *et al.*[6] in 2D, Dubson and Garland[7] measured the conductivity exponents for a site percolation system and a random-void percolation system. They found that the conductivity exponents for these two systems were the same within experimental error as predicted by Halperin *et al.*[6] Even though this work was the first experimental effort to explicitly compare the conductivity exponent of a lattice system with that of a continuum system, the dimensionality of their system prevented them from testing the *nonuniversal* behavior of the conductivity exponents. Thus, as far as we know, there is no explicit experimental evidence which shows that the conductivity exponent of a continuum percolation system is *not* universal.

In this paper, we report the results of experiments designed to test for nonuniversal behavior in the conductivity exponent of 3D continuum systems. We prepared two different kinds of continuum systems, i.e., silver-coated-glass—Teflon (SCG-Teflon) composites and indium-glass composites. For both composite systems we measured the percolation threshold p_c and the conductivity exponent t. The comparison of the values of t obtained for these two complementary systems with the accepted value for 3D lattice systems, $t_{\text{latt}}\sim 1.9$ constitutes the test for nonuniversality.

The SCG-Teflon composites were prepared by conventional mixing and pressing techniques.[8] We used Dupont DLX 6000 Teflon powder,[9] which is composed of particles about 1 μm in diameter. The Teflon powder was ground using a freezer mill operator at 77 K in order to obtain very fine powder with particle diameters less than 1 μm. The commercially available[10] silver-coated-glass spheres used in this study are well-separated glass particles with a mean diameter of about 10 μm. These glass particles are coated with a 600-Å silver layer which provides a relatively high conductivity. The preweighed mixture of Teflon and silver-coated-glass spheres was mixed for 5 min. using a vortex mixer. The mixture was then poured into a die and vacuum (about 10^{-5} torr) pressed (for about 20 min at 90 kpsi) into a pellet. The final pellets were cylindrical in shape, $\frac{1}{4}$ inch in diameter and about 1.5 cm long. The scanning electron microscope (SEM) pictures of fracture surfaces [refer to Fig. 1(a)] show that the glass spheres were free from damage and that the contacts between spheres were made without any visible deformation of the glass spheres. Since overlapping of the glass was not allowed, the SCG-Teflon composites should be considered to be conducting hard spheres randomly embedded in a continuous insulating background.

The complementary systems, the indium-glass composites, were prepared by following the same procedure as that used for the SCG-Teflon composites. We used commercially available glass spheres[11] with a mean diameter of 30 μm. These glass spheres had no conducting coating so they played the role of insulating hard spheres. To provide a continuous conducting host, we used indium spheres which had a typical diameter of about 20 μm. When pressed into a pellet, the In powder had a resistivity of 9.4 $\mu\Omega$ cm, reasonably close to the bulk resistivity value for pure indium $\rho(\text{In})=8.37$ $\mu\Omega$ cm.[12] The near agreement of these two values and SEM pictures of the indium-glass composites [refer to Figure 1(b)] show that, under high pressure, the indium flows like plastic and fills the gaps between the glass spheres. We used four different pressures (60, 90, 120, and 180 kpsi) to make the pellets since we found that the percolation threshold of these composites depended on the applied pressure.

Some of the glass spheres for the Indium-glass composites, near p_c, were fractured at a pressure of 180 kpsi according to the SEM studies. However, samples far from p_c did not show much damage. Moreover, most of the samples below 120 kpsi were nearly free from fractures, so our indium-glass composites (made below 120 kpsi) should be considered to be randomly distributed, insulating hard spheres, in a continuous conducting background. Our indium-glass composites were different from the random-void model because the hard glass spheres did not overlap. For samples with a low-volume fraction of indium, void spaces exist inside the sample. Nevertheless, as can be seen in Figure 1(b), narrow necks of the conducting paths actually exist, providing a distribution of the conductance.

SEM studies of the indium-glass composites near p_c and those of the SCG-Teflon composites near $p=1$ indi-

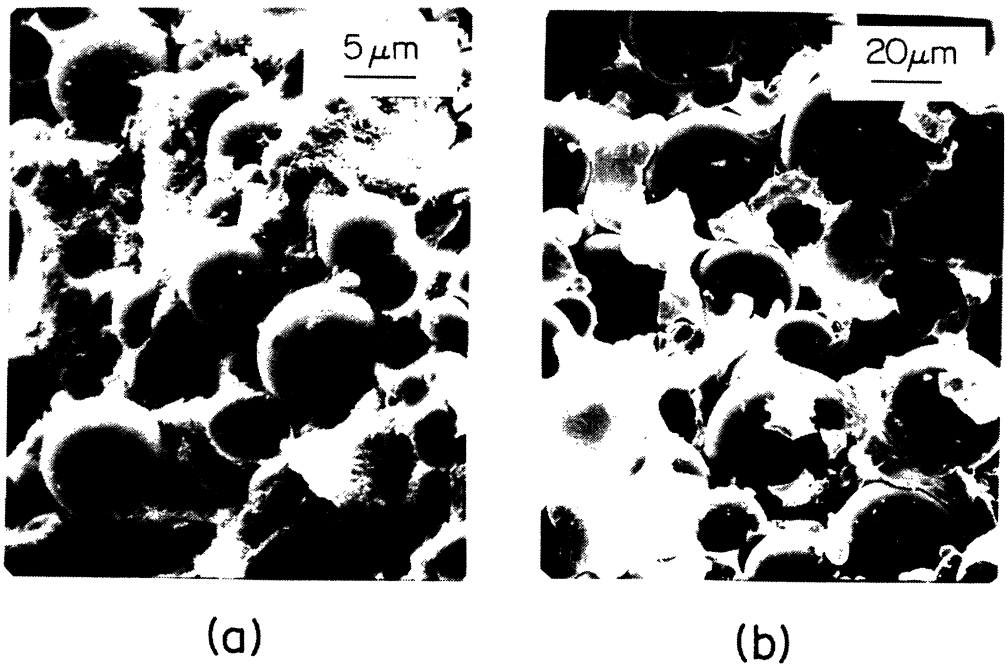

FIG. 1. (a) A SEM picture of a SCG-Teflon composite. The spherical particles are silver-coated-glass particles. The silver coating provides a relatively high conductivity. In this composite, conduction is only possible through the contact points between the spheres. (b) A SEM picture of an indium-glass composite. The spheres are insulating glass particles. As shown in this picture, conduction is possible through the small necks of the indium continuum.

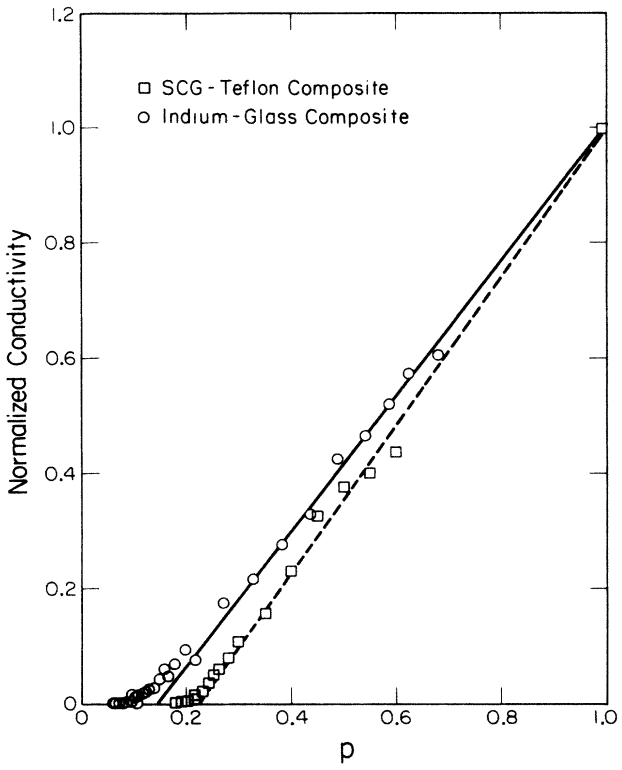

FIG. 2. The normalized conductivity of SCG-Teflon composites and indium-glass composites is plotted as a function of p. The lines shown are the best fit curves with $t=1$ as predicted by the EMA. Straight lines can describe the conductivity of the samples far from p_c.

cated that each had a substantial void volume. This is understandable since the glass spheres do not allow overlapping and the maximum packing fraction of such hard spheres is about 0.7. Since the empty space does not allow any electrical conduction, the volume of these empty spaces should be considered as an insulator. Therefore, for each sample, we estimated the volume of void spaces by measuring the weight and actual dimensions, and made a proper correction to the metal volume fraction, i.e., p.

The room-temperature resistance of our samples was measured using a four-probe method with separate voltage and current electrodes. Low-resistance current contacts were made by pressing polished copper blocks against the ends. Voltage contacts were made by attaching point contact electrodes directly to the sample. Several resistance measurements were performed for each sample by choosing different points on the sample as voltage contacts, and the final resistance of each sample was determined by averaging the measured values. The measured resistance of most of the samples did not fluctuate significantly when the voltage contact points were changed. However, samples near p_c showed large resistance fluctuations (sometimes, as large as a factor of 10) which might be due to statistical fluctuations near p_c. We did not include the resistance of such samples in our data analysis. The current-voltage characteristics of all the samples were linear (Ohmic) in our measurement region. Since the current we used was very small, destructive effects or resistance drifts due to joule heating were not observed during the measurements.

The normalized conductivities of the SCG-Teflon composites and those of the indium-glass composites are plotted in Fig. 2. Far from p_c, the experimental data for each sample can be fitted to Eq. (1) with $t=1$, which agrees

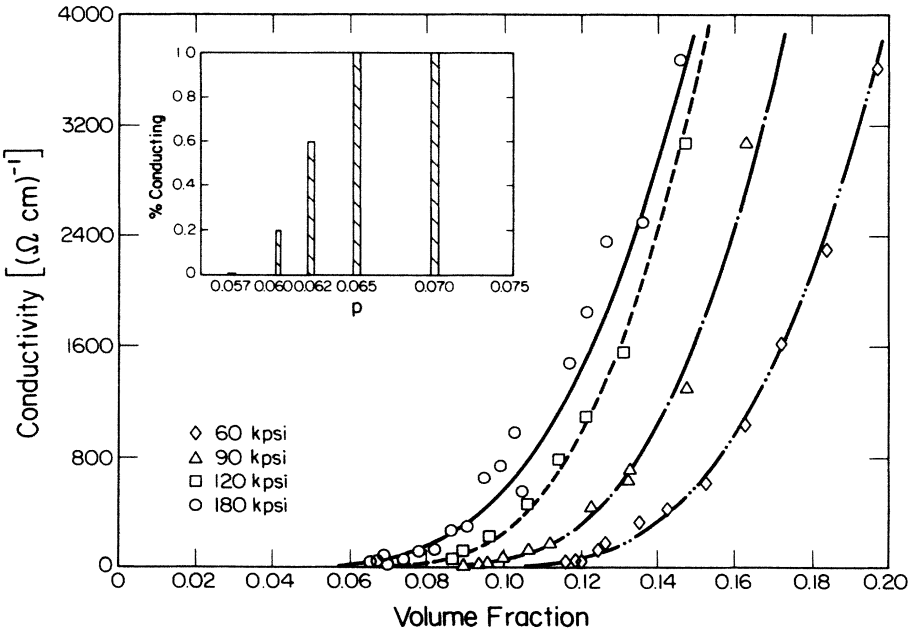

FIG. 3. The conductivity of indium-glass composites near the percolation threshold. Insert: A histogram of the percolation probability for the indium-glass samples made at a pressure of 120 kpsi. From this histogram, we can experimentally determine the percolation threshold of the indium-glass composites made at 120 kpsi.

TABLE I. The percolation threshold and conductivity exponent of indium-glass composites made at different pressures

Pressure in kpsi	Three-parameter fitting $p_c(\%)$	t	Real measurement $p_c(\%)$	t
60	10.0	2.6	9.3±0.3	3.0±0.3
90	7.7	3.0	7.5±0.3	3.2±0.3
120	6.5	2.9	6.1±0.3	3.1±0.3
180	4.3	3.0	4.1±0.4	3.1±0.4

with the prediction of the effective medium approximation (EMA) developed by Bruggeman.[13] Therefore, the EMA adequately describes the critical behavior of metal-insulator composites far from the percolation threshold. However, in the critical region near the percolation transition, the conductivity data does not follow the EMA predictions. In 2D percolating systems, some workers[7,14] have found that the critical region can be extended to $p=1$ so it is possible to fit their data over the entire range of $p>p_c$ to Eq. (1) with single value of p_c and t. However, in our 3D composites, the critical region is limited to p near p_c.

The detailed conductivity changes of our indium-glass composites, in the critical region, are plotted in Fig. 3. This figure demonstrates that p_c is reduced as we increase the pressure used to make samples. (Refer to Table I.) These changes in p_c may reflect the fact that there is less space to be filled at higher pressures and the indium itself flows better at high pressure forming more conducting paths. However, this explanation is rather speculative. Another point of interest is that the p_c's of the indium-glass composites fall between $p=0.04$ and $p=0.1$, making them much smaller than the conventionally accepted value $p_c=0.17\pm0.02$ for 3D random composites. However, such a low value of p_c is not impossible. For example, the percolation threshold of *soft* insulating spheres whose centers are chosen from a Bernal distribution[15] is about 0.03.

In order to find the conductivity exponent, we tried a conventional three-parameter (p_c, t, and σ_0) fit for each series of samples made at the same pressure. The "best-fit" curves for each series are plotted in Fig. 3 as solid lines with the best values of p_c and t listed in Table I. For the samples made at pressures of 60, 90, or 120 kpsi, the three-parameter fit to Eq. (1) is rather good. However, the resistance of samples made at a pressure of 180 kpsi scatters significantly about the best-fit curve. This scattering may be due to the fracture problems noted earlier for samples made at 180 kpsi.

The three-parameter fit mentioned above was not an accurate way to find the conductivity exponent. In fitting our data, we took the logarithm of Eq. (1) to obtain $y=tx+b$, where $y=\ln\sigma$, $x=(p-p_c)$, and $b=\ln\sigma_0$, and performed a nonlinear fit. To check the success of this fitting process, we defined the statistical variable[16] $\chi^2=\sum_i(y_i-Y_i)^2/\sigma_i^2$, where y_i is calculated from $y=tx+b$, Y_i is the measured value, and σ_i is the standard deviation of Y_i. Then we varied p_c from the result of the nonlinear fit and then tried to minimize χ^2 using a least-squares linear fit. We found that χ^2 did not change much even though we changed p_c from the nonlinear fitting result by 0.5%; however, the change of p_c by 0.5% produced changes in t by about 0.5. Therefore to increase our accuracy on t, we decided to measure p_c directly and use that value in our fit to Eq. (1).

The experimental determination of p_c is difficult because each sample yields only one data point. Due to large statistical fluctuations in the critical region, we had to make as many samples as possible and take the average to pinpoint the value of p_c. Moreover, since the indium-glass samples were very brittle near p_c, extreme care in handling them was necessary. For each pressure, we typically chose five different values of p bracketing the estimated p_c and then made five samples for that volume fraction. The percolation threshold was determined as the volume fraction where about half of the samples were conducting. A typical graph of the probability of obtaining a conducting sample for a given p is inserted in Fig. 3. We believe that it is important to determine p_c experimentally as this eliminates some of the ambiguity present in the three parameter fit. After p_c was determined, we fitted our data to Eq. (1) by adjusting σ_0 and t (a two parameter fit). The results of these two parameter fits are also given in Table I. In general, the conductivity exponents from the two-parameter fits are slightly larger than those of the three-parameter fits.

For SCG-Teflon composites, we also measured p_c directly, obtaining a value of $p_c=0.170\pm0.002$. A two-parameter least-squares fit gave for the conductivity exponent $t=2.0\pm0.2$. [Refer to Fig. 4(a).] These values of p_c and t agree with the conventionally accepted values for a three-dimensional random composite. A typical log-log plot for the indium-glass composites is also given in Fig. 4(b). As can be seen in Table I, the conductivity exponent obtained was $t=3.1\pm0.3$. Even though the p_c values changed with the pressure used to make the sample, t turned out to be independent of the pressure. The value of the conductivity exponent for the indium-glass composites is much higher than that of SCG-Teflon glass composites. Therefore, *the conductivity exponent is not universal for the continuum percolation system.*

The difference in the conductivity exponents may be understood in terms of the distribution of conductance for the conducting component. As pointed out in the work of Halperin *et al.*[6] the nodes-links-blobs (NLB) picture[17] of the percolation backbone can provide a plausible explanation of nonuniversal behavior of t. In the NLB picture, the conducting backbone of the infinite cluster is imagined to consist of a network of quasi-one-dimensional string segments (links), tying together a set of nodes

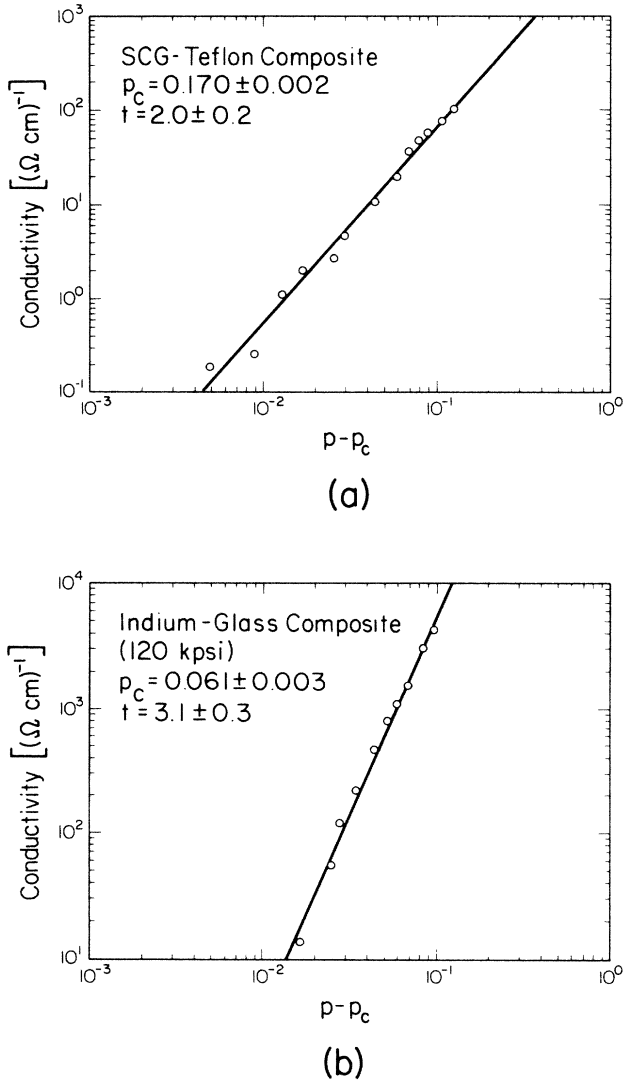

FIG. 4. (a) A log-log plot of the conductivity of SCG-Teflon composites versus p. (b) A log-log plot of the conductivity of Indium-glass composites versus p.

whose typical separation is the percolation length $\xi \sim (p - p_c)^{-\nu}$. Neglecting the multiply connected bonds (blobs) in each string, we can approximate the conductance G of a string by

$$G^{-1} = \sum_{i=1}^{L_1} g_i^{-1} , \tag{2}$$

where the sum is restricted to the L_1 singly connected bonds on the string. It has been shown[17] that the typical value of L_1 is proportional to $(p - p_c)^{-1}$.

For SCG-Teflon composites, the conduction of the samples is only possible through the contact points between the spheres, so the conductance between such points will be identical. Since there is no distribution of the conductances, G of a string will be proportional to L_1^{-1}, and the conductivity of the network will be $\sum \sim \xi^{2-d} L_1^{-1}$, where d is the spatial dimension. Thus, this analysis based on the NLB picture predicts $t = 1 + \nu(d-2) = t_1 \approx 1.8$ (in $d = 3$), a result which slightly underestimates the true value of $t_{\text{latt}} \sim 1.9$ and which approximately agrees with our experimental results.

For indium-glass composites, the SEM pictures show the existence of narrow necks in the conducting paths, and this existence of narrow neck and the existence of voids will provide the distribution in conductance of the bonds, which will make the value of t larger than that for the SCG-Teflon system. In the NLB picture, these narrow necks can be treated as singly connected bonds with conductance g dependent upon the neck size δ, such that $g(\delta) = A\delta^a$. If we denote $p(g)dg$ as the probability that a given bond has conductance between g and $g + dg$, then Eq. (2) should be written

$$G^{-1} \approx L_1 \int_{g_{\min}}^{\infty} \frac{p(g)}{g} ,$$

where $g_{\min}$ is the minimum value of g for the singly connected bonds on the string. Assuming $p(g) \propto 1/|dg/d\delta| \sim g^{(1-a)/a} \equiv g^{-\alpha} (\alpha = 1 - 1/a)$, the conductance of a string will be proportional to $L_1^{-1} g_{\min}^{\alpha}$. With $g_{\min} \sim (\delta_{\min})^a \sim (1/L_1)^a$, the conductivity exponent for this system will become $\bar{t} = t_1 + \alpha/(1-\alpha)$. The random-void continuum model predicts $\alpha = \frac{1}{3}$ $(a = \frac{3}{2})$, so for this model $\bar{t} - t = 0.5$.

For our indium-glass composites, it was not possible to determine $p(g)$ with the experimental techniques available to us. Our indium-glass composites are different from the random-void continuum model since there is no overlap of the glass spheres, so the conductance distribution of the indium-glass composites may be different from that of the random-void model. However, if we assume that the narrow necks of indium and the voids make α effectively $\frac{1}{2}$, then we can explain our experimental result, i.e., $\bar{t} - t = 1.0$.

In conclusion, we have measured the conductivity critical exponent, t, of silver-coated-glass—Teflon composites, and indium-glass composites. In the silver-coated-glass—Teflon composites, conducting hard spheres are randomly distributed inside the Teflon host, and the conduction between the spheres occurs through the contact point. For this composite, the conductivity exponent was found to be $t = 2.0 \pm 0.2$, in agreement with the "universal" value of $t_{\text{latt}} \sim 1.9$. In the indium-glass composites, insulating hard spheres are randomly distributed inside the conducting medium, i.e., indium. Scanning-electron-microscope pictures show that narrow necks of conducting paths exist, and we obtained a value of $t = 3.1 \pm 0.3$. The difference between these two values proves that the conductivity exponent for continuum percolation systems is not universal.

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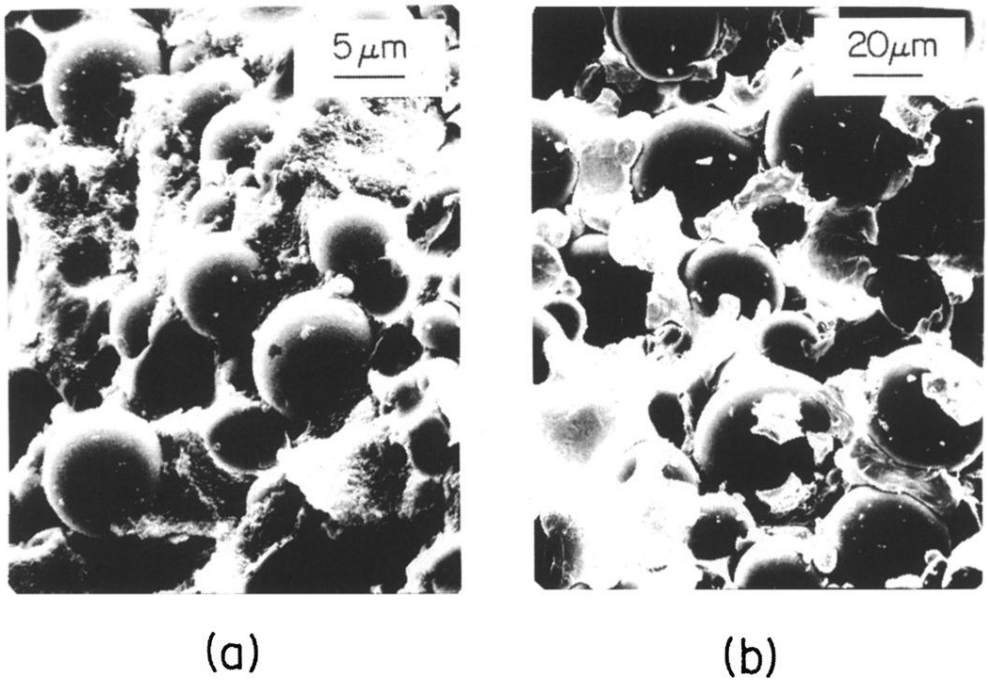

FIG. 1. (a) A SEM picture of a SCG-Teflon composite. The spherical particles are silver-coated-glass particles. The silver coating provides a relatively high conductivity. In this composite, conduction is only possible through the contact points between the spheres. (b) A SEM picture of an indium-glass composite. The spheres are insulating glass particles. As shown in this picture, conduction is possible through the small necks of the indium continuum.