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Controlling percolation in field-structured particle composites: Observations of giant thermoresistance, piezoresistance, and chemiresistance

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Composites of conductive particles in an insulating phase are conductive if the particle volume fraction exceeds the percolation threshold. Composites prepared slightly above the percolation threshold have a conductivity that is sensitive to small volume changes, and thus have potential as temperature, pressure, or chemical sensors. In practice it is difficult to prepare composites close to the percolation threshold, and the critical current-carrying path gives a rather low sample conductivity. We find that magnetic-field-structured composites, consisting of gold-coated magnetic particle chains in a polymeric resin, can be reproducibly brought to the percolation threshold, regardless of particle concentration. The low-dimensionality conducting chains form a dense population of critical current paths with extreme sensitivity to composite volume changes. These field-structured composites thus exhibit giant thermoresistance, piezoresistance, and chemiresistance, and should be useful as sensor materials.

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I. INTRODUCTION

Composites of conductive particles in an insulating phase can be made conductive if the particle volume fraction exceeds the percolation threshold.[1] This is the basis for such useful materials as conducting silver-filled epoxy resins, electromagnetic interference shields, etc. In noncrystalline polymers, the resistivity of such composites is typically found to increase weakly with temperature,[2] the so-called positive temperature coefficient of resistance (PTC) effect.[3] In crystalline polymers the PTC effect can be quite large, an abrupt, six-decade resistance change occurring at the polymer melting temperature, due to the large associated specific volume change, which apparently pulls the particles apart.[4] This has led to the development of these materials for applications as current-limiting thermistors, temperature sensors, and self-regulating Joule heating elements. In this paper the properties of magnetic-field-structured composites of conducting particles in amorphous polymers are examined. These materials are found to have an exceedingly large PTC effect.

Composites prepared slightly above the percolation threshold have a conductivity that is low, but sensitive to small specific volume changes of the composite. Such materials have potential as sensitive temperature,[4,5] pressure, or chemical sensors,[6] but it is difficult to prepare composite materials near the percolation threshold reproducibly. To avoid these problems and to achieve great sensitivity, we have begun to study the conductivity of *field-structured composites* (FSC's) whose conducting magnetic particles are structured into chains by a uniform magnetic field.[7] These materials are conductive even at low particle concentrations, and are essentially at a conductivity critical point regardless of the particle concentration.

Before proceeding, it is useful to consider the percolation threshold in disordered particle systems. The percolation threshold for a *random* composite of monodisperse conducting hard spheres in a continuum is just the random close-pack volume fraction of ~64 vol %.[8] In real materials the observed volume fraction is generally much lower, in the range of 5–25 vol %.[9] This difference is due to attractive particle interactions. If the contact interactions are much less than k_BT then one might expect an equilibrium model to describe the composite. *Correlated percolation* predicts a nonuniversal percolation threshold that can be considerably reduced in the case of attractive interactions.[10–12] If the particle interactions are much larger than k_BT, then in a *quiescent* system one might expect rough particles to stick irreversibly, forming fractal aggregates whose dimension is determined by the growth kinetics. As the fractal aggregates grow, the volume fraction of solution occupied by the aggregates increases, until the semidilute condition is reached, where the hydrodynamic volume of the aggregates is roughly the solution volume. Further agglomeration of the nearly immobilized aggregates then occurs by percolation, which is both an equilibrium and a kinetic process. In essence, the fractal aggregates merely serve as renormalized particles. The percolation threshold is completely nonuniversal; gels can easily be prepared from solutions containing only 0.1 vol % particles.[13] If the composites are prepared by stirring the particles into the pre-polymer, the situation is complex. Stirring can initially increase the rate of aggregation, but can also limit this, due to fragmentation processes. Restructuring of the aggregates to a denser state can also occur. Suffice it to say that agglomerates do occur in real composites,[14] causing nonuniversality in the observed threshold, which has no simple explanation. By structuring, we remove these uncertainties and consistently evolve to a well-defined state.

To understand why field structuring brings a particle suspension to a conductivity critical point, consider why the random composite conductivity is so sensitive when prepared near the percolation threshold. For simplicity we will assume in the following that the contact interactions between particles are negligible. Simulations of three-dimensional (3D) systems *exactly* at the percolation threshold (*critical composites*), show that an infinite cluster exists with a fractal dimension of ~2.5.[1] When a potential is applied across this critical composite, current will flow through a subset of this infinite cluster called the *conducting backbone*, which has a fractal dimension of $\sim$1.66, and is thus a set of measure zero on the infinite cluster itself. In consequence, the conductivity of a critical composite is a nonintensive property that scales as an inverse power of the size of the composite.[1] This conducting backbone is sparsely connected and its conductivity is infinitely sensitive to bond breaking processes, such as the separation of particles in Ohmic contact due to an increase in the specific volume of the resin, or some type of elastic deformation.

Real conducting composites can at best be prepared slightly above the percolation threshold. We call these *near-critical composites*. Here the particles form a open-porous conducting network whose cavities are filled with electrically isolated fractal clusters. The network itself contains many branches that do not conduct, and its structure can be partially described by its pair-correlation function. This pair-correlation function has a *correlation length* that can be roughly thought of as the largest cavity size that is reasonably likely to occur (really big cavities are exponentially rare) or, alternatively, as the size of the largest finite clusters embedded in the network. This correlation length is infinite at the percolation threshold, and decreases as an inverse power of particle volume fraction minus threshold fraction for particle composites prepared above the percolation threshold. On length scales small compared to this length the network is fractal, and on larger length scales the network is homogeneous.[1]

For a composite sample larger than the connectivity correlation length, the conductivity is an intensive property whose sensitivity to breaking conducting particle ''bonds'' depends on the magnitude of the connectivity correlation length. Swelling or deforming these composites will break some of these particle bonds, in a process that can be described as *bond percolation* on a site percolation network. Purely affine swelling would in reality break all particle contacts simultaneously—a first-order change, but fluctuations undoubtedly exist that map the composite conductivity problem onto bond percolation.

In a real material many particles are probably in Ohmic contact, and would have rather large contact pressures in thermocured polymers with a large coefficient of thermal expansion.[15] As particles separate, it has been suggested that tunneling conduction will occur,[16] which decreases exponentially with the gap, and has a characteristic length of tens of angstroms. In any case, one can expect a distribution of contact resistances in a real material, and unless this distribution is pathological, such as a power law, one can expect real behavior to fall into the bond percolation universality class. In the particular case of FSC's prepared in a low viscosity pre-polymer, it seems especially reasonable to assume that the interactions between particles brings them into Ohmic contact. Polymerization is accompanied by cure shrinkage, which creates positive contact pressure, and cooling the polymer creates greater contact pressure, especially if a glassy transition occurs during cooling.

Bond percolation on a percolative network is a quite different concept than the idea that increasing the volume of the matrix decreases the volume fraction of particles, moving the composite toward the percolation threshold from above, and thus decreasing the conductivity. The flaw in this latter view can be seen from the following argument. A random composite of hard spheres has a liquid state structure factor for the particle centers of mass which has extremely strong peaks when prepared at the percolation threshold of 64 vol %. Swelling the continuous phase by a large amount is equivalent to decreasing the particle size, and one can imagine doing this until the particle volume fraction is, say 1%. A random composite at this concentration should have a structure factor that is essentially uniform beyond the hard-sphere diameter, but in this affine swelling process the structure factor does not change, and still has strong peaks. In essence, for this swelling description to be correct the particles would have to randomize, but they cannot because they are trapped in a solid matrix.

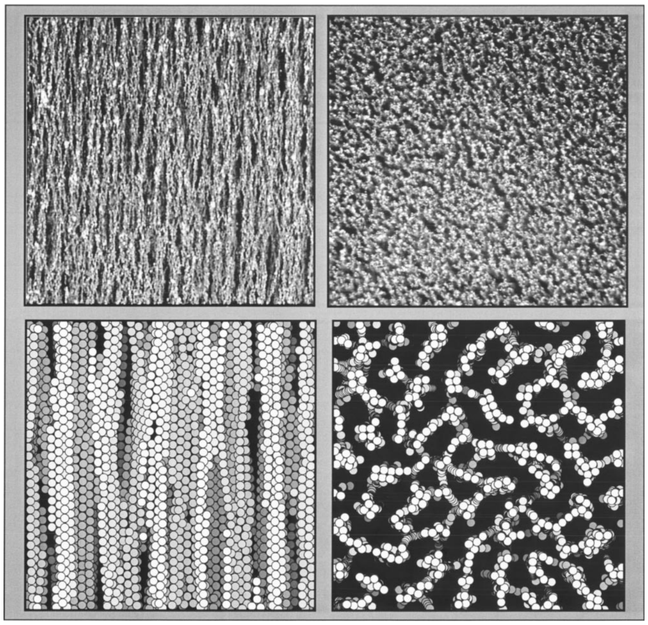

FIG. 1. Uniaxial FSC viewed perpendicular (top left) and parallel (top right) to the field structuring axis. Simulated uniaxial FSC viewed perpendicular (bottom left) and parallel (bottom right) to the field structuring axis. Particle volume fraction is 10.0%.

Bond percolation produces large changes in conductivity for fractal particle agglomerates, such as the conducting backbone that exists in random percolation. But no structure is more sensitive than a chain of particles, where one broken particle contact reduces the chain conductivity to zero. Thus the conductivity of magnetic-field-structured composites (FSC's), consisting of many chainlike structures, should exhibit extraordinary sensitivity to deformations and volume changes. Over the last few years we have been studying the magnetic,[17] dielectric,[18] and transport properties of FSC's formed when magnetic or dielectric particle suspensions are exposed to structuring magnetic or electric fields, respectively, and the fluid phase polymerized, as in Fig. 1. In this paper we show that conducting field-structured composites, consisting of Au-coated magnetic particles in a polymeric resin, can reproducibly be brought to a percolation threshold,

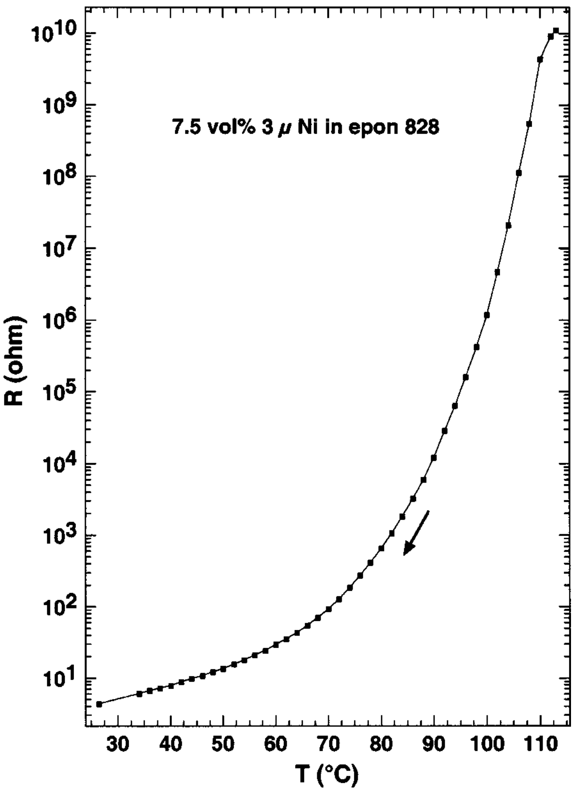

FIG. 2. Thermoresistance of an FSC of Au-coated Ni particles in epoxy. These data are taken below the glass transition temperature.

forming a dense population of critical current paths with extreme sensitivity to specific volume changes of the resin. Uniaxial FSC's exhibit giant thermoresistance, piezoresistance, and chemiresistance, and appear to have potential as sensors.

II. SENSOR EXPERIMENTS

A. Thermoresistance

Nickel particles with a mean particle size of 3 μm were coated with Au using an electroless plating solution obtained from Oromerse™. These particles were then dispersed in an epoxy resin to a volume fraction of 7.5%, the suspension was degassed in a vacuum oven at 50 °C for 20 min, placed in a 1-cm-square cuvette with inner Cu electrodes, and cured in a 500-G magnetic field at 70 °C for 4 h, followed by a 110-°C cure for 10 days. The thermoresistance of the composites was measured with a Keithley model 619 digital ac electrometer, and a resistance change of almost ten decades over a temperature range of 85 °C was observed (Fig. 2).

Further experiments with epoxy-based composites showed a dependence of the thermoresistance on the cure schedule, with longer cure times generally giving greater response. The epoxy we chose (epon 828) has complex cure kinetics, and the final material had a glassy transition temperature of 100 °C, which is close enough to the final cure temperature that the cure rate becomes very slow. The mismatch between the coefficients of thermal expansion of the epoxy and Ni phases creates compressive stresses on the particles upon cooling, and the increased contact pressure probably leads to improved conductance in the particle chains.

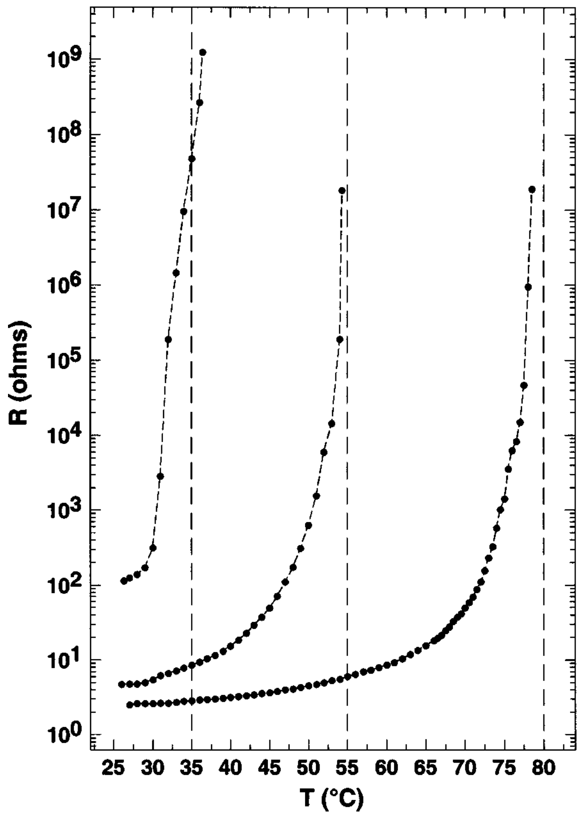

FIG. 3. Thermoresistance measurements of an FSC of Au-coated Ni particles in silicone show a conductivity divergence at, or close to, the cure temperature, each of which is indicated by a vertical dashed line.

Epon 828 is glassy throughout most of the temperature range of these experiments, and the slow volume relaxation leads to some hysteresis in the thermoresistance data. To attempt to reduce this hysteresis we used a silicone encapsulant with a T_g far below room temperature. Samples at 5 vol % Ni particles were prepared by curing at 35, 55, and 80 °C. Thermoresistance measurements show that these samples have a permanent memory of the cure temperature, in the form of a resistance divergence, indicating that they were successfully prepared at the percolation threshold (Fig. 3). To obtain great sensor sensitivity, one need only cure the sample at a temperature somewhat larger than the operating temperature, as shown in the results of chemiresistance measurements below.

The resistance divergence is insensitive to the particle concentration. Samples ranging from 1–5 vol % Ni were shown to have a resistance divergence at the cure temperature of 55 °C. The only effect of particle concentration is to create greater or fewer essentially parallel conducting paths in the composite.

B. Piezoresistance

To investigate the piezoresistance of FSC's we prepared epoxy/Ni samples and cured these for only 24 h. Upon cool-

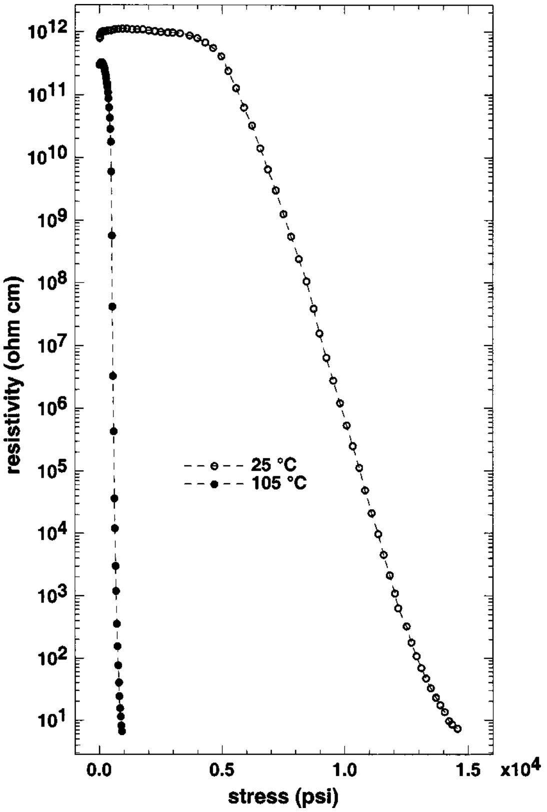

FIG. 4. Piezoresistance of an FSC of Au-coated Ni particles in epoxy. At 25 °C the epoxy is glassy, but at 105 °C it is rubbery and requires much less stress to deform.

ing to room temperature these samples generally show little conductance. We sputtered Au electrodes onto a solid rectangular FSC and subjected this sample to uniaxial compression in an Instron™, isolating the electrodes from the instrument with Mylar™, and electrically shielding the sample and coaxial cable leads with a surrounding grounded oven. Measurements were made with an antique, battery operated, analog Keithley model 602 dc electrometer, which provided greater accuracy at low conductance than any other instrument at our disposal. The empty Instron™ load cell assembly was calibrated for displacement throughout the applied load range, and this measured displacement was subtracted from the displacement measured with the sample in place, to compute the true sample strain. Piezoresistance measurements were made both well below and above the glassy transition temperature of this sample, which was $\sim$95 °C, with the results in Fig. 4. Beneath the glassy transition temperature the resistance decreases nearly exponentially with applied stress after an initial load of 5000 psi. Eleven decades of resistance change were observed over an additional stress of 10 000 psi, which is still beneath the yield stress of this material. Above the glassy transition temperature a comparable resistance change is observed with a stress of 1000 psi, again below the yield stress. When these data are plotted against the sample strain, the data nearly superimpose (Fig. 5), indicating that this is the important dependent variable.

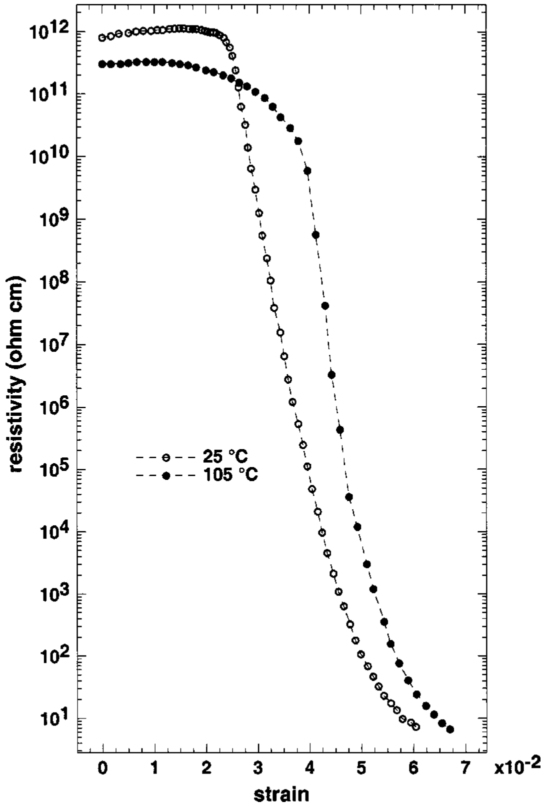

FIG. 5. The piezoresistance data of Fig. 4 nearly form a master curve when plotted against strain.

C. Chemiresistance

There is much current interest in developing chemical sensors that are simple and inexpensive. One approach is the so-called chemiresistor, formed by dispersing conducting particles at a loading slightly above the percolation threshold, into a polymeric matrix.[6] When these random particle composites are exposed to chemical vapors the polymer can swell, causing an increase in the composite resistance. Some degree of specificity can be achieved by having an array of these chemiresistors, each composed of a different polymer, with different chemical affinities. Again, great sensitivity is achieved when the random composites are prepared close to the percolation threshold, and this is difficult to achieve. In practice, the response of a chemiresistor might be of the order of 1 decade.

FSC chemiresistors were constructed by evaporating gold/niobium electrodes onto a glass slide. A 10-vol % suspension of 4–7 μm Au coated Ni particles in a silicone encapsulant was dispensed onto the slide and cured at 40 °C, with the uniaxial magnetic field in the plane of the slide, oriented to form chains spanning the electrodes. After curing the silicone this device was exposed to saturated toluene vapors, which caused a nine-decade increase in the resistance after roughly two minutes (Fig. 6). The sample was $\sim$1 mm thick at the center, which accounts for the long response time. The chemiresistor slowly recovered when removed from the toluene vapors. Devices made at other particle loadings responded similarly.

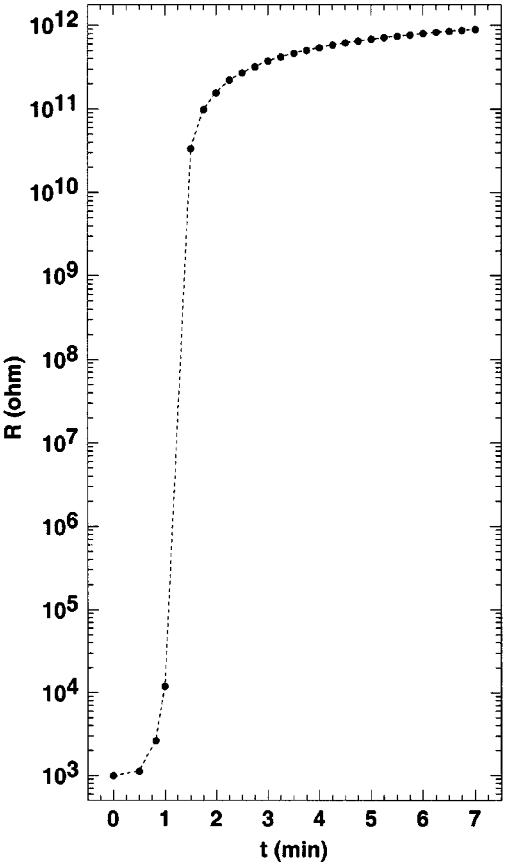

FIG. 6. Chemiresistance of an FSC of Au-coated Ni particles in silicone subjected to saturated toluene vapors (100 torr).

D. Nonlinear conduction

The extremely large PTC effect suggests that FSC's might exhibit current-limiting thermistor behavior. A 7.5-vol % Ni/epoxy composite 1 cm thick was subjected to a range of potentials, and the time-dependent current was measured with a Fluke model 8842A programmable multimeter capable of making a current measurement every 40 ms. At low applied voltages the current is proportional to the applied voltage, so the response is Ohmic, as in the 8-V data in Fig. 7. At a moderate potential of 44 V the conduction becomes non-Ohmic, and a rapid current spike is followed by a low, essentially noiseless, steady-state current. Finally, as the potential is increased to 100 V, a large current spike is followed by a small, but extremely noisy steady-state current. The composite was undamaged by these current-limiting effects, but it is clear that in using these composites as sensors the applied fields must be sufficiently small to insure that current limiting does not occur.

The I-V plot, Fig. 8, clearly shows a linear conduction regime followed by current-limiting behavior commonly observed in carbon-black composites. This existence of a linear regime is not obvious in a composite of chains, since the fields in the gaps are enhanced over the macroscopic field by a factor that is roughly the particle diameter divided by the gap. The onset of current-limiting behavior is beyond the scope of this paper, but some interpretations of this effect take into consideration the change in contact resistance due to local heating at particle contacts. In some models the change in contact resistance is irreversible and first order, precipitated by crossing a current threshold.[19–21] These models show the formation of a 2D Joule dissipation instability in the composite, in the form of a 2D hot zone normal to the applied field. Another point of view is that the contact resistance changes continuously and reversibly with the power dissipation at the particle contact.[22] This model shows that current-limiting behavior is always associated with a Joule dissipation instability. Others have taken a continuum approach to current-limiting behavior, which is more appropriate when sources of circuit inductance limit the rate of current rise through the composite.[23]

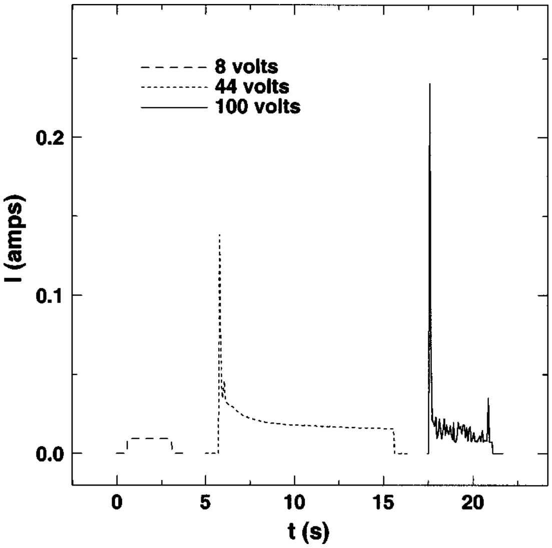

FIG. 7. When a potential is suddenly applied to a 1-cm-thick FSC of Au-coated Ni particles in epoxy resin, current limiting behavior can occur. The 8-V response is Ohmic, the 44-V response shows an initial current spike followed by current limiting behavior, and at 100 V the limiting current becomes extremely noisy.

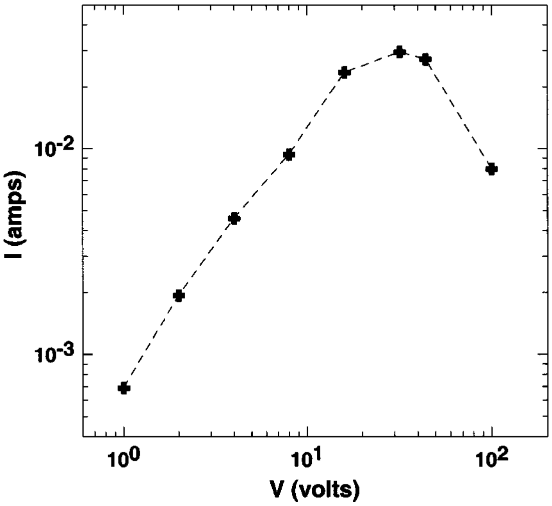

FIG. 8. The steady-state currents from the sample used to make Fig. 7 show an Ohmic regime followed by current-limiting behavior. The effect is reversible.

The large noise amplitude in the current limiting regime is an interesting aspect of these materials and is not understood at this time. However, we speculate that a reversible microscopic model that accounts for the coupling between heat generated at various particle contacts might drive the system into chaos.

III. PERCOLATION MODELS

Before discussing experiments designed to understand why field-structuring produces composites whose conductance is exceptionally sensitive to bond breaking, we would like to provide some motivation based on percolation concepts. We will not be able to provide a quantitative treatment; in fact, this has never been accomplished even for bond and site percolation on a periodic lattice. Nonetheless, some general trends can be anticipated.

A. Contact resistance

In the introduction some remarks were made about current thoughts on the mechanism of contact resistance, and some elaboration of this is needed for FSC's. The primary mechanisms are Ohmic contact, where the electron orbitals of vicinal particles overlap in the contact zone; quantum-mechanical tunneling, where the electron orbitals on vicinal particles are separate, but close; and for larger gaps, continuum conduction.

Structuring particles in a magnetic field creates large contact forces that are much more likely to create Ohmic contact, especially when CTE mismatch in glassy thermosetting resins create large positive contact pressures. Chain formation is also likely to have a large effect on continuum conduction, so it is helpful to quantify this. Consider a single particle chain spanning two electrodes, with equally spaced gaps between the particles. The field inside the particles is zero, so the potential must drop in the particle gaps alone. Along the axis of the chain the average field in the gaps is thus enhanced by the ratio of the particle diameter to the particle gap. Ten-micron particles spaced by 1 nm have a field enhancement of 10^4, so a conductance-measuring potential of 1 V across a 1-cm sample leads to an average gap field of 10 kV/cm. The capacitance of a chain of such particles has been computed, and from this the conductance can be obtained, since these continuum problems are isomorphic. For a FSC of chains the particle contribution to the effective composite conductivity is $\sigma_{\mathrm{eff}}-\sigma_c \approx 3\sigma_c\phi\ln(1+1/2\delta)$, where σ_c is the conductivity of the continuous phase, ϕ is the particle volume fraction, and δ is the ratio of the particle gap to the particle diameter. Even for extremely small relative gaps, continuum conduction leads to an effective conductivity that is merely a few times the matrix conductivity and cannot account for the effects we have observed. Furthermore, the existence of a linear conduction regime demonstrates that the gap fields are not large enough in normal measurements for nonlinear conduction to be important. We conclude that Ohmic contact and tunneling are the important conduction mechanisms in these materials. These mechanisms are so sensitive to the details of particle contact that enormous contact resistance fluctuations must exist in these materials.

The following arguments are based on the fact that both simulated and real uniaxial FSC's are not an ensemble of simple parallel chains, but are more like networks of columns. These columns can consist of one or more chains and are often highly defective. Neighboring columns frequently tilt to collide, forming current junctions or cross links. It is interesting to explore some of the consequences of this, and we shall do so in the language of site percolation, to connect clearly with experiments described below, wherein nonconducting particles are randomly mixed with conducting particles.

B. Single chain

The single chain is easily treated. If s is the fraction of nonconducting particles in a chain of N particles, the probability that the chain will conduct is $P_1(N)=(1-s)^N \approx e^{-sN}$. The conductivity of a composite of thickness T will be

$$G=c\phi e^{-T/\xi_1}, \tag{1}$$

where c is a constant that depends on the contact resistance, $\xi_1=d/s$ is the average distance between nonconducting particles, and d is the average particle size. This composite conductivity is nonintensive, decreasing exponentially with sample thickness, which does not agree with experimental measurements we have made.

In real composites chains can aggregate into columns, routing the current around nonconducting particles. Second, chains actually contact each other, forming cross links and introducing an internal length scale that makes the conductivity an intensive property. Both of these features can be seen in the simulated structure of Fig. 9.

C. Columns

To understand the sensitivity of columns to the presence of nonconducting particles, we take as an example two chains of N particles each that have aggregated to form a column, with each particle sitting on a saddle site of the neighboring chain (dipolar forces join chains in this fashion). The probability that any particular particle in chain 1 is nonconducting is s. The probability that a contacting particle in the other chain is nonconducting is $2s$, giving $2s^2$ for the probability of a current-blocking configuration of nonconducting particles. The probability that this two-chain column conducts is $P_2(N)=(1-2s^2)^N \approx e^{-2s^2N}$. The characteristic length of conducting column scales as $\xi_2 \sim d/s^2 \sim \xi_1/s$, so in the regime where the network still conducts, $\xi_2 \gg \xi_1$. For a column of n chains of N balls each the result will be

$$P_n(N)=(1-\Omega_n s^n)^N \approx e^{-\Omega_n s^n N}, \tag{2}$$

where Ω_n is in general a nontrivial combinatorial factor, and the characteristic conductivity length is $\xi_n \sim \xi_1/s^{n-1}$.

Column structures obtained from simulation are complex, with a single column being a mixture of single chains, double chains, etc. Consider the simple example of a particular column that can be thought of as a single chain of N balls, to which a shorter chain of M balls has accreted. The prob-

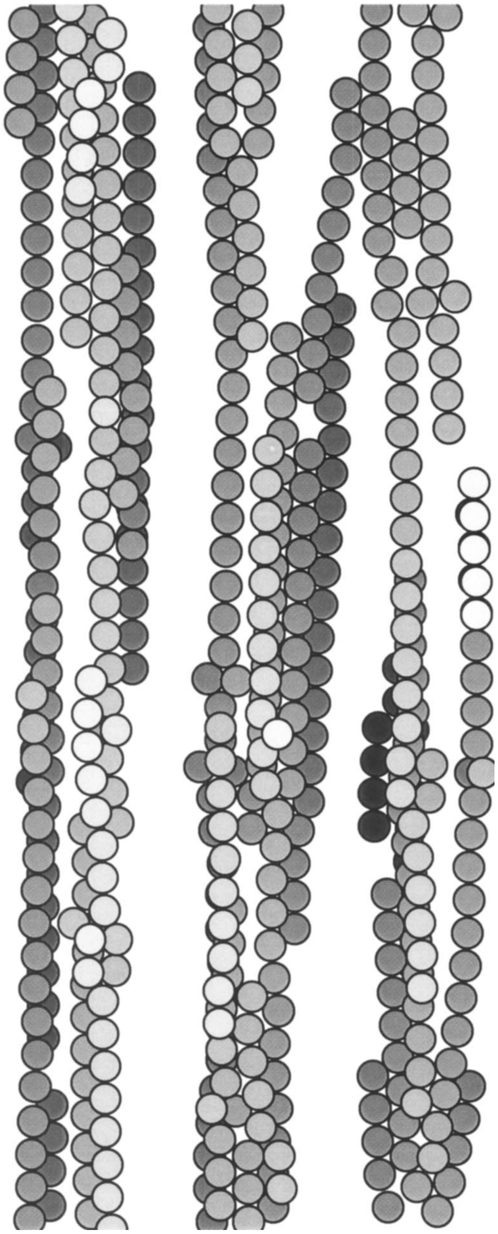

FIG. 9. Fragment of a large-scale simulation shows highly defective columns that bridge, forming cross links between chains.

ability that the single chain part of the column will conduct is $P_1(N-M)$, the probability that the double chain part will conduct is $P_2(M)$, so the probability that the entire column will conduct is $P_1(N-M)P_2(M) \approx e^{-s(N-M)-2s^2M}$. For failure of the double chain part to be comparable to the single chain part requires $(N-M)/M=2s$, so at small fractions of nonconducting particles only the single chain parts of a column will lead to a loss of conduction. Under these conditions the double chain part can be ignored and Eq. (1) will describe the conductance if the bare correlation length ξ_1 is replaced by the much larger renormalized length $\xi_1' = \xi_1/c$, where c is the fraction of the length of a column that is composed of a single chain.

D. Network of chains

Cross linking can be understood at some level by considering a model simple cubic network of chains. The interlinking chains that span current junctions can be thought of as bonds that conduct with some probability $p \approx e^{-sN}$, where N is the number of particles in an interlinking chain. Slightly above the bond percolation threshold p_c, the results of many three-dimensional simulations show that the conductivity scales as $G \propto (p-p_c)^t$, where the conductivity exponent is found to have the universal value $t \approx 2.0$.[1] The bond percolation threshold is not universal, but for a simple cubic lattice is $p_c \sim 0.25$. The conductivity is now expected to be an *intensive* quantity, and should be given by an expression like

$$G \propto (e^{-sN}-p_c)^{2.0}. \tag{3}$$

For long interlinking chains the chain length is related to the volume fraction ϕ through $N \approx \sqrt{\pi/2\phi}$. For large N the *site* percolation threshold is $s^* \cong (\ln 4.0)/N$, so a small fraction of nonconducting particles can easily reduce the conductivity to zero. Equation (3) gives a conductance that initially decays exponentially, then has an abrupt, superexponential decay to zero conductance at finite s.

Real networks are composed of interlinking columns, not interlinking chains, making the real behavior too complicated to model analytically. Site-percolation computations on simulated structures are given below, and these show that the general features of Eqs. (1)–(3) are evident. However, before discussing these simulations, we present the experiments that motivated these.

IV. SITE PERCOLATION EXPERIMENTS

We have seen that the conductance of real FSC's can depend sensitively on the small overall deformations of the composite. We have argued in the section above, but not demonstrated in any direct way, that this sensitivity is due to the loss of only a small percentage of Ohmic contacts in the composite. We cannot think of any way in which we can actually measure the percentage loss of Ohmic contacts in a real sample, so we have opted for the next best thing, the introduction of nonconducting magnetic particles into the composite. If the above analysis is correct, a small percentage of nonconducting particles should have a significant impact on the composite conductance. In these site percolation experiments we create a suspension of a mixture of conducting and nonconducting magnetic particles. This suspension is structured in a magnetic field and the conductance is measured. We expect that at low total particle volume fractions the conductance of the structured suspension will be sensitive to the introduction of nonconducting particles.

Ni particles with a nonconducting surface oxide were mixed with 50-μm Ni particles (Fisher Scientific) coated with a conducting layer of Au. The particles were dispersed in immersion oil to a concentration of 5.0 vol %, particle chains were formed in a 500-G induction field, and the conductance was measured with the Keithley model 602 dc electrometer.

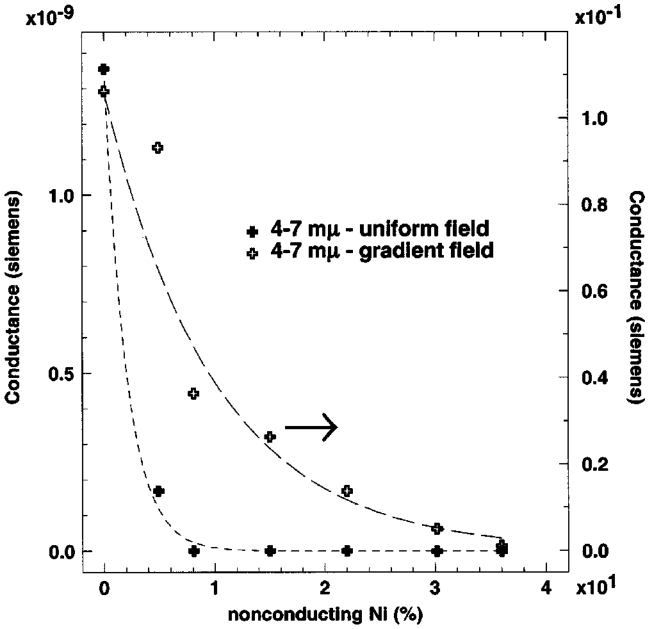

FIG. 10. Site percolation experiments on FSC's show an extremely rapid drop in sample conductance with the addition of nonconducting particles. The same particle suspensions show extremely large conductance when structured into dense powders using magnetic-field gradients.

The highly uniform magnetic field was provided by an open-air Helmholtz coil pair. This Helmholtz pair has thick coils designed for low power dissipation. Each coil is 410 turns of 1.83×1.83-mm-square Cu wire, the coil mean diameter is 11.0 cm, and the coil spacing is set to optimize the field homogeneity along the cylindrical axis. This coil spacing was determined by modeling the field in the coil, and over the $\sim$1-cm^3 sample volume the field should be uniform to better than 0.001%, though we are unable to verify this experimentally. Nonetheless, the field is sufficiently uniform that with a Hall probe connected to a four-place, Walker Scientific Gauss-meter 5DAR, we are unable to observe field variations in the sample volume. In any case, the demagnetizing field produced by the roughly cubical solid rectangular sample itself will introduce gradients in the internal macroscopic field that are more significant.

The macroscopic magnetic field within the sample is reduced by the demagnetizing field produced by the roughly cubical sample itself. However, this effect is not terribly large for chained particle suspensions. The measured mks susceptibility of the chained suspensions at the 5.0-vol % Ni concentrations we used is $\sim$0.74, and at this susceptibility we have computed that the demagnetizing factor for the average field along the cylindrical axis within a cube is $n \sim 0.3192$, giving an average macroscopic field, $H_{\mathrm{macro}}=H_0-nM$, within the cube of $H_{\mathrm{macro}}=H_0/(1+n\chi)\cong 0.81H_0$.

In accordance with expectations for low-dimensionality structures, we find that only a small percentage of nonconducting particles is required to greatly reduce the conductance of uniaxial FSC's (Fig. 10). This effect is not field dependent. Experiments with a highly uniform 15 000-G induction field provided by a commercial electromagnet had no appreciable effect on the suspension conductivity, but further experimentation showed that magnetic-field gradients can have an enormous effect. By judiciously applying small permanent magnets to the sample cell, field gradients could be created that formed the Ni particles into a dense solid with a conductance 8 orders of magnitude greater than the chained suspensions (Fig. 10). The conductance of this dense mass was reproducible, and much less sensitive to the introduction of nonconducting Ni particles, showing that the dimensionality of the structures is the dominant factor in their conduction sensitivity.

V. SITE PERCOLATION SIMULATIONS

Computer simulations of these site percolation experiments further demonstrate the importance of the low dimensionality structures in achieving high sensitivity. These simulations were performed in two steps; structure formation and conductivity calculations. A Brownian dynamics code was developed to generate 10 000-particle FSC structures. This code treats the magnetic interactions between particles in the self-consistent point dipole approximation. The moment of each dipole is determined by the local field, which is the applied field plus the field due to the other dipoles. Cyclic boundary conditions are used, and a Lorentz cavity field is applied to account for the fact that the local dipole sum is over a spherical volume centered on each particle. Particle diffusion is included, inertia is neglected (a good approximation at low Reynolds numbers) and the hydrodynamics are approximated by Stokes drag. (Hydrodynamic interactions are not known to affect structure.) This is an improvement on our previous code, which used the fixed point dipole approximation, and should give more accurate structures, such as that in Fig. 1. As the volume fraction of particles increases, the simulated structures become less anisotropic, and should become much less sensitive to the introduction of nonconducting particles, i.e., the site percolation threshold for conducting particles should decrease. All anisotropy is lost at the random close-pack concentration of 64 vol %, where Powell[8] has determined that site percolation occurs when 31% of the spheres conduct.

To compute the sensitivity of these simulated FSC structures to incorporated nonconducting particles, we randomly select a subset of particles to be nonconductive. Conductive particles in contact are then assigned a fixed contact resistance, and the conductance of the equivalent resistor network (typically $\sim$60 000 resistors) is computed by solving Kirchhoff's laws with an efficient Gauss-Seidel overcorrection method. Plate electrodes are used in this calculation, and the cyclic boundary conditions in the planes orthogonal to the applied field are maintained. For each nonconducting fraction the random selection of nonconducting particles is repeated 100 times to reduce the error. The results for particle volume fractions ranging from 5 to 50 vol % are shown in Fig. 11(a). We have not attempted to correct these data for finite-size scaling effects, but for infinite simulation volumes the percolation thresholds would be somewhat larger.

At the highest particle concentration, the observed percolation threshold occurs when $\sim$30.3% of the particles con-

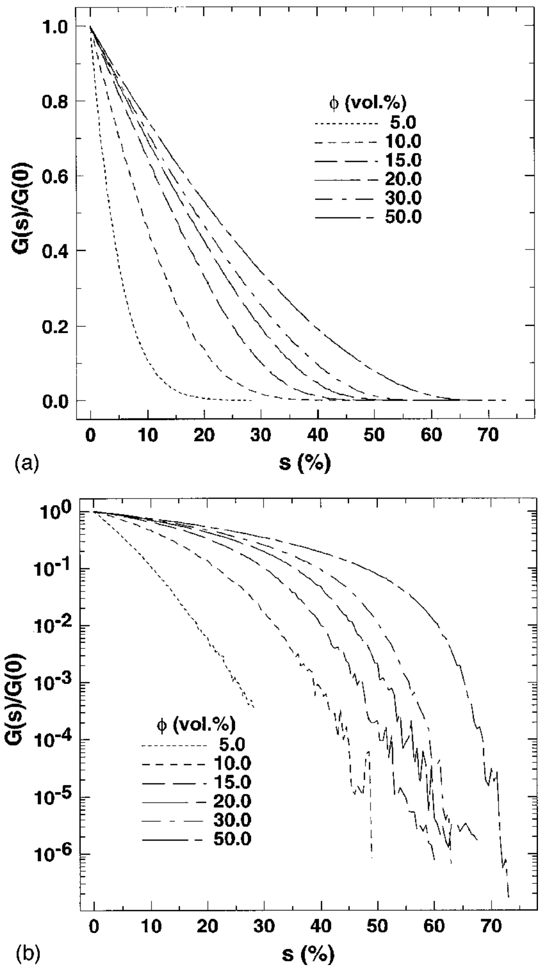

FIG. 11. (a) Conductivity of site percolation simulations on uniaxial FSC's of a wide range of concentrations show that at low concentrations, where chains are dominant, rendering only a small percentage s of particles nonconducting rapidly decreases the conductivity. (b) Plotting the data logarithmically shows a crossover from exponential behavior at low particle concentration to faster-than-exponential decay at higher concentrations.

duct, close to the random-packed hard-sphere result. As the FSC particle concentration decreases, the site percolation threshold increases, reflecting the importance of structure dimensionality to sensitivity. This behavior is qualitatively similar to the site percolation experiments, that show that when a low concentration particle dispersion is chained in a uniform field, the introduction of a small percentage of nonconducting particles reduces the conduction appreciably, whereas when field gradients are used to draw the particle into this dispersion into a concentrated mass, the introduction of nonconducting particles has little effect. At the lowest particle concentrations (5 and 10%) the *apparent* percolation threshold is high, but it is also here that the finite size of the simulation volume causes an underestimation of the true increase in the percolation threshold at low volume fraction.

Some interesting aspects of the simulation data can be seen by plotting these data semilogarithmically [Fig. 11(b)]. At the particle concentration of 5 vol % the conductance decays nearly exponentially, in accordance with the simple chain prediction of Eq. (1). Examination of the simulated structure reveals essentially no cross linking between chains, and much less column formation than at higher concentrations, so an exponential dependence is expected. The number of particles is takes to span the simulation volume is $N=(\pi n/6\phi)^{1/3}$, where n is the number of particles in the simulation volume and ϕ is the volume fraction. In this simulation $n=10\,000$ and $\phi=0.05$, so $N\approx 41$ particles. If all of the chains were perfect, this value of N substituted into Eq. (1) would give an excellent fit to the simulation data. In fact, a good fit is obtained with $N\approx 21$, indicating that about 50% of each spanning column is a single chain, and the rest is a double chain or more, the latter being insensitive to the introduction of nonconducting particles at the concentrations that render the single chains nonconductive, as shown by Eq. (2).

The simulation results at 5 vol % are definitely affected by the finite size of the simulation volume, since there was no cross linking between the columns, i.e., percolation does not occur transverse to the direction of the structuring field. We expect that a *much* larger simulation at 5.0 vol % would indeed show cross linking between chains, but there is no practical way to increase significantly the number of particles in the structural evolution simulation at this time, due to the long range of dipolar interactions. Even a 10 000 particle structure takes $\sim$150 h of cpu time to develop on a 833-MHz Macintosh. Furthermore, real structures at the same concentration show a greater tendency to cross link, probably due to friction between particles causing pinning of structures, an effect that is in fact extremely time consuming to simulate, and would not permit the simulation of structure formation in systems containing large numbers of particles. The effect of the finite size of the simulation volume is appreciable. If we were to double the size of the simulation cell $(n=80\,000)$, and cross linking between columns still did not occur, then we would expect the value of N to double, halving the concentration of nonconducting particles needed to reduce the conductivity by some fixed fraction.

At 10 vol % the simulated structure shows pronounced column formation, but still very little cross linking, so a faster-than-exponential decay is expected, with additional terms as in Eq. (2). A function of the form $\exp(-as-bs^2-cs^3)$ gives a fit to these data with no apparent systematic deviations, yielding the physically reasonable parameters $a=6.0$, $b=10.0$, and $c=54.0$. Again, we expect that these results would change in a larger scale simulation, with greater sensitivity to the introduction of nonconducting particles expected.

At higher concentrations, the simulated 10 000-particle structures percolate in the direction transverse to the structuring field, indicating that cross linking is significant enough to create a network. Now a very sharp cutoff is expected in the conductance with increasing s, in general accordance with Eq. (3). However, although Eq. (3) captures the general behavior of the conductance data, fits to this equation are not extremely compelling, because this equation really only applies in the critical regime close to the percolation threshold p_c. Furthermore, Eq. (3) ignores the extensive column formation that occurs in these high volume fraction structures.

Developing a quantitative theory of site percolation on these anisotropic structures is an extremely complex problem, but the qualitative features predicted by Eqs. (1)–(3) are seen in the simulation data, and these data demonstrate the importance of low-dimensionality structures.

VI. DISCUSSION

The extreme sensitivity of the conductance of field structured composites to specific volume changes of the matrix material is fundamentally due to changes in the contact resistance between particles. Continuum conduction cannot account for the magnitude of changes we have observed, and so Ohmic contacts and tunneling must be the source of these effects.

In the modeling described above, we have assumed that the contact resistance is either some fixed, finite value, or is infinite. Reality is undoubtedly more complex, with a spectrum of contact resistances throughout the sample. The contact resistance is a complex issue, since both Ohmic contacts and charge tunneling are possible. The resistance of an Ohmic contact will depend greatly on the contact pressure, deformation of the Au coating, etc. For very small gaps quantum-mechanical tunneling can occur, with its exponential gap dependence. In either case, the contact resistance depends strongly on the gap between particles, and because the particles are much more rigid than the polymeric matrix, small macroscopic deformations can lead to large gap changes.

If we suppose that in the sensor experiments described above perhaps 20% of the particle contacts are broken, then the importance of chainlike structures to sensitivity can be understood from the site percolation experiments and simulations, which show that large conductance changes are indeed possible with chain structures, whereas a dense particle compact will scarcely change at all. For this reason, FSC's apparently offer an ideal method of achieving high sensor sensitivity. At this point we do not know the relationship between polymer swelling and the loss of conducting contacts between particles, so our understanding of these materials is incomplete. This problem is probably complex and nonuniversal, involving such issues as cure shrinkage, elastic and inelastic particle deformations, local stress fluctuations, and so forth. Perhaps future work will be able to shed some light on these factors, but much progress can be made in developing these materials without such a detailed understanding.

One fruitful avenue for future research is the use of complex magnetic fields to control the dimensionality of the conducting particle aggregates. In this paper we have restricted our attention to 1D linear chain structures created by a uniaxial field. It is also possible to create 2D sheetlike particle structures using an ac biaxial field, such as a rotating field,[24] and a rich variety of 3D structures—particle chain networks and various particle foams—can be formed in triaxial[25] magnetic fields. With these techniques the conductivity of FSC's can be controlled over a wide range, and using such structures we expect to be able to moderate, to a desired extent, the sensitivity of these materials, ideally being able to tune the dynamic range of the response to the anticipated sensor environment.

VII. CONCLUSIONS

We have shown that it is possible to prepare composites that are effectively very close to the percolation threshold by using magnetic fields to first structure the particles into chains. The approach gives reproducible materials with an extremely large dependence of the effective conductivity on strain or elastic deformation, and thus have potential as temperature, pressure, or chemical sensors. Reversible current-limiting thermistor behavior has also been demonstrated. Composites made with an elastic silicone polymer have a divergence in the resistivity at the cure temperature of the polymer, which can be controlled over a wide range. By selecting the cure temperature to correspond to the temperature at which these composites are used as sensors, extreme sensitivity can be obtained. It is suggested that the mechanism by which the observed resistance changes occur is one in which polymer specific volume changes make or break Ohmic contacts where they exist, and alter tunneling currents. Under these circumstances one can expect large fluctuations in contact resistance, which we have modeled as a simple bond percolation process. To demonstrate that these structured particle composites have high sensitivity, we have conducted site percolation experiments and simulations on structured materials, and have found that enhanced sensitivity to the introduction of nonconducting particles does indeed exist.

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[1] D. Stauffer, *Introduction to Percolation Theory* (Taylor & Francis, London, 1985).

[2] L. Lamaignere, F. Carmona, and D. Sornette, Physica A **241**, 328 (1997).

[3] F. Carmona and C. Mouney, J. Mater. Sci. **27**, 1322 (1992).

[4] M. B. Heaney, Appl. Phys. Lett. **69**, 2602 (1996).

[5] M. B. Heaney, Physica A **241**, 296 (1997).

[6] S. V. Patel, M. W. Jenkins, R. C. Hughes, W. G. Yelton, and A. J. Ricco, Anal. Chem. **72**, 1532 (2000).

[7] J. E. Martin, R. A. Anderson, and C. P. Tigges, J. Chem. Phys. **108**, 3765 (1998).

[8] This is a point of some confusion in the literature, where it is

often stated that for a random composite of particles in a continuum the percolation threshold is 0.183. The justification for this comment is a misinterpretation of M. J. Powell, Phys. Rev. B **20**, 4194 (1979). Powell considered site percolation in *contacting* randomly packed conducting and nonconducting hard spheres, finding that conducting spheres percolate when they comprise 31.0% of the total number of spheres. Multiplying this result times the hard-sphere packing density gives the volume fraction of 0.183 for conducting spheres at percolation. This result is meaningful for mixtures of particles, but is irrelevant to conducting spheres in a continuum. For conducting hard spheres in a continuum at high particle density (but smaller than random close packed), each sphere finds itself restricted to a cavity. The center of mass of this sphere is allowed to explore a small volume, the surface of which is defined by contact with its neighbors. This surface is a set of measure zero on the volume, so the contact probability is zero. From a kinetic point of view, hard-sphere collisions occur instantaneously.

[9] F. Carmona, Physica A **157**, 461 (1989).

[10] T. Odagaki, N. Ogita, and H. Matsuda, J. Phys. Soc. Jpn. **39**, 618 (1975).

[11] A. Coniglio, C. R. Nappi, F. Peruggi, and L. Russo, J. Phys. A **10**, 205 (1977).

[12] C. Domb and E. Stoll, J. Phys. A **10**, 1141 (1977).

[13] J. E. Martin and J. P. Wilcoxon, Phys. Rev. A **39**, 252 (1989).

[14] C. D. Mukerjee, K. K. Bardhan, and M. B. Heaney, Phys. Rev. Lett. **83**, 1215 (1999).

[15] F. Kohler, US Patent No. 3,243,753 (issued 29 March 1966).

[16] K. Ohe and Y. Naito, Jpn. J. Appl. Phys., Part 1 **10**, 99 (1971).

[17] J. E. Martin, R. A. Anderson, and C. P. Tigges, *Nanostructured Materials: Clusters, Composites, & Thin Films*, edited by V. M. Shalaev and M. Moskovits, ACS Symposium Series Vol. 679 (American Chemical Society, Washington, DC, 1996).

[18] J. E. Martin, E. Venturini, J. Odinek, and R. A. Anderson, Phys. Rev. E **61**, 2818 (2000).

[19] P. M. Duxbury, P. L. Leath, and P. D. Beal, Phys. Rev. B **36**, 367 (1987).

[20] B. Kahng, G. G. Batrouni, S. Redner, L. de Arcangelis, and H. J. Herrmann, Phys. Rev. B **37**, 7625 (1988).

[21] C. Vaneste and D. Sornette, J. Phys. I **2**, 1621 (1992).

[22] J. E. Martin and M. B. Heaney, Phys. Rev. B **62**, 9390 (2000).

[23] R. A. Dougal, IEEE Trans. Power Electron. **11**, 304 (1996).

[24] J. E. Martin, R. A. Anderson, and C. P. Tigges, J. Chem. Phys. **108**, 7887 (1998).

[25] J. E. Martin, R. A. Anderson, and R. L. Williamson, J. Chem. Phys. **118**, 1557 (2003).