J Mater Sci (2008) 43:1128–1134
DOI 10.1007/s10853-007-2117-5

Strain effects on percolation conduction in conductive particle filled composites

Thomas A. Godfrey

Received: 15 March 2007 / Accepted: 15 August 2007 / Published online: 4 December 2007

Abstract The effect of uniaxial and multiaxial mechanical strain on the electrical conductivity of particle filled polymer composites is investigated in the framework of concentration-driven percolation. For composites consisting of low aspect ratio, rigid conductive particles in a compliant polymer matrix, a simple argument leads to the conclusion that the effective volume fraction of conductive particles (the ratio of total particle volume to the total volume of the deformed composite) plays a dominant role, with conductivity remaining isotropic despite the directional bias of the strain state. As such, conductivity is expected to exhibit classical power, law-dependence on concentration, which in this case takes the form of a strain-dependent effective volume fraction. Consideration of deformation effects on particle agglomerates suggest, however, that particle-to-particle network connections are likely to be affected most significantly along directions experiencing the most severe strains, introducing a directional bias in network connectivity at a higher length scale. To assess the importance of this possible directional bias, random resistor network models are used to study the conductivity of uniaxially strained composites. For conservative assumptions on the severity of the bias in bond probabilities, network conductivities exhibit approximately isotropic, concentration-driven behavior for moderate strains, supporting the predictive utility of the simple percolation conduction-effective volume fraction approach. Further corroboration is provided by experiments in the literature on silicone-graphite composites subjected to uniaxial compressive strain, where good agreement is obtained through moderate strains for the theoretically correct value of the conduction exponent in concentration-driven percolation.

T. A. Godfrey (✉)
US Army Natick Soldier Research Development & Engineering Center, Natick, MA 01760-5020, USA
e-mail: Thomas.Godfrey@us.army.mil

Introduction

Conductive polymers are used in a variety of applications where material is required to be both electrically conductive and mechanically compliant. Recently, interest in conductive polymeric fibers has been motivated by *electronic textiles* applications, such as the integration of sensors and signal/data transmission lines into military combat clothing. One avenue being pursued is a composite fiber approach, where sufficient concentration of suitable conductive filler (e.g., graphite platelets) in the polymer provides a percolating conductive network. Ideally, such fibers should be durable and exhibit little change in electrical resistance during extension. The changes in the percolating network that occur during extension, are key to the strain dependence of the fiber's electrical resistance. Our investigation here of strain effects on percolation conduction in particle filled composites is part of a broader study of the basic mechanical and electrical behavior of conductive fibers and fibrous assemblies for potential electronic textile applications.

Kirkpatrick [1] demonstrated that random resistor networks follow a percolation conduction law of the form

$$\sigma \propto (p - p_c)^{\mu} \tag{1}$$

where in, say, the simplest case of nearest neighbor bond percolation, p is the probability that a given bond in the lattice is conductive, and p_c is the percolation threshold value of p. The conductivity exponent has a value of about 2 for three-dimensional networks [2], and, as with critical exponents in percolation phenomena generally, it is sensitive to the dimensionality of the system, but not the specifics of the lattice. The probabilities model the concentration of the conductive phase in the mixture, so p and p_c may be replaced with volume fractions V and V_c or area fractions A and A_c for three- and two-dimensional systems, respectively. Experiments on many mixed conductor/insulator systems have demonstrated the validity of Eq. 1 with the aforementioned substitution [3]. Most real systems of interest do not possess a regular lattice structure and are denoted *random lattices* [4] in early literature, though, more recently, percolation in such systems is termed *continuum percolation*. It is noteworthy that, while values of V_c vary considerably [5], values of the conductivity exponent are remarkably consistent, whether arising from regular lattice resistor network models, experiments on real composite materials, or experiments on model regular and random lattice systems [3]. For example, for two-dimensional systems, μ has been found to be 1.35 and 1.38 in experiments [3] (graphite paper with randomly punched holes, and wire mesh with randomly severed segments, respectively), while square random resistor networks simulations [2] yield a value of about 1.3.

Given the success of the concentration driven conduction law, and the direct role of mechanical strain in altering particle concentration, it is natural to extend the concept to treat the response of composites to strain. Chelidze and Gueguen [6] consider hydrostatic compression of a composite comprised of rigid conductive inclusions in a deformable insulative matrix. For initial concentrations below the percolation threshold, they identify a pressure-induced percolation transition occurring at a critical volumetric strain ε_c (depending on the initial concentration) and show that the strain dependence of conductivity scales with the conductivity exponent μ, $\sigma \propto (\varepsilon - \varepsilon)^{\mu}$. In experiments on silver coated glass microspheres embedded in fine talcum powder near the percolation threshold, the exponent on the strain increment was found to be much less than the expected two for a three dimensional system. Chelidze and Gueguen speculate that the slower than expected increase in conductivity with compression is due to the tenuous nature of contact between spheres near the threshold, where compression increments may cause slight disturbances that destroy existing connections as well as form new ones, and where the percolating network cluster has yet to establish much redundancy. Their experimental set-up, which constrained the samples within a cylinder and compressed them via a piston, applies an uniaxial strain. However, since the initial state of the samples was unconsolidated, Chelidze and Gueguen argue that the state of strain in the compressed samples, under constraint by the cell wall, is quasi-hydrostatic. They did not consider the sensitivity of percolation conduction to the particular case of uniaxial strain or a general state of multiaxial strain.

Although their experiments [6] did not corroborate theory, Chelidze and Gueguen's extension of percolation conduction in rigid conductive particle/insulative matrix composites to address hydrostatic strain piezoresistivity is straightforward and compelling. Our interest here is how the concept may be generalized to treat the piezoresistive response of such composites to an arbitrary state of multiaxial strain. Considering only first order effects, in the next section we present an argument based on the resistor network model that suggests, for any arbitrary direct strains applied to the composite, it is the resulting *effective volume fraction* of conductive particles (the ratio of total particle volume to the total volume of the deformed composite) that dominates strain-dependence. A consequence of this simple dependence on effective volume fraction, a scalar, is that the conductivity of the deformed composite remains approximately isotropic.

The simple effective volume fraction argument we make here, deals only with average properties and neglects effects arising from the detailed spatial distribution of particles in the deformed composite. Conductivity in the composite arises from networks of conductive pathways established through particle-to-particle contact. We hypothesize that inter-particle contacts will be most significantly affected along the most highly strained directions in the specimen, introducing a strain-dependent directional bias in the bond probabilities. To investigate the possible magnitude of the deviation from simple effective volume fraction behavior due to these effects, in section "Random resistor network simulations" of this article we use random resistor networks to simulate the conductivity of strained composites where inter-particle contact effects are modeled by directionally biased bond probabilities. It turns out that, even for a fairly severe strain-dependent directional bias based on conservative assumptions, network conductivities exhibit piezoresistive behavior for small to moderate strains that is fairly close to predictions based on the effective volume fraction assumption.

The treatment given in the present article is intended as a preliminary approach, subject to extension and refinement in follow-on work. A significant limitation is that particle reorientation effects during straining are neglected. For high-aspect ratio conductive particles, such effects may dominate piezoresistive response, becoming increasingly important as strains grow to moderate values. However, the present approach may be useful for particles with moderate aspect ratios, as will be shown in section "Experiments on silicone-graphite composites". The work here considers homogeneous states of strain in the interest of developing a simple piezoresistive material model for composites. Such a model could be used to investigate the resistance behavior of composite structures experiencing non-homogeneous strains arising from contact with external bodies (a problem of considerable interest) through combination with an appropriate finite element analysis of the coupled electrical and mechanical behavior of the deforming structure.

Development of simple effective volume fraction model

Consider a composite comprised of low aspect ratio rigid conductive particles embedded in a compliant polymeric matrix, denoted the RCPCPM composite. There are no directional effects in the distribution of the particles, i.e., the composite is macroscopically isotropic, and effects of particle orientation for these low aspect ratio particles are neglected. To model concentration driven conduction in such a composite using a simple cubic lattice, one regards the probability of a conductive bond in a given position as proportional to the volume fraction, V_0, of the conductive phase. This correspondence between bond probability and conductive phase concentration has been established, as discussed previously, through the success of Eq. 1 in describing percolation conduction in both lattice simulations and real isotropic composites. As necessary for isotropy and correspondence to conductive phase volume fraction (a scalar), bond probabilities are identical along the x, y, and z directions of the lattice.

Suppose the composite is deformed homogeneously by direct average strains ε_x, ε_y, ε_z, where, by *average* we refer to the nominal strain in a volume element of the composite containing many particles. Consider the case that the deformation of the composite is approximately affine. Here we define an approximately affine deformation of the composite to be one in which the displacements of the mass centers of the conductive particles from their initial positions in the unstrained composite are approximately the same as the displacement of points on an ideal homogeneous solid subjected to the identical strain state. Since the conductivity of the composite in the unstrained state is macroscopically isotropic, the conductivity of the composite after an approximately affine deformation will also be macroscopically isotropic and dependent on the conductive phase volume fraction in the strained state.

The notion that conduction is isotropic in the deformed composite can be illustrated by assuming, for the moment, that conductivity in the strained composite is non-isotropic. In the simple cubic lattice model of the non-isotropic strained composite, the links in the x, y, and z directions, which represent interparticle bonds along those directions, would have different bond probabilities. If we interpret the bond probability as proportional to the density of particles along the specified coordinate direction, we recognize immediately that, since the density of particles has no directional dependence (it is simply the particle volume fraction), the bond probabilities in each direction are equal and, therefore, the strained composite must exhibit isotropic conductivity.

Since the conductive particles are rigid in comparison with the matrix, the conductive phase volume fraction in the deformed composite (which we denote *effective* volume fraction) can be expressed as the particle volume divided by the total volume of the deformed composite simply as, $V_0/(1 + \varepsilon_x)\,(1 + \varepsilon_y)\,(1 + \varepsilon_z)$. As such, the conductivity of the strained composite, following the discussion given after Eq. 1, may be seen to be

$$\sigma = \left\{ \frac{V_0}{(1+\varepsilon_x)\,(1+\varepsilon_y)\,(1+\varepsilon_z)} - V_{\mathrm{c}} \right\}^{\mu} \tag{2}$$

In section "Random resistor network simulations", we consider how local spatial inhomogeneity and particle agglomeration in deformation may affect particle-to-particle bonds and associated piezoresistive response.

Random resistor network simulations

Consider again a composite consisting of rigid conductive particles embedded in a complaint insulative polymeric matrix (i.e., the RCPCPM material). The material is originally macroscopically isotropic, therefore the bond probabilities of a corresponding cubic lattice resistor network model are identical in the x, y, and z lattice directions. As the composite is deformed by direct strains along the x, y, and z directions, we expect these network bond probabilities, reflecting the probability of particle-to-particle connectivity in the composite, to change. If the composite deformation is affine, as discussed in the previous section, bond probabilities will vary with the effective volume fraction of the conductive particles. Such an approximately affine deformation would arise if particle displacements closely match the prescribed global deformation of the composite. If, however, particles tend to agglomerate, deformation will not be nearly spatially homogeneous and affine; instead particle clumps or rafts will form with much of the deformation occurring in localized bands between clumps. In this article, a simple approach is adopted to roughly estimate the degree to which the piezoresistive response of RCPCPM agglomerating particle composites may be affected by such deformation; the composite is modeled as a cubic lattice random resistor network where the possible effects of particle agglomeration on network connectivity are simulated by reasonable adhoc assumptions on the evolution of bond probabilities during deformation.

In an agglomerating particle composite with an established network of particle-to-particle connections (i.e., above the percolation threshold), it is natural to expect particle connectivity to be affected most significantly along the most severely strained directions in the composite. For example, in the case of uniaxial extension of the composite, particle-to-particle connections will be preferentially broken along the strained direction, leading eventually to the development of a pattern of *microcracks* in particle connectivity largely perpendicular to the direction of extension. Similarly, for uniaxial compression of the composite, new particle-to-particle connections are created along the direction of compression at a rate higher than in proportion to the increase in particle volume fraction. Lateral particle-to-particle connections (y or z direction) are affected to a lesser degree by x-axis extension or compression because the global deformation tends to place less stress on these connections.

We investigate here the case of uniaxial compression with lateral constraint. Such a mode of deformation is realized experimentally through compression of a specimen confined in a cavity. Experiments on the compression of a very thin specimen between platens with high friction at the material/platen interface also approximately reproduce this deformation state. As a conservative bound on the severity of directionally biased behavior of such composites we assume that: (1) Lateral inter-particle connections are unaffected by the deformation and all deformation-induced changes in inter-particle connection occur longitudinally (i.e., along the axis of compression) (2) The directionally averaged inter-particle connectivity (i.e., the average of x, y, and z direction bond probabilities) in the composite is proportional to the effective volume fraction of the particles in the deformed composite. The first assumption is straightforward. The second assumption provides a reasonable means of indexing the behavior of the composite to the concentration of the conductive phase.

Following the assumptions given above, we derive expressions for the directional bond probabilities in a cubic lattice resistor network model simulating the compression of an RCPCPM composite along the x-direction under lateral (i.e., y and z direction) constraint. From assumption 1, we require the bond probabilities in the y and z directions remain equal to the initial bond probability before deformation,

$$p_y = p_z = p_0 \tag{3}$$

From assumption 2, we require the average bond probability to vary in proportion to the volume fraction of particles in the deformed composite. Due to lateral constraint, $\varepsilon_y = \varepsilon_z = 0$, therefore, the effective conductive particle volume fraction discussed in connection with Eq. 2 reduces in this case to $V_0/(1 + \varepsilon_x)$, where a compressive strain is taken as negative. Using $p \propto V$, we write,

$$\frac{1}{3}\left(p_x + p_y + p_z\right) = \frac{p_0}{1+\varepsilon_x} \tag{4}$$

where the left hand side represents the directional averaged bond probability and the right hand side is proportional to the conductive phase effective volume fraction. Combining Eqs. 3 and 4, the x-direction bond probability may be written as,

$$p_x = \frac{1-2\varepsilon_x}{1+\varepsilon_x} p_0 \tag{5}$$

In this work, 17 × 17 × 17 element resistor networks are used, where the resistors are selected to have a conductance of one (bond is occupied) or 1×10^{-12} (bond is unoccupied) in accord with the specified bond probability. A system of equations for the voltage at each node in the resistor network is then generated by applying the Kirchoff current law. A unit voltage difference is applied from the left to the right hand sides of the network and the total conductance of the network is determined as the total current flowing into the network divided by the voltage difference (=1 V). Conductivity, σ, is normalized so that the conductivity of a network with all bonds occupied is one. The top surface is joined to the bottom surface, and the front surface is joined to the back surface of the network through extra planes of resistors so that the network is effectively periodic and infinite in extent in the y and z directions. The simulation approach is depicted schematically in Fig. 1. The MATLAB® technical computing language was used to perform the simulations.

Simulations were conducted for isotropic networks ($p_x = p_y = p_z = p$) and for networks simulating compression with the directionally biased bond probabilities given by Eqs. 3 and 5. The percolation threshold, p_c and

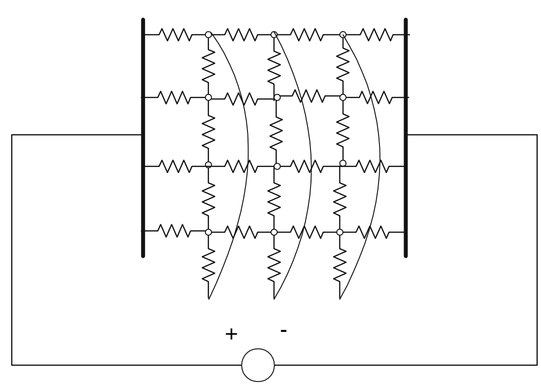

Fig. 1 Schematic representation of resistor network simulation. Two dimensional 4 by 4 resistor network is shown; Actual networks are 3-D 17 by 17 by 17. Conductance of resistors is selected to be one (bond) or 10^{-12} (no bond)

exponent μ are determined by linear fits of $\ln(p - p_c)$ versus $\ln(\sigma)$, where p_c is adjusted for best fit, and the slope of the line gives μ. Using the averages from 30 realizations of the $17 \times 17 \times 17$ networks with $0.25 \leq p \leq 0.35$, p_c and μ are found to be 0.24 and 1.85, respectively. The percolation threshold for bond percolation on a cubic lattice, properly defined as the threshold value for formation of an infinite spanning cluster of bonds, has been found to be 0.2488 [2]; our result is slightly lower due to the small size of the networks used here.

The isotropic network results for a range of bond probabilities used to simulate compression in the affine deformation case, where a compressive strain may be related to the bond probability by,

$$\varepsilon_x = p_0/p - 1. \tag{6}$$

Eq. 6 is obtained from Eq. 4 using $p_x = p_y = p_z = p$.

Results for compression with lateral restraint of a composite with initial bond probabilities p_0 of 0.26 and 0.29 are exhibited in Figs. 2 and 3, respectively. These results may be compared with compression of actual composites with V_0/V_c equal to p_0/p_c, which for these cases is 1.083 and 1.208. Compressive strain is shown positive for convenience. The power law curve is obtained from Eq. 2 with p_0 and p_c replacing V_0 and V_c, respectively, and $\varepsilon_y = \varepsilon_z = 0$, as,

$$\sigma = \sigma_0 \left(\frac{p_0}{1 + \varepsilon_x} - p_c \right)^{\mu} \tag{7}$$

For the results exhibited in Figs. 2 and 3, p_c and μ are as determined previously and the constant σ_0 is fitted to the isotropic simulation results. The directionally biased network simulation results are averages of 40 realizations of

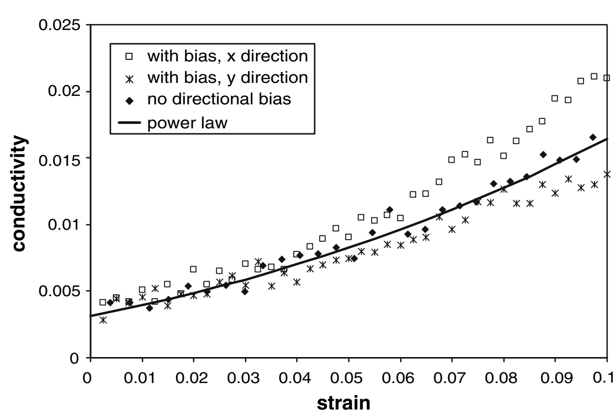

Fig. 2 Analytical and resistor network results for simulated compression of composite with lateral constraint. Initial bond probability $p_0 = 0.26$

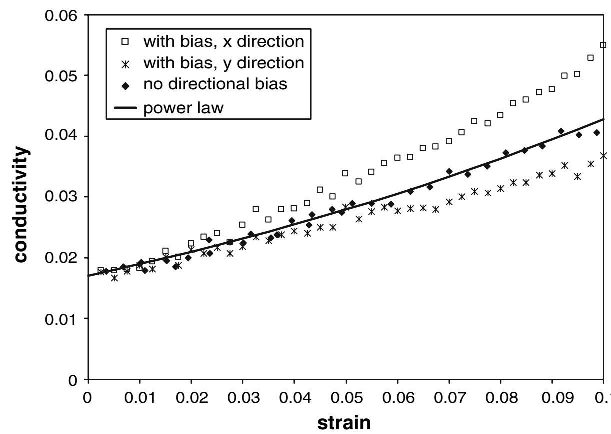

Fig. 3 Analytical and resistor network results for simulated compression of composite with lateral constraint. Initial bond probability $p_0 = 0.29$

the network. Conductivities in the direction of compression (i.e., x direction) and in the lateral direction (i.e., y direction) for the directionally biased cases are seen to remain close to the isotropic results for moderate values of strain up to about 4%. At higher strains, the assumptions made on directional bias in bond probabilities lead to significant divergence from the isotropic results, with x direction conductivities becoming significantly higher, and y direction conductivities becoming significantly lower, than in the concentration-driven isotropic case. Conductivity in the $p_0 = 0.29$ case is significantly higher than in the $p_0 = 0.26$ case due to the higher probability of conductive bonds.

Experiments on silicone-graphite composites [7]

Beruto et al. [7] investigated the piezoresistance properties of silicone matrix graphite powder composites at graphite volume fractions near the percolation threshold, measuring the through-the-thickness electrical resistance of disc-shaped specimens 13 mm in diameter and 2 mm thick as they were compressed between parallel plates. The relative thinness of these discs compared to their diameter suggests that, due to friction at the plate/specimen interface, the overall deformation of the disc is approximately laterally constrained (i.e., friction at the top and bottom surfaces inhibits lateral expansion of the specimen, and specimen thinness inhibits significant barrel-shaped lateral bulging). The graphite platelet particles used have in-plane dimensions ranging between 5 µm and 15 µm and thickness of 1–2 µm. Beruto et al. report the resistance versus compressive strain behavior for a 32% graphite volume fraction composite for strains greater than 2%. The percolation threshold for these composites was found to be 31% graphite at 2% compressive strain. Although reference [7] contains results for composites with graphite volume fractions of 33% and 35%, these results could not be extracted with sufficient accuracy for use here.

For the purpose of comparing with the analysis of this article, we treat the 2% pre-compression as the initial state of the material (i.e., zero compressive strain). As such, the volume fractions are corrected to represent the volume fraction in the precompressed state, where V_0 and V_c are seen to be 0.3265 and 0.3163, respectively. For convenience, conductivity is normalized by the conductivity of the composite in the initial state. It is straightforward to obtain the normalized conductivity, σ/σ^*, from the resistance of the 2 mm thick disc as,

$$\frac{\sigma}{\sigma^*} = \frac{R^*}{R}(1 - \bar{\varepsilon}), \tag{8}$$

where a star superscript denotes that the value is to be taken in the initial state, R is the resistance of the 2 mm thick disc, and $\bar{\varepsilon}$ is the compressive strain relative to the initial state, taken to be positive for increasing compression. The area of the disc has been assumed constant during compression due to the effects for lateral constraint discussed previously. The power law relationship for compression with lateral constraint can be written for normalized conductivity from Eq. 7 as,

$$\frac{\sigma}{\sigma^*} = \left\{\frac{V_0}{(V_0 - V_c)(1 - \bar{\varepsilon})} - \frac{V_c}{V_0 - V_c}\right\}^{\mu}, \tag{9}$$

where V_0 and V_c have replaced the p_0 and p_c seen in Eq. 7. The normalized conductivities obtained from the experiments by Beruto et al. [using Eq. 8] are exhibited in Fig. 4 along with strain biased resistor network simulation results and the effective volume fraction power law prediction using Eq. 9. The experimental results include the average resistance values for the nominally 32% graphite composites extracted from [7] and the resistance values for a typical specimen of the data set, provided in [8]. For the directionally strain biased network simulation, $p_0 = 0.2477$, such that $p_0/p_c = V_0/V_c = 1.032$. For the power law prediction, the theoretically accepted value [2] for the conductivity exponent in three-dimensional systems, $\mu = 2$, has been used. The conductivity of the silicone–graphite composites is seen to increase rapidly with increasing strain and agrees well with the effective volume fraction power law prediction and the directionally biased simulation prediction through about 4% strain. For strains above 4%, the silicone-graphite composites are more highly conductive than the predicted values. Speculatively, the rapid increase in conductivity of the silicone-graphite composites at strains above 4% could arise due to the effects of changing particle orientations [7], which would tend to become more significant at higher strains.

Conductivity increases much more rapidly with strain in this case, as compared with the theoretical and network simulations considered in section "Random resistor network simulations", due to the closeness of the initial volume fraction to the percolation threshold, here $V_0/V_c = 1.032$. The directionally biased resistor network simulation, while exhibiting generally higher conductivity in the through thickness (x) direction, does not diverge from the isotropic power law results as in the cases studied in section "Random resistor network simulations" (Figs. 2 and 3). Speculatively, near the percolation threshold, directional biases in the conductive pathways may have less of an influence over the macro-conductivity of a composite than seen at higher conductive phase concentrations.

Conclusions

The effect of uniaxial and multiaxial mechanical strain on the electrical conductivity of particle filled polymer composites has been investigated in the framework of concentration driven percolation. A simple argument has been presented for composites consisting of low aspect ratio rigid conductive particles in a compliant polymer matrix undergoing approximately affine deformation, suggesting that the effective volume fraction of conductive particles (the ratio of total particle volume to the total volume of the deformed composite) plays a dominant role in the piezoresistive response, with the composite's conductivity remaining isotropic for a general state of three-dimensional direct strain. As such, conductivity is expected to exhibit classical power law dependence on concentration, which in this case takes the form of a strain-dependent effective volume fraction. The effects of a degree of

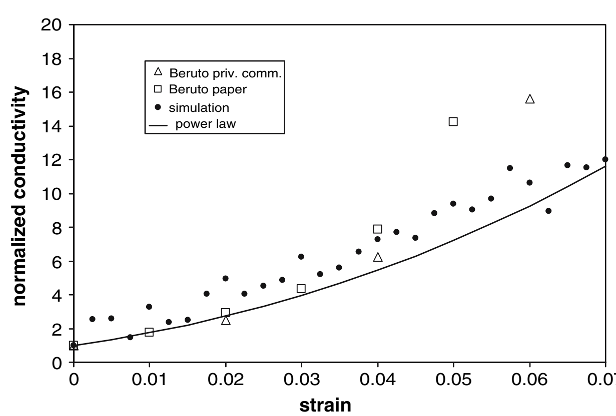

Fig. 4 Comparison of analytical power law and directionally biased resistor network results with experiments on compression of silicone-graphite composites. Data labeled Beruto private communication represents results for an individual specimen typical of the data set

non-affine deformation due to particle agglomeration on composites under compression with lateral constraint were investigated using random resistor network models with directionally biased bond probabilities. For conservative assumptions on the severity of the bias in bond probabilities, network conductivities exhibited approximately isotropic, concentration driven behavior for moderate strains (up to 4%) at reasonable values of the initial conductive volume fraction (ratios of 1.08–1.21 relative to the percolation threshold), supporting the predictive utility of the simple percolation conduction-effective volume fraction approach. At higher compressive strains, resistor network simulation results suggest that composites will become significantly more conductive in the direction of compression than in the lateral direction. The effective volume fraction approach to the piezoresistive response of rigid conductive particle complaint matrix composites was further corroborated by comparison to experiments in the literature on silicone-graphite composites subjected to uniaxial compressive strain, where good agreement was demonstrated for the theoretically correct value of the conduction exponent in concentration driven percolation.

References

1. Kirkpatrick S (1973) Rev Mod Phys 45:574
2. Stauffer D, Aharony A (1994) Introduction to percolation theory. Taylor & Francis, Philadelphia, p 93
3. Coutts TJ (1976) Thin Solid Films 38:313
4. Pike GE, Seager CH (1974) Phys Rev B 10:1421
5. Seager CH, Pike GE (1974) ibid 10:1435
6. Chelidze T, Gueguen Y (1998) J Phys D: Appl Phys 31:2877
7. Beruto DT, Capurro M, Marro G (2005) Sens Actuators A 117:301–308
8. Beruto DT (2006) private communication (February 1, 2006)