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Piezoresistivity of a short fiber/elastomer matrix composite

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Abstract

If the electrical resistance of a material depends upon external straining, the material exhibits 'piezoresistivity'. The piezoresistive behavior has been realized in an electrically conductive elastomer composite where the microstructure of conductive fillers can be changed under finite deformation of elastomer, resulting in the change of the composite resistivity. In this paper, we analyze the piezoresistive behavior of a conductive short fiber/elastomer matrix composite by applying a percolation model. Fiber reorientation model is applied to the composite system with the aim of predicting the relation between the applied finite strain and the reorientation of conductive short fibers. It is found that the piezoresistive behavior of a conductive short fiber/elastomer composite is attributed to the degeneration of initially percolating network under the finite strain. Some numerical results are then compared with our previous experimental data, showing a reasonably good agreement.

Keywords: Piezoresistivity; Short fiber/elastomer matrix composite; Percolation; Threshold volume fraction; Tunneling effect; Fiber reorientation model

1. Introduction

Electrically conductive polymer matrix composites have attracted a great deal of scientific and commercial interests during the last few decades because these materials provide unique electrical and mechanical properties as well as many excellent properties of polymeric materials, such as light weight, low cost, ease of processing and corrosion resistance, compared with metals. The mechanism of electrical conduction in an electronic composite is the formation of a continuous network of conductive fillers throughout the insulating polymer matrix. These conductive composites have been widely used in the areas of electromagnetic/radio-frequency interference (EMI/RFI) shielding, electrostatic discharge (ESD), and conductive adhesives for die attach in electronic packaging applications.

It has been observed that in a conductor–insulator composite, as the volume fraction of conductor (f) increases gradually, a sharp upturn in the electrical conductivity occurs when the volume fraction reaches a certain critical value, the threshold volume fraction of filler (f^*). In order to obtain the minimum f^* in conductive composites, a knowledge of factors controlling the formation of conductive networks is prerequisite. The threshold phenomena can be well described by a percolation theory. Broadbent and Hammersley (1957) first introduced the term 'percolation', and explained it with geometrical and proba-

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bilistic concepts. Subsequent studies (Gurland, 1966; Kirkpatrick, 1973; Cohen et al., 1978) showed that the percolation concept can be applied to many physical processes in disordered systems, especially various transport processes in composite materials.

Based on the studies of Pike and Seager (1974) and Balberg and Binenbaum (1983), Ueda and Taya (1986) proposed a fiber percolation model (FPM) which can predict the electrical conductivity of a two-dimensionally misoriented short fiber composite. Subsequently, the FPM was extended to the three-dimensional short fiber composite (Taya and Ueda, 1987). It was found in the FPM analysis that the key microstructural factors on the composite conductivity are fiber volume fraction (f), fiber aspect ratio (L/D) and fiber orientation distribution: a short fiber composite with larger fiber aspect ratio and more randomly distributed fibers becomes conductive at smaller volume fraction of fiber, resulting in smaller threshold volume fraction.

It has been known that the electrical conductivity of a conductive polymer composite depends markedly on external loading, showing the piezoresistive effects; see Lundberg and Sundqvist (1986), Carmona et al. (1987), Pramanik et al. (1990), Yoshikawa et al. (1990), McLachlan et al. (1990), Narita (1990), Carmona and El Amarti (1992), and Taya et al. (1994). While the piezoresistive effects of conductive polymer composites have been mainly studied experimentally, there exist very few theoretical studies on piezoresistive behavior of the conductive composites. Carmona et al. (1987) proposed an extended percolation theory involving an appropriate function that describes the changes in filler volume fraction due to external loading. They showed that the sensitivity of piezoresistive effect of the composite depends on the elastic properties of the matrix material and on the mode of applied loading, hydrostatic or uniaxial. McLachlan et al. (1990) pointed out that the approach of Carmona et al. (1987) may not work because the expansion or movement of one phase with respect to the other is not equivalent to changing the volume fraction by varying the volume ratio of the two phases, and proposed a simple equation which describes threshold f^* in terms of external loading, assuming a linear dependence of the contact density of particle (average contact number per particle) on external loading.

It has been shown that an initially electrically conductive short fiber composite becomes less-conductive as straining increases, and suddenly non-conductive at and beyond a critical strain, exhibiting switching behavior (Narita, 1990; Taya et al., 1994). This is mainly due to the reorientation of conductive short fibers upon straining, as shown in Fig. 1, where initially electrically percolating network is degenerated to non-percolating network. When the insulator matrix is soft, such as elastomer, external loading causes the microstructural change of the composite, resulting in the change in the overall mechanical properties and electrical properties (Taya et al., 1994; Aspden, 1986). Electrically conductive elastomer composites, which exhibit variable conductivity in response to varying external loading, are widely used for various electronic applications, touch control switches and strain and pressure sensors for applications such as robot hands or artificial limbs (Pramanik et al., 1990). However, no quantitative analysis of these switchable composites has been conducted.

The aim of this paper is to predict the effective electrical conductivity of a three-dimensional (3D) misoriented conductive short fiber/elastomer matrix composite under finite strains. In order to account for the piezoresistive effects of the composite, we propose to use the percolation theory involving the microstructure change of the composite under finite strains. The relation between the applied finite strain and the consequent change in the microstructure of short fiber network is predicted by using fiber reorientation model, and the threshold volume fraction of fiber is computed for a given microstructure by applying the fiber percolation model. The effective conductivity of a composite is then calculated by using a power-law-type conductivity equation.

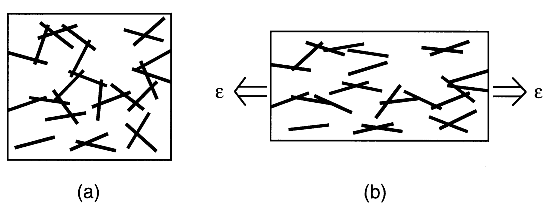

Fig. 1. The expected microstructure change of a composite under straining; (a) percolating before straining (electrically conductive) and (b) non-percolating after straining (non-conductive).

2. Analytical formulation

2.1. Percolation model

The fiber percolation model, based on the bond percolation and Monte Carlo method (Ueda and Taya, 1986; Taya and Ueda, 1987), is used for computation of the threshold volume fraction of fiber. In Monte Carlo simulation, the center coordinates (x_i, y_i, z_i) of the i-th fiber $(i = 1, \dots, N)$ and its orientations (θ_i, ϕ_i) are homogeneously and randomly generated within a rectangular specimen with a dimension of $L_x \times L_y \times L_z$ by using a pseudo-random number generator (RNUNF), where RNUNF produces a sequence of pseudo-random numbers uniformly distributed on the interval [0,1]. The initial 3D fiber misorientation (before straining) can be simplified as uniform distribution with the in-plane (α) and the out-of-plane (β) limit angles where $\theta \leq |\alpha|$ and $90\text{-}\beta \leq \phi \leq 90 + \beta$, Fig. 2. The short fiber used in this study is cylinder with length L and radius $D/2$ which is capped at the two ends by semi-sphere of radius $D/2$. It is assumed that short fibers are not allowed to be overlapped (or penetrated). As shown in Fig. 3, the actual short fiber (solid line) is simulated as non-penetrable portion and the penetrable shell of thickness d_c indicates the range across which electric charge transfer can take place between fibers, showing tunneling effect (Balberg and Binenbaum, 1987; Wang and Ogale, 1993). Thus, the tunneling distance (or twice the penetrable shell thickness) between fibers ranges from zero (touching fibers) to $2d_c$. Two fillers are said to be connected if their shells penetrate each other without overlapping actual filler. The tunneling distance distribution of conducting fillers has an important effect on the electrical conductivity in the percolation theory (Balberg, 1987). For simplicity, we assume a constant conductance between fibers within the tunneling distance $2d_c$ and focus on the computation of the threshold volume fraction of fiber.

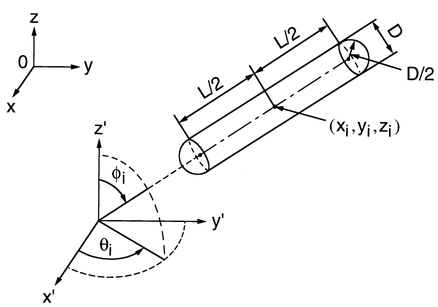

Fig. 2. A capped cylindrical fiber in a 3D space.

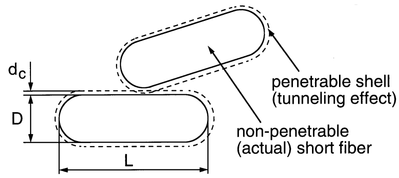

Fig. 3. The simulation of non-penetrable model (D = actual fiber diameter, d_c = tunneling distance).

If two fibers were found to be connected, they are assigned a cluster identification number (CIDN). All fibers within the same cluster have the same CIDN. The CIDN is updated as each pair of fibers is being checked so that if a fiber in a cluster is found to contact a new fiber which previously belonged to a different cluster, two clusters will be assigned the same CIDN (the smaller one of two CIDNs). If in a cluster there are fibers which intersect the opposite boundaries of the rectangular composite specimen along a particular axis, it is said that a percolating cluster is established along the axis.

In the percolation model of a conductor–insulator composite with conductor volume fraction f, there is a critical conductor volume fraction f^*, above which a percolating network of conductors is just established through the composite. Then, the effective conductivity of a composite can be expressed as (Cohen et al., 1978);

$$\sigma_c = \sigma_f (f - f^*)^t \text{ for } f > f^*, \tag{1}$$

where σ_f is the conductivity of fiber and t is a conductivity exponent. Due to the power-law-type conductive behavior, small changes in f or f^* can lead to large changes in the composite conductivity, especially close to the threshold. The effective electrical conductivity of a composite is computed by predicting the threshold volume fraction of fiber of a given composite system.

2.2. Fiber reorientation model

Reorientation and relocation of fibers in an elastomer composite are expected to take place under large straining. If the microstructure of conductive

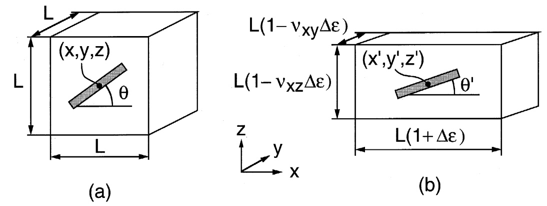

Fig. 4. The 3D fiber reorientation model where only angle θ is shown for illustrative purpose; (a) before straining and (b) after straining.

short fibers was initially percolating, then the percolating microstructure is degenerated to less- or non-percolation network as the applied strain ε increases.

It is assumed that upon incremental uniaxial straining $\Delta\varepsilon$ along the x axis, the changes in the orientation and location of a short fiber are taken into account by following affine transformation, as pictured in Fig. 4, where (a) and (b) denote, respectively, the configuration before and after the incremental straining $\Delta\varepsilon$. Affine transformation assumes that under the external loading the length components of a fiber change by the same ratio as the corresponding dimensions of the matrix. Under the assumption of incompressibility of an elastomer composite and incremental strain along the x-axis ($\Delta\varepsilon$), the dimensions of a rectangular specimen (L_x, L_y, and L_z) and the center coordinates (x_i, y_i, z_i) of the i-th fiber are changed to

$$L'_x = L_x(1+\Delta\varepsilon),\ L'_y = L_y(1-\nu_{xy}\Delta\varepsilon),$$
$$L'_z = L_z(1-\nu_{xz}\Delta\varepsilon) \tag{2-a}$$
$$x'_i = x_i(1+\Delta\varepsilon),\ y'_i = y_i(1-\nu_{xy}\Delta\varepsilon),$$
$$z'_i = z_i(1-\nu_{xz}\Delta\varepsilon) \tag{2-b}$$

where the prime indicates the current variables after straining by $\Delta\varepsilon$, and υ_{ij} is Poisson's ratio of a composite, defined as $|\varepsilon_j/\varepsilon_i|$. The length components in Cartesian coordinates of the i-th fiber before and after uniaxial straining are expressed as

$$u_{xi} = u\sin\phi_i\cos\theta_i,\ u_{yi} = u\sin\phi_i\sin\theta_i,$$
$$u_{zi} = u\cos\phi_i \text{ before straining,} \tag{3-a}$$
$$u'_{xi} = u'\sin\phi'_i\cos\theta'_i,\ u'_{yi} = u'\sin\phi'_i\sin\theta'_i,$$
$$u'_{zi} = u'\cos\phi'_i \text{ after straining,} \tag{3-b}$$

where u (u') is the length of fiber before (after) straining. Applying affine transformation with Eqs. (2-a), (2-b), (3-a) and (3-b), the following relations are obtained

$$1+\Delta\varepsilon = \frac{u'\sin\phi'_i\cos\theta'_i}{u\sin\phi_i\cos\theta_i},\ 1+\varepsilon_y = \frac{u'\sin\phi'_i\sin\theta'_i}{u\sin\phi_i\sin\theta_i},$$
$$1+\varepsilon_z = \frac{u'\cos\phi'_i}{u\cos\phi_i}. \tag{4}$$

By using Eq. (4), the reorientation angles of a fiber after straining are derived as

$$\theta'_i = \tan^{-1}\left[\frac{(1-\nu_{xy}\Delta\varepsilon)}{(1+\Delta\varepsilon)}\tan\theta_i\right] \text{ and}$$
$$\phi'_i = \tan^{-1}\left[\frac{(1-\nu_{xy}\Delta\varepsilon)}{(1-\nu_{xz}\Delta\varepsilon)}\frac{\sin\theta_i}{\sin\phi'_i}\tan\phi\right]. \tag{5}$$

Following Eqs. (2-a), (2-b) and (5), the dimensions of a rectangular composite specimen and the center coordinates and orientation of the i-th fiber are changed under the incremental straining.

3. Results and discussion

It is expected that in a 3D short fiber composite electric current flows by a tunneling mechanism. The overall (including tunneling shell d_c) and actual fiber volume fractions at the percolation threshold for a 3D random system are plotted in Fig. 5 as a function of ratio of tunneling distance to actual fiber

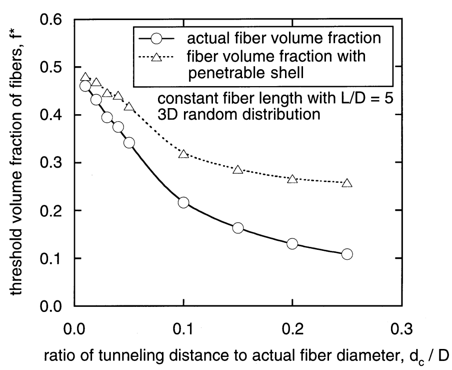

Fig. 5. The threshold volume fractions of actual (circles with solid line) and overall (triangles with dotted line) fibers as a function of the ratio of tunneling distance (d_c) to actual fiber diameter (D).

diameter (d_c/D), where fiber length and diameter are fixed and fiber aspect ratio (L/D) is 5. The 3D fiber orientation is simulated as a uniform random distribution. The circles with solid line and triangles with dotted line represent the volume fractions of actual and overall fiber, respectively. It is depicted from Fig. 5 that as the ratio d_c/D decreases, the volume fraction of fiber increases. When d_c/D approaches zero, these two curves should converge to a single value. Thus the d_c/D ratio in a non-penetrable model is an important parameter on the threshold volume fraction and the electrical conductivity. The tunneling distance is a characteristic electrical property of the matrix polymer. However, since electrical transport process consists of several different mechanisms, determination of the tunneling distance in a given system is difficult. Thus the tunneling distance will be approximated by matching the experimental value of threshold volume fraction f^* to the predictions by the present model.

Next the change in the microstructure of a short fiber/elastomer composite under straining is examined. Fig. 6 illustrates the orientation distributions of in-plane fiber angles (θ) where (a) and (b) denote, respectively, the initial orientation of a 3D randomly

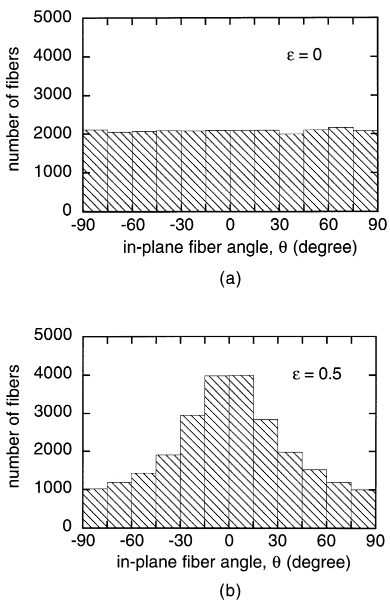

Fig. 6. The reorientation of fibers under straining of an isotropic composite (total number of fibers = 25,000); (a) before straining ($\varepsilon = 0$) and (b) after straining ($\varepsilon = 0.5$); $L/D = 55$.

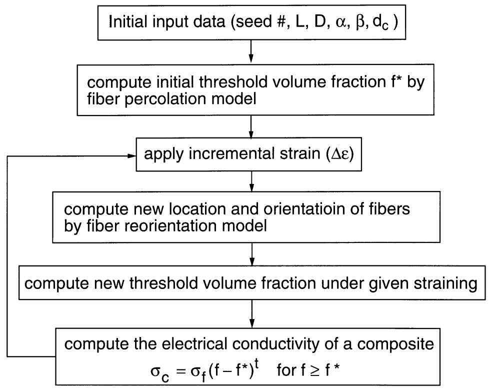

Fig. 7. The computation procedure of the present model.

isotropic composite with $L/D = 55$ before straining and the reorientation after the final strain (ε) of 0.5 is reached. The reason for using $L/D = 55$ is to compare the predictions with the experimental data where $L/D = 55$ was used (Narita, 1990). The final strain of 0.5 is reached by incremental strain $\Delta\varepsilon$ of 0.05. It is found in Fig. 6 that the initially uniform distribution is changed to non-uniform type distribution, becoming narrower distribution as straining increases. For out-of-plane angles (ϕ), although it is not shown here, similar trends of fiber reorientation distribution are observed. It is also found that the change in volume fraction of fiber (f) is negligibly small since the matrix is elastomer (Poisson's ratio $\nu \cong 0.5$).

On the basis of the analytical formulation in Section 2, the computational process of the piezoresistive behavior is illustrated in Fig. 7. First initial input data, including of seed number, fiber length and diameter, fiber orientations and tunneling distance are assigned, and for a given microstructure of a composite system, the threshold volume fraction of fiber is computed by applying the fiber percolation model. Subsequently, incremental strain along the x-axis is applied and new microstructure of the composite with relocation and reorientation of conductive fibers is established by applying the fiber reorientation model. The microstructure is examined to see if it forms a percolation network, and new threshold fiber volume fraction is then computed. Finally the effective electrical conductivity is calculated for the composite with the changed microstructure by using Eq. (1).

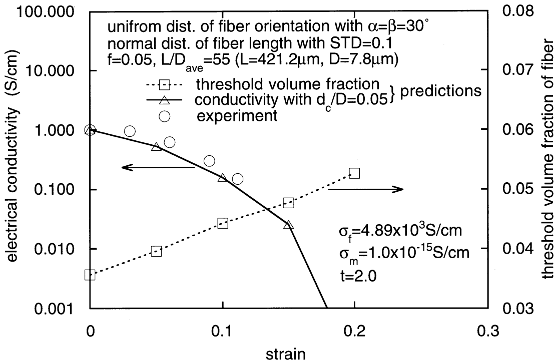

Fig. 8. The electrical conductivity of a composite and threshold volume fraction of conductive fiber as a function of the applied strain.

The numerical results of the present model are compared with the previous experimental data of a Ni-coated graphite fiber/natural rubber composite with fiber volume fraction (f) of 0.05 and average fiber aspect ratio (L/D) of 55, i.e., $L = 421.2$ μm and $D = 7.8$ μm (Narita, 1990). The specimen dimension is $1 \times 1 \times 1$ mm^3. It is assumed that fiber orientations of the composite consist of initially ($\varepsilon = 0$) uniform fiber distributions with in-plane limit angle $\alpha = 30°$ and out-of-plane limit angle $\beta = 30°$, and fiber length is composed of a normal distribution with standard deviation of 0.1. The ratio of tunneling distance to fiber diameter ($d_c/D = 0.05$) was approximately determined by matching the threshold volume fractions predicted by the present model with the experimental value of f^*, 0.035. The predicted effective electrical conductivities (triangles with solid line) along the x-axis (see Fig. 4) are plotted as a function of applied uniaxial strain (ε) in Fig. 8, where the experimental data are also shown as circles. Fig. 8 also illustrates the change in the threshold volume fraction (squares with dotted line) under the applied strain. The threshold fiber volume fraction is seen to increase with the applied strain. This explains that the initially percolating fiber network is degenerated by separation of the previously existing contacts between fibers due to reorientation of conductive fibers. This result is also supported by the fact that the fiber orientation distribution becomes narrower (more aligned toward the x-direction) due to straining in the x-axis (see Fig. 6) and the narrower distribution gives rise to higher threshold volume fraction of conductive fiber (Taya and Ueda, 1987). The electrical conductivity of the composite is calculated by using Eq. (1) with an experimentally obtained conductivity exponent t of 2.0 (Narita, 1990), which is known as a universal value for a 3D system (Stauffer, 1985), and the computed f^* by the fiber percolation model, where conductivities of coated fiber and matrix are 4.89×10^3 S/cm and 1.0×10^{-15} S/cm, respectively, and the Poissons' ratio of the composite is 0.5. Fig. 8 clearly demonstrates a piezoresistive behavior of the composite where the composite becomes less-conductive as the applied strain increases and non-conductive at and beyond a critical strain of 0.2, exhibiting a switching behavior. As seen in Fig. 8, the numerical data have a reasonably good agreement with the experimental data.

4. Conclusion

A new analytical modeling was developed to study a piezoresistive behavior of a conductive short fiber reinforced elastomer composite. The analytical prediction was deduced from a fiber percolation model when the change in the threshold volume fraction (f^*) of fiber under straining is taken into account. The change in the threshold volume fraction of fiber is mainly attributed to the change in microstructure of a composite under straining. The reorientation distributions of fibers due to straining were computed by using a fiber reorientation model. It was found that the threshold fiber volume fraction increases as the applied strain increases. It was also found in this study that an initially conductive composite becomes non-conductive around the critical strain, exhibiting a switching behavior.

Acknowledgements

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References

Aspden, R.M., 1986. Relation between structure and mechanical behavior of fiber-reinforced composite materials at large strains. Proc. R. Soc. London A 406, 287.

Balberg, I., 1987. Tunneling and nonuniversal conductivity in composite materials. Phys. Rev. Lett. 59, 1305.

Balberg, I., Binenbaum, N., 1983. Computer study of the percolation threshold in a two-dimensional anisotropic system of conducting sticks. Phys. Rev. B 28, 3799.

Balberg, I., Binenbaum, N., 1987. Invariant properties of the percolation thresholds in the soft-core–hard-core transition. Phys. Rev. A 35, 5174.

Broadbent, S.R., Hammersley, J.M., 1957. Percolation processes: I. Crystals and mazes. Proc. Cambridge Philos. Soc. 53, 629.

Carmona, F., El Amarti, A., 1992. Temperature and pressure dependence of the conductivity anisotropy of unidirectional short carbon fiber filled polymers. J. Mater. Res. 7, 117.

Carmona, F., Canet, R., Delhaes, P., 1987. Piezoresistivity of heterogeneous solids. J. Appl. Phys. 61, 2550.

Cohen, M.H., Jortner, J., Webman, I., 1978. The electronic properties of inhomogeneous materials; metal–nonmetal transitions. In: Garland, J.C., Tanner, D.B. (Eds.), Electrical transport and optical properties of inhomogeneous Media, AIP Conf. Proc. No. 40, American Institute of Physics, New York, p. 63.

Gurland, J., 1966. An estimate of contact and continuity of dispersions in opaque samples. Trans. Metall. Soc. AIME 236, 642.

Kirkpatrick, S., 1973. Percolation and conduction. Rev. Mod. Phys. 45, 574.

Lundberg, B., Sundqvist, B., 1986. Resistivity of a composite conducting polymer as a function of temperature, pressure and environment; Applications as a pressure and gas concentration transducer. J. Appl. Phys. 60, 1074.

McLachlan, D.S., Blaszkiewicz, M., Newnham, R.E., 1990. Electrical resistivity of composites. J. Am. Ceram. Soc. 73, 2187.

Narita, Q., 1990. Percolation conductivity model and mechanical properties of short fiber/polymer composites, MS Thesis, Tohoku Univ., Department of Mater. Process.

Pike, G.E., Seager, C.H., 1974. Percolation and conductivity: A computer study I. Phys. Rev. B 10, 1421.

Pramanik, P.K., Khastgir, D., De, S.K., Saha, T.N., 1990. Pressure-sensitive electrically conductive nitrile rubber composites filled with particulate carbon black and short carbon fiber. J. Mater. Sci. 25, 3848.

Stauffer, D., 1985. Introduction to Percolation Theory, Taylor and Francis, London.

Taya, M., Ueda, N., 1987. Prediction of the in-plane electrical conductivity of a misoriented short fiber composite: Fiber percolation model versus effective medium theory. Trans. ASME, J. Eng. Mater. Technol. 109, 252.

Taya, M., Kim, W.J., Ono, K., 1994. Electro-mechanical coupling behavior of conductive short fiber reinforced elastomers. In: Mechanics and Materials for Electronic Packaging, Vol. 3: Coupled Field Behavior in Materials, American Society of Mechanical Engineers (AMD-Vol. 193, NY), p. 61.

Ueda, N., Taya, M., 1986. Prediction of the electrical conductivity of two-dimensionally misoriented short fiber composites by a percolation model. J. Appl. Phys. 60, 459.

Wang, S.F., Ogale, A.A., 1993. Continuum space simulation and experimental characterization of electrical percolation behavior of particulate composites. Comp. Sci. Technol. 46, 93.

Yoshikawa, S., Ota, T., Newnham, R., Amin, A., 1990. Piezoresistivity in polymer-ceramic composites. J. Am. Ceram. Soc. 73, 263.