Spatial Distribution of Metal Fillers in Isotropically Conductive Adhesives

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The dc electric conductance of isotropically conductive adhesive (ICA) was studied. Assuming completely random distribution of the metal fillers in the ICA, it was demonstrated that the percolation volume percentage of the metal fillers can be significantly reduced by adding nano-size fillers (nanofillers) into the system originally containing only micro-size fillers (microfillers). However experiments show that, due to the surface tensions, nanofillers tend to gather around microfillers as well as to form clusters themselves so the resistivity of the ICA increases following the increase of the nanofillers' volume percentage. In the present work, these cluster effects are investigated by simulating the detailed random walks of the nanofillers and microfillers in the system. It is concluded that the cluster effects of the nanofillers deteriorate the electric conductivity of the ICA because the microfillers separate from each other so that it is more difficult to form the electrical conduction path in the ICA.

Key words: ICA, nanofillers, microfillers

INTRODUCTION

An isotropically conductive adhesive (ICA) consists of a polymer matrix filled with conductive particles. The most commonly used fillers are metals such as Ag or Cu. The metal fillers must reach and exceed the percolation threshold of the electric conducting network for an insulator-conductor transition.[1] Adhesive failure is often observed due to the poor impact strength because of the heavy metal loading required in the range of 80–90 wt.% that is essential to guarantee effective electrical conduction.[2,3] It is desirable to decrease the loading of the metal-fillers to improve the impact strength.[2,4] The trade-off between electrical and mechanical properties is the subject of continued research. A bimodal distribution of nano-size and micro-size metal fillers was proposed to reduce the metal loading for better mechanical performance while the electrical and manufacturing processing properties remain unchanged.[5] Nano-size metal particles were used to improve the electrical conduction of the ICA.[6] However, the electrical conductivity was reduced when the volume percentage of the nano-size fillers was increased in the system.[7]

Extensive modeling of the ICA has been undertaken recently.[8] However, a well-behaved particle distribution is normally assumed. In this work, a model is presented to investigate the metal filler distribution in the ICA. Two types of metal fillers are studied, one nano-size (nanofillers) and the other micro-size (microfillers). Instead of the ideal random distribution of the metal fillers, that is the basis of the percolation theory for the functioning ICA, the spatial distributions of the metal fillers are modeled by random walking simulations.

The ICA preparation process is modeled by randomly walking metal fillers through the adhesive matrix, from complete separation of the metal fillers from the adhesive matrix to completely random distribution of the metal fillers in the adhesive matrix. The effect of clustering of the metal fillers on the electric conductance of the whole ICA system is studied by introducing spatial preferences to the random walking of the metal fillers toward their neighbors.

(Received September 28, 2000; accepted December 8, 2000)

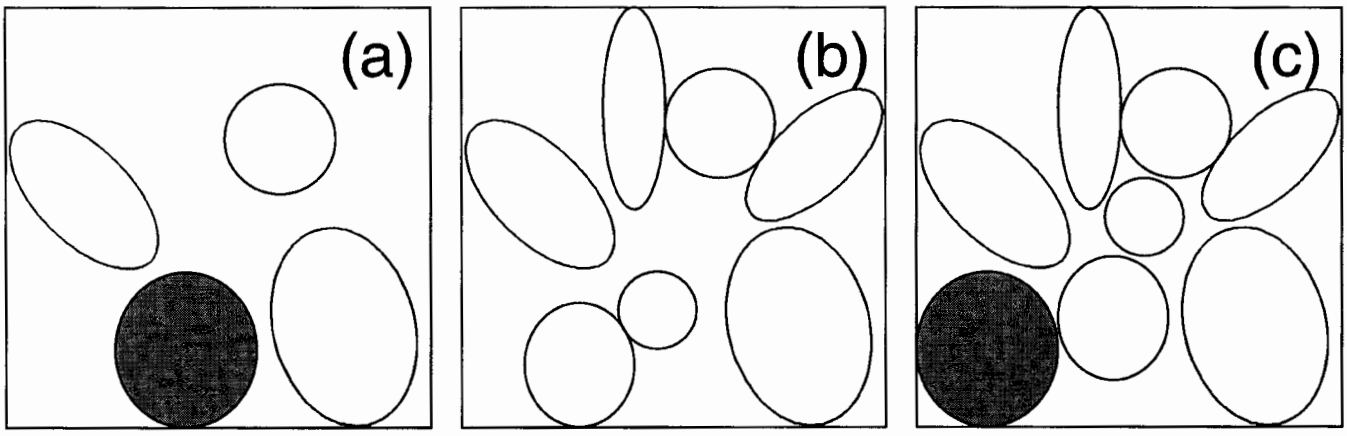

Fig. 1. (a) New (gray) filler can be added to the ICA having a low volume percentage of metal fillers. (b) It is impossible to add the same gray filler to this ICA already having a high volume percentage of metal fillers. (c) ICA with same high volume percentage as in (b) can have even higher volume percentage.

ELECTRIC CONDUCTION OF ICA WITH RANDOMLY DISTRIBUTED METAL FILLERS

Various metal fillers are simulated in the form of ellipsoids

$$\frac{(X-x_0)^2}{a^2}+\frac{(Y-y_0)^2}{b^2}+\frac{(Z-z_0)^2}{c^2}\le 1 \qquad (1)$$

centered at (x_0, y_0, z_0), where (a, b, c) are three parameters describing the geometric shape of the filler in the principal XYZ-coordinate of the ellipsoid. The orientation of the metal filler in the real xyz-coordinate with respect to the XYZ-coordinate is described by three Euler angles (θ, ψ, ϕ). The nine parameters $(x_0, y_0, z_0, a, b, c, \theta, \psi, \phi)$ describing the filler in the computer simulation are determined by random numbers when the distributions (spatial distribution, spatial orientation and geometric shape) of the metal fillers in the ICA are random. This can easily simulate metal fillers in the form of disk flakes by this formula. The generation of the metal filler is repeated in the computer until the predetermined volume percentage of the metal fillers is achieved.

To numerically determine the electrical characteristics of the ICA and to avoid constriction resistance in the numerical treatment.[9,10] Two types of electric conductance can occur: (a) conductance within unit cell i which is denoted as ρ_i, and (b) conductance between two adjacent unit cells i and j, that is calculated by

$$\frac{2}{\rho_{ji}}=\frac{1}{\rho_j}+\frac{1}{\rho_i} \qquad (2)$$

by Ohm's law. Knowing the conductance ρ_{ji} between cells j and i, Kirchoff's linear equations can be applied

$$\sum_j (V_j - V_i)\rho_{ji} = 0 \qquad (3)$$

from which the voltage at cell i, V_i is determined. The cells included in the above Kirchoff's equations are not at the external terminals. At external electrodes the following boundary conditions exist

$$V(0) = 0,\ V(L_z) = V_{ex} \qquad (4)$$

where V_{ex} is the externally applied bias. Knowing the distribution of the electric potential, the electric conductance of the system can be calculated.

The geometric size of a realistic ICA is too large to be simulated completely, so a sampling of the ICA with a limited spatial volume and its electric conduction along the z-direction are considered. The sampling ICA is embedded between two metal contacts located at $z \le 0$ and $z \ge L_z$. The xy-extension of the ICA is $L \times L$. The electric conduction of the sampling ICA is not exactly isotropic because of the limited spatial volume. However properly averaging the electric conductance of many sample ICAs can result in typical electric characteristics of a real ICA sample. For example, 27 samples of $L \times L \times L_z$ ICA's gives us the conductance of one ICA with $3L \times 3L \times 3L$, by

$$\frac{1}{\rho_{3L\times 3L\times 3L_z}}=\frac{1}{\sum_1^9 \rho_n}+\frac{1}{\sum_{10}^{18} \rho_n}+\frac{1}{\sum_{19}^{27} \rho_n} \qquad (5)$$

when sampling ICAs, n = (1, 9), (10,18), and (19, 27) are first parallel-connected and then series-connected.

Mixing different metal fillers could theoretically reduce the volume percentage of the metal fillers in the ICA,[5] so a mixture of two types of metal fillers is considered in the adhesive, one nano-size (having radius of 25 nm) and the other micro-size (a =: b = 2c = 2 μm).

When the volume percentage of the metal fillers is rather small in the isotropically conductive adhesives, metal fillers are not correlated with one another. The fillers distribute in the ICA freely and uniformly so the simulation is straightforward. When the volume percentage increases to a value where the metal fillers interact with one another in the ICA, spatial correlations among metal fillers begins to appear, especially when the spatial geometry of the metal fillers is not regular. Under such circumstances

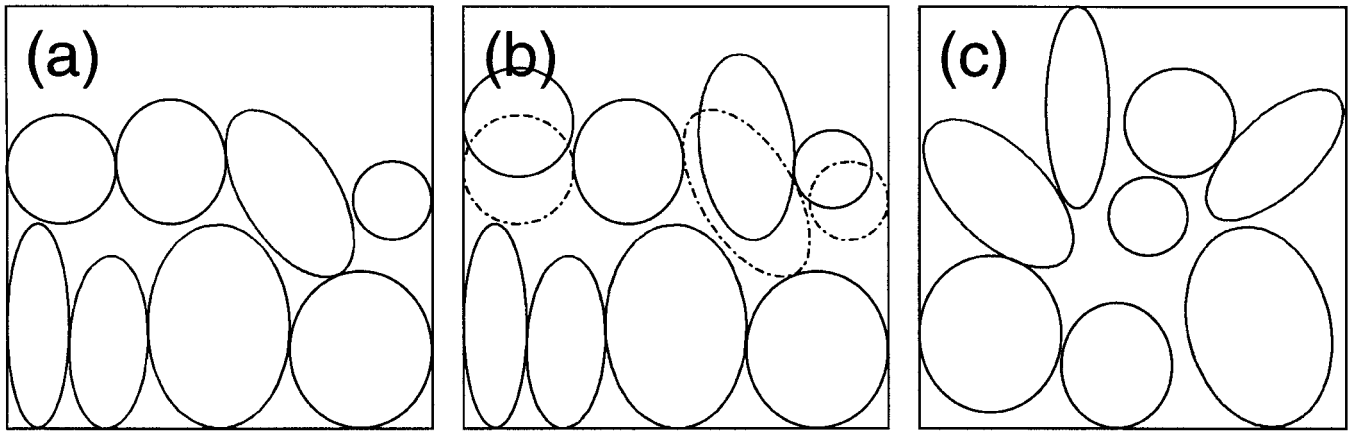

Fig. 2. Fabrication process of an ICA. (a) Metal fillers, closely packed up, are added to the adhesive matrix (segregation phase); (b) Metal fillers at the outskirt of the closely packed cluster (dashed lines) are first to outspread them into adhesive matrix; (c) the whole system is mixed up (alloying phase).

the complete-random-number generation in the computer is not proper because it is computationally intensive and may be not possible to reach the predetermined volume percentage. A simple example is demonstrated in Fig. 1. It is straightforward to add the gray filler to the ICA in Fig. 1a while it is impossible in Fig. 1b. But a slight modification in the configuration of the initial metal fillers can enable a high volume percentage of fillers. However, the distributions of metal fillers become correlated at high volume percentages.

The fabrication process of the ICA samples does not put metal fillers one after another and randomly into the adhesive matrix. Instead, the metal fillers, first closely packed, are added to the adhesive matrix (as a segregation phase) and then the whole system is mixed to reach a random distribution of the metal fillers (an alloying phase). The physical process is schematically represented in Fig. 2.

A simulation of the physical preparation in the ICA is shown in Fig. 2. The size of the ICA sample is $L = L_z = 20$ μm. Numerical simulations of the electric dc conduction are presented in Fig. 3.

Scattering of the electric conductances for different samples of ICA are extended in the logarithmic scale, below the percolation volume percentage where the electric conductances are essentially zero. In Fig. 3 two simple averaging results of the ten sampling ICAs are presented. The solid lines are obtained when the ten sampling ICAs are parallel connected so that the averaged electric conductance is the sum of the ten individual conductances (ρ_n, n = 1,2 ... 10) divided by ten

$$\rho_{parallel} = \frac{1}{10}\sum_{n=1}^{10} \rho_n \tag{6}$$

The $\rho_{parallel}$ is determined by the largest ρ_n. The dotted lines represent the conductance when the ten sampling ICAs are in series connection so that

$$\frac{10}{\rho_{series}} = \sum_{n=1}^{10} \frac{1}{\rho_n} \tag{7}$$

which is determined by the lowest ρ_n. The difference between ρ_{series} and $\rho_{parallel}$ decreases when the sampling ICAs are conductive. It is expected that $\rho_{series} = \rho_{parallel}$ when the spatial volume of the sampling ICA ($L \times L \times L_z$) and the number of the ICA samples are significantly increased.

Three series of ICA samples having 0%, 13.8%, 27.6% volume percentage of the nanofillers are considered. Figure 3 shows the increase of the electric conductance of the system following the increase of the volume percentage of the metal fillers. This is the functioning mechanism of the ICA, namely, for an electric conduction network there exists a critical probability of a metal filler occupying a lattice site with which electric percolation occurs.[11] Assuming that the particles (both the nanofillers and microfillers) distribute and orient randomly in the ICA, i.e., (x_0, y_0, z_0, θ, ψ, ϕ) are completely random, Fig. 3 shows a drastic reduction in the volume percentage of the microfillers at which the electric conductance becomes significant (percolation in the electric network). The total critical volume percentage of the metal fillers (microfillers plus nanofillers) decreases from 47% to 44% and 41% when the nanofillers increase their volume percentages from 0 to 13.8% and 27.6%, respectively.

To understand the results, a two dimensional electric network with a square lattice in the form of $\mathbf{r} = n_x\mathbf{x}_0 + n_y\mathbf{y}_0$ is considered, where n_x and n_y are integers and $\mathbf{x}_0$ and $\mathbf{y}_0$ are unit vectors along the x and y axes. It is assumed that the size of metal fillers is uniform and the metal fillers distribute randomly in the network. The occupation probability of a lattice point by a metal filler is denoted as p, and it is known by percolation theory[11] that the critical probability of percolation, p_c, is 1/2. For a three-dimensional electrical network, the maximum number of nearest metal fillers is 12. However, far below the maximum volume percentage under the normal ICA conductive condition, the statistical number of nearest metal fillers is less than 6. We approximate the same $p_c = 1/2$ for the three-dimensional ICA. Denoting a as the radius of the metal fillers, the maximum volume percentage is

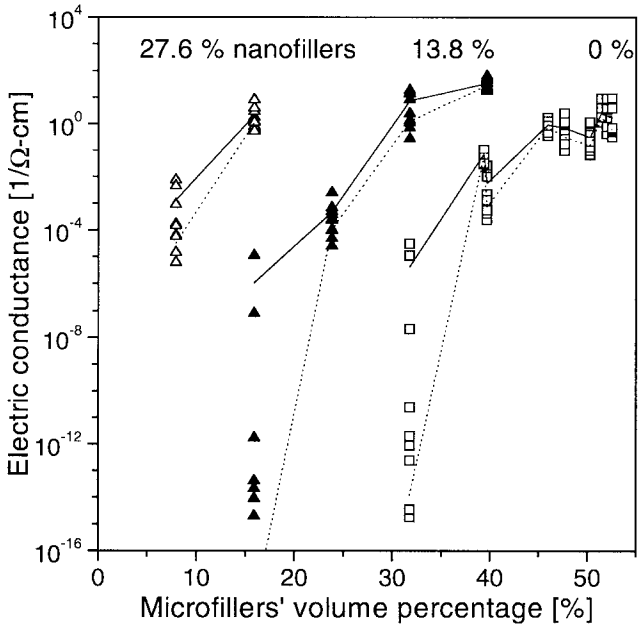

Fig. 3. Electric conductance along the z-direction of ICA $L \times L \times L_z$ with randomly distributed micro- and nanofillers. Square symbol: 0%; Solid triangle symbol: 13.8%; Open triangle symbol: 27.6% volume percentage of nano-size fillers in the ICA. Solid lines: parallel connection; Dotted lines: series connection.

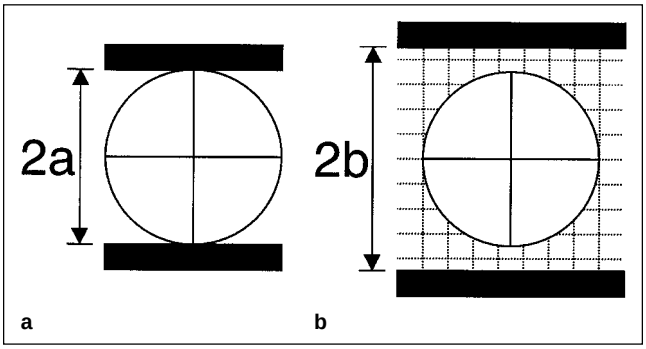

Fig. 4. (a): Single electrical network (solid lines) of microfillers. (b): Composite network of microfillers (solid lines) and nanofillers (dotted lines).

achieved when the fillers have a hexagonal close-packed structure. Starting with a close-packed triangular lattice as the first layer, the next layer is formed by placing a metal filler in the depressions left in the center of every other triangle in the first layer, thereby forming a second triangular layer, shifted with respect to the first. The third layer is formed by placing metal fillers in the alternate depressions in the second layer, so that they lie directly over the metal fillers in the first layer. The resulting lattice is hexagonal close-packed. The distance between the first layer to the third layer, $c = 2a\sqrt{8/3}$. Its volume is $a^2 = \sqrt{3}C = 4\sqrt{2}a^3$. The maximal volume percentage is

$$v_{max} = \frac{(4/3)\pi a^3}{4\sqrt{2}a^3} = 74.05\% \qquad (8)$$

where $4\pi a^3/3$ is the volume of a metal filler with radius, a. The percolation volume percentage is expected to be $\beta_c = p_c v_{max} = 37.02\%$ which is very close to that obtained numerically from Fig. 3 for a three-dimensional ICA where the metal fillers distribute freely.

Now consider an ICA that consists of two types of metal fillers, one a nanofiller and the other a microfiller. If the two types of fillers distribute randomly, we can divide the system into two subsystems. The first subsystem is composed only by the microfillers. The nanofillers form a sub-network in the space between microfillers. Consider the electrical network of Fig. 4 where there is one microfiller. Between the upper and lower contacts, the volume percentage of the microfiller is

$$v_{micro} = \frac{(4/3)\pi a^3}{8a^3} = 52.36\% \qquad (9)$$

Increasing the size of the ICA from 2a to 2b, the vacancy between the microfiller and the contacts becomes $8b^3 - (4/3)\pi a^3$. The vacant space is now filled with nanofillers that becomes conductive at a critical volume percentage of 37.02%. The total volume percentage of metal fillers is

$$v_{mix} = \frac{\beta_c[8b^3 - (4/3)\pi a^3] + (4/3)\pi a^3}{8b^3} = \beta_c + (1-\beta_c)\frac{\pi}{6}\left(\frac{a}{b}\right)^3 \qquad (10)$$

which is 46.7% when $\beta_c = 37.02\%$ and $b = 1.5a$. Figure 5 shows v_{mix} as a function of b/a with respect to v_{micro}. It is observed here that b/a must be larger than a certain critical value in order to obtain a reduced v_{mix}. This is due to the consideration of only one microfiller.

CLUSTER EFFECT OF METAL FILLERS ON ICA ELECTRIC CONDUCTION

Thus far the electric conduction of an ICA has been modeled when the metal fillers are distributed randomly in the space. However, this does not occur in samples of Ag-filled adhesive composite materials studied experimentally. Three types of silver fillers were used in Ref. 7 to study the effect of particle size on the electrical conductivity, nanofillers approximately 50–150 nm in diameter, microfillers with diameter of 5–8 μm and flake Ag of 10 μm in length. The measured resistivities [Ω·cm] of ICAs are: Ag-flake, 4.23×10^{-3}; Microfillers: 7.21×10^{-3}; 80% microfillers+20% nanofillers: 0.36; 50% microfillers+50% nanofillers: 5.88; Nanofillers: nonconductive.

Transmission electron microscope (TEM) images showed[7] that clusters of nanofillers float among bigger particles so that adding small particles into the system provides less possibility of forming conductive continuous linkages through the electrical network.

The cluster effect is modeled by rearranging the spatial locations of nanofillers in the following manner. A random distribution of all types of fillers in the sampling ICA is assumed. The spatial location and orientation of every metal filler are moved around in

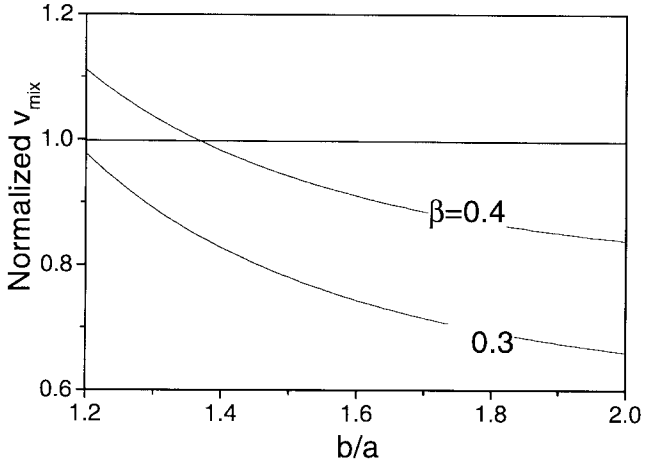

Fig. 5. Normalized v_{mix} as a function of the b/a for different percolation volume percentage of the nanofillers.

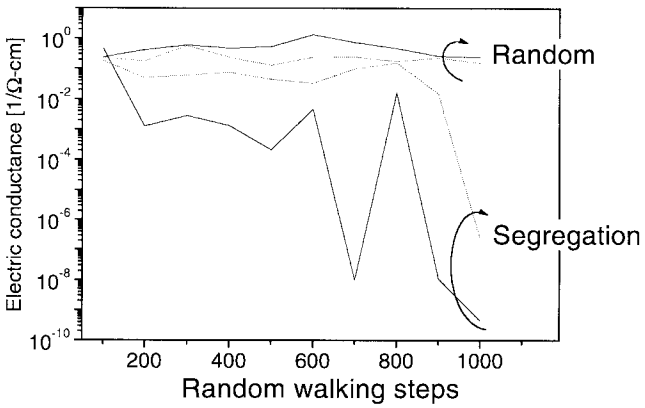

Fig. 6. The electric conductances of sampling ICAs as functions of the cluster formation process. Dotted lines: sample A with 31.45% volume percentage of microfillers and 13.80% of nanofillers); Solid lines: sample B with 15.73% of microfillers and 27.60% nanofillers.

the ICA as in the sample preparation processes (Figs. 1 and 2) using random walk simulation. The nanoparticles also move in the manner of random walk but with certain spatial preference directions. As demonstrated by the experiments, nanofillers prefer to form clusters or gather around microfillers.

First consider a specific nanofiller located at (x_0^n, y_0^n, z_0^n) (superscript n here stands for "nanofiller") gathering around a microfiller. The simulation locates the microfiller at (x_0^m, y_0^m, z_0^m) (superscript m stands for "microfiller"), the random walking step (δ_x, δ_y, δ_z) in the unit length of the unit cell is determined by three random numbers (i_1, i_2, i_3) [i_1, i_2, $i_3 \in (0,1)$], such that $x_0^m - x_0^n > 0$

$$\delta_x = \begin{cases} -1 & \text{if } i_1 \le 0.25 \\ 0 & \text{if } 0.25 < i_1 \le 0.5 \\ 1 & \text{otherwise} \end{cases} \tag{11}$$

$x_0^m - x_0^n = 0$

$$\delta_x = \begin{cases} -1 & \text{if } i_1 \le 0.25 \\ 0 & \text{if } 0.25 < i_1 \le 0.75 \\ 1 & \text{otherwise} \end{cases} \tag{12}$$

and finally when $x_0^m - x_0^n < 0$,

$$\delta_x = \begin{cases} -1 & \text{if } i_1 \le 0.5 \\ 0 & \text{if } 0.5 < i_1 \le 0.75 \\ 1 & \text{otherwise} \end{cases} \tag{13}$$

δ_y and δ_z are determined similarly. In other words, the nanofiller prefers to move toward its nearby microfiller and its new location becomes $(x_0^n + \delta_x, y_0^n + \delta_y, z_0^n + \delta_z)$ after the walk.

When the two nearest-neighbor fillers touch each other, they become a composite filler. The simulation then tries to find a new nearest-neighbor filler. A cluster thus gradually builds up from the composite fillers. Similarly, the case of the nanofiller clusters and the mixture of nanofillers clustering around nearby microfiller and around nearby nanofiller can be considered.

The effect of cluster formations on the electric property of the sampling ICA is presented by calculating the resistivity of the ICA as a function of the number of walks started from a completely random distribution of the metal fillers. Two ICA samples ($20 \times 20 \times 20$ μm^3) containing three types of metal fillers are studied: N_1 microfillers of type 1: a = b = c = 2 μm (spherical); N_2 microfiller 2: a = b = 2c = 2 μm (disk-like to account for the experimental flake fillers); N_3 nanofillers: a = b = c = 50 nm. In sample A, $N_1 = N_2 = 100$, $N_3 = 2000$ (31.45% volume percentage of microfillers and 13.80% of nanofillers). Sample B has $N_1 = N_2 =: 50$ and $N_3 = 4000$ (15.73% and 27.60% volume percentages). The electric conductance is recorded for every 100 walking steps of all fillers in the system. We do not distinguish the nanofillers and microfillers during the cluster formation processes.

The resulting electric conductances are presented in Fig. 6. Along with the results of completely random walk (when the spatial preferences of the random walks are removed in the simulation) for comparison. A completely random distribution of metal fillers, sample A and sample B, which contains 45.25% and 43.33% metal fillers, respectively, are electrically conductive. However, switching on the spatial preferences of the random walks, the differences between the two samples are observed. Sample A has 2000 nanofillers and the cluster effect on the electric conductance is observed only after 800 random walking steps. The amount of the nanofillers in sample B is increased by a factor of 2 and the cluster effect appears already after only 200 walking steps.

By comparing Fig. 6 with experimental results, a spatial preference of random walks of nanofillers during the ICA preparation deteriorates the electric conductance of the ICA. Keeping the rate of the spatial preference constant during the random walk

process, the deterioration rate in the electric conductance increases following the increase of the nanofiller concentration in the ICA. Moreover, the fluctuation in the electric conductance is stronger when the nanofiller concentration in the ICA is high.

Further investigations, both theoretically and experimentally, on the origin of the clusters, e.g., the interactions among metal fillers[12] and self-sintering during the powder manufacturing process,[13] are of great importance to determine the absolute formation rate of the cluster effect, and to optimize and design the isotropically conductive adhesives.

SUMMARY

Metal-based conductive adhesives have been extensively studied. High metal loading is essential to guarantee effective electrical conduction, which often causes adhesive failure. To decrease the loading of the metal-fillers, a bimodal distribution of nano-size and micro-size metal fillers has been proposed. By combination of the percolation theory and detailed numerical simulation, a reduction in the metal-filler volume percentage of 10% can be achieved when the volume percentage of the nanofillers in the isotropically conductive adhesive (ICA) increases from 2.8% to 13.8%. The simulation assumes a completely random distribution of both the microfillers and nanofillers.

However the TEM showed[7] that the chances of direct contact among microfillers are reduced when nanofillers are introduced into the system. Nanofillers tend to form clusters with significant spatial gaps among the clusters. Thus the electrical conductivity reduces when increasing the volume percentage of the nanofillers.

Including the effects of metal fillers (both microfillers and nanofillers) gathering around nearby fillers to form clusters, the spatial distributions of metal fillers are simulated in a bimodal ICA by preferential random walks. Starting from a completely random distribution of metal fillers, both the microfillers and nanofillers are programmed to move more preferentially towards corresponding nearby fillers or clusters. Numerical calculations show the conductivity reduction following the progress of the cluster formation.

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