Conductive percolation threshold of conductive-insulating granular composites

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The percolation phenomenon of conductive-insulating composites has been extensively studied because of their wide applications in the electronic industry [1–7]. Such materials possess special physical properties different from metals, for example the thermal conductivity of conductive polymers is lower, the wear resistance of conductive ceramics is higher. Conductive-insulating composites can be made by dispersing conductive particles into the melt of an insulating matrix, such as a polymer [1–3], by thermal pressing of a mixture of conductive-insulating powders, such as metal and ceramic powders [4–6], and by growing a thin film on a substrate [7]. In such a material, when the volume fraction of the conductive powders is lower than a critical valve, it behaves as an insulator; as the volume fraction of the conductive powders reaches the critical valve, its electrical conductivity sharply increases by several orders of magnitude. This critical valve is referred to as the percolation threshold at which a conductive network is formed to span the entire cross section of the body of the material. For materials with crystal structures, such as simple cubic, body centered cubic (BCC) and face centred cubic (FCC) lattices, the exact or very accurate values of the percolation thresholds have been obtained by theoretical analysis or by computer simulation. For example, the site percolation threshold is about 0.3116 for the simple cubic lattice and is about 0.246 for the BCC lattice [8]. However, for composites with amorphous structures, such as a compact of a mixture of conductive-insulating powders, only experimental data and simplified analytical models are available.

Using a Monte Carlo simulation model, we studied the percolation behavior of such granular composites with amorphous structure. In this letter we briefly review the simulation model first; then we report our simulation result on conductive and insulating powders with equal particle size. The assumptions made in this study are that the particles have spherical shape and are rigid so that overlap is not allowed. For convenience, the particle diameter is set to one unit.

The simulation model is composed of two parts. The first part is the generation of the composite structure using a random particle-packing model. Initially the particles are randomly generated within a cubic space with high packing density and overlaps. Then a relaxing procedure is applied to reduce or eliminate the overlaps; meanwhile, the cubic space is slightly expanded depending on the overlap situation. By repeating the relaxation and expansion procedures, overlap free random packing can be finally obtained. In the second part, for a given conductive volume fraction φ we randomly sample $n_c = \varphi n$ conductive particles in the random packing; we then apply a from-neighbour-to-neighbor propagation method to count the conductive particles belonging to the same cluster and the number of clusters in the packing; finally we check if there exists a percolating cluster that spans the packing space in a given direction. It is a feature of this simulation model that neighbouring particles are either slightly overlapped or separated, if the gap between two particles is smaller than 0.005, we consider they contact each other. Fig. 1 shows the three-dimensional view of the random packing of one thousand particles and the projection of the largest conductive cluster on the $x-z$ plane that spans the packing space in the z direction. Details of the simulation model and cluster identification method are given in [9 , 10].

In the simulation we employed n =1,000, n = 5,000 and n = 20,000 particles respectively. With a given value of φ, in each case we randomly took 10,000 samples by repeating the second part of the simulation model, and then counted the percentage $G'(\varphi)$ of those in which there existed percolating clusters. The values of $G'(\varphi)$ in the x, y and z directions were counted respectively and then averaged, thus the average value of $G'(\varphi)$ was calculated from 30 000 samples, which could be taken as the percolation probability at φ. Fig. 2 shows $G'(\varphi)$ as a function of φ. In infinite systems, $n \to \infty$, $G'(\varphi) = 0$ as $\varphi < \varphi_c$, and $G'(\varphi) = 1$ as $\varphi \geq \varphi_c$, where φ_c is the percolation threshold. However, for finite systems $G'(\varphi)$ is a probability depending on the system size n and the

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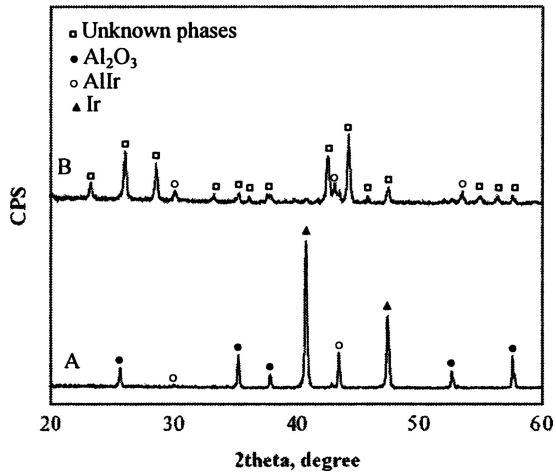

Figure 1 Views of the random packing and the percolating cluster, $n = 1000$, $\varphi = 0.287$.

volume fraction φ, and as φ increases $G'(\varphi)$ gradually approaches one. For finite three-dimensional systems with a free boundary at percolation threshold φ_c, it has been shown that $G'(\varphi_c) = 0.28 \pm 0.01$ which is independent of the particle arrangement and the system size n [11]. Fig. 2 shows that, for random packings with system sizes $n = 5000$ and $n = 20\,000$, the percolation probabilities also cross at $G'(\varphi) = 0.286$, which is in excellent agreement with 0.28 ± 0.01. Fig. 2 also shows our simulation results on simple cubic lattices. In Fig. 2, corresponding to $G'(\varphi_c) = 0.286$ we can estimate that the percolation threshold φ_c of the random packing is about 0.285. For a simple cubic lattice the site percolation threshold $\varphi_c = 0.3116$ with packing density about 0.524, and for a BCC lattice $\varphi_c = 0.246$ with packing density about 0.680. The random packing density we obtained is about 0.630 which falls between the simple cubic and BCC packing densities, thus it is expected that the percolation threshold should also fall between the simple cubic and BCC site percolation thresholds, 0.3116 and 0.246. From the above argument one can conclude that a value around 0.285 is a reasonable estimation of φ_c for random packing. It should be mentioned that the packing density we obtained approaches the close random packing density 0.633 [12], for random loose packing with density around 0.6 the

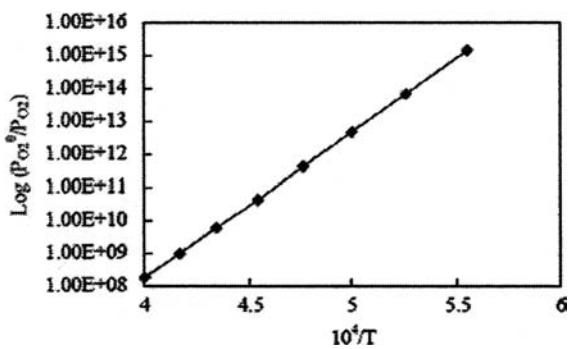

Figure 2 Percolating probability $G\prime(\varphi)$ as function of φ.

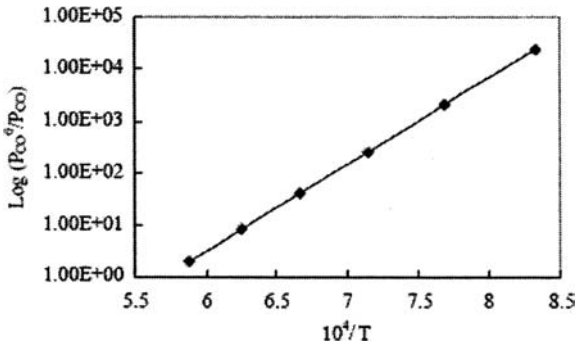

Figure 3 Virtual-percolation threshold φ_c as function of gap δ.

percolation threshold should be higher than 0.285 but still lower than 0.3116.

The above percolation threshold $\varphi_c = 0.285$ was obtained under the condition that the particles belonging to the same cluster must contact each other. However, lower percolation thresholds and nonlinear voltage–current (V-I) characteristics have been observed in conductive-insulating composites [7, 13, 14]. This is distinguished from the above definition and we call it the virtual-contact percolation threshold. For a composite with nanosize conductive particles dispersed in a continuum-insulating matrix, this is due to the tunneling of single electrons between neighboring particles. A simple geometrical model shows that, at a constant volume fraction, the average gap between neighboring particles decreases with decreasing particle size [15]. Thus, as the gap becomes sufficiently small the electron can overcome the Coulomb charging energy and the onset of conduction occurs. For composites with particles of micro-size or larger, one of the explanations of the lower percolation threshold is due to the dielectric breakdown between the neighboring particles [14]. In such composites there exist no real percolating clusters. However, when an electric field is applied to the opposite sides of a specimen, the medium in the gap between near contact particles belonging to different clusters will be polarized. As the applied field exceeds the dielectric breakdown limit the onset of conduction occurs. Our simulation provides detailed structural information that allows the prediction of the noncontact percolation threshold. We set a limit δ such that when the gap between two conductive particles is smaller than δ, we consider then to virtually contact each other. Thus, applying the second part of the simulation model, we can estimate the percolation threshold φ_c at a given value of δ. Fig. 3 shows φ_c as a function of δ, from which we see that as δ increases to 0.2, φ_c drops to about 0.224. At constant volume fraction φ, we also found that the size of the virtual-percolating cluster increases with the dielectric breakdown gap δ. This implies that as the applied voltage increases more conductive particles will carry current, which leads to a drop in the electrical resistance of the percolating cluster resulting in the nonlinear V–I characteristics.

In summary, Monte Carlo simulation has been applied to study the percolation phenomenon of conductive-

insulating granular composites with amorphous structure. Results show that the percolation threshold φ_c of such composites falls between the simple cubic and BCC percolation thresholds. Results also provide quantitative structure information that can be used to explain the nonlinear V–I characteristic of composites at lower virtual-percolation threshold. Conductive-insulating composites are widely used in electronic and semiconductor industries. Our work provides a window for material design to obtain desirable physical properties.

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