Simulation and research of percolation phenomenon in T-ZnOw resin matrix composite*

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Abstract: A novel three-dimensional lattice model of tetrapod-like zinc oxide whisker (T-ZnOw) resin matrix composite with a coordination number of 12 is constructed based on the special structure of T-ZnOw; the percolation phenomenon of the system is simulated by the Monte Carlo method, and the percolation threshold is obtained at 23.2%. The critical mixing ratio of T-ZnOw is calculated by considering the practical factors, and the result basically agrees with the reported one. Theoretical calculation shows that the critical mixing ratio mainly depends on the L/D ratio of T-ZnOw, and is also related to the size of T-ZnOw as well as the preparation method of the composite. The microwave absorbing mechanism of T-ZnOw composite is discussed, and conductivity loss and point discharge caused by the polarization effect are regarded to be two important means of energy dissipation.

Key words: T-ZnOw; percolation; microwave absorbing property
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1. Introduction

Microwave absorbing materials have attracted considerable attention for their great application potential in both civil and military areas on account of their ability to eliminate electromagnetic wave pollution and to reduce radar signals[1−3]. A number of magnetic and dielectric materials in powder form are used to be loaded in polymeric matrices to make microwave absorbing materials, among which T-ZnOw is considered to be a candidate[4]. As the microwave absorbing property varies along with the electrical conductivity of the composite[5], which changes when the filler concentration is different, it is meaningful to figure out the relationship between the conductivity and the filler concentration. The phenomenon that the conductivity increases dramatically at a certain filler concentration commonly exists in the binary system of conductive particle reinforced polymer. The percolation theory can be used to model this kind of conductive behavior accurately and predict the percolation threshold where a connected network of sites that spans the sample is formed, causing the system to "percolate"[6]. A wide range of lattices under different dimensions have been calculated; the results show that the percolation threshold is related to the dimension as well as the coordination number which represents the connectivity of the lattice. Recently, computation research into percolation has been carried out with systems of polymers reinforced by carbon powder or carbon nanotubes and the like[7−9], but considering the special spatial structure and connectivity of T-ZnOw there is no existing method that can be used directly to obtain the critical mixing ratio of T-ZnOw resin matrix composite, and it is necessary to construct a novel desirable 3D lattice based on which the percolation threshold can be calculated.

In this paper, we build a novel three-dimensional lattice model of T-ZnOw resin matrix composite to carry out a simulation of the percolation phenomenon based on the special spatial structure of T-ZnOw; the critical mixing ratio is calculated and the microwave absorbing mechanism is discussed.

2. Simulation of percolation

2.1. Model construction

Considering that the size of a microwave absorber is much larger than that of T-ZnOw, a three-dimensional infinite lattice is chosen to be constructed. The T-ZnOw is constituted of a central part and four needle-like legs with an angle between every two of which of about 109°, as shown in Fig. 1(a). The four legs with the same length together define a regular tetrahedron, which is just like the tetrahedral unit in the diamond structure. Every adjacent unit of T-ZnOw is likely to be connected with each other through the extending legs. Figure 1(b) shows the spatial arrangement of T-ZnOw by which T-ZnOw units at adjacent positions are considered to be connected. As the spatial arrangement is extended periodically, a novel three-dimensional lattice is obtained as shown in Fig. 1(c) with every lattice point representing each T-ZnOw unit. Each point of the lattice has 6 nearest neighbors in the same layer at the vertexes of a regular hexagon with its center at this point, and has 3 nearest neighbors in both the upper layer and the lower layer at the vertexes of a regular triangle whose center corresponds to this point. That is, the lattice has a coordination number of 12.

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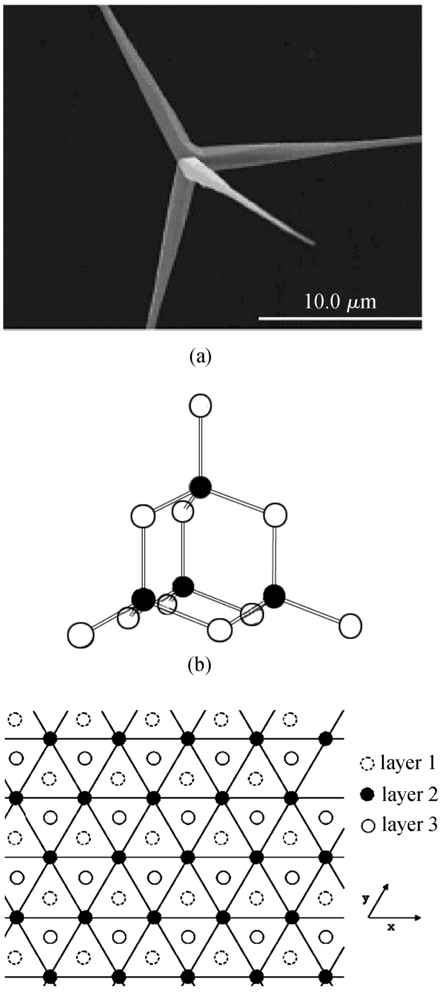

Fig. 1. (a) SEM image of T-ZnOw[10]. (b) Spatial arrangement model of T-ZnOw. (c) 3-D lattice of T-ZnOw composite.

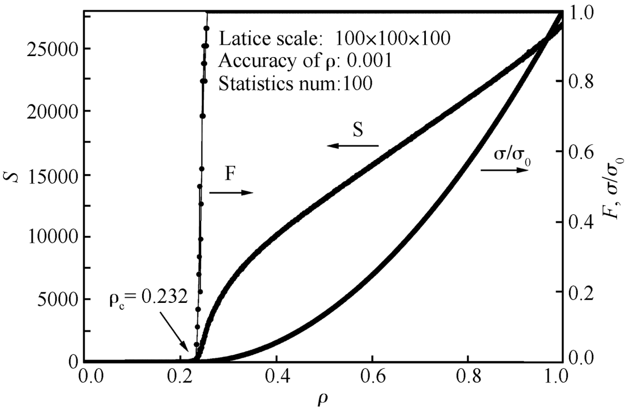

Fig. 2. Computational results for 3-D lattice of T-ZnOw composite.

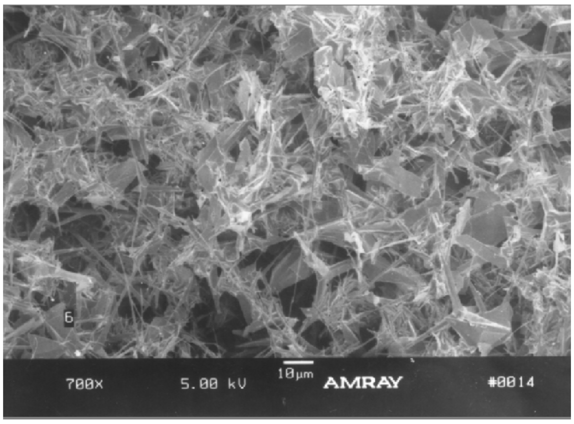

Fig. 3. SEM image of T-ZnOw composite[12].

The simulation is carried out by the Monte Carlo method with a lattice having a finite number of sites. Firstly, the sites are distributed randomly on the lattice by a random number generator with a portion of p from 0 to 1; then, the connectivity between the occupied sites is checked, a site positioned at one of the 12 nearest neighbor positions of the other one is considered to be connected with it, and all those sites connected with each other are designated as a cluster. The average cluster size S and global connectivity factor F of the lattice are calculated by a statistical method, wherein the value of F is 1 if the lattice is globally connected and is 0 if the lattice is not globally connected. As the connectivity property of the lattice is isotropic, we define that when the top layer and the bottom layer share occupied sites belonging to one cluster, the lattice is regarded as being globally connected.

2.2. Computational results and discussion

The size of the lattice is $100 \times 100 \times 100$, the statistics number is 100, and the accuracy of the site occupation proportion is 0.1%. The average cluster size S and global connectivity factor F under different occupation proportions are calculated, and the results are shown in Fig. 2. It is obvious that S increases abruptly when p is 23.2%. Before p gets to 23.2%, S increases slowly along with the increment of p and reaches no more than 200, which means clusters in the lattices are independent of each other. When p is over 23.2%, S begins to increase dramatically from about 200 to 5000, and the clusters in the lattices begin to connect with each other to form large scale clusters. It is noticed that S increases almost linearly when p is larger than 40%, which means the number of clusters in the lattice is very small. F changes from 0 to 1 abruptly at the point of 23.2%, showing a phase transition of the global connectivity of the system, and the percolation threshold is determined at 23.2% where a connected network of sites begins to span the whole system. The conductance of the system can be described by a simple power law of:

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

in the vicinity of the percolation threshold, where p is the proportion of occupied sites, p_c is the percolation threshold and t is the critical exponent which is about 1.3–1.7 in 3-D systems[11]. The normalized conductance of the system is obtained according to Eq. (1) and the conductance is shown to have a great increment around the percolation threshold.

3. Calculation of critical mixing ratio

T-ZnOw resin matrix composite can be prepared according to the following method: firstly, a certain amount of T-ZnOw was added into a mixture of anhydrous ethanol and oleic acid in proper proportions and mechanically stirred for half an hour; secondly, the mixture was added into diluted ethoxyline resin, treated by mechanical stirring and ultrasonic dispersion to make sure that T-ZnOw was well dispersed into the ethoxyline resin, and then the residual anhydrous ethanol was removed by heating; finally, the mixture was well mixed with a certain volume of ethylenediamine and solidified for about an hour under room temperature.

Considering the spatial structure of T-ZnOw, the central part is approximate to a sphere with a radius of r and the needle-like legs are approximate to four circular cones with a base radius of r and a height of h, and the volume of T-ZnOw is expressed as:

$$V_{\text{T-ZnOw}} = \frac{4}{3}\pi r^3 + 4 \times \frac{\pi}{3} r^2 h. \tag{2}$$

From Fig. 3, which gives an SEM image of T-ZnOw composite, it can be found that each T-ZnOw overlaps with each other to form a network. The effective volume that each T-ZnOw occupies is expressed as:

$$V_{\text{r}} = \frac{4\pi}{3}(\kappa h + r)^3, \tag{3}$$

where κ is constant between 0 and 1, and the ideal critical mixing ratio by volume of T-ZnOw composite can be expressed as:

$$\rho_{\text{vci}} = p_{\text{c}} \frac{V_{\text{T-ZnOw}}}{V_{\text{r}}} = p_{\text{c}} \frac{1 + 2\chi}{(1 + 2\kappa\chi)^3}, \tag{4}$$

where $\chi = \frac{h}{2r}$ is the L/D ratio of T-ZnOw.

Several non-ideal effects should be considered when calculating the critical mixing ratio in a practical situation: (1) the size of T-ZnOw is inhomogeneous, which results in the possibility that T-ZnOw at adjacent positions are not connected with each other; (2) the needle-like legs of T-ZnOw will be unavoidably broken during the process of preparation, which reduces the connectivity of the system as a whole; (3) T-ZnOw may get disconnected by rotating to a certain degree, which also affects the global conductivity to some extent. As a result, the critical mixing ratio should be modified as:

$$\rho_{\text{vc}} = p_{\text{c}} \frac{1 + 2\chi}{(1 + 2\kappa\chi)^3} \frac{\gamma}{\alpha\beta}, \tag{5}$$

where α is the inhomogeneity factor, which is related to the purity and uniformity of the T-ZnOw; β is the breaking factor, which is related to the preparation method and the size of T-ZnOw; and γ is the rotation factor, which depends on the size of T-ZnOw. Adjacent T-ZnOws with small size may be connected through the quantum tunneling effect even if they depart from each other, but the range of angles by which T-ZnOw rotates to get disconnected is much larger for the T-ZnOw with large size.

For a practical composite system having T-ZnOw with a density of 5.8 g/cm^3 and a whisker length of 30–100 μm[13], the value of the parameters can be taken as: $\chi = 10$, $\kappa = 0.6$–0.7, $\alpha = 0.8$–0.9, $\beta = 0.6$–0.8, $\gamma = 2$–3. The critical mixing ratio of T-ZnOw by volume is calculated, and the result of $V_{\text{c}} = 0.40\%$–1.39% obtained basically agrees with the reported one[13]. The calculation shows that the critical mixing ratio of T-ZnOw mainly depends on the L/D ratio χ; the larger the L/D ratio, the smaller the critical mixing ratio. When the size is larger, the possibility that adjacent T-ZnOws with a certain degree of rotation disconnect with each other is larger, which ultimately increases the critical mixing ratio. Furthermore, the whisker breaking effect caused by the preparation method will also give rise to the increment of the critical mixing ratio to some extent.

It is commonly accepted that microwave absorption for T-ZnOw composite mainly results from dielectric loss[14], which comprises polarization loss and conductivity loss. The polarization loss comes from the orientation polarization of the dipole under an alternative electric field as well as the interfacial polarization at the interface of T-ZnOw and the resin matrix. Much polarization charge is produced and accumulated on the tip surface of the whisker where a large localized electric field is produced, and the energy may be dissipated through point discharge. The conductivity loss mainly comes from the flow of charge; when T-ZnOw in the resin matrix forms a globally connected conductive network, the conductivity loss will be enhanced. It is noted that the microwave absorbing property is obviously improved when the mixing ratio of T-ZnOw is higher than the critical mixing ratio[4, 14], which confirms the idea of conductivity loss. As the T-ZnOw with smaller size behaves better in microwave absorption, it is supposed that point discharge may play an important part in energy dissipation.

4. Conclusions

We constructed a novel 3-D lattice mode of T-ZnOw resin matrix composite based on which the percolation phenomenon is simulated and the percolation threshold is obtained at 23.2%. The critical mixing ratio of T-ZnOw is calculated by considering practical factors like nonuniformity, the whisker breaking effect and rotating disconnection, and the result basically agrees with the reported one. Theoretical calculation shows that the critical mixing ratio mainly depends on the L/D ratio of T-ZnOw, and is also related to the size of T-ZnOw as well as the preparation method of the composite. Furthermore, conductivity loss and point discharge are considered to be important ways to dissipate the incident microwave energy.

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