Theoretical estimation on the percolation threshold for polymer matrix composites with hybrid fillers

Yuli Chen *, Fei Pan, Shengtao Wang, Bo Liu, Jianyu Zhang

Institute of Solid Mechanics, Beihang University, Beijing 100191, PR China

A B S T R A C T

Hybrid particles can improve the performance and reduce the cost of polymer matrix composites (PMCs), and thus increasingly used as fillers in multifunctional and structural materials. For these materials, the percolation threshold is of great importance because it determines whether or not the excellent mechanical, electrical and thermal properties of fillers can be fully utilized in the composites. However, the existing theoretical methods have limitations in percolation threshold predictions, and moreover, they are not applicable for hybrid filler systems. In this paper, an approach to predict the percolation threshold of hybrid filler systems is developed based on the modified average intersection number, which is proposed in this paper and revealed to be an invariant at the threshold. The theoretical expression for the percolation threshold of PMCs with fillers of different shapes is developed, and especially, the analytical expression for systems with spherical and cylindrical particles is obtained and validated by Monte-Carlo simulations. The proposed method on percolation threshold prediction can well explain the synergistic effect of fillers with different shapes, and provides great convenience for the design of conductive PMCs with hybrid fillers.

1. Introduction

Polymer matrix composites (PMCs) reinforced with micro- and nano-scale particles possess outstanding mechanical, electrical and thermal properties, and thus has been applied widely as functional structural materials, as well as electromagnetic interference shielding, thermal conductive materials and other multifunctional materials [1–4]. In recent years, the allotropes of carbon, e.g. carbon black (CB), carbon nanotubes (CNTs) and graphene [5–11], have been considered as multifunctional fillers for their extraordinary properties such as low density, high strength, high electrical and thermal conductivity, and thus used to reinforce the mechanical, electrical and thermal properties of composites. Remarkably, hybrid filler reinforced PMCs, such as PMCs with both CNT and CB particles [12–15], are drawing more and more attentions from researchers because they can achieve a good balance between comprehensive performances and economy.

However, the excellent properties of reinforcement particles cannot be fully utilized unless they interact with each other [16]. Taking the electrical conductive particle reinforced PMCs for example, only when the volume fraction of particles exceeds

the electrical percolation threshold, the conductive paths could be formed and the material could be well conductive [17]. Similarly, for heat and load transfer, the reinforcing particles, which generally have better thermal and mechanical properties than the matrix, need contact each other to construct connecting paths in the matrix so that their excellent properties can be performed. The process of forming connecting paths can be well explained by the percolation theory, and the critical point is defined as percolation threshold, which is very important for the performance of composites.

The percolation threshold is crucial for the electric conduction and heat transfer of the composites, and also important for the load transfer. Because electrons and heat can transfer from one particle to another only when the two particles contact each other, and the capacity of load transfer of composites can be improved effectively when the particles contact and restrain each other. Studies show that the threshold for load transfer is equal to or a little larger than the percolation threshold when the effect of matrix is not considered [18], and in composites with matrix and nano-scale interaction in consideration, the load transfer threshold can be estimated by the percolation threshold due to the interfaces between particles and matrix. For example, Baxter and Robinson [19] have observed a sudden increase in the stiffness of polymer nanocomposites at the electrical percolation threshold.

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* Corresponding author. Tel.: +86 10 82338410.
  E-mail address: yulichen@buaa.edu.cn (Y. Chen).

Therefore, for PMCs, percolation threshold is one of the most important design parameters, which has sparked intense interests and leaded to a large number of experimental, numerical and theoretical studies [3,17,20–23]. Among these studies, theoretical methods are convenient, economical and highly optimized for general use, and thus play an irreplaceable role to guide experimental trials and material designs. There are two widely accepted theoretical methods for percolation threshold estimation: average bond number method [24] and excluded volume method [20]. Both methods are based on the statistical percolation model [17,22], which can obtain simple forms of the volume fraction of particles at the percolation threshold by deducing some invariants at the percolation threshold through the relationship between the system statistical parameters and the distribution, shape, size and density of the conductive particles.

The average bond number method, or average coordination number method [24], is based on calculating the average bond number of each particle in lattice or continuum. When the system reaches the percolation threshold, the average bond number (i.e. the average number of particles which one particle contact with) is a constant B_c. Gurland [24] found B_c = 1.3–1.5 in sliver powder/phenolic aldehyde system, and the value of B_c was independent of the type of fillers. Aharoni [25] also reported that B_c is between 1 and 2. When B_c = 1, conductive paths begin to be formed, and when B_c = 2, conductive paths have been formed completely. Malliaris and Turner [26] observed a sudden increment of conductivity when B_c = 2 in Ni/HDPE system. So according to the previous studies, the average bond number method can predict the thresholds of many mental powder systems well. However, this method cannot interpret the mechanism of the thresholds for lacking in theoretical basis. Besides, the average bond number B_c changes for different materials. Thus this method cannot predict the percolation threshold independent of experimental result for new materials, and experiments need to be carried out to obtain the constant B_c for each type of composite materials.

The excluded volume method [20] mainly studies the excluded volume V^{ex} of particles with similar shape. At the percolation threshold, the average excluded volume of particles in a unit element $\langle V^{ex} \rangle n$ is considered to be a constant, which has been validated by many experiments [17,18], especially in the systems with large-aspect-ratio particle fillers. In fact, for continuously distributed permeable particles, $\langle V^{ex} \rangle n$ is equivalent to the average bond number B. However, the excluded volume method can hardly be used to solve the percolation threshold of systems with particles of different shapes.

To predict the percolation threshold of a system with hybrid fillers (i.e. fillers with different shapes), Sun et al. [27] proposed a simple formula based on excluded volume method, i.e.

$$\frac{F_i}{\Phi_i^{th}} + \frac{F_j}{\Phi_j^{th}} = 1 \tag{1}$$

where Φ^{th} is the percolation threshold of single filler system, F is the real volume fraction of particles in the mixed system, and the subscript i and j denote the types of particles. By the linear superposition, Sun's formula can be used to calculate the percolation threshold of a mixed system if the percolation thresholds of single filler system are known. However, it cannot explain the synergism of different fillers [23] because it does not take into consideration the degree of mix.

This paper aims to develop a universal statistical invariant for theoretical estimation on the percolation threshold of polymer matrix composites with hybrid micro- and nano-scale fillers. This proposed method can account for both the shape effect and the synergism of different fillers to overcome the limitations of previous methods, and thus provides great convenience for the composite design and applications.

2. Probability analysis on intersections between particles

In composites, the percolation threshold is determined by the formation of conductive paths, which may be reflected by the intersections between fillers. So a geometric probability analysis is carried out in this section to obtain the average number of intersections on each particle.

For the particles randomly distributed in space, the probability to intersect with each other affects the possibility to construct connected conductive paths, and also determines the average number of intersections on each particle. Assuming that all the particles are independent, the position and direction of the particles are not affected by others and the penetration between particles is allowed, same as the definition of "soft core" particles [28,29]. For simplicity, the particles are hypothesized as spherocylinders, i.e. cylinders capped with hemispheres on the two ends, with the length l, cap diameter d and aspect ratio $\lambda = l/d$. When $\lambda = 0$, the particles degenerate to spheres, and when λ is large enough, the hemisphere on the end can be neglected.

For two arbitrary particles i and j with the angle between their axial directions θ, the particles intersect only when the geometric center of j enters the "general excluded volume" V_{ij}^{ex} of particle i, or the geometric center of particle i enters the "general excluded volume" V_{ji}^{ex} of particle j. It should be noted that the "general excluded volume" here is similar to the "excluded volume" proposed by Balberg et al. [20], and both of them mean a volume which a particle occupied and intersecting happens if the geometric center of another particle enters. In Balberg's theory, only particles with the same shape and size are considered, while the general excluded volume proposed in this paper can account for different particles, expressed as below (see Appendix A for more details).

$$V_{ij}^{ex}(\theta) = V_{ji}^{ex}(\theta)$$
$$= \frac{1}{6}\pi(d_i + d_j)^3 + \frac{1}{4}\pi(d_i + d_j)^2(l_i + l_j) + (d_i + d_j)l_i l_j \sin\theta \tag{2}$$

Here d_i, d_j and l_i, l_j are the diameters and lengths of particles i and j respectively. When particles i and j are of the same shape, i.e. $d_i = d_j = d$, and $l_i = l_j = l$, Eq. (2) degenerates to Balberg's result [20] as

$$V_{ii}^{ex}(\theta) = \frac{4}{3}\pi d^3 + 2\pi d^2 l + 2dl^2 \sin\theta \tag{3}$$

For spherical particles with the same diameter, the excluded volume can be obtained by setting the length $l = 0$ in Eq. (2) as

$$V_{ij}^{ex} = \frac{1}{6}\pi(d_i + d_j)^3 \tag{4}$$

Eq. (4) is independent of the angle θ due to the nature of spheres. However, for other shapes, the general excluded volume is a function of θ.

In a cuboid represent volume element (RVE) of $L_1 \times L_2 \times L_3$, supposing there are two different shapes of particles, i and j, if their geometric centers distribute uniformly and their directions follow the probability density of $\eta(\theta)$, the probability of intersecting between particles is

$$p_{ij} = \frac{\langle V_{ij}^{ex} \rangle}{V_{ele}} \tag{5}$$

where $V_{ele} = L_1 L_2 L_3$ is the volume of the RVE, and $\langle V_{ij}^{ex} \rangle$ is the average general excluded volume of different angles, expressed as