Critical concentration in percolating systems containing a high-aspect-ratio filler

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We examine the percolation threshold for composites made by dispersing anisometric, single-crystal graphite flakes in either an epoxy resin or a polyurethane polymer matrix. Analysis is based on empirical and excluded-volume approaches and the results are compared with a similar treatment using literature data of carbon-fiber based composites.

I. INTRODUCTION

Percolation theory has been applied to a wide range of materials and phenomena over the past years[1] and the fundamental mathematics are well understood.[2] Application to electrical conductivity has been reviewed in detail by several authors.[3–5] Many model systems have been treated and a vast literature exists comparing experiment with theory. One of the less well established points concerns the capacity of percolation concepts to predict the threshold of a conducting filler in an insulating matrix in real systems for other than the most simply shaped filler objects.

In the present work, based on two types of graphite, the particles of which can be assimilated to very thin disks, we have made composite materials by dispersing this conducting filler in two types of polymers, an epoxy resin and a polyurethane resin. The critical concentration ϕ_c, expressed as a volume percentage of graphite, was determined through dc electrical conductivity measurements on a large number of samples covering the range of ϕ from 0 to 10 % as discussed elsewhere.[6] We will show here that it is possible, through different approaches, to calculate this observed value. In particular, it will be seen that the concept of excluded volume[7] is particularly efficient in treating the problem of percolating systems in which the objects possess a large aspect ratio, such as disks. Through the same type of calculation, we will determine the critical concentrations of another type of anisometric filler, namely fibers. In order to do so, we have analyzed much literature data concerning ϕ_c and compared them to the excluded volume calculations presented here. For disks, as for fibers, a brief discussion will center on orientation effects of the particles and specific properties of the insulating matrices.

II. POLYMER–GRAPHITE FLAKE COMPOSITES

A. Materials and determination of the threshold

The conducting filler used in this work, termed FMG_1 (flat micronic graphite), is constituted of single-crystal particles of graphite made through exfoliation.[8] They were characterized by scanning electron microscopy which showed that their thickness is of the order of 0.1 μm. Laser counting furnished a particle size distribution histogram with an average diameter of 10 μm. A typical flake of FMG_1 is thus roughly disk-shaped with an aspect ratio (diameter/thickness) of the order of 100. Furthermore, krypton adsorption on these particles showed a specific surface area of about 20 m^2/g.

The second type of particle, designated FMG_2 is characterized by a size distribution identical to that of FMG_1, thus an average diameter of 10 μm. Its specific surface area, however, is 40 m^2/g, a measurement from which we conclude that these particles are twice as thin as those of FMG_1 and possess therefore an aspect ratio of about 200.

Using these two types of disk-shaped particles, we have made polymeric composites of different filler concentrations ϕ based on two thermally cured resins. The protocol used[6] leads to materials in the form of thick films with preferentially oriented particles. The degree of disorientation, or mosaic spread, is defined as the full width at half maximum of the curve of intensity versus angular rotation α about the (002) graphite reflection. If all the particles were perfectly aligned parallel to the plane of deposition, the reflection would primarily be only instrumentally broadened: in our case, rotation of the sample within the x-ray beam places greater or fewer graphite flakes into Bragg diffraction conditions yielding a mosaic spread of approximately $\pm 20°$, independent of ϕ. We will return to this later. The percolation threshold was determined through conductivity measurements, both parallel ($\sigma_\parallel$) and perpendicular ($\sigma_\perp$) to the plane of the films, as illustrated in Fig. 1: the corresponding critical concentrations ϕ_c are presented in Table I. All values are below 2%, much less than is the case for spherical filler materials. In the following, we will compare these values with those that can be obtained theoretically using the characteristics at our disposal and three different approaches.

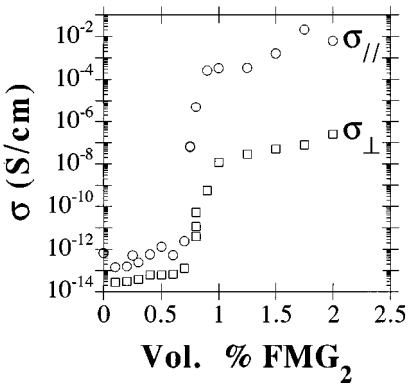

FIG. 1. Experimentally determined curves of conductivity $\sigma(\phi)$ for a polyurethane-FMG_2 composite.

B. Theoretical determination of the threshold

1. Mean-field theory

To calculate the critical concentration of an ensemble of thin spheroids dispersed in an insulating matrix, a mean-field approach was used by Helsing and Helte.[9] Such an approach consists in calculating the average effects of the random resistor network representing the binary heterogeneous mixture of insulator and conductor by a homogeneous effective medium. An overall conductivity equation can be determined which is then, in principle, applicable over the full range of compositions. Thus for flat ellipsoids of major and minor axis lengths R and ϵR ($\epsilon \ll 1$), the conductivity threshold for a critical concentration ϕ_c was found, to first order, to be such that,

$$\phi_c = 1.18\epsilon. \tag{1}$$

If we suppose that a FMG particle can be approximately described by this type of object with a ratio of diameter to thickness of 100 for FMG_1 ($\epsilon = 0.01$), then

$$\phi_{c1} = 1.18\%.$$

For the FMG_2 we have $\epsilon_2 = \epsilon_1/2 = 0.005$, so

$$\phi_{c2} = 0.59\%.$$

These values are indeed of the order of magnitude of those in Table I. Furthermore, the calculations of Helsing and Helte modeled a medium containing an unoriented filler; knowing that the particles are more or less well oriented in the present case, it is thus natural to find a percolation threshold which is slightly higher; this point will be further developed below.

TABLE I. Values of critical concentrations expressed in vol % of conducting particles determined experimentally for polymer–graphite flake composites.

Composite	Critical concentration ϕ_c (vol %)
Epoxy-FMG_1	1.3
Polyurethane-FMG_1	1.7
Polyurethane-FMG_2	0.7

2. Empirical method

The above determined critical concentrations can also be determined somewhat more empirically by the idea[10] according to which the percolation threshold of a conducting powder is linked with the empty volume between the particles. This, of course, is directly related with the notion of excluded volume which will be developed in the following paragraph. A composite can thus be considered as a conducting backbone with a certain packing density which differs with the conducting powder according to the particle morphologies. For example, the greater the aspect ratio, the less the packing density and the lower one would expect to find the critical volume concentration. Good qualitative correspondence has thus been found between the quantities ϕ_c and ϕ_p where

$$\phi_p = \frac{\text{density of unpacked powder}}{\text{density of material constituting this powder}}.$$

ϕ_p is thus equivalent to a filling factor. For a certain number of materials with ϕ_c values between 20 and 55%, the following empirical relationship was put forward:

$$\phi_c \approx \phi_p - 5\%. \tag{2}$$

However, it was noted that as ϕ_c diminished below 20% ϕ_c and ϕ_p more closely approached each other, and $\phi_c \approx \phi_p$. Consequently, the lesser the packing density, the lower the value of ϕ_p (and the easier the percolation in a matrix for a low value of ϕ).

We would now like to apply this relationship to FMG; however, ϕ_p is not an easy parameter to work with since it must strongly depend on the experimental conditions. Indeed, the apparent density of the FMG_1 powder is about 10 g/l. Graphite, having a mass density of 2.2 g/cm^3, a percolation threshold of about 0.45% should then be observed. Similarly, an apparent density of about 8 g/l was found for FMG_2 which would then lead to a critical concentration of 0.36%. These results are, of course, approximate, and serve mainly to compare the different types of graphite powders with each other using a well defined protocol for defining the apparent density.

3. Excluded volume

Application of this concept, which associates a volume with objects which do not necessarily possess a true volume (e.g., infinitely thin rods and disks) results in very low values of threshold concentration. Indeed, real particles can have a true volume which is extremely modest compared to the excluded volume when they are not densely packed. Let us use this concept and define the excluded volume[7] [excluded area in two dimensions (2D)] as the volume around an object in which the center of another similarly shaped object is not allowed to penetrate. The underlying idea is that the percolation threshold is not linked to the true volume of the object itself but rather to its excluded volume. Thus, if N_c is the critical number density of objects in the system, V is the volume of one of these objects, and V_e is the associated excluded volume, then the invariance properties of the quantity $N_c V$ established for network percolation[11] are no longer valid in the continuum in which the dimensionless invariant

TABLE II. Total excluded volumes $\langle V_{ex}\rangle$ of objects cited in this paper.

System (3D)	$\langle V_{ex}\rangle$	Reference
Continuum, deformable spheres or parallel objects	2.8	7
Continuum, randomly oriented, infinitely thin rods	1.4	12
Continuum, randomly oriented, infinitely thin disks	1.8	13

is then $N_c V_e$. Indeed, in the continuum, V_e is often very different from V and the difference between the two increases as the complexity of the objects' geometry rises.

The argument based on excluded volume thus allows evaluating the threshold of more complex systems, in which it is possible to introduce not only a distribution function describing the orientations of the objects with respect to each other, but also aspect ratios different from unity. This allows more closely approximating real random media than through the use of a well defined geometric network. The total excluded volume $\langle V_{ex}\rangle$ is defined by the relation

$$\langle V_{ex}\rangle = N_c\langle V_e\rangle \approx \text{const}, \tag{3}$$

where $\langle V_e\rangle$ represents the excluded volume of an object averaged over the orientational distribution characterizing the system objects.

$\langle V_{ex}\rangle$ is, in fact, not a true invariant beyond the case of parallel objects and is situated, for each type of object, within a range of values, the extremal values corresponding to the system characterized by a random orientation (lower limit) and a system of strictly parallel objects (upper limit). The upper limit is the same as that which corresponds to the case of permeable spheres. Table II summarizes the values of total excluded volume that we use in this paper.

In three dimensions (3D), the critical volume fraction is linked[14] to $\langle V_{ex}\rangle$ through

$$\phi_c = 1-\exp\left(-\frac{\langle V_{ex}\rangle V}{\langle V_e\rangle}\right) = 1-\exp(-N_c V). \tag{4}$$

The problem of thin disks of radius r randomly dispersed in space has been studied by Charlaix, Guyon, and Rivier.[15] The quasi-invariant was found to be $\langle V_{ex}\rangle = N_c r^3$ where N_c is the critical number of objects per unit volume. The mean excluded volume of a disk was calculated as,

$$\langle V_e\rangle = 4\pi r^3 \int_0^{\theta} \sin^2\beta \; d\beta, \tag{5}$$

where β is the angle between the planes of two disks in contact with each other and θ represents the angle of greatest disorientation of the system of disks. In other words,

$$-\theta \leqslant \beta \leqslant +\theta.$$

For randomly oriented disks (isotropic system), $\theta = \pi/2$ and consequently, the excluded volume of a disk of radius r is

$$\langle V_e\rangle = \pi^2 r^3.$$

Thus, based on Eq. (4), determination of the percolation threshold of a system of randomly oriented disks thus necessitates calculating

$$\phi_c = 1-\exp\left(-\frac{\langle V_{ex}\rangle \pi r^2 t}{\pi^2 r^3}\right) = 1-\exp\left(-\frac{\langle V_{ex}\rangle t}{\pi r}\right), \tag{6}$$

where t is the thickness of the disks. $\langle V_{ex}\rangle$ is known in the extreme cases of infinitely thin disks (1.8) and of spheres (2.8); it is thus expected that the value of $\langle V_{ex}\rangle$ corresponding to disks of thickness t will lie between 1.8 and 2.8. We thus have the following double inequality:

$$1-\exp\left(-\frac{1.8t}{\pi r}\right) \leqslant \phi_c \leqslant 1-\exp\left(-\frac{2.8t}{\pi r}\right).$$

With $r=5$ μm and $t_1=0.1$ μm for the FMG_1 and $t_2=0.05$ μm for the FMG_2, we find the following critical concentration ϕ_{c1} and ϕ_{c2} such that:

$$1.14\% \leqslant \phi_{c1} \leqslant 1.77\%,$$

$$0.57\% \leqslant \phi_{c2} \leqslant 0.89\%.$$

The values found above are thus close to the critical concentrations experimentally determined for the two types of conducting charge (Table I). The lower limits for ϕ_c are very similar to those given by Eq. (1); however, the calculations that we present suppose randomly oriented disks, whereas as we have indicated above, there is an experimental mosaic spread of $\pm 20°$ in our materials. In order to observe the sensitivity of the threshold to the particle orientation, we recalculated the excluded volume taking different values of θ based on Eq. (5), which after integration becomes

$$\langle V_e\rangle = r^3[2\pi\theta - \pi \sin(2\theta)],$$

where the disks are oriented at $\pm\theta$ with respect to each other. The results are summarized in Fig. 2 for the two types of FMG. It is clear that particle orientation has considerable influence on the position of the percolation threshold. If, in our composites, the particles were disoriented by $\pm 20° = \pm\pi/9$ at the most, then using the same limits of $\langle V_{ex}\rangle$ as before, the critical concentrations ϕ_{c1} and ϕ_{c2} corresponding, respectively, to the FMG_1 and FMG_2 become

$$47.8\% \leqslant \phi_{c1} \leqslant 63.6\%,$$

$$27.8\% \leqslant \phi_{c2} \leqslant 39.7\%.$$

Agreement between these values and those of Table I is no longer observed; two factors underlie this. First, as discussed above, although the graphite flakes are on the *average* oriented at $\pm\theta$, this is by no means the upper limit: there is a non-negligible number within the tails of the curve, beyond 20°, which strongly influence ϕ_c as brought out by Fig. 2. Secondly, the laser counting carried out on the suspension of the particles reveals that the size (diameter) distribution is asymmetrically extended on the side of the higher-than-average values, up to diameters of about 50 μm. This fact in itself tends to reduce the threshold since it has been shown[16,17] that when percolating objects have a large aspect ratio, the critical concentration diminishes as the size distribution increases. Furthermore, in their concluding remarks

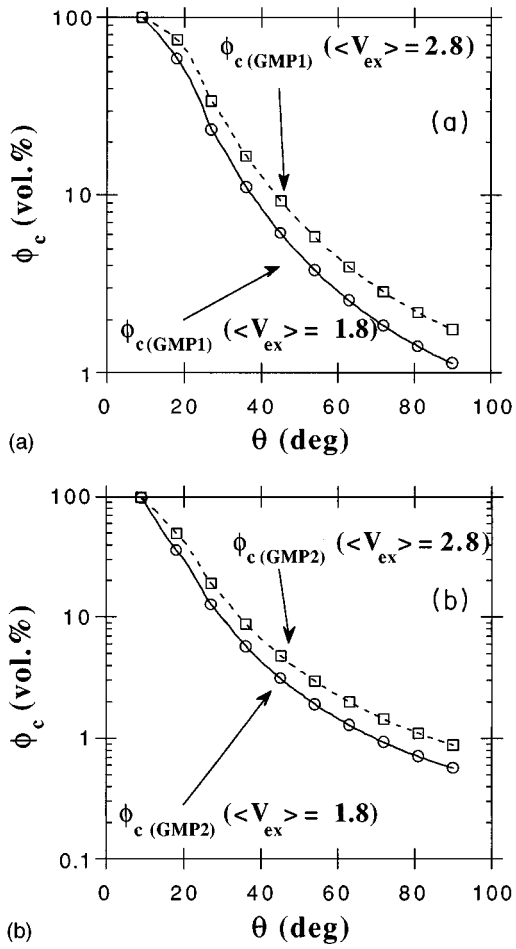

FIG. 2. Critical concentration calculated for a system of disk-shaped particles of 10 μm diameter and thickness (a) 0.1 μm and (b) 0.05 μm (corresponding, respectively, to fillers FMG_1 and FMG_2) as a function of θ, the maximum angular orientation between the disks. The calculation uses the two extreme values of 1.8 and 2.8 for the total excluded volume $\langle V_{ex}\rangle$.

on the effects of polydispersed particles, Charlaix, Guyon, and Rivier[15] specifically noted that a "larger statistical weight" was given to larger disks in evaluating $\langle V_{ex}\rangle = N_c r^3$. ϕ_c is thus a maximum when the objects are of fixed size, otherwise it is the larger objects which determine the threshold.

As concerns the values of 1.3% and 1.7% found for the critical concentrations in the epoxy-FMG_1 and polyurethane-FMG_1 composites, respectively, it should be noted that the particles, their mode of incorporation and the conditions used for the dispersion of the particles within the matrix are all rigorously the same in the two types of composites. This leads to believing that the different thresholds arise from different physicochemical properties of the polymeric matrices. Whatever the case, the concept of excluded volume leads, as suggested by Eq. (6) for disoriented particles, to the following relation of proportionality:

$$\phi_c \propto \frac{t}{r}. \tag{7}$$

This relationship is thus relatively well verified in the real composite materials, since we have verified that a system of disks of thickness t has a percolation threshold twice that of a system of disks of thickness $t/2$.

III. POLYMER–CARBON-FIBER COMPOSITES

So as to verify the applicability of the concept of excluded volume to this type of composite, we have gathered together a certain number of literature results. In all cases, the conducting filler can be geometrically considered as capped, cylindrical objects.

A. Experimental literature results

Table III illustrates a certain number of values of critical concentration relative to composite materials comprising a polymer and either carbon fibers or elongated carbon black aggregates.

B. Calculation of excluded volume

Calculation of the excluded volume of a capped cylinder modeled as a cylinder of length L and diameter W and comprising at each end a half sphere of diameter $W/2$ was carried out by Balberg *et al.*[7] If γ is the angle between the two cylinders in contact with each other, one oriented at an angle θ_i with respect to the z axis of the system, the other by an angle θ_j, then the average excluded volume $\langle V_e\rangle$ is such that

TABLE III. Critical concentrations for indicated particles dispersed in a polymer matrix determined experimentally (indicated reference) and calculated here based on concept of excluded volume.

Case	Particles	Diameter	Length	ϕ_c (vol %)	Calculated ϕ_c	Reference
1	Elongated carbon black aggregates	≈800 Å	≈5000 Å	7.2	$7.00 \leqslant \phi_c \leqslant 13.51$	17
2	Carbon fibers	10 μm	1 mm	0.52; 0.69; 0.72; 0.71; 0.86; 0.93; 1.1	$0.67 \leqslant \phi_c \leqslant 1.35$	18
3	Carbon fibers	10 μm	1.15 mm	1.4; 1.47; 1.55	$0.59 \leqslant \phi_c \leqslant 1.18$	19
4	Carbon fibers	10 μm	2.85 mm	0.24; 0.25; 0.265	$0.24 \leqslant \phi_c \leqslant 0.48$	19
5	Carbon fibers	8 μm	1 mm	0.98	$0.54 \leqslant \phi_c \leqslant 1.08$	20
6	Carbon fibers	10 μm	1.1 mm	3	$0.62 \leqslant \phi_c \leqslant 1.23$	21
7	Carbon fibers	8 μm	1 mm	0.90	$0.54 \leqslant \phi_c \leqslant 1.08$	22

$$\langle V_e\rangle = \frac{4\pi}{3} W^3 + 2\pi W^2 L + 2WL^2 \langle \sin\gamma\rangle_\mu , \qquad (8)$$

where $\langle \sin\gamma\rangle_\mu$ is the average of $\sin\gamma$ when θ_i and θ_j are confined within an angle $2\theta_\mu$ around the z axis of the system. The calculation of $\langle \sin\gamma\rangle_\mu$ is complex[7] and leads to the following when the cylinders are randomly oriented (i.e., $\theta_\mu = \pi/2$):

$$\langle \sin\gamma\rangle_\mu = \frac{\pi}{4},$$

in other words, an excluded volume of

$$\langle V_e\rangle = \frac{4\pi}{3} W^3 + 2\pi W^2 L + \frac{\pi}{2} WL^2 .$$

Using Eq. (4) once again, linking the excluded volume and the critical concentration, we thus have for a system of randomly oriented, capped cylinders of volume V:

$$\phi_c = 1 - \exp\left(- \frac{\langle V_{\rm ex}\rangle V}{\langle V_e\rangle} \right)$$

$$= 1 - \exp\left(- \frac{\langle V_{\rm ex}\rangle [(\pi/4) W^2 L + (\pi/6) W^3]}{[(4\pi/3) W^3 + 2\pi W^2 L + (\pi/2) WL^2]} \right).$$

As concerns $\langle V_{\rm ex}\rangle$, the value of 1.4 (see Table I) was obtained by simulation based on infinitely thin cylinders. Once again calculation of the critical concentration of the system of real cylindrical particles should be carried out using for $\langle V_{\rm ex}\rangle$ the lower limit 1.4 and as an upper limit that corresponding to spheres, 2.8. We can therefore write

$$1 - \exp\left(- \frac{1.4V}{\langle V_e\rangle} \right) \leqslant \phi_c \leqslant 1 - \exp\left(- \frac{2.8V}{\langle V_e\rangle} \right).$$

Based on this double inequality, the critical-concentrations corresponding to objects the geometry of which is described in Table III were calculated. The results are presented in the second last column of Table III.

All these different results concern systems of randomly dispersed, anisometric objects. As we have noted above, the agreement between measured and calculated critical concentrations is good. Sometimes, however, the experimental value lies outside the range of estimated values. This can probably be explained in terms of interactions between the polymeric matrix and the conducting particles, these interactions influencing the state of dispersion of the filler within the matrix. These have been shown to modify the critical concentration through the physicochemical properties of the matrix, in particular, the viscosity and surface tension at the time of synthesizing the composite.[18] Furthermore, this explains the range of different values cited in Ref. 18. In this case it was observed that the threshold rose preparing the polymer-particle mixtures at increasingly higher temperatures which resulted in increasingly lower values of viscosity; this reference cites a value of $\phi_c = 1.6\%$ for a composite prepared using a low viscosity solution.

TABLE IV. Calculated critical concentration of polymer–partially oriented carbon-fiber composites, as a function of the maximum disorientation angle θ_μ.

θ_μ	$\langle \sin\gamma\rangle_\mu$	Calc ϕ_c (% vol)
0	0	$16.05 \leqslant \phi_c \leqslant 29.53$
$\pi/6$	0.44	$1.00 \leqslant \phi_c \leqslant 1.99$
$\pi/4$	0.60	$0.75 \leqslant \phi_c \leqslant 1.49$
$\pi/2$	$0.78 = \pi/4$	$0.58 \leqslant \phi_c \leqslant 1.15$

Finally, we must examine the case of materials comprising oriented cylindrical particles. A study carried out on carbon fibers[23] of diameter $= 8-9$ μm and length 1 mm oriented in an epoxy resin yield a critical concentration of 1.6 vol,%. Although the authors gave no specific details on the fiber orientation, one can attempt to find this value by calculating the excluded volume using, as before, 1.4 and 2.8 for the limiting values of $\langle V_{\rm ex}\rangle$. Table IV regroups the critical concentrations that can thus be determined through use of Eqs. (4) and (8) as well as the results of calculating $\langle \sin\gamma\rangle_\mu$ given by Balberg *et al.*[7] for certain values of θ_μ. We recall that the case $\theta_\mu = \pi/2$ corresponds to a system of objects with no preferential orientation whereas $\theta_\mu = 0$ is identified with a system of perfectly parallel objects. An average diameter of the fibers of 8.5 μm was used in these calculations.

As in the case of disks, the effect of orienting the cylinders on the position of the threshold is significant. Based on the values of Table IV, and assuming that the polymer does not affect the dispersion of the particles, it is seen that an experimental percolation threshold of 1.6% would correspond to a maximum orientation of $\pm 30°$.

IV. CONCLUSIONS

In this paper, through the use of several different methods, we have treated the problem of determining the percolation threshold for composites comprising an insulating matrix charged with conducting disks. Among the three approaches used, that based on the excluded volume yields the best results and it is observed that the calculated critical concentration is a strong function of both particle orientation and size distribution. The concept of excluded volume was also applied to analysis of polymer–carbon-fiber composites based on literature data and was found to give good results. For both disk-and fiber-based composites, notable deviations from predicted values of ϕ_c may be observed according to the intrinsic properties of the polymers utilized (viscosity, surface tension, particle wetting, crystallinity, presence of surfactants, etc.). In spite of all these possible contributions, it has been shown here that reasonably good agreement can be observed between calculated and experimental values of critical concentration taking into account only the particle morphology. Work is currently in progress concerning the variation of electrical conductivity with temperature and pressure so as to understand the conduction processes and in particular the role and nature of the particle-particle interface.

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