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Three-dimensional electrical percolation behaviour in conductive short-fibre composites

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The percolation behaviour and electrical conductivity in unidirectional composites made of short conductive fibres embedded in an insulating matrix were examined by Monte Carlo simulation as a function of aspect ratio, volume fraction and angle. The unidirectional composite exhibited a highly anisotropic percolation behaviour with respect to the fibre direction for both fibre normal and fixed-length distribution. For the direction parallel to the fibre, the electrical conductivity increased exponentially with the volume fraction and the exponent increased as the aspect ratio increased. The conductivity in the transverse direction exhibited a sharp transition, from zero to nearly the same level as parallel conductivity at the critical volume fraction. The percolation threshold for the transverse direction also increased with aspect ratio up to 20, above which it decreased in parabolic manner. Both the threshold volume fraction and transient increase in conductivity in the transverse direction varied parabolically with aspect ratio, the maximum being an aspect ratio of 20.

1. Introduction

The electrical conductivity of composites made of conductive filler and a polymer matrix is adjustable within a certain range by changing volume fraction and arrangement of filler. Therefore, the potential areas for application are situations with varying electrical conductivity [1–5], such as materials with electrical conductivity which can be used for electrostatic discharge properties and electromagnetic interference shielding purposes of electrical equipment housing [6, 7]. This understanding is based on the realization that the electrical or thermal conduction in such systems is a percolative process.

So far the study of percolation in three dimensions has centred on percolation in the lattices. Pike and Seager's [8] work on percolation is concerned with various types of regular and random lattice using Monte Carlo techniques. Balberg and co-workers [9, 10] extended this approach to line percolation in two and three dimensions, but the line percolation model is not appropriate for real physical situations in composites because the filler of composites is not line segments but usually spheres or sticks.

In the present work, the d.c. electrical conductivity, percolation threshold and their angular dependency were calculated for the stick percolation in three dimensions by Monte Carlo simulation in unidirectional conductive short-fibre composites by varying the fibre length distribution, aspect ratio and volume fraction.

2. A percolation model

Composites made of short conductive fibres were generated using Monte Carlo simulation in three dimensions. To give the coordinates of N sites, a seed was selected and all N of the x_i, y_i, and z_i were generated likewise by picking another seed using the RAND pseudo-random number generator. This procedure produces a random array of N_s sites in a unit cube of side unity and the site density is also given by N_s following Pike and Seager's method. A seed was selected and the length, L, of a stick, radius a and angles θ and φ of a spherical coordinate system were chosen. Thus, information about the sticks in the unit cube was generated.

The shortest distance of two sticks was calculated by the bisection algorithm for selecting bonding sticks. To reduce access time, a comparison was made of the distance of four end points (D_1, D_2, D_3, D_4) between two sticks (L_1, L_2) (see Fig. 1) and all the sticks existing in the longest distance between them were selected. If the condition is min. $(|D_1|, |D_2|, |D_3|, |D_4|) \leq$ max. (L_1, L_2), then the connected sticks are selected by the contact condition between two sticks, by setting the minimum distance between two sticks as $D_i \leq 2a$, where $i = 1, 2, 3, 4$, and the minimum distance between two sticks is zero for $\theta = \varphi = 0°$.

For a given bonding criterion, every stick is checked against every other stick. If any two sticks satisfy the bonding criterion, identification numbers are

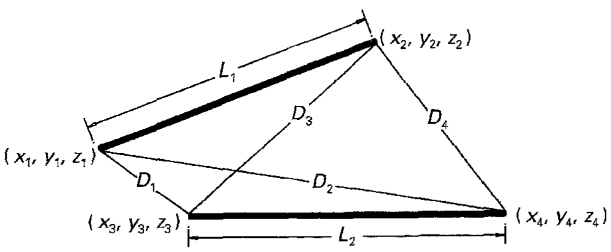

Figure 1 The measured distances between two sticks.

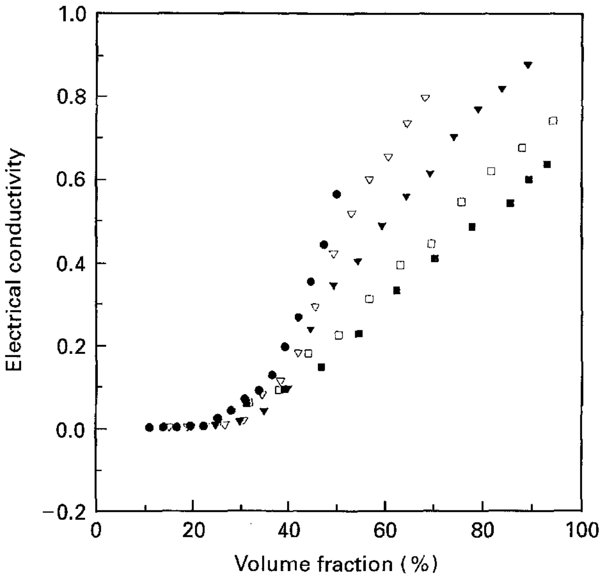

Figure 2 The variation of parallel electrical conductivity with volume fraction of conductive fibre for the NLD. AR: (●) 22.86, (△) 22.66, (▼) 20, (□) 17.78, (■) 16.

assigned. If any two sticks in opposite boundary regions have the same identification number, then the stick is considered to be percolating in the direction perpendicular to that boundary. The numbers of clusters and fibres generated in a percolation were calculated by increasing the fibre volume fraction and aspect ratio.

3 Results and discussion

3.1. The dependence of conductivity on fibre length distribution

The aspect ratio, AR, and volume fraction, V_f, were varied by changing the fibre length, L, radius, a, and the number of fibres with fixed angle distribution in unit volume. The lengths of fibre were generated with normal length distribution (NLD), i.e. the fibre lengths were distributed with normal distribution, and fixed length distribution (FLD).

The electrical conductivity along a direction parallel to the fibre, $\sigma_{\|}$, increases exponentially with volume fraction as $\sigma = \sigma_0 \exp \alpha V_f$. Results for various aspect ratios are shown in Fig. 2. Also, the conductivity exponent of NLD, α, is shown to be higher for greater aspect ratio. Fig. 3 shows the variation of $\sigma_{\|}$ for the FLD, i.e. $L =$ fixed, $\theta = \varphi = 0°$. The behaviour of electrical conductivity and the percolation threshold of volume fraction V_c, are similar to those of NLD,

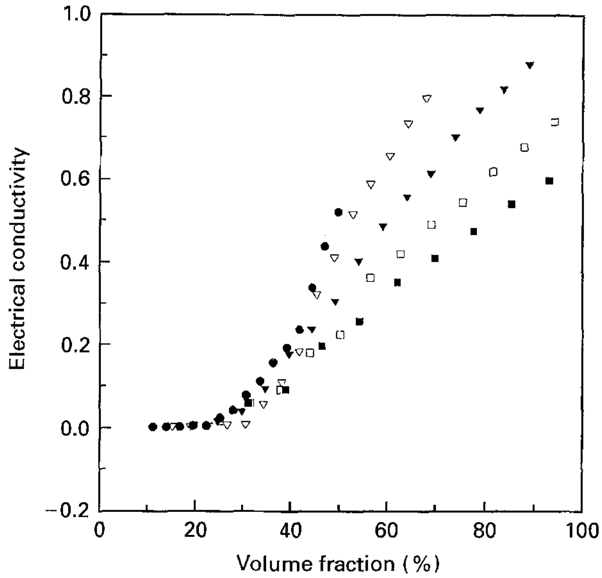

Figure 3 The variation of parallel electrical conductivity with volume fraction of conductive fibre for the FLD. For key, see Fig. 2.

TABLE I The exponent of conductivity increment of NLD and FLD

	AR				
Exponent	22.86	22.66	20	17.78	16
α (NLD)	1.65	1.28	1.40	1.08	0.95
α (FLD)	1.66	1.25	1.35	1.08	0.88

TABLE II The percolation threshold and aspect ratio

Reference	AR	V_c	Fibre dist.	Remarks
Bigg [1]	24	0.06	NLD	Fibre composite
	12.5	0.11		
Carmona [18]	20	0.14	NLD	Fibre composite
Whitehouse [12]	4	0.14	FLD	Unidirectional fibre composite
Gurland [11]		0.38		Spherical particulate
Present work	22.86	0.113	FLD	Unidirectional fibre composite
	22.66	0.154		
	20	0.20		

which indicates that the percolation threshold does not depend on fibre-length distribution. Table I presents the exponent α of parallel conductivity for various AR, where α of NLD and FLD were nearly the same for the same AR and decrease as AR decreases.

Previous work on the percolation threshold, V_c, associated with aspect ratio AR did not cover a sufficient range to see the relationship between V_c and AR as in Table II. However, the present results show that the threshold V_c decreases as AR increases, because the stick volume is inversely proportional to the square of aspect ratio, i.e. $V = \pi l^3/4\ (\mathrm{AR})^2$. Thus a lower fibre volume is required for a given percolation as AR increases.

3.2. The angular dependency of conductivity

The electrical conductivity of unidirectional short-fibre composites of FLD is plotted as a function of volume fraction for various angles in Fig. 4. The conductivity increases exponentially as the volume fraction increases and the exponent increases with the angle for $\xi \leq 45°$, then it decreases with further increase in the angle. However, the percolation threshold remains constant, regardless of the angle, for $\xi = 0°–60°$. A sharp transition, from zero to nearly the same level as parallel conductivity, was observed for the transverse direction, $\xi = 90°$, at the critical volume fraction, $V_{c\perp}$.

The conductivity exponents for various fibre angles are summarized in Table III and the exponent reached a maximum at 45° and decreased markedly at 60°. The exponent for the transverse direction $\xi = 90°$, where a critical transition takes place, was obtained from the conductivity for $V_f > V_{c\perp}$ in Fig. 4.

For the parallel direction, the minimum number of fibres required for a percolation is $N = l/L$, which indicates that the percolation probability, $P_{p\parallel}$, is given as function of length and the number of the fibres, N, i.e. $P_{p\parallel} = P_{p\parallel}(L, N)$. Thus, the fibre length has a dominant role for the percolation in the parallel direction and the percolation probability depends on the length of stick, like a line percolation [10].

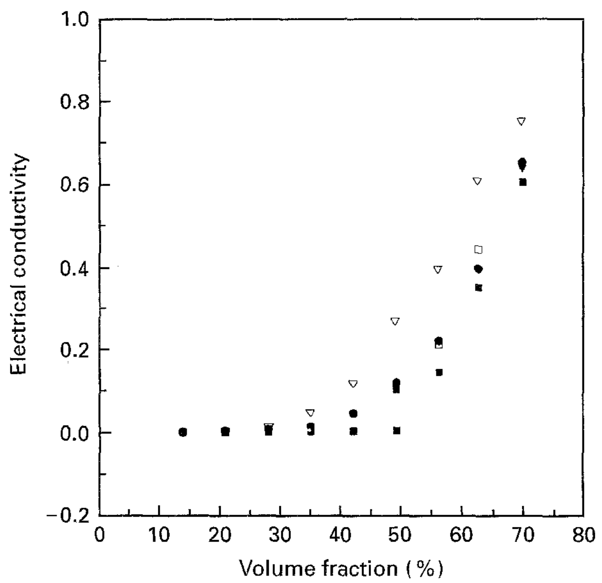

Figure 4 The angular dependence of electrical conductivity with respect to fibre direction of the unidirectional composites with the same volume fraction, and FLD. AR = 33; ξ: (□) 0°, (●) 30°, (△) 45°, (▼) 60°, (■) 90°.

TABLE III The variation of conductivity exponent with angle with respect to the fibre

	ξ (deg)				
	0	30	45	60	90[a]
Conductivity exponent	0.82	1.075	1.234	0.074	1.924

[a] Angle of critical transition.

However, for the transverse direction, the minimum number of fibres for a percolation is $N = l/a$, so the percolation probability for the transverse direction is given as $P_{p\perp} = P_{p\perp}(a, N)$. Thus the diameter of the fibre plays an important role through aspect ratio like a sphere percolation in two dimensions [11].

As the angle with respect to the fibre increases, the influential parameter for the percolation probability changes from the length to the diameter of the fibre. Both a and L have the same weighting for percolation probability in the 45° case, resulting in the maximum increment of conductivity.

3.3. The critical transition in unidirectional composites

In Fig. 5, the electrical conductivity of composites for parallel and transverse directions for FLD with the same AR = 26.66 are compared as a function of volume fraction. The percolation thresholds of the parallel and transverse directions were 0.113 and 0.4422, respectively, and the normalized electrical conductivity for the parallel direction was 0.316 at $V_{c\parallel} = 0.44$, while that in the transverse direction was zero at $V_{c\perp}$.

Whitehouse *et al.* [12] reported the variation of conductivity with volume fraction in a composite of copper reinforced with short aligned carbon fibre. The conductivity, $\sigma_{\parallel}$, for the parallel direction, increased as the volume fraction increased for FLD; however, the data on the conductivity for the transverse direction were limited to $V_f > V_{c\perp}$ (= 0.14), without comment on the conductivity for $V_f < V_{c\perp}$. Whitehouse *et al.* were concerned about the difference in the conductivity between both directions to determine the effects of porosity. The change of conductivity with volume fraction of carbon fibre was explained using the Eshelby model [13, 14], which is applicable to the conductivity for non-dilute composites with spherical filler. However, although this model is based on the

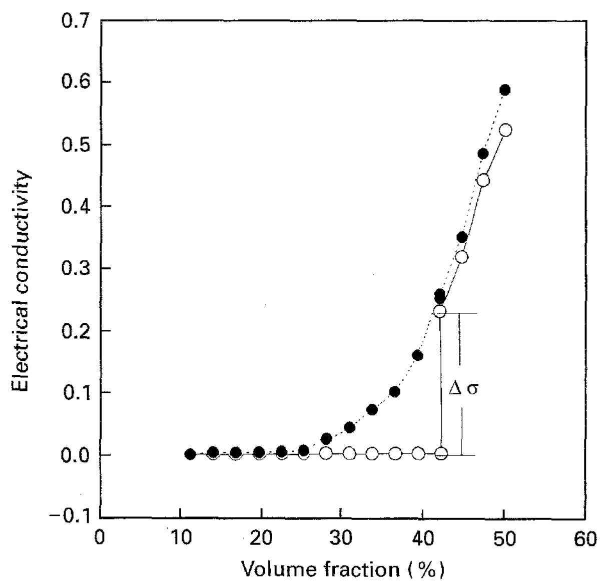

Figure 5 The variation of electrical conductivity in the (●) parallel and (○) transverse directions to the fibre with volume fraction. AR = 26.66.

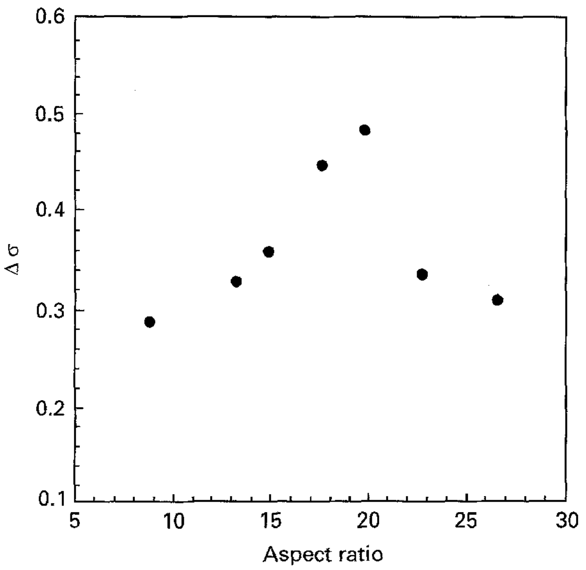

Figure 6 Δσ as a function of aspect ratio.

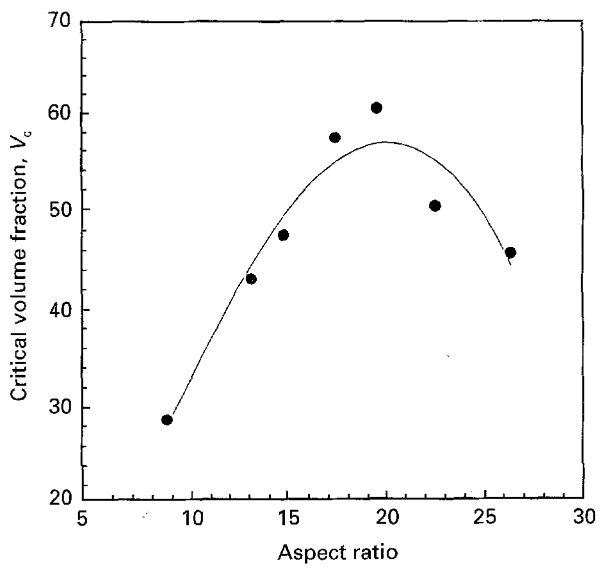

Figure 7 The variation of critical volume fraction for the parallel direction to the fibre with the aspect ratio.

mean field approximation [15], and gives a reasonable agreement for composites of ellipsoidal particulates [16], such was not the case for the conductivity behaviour of fibre composites. However, the present work clarifies that there is no conductivity below the critical volume fraction, $V_{c\perp}$, for the transverse direction.

3.4. The variations V_c and $\Delta\sigma$ with aspect ratio

The percolation threshold, $V_{c\perp}$, increases for the transverse direction with aspect ratio up to 20, above which V_c decreases in a parabolic manner, which is in contrast to the work of Ueda and Taya [17], in which a hyperbolic decrease with aspect ratio was found between 50 and 150. It is envisaged from these two results that $V_{c\perp}$ varies in a parabolic manner with AR.

Fig. 6 shows the variation of the transient increase in conductivity for transverse direction at the percolation threshold, $\Delta\sigma$, as a function of aspect ratio AR. The variation is similar to that of the critical volume fraction $V_{c\perp}$ with aspect ratio in Fig. 7, in which the maximum transient increase of conductivity was observed at the same aspect ratio of 20.

4. Conclusions

The electrical conductivity made of conductive short fibre embedded in an insulating matrix showed a highly anisotropic variation, depending on the fibre direction. The conductivity increased exponentially as the volume fraction increased and the exponent was shown to be higher for greater aspect ratio. In addition, the percolation thresholds decreased as the aspect ratio increased and did not depend on the fibre-length distribution.

The electrical conductivity varied with angle with respect to the fibre direction of FLD and the conductivity exponent increased with angle for $\xi \leq 45°$, then it decreased with further increase in angle, the maximum being at 45°, and decreased markedly at 60°.

A sharp transition, from zero to nearly the same level as parallel conductivity, was observed for the transverse direction. The percolation threshold for the transverse direction increased with aspect ratio up to 20, above which the V_c decreased in a parabolic manner. The variation of the transient increase of conductivity at the percolation threshold was similar to that of the V_c with respect to the aspect ratio.

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