Fractal approach to the critical filler volume fraction of an electrically conductive polymer composite

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It has been known for quite a long time that polymers filled with electrically conductive particles, foils or fibres exhibit a distinctive dependence of conductivity on filler volume fraction. With a rise in filler content, there is always a drastic increase in composite conductivity by the order of ten magnitudes at a certain threshold, namely, the critical volume fraction. Such a transition-like change in conductivity is usually interpreted as percolation. Many models have been proposed for explaining the conduction mechanism involved, but often they possess evident drawbacks mainly due to the negligence of relative filler arrangements or the Euclidean geometric description of the arrays. The present work focused on the prediction of the critical volume fraction by a new electrical conductive model, based on the fractal technique and the generalized unit-cell method proposed by Pitchumani and Yao for modelling the thermal conductivity of fibrous composites. It was found that the electrical conduction behaviour of a polymer composite is governed by both a filler geometry factor and a material factor of the components. The critical volume fractions estimated by the model are in good agreement with experimental results taken from the literature. In addition, possible improvements of the present approach are discussed.

1. Introduction

As a member of the functional composite materials family, an electrically conductive polymer composite comprised of conductive fillers (e.g. graphite, metal powder or carbon fibre) and an insulating polymer matrix, plays an important role in modern industries owing to its advantages of light weight, good processability, chemical stability, cost effectiveness and easy regulation of electrical conductivity and mechanical performance within a wide range. In recent years, conductive polymeric composites have been successfully used, e.g. for electrostatic discharge (ESD) protection, electromagnetic–radio frequency interference (EMI/RFI) shielding, self-control heating and deformation–conductivity transducers [1, 2].

The mechanical and physical properties of the composite are mostly dominated by the nature of the filler, whereas the polymer matrix determines the environmental characteristics of the composite. Therefore, the overall composite properties can be tailored to fit the desired application through proper choice of filler and matrix resin [3].

With respect to the mechanisms of conductivity, usually two considerations must be made. One deals with the formation of electrical paths through the composite, and the other looks into the movement

details of electrons along these electrical paths. Both mechanisms are highly dependent on the filler content [4]. In the case of very low filler concentration, the composite's conductivity remains almost the same as that of the polymeric matrix. If the filler loading exceeds a certain critical value, however, a drastic rise in the composite's conductivity by ten orders of magnitude can occur, meaning that at least one conductive network is formed. The subsequent change in electrical conductivity with a further increase in filler fraction takes place again rather slowly. In order to model such an S-shaped conductivity versus filler content curve, many theoretical treatments have been proposed; in all of these cases the critical filler volume fraction necessary to support a continuous electrical path in the composite received special attention [5]. Evidently, this is a problem of scientific value, but it is of practical importance as well. For example, it is often expected to achieve sufficient conductivity (a) at lowest carbon black content so as not to lower substantially the composite's strength, or (b) at lowest carbon fibre content for economic reasons.

Generally, the transition in composite conductivity is attributed to the percolation phenomenon which is based on the fact that the conductive fillers are sufficient to come into contact with one another as the

filler loading exceeds the threshold concentration. It has been experimentally demonstrated that the critical filler content depends upon the structure, conductivity, dimension, geometry, and distribution of the fillers in the composite. Further factors are the rheology and thermal behaviour of the polymer matrix, and the thermodynamic interaction between filler and polymer. Hence, many investigators have attempted to interpret the percolation and to predict the critical filler volume fraction from these aspects. Two typical approaches are briefly described below. Kirkpatrick [6] and Zallen [7] developed a statistical model that assumes site or bond percolation in the lattice coordination. They derived the scaling relation

$$\sigma = \sigma_0 (V - V_c)^t \qquad (1)$$

where σ is the composite conductivity, σ_0 the filler conductivity, V the filler volume fraction, V_c the critical filler volume fraction, and t the critical index of conductivity. The theory has been experimentally verified in some composites containing carbon black [8]. However, the limitation of this model lies in the fact that V_c and t are only functions of the lattice dimension, and many studies found that the predicted V_c deviated greatly from the values measured [9]. In another approach to explain the reason why V_c varied with the species of filler and matrix resin, Miyasaka et al. [10] avoided the complicated geometry effects. Instead they proposed a model from the view point of thermodynamics, assuming that the coagulation of conductive fillers forms networks at a certain interfacial excess energy, Δg^*. The critical concentration in the case of spherical particles was thus given as

$$V_c = [1 + 3(\gamma_c^{1/2} - \gamma_p^{1/2})^2/(\Delta g^* R)]^{-1} \qquad (2)$$

where γ_c and γ_p are the surface tensions of filler particles and polymer, respectively, and R is the radius of filler particles. By considering the melt viscosity of the polymer and the moulding time during composite processing, a modified version of Equation 2 was subsequently suggested by Sumita et al. [11], and it was supported by their experimental results. Owing to the limitation of their initial basic assumptions, this thermodynamic model is only applicable for non-polar systems, e.g. polyethylene or polypropylene. However, it sets an example that geometry problems should not be emphasized too much in the study of a composite's conduction mechanisms.

It can be concluded from the literature that a model which is able to describe the electrical conductivity of a composite might be at least of the form

$$\sigma = f(V, \sigma_0, \text{"filler arrangement"}) \qquad (3)$$

In the view of composite manufacturing, filler arrangement is a key factor controlling ultimate material performance; it is factually related not only to the particular processing technique but also to the filler dimension and geometry, the species of filler and matrix, and filler–matrix interfacial effects. The available models, however, usually neglect the relative filler arrangement or treat the problem by means of Euclidean geometry, which is not useful in the practical disordered distribution. Therefore, an appropriate

characterization of filler arrangements should have a top priority for developing a more rational model.

In the present work, attempts were made to find a universal method for estimating the critical filler volume fraction in conductive composites, with the hope of providing a scientific basis for subsequent work on a new and further improved model. As the first step, the filler arrangements were quantified by using fractals in accordance with Pitchumani and Yao's analysis of thermal conductivities in fibrous composites [12]. This allows the geometric complexity and the enormous computation time required for statistical simulation to be reduced. In particular, the fractal concept developed by Mandelbrot [13], is used to describe a material microstructure that is not Euclidean, but with a non-integral, so-called fractal dimension [14]. Pitchumani and Yao [12] demonstrated that a cross-section of a fibrous composite exhibits self-similarity over a small range of scaling. They determined the fractal dimensions of such a system, based on this concept, and a generalized unit cell representing the geometric pattern of the cross-section was constructed (i.e. filler arrangement in the composite was thus characterized), and then a thermal model was derived [12]. Because the fractal dimension could reflect the connectedness of the fillers, it might also be directly correlated to the probability of the formation of electrically conductive networks in the composite at various filler fractions.

By considering the electrical conduction model, a two-phase composite system is employed and its electric conductivity is written as

$$\sigma = \sigma_p^G \sigma_s^{1-G} \qquad (4a)$$

with

$$\sigma_p = V\sigma_0 + (1 - V)\sigma_m \qquad (4b)$$

$$\sigma_s = [V/\sigma_0 + (1 - V)/\sigma_m]^{-1} \qquad (4c)$$

where σ_m denotes the matrix conductivity, σ_p and σ_s are the conductivity of the composite in the limiting cases of parallel and serial connection, respectively, and G is a distribution function that has the value of 1 for the parallel and 0 for the serial model (Fig. 1). It is clear that G reflects the contact probability of fillers to form conductive networks, and it concerns the relative filler arrangement as well as other microscopic details of the composite. As long as the measure of G is obtained, the composite electric conductivity can be deduced from Equation 4a, which coincides factually with the same functional form as proposed in Equation 3.

2. Modelling

For the convenience of evaluation, the fillers are assumed to be spherical particles of identical diameter, D, distributing in the matrix in the form of a face-centred cubic (fcc) structure (Fig. 2a). A cross-section of the composite is randomly sampled in the x–y plane (Fig. 2b). Following the technique employed elsewhere [12], the section is divided into small grids (about one-tenth the particle diameter in size) in accordance
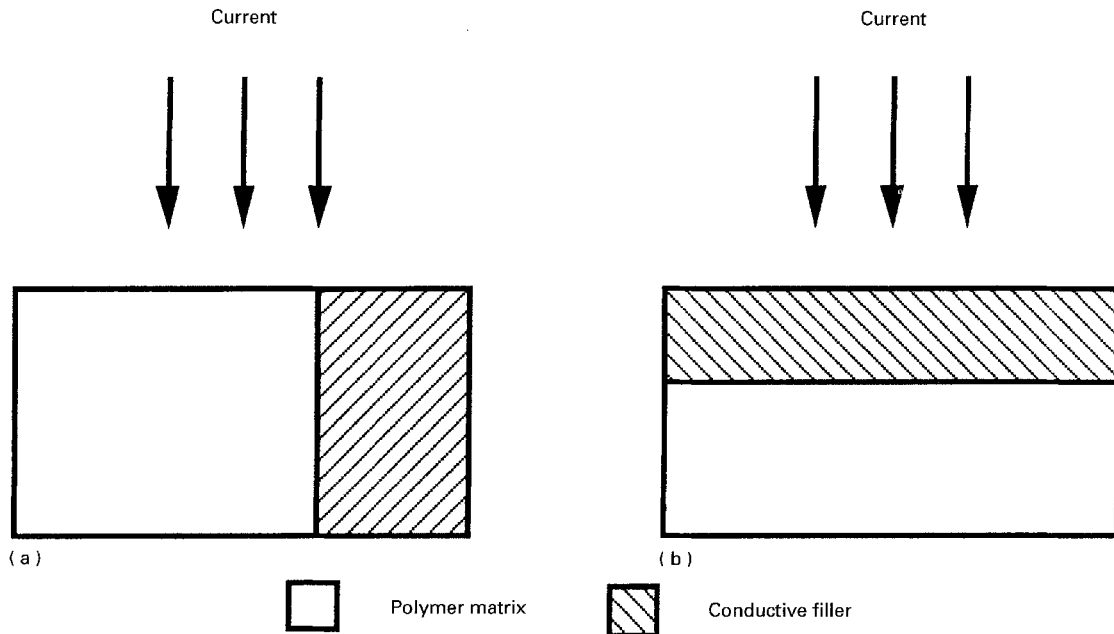
Figure 1 The electrical conduction model proposed for a two-phase composite. (a) Parallel model; (b) serial model.

with the sandbox method, in order to measure the fractal dimension. A line scale of length L is put inside the cross-section and scans the whole section in the x-direction. When the centre of the line scale falls on the fillers, the intercepts' length between the line scale and fillers is added together and denoted as $M(L)$ (Fig. 2c). The averaged length of the intercepts scaling with the line scale L, $\overline{M(L)}$, equals the total $M(L)$ divided by the interception times. A series of values of $\overline{M(L)}$ can be yielded by changing the length of L. By plotting $\log \overline{M(L)}$ against $\log L$, the slope estimated with the least-square method gives the fractal dimension in the y-direction. It should be noted that the length of the line scale cannot be varied freely. As mentioned earlier, an overall composite cross-section might not be a real fractal and shows self-similarity only within a small scaling range, therefore the definition of the range of L values is absolutely necessary. Owing to the facts that the relative filler arrangement is a very important factor in this research and that the most fundamental pattern of the cross-section illustrated in Fig. 2b is one filler particle, the lower bound of L must be the particle diameter, D. On the other hand, the approach made by Pitchumani and Yao [12] suggested that the maximum length scale must not exceed the interfiller distance between three to four fillers. The upper bound of L corresponding to a given filler volume fraction is set to $\Delta = (2\pi/3V)^{1/3}D/\cos(\pi/4)$.

Owing to the configuration of fcc, filler arrangement is identical in both the direction x and y. So the fractal dimension in the x-direction is just the same as that in the y-direction, and it is represented by an identical symbol, d. According to the procedures above, the fractal dimensions of composites with different filler volume fractions can be calculated.

As a simplified but effective method, it is usually possible to obtain information on a complicated system through investigation of a generalized unit cell. In order to relate the macroscopic performance to the filler content and the fractal dimensions, Pitchumani and Yao constructed the polygonal Wigner–Seitz cells of different sizes around each fibre in a composite section [12, 15], which were then represented by an equivalent rectangular cell having the same physical behaviour. Finally, they yielded a dimensionless generalized unit cell which was only the function of filler volume fraction and relative filler arrangement. Applying their results to the case here, a simplified description of the generalized unit cell containing a generalized filler particle of dimensionless diameter D' (as adjusted to the present system) can be expressed as follows

$$L' = \left(\frac{\pi}{4V}\right)^{1/2} D' \tag{5a}$$

with

$$D' = \left(\frac{4V}{\pi}\right)^{d/(2d-2)} \tag{5b}$$

where L' is the size of the square generalized unit cell (Fig. 3).

The filler volume fraction dependence of the size of the generalized unit cell representing composites filled with particles of different diameters is shown in Fig. 4. L' decreases with increasing V in such a way that at lower filler content, L' drops rapidly, but in the case of higher loadings varies slowly. It becomes clear from this figure, that at lower filler fraction (i.e. at a longer interfiller distance), the value of L' is larger. Fig. 4 further reveals that the drastic decrease occurs in the range of $V < 15$ vol%, which is analogous to the conventional electrical resistivity versus filler volume fraction plot. The critical volume fractions of most particle-filled composites lie at about 10%. In addition, the curves of Fig. 4 exhibit that at the same filler content, L' decreases with decreasing particle diameter. For a given volume fraction the total filler amount in a composite filled with small particles is

(a)

(b)

(c)

$$\Delta = (2\pi / 3V)^{1/3} D / \cos (\pi / 4)$$

$$\Delta \geq L \geq D$$

$$M(L)$$
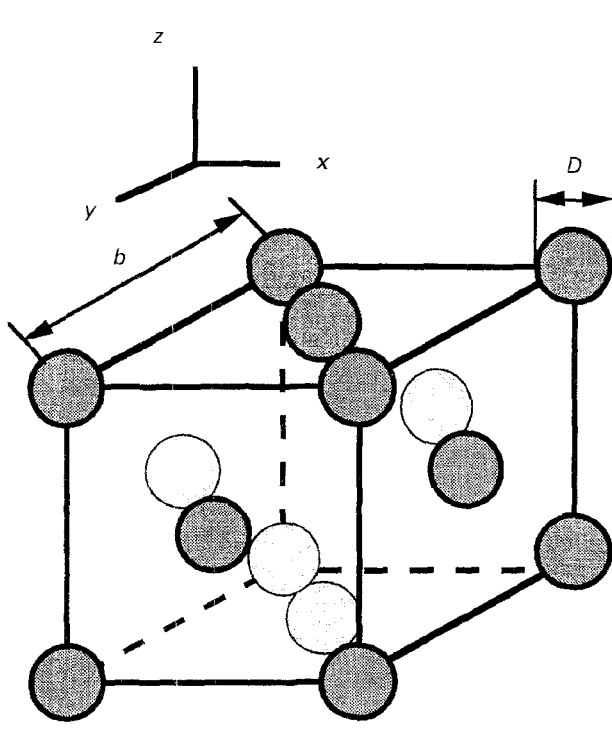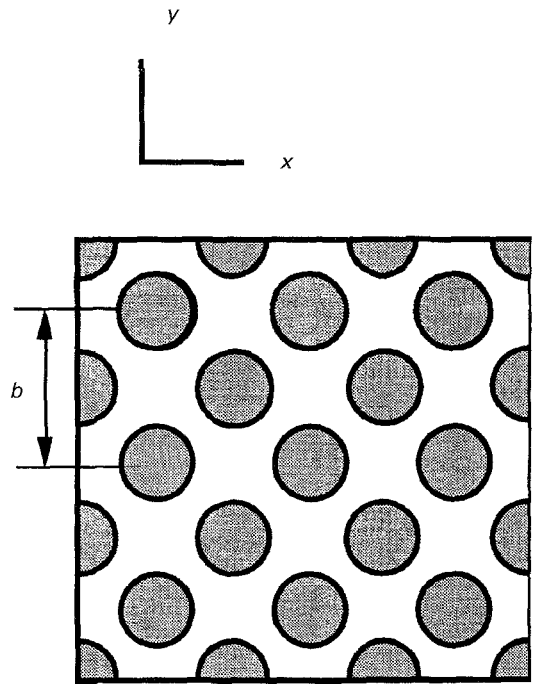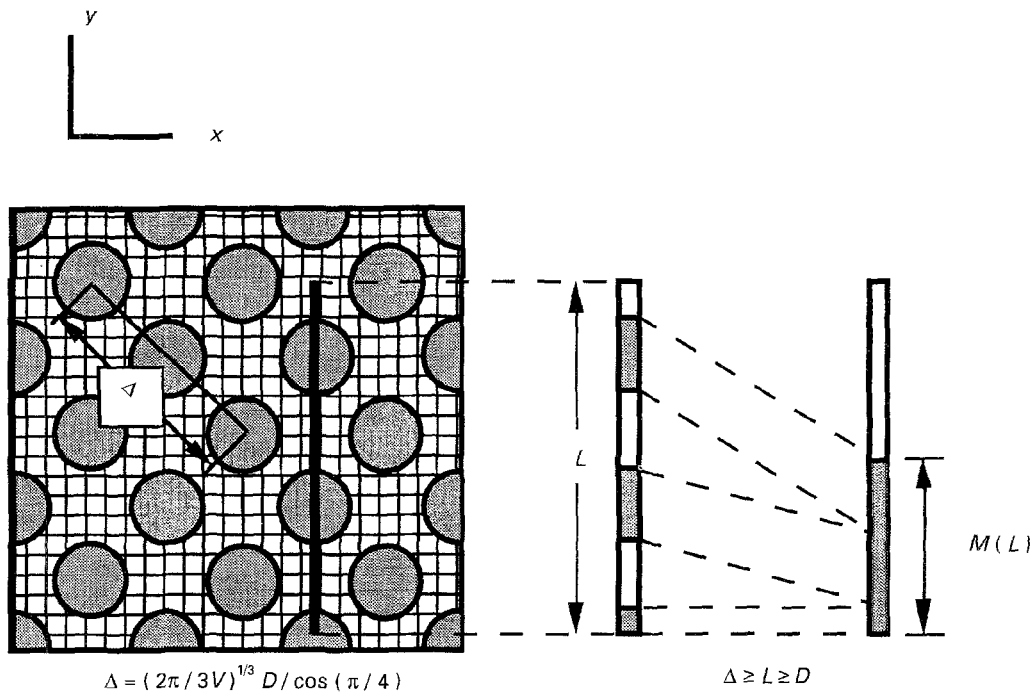
always larger than in one filled with large particles, usually meaning that the contact possibility of the larger particles is rarer. As a result, it might be deduced that the formation probability of conductive paths throughout a composite is closely related to L'.

Kirkpatrick derived the relationship between percolation probability, $P(V)$, and filler concentration from his model introduced earlier [6]

$$P(V) \propto (V - V_c)^{1.5-1.6} \qquad (6)$$

An important enlightenment is that the probability of the conductive network formation might be exponentially related to the filler content. Considering the meaning of L' implied by Fig. 4, the expression for G appearing in Equation 4a is written as

$$G = V^{aL'} \qquad (7)$$

where a is defined as a material factor that will be discussed later. At the present stage, the dependence of the composite's conductivity on filler volume fraction can be evaluated from Equation 4 as long as a proper
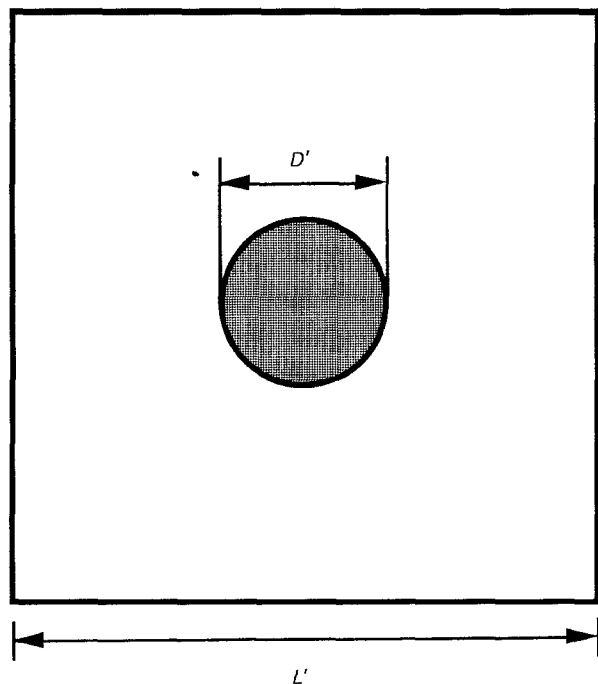
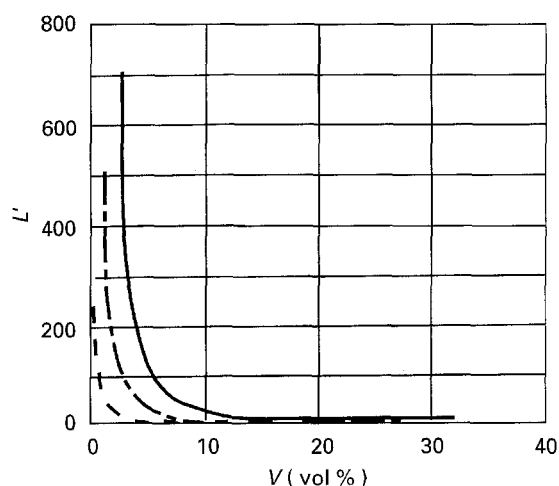*Figure 3* A generalized unit cell.

Figure 4 The size of the generalized unit cell versus filler volume fraction. D: (—) $10\,\mu m$, (— — —) $5\,\mu m$, (— · —) $2\,\mu m$.

value of a is known. However, the effect of contact resistance on filler conductivity should also be taken into consideration.

The composite model that regards the conductive filler and matrix resin as two separate regimes of the two phases is very rough (Fig. 1), because there are unavoidable microgaps, voids and resin bridges between the filler particles even in the case of closest packing. That is, σ_0 in Equation 4b and c only represents the apparent filler conductivity. For the conduction performance of a particle-filled composite at very high loading regime, the composite resistivity, ρ, is [16]

$$\rho = R_{p'}/D + \rho_0/0.59 \qquad (8)$$

where $R_{p'}$ is the sum of constriction and tunnelling resistance ($\Omega\,cm^2$), and ρ_0 is the filler resistivity. Replacing σ_0 in Equations 4b and c with the inverse of ρ, one can obtain a more reasonable expression for

Equation 4a

$$\sigma = \sigma_p^G \sigma_s^{1-G} \qquad (9a)$$

with

$$\sigma_p = V/\rho + (1 - V)\,\sigma_m \qquad (9b)$$

$$\sigma_s = [V_\rho + (1 - V)\,/\sigma_m]^{-1} \qquad (9c)$$

3. Discussion

The critical volume fractions for carbon black (CB)-filled LDPE and PP and powdered silver (Ag)-filled silicone rubber composites were reported elsewhere [9, 10]. In order to examine the model approach suggested here, these literature results and some performance data [10, 16] are cited for comparison and calculation, e.g. ρ (CB) $= 10^{-3}\,\Omega\,cm$, ρ (Ag) $= 1.6 \times 10^{-6}\,\Omega\,cm$, ρ (polymer) $= 10^{-15}\,\Omega\,cm$, $R_{p'} = 7.0 \times 10^{-8}\,\Omega\,cm^2$ and data in Table I.

Using Equation 9a and these data, the numerical expression of composite conductivity can be obtained. On a trial basis, 0.2 is found to be an appropriate value for the material factor a in Equation 7. Fig. 5 shows the results of silver/silicone composites. The critical volume fraction, V_c, is determined by the conventional method, i.e. the peak position of $d\log\sigma/dV$ in the drastically increasing regime. It becomes

TABLE I Comparison of observed critical volume fractions (from [9, 10]) and the calculated ones (according to Equation 9)

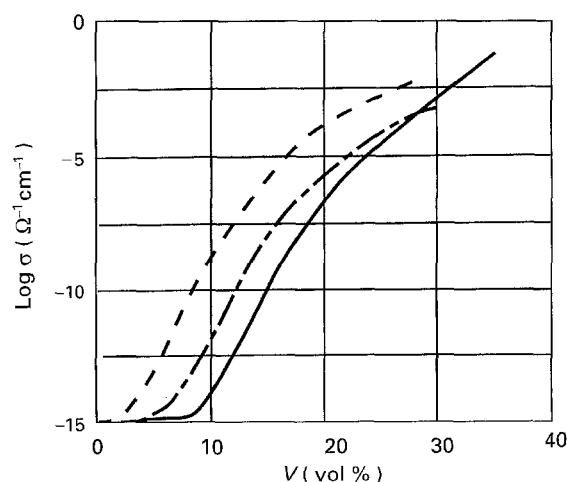| Fillers	Filler diameter (μm)	V_c (vol %)	
		Observed	Calculated
Ag [9]	9	20	20
	5	15	16
	4	16	12.5
	1	10	11
	0.5	5	5
CB [10]	10		21
	5		15
	2		10.5
	0.37	4.7	6

Figure 5 Calculated electrical conductivity versus filler volume fraction of silver/silicone rubber composites. D: (—) $10\,\mu m$, (— — —) $5\,\mu m$, (— · —) $2\,\mu m$.
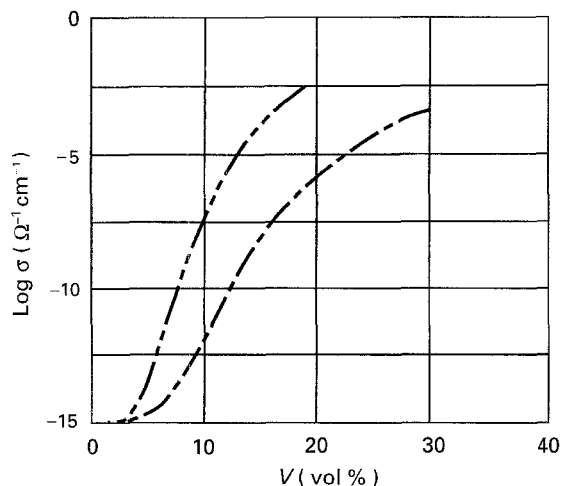
Figure 6 Effect of the material factor, *a*, on the estimated volume fraction dependence of conductivity of a silver/silicone rubber composite. *a*: (---) 0.1, (———) 0.2.

evident, that the theoretical σ-V curves describe the known S-shaped relation very well. In addition, the calculated critical volume fractions coincide exactly with the experimental results published in the literature (Table I). It is also seen that the calculated and observed V_c values increase with increasing diameter of filler particles. These results confirm that the model approach of this study is effective in predicting the critical volume fractions of conductive particle-filled composites.

It is worth noting that the material factor, *a*, is an important parameter, and cannot be simply regarded as a meaningless constant. Obviously, different values of *a* will result in different shapes of the σ-V curve, and therefore in different values of V_c (Fig. 6), greater value of *a* corresponds to greater values of V_c. Only for a certain value, e.g. 0.2 (in the case of the silver and carbon black particle-filled systems evaluated here) there is good agreement between the predictions and experiments. In fact, the conductive behaviour of a composite material manufactured by a given processing technique is basically controlled by two types of factors: (1) a geometry factor (including filler dimension, morphology, packing density, relative arrangement), and (2) a material factor (accounting for the filler and matrix species, macroscopic and microscopic properties, filler–matrix compatibility). Both of these factors are related to and affect each other. This explains why some composites filled with different species of conductive particles of similar dimensions have quite different critical volume fractions. Miyasaka *et al.* [10] also indicated that the critical volume fraction depends to a great extent upon the surface tensions of fillers and matrix resins. By analysing Equation 7, it is evident that L' obtained from the fractal-based consideration reflects the effect of geometrical factors on the probability of a conductive network formation, whereas the value of *a* takes the effects of material parameters into consideration. This is also the reason why *a* is termed a material factor. The present work arranges the influence factors under

two categories and correlates them through Equation 7, but the exact expression of *a*, as well as its dependence on material properties, still remains unknown. Furthermore, the fillers in the model composite applied to the work are assumed to be spherical particles of identical diameter and distributed in an f c c order. Such an approximation disagrees with the practical cases. Solving these problems might result in a more satisfactory conduction model.

Future work should, therefore, be focused on the clarification of the exact physical meaning of the material factor. Furthermore, the values of L' should be obtained from experimentally measured fractal dimensions of real composite cross-sections, so that the assumption about filler dimension, shape and distribution made in the present work need no longer be used. This will help in eliminating the resultant deviation from disordered arrays.

4. Conclusion

A generalized unit cell that characterizes the geometrical details of a composite cross-section has been built up using the fractal technique developed by Pitchumani and Yao [12]. The dependence of the unit-cell dimension on filler volume fraction is quite similar to the conventionally determined electrical resistivity versus volume fraction of a bulk material. Based on this analogy as well as on the work of Kirkpatrick [6], a generalized unit-cell conductive model is proposed, which can effectively predict the critical volume fraction of a conductive composite. The estimations are demonstrated to be rather close to the experimental data reported by other researchers. The approach can also be applied to composites filled with other fillers, such as fibres, hybridized particles and fibres, as long as minor revisions are made on the numerical simulations of the composite microstructure.

The electrically conductive behaviour of a composite material is dominated by both a geometry factor and a material factor. Although the relationship between them and their combined influence on conduction may be derived from the present work, efforts must be made to reveal the exact expression for the material factor for a satisfactory model which is able to predict not only the critical volume fraction (as demonstrated in the present approach) but also the overall conduction performance of electrically conductive composites.

Acknowledgements

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