

A simple theoretical model for the bulk properties of nanocomposite materials.

M. Praeger, T. Andritsch, S. G. Swingler and Alun S. Vaughan

University of Southampton,
SO17 1BJ,
United Kingdom

Abstract— Nanocomposites may be produced simply by combining two materials in such a manner as to produce domains of nanometric scale in the resulting composite [1]. True nanocomposites are distinct from simple mixtures in that they exhibit material properties that do not vary monotonically in proportion to the ratio of the constituent materials – throughout this paper this behavior will be labeled as a “nano effect”. It is widely supposed that “nano effects” are produced by interactions that occur at the interface of the nanometric domains [2]. In typical polymer-nanofiller systems, it is proposed that these interactions act to modify the material properties in a region of the polymer matrix near to the surface of the nanoparticle fillers. We shall refer to this volume of modified material as the interphase.

A simple theoretical model is presented which links the interphase volume (and the nature of the material within that volume) with the externally measured properties of the nanocomposite. An equation for the probability that inserting an additional nanoparticle will increase the interphase volume is defined. This equation is applied in a Monte Carlo type calculation to evaluate the interphase volume as a function of filler loading. The resulting properties of the nanocomposite are calculated simply by combining the material properties of the constituents (nanoparticle, matrix and interphase) in the appropriate volume ratios. The strength of this approach is that its simplicity both minimises the number of free-parameters and ensures wide applicability.

In this work the model is fitted to measured values of permittivity in nanodielectrics, however, the same approach may readily be applied to a range of other material properties. Statistical calculations are provided that demonstrate the generality of this result. Analysis of the model parameters is shown and provides insight into the extent and type of modification that occurs within the interphase.

Keywords— *nano; composite; effective medium; permittivity;*

I. INTRODUCTION

In the literature, there exist numerous theoretical models which describe the mixing of two materials and allow calculation of the bulk properties of the resulting composite. These effective medium calculations are frequently applied to the problem of calculating the permittivity of composite dielectric materials; a helpful comparison of some of these models can be found in [3]. Effective medium theories such as those of Bruggeman and Maxwell-Garnet are predicated on the

basis that the composition of the resulting material is always identical to sum of the constituent components, i.e. when two materials are combined to produce a composite, only these two initial components exist in the resulting mixture and they are present in exactly the same ratios as before mixing. This constitutes “simple mixing”, in which the properties of the resulting composite are rigidly limited to fall within the interval defined by the properties of the constituent materials, the “absolute bounds”. Furthermore, since most effective medium theories do not incorporate any knowledge of the size of the material domains it is evident that they cannot account for variation of material properties that results from a change in filler particle size. In the field of nanocomposites, a material which demonstrates a “simple mixing” type of behavior is likely to be uninteresting, as this means that the same effective properties could be achieved with micro-scale or larger inclusions. For nanocomposite materials a particle size dependent variation or non-monotonic variation in material properties with filler loading is highly desirable as this demonstrates a “nano effect” and therefore the potential for enhancement of material properties due to the presence of the nano filler. For example, “nano effects” are observed in the mechanical properties of carbon black reinforced rubber, particularly in the cases of tensile strength and abrasion resistance [4].

The widely accepted explanation for these observed “nano effects” is based on the concept that the material properties are modified at the interface between the filler and the matrix. There are many possible mechanisms, for modification of the material properties: Chemical reactions could occur between the filler material and the matrix in order to create a shell of a different compound. Polymer chains in the vicinity of the filler particles may become aligned and therefore display modified properties whilst, in regions far from the interface, the properties are amorphous. For polymer chains which in the matrix are only weakly bound to their neighbours, bonding to the surface of a nanofiller can significantly increase the distance over which polymer chains can influence one another (i.e. the radius of gyration). For the purposes of this theoretical model, the exact mechanism which is responsible for the change in material property is unimportant. The key point is that, in the vicinity of each nanoparticle, there will be a region in which the material properties are modified (the “interphase”). Crucially, the properties in the interphase need not be within the bounds defined by the initial constituents (the matrix and the nanofiller) this can allow the classical bounds

for “simple mixing” such as the Wiener and “absolute” bounds to be violated. Typically (and in this model), the interphase region is assumed to be produced by modification of the surrounding matrix material with the nanoparticle filler retaining its initial size and composition. The link between filler particle size and the interphase volume arises from the assumption that the interphase material occurs as a layer of approximately constant thickness that surrounds each nanoparticle. If the filler particle size is reduced then their surface area and hence the interphase volume will increase. It is through this link that this model can account for variation in material properties as a function of filler particle size.

II. METHOD

A. Calculation of the interphase volume fraction

In order to calculate the volume fraction of the interphase material as a function of nanofiller loading, a Monte-Carlo type calculation is performed. Conceptually, the simulation runs as follows.

A hypothetical simulation volume is defined (V_s); this volume is divided into an integer number of domains each with volume equal to that of the average nanoparticle (V_p). Initially, all domains are filled with matrix material. At each iteration a nanoparticle is added to one of these domains and matrix material in a shell surrounding that particle is converted to interphase. Nanoparticles are sequentially added at random locations in the simulation volume in order to sweep all possible filler loading levels.

This procedure is formulated mathematically by calculating, at each iteration step, the probability that adding another particle will increase the volume fraction of interphase material. In (1) the volume fraction of matrix, nanoparticles and interphase (all ranging between 0 and 1) are given by M , P and I respectively whilst k represents the coordination number. The parameter n or $n+1$ within parenthesis denotes the iteration number, which is equivalent to the number of particles added.

$$I(n+1) = I(n) - (V_p / V_s) \cdot [I(n) / (I(n) + M(n))] \dots + (k \cdot V_p / V_s) \cdot M(n) \quad (1)$$

$$P(n) = n \cdot V_p \quad (2)$$

$$M(n) = 1 - I(n) - P(n) \quad (3)$$

The first term on the right of (1) merely carries over the interphase volume fraction from the previous iteration. The second term calculates the probability of removing an interphase filled domain by replacing it with the nanoparticle. That is, (V_p / V_s) is the probability that any individual domain will be selected at random for replacement by a filler particle. Whilst $[I(n) / (I(n) + M(n))]$ is the probability that this domain already contains interphase and is allowed (i.e. is not a nanoparticle). The third term calculates the probability that the interphase volume will be increased. That is, for the first nanoparticle $M(1) = 1$ and therefore k nanoparticle domains (a volume of $k \cdot V_p$ out of the total simulation volume V_s) will be converted to interphase.

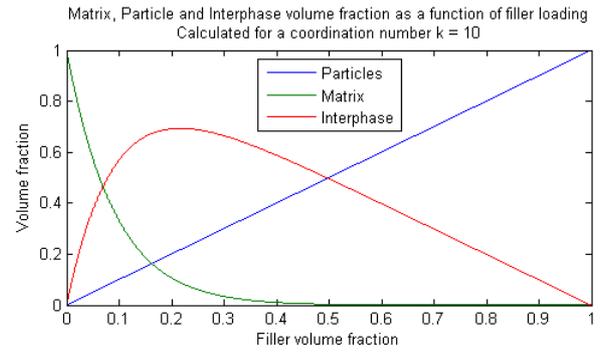


Fig. 1. The curves show the volume fraction of nanoparticles, matrix and interphase as calculated using equations 1-3. Note that the interphase volume fraction is non-monotonic as a function of filler loading.

Figure 1 shows the typical form that (1) produces; in this case the coordination number $k = 10$. Notice that, initially, there is a sharp increase in interphase volume fraction as filler material is added. In Figure 1, for filler fractions greater than approximately 0.2 some matrix material remains, but the sample volume is beginning to saturate with interphase. Above this filler loading level it becomes increasingly likely that adding an additional particle will reduce the interphase volume fraction. This saturation of interphase is the source of filler loading dependency in the calculated output of this model and is what allows it to explain “nano effects”.

The curves shown in figure 1 were computed using Matlab. The calculation is computationally simple with a solution time proportional to the number of nanoparticle sites, i.e. on (V_s / V_p) . Using a million possible nanoparticle sites the calculation takes less than 100 ms and achieves a Mean Squared Error (MSE) lower than 5×10^{-13} .

The only model input which significantly modifies the shape of the curves shown in figure 1 is the coordination number k (see figure 2). High values of k cause a sharp increase in interphase volume fraction at low filler loading; thereafter, interphase volume is progressively reduced as filler loading increases. For lower values of k the peak in interphase volume fraction is lower and occurs at a higher filler loading.

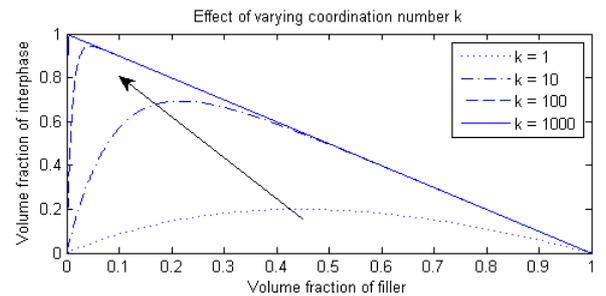


Fig. 2. The curves show the volume fraction of nanoparticles, matrix and interphase as calculated using equations 1-3. Note that the interphase volume fraction is non-monotonic as a function of filler loading.

B. Calculation of material properties

Once the volume fractions of nanoparticles, interphase and matrix have been established (P , I and M respectively) it is

possible to calculate the value of an arbitrary material property G as a function of filler loading:

$$G_{eff} = I.G_I + M.G_M + P.G_P \quad (4)$$

Although it is possible to modify the form of (4) to use an existing effective medium theory (which could be specific to a particular material property) and adapt this to the case of a three component system; we opt to take the simplest possible approach and merely sum the properties of the constituent materials in the appropriate volume fractions. This highly simplistic method has the dual benefits that it is directly applicable to any material property and does not introduce additional unknown quantities into the calculation.

The volume fraction of interphase and matrix (I and M) can be calculated using the method described in Section II A. I and M are therefore functions of the particle volume fraction P and the coordination number k . It then remains to find appropriate values for G in the interphase (G_I), matrix (G_M) and in the particles (G_P). The bulk material properties for the matrix and the particles respectively should provide good estimates for G_M and G_P . G_I and k are therefore the primary unknowns in any material system. The fitted value of G_I gives us information about the interphase which cannot be measured directly.

In the specific examples given in the remainder of this paper the material property that will be investigated in place of G is the real component of relative permittivity. (We will take the value at 1000 Hz as being representative of the sample).

Note that for consistency with the experimental data it is often necessary to make a conversion to filler loading as weight % whereas the values of I , M and P used in the model are all expressed as volume fractions. The following expression for weight % (W) may be used:

$$W = 100.P.d_p / (I.d_i + M.d_m + P.d_p) \quad (5)$$

where d_i , d_m and d_p are the densities of the interphase, matrix and particles respectively. Optionally these density values can be freely fitted by the model; however, we have made the assumption that $d_i = d_m$ and that d_m and d_p are equal to the literature values for bulk material. This minimizes the number of unknowns and therefore constrains the fit on the remaining unknown parameters (k and G_I) more tightly.

III. RESULTS

A. Model fit results for nano Al_2O_3 and MgO in epoxy

Nanocomposite samples with varying filler loadings, were prepared and dielectric spectroscopy measurements were made as described in [5]. The real permittivity at 1 kHz is plotted as the marker points in figure 3 (for Al_2O_3 and MgO nanoparticles in epoxy). In each case the fit line is calculated using a nonlinear least-squares fit in matlab. The matlab software allows all fit parameters either to be given fixed values (where these are well known) or to be freely fitted (within user specified bounds). The only restriction is that you must have at least one more data point than you have free parameters or the fit will be inadequately constrained.

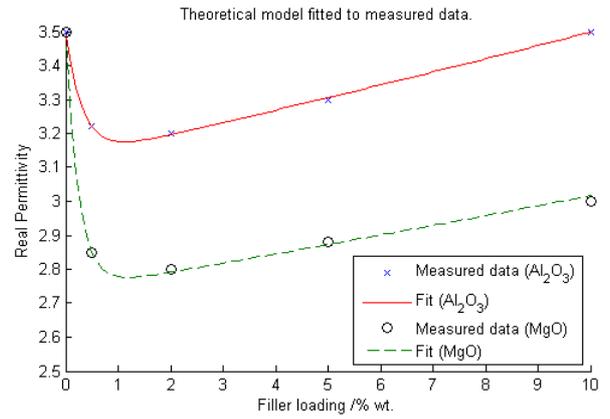


Fig. 3. Measured data (markers) and model fit for the real permittivity of Al_2O_3 filled epoxy (green dashed line) and of MgO filled epoxy (red solid line). Values of the fit parameters are given in Table 1.

In figure 3, at 0 % filler loading, the real permittivity of the matrix material is directly measured and can therefore be fixed in the fit. Selecting an appropriate value for the permittivity of the particles is more problematic as the literature may contain a range of values (i.e. for solid bulk material and for compacted nanoparticles). This uncertainty means it is appropriate to use a free fit for G_P with the bounds being defined by the literature values. The other free parameters are the coordination number k and the real permittivity of the interphase G_I . The lower and upper limits for G_I are set as 1 and $2G_P$ respectively.

Figure 3 demonstrates that the model was able to fit closely to the measured data (for both MgO and Al_2O_3 filled epoxy nanocomposites) whilst varying only the coordination number k and the relative permittivity of the interphase material G_I .

B. Further analysis of the results

Further analysis can help us to relate the coordination number k to the real-world physical properties of the material. In order to fit with the proposed model where interphase is added in a shell surrounding each nanoparticle; values of k can be converted from multiples of the nanoparticle volume V_p to give the effective thickness T_{eff} of such a hypothetical shell. When the average radius of the nanoparticles is r .

$$T_{eff} = [3.V_p.(k+1) / 4.\pi]^{1/3} - r \quad (6)$$

$$V_p = 4.\pi.r^3/3 \quad (7)$$

In figure 4, $T_{eff}/2.r$ is plotted in order to show the relationship between coordination number k and the effective interphase thickness. (The dashed lines show the values of k obtained from the fits in figure 3). The effective interphase thickness grows rapidly at low k but then slows. This is because as the interphase shell grows (with k) an increasingly large change in interphase volume is required to produce the same small change in interphase thickness.

From the fits made to the data in figure 3 and with knowledge of the nominal particle size (obtained by SEM) we can calculate the nominal interphase thickness and the change of permittivity in the interphase region (relative to the permittivity of the matrix) see table 1:

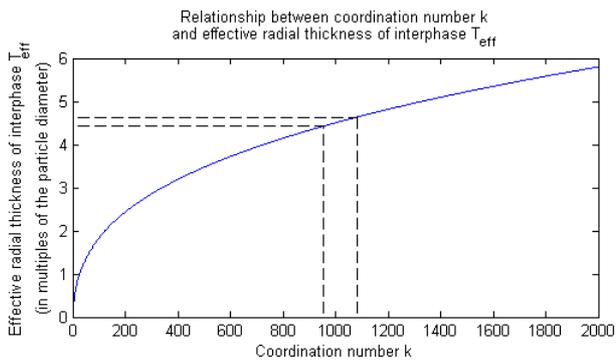


Fig. 4. Plot showing the relationship between coordination number k and the thickness of a hypothetical interphase shell surrounding each nanoparticle. Interphase thickness is expressed in multiples of mean nanoparticle diameter.

TABLE I. FIT PARAMETERS

Filler Material	Nominal (diameter)	Coordination number (k)	Interphase thickness	Change in permittivity
Al ₂ O ₃	22 nm	953	97 nm	-0.37
MgO	50 nm	1084	232 nm	-0.71

For both filler materials the nanoparticle diameters are of the same order of magnitude; this explains the similarity in the values for the coordination number k . However, the calculations for interphase thickness and permittivity indicate that there is a stronger interaction between the MgO particles and the epoxy matrix than there is for the Al₂O₃ ones. This is despite the fact that the Al₂O₃ particles provide a higher contrast in permittivity relative to the matrix material.

IV. CONCLUSIONS

In conclusion, the model presented here is capable of fitting to the externally measured properties of materials that exhibit non-monotonic filler loading dependence. This type of non-monotonic behavior is by definition a “nano effect” and cannot be produced by simple two component effective medium theories. The model is presented with the following caveats:

Fit values for k and derived values such as T_{eff} are all critically dependent upon the form of the equation used to calculate the material properties from the volume fractions (4). Nevertheless, if the same equations are used, then the values obtained may be used for comparison between materials.

The permittivity and the thickness of the interphase that are determined by this model represent the “effective” material properties of a hypothetical interphase volume. However, to some extent, dielectric spectroscopy is always concerned with “effective” material properties since in reality permittivity varies dramatically on the microscopic/atomic level.

In the simulation, as set out in equations 1 to 3, it is possible to reach 100 % filler loading whilst in real materials imperfect tessellation leaves trapped regions of interphase or matrix material which cannot be occupied by filler. (The packing density for spheres is just 64 %). As a result the model is expected to deviate from reality for very high filler loadings.

The authors gratefully acknowledge the RCUK's Energy Programme for the financial support of this work through the Top & Tail Transformation programme grant, EP/I031707/1.

Despite the above caveats, the relative simplicity of the model allows us to be confident of certain conclusions drawn from the fits. For example, the nanocomposites presented in figure 3 are both inorganic fillers dispersed a polymer. In both cases (and for a variety of similar material systems studied by the authors) the modification of properties that occurs in the interphase region of the matrix manifests as a reduction in permittivity. This is an important result which is not yet widely appreciated in the field.

Since reduced permittivity is observed in the interphase regions of many diverse material systems this effect may be primarily driven by mechanical/spatial factors. For example, disordering or immobilization of the polymer chains near to the nanoparticle could result in increased free volume or even the presence of microscopic air filled voids – lowering the effective permittivity [6]. One implication of this finding is that this type of “nano effects” in dielectric spectroscopy will be most clearly measurable at low filler loadings and when there is a relatively low contrast in permittivity between the matrix and the filler materials.

An interphase region with differing material properties is frequently presented as an explanation for observed “nano effects”. The end result of this hypothesis is to produce a material composition (i.e. the volume fraction of each component) which changes as a function of filler loading and of nanoparticle size. If it is possible to calculate the resultant properties of the composite simply by using a three component effective medium equation then logically it would have been possible to achieve the same properties by directly mixing the three components in the appropriate ratios without needing to produce nano scale domains. This discussion points towards a distinction between different types of “nano effects”. That is, those that are driven by compositional change as described here, and those where the source of the particle size dependency is the physics which determines the material properties. In the latter case, it would be possible to see a “nano effect” in a purely two component system.

If by invoking an interphase we change the net composition of the material - does that material truly show a “nano effect”?

REFERENCES

- [1] M. F. Frechette, M. L. Trudeau, H. D. Alamdari, and S. Boily, "Introductory remarks on nanodielectrics," *Ieee Transactions on Dielectrics and Electrical Insulation*, vol. 11, pp. 808-818, Oct 2004.
- [2] T. J. Lewis, "Interfaces are the dominant feature of dielectrics at the nanometric level," *Ieee Transactions on Dielectrics and Electrical Insulation*, vol. 11, pp. 739-753, Oct 2004.
- [3] A. H. Sihvola, "How strict are theoretical bounds for dielectric properties of mixtures?," *Ieee Transactions on Geoscience and Remote Sensing*, vol. 40, pp. 880-886, Apr 2002.
- [4] D. Parkinson, "The reinforcement of rubber by carbon black," *British Journal of Applied Physics*, vol. 2, p. 273, 1951.
- [5] R. Kochetov, T. Andritsch, P. H. F. Morshuis, and J. J. Smit, "Anomalous Behaviour of the Dielectric Spectroscopy Response of Nanocomposites," *Ieee Transactions on Dielectrics and Electrical Insulation*, vol. 19, pp. 107-117, Feb 2012.
- [6] M. F. Frechette, A. Vijn, M. L. Trudeau, D. Fabiani, L. Utracki, S. Gubanski, *et al.*, "Nanodielectrics: A panacea for solving all electrical insulation problems?," in *Solid Dielectrics (ICSD), 2010 10th IEEE International Conference on*, 2010, pp. 1-29.