Physica B 405 (2010) 2014–2017

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Study on permittivity of composites with core–shell particle

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ARTICLE INFO

Article history:
Received 1 December 2009
Received in revised form
15 January 2010
Accepted 15 January 2010

Keywords:
Composite
Effective permittivity
Core–shell particle
Interface

ABSTRACT

An effective permittivity model of composite with interfacial shell is established. The concentric core–shell ellipsoidal particle randomly mixed with matrix is replaced by solid particle mixed with the same matrix, and the equivalent solid particle has the same radius as the original coating shell. Based on the effective medium theory, the formula for the effective permittivity of two-phase composite with interface is derived, then a simple self-consistent method is applied to modify the formula. With the modified formula, the influence of the structure parameter, the permittivity of the shell, the shape and the volume content of the core on the effective permittivity are investigated. The theoretical results on the effective permittivity of polystyrene–barium titanate composites with interfaces are in agreement with the experimental data.

1. Introduction

The optical, electrical and magnetic properties of two-phase randomly mixed composite are closely related to its dielectric property. Therefore extensively experimental and theoretical research has continuously gone into studying the macroscopic electrical conductivity and the permittivity of the binary composite [1–3]. During the investigation, the layers between two components are often regarded as an ideal contact. In other words, the interfaces are considered as nonexistent [4,5]. However, in fact, there exist interfaces between the scattered particles and the host matrix due to diffusion, penetration, combination, etc. The dielectric properties of the interfacial coating shells (the third component) are different from both the scattered particle and the host matrix. The size of scattered particles in nano-composite is so small that the total interfacial area is large. Therefore, it is more significant to investigate three-phase composite than two-phase composite.

This paper presents an equivalent method to investigate the effective permittivity of a composite system. Considering the interfaces between two components, a new complex model of permittivity of two-phase composites is established, and then an equivalent method is utilized to simplify a three-phase composite system to a two-phase composite system. On the basis of the average polarization theory and Maxwell–Garnett theory, the forecasting formula for the effective permittivity of two-phase composite with interfacial shell is presented. Considering the interaction of particles, a single self-consistent method is applied to modify this formula. According to the proposed formula, the influence of the structure parameter, the permittivity of the shell, the shape and the volume content of the core on the effective permittivity are investigated. The theoretical results on dielectric properties of polystyrene–barium titanate composite with interfacial shell are in good agreement with experimental data. The achieved conclusions can provide theoretical guidance for the design of core–shell structure composites to optimize some desired electromagnetic properties.

2. The effective theory of composites with core–shell particles

2.1. The equivalency to core–shell spherical particles

A two-phase composite is investigated in which ellipsoidal particles with interfacial shells are randomly embedded in a homogeneous matrix. Combining the interfacial shell and the filler particle can be regarded as a "complex particle". Therefore, the three-phase random composite system can be regarded as the complex particles embedded in the matrix. For simplicity, the permittivity is assumed to be unchangeable inside the interfacial layer. Usually, the scattered particles can be considered as spherical particles. We postulate that R_1 and R_2 are the radius of core with permittivity ε_1 and shell with permittivity ε_2 of the complex particle, respectively. The thickness of the shell is $t=R_2-R_1$, and the permittivity of the matrix is ε_m. Under quasi-static approximation, when an electromagnetic field E_0 is incident perpendicularly to the complex particle, the electric potential in each component in composite is given by the Laplace equation:

$$\phi_c = -AE_0 r\cos\theta, \quad r < R_1 \tag{1}$$

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doi:10.1016/j.physb.2010.01.093

$$\phi_s = -E_0\left[Br - \frac{CR_1^3}{r^2}\right]\cos\theta, \quad R_1 < r < R_2 \tag{2}$$

$$\phi_m = -E_0\left[r - \frac{DR_2^3}{r^2}\right]\cos\theta, \quad r > R_2 \tag{3}$$

Coefficients A, B, C and D are determined by the boundary conditions, respectively. As shown in Eq. (3), the outer electric potential contains two parts: one is the contribution of outfield and the second can be considered as the contribution of the electrical dipole moment of medium sphere. The overall electrical dipole moment of the spherical particle with interfacial shell is calculated through the electric potential generated by the electrical dipole moment in the space [3]:

$$\vec{p} = \frac{\gamma\varepsilon_1 - \varepsilon_m}{\gamma\varepsilon_1 + 2\varepsilon_m} 4\pi\varepsilon_m R_2^3 \vec{E}_0 \tag{4}$$

where

$$\gamma = \frac{\beta(1+2\beta)+2\alpha\beta(1-\beta)}{(1+2\beta)-\alpha(1-\beta)}$$

and $\alpha = R_1^3/R_2^3$ are called equivalent coefficient and structure parameter, respectively. $\beta = \varepsilon_2/\varepsilon_1$.

Solid spherical particles with permittivity ε_1 and radius R_1 embedding in the same homogeneous matrix can be made up of another composite. Illuminated perpendicularly by electromagnetic field $\vec{E}_0$, the overall electrical dipole moment of the solid particle is calculated with the following formula:

$$\vec{p} = \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} 4\pi\varepsilon_m R_1^3 \vec{E}_0 \tag{5}$$

The comparison of Eq. (4) and Eq. (5) shows that the difference in the two equations is just replacing $\gamma\varepsilon_1$ and R_2 in Eq. (4) to ε_1 and R_1 in Eq. (5). The equivalent permittivity of the spherical particle with interfacial shell is

$$\varepsilon_c = \frac{\beta(1+2\beta)+2\alpha\beta(1-\beta)}{(1+2\beta)-\alpha(1-\beta)}\varepsilon_1 = \gamma\varepsilon_1 \tag{6}$$

Therefore a spherical particle with interface equates another spherical particle without interface, and this leads to a result where the system can be replaced by solid sphere with equivalent permittivity $\gamma\varepsilon_1$ and equivalent radius R_2 mixed with the same matrix. Consequently, the system is simplified from trinary components to binary components.

2.2. The equivalency to core–shell ellipsoidal particles

The equivalent thought mentioned above was popularized to apply it to the composite system filled with coated ellipsoidal particles. It is supposed that the thickness of the shell is fixed and that ε_1 and ε_2 are the permittivity of core and shell of the complex ellipsoidal particle, respectively. Similarly, the core–shell ellipsoidal particle can also be replaced by a solid ellipsoidal particle mixed with the same matrix. The equivalent solid particle has a semi-radii equal to the original coating shell, and the equivalent permittivity is

$$\varepsilon_{c,kk} = \frac{\beta^2(1-L_{c,k})(1-\alpha)+\beta[L_{c,k}+(1-L_{c,k})\alpha]}{\beta[(1-L_{c,k})+L_{c,k}\alpha]+L_{c,k}(1-\alpha)}\varepsilon_1 = \gamma_k\varepsilon_1 \tag{7}$$

where

$$\gamma_k = \beta\frac{\beta(1-L_k)(1-\alpha)+[L_k+(1-L_k)\alpha]}{\beta[(1-L_k)+L_k\alpha]+L_k(1-\alpha)}$$

and $\alpha = (abc)/[(a+t)(b+t)(c+t)]$ represent equivalent coefficient and structure parameter of ellipsoidal particle; $\beta=\varepsilon_2/\varepsilon_1$; a, b, and c are noted as the semi-radii, and t is the thickness of interfacial shell. $L_{c,k}$ is the depolarization factor of the particle along the k-axis (k=x, y, z). The equivalent permittivity of the equivalent particle is anisotropic owing to different equivalent coefficient induced by polarization.

2.3. The effective permittivity of composites with core–shell particles

The effective medium theory and the Maxwell–Garnett theory are usually regarded as a convenient method to deal with the linear response of such a homogeneous composite system according to its microstructure [5–8]. Considering the probability of the orientation of the particles in the composite random, the effective permittivity of the composite with single shape distribution is derived according to the average polarization theory [8–10]:

$$\sum_{k=x,y,z}\left[V\frac{\varepsilon_{1,kk}-\varepsilon_{eff}}{\varepsilon_{eff}+L_{1,k}(\varepsilon_{1,kk}-\varepsilon_{eff})}+(1-V)\frac{\varepsilon_{m,kk}-\varepsilon_{eff}}{\varepsilon_{eff}+L_{m,k}(\varepsilon_{m,kk}-\varepsilon_{eff})}\right]=0 \tag{8}$$

where V and 1–V are the volume fractions of particles and matrix, respectively; ε_{eff} is the effective permittivity of composite; $\varepsilon_{1,kk}$ and $\varepsilon_{m,kk}$ are the permittivity of filler particle and the matrix particle along the k-axis (k=x, y, z), respectively; and $L_{1,k}$ and $L_{m\ k}$ are the depolarization factors of the filler particle and the matrix particle along the k-axis, respectively.

For simplicity, it is assumed that all the matrix particles are balls and all the filler particles are the same rotational elliptical particles with semi-radii a, b, and c (a=b). As $L_{1,x}$=$L_{1,y}$=(1–$L_{1,y}$)/2, Eq. (8) can be simplified to the following equation:

$$9(1-V)\frac{\varepsilon_m-\varepsilon_{eff}}{\varepsilon_m+2\varepsilon_{eff}}+V\left[\frac{\varepsilon_{1,zz}-\varepsilon_{eff}}{\varepsilon_{eff}+L_{1,z}(\varepsilon_{1,zz}-\varepsilon_{eff})}+\frac{4(\varepsilon_{1,xx}-\varepsilon_{eff})}{2\varepsilon_{eff}+(1-L_{1,z})(\varepsilon_{1,xx}-\varepsilon_{eff})}\right]=0 \tag{9}$$

The effective permittivity of composite is given by Eq. (9) when only dipole interactions are present. For regular arrays this case occurs in the limit of low volume loading. However, higher multipole interactions become significant when particles approach contact, so Eq. (9) is inapplicable in regular arrays at high volume filling. In random or disordered distributions close encounters can occur at any volume filling, so higher multipole corrections are necessarily considered in disordered medium even at low volume filling. Furthermore, the higher multipole interactions intensify rapidly on enhancing the volume fraction of filler particles. In order to take the higher multipole interactions into account, we give a set of permittivity (ε_1^b, ε_m^b) to replace the real permittivity (ε_1, ε_m). The set of permittivity (ε_1^b, ε_m^b) has something to do with permittivity (ε_1, ε_m) and the shape of the particles. Based on the Maxwell–Garnett theory and the relation between two distinct topological structures (symmetry structure and dissymmetry structure) [10], ε_1^b and ε_m^b can be expressed as

$$\varepsilon_1^b = \frac{2V}{3-V}\varepsilon_1, \quad \varepsilon_m^b = \frac{2(1-V)}{2+V}\varepsilon_m \tag{10}$$

Substituting Eq. (10) into Eq. (9), we obtain the equation for the effective permittivity of two-phase randomly mixed composite:

$$9(1-V)\frac{\varepsilon_m^b-\varepsilon_{eff}}{\varepsilon_m^b+2\varepsilon_{eff}}+V\left[\frac{\varepsilon_{1,zz}^b-\varepsilon_{eff}}{\varepsilon_{eff}+L_{1,z}(\varepsilon_{1,zz}^b-\varepsilon_{eff})}+\frac{4(\varepsilon_{1,xx}^b-\varepsilon_{eff})}{2\varepsilon_{eff}+(1-L_{1,z})(\varepsilon_{1,xx}^b-\varepsilon_{eff})}\right]=0 \tag{11}$$

The following step investigates the composite containing core–shell ellipsoidal particles randomly distributed in a homogeneous matrix. According to the equivalent method, only by substituting Eq. (7) into Eq. (9), we can get the equation for effective