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A fundamental study of the extent of meaningful application of Maxwell's and Wiener's equations to the permeability of binary composite materials. Part I: A numerical computation approach

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H I G H L I G H T S

- Numerical calculations of gas permeation are performed on binary composite materials.
- Wide range of composition and particle aspect ratio is explored in a s.c. lattice.
- Maxwell's equation was found to be accurate even at high loadings of inclusions.
- A simple method accounts for inclusions aspect ratio on effective permeability.

A R T I C L E I N F O

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In studies of the permeability of composite materials, consisting of solid isometric particles A dispersed in a polymeric matrix B, Maxwell's classical equation, rigorously valid only for very low fractional volumes (ν_A) of spherical particles, is often used for data analysis up to much higher ν_A values. Theoretical justification for this practice can be provided, only up to $\nu_A \approx 0.5$, by current analytical models based on cubic lattices of congruent spheres. Replacing spheres by cubes yields a model covering the full composition range $\nu_A = 0 - 1$, but lacking convenient general analytical tractability. Accordingly, to explore unrestrictedly the practical validity of the Maxwell equation, a simple cubic lattice-of-cubes model was combined with an appropriate numerical computation tool. The results establish satisfactory applicability of the Maxwell equation for isometric particles A, at all compositions and over a wide range of component permeability ratios ($\alpha = P_A/P_B = 0 - 100$).

The practical applicability of the corresponding classical equation of Wiener (which extends Maxwell's treatment to anisometric particles via the value of a single geometrical parameter A_W) was similarly explored, using appropriate model s.c. lattices of (a) unidimensionally anisometric particles (transverse square rods of varying length) or (b) bidimensionally anisometric particles (transverse square platelets of varying area). The computations covered the same ν_A and α ranges as above, as well as a range of aspect ratios in each of the cases (a) and (b). The results obtained enable determination of values of A_W , independent of ν_A and α , linked directly to the aspect ratio of the embedded particles, and demonstrate very good practical applicability of the Wiener equation (with the proper A_W value) under all conditions studied.

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1. Introduction

The description of properties of mass transport for low molecular weight species in heterogeneous polymeric systems is of

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great importance. The theoretical analysis of composite materials behavior is indeed fundamental for proper material design in a variety of different applications (Wijmans and Baker, 1995; Del Nobile et al., 1996; Grate and Abraham, 1991). Among others, immiscible polymer blends (Barlow and Paul, 1981) as well as block copolymers (Lazzari and López-Quintela, 2003) are often of interest for the opportunity they offer of combining properties of two or more homogeneous materials. On the other hand,

semicrystalline polymers constitute a substantial percentage of polymers employed in many different fields (Hedenqvist and Gedde, 1996). The aforementioned general approach is thus obviously required for many common polymers containing impermeable crystalline domains, such as polyethylene (PE) or polyethylene terephthalate (PET), as well as for the analysis of enlarged regular structures, such as poly(4-methyl-1-pentene) or syndiotactic polystyrene (Puleo et al., 1989; Larobina et al., 2004).

In recent years, the development of nanocomposite materials, prepared by incorporating impermeable platelets in polymeric phases, was largely undertaken for barrier applications (Choudalakis and Gotsis (2009)). This technology is also suitable for the design of membranes for gas separation, with particles highly selective for one or more gases, such as zeolites (Mahajan and Koros, 2002) or metallic organic frameworks (Adams et al., 2010), dispersed in the polymer phase (Aroon et al., 2010).

All these examples refer to composite materials constituted by at least two distinct and well defined regions or domains i (of different length scale), characterized by different values of gas permeability P_i . The resulting permeability of the complete heterogeneous medium is then related to the P_i values ($i=A, B, \dots$), as well as to the volume fractions v_i of the component phases and the system morphology, notably the shape and geometrical arrangement of the respective domains i .

The aim of this work is to develop and apply a valuable computation tool for the description of key features of the mass transport properties of binary composite media, consisting of particles A dispersed in a polymer matrix B, as a function of system composition and morphology. Numerical calculations were thus performed to evaluate the permeability of suitable model systems over a range of composition and of component characteristics much wider than that accessible to previous analytical treatments. The results were then compared with the predictions of two major existing model equations, in order to investigate their physical significance and range of validity, and thus confirm and/or extend the conclusions drawn in a previous study conducted along these lines (Petropoulos, 1985).

1.1. Review of some significant modeling approaches

The behavior of overall permeability P of a heterogeneous medium involving a dispersed phase A in a continuous phase B has been investigated by many authors. The main modeling parameters used are (i) the permeability coefficients of the component phases, P_A and P_B , (assumed to be constant for a given permeating species, i.e. independent of the concentration of permeant), (ii) the composition of the system, expressed as volume fraction v_A of dispersed phase A, and (iii) the shape of the dispersed particles, as well as their arrangement in the composite. Different expressions of the type indicated in Eq. (1) have been developed for different system morphologies:

$$\frac{P}{P_B} = f(\alpha, v_A) \quad (1)$$

where α indicates the permeability ratio between dispersed and continuous phase in the composite system, i.e.

$$\alpha = \frac{P_A}{P_B} \quad (2)$$

The study of composite structures and of the methods for averaging gas transport properties starts from the simplest configurations, in which the component phases are laminated in alternating domains (ABAB...) parallel or normal to the direction of permeation. The resulting overall permeability P is given by Eqs. (3) or (4),

respectively:

$$\frac{P}{P_B} = 1 + v_A(\alpha - 1) \quad (3)$$

$$\frac{P}{P_B} = \left[1 + v_A \left(\frac{1}{\alpha} - 1 \right) \right]^{-1} \quad (4)$$

These equations are readily derived. Their relevance here is that they represent, respectively, the maximum and minimum value of P/P_B obtainable for any given pair (α, v_A) , when different morphologies are considered for A and B phases.

For the composite materials under consideration here, pioneer work has been carried out by Maxwell. He derived a rigorous expression for a highly dilute dispersion of congruent spheres (Maxwell, 1873; Barrer, 1968), wherein interparticle distances are large enough to ensure that the permeant flow pattern around one sphere is undisturbed by the presence of the others; which may be written as follows:

$$\frac{P}{P_B} = 1 + \frac{3v_A}{(\alpha + 2)/(\alpha - 1) - v_A} \quad (5)$$

The same treatment may also be applied to the 2-D problem resulting from the dispersion of parallel congruent long cylinders oriented transversely to the direction of permeation; which is included, as a special case, in the general Wiener equation (Wiener, 1912; Nielsen, 1974):

$$\frac{P}{P_B} = 1 + \frac{(1 + A_W)v_A}{(\alpha + A_W)/(\alpha - 1) - v_A} \quad (6)$$

Parameter A_W is a function of the arrangement and geometry of the dispersed phase with respect to the continuous one. In particular, $A_W \rightarrow \infty$ or $A_W = 0$ lead to Eqs. (3) or (4) respectively, whereas $A_W = 2$ or $A_W = 1$ yield the Maxwell equation for spheres (3-D) or long transverse cylinders (2-D), respectively.

The physical meaning of the above Maxwell 3-D and 2-D models is most commonly considered (in accord with their original derivation) to be limited to the range of very low concentrations of dispersed phase. However, in practice, the said models may be usefully applied over a substantially wider range of v_A (and used as a conservative estimate of the expected change in permeability caused by the presence of the particles for given α and v_A , as pointed out in Petropoulos, 1985). In addressing the case of non-dilute dispersion of inclusions, the question of their arrangement arises. To enable analytical calculations, a regular arrangement of congruent particles has most commonly been adopted. For present purposes, a simple orthogonal lattice will be considered in all cases, with a unit cell extending along each space coordinate, in strict geometrical similarity with the shape of the single particle. To this category belongs the case of a non-dilute dispersion of spherical particles arranged in a simple cubic (s.c.) lattice, as illustrated in Fig. 1, for which an extended Maxwell expression for permeability was obtained (in the form of an infinite series) by Lord Rayleigh (1892), which was subsequently reworked by Meredith and Tobias (1960), and presented as a truncated series:

$$\frac{P}{P_B} = 1 + 3v_A \left(\frac{\alpha + 2}{\alpha - 1} - v_A - \frac{k_1 v_A^{10/3}}{(\alpha + (4/3))/(\alpha - 1) - k_2 v_A^{7/3}} - \frac{k_3(\alpha - 1)v_A^{14/3}}{\alpha + (6/5)} \right)^{-1} \quad (7)$$

where $k_1 = 1.315$, $k_2 = 0.409$ and $k_3 = 0.016$.

It is worthwhile to note that the applicability of results similar to that represented by Eq. (7) is restricted to v_A values sensibly below that ($v_{A,max}$) imposed by the closest possible packing of the particles in each particular arrangement. The cases of congruent spherical, or transverse long cylindrical, particles arranged in

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