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EFFECTIVE MODULI OF MULTIPHASE MATRIX COMPOSITES

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An extensive literature [1-3] addresses the question of calculating the effective characteristics of granulated matrix composites. However, these studies are generally concerned with two-phase composites, i.e., composites consisting of a matrix with inclusions having the same physical and geometric characteristics. The polydisperse model proposed by Hashin [4] has several important deficiencies which make it unsuitable for the design of actual composites: first of all, it is invalid for multiphase mixtures whose fractions differ in density; second, it does not account for the geometry of the filler and the associated arrangement of the filler material in the matrix.

In the present study, we construct a theory to calculate the effective moduli of particulate matrix composites which is free of these problems. Our theory is in turn based on the theory of composite media proposed by Hill [5] and a generalized singular approximation of Shermergor's theory of random functions [1]. As an example of the use of the results obtained here, we examine the determination of the elastic moduli of polymer composites consisting of a polymer matrix and whole spherical inclusions introduced into the matrix.

We will study a medium consisting of a homogeneous, isotropic matrix and spherical or ellipsoidal particles introduced into the matrix. The introduced particles are randomly located and oriented in the matrix. It is assumed that the filler consists of n − 1 isotropic phases differing in density and elastic characteristics and − in the case of spheres − in external diameter. Given the volume content of inclusions in the composite v_s, it is assumed that we know the histogram describing the distribution of the phases with respect to their volume content in the filler $v_s^{(i)}$. The latter quantity is determined by the vector function

$$\mathbf{p} = \mathbf{p}(p_1, p_2, \ldots, p_{n-1}); \quad \sum_{i=1}^{n-1} p_i = 1 \tag{1}$$

so that $v_s^{(i)} = p_i v_s$.

If the components of the filler differ in density, then the below vector-function describing the distribution of the densities of the phases is assigned

$$\boldsymbol{\rho}_s = \boldsymbol{\rho}_s\left(\rho_s^{(1)}, \rho_s^{(2)}, \ldots, \rho_s^{(n-1)}\right). \tag{2}$$

In the case when the filler is spherical, we should also know the histogram describing the distribution of the fractions with respect to external diameter

$$\mathbf{d} = \mathbf{d}(d_1, d_2, \ldots, d_{n-1}). \tag{3}$$

Equations (1)-(3) describe the structure and geometry of the filler of a particulate matrix composite.

In accordance with the generalized singular approximation [1], the tensor of the effective moduli of a multiphase nonmatrix mixture is found from one of the equivalent expressions

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$$(L_* + L_0)^{-1} = \sum_{i=1}^{n} v_s^{(i)} (L_s^{(i)} + L_0)^{-1}; \quad \sum_{i=1}^{n} v_s^{(i)} = 1 \tag{4}$$

or

$$L_* = \left(\sum_{i=1}^{n} v_s^{(i)} (L_s^{(i)} + L_0)^{-1} \right)^{-1} - L_0,$$

where L_0 is an isotropic tensor dependent on the elastic moduli of the reference body (Hill tensor [5]). For matrix composites, its properties are determined by the elastic characteristics of the matrix ($L_0 = L_0^{(m)}$ in the sense of equality of the volumetric and deviatoric components of the tensors).

We multiply the left and right sides of (4) by the isotropic tensor $(L_m + L_0^{(m)})^{-1}$ (L_m is the tensor of the elastic moduli of the matrix). We thus obtain

$$L_* = L_m + \left(\sum_{i=1}^{n-1} (L_s^{(i)} - L_m) v_s^{(i)} \alpha_s^{(i)} \right) \left(v_m I + \sum_{i=1}^{n-1} v_s^{(i)} \alpha_s^{(i)} \right)^{-1}, \tag{5}$$

where I is a unit tensor of rank four; $\alpha_s^{(i)} = (L_0^{(m)} + L_m) \times (L_s^{(i)} + L_0^{(m)})^{-1}$ is the tensor coefficient of strain concentration for a single inclusion of the i-th fraction in an infinite matrix; $L_s^{(i)}$ is the tensor of the elastic moduli of the i-th phase of the filler. Here and below, by the product of tensors we mean their convolution with regard to the internal indices.

If we now introduce the tensor coefficient for the stress concentration on a single inclusion in an infinite matrix $\beta_s^{(i)}$, connected with $\alpha_s^{(i)}$ by the relation [6] $\beta_s^{(i)} = L_s^{(i)} \alpha_s^{(i)} L_m^{-1}$, then we can reduce (5) to the form

$$L_* = L_m \left(v_m I + \sum_{i=1}^{n-1} v_s^{(i)} \beta_s^{(i)} \right) \left(v_m I + \sum_{i=1}^{n-1} v_s^{(i)} \alpha_s^{(i)} \right)^{-1}. \tag{6}$$

Equations (5) and (6) give the solution to the problem of determining the effective elastic moduli of a multiphase matrix composite without allowance for the geometry of the phases.

The below equalities follow from the theory of composites developed by Hill [5]

$$L_* = \sum_{i=1}^{n} v_s^{(i)} A_s^{(i)} L_s^{(i)}, \quad \sum_{i=1}^{n} A_s^{(i)} v_s^{(i)} = I \tag{7}$$

where $A_s^{(i)}$ is the strain-concentration tensor for an inclusion of the i-th fraction in the composite. Assuming that one of the phases has the properties of the matrix and allowing for the second relation in (7), we write

$$L_* = L_m + \sum_{i=1}^{n-1} v_s^{(i)} (L_s^{(i)} - L_m) A_s^{(i)}. \tag{8}$$

Comparing (5) and (8), we find that

$$A_s^{(i)} = \alpha_s^{(i)} \left(v_m I + \sum_{i=1}^{n-1} v_s^{(i)} \alpha_s^{(i)} \right)^{-1}. \tag{9}$$

It follows from (9) that the strain-concentration tensor for an inclusion of the i-th fraction can be represented in the form of the convolution of two tensors. One of these tensors characterizes the strain field of a single inclusion in an infinite matrix, while the other tensor characterizes the distortion of this field due to the presence of other inclusions.

If we take into account the relation obtained in [7],

$$A_s^{(i)} L_s^{(i)} = B_s^{(i)} L_*, \tag{10}$$

where $B_s^{(i)}$ is the stress concentration tensor for an inclusion in a composite. With allowance for (6) and (10), the value of this quantity will be

$$B_s^{(i)} = \beta_s^{(i)} \left(v_m I + \sum_{i=1}^{n-1} v_s^{(i)} \beta_s^{(i)} \right)^{-1},$$

i.e., the structures of the tensors $B_s^{(i)}$ and $A_s^{(i)}$ coincide.

We find expressions for the compressive bulk modulus K_* and shear modulus G_* of the composite from (6) by separating the tensors in this expression into volumetric and deviatoric components:

$$\frac{K_*}{K_m} = \frac{v_m + v_s \langle \beta_s^{(v)} \rangle}{v_m + v_s \langle \alpha_s^{(v)} \rangle}, \quad \frac{G_*}{G_m} = \frac{v_m + v_s \langle \beta_s^{(d)} \rangle}{v_m + v_s \langle \alpha_s^{(d)} \rangle}; \tag{11}$$

$$\langle \beta_s^{(v)} \rangle = \sum_{i=1}^{n-1} \frac{p_i \xi_i (1+\rho)}{\xi_i \rho + 1}; \quad \langle \alpha_s^{(v)} \rangle = \sum_{i=1}^{n-1} \frac{p_i (1+\rho)}{\xi_i \rho + 1}; \tag{12}$$

$$\langle \beta_s^{(d)} \rangle = \sum_{i=1}^{n-1} \frac{p_i \xi_{1i} (1+\rho_1)}{\xi_{1i} \rho_1 + 1}; \quad \langle \alpha_s^{(d)} \rangle = \sum_{i=1}^{n-1} \frac{p_i (1+\rho_1)}{\xi_{1i} \rho_1 + 1};$$

$$\rho = \frac{3K_m}{4G_m}; \quad \rho_1 = \frac{2\rho + 3}{3\rho + 2}; \quad \xi_i = \frac{K_s^{(i)}}{K_m}; \quad \xi_{1i} = \frac{G_s^{(i)}}{G_m};$$

where K_m and G_m are the compressive bulk modulus and shear modulus of the matrix; $K_s^{(i)}$, $G_s^{(i)}$ are the corresponding elastic moduli of the i-th fraction.

If the filler consists of hollow glass microspheres, then in (12) we should take [8]

$$K_s^{(i)} = \frac{K_c \psi^{(i)}}{1 + \rho_0 (1 - \psi^{(i)})}; \quad G_s^{(i)} = \frac{3(1 - \nu_s)}{2(1 + \nu_s)} K_s^{(i)}$$

where K_c is the bulk modulus of elasticity of the material of the microspheres; $\psi^{(i)} = \rho_s^{(i)}/\rho_c$; ρ_c is the density of the material of the microspheres; $\rho_0 = (1 + \nu_c)/(2(1 - 2\nu_c))$; ν_c is the Poisson's ratio of the glass; ν_s is the corrected transverse-strain coefficient of a hollow sphere. For thin spherical shells, its approximate value $\nu_s = (3 + 5\nu_c)/(11 + 5\nu_c)$. The exact value of ν_s for a hollow sphere of arbitrary thickness was also given in [8].

The results calculated for the effective moduli of a composite containing spherical inclusions of different diameters and densities can be refined further on the basis of a model which accounts for the geometry of the arrangement of the filler in the matrix.

The model presented below follows from the features of the process of making high-filler-content polymer composites by the impregnation method [9].

Let us assume that a filler consisting of spherical inclusions of different diameters and densities given by known vector-functions $\mathbf{d}$ and $\mathbf{p}$ is densely arranged in space, as shown in Fig. 1a. With the introduction of the matrix material in the interstices between the inclusions, the inclusions move apart from one another. This leaves the structure depicted in Fig. 1b.

We will surround each inclusion by a spherical layer of matrix in such a way that the newly formed two-layer composite cells will have the distribution of external diameters $\mathbf{d}^{(*)} = \mathbf{d}^{(*)}(d_1^{(*)}, d_2^{(*)}, \ldots, d_{n-1}^{*})$. This distribution is similar to $\mathbf{d}$, so that $d_i/d_i^{(*)} = \lambda$, where λ is the similarity parameter. This parameter is yet to be determined.

By virtue of having assumed the existence of similitude between $\mathbf{d}$ and $\mathbf{d}^{(*)}$, we find that the coefficient describing the packing of the composite spherical cells D will be equal to the coefficient describing the packing of the filler in the consolidated state. Its value, dependent on $\mathbf{d}$ and $\mathbf{p}$, can be found from experimental studies [10, 11] or can be approximately calculated for multiphase mixtures [12].

We now need to construct a vector function describing the distribution of the composite cells with regard to their volume content in the mixture

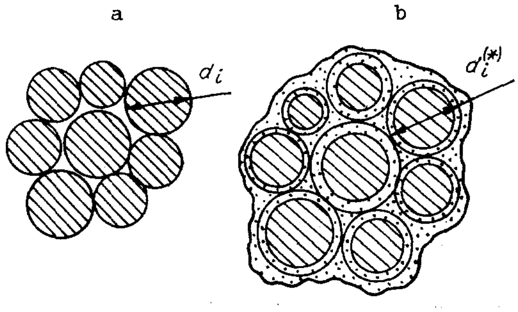

Fig. 1

$$\mathbf{v}_c = \mathbf{v}_c\left(v_c^{(1)}, v_c^{(2)}, \ldots, v_c^{(n-1)}\right), \quad \sum_{i=1}^{n-1} v_c^{(i)} = D. \tag{13}$$

The components of the vectors $\mathbf{v}_c$ and $\mathbf{p}$ are connected by the relation

$$v_c^{(i)} = p_i v_s/\lambda^3. \tag{14}$$

Insertion of (14) into (13) leads us to the value of the similarity parameter

$$\lambda = \sqrt[3]{v_s/D}. \tag{15}$$

It should be pointed out that the expression for λ, valid for regular packings of spheres of one size, retains the same form in the present model for a random packing of spherical particles with arbitrary diameters. It remains to be proven that the densities of the composite and the model are the same for the resulting value of λ.

The density of a multiphase matrix composite

$$\rho_* = \sum_{i=1}^{n-1} \rho_s^{(i)} v_s^{(i)} + \rho_m v_m, \tag{16}$$

where ρ_m is the density of the matrix. The density of the model

$$\rho_{\text{mod}} = \sum_{i=1}^{n-1} \rho_0^{(i)} v_c^{(i)} + \rho_m (1 - D) \tag{17}$$

[$\rho_0^{(i)} = \rho_s^{(i)}\lambda^3 + \rho_m(1 - \lambda^3)$ is the apparent density of the composite cell]. Inserting $\rho_0^{(i)}$ into (17) and performing some simple transformations, we arrive at expression (16) for the density of the composite.

The effective moduli of the matrix mixture representing the second model are calculated in the following sequence. First we find the corrected elastic characteristics of the composite spherical cells. This can be done using the concentrically spherical model in [4].

As a result, the original n-phase composite is replaced by another n-phase composite with a volume content of composite cells D and a volume content of matrix 1 − D. It is convenient to make use of the self-consistent method [13] to calculate the initial moduli of such a composite. The validity of taking this approach for a two-phase matrix mixture was proven in [14].

With allowance for (5) and the results in [13], we find the final expressions for the effective moduli of an n-phase matrix mixture by combining the self-consistent method with the concentrically spherical model in the form

$$\widetilde{K}_* = 1 + \frac{D \sum_{i=1}^{n-1} p_i \alpha_{*(v)}^{(i)} \left(\xi_i^{(*)} - 1\right)}{1 - D + D \sum_{i=1}^{n-1} p_i \alpha_{*(v)}^{(i)}};$$

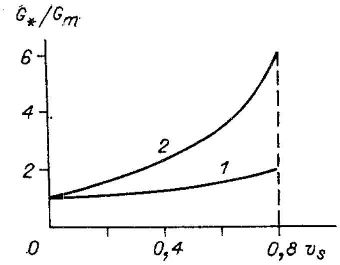

Fig. 2

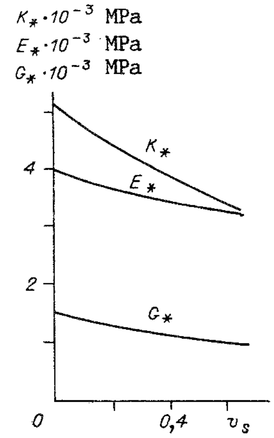

Fig. 3

$$\widetilde{G}_* = 1 + \frac{D\sum\limits_{i=1}^{n-1} p_i\alpha_{*(d)}^{(i)}\left(\xi_{1i}^{(*)} - 1\right)}{1 - D + D\sum\limits_{i=1}^{n-1} p_i\alpha_{*(d)}^{(i)}}, \tag{18}$$

where $\xi_i^{(*)} = \overline{K}_s^{(i)}/K_m$; $\xi_{1i}^{(*)} = \overline{G}_s^{(i)}/G_m$; $\alpha_{*(v)}^{(i)} = (\widetilde{K}_* + \varphi)/(\widetilde{K}_* + \xi_i^{(*)}\varphi)$; $\alpha_{*(d)}^{(i)} = \dfrac{\widetilde{G}_* + \varphi_1}{\widetilde{G}_* + \xi_{1i}^{(*)}\varphi_1}$; $\widetilde{K}_* = \dfrac{K_*}{K_m}$; $\widetilde{G}_* = \dfrac{G_*}{G_m}$;

$\varphi = \dfrac{3K_*}{4G_*}$; $\varphi_1 = \dfrac{2\varphi+3}{3\varphi+2}$; $\overline{K}_s^{(i)}$, $\overline{G}_s^{(i)}$ are the elastic bulk modulus and shear modulus of a composite spherical cell of the i-th fraction of the filler;

$$\frac{\overline{K}_s^{(i)}}{K_m} = 1 + \frac{\lambda^3(\xi_i - 1)(1+\rho)}{(1-\lambda^3)(\xi_i - 1)\rho + 1 + \rho};$$

$$\frac{\overline{G}_s^{(i)}}{G_m} = 1 + \frac{\lambda^3(\xi_{1i} - 1)(1+\rho_1)}{(1-\lambda^3)(\xi_{1i} - 1)\rho_1 + 1 + \rho_1}.$$

The sought values K_* and G_* are readily determined from a system of nonlinear algebraic equations by the method of successive approximation.

In conclusion, we will examine two examples of the use of the solutions obtained above.

1. Let us find the shear modulus of a mixture of rigid spherical inclusions in an incompressible matrix containing pores. One feature of this system is the indeterminateness of both the upper and lower bounds of the Hill and Hashin–Shtrikman forks. The composition of the filler: relative volume of inclusions $p_1 = 0.7$; relative volume of pores $p_2 = 0.3$. The ratio of the diameter of the inclusions to the diameter of the pores is equal to 7. In accordance with [11], the packing coefficient D = 0.8 for such a filler.

In the case where no allowance is made for the geometry of the packing in accordance with (11)

$$\frac{G_*}{G_m} = \frac{v_m + (5/2)\,p_1 v_s}{v_m + (5/3)\,p_2 v_s}. \tag{19}$$

The results of the calculation are shown in Fig. 2. Curve 1 was plotted from Eq. (19), while curve was plotted from Eqs. (18). It can be seen that allowing for the arrangement of the inclusions in the matrix is mandatory for high-filler-content mixtures characterized by large fluctuations in the elastic moduli of the components.

2. Let us calculate the effective moduli of a polymer composite having the following initial data. Matrix) epoxy binder; $K_m = 5.12\cdot 10^3$ MPa, $\nu_m = 0.37$. Filler) hollow glass microspheres having a composition characterized by the following distributions: p = 0.015;

0.060; 0.176; 0.178; 0.251; 0.276; 0.046, ρ_s = 0.44; 0.35; 0.24; 0.19; 0.18; 0.18; 0.16 (g/cm³), **d** = 15, 25, 33, 40, 48, 58, 68 (μm), $K_c = 4.2 \cdot 10^3$ MPa, $\nu_c = 0.21$, D = 0.72, $\rho_m = 1.2$ g/cm³, $\rho_c = 2.4$ g/cm³.

Figure 3 shows the compressive bulk moduli K_*, shear moduli G_*, and longitudinal elastic moduli E_* of the composite.

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