

The Elastic Moduli of Particulate-Filled Polymers

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Synopsis

The static and dynamic elastic moduli of particulate composites, consisting of two phases, one of which has isotropic-elastic and the other linear viscoelastic properties, were studied. For this purpose a model defining the approximate equations for determining the elastic modulus of a composite from the properties of the constituent materials was used. Classical theory of elasticity was applied to this simplified model of a composite-unit cell. The following assumptions are made: (i) filler particles are spherical; (ii) fillers are completely dispersed; and (iii) the volume fraction of fillers is sufficiently small, so that any interaction among fillers may be neglected. A class of iron-filled epoxy composites was subjected to tests in order to compare the theoretical values with the experimental results. The elastic modulus calculated by the expression derived in this study seems to corroborate with the experimental results fairly well. Finally, by applying the correspondence principle to this expression, theoretical relationships for the dynamic storage and loss moduli were also derived.

INTRODUCTION

Metal particles added in polymer matrices produce composites of greater density, improved electrical conductivity, better thermal conductivity, and, consequently, improved behavior at high operating temperatures, etc., and, above all, highly improved mechanical properties. Metals and plastics can be combined in several ways to form composites, such as impregnated metal castings with plastics, thus reducing porosity of the metals, plastic layers on surface to prevent corrosion, or to introduce vibration damping, pressing and sintering of metal powders and powdered thermoplastics, chemical combinations in organometallic complexes and, finally, metal powders dispersed into thermoplastic solutions or into the liquid mixture of thermosetting resins and their curing agents.¹

Epoxy resins are the most suitable polymers for composite matrices, and extensive research has been carried out on their rheological behavior²⁻⁴ and their mechanical properties.^{5,6} Indentation studies of these latter materials were also carried out.⁷

On the other hand, metal oxides and metal powders have been applied in the past in combination with epoxy matrices to create composites. The mechanical and thermal properties of such resins filled with iron particles have been investigated, and the effect of particle size on the same properties of iron-filled epoxies has been extensively studied.^{8,9}

A rigorous description of a composite system consisting of a matrix, in which filler particles have been dispersed, is not an easy task. In fact, a great number of geometrical, topological, mechanical, etc., parameters are necessary, the majority of which varies statistically or is simply unknown.

Theoretical treatments usually attempt to exploit, as much as possible, readily available information, which, in most cases, consists of the mechanical properties of the matrix and the filler and the volume fraction of the latter, while suitable assumptions cover missing data. The best approximation appears to be the determination of upper and lower bounds for the effective moduli of the composite, based on variational principles of mechanics, developed by Hashin.¹⁰

Analytical solutions are valid up to some fairly low filler-volume fraction, as they have to ignore, for reasons of efficiency, any mechanical interaction between neighboring inclusions. Referring, in particular, to the moduli, a great number of empirical or semiempirical expressions exist, which either express a kind of *law of mixtures*, or are simply an attempt to match theoretical curves to experimental data. In most of them a perfect adhesion between matrix and filler was assumed as existing between phases of the composite.

One of the theories concerning inclusions in a viscous matrix has been developed by Einstein.¹¹ He has considered rigid-spherical nonsolvated particles in a Newtonian viscous fluid, and he expressed the viscosity in the form

$$E_c/E_m = 1 + av_f \quad (1)$$

where E_c and E_m are the elastic moduli of the composite and matrix, respectively, and v_f is the filler-volume fraction. The constant a is equal to 2.5.

According to the equation of Guth and Smallwood,^{12,13} which is an extension of the Einstein equation, it is valid that

$$E_c/E_m = 1 + 2.5v_f + 14.1v_f^2 \quad (2)$$

An equation based on a mathematical model valid for the glassy behavior of composites is due to Kerner,¹⁴ which, for rigid fillers, simplifies to the expression

$$\frac{E_c}{E_m} = 1 + \frac{v_f}{v_m} \left[\frac{15(1 - \nu_m)}{8 - 10\nu_m} \right] \quad (3)$$

where ν_m is the Poisson ratio of the matrix material.

A relation taking into account the effect of adhesion efficiency between the two phases has been suggested by Sato and Furukawa^{15,16} and is expressed by

$$\frac{E_c}{E_m} = \left[\left(1 + \frac{1}{2} \frac{Y^2}{1 - Y} \right) \left(1 - \frac{Y^3 k}{3} \frac{(1 + Y - Y^2)}{(1 - Y + Y^2)} \right) - \frac{Y^2 k}{3(1 - Y)} \frac{(1 + Y - Y^2)}{(1 - Y + Y^2)} \right] \quad (4)$$

where $Y = v_f^{1/3}$ and k is an adhesion factor, taking the value of zero for perfect adhesion and the value of 1 for zero adhesion.

On the other hand, the Mooney equation¹⁷ can take into consideration a number of effects of the filler agglomeration:

$$\frac{E_c}{E_m} = \exp\left(\frac{2.5v_f}{1 - Sv_f}\right) \quad (5)$$

by means of a *crowding factor* S , expressing the ratio of the apparent volume occupied by the filler over its own true volume. This factor takes values from 1 to 2, depending on the type of particle distribution into the matrix material. For closely packed spheres of a uniform size, this is $S = 1.35$. In the equation proposed by Eilers and van Dyck,¹⁸

$$\frac{E_c}{E_m} = \left(1 + \frac{kv_f}{1 - S'v_f}\right) \quad (6)$$

k and S' are constants usually equal to 1.25 and 1.20, respectively. The effect of filler concentration on the elastic modulus is also expressed by an empirical relation proposed by Bills et al.,¹⁹ which is written as

$$E_c/E_m = \exp\left[A v_f / (1 - B v_f)\right] \quad (7)$$

where A and B are experimental constants. They have found that constant A takes the value 2.5, while B is given by

$$B = -6.4 \times 10^{-3}T + 2.51 \quad (8)$$

in which T corresponds to the test temperature. Thus, eq. (7) may be written in the form:

$$E_c/E_m = 1 + \left[2.5v_f/(1 - Bv_f)\right] + (1/2!) \left[2.5v_f/(1 - Bv_f)\right]^2 + \dots \quad (9)$$

A semiempirical single-parameter equation describing the moduli of particulate systems has been formulated by Narkis²⁰ as follows:

$$E_c/E_m = 1/K(1 - v_f^{1/3}) \quad (10)$$

where K is an empirical parameter related to a stress concentration factor with usual values in the range of 1.4–1.7.

Analytical equations for the elastic modulus of a composite containing spherical fillers have also been derived by Takahashi et al.²¹ In the case of perfect adhesion they gave the relationship

$$\frac{E_c}{E_m} = 1 + (1 - v_m) \left[\frac{E_f(1 - 2v_m) - E_m(1 - 2v_f)}{E_f(1 + v_m) + 2E_m(1 - 2v_f)} \right]$$

$$+ \frac{10(1 + \nu_m) [E_f(1 + \nu_m) - E_m(1 + \nu_f)]}{2E_f(4 - 5\nu_m)(1 + \nu_m) + E_m(7 - 5\nu_m)(1 + \nu_f)} \Big] \nu_f \quad (11)$$

On the other hand, the effect of adhesion between phases on the elastic modulus has been studied in Ref. 22. In this paper the concept of the boundary interphase was used in order to predict the elastic modulus of a particulate composite. According to this theory, the elastic modulus is given by

$$E_c = kE_f\nu_f + E_m\nu_m + E_i\nu_i \quad (12)$$

where subscript i refers to mesophase properties and k is a parameter which describes the degree of bonding between filler and mesophase.

Various other equations have been developed for the plastic modulus of materials filled with spherical inclusions. Only a few of them but the most important have been presented here.

THEORETICAL CONSIDERATIONS

A theoretical analysis now will be based on the following assumptions:

- (i) The matrix and the fillers are elastic, isotropic, and homogeneous.
- (ii) Fillers are perfectly spherical in shape.
- (iii) Fillers are large in number, and their distribution is uniform, so that the composite may be regarded as a quasihomogeneous isotropic material.
- (iv) The volume fraction of fillers is sufficiently small that the interaction among fillers may be neglected.
- (v) The deformations applied to the composite are small enough to maintain linearity of stress-strain relations.

In order to find the relationships, which give the expression for the elastic modulus, it will be assumed that classical theory of elasticity is applied to the representative volume element, whose mechanical properties equal the average properties of the particulate and which can be represented by two concentric spheres as was used by Hashin and Rosen.²³

A hollow sphere is considered with an inner radius $r_f = a$ and an outer radius $r_m = b$. Let a pressure P_0 be applied on the inner surface and a pressure P_1 on the outer surface. This simulates the matrix. A solid sphere of radius $r_f = a$, to which a pressure P_0 is applied, simulates the inclusion (Fig. 1). Pressure P_0 is the interaction between matrix and filler and P_1 is the applied pressure on the matrix. Because of the spherical symmetry, it is advantageous to use spherical coordinates (r, θ, φ) . Of the three components of the displacement vector u_φ, u_θ, u_r , only u_r is different from zero.

The solution to this problem is furnished by a stress function expressed by²⁴

$$\phi = L/r + Mr^2$$

If we apply this function for the matrix and the filler separately, we obtain

$$\phi_f = A/r + Br^2 \text{ and } \phi_m = C/r + Dr^2$$

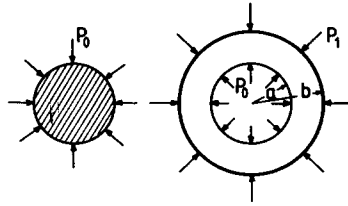


Fig. 1. Loading mode of the components of the representative volume element.

In order to avoid infinite stresses at $r = 0$, the constant A must take the value $A = 0$.

Thus,

$$\phi_f = Br^2$$

The displacements are given by

$$u_{r,f} = \frac{Br}{G_f}, \quad u_{r,m} = \left(-\frac{C}{r^2} + 2Dr \right) / 2G_m \quad (13)$$

and

$$u_{\theta,f} = u_{\theta,m} = u_{\varphi,f} = u_{\varphi,m} = 0 \quad (14)$$

The stresses are given by

$$\sigma_{r,f} = \frac{2(1 + \nu_f)}{1 - 2\nu_f} B \quad (15)$$

$$\sigma_{\theta,f} = \frac{2(1 + \nu_f)}{1 - 2\nu_f} B \quad (16)$$

$$\sigma_{\varphi,f} = \frac{2(1 + \nu_f)}{1 - 2\nu_f} B \quad (17)$$

$$\sigma_{r,m} = \frac{2C}{r^3} + \frac{2(1 + \nu_m)}{1 - 2\nu_m} D \quad (18)$$

$$\sigma_{\theta,m} = -\frac{C}{r^3} + \frac{2(1 + \nu_m)}{1 - 2\nu_m} D \quad (19)$$

$$\sigma_{\varphi,m} = -\frac{C}{r^3} + \frac{2(1 + \nu_m)}{1 - 2\nu_m} D \quad (20)$$

The boundary conditions are

$$\text{at } r = a, \quad \sigma_{r,f} = \sigma_{r,m} = -P_0 \quad (21)$$

$$\text{at } r = b, \quad \sigma_{r,m} = -P_1 \quad (22)$$

The solution of this system gives the values for the constants B , C , and D as follows:

$$B = \frac{-P_0(1 - 2\nu_f)}{2(1 + \nu_f)} \quad (23)$$

$$C = \frac{(P_1 - P_0)a^3b^3}{2(b^3 - a^3)} \quad (24)$$

$$D = \frac{(a^3P_0 - b^3P_1)(1 - 2\nu_m)}{2(b^3 - a^3)(1 + \nu_m)} \quad (25)$$

If we substitute these values in Eqs. (13) and (14), we find the following expressions for the displacements:

$$u_{r,f} = \frac{r}{2G_f} \left[-\frac{(1 - 2\nu_f)}{1 + \nu_f} P_0 \right] = \frac{-P_0(1 - 2\nu_f)r}{E_f} \quad (26)$$

$$u_{r,m} = \frac{a^3b^3(P_0 - P_1)(1 + \nu_m)}{2(b^3 - a^3)E_m} \frac{1}{r^2} + \frac{(1 - 2\nu_m)(a^3P_0 - b^3P_1)}{E_m(b^3 - a^3)} r \quad (27)$$

The boundary conditions must account for continuity of displacements at the interface, and they are expressed as follows:

$$\text{for } r = a \quad , \quad u_{r,m} = u_{r,f} \quad (28)$$

With $a^3/b^3 = \nu_f$ we obtain

$$\frac{-P_0(1 - 2\nu_f)}{E_f} = \frac{(1 - 2\nu_m)(P_0\nu_f - P_1)}{E_m(1 - \nu_f)} + \frac{(1 + \nu_m)(P_0 - P_1)}{2(1 - \nu_f)E_m} \quad (29)$$

Solving this equation with respect to P_0 , we obtain

$$P_0 = \frac{3(1 - \nu_m)E_f}{[2\nu_f(1 - 2\nu_m) + 1 + \nu_m]E_f + 2(1 - 2\nu_f)(1 - \nu_f)E_m} P_1 \quad (30)$$

A coefficient λ is defined as the ratio of P_0 and P_1 , that is

$$\lambda = P_0/P_1 \quad (31)$$

Then, λ takes the form

$$\lambda = \frac{3(1 - \nu_m)E_f}{[2\nu_f(1 - 2\nu_m) + 1 + \nu_m]E_f + 2(1 - 2\nu_f)(1 - \nu_f)E_m} \quad (32)$$

The elastic modulus E_c of the composite can be derived by an energy balance applied to the representative volume element. This strain energy, applied

to the composite, must be equal to the sum of the strain energies in the filler and matrix, that is,

$$\begin{aligned} \frac{1}{2} \int_{u_c} \frac{P^2}{K_c} dvc = \frac{1}{2} \int_{u_f} (\sigma_{r,f} \epsilon_{r,f} + \sigma_{\theta,f} \epsilon_{\theta,f} + \sigma_{\varphi,f} \epsilon_{\varphi,f}) dv_f \\ + \frac{1}{2} \int_{u_m} (\sigma_{r,m} \epsilon_{r,m} + \sigma_{\theta,m} \epsilon_{\theta,m} + \sigma_{\varphi,m} \epsilon_{\varphi,m}) dv_m \end{aligned} \quad (33)$$

where K_c is the bulk modulus of the composite. Then, the following relations hold for the spherical components of stresses and strains in the matrix material:

$$\begin{aligned} \sigma_{r,f} = \sigma_{\theta,f} = \sigma_{\varphi,f} = -P_0, \quad \epsilon_{r,f} = \frac{du_{r,f}}{dr} = \frac{-P_0(1 - 2\nu_f)}{E_f} \\ \epsilon_{\theta,f} = \epsilon_{\varphi,f} = \frac{u_{r,f}}{r} = \frac{-P_0(1 - 2\nu_f)}{E_f}, \quad \sigma_{r,m} = \frac{a^3 b^3 (P_1 - P_0)}{(b^3 - a^3)} \frac{1}{r^3} + \frac{a^3 P_0 - b^3 P_1}{b^3 - a^3} \\ \epsilon_{r,m} = \frac{du_{r,m}}{dr} = \frac{-a^3 b^3 (P_0 - P_1) (1 + \nu_m)}{(b^3 - a^3) E_m} \frac{1}{r^3} + \frac{(1 - 2\nu_m) (a^3 P_0 - b^3 P_1)}{E_m (b^3 - a^3)} \\ \sigma_{\theta,m} = \sigma_{\varphi,m} = -\frac{a^3 b^3 (P_1 - P_0)}{2(b^3 - a^3)} \frac{1}{r^3} + \frac{a^3 P_0 - b^3 P_1}{b^3 - a^3} \\ \epsilon_{\theta,m} = \epsilon_{\varphi,m} = \frac{u_{r,m}}{r} = \frac{a^3 b^3 (P_0 - P_1) (1 + \nu_m)}{2(b^3 - a^3) E_m} \frac{1}{r^3} + \frac{(1 - 2\nu_m) (a^3 P_0 - b^3 P_1)}{E_m (b^3 - a^3)} \end{aligned}$$

If these relationships are introduced into eq. (33) with the substitutions

$$a^3/b^3 = \nu_f, \quad P_0 = \lambda P_1, \quad \text{and} \quad K_c = E_c/3(1 - 2\nu_c) \quad (34)$$

and if all terms of the relationship are divided by P_1^2 , we obtain the final form for the expression of the elastic modulus of the composite:

$$\begin{aligned} \frac{2(1 - 2\nu_c)}{E_c} = \frac{2\lambda^2 \nu_f (1 - 2\nu_f)}{E_f} \\ + \frac{1}{E_m} \left\{ \frac{\nu_f (1 - \lambda)^2 (1 + \nu_m) + 2(\lambda \nu_f - 1)^2 (1 - 2\nu_m)}{1 - \nu_f} \right\} \end{aligned} \quad (35)$$

where the Poisson ratio μ_c of the composite may be calculated by the simple relation derived from the law of mixtures, which is expressed by

$$\frac{1}{\nu_c} = \frac{\nu_f}{\nu_f} + \frac{\nu_m}{\nu_m} \quad (36a)$$

This relation is a good approximation for the Poisson ratio of the composite given in Ref. 25 for the case of small differences between the Poisson ratios of the filler and the matrix.

APPLICATION TO DYNAMIC MODULI

When a viscoelastic material is subjected to a sinusoidally varying strain, the relation between complex stresses and complex strains developed in the specimen is formally the same as that between stresses and strains in an elastic material, but the moduli are now complex quantities. Thus, any algebraic expression for the moduli of an elastic composite, derived from the fundamental equations of elasticity, also applies to the complex moduli of a linear viscoelastic composite with the same geometry.

A considerable amount of work on the dynamic properties of particle-reinforced composites has been carried out;²⁶⁻²⁹ therefore, a detailed review need not be given. Especially, the main problem is the determination of the dynamic properties of the composites in terms of the respective properties of the constituent materials. Two main groups of methods have been developed: (i) direct methods for deriving the overall moduli of the composite from the micromechanical stress fields, developed around filler particles by means of energy considerations, for which a large number of simplifying assumptions are usually required,³⁰ and (ii) methods based on the variational principles of elasticity, providing upper and lower bounds for the moduli.³¹ While the latter method has been used for determining the complex moduli of viscoelastic composites,³² the former one is not yet used.

In order to find the storage and loss moduli of a particle-reinforced composite, we used the same model, described in previous sections, with a transformation of eqs. (32) and (35), by applying the above-mentioned correspondence principle of viscoelasticity with the assumption that the matrix is viscoelastic and the filler is elastic. In this way we tried to find expressions for the storage and loss moduli of the composite in terms of the properties of filler and matrix.

The behavior of a viscoelastic material can be described by a complex frequency-dependent modulus $E_m^*(\omega)$, $E_c^*(\omega)$, where $\omega = 2\pi f$ is the angular frequency. The following well-known expressions hold:

$$E_m^*(\omega) = E'_m(\omega) + iE''_m(\omega) \quad \text{and} \quad E_c^*(\omega) = E'_c(\omega) + iE''_c(\omega)$$

where $E'_m(\omega)$ and $E'_c(\omega)$ are the storage moduli and $E''_m(\omega)$ and $E''_c(\omega)$ are the loss moduli of the matrix and composite, respectively. The expression for the loss factor is

$$\tan \delta_E = E''/E'$$

where δ_E is the phase lag between stresses and strains in extension. For isotropic viscoelastic materials the complex Poisson ratios $\nu_m^*(\omega)$ and $\nu_c^*(\omega)$ can be expressed by

$$\nu_m^*(\omega) = \nu'_m(\omega) - i\nu''_m(\omega) \quad \text{and} \quad \nu_c^*(\omega) = \nu'_c(\omega) - i\nu''_c(\omega)$$

If we substitute the complex moduli in the elastic relationship between the shear moduli $G^*(\omega)$ the elastic moduli $E^*(\omega)$ and Poisson's ratios $\mu^*(\omega)$, we derive

If we substitute the complex moduli in the elastic relationship between the shear moduli $G^*(\omega)$ the elastic moduli $E^*(\omega)$ and Poisson's ratios $\mu^*(\omega)$, we derive

$$G'_m = \frac{E'_m(1+\nu'_m) - E''_m\nu''_m}{2[(1+\nu'_m)^2 + \nu''_m{}^2]}, \quad G''_m = \frac{E''_m(1+\nu'_m) + E'_m\nu''_m}{2[(1+\nu'_m)^2 + \nu''_m{}^2]} \quad (36b)$$

The solution of this system gives for $\nu'_m(\omega)$ and $\nu''_m(\omega)$ the expressions

$$\nu'_m = \frac{E'_m G'_m + E''_m G''_m - 2(G_m{}^2 + G_m{}^{\prime 2})}{2(G_m{}^2 + G_m{}^{\prime 2})} \quad (37)$$

$$\nu''_m = \frac{E'_m G''_m - G'_m E''_m}{2(G_m{}^2 + G_m{}^{\prime 2})} \quad (38)$$

Equation (32), by applying the correspondence principle, can be written as follows:

$$\lambda^* = [3(1 - \nu'_m + i\nu''_m)E_f] \{ [(2\nu_f + 1)E_f + \nu'_m(1 - 4\nu_f)E_f + 2(1 - 2\nu_f)(1 - \nu_f)E'_m] - i[\nu'_m(1 - 4\nu_f)E_f - 2(1 - 2\nu_f)(1 - \nu_f)E''_m] \}^{-1}$$

This relationship, by substitution of the expressions

$$A = (2\nu_f + 1)E_f + \nu'_m(1 - 4\nu_f)E_f + 2(1 - 2\nu_f)(1 - \nu_f)E'_m \quad (39a)$$

and

$$B = [\nu'_m(1 - 4\nu_f)E_f - 2(1 - 2\nu_f)(1 - \nu_f)E''_m] \quad (39b)$$

and after separation of the real from the imaginary parts, yields

$$\lambda_1 = \frac{3E_f[(1 - \nu'_m)A - \nu''_m B]}{A^2 + B^2} \quad (40)$$

and

$$\lambda_2 = \frac{3E_f[(1 - \nu'_m)B + \nu''_m A]}{A^2 + B^2} \quad (41)$$

where $\lambda^* = \lambda_1 + i\lambda_2$ and $\lambda^{*2} = \lambda_1^2 - \lambda_2^2 + 2i\lambda_1\lambda_2$. Equations (35) and (36), by applying the correspondence principle, can be written as

$$\frac{2(1 - 2\nu_c^*)}{E_c^*} = \left[\frac{2\nu_f(1 - 2\nu_f)}{E_f} + \frac{1}{E_m^*} \frac{\nu_f + \nu_m^* \nu_f + 2\nu_f^2 - 4\nu_m^* \nu_f^2}{(1 - \mu_f)} \right] \lambda^{*2} + \frac{6\mu_m^* \nu_f - 6\nu_f}{E_m^* (1 - \nu_f)} \lambda^* + \frac{(\nu_f + \mu_m^* \nu_f - 4\mu_m^* + 2)}{E_m^* (1 - \nu_f)} \quad (42)$$

with

$$\frac{1}{\nu_c^*} = \frac{\nu_f}{\nu_f} + \frac{\nu_m}{\nu_m^*} \rightarrow \frac{1}{(\nu_c' - i\nu_c'')} = \frac{\nu_f}{\nu_f} + \frac{\nu_m}{\nu_m' - i\nu_m''} \quad (43)$$

If we replace eq. (43) in the left-hand side of eq. (42), after some algebra we obtain

$$\frac{2(PE_c' + QE_c'')}{R(E_c'^2 + E_c''^2)} - i \frac{2(PE_c'' - QE_c')}{R(E_c'^2 + E_c''^2)} \quad (44)$$

with

$$P = (\nu_f \nu_m + \nu_m' \nu_f')^2 + \nu_m'' \nu_f^2 - 2\nu_f \nu_m' (\nu_f \nu_m + \nu_m' \nu_f) - 2\nu_f \nu_m'' \nu_f'$$

$$Q = 2\nu_f [\nu_m'' (\nu_f \nu_m + \nu_m' \nu_f) - \nu_m' \nu_m'' \nu_f']$$

$$R = (\nu_f \nu_m + \nu_m' \nu_f')^2 + \nu_m'' \nu_f^2$$

The first term of the right-hand side of eq. (42) can be written as

$$\frac{2\nu_f(1-2\nu_f)}{E_f} (\lambda_1^2 - \lambda_2^2) - 4i \frac{\nu_f(1-2\nu_f)}{E_f} \lambda_1 \lambda_2 \quad (45)$$

For the second term of eq. (42) with

$$C = \nu_f + 2\nu_f^2 + \nu_m' (\nu_f - 4\nu_f^2)$$

$$D = \nu_m'' (\nu_f - 4\nu_f^2)$$

$$L = C(\lambda_1^2 - \lambda_2^2) + 2D\lambda_1 - \lambda_2$$

and

$$M = 2C\lambda_1\lambda_2 - D(\lambda_1^2 - \lambda_2^2)$$

we obtain

$$\frac{LE_m' + ME_m''}{(1-\nu_f)(E_m'^2 + E_m''^2)} - i \frac{(LE_m'' - ME_m')}{(1-\nu_f)(E_m'^2 + E_m''^2)} \quad (46)$$

Moreover, the third term of Eq. (42) can be written as

$$\frac{6\nu_f(\nu_m' - i\nu_m'' - 1)}{(E_m' + iE_m'')(1-\nu_f)} (\lambda_1 + i\lambda_2)$$

which, after some algebra, gives

$$\frac{F\lambda_1 + G\lambda_2}{(E_m'^2 + E_m''^2)(1-\nu_f)} + i \frac{F\lambda_2 - G\lambda_1}{(E_m'^2 + E_m''^2)(1-\nu_f)} \quad (47)$$

where F and G are given by

$$\begin{aligned} F &= 6v_f(v'_m - 1)E'_m - 6v_f v''_m E'_m \\ G &= 6v_f(v'_m - 1)E''_m + 6v_f v''_m E''_m \end{aligned}$$

The fourth term can be written as

$$\frac{(HE'_m - KE''_m)}{(E'^2_m + E''^2_m)(1 - v_f)} - i \frac{(HE''_m + KE'_m)}{(E'^2_m + E''^2_m)(1 - v_f)} \quad (48)$$

with $H = (v_f + 2) + v'_m(v_f - 4)$ and $K = (v_f - 4)\mu''_m$.

If all these relationships are substituted into eq. (42), we obtain the final expression:

$$\begin{aligned} & \frac{2(PE'_c + QE''_c)}{R(E'^2_c + E''^2_c)} - i \frac{2(PE''_c - QE'_c)}{R(E'^2_c + E''^2_c)} = \frac{2v_f(1 - 2v_f)}{E_f} (\lambda_1^2 - \lambda_2^2) \\ & + \frac{(LE'_m + ME''_m) + (F\lambda_1 + G\lambda_2) + (HE'_m - KE''_m)}{(1 - v_f)(E'^2_m + E''^2_m)} - \\ & - i \left[\frac{4v_f(1 - 2v_f)}{E_f} \lambda_1 \lambda_2 + \frac{(LE''_m - ME'_m) + (G\lambda_1 - F\lambda_2) + (HE''_m + KE'_m)}{(1 - v_f)(E'^2_m + E''^2_m)} \right] \end{aligned} \quad (49)$$

The solution of this complex equation gives the storage and loss moduli of the composite material expressed by the following expressions:

$$E'_c = \frac{2(PT - QU)}{R(T^2 + U^2)} \quad (50)$$

$$E''_c = \frac{2(PU + QT)}{R(T^2 + U^2)} \quad (51)$$

with

$$\begin{aligned} T &= \frac{2v_f(1 - 2v_f)}{E_f} (\lambda_1^2 - \lambda_2^2) + \frac{(LE'_m + ME''_m) + (F\lambda_1 + G\lambda_2) + (HE'_m - KE''_m)}{(1 - v_f)(E'^2_m + E''^2_m)} \\ U &= \frac{4v_f(1 - 2v_f)}{E_f} \lambda_1 \lambda_2 + \frac{(LE''_m - ME'_m) + (G\lambda_1 - F\lambda_2) + (HE''_m + KE'_m)}{(1 - v_f)(E'^2_m + E''^2_m)} \end{aligned}$$

EXPERIMENTAL PROCEDURE

In order to verify the theoretical values given by eq. (35), experiments were carried out with metal-particle composite materials. The matrix material was in all cases a cold-setting system, based on a diglycidyl ether of bisphenol-A resin, cured with 8% triethylenetetramine. The epoxy matrix was filled with iron particles of average diameter 150 μm , in order to produce composite specimens. The composites were manufactured in the way presented in Ref. 8. The properties of the constituent materials are

given in Table I. Dogbone specimens with constant dimensions at the measuring area $0.006 \times 0.003 \text{ m}^2$ and length 0.045 m were used during the tests.

Tensile measurements were carried out with a conventional Instron-type tester at room temperature. The specimens were tested in three different rates of extension ($c = 0.1, 0.5,$ and $1.0 \times 10^{-3} \text{ m/min}$). Four distinct filler concentrations (5%, 10%, 15%, and 20%) were used in order to study the effect of filler-volume fraction on the elastic modulus of composites. Five specimens per each strain rate and per each filler-volume fraction were tested, and the given values correspond to their arithmetic-mean value.

RESULTS AND DISCUSSION

Figure 2 shows the values of the elastic modulus of the composite calculated by eq. (35) for different extension rates. We observe that the increase of this rate gives also increased values for theoretical and experimental results of the elastic modulus of the composite material. We can also observe that for lower filler volume fractions the experimental values are slightly below the theoretical values, while for higher volume fractions the experimental values begin to be above the theoretical ones. We can explain this phenomenon by the adhesion efficiency at the interface of the two phases. It is a decisive factor for the behavior of the composite. In most theoretical models describing the mechanical behavior of a composite material, this adhesion is considered as perfect, i.e., the interface can ensure continuity of stresses and displacements. However, such a condition is hardly fulfilled in real composites. In reality, around an inclusion, embedded in a matrix, a rather complex situation develops, consisting of areas of imperfect bonding, mechanical stresses, due to shrinkage, or even stress singularities, due to the geometry of the inclusion. These factors, which influence the adhesion efficiency, become greater when filler volume fraction is increased. So the theory which does not take it into account begins to give values less than in the reality.

Moreover, the interaction of the surface of the filler with the matrix material is usually something much more complicated than a simple mechanical effect. The presence of the filler restricts the segmental and molecular mobility of the polymeric matrix, as absorption interaction in polymer surface layers into filler particles occurs. Although it was assumed

TABLE I

	Iron	TETA-cured DGEBA resin
Elastic modulus (N/m^2)	21.0×10^{10}	0.35×10^{10a}
Bulk modulus (N/m^2)	16.7×10^{10}	0.421×10^{10a}
Poisson's ratio	0.29	0.36 ^a
Density (g/m^3)	7.80	1.19
Thermal expansion Coefficient ($^{\circ}\text{C}^{-1}$)		
α_1		65.26×10^{-6}
α_2	15.0×10^{-6}	168.48×10^{-6}

^a Properties determined during creep tests of 20°C and time $t = 15 \text{ s}$ by means of an Instron tester.

that the volume fraction of fillers is sufficiently small, so that the interaction among fillers may be neglected, in reality such an interaction always exists. Its effect becomes greater when filler volume fraction is increased.

From Figure 2 we can also observe that, as the filler volume fraction is increased, a more linear elastic response is obtained. This kind of behavior is due to the filler material which is strongly elastic, so that, as its volume fraction is increased, the viscoelastic response of the composite is decreased.

In Figure 3, the moduli E_c , normalized to the respective moduli E_m of the matrix material, were plotted against filler volume fraction for $c = 0.5 \times 10^{-3}$ m/min. Theoretical curves obtained by other theories are also plotted in the same diagram for comparison. From this figure we can observe that the experimental results fit well with those derived from eq. (35), as well as the values of the theoretical curve (C), given by Kerner. The theoretical curves labeled A, B, D, E do not fit with the experiments.

Thus, we can conclude that eq. (35) yields satisfactory results for the elastic modulus of particulate composite for low-filler volume fractions. For higher volume fractions its validity will be limited. For these cases a theory, which will take into consideration the adhesion efficiency and the interaction between inclusion and matrix, is necessary in order to obtain more valid values of the elastic modulus of a composite material.

The analysis presented here for the dynamic moduli may be regarded as a step in the theoretical prediction of the viscoelastic properties of a particle-filled composite material. The composite sphere assemblage model is a geometrical idealization of a real-particle-filled composite material. However,

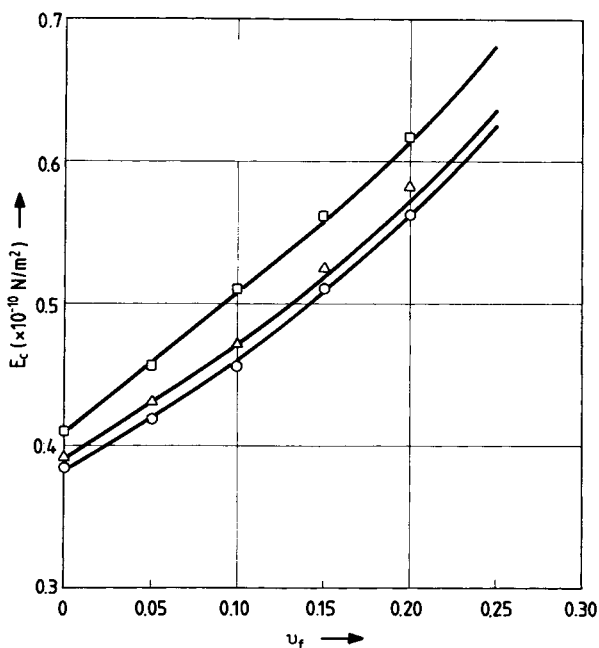


Fig. 2. Theoretical values of elastic modulus obtained from eq. (35) for various filler volume fractions and comparison with experimental values for different rates of extension. $c = (\square) 1.0 \times 10^{-3}$ m/min; $(\triangle) 0.5 \times 10^{-3}$ m/min; $(\circ) 0.1 \times 10^{-3}$ m/min.

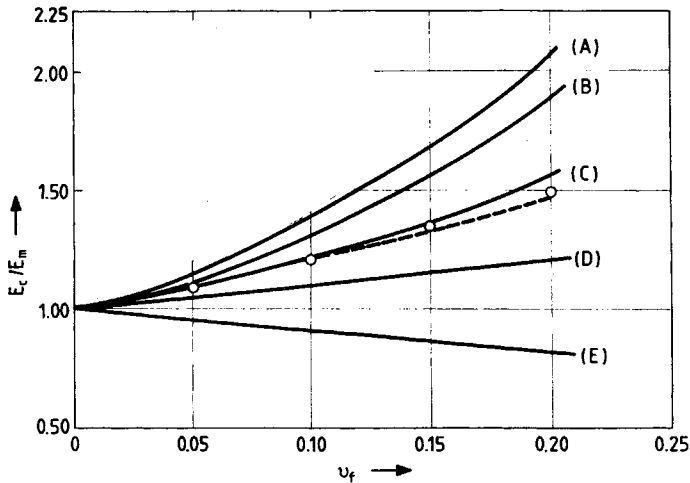


Fig. 3. Comparison of the relative elastic modulus given by eq. (35) with the values given by other theories for varying filler volume fractions. (A) Guth-Smallwood, eq. (2); (B) Money, eq. (5), $\beta = 1.4$; (C) Kerner, eq. (3); (D) Einstein, eq. (1), $a = 1$; (E) Sato-Furukawa, eq. (4); (- -) eq. (35); (O) experimental values for $c = 0.5 \times 10^{-3}$ m/min.

given that, in the elastic case, the results obtained on the basis of this model were close to the experimental results, it may be hoped that the viscoelastic results obtained by an analogous method will be of similar value.

References

1. J. Delmonte, *Metal-Filled Plastics*, Rheinhold, New York, 1961.
2. P. S. Theocaris, *Rheol. Acta*, **2**(2), 92 (1962).
3. P. S. Theocaris, *J. Appl. Polym. Sci.*, **8**, 399 (1964).
4. P. S. Theocaris, *Exp. Mech.*, **5**, 105 (1965).
5. T. Hirai and D. E. Kline, *J. Appl. Polym. Sci.*, **16**, 3145 (1972).
6. T. Hirai and D. E. Kline, *J. Appl. Polym. Sci.*, **17**, 31 (1973).
7. P. S. Theocaris, S. A. Paipetis, and G. C. Papanicolaou, *J. Appl. Polym. Sci.*, **22**, 2245 (1978).
8. G. C. Papanicolaou, S. A. Paipetis, and P. S. Theocaris, *J. Appl. Polym. Sci.*, **21**, 689 (1977).
9. P. S. Theocaris, G. C. Papanicolaou, and E. P. Sideridis, *J. Reinforced Plast. Comp.*, **1**, 92 (1982).
10. Z. Hashin, *Int. J. Solids Structures*, **6**, 539, 797 (1970).
11. A. Einstein, *Ann. Phys.*, **19**, 289 (1906); **34**, 591 (1911).
12. E. Guth, *J. Appl. Phys.*, **16**, 20 (1945).
13. H. M. Smallwood, *J. Appl. Phys.*, **15**, 758 (1944).
14. E. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
15. Y. Sato and J. Furukawa, *Rubber Chem. Tech.*, **35**, 857 (1962).
16. Y. Sato and J. Furukawa, *Rubber Chem. Tech.*, **36**, 1081 (1963).
17. M. Mooney, *J. Colloid Sci.*, **6**, 162 (1951).
18. H. Eilers and Van Dyck, *Kolloid Z.*, **97**, 313 (1941).
19. K. Bills, K. Sweeny, and F. Salcedo, *J. Appl. Polym. Sci.*, **12**, 259 (1960).
20. M. Narkis, *Polym. Eng. Sci.*, **15**, 316 (1975).
21. K. Takahashi, M. Ikeda, K. Harakawa, K. Tanaka, and T. Sakai, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 415 (1978).
22. G. D. Spathis, E. P. Sideridis, and P. S. Theocaris, *Int. J. Adhesion Adhesives*, **1**, 195 (1981).
23. G. C. Papanicolaou and P. S. Theocaris, *Colloid Polym. Sci.*, **257**, 239 (1979).

24. A. Saada, *Elasticity*, Pergamon Unified Engineering Series, Pergamon, New York, 1974.
25. R. M. Jones, *Mechanics of Composite Materials*, McGraw-Hill, New York, 1975.
26. P. S. Theocaris, *Coll. Polym. J.*, **235**(1), 1182 (1969).
27. P. S. Theocaris and S. A. Paipetis, *J. Strain Anal.*, **8**(4), 286 (1973).
28. S. A. Paipetis, G. C. Papanicolaou, and P. S. Theocaris, *Fiber Sci. Tech.*, **8**, 221 (1975).
29. S. A. Paipetis and P. Grootenhuys, *Fibre Sci. Tech.*, **11**, 377 (1979).
30. L. Holiday, Ed., *Composite Materials*, Elsevier, Amsterdam, London, New York, 1966.
31. Z. Hashin and S. Shrikman, *J. Mech. Phys. Solids*, **10**, 335 (1962).
32. Z. Hashin, *Int. J. Solids Structures*, **6**, 539 (1970).

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