DETERMINATION OF THE DYNAMIC MODULI OF PARTICULATE COMPOSITES BY MEANS OF THE BASIC THREE-COMPONENT MODELS IN CUBE-WITHIN-CUBE FORMATION

By

G. Bourkas, V. Kytopoulos, E. Sideridis, C. Younis

National Technical University of Athens
Faculty of Applied Mathematical and Physical Sciences
Department of Mechanics
Laboratory of Testing and Masterials
Zografou Campus
GR – 15773, Athens, Greece

Abstract

In this work, the dynamic elastic moduli of particulate composites are evaluated, by means of two models in cube-within-cube formation, each consisting of three components. For this purpose the correspondence principle is applied to the existing equations which provide the static elastic modulus of particulate composites, by means of these two models. Two general equations providing the storage and loss modulus respectively, of particulate composites which are valid for both models, are obtained. The theoretical results are compared with dynamic experimental results in iron / epoxy particulate composites as well as with existing formulae in the literature. Since the dynamic experiments and ultrasonic measurements have as a common parameter the frequency, an extrapolation of the storage modulus curves, predicted by dynamic experiments, is made as far as the respective values of ultrasonic measurements in iron / epoxy particulate composites.

Introduction

The addition of fillers to polymers can produce compositions with a variety of desirable properties. In general fillers increase the elastic modulus and many theories have been developed to explain this effect. The discrepancy between theoretical predictions and experimental results for the moduli of particulate reinforced polymers is a limitation to the understanding of composite materials.

There is a considerable volume of literature dealing with the dynamic behavior of heterogeneous systems, where the dispersed phase is a relatively rigid inclusion. A good approximation appears to be the determination of upper and lower bounds for the effective moduli of the composite, based on variational principles of mechanics [1]. In ref [1] a correspondence principle is developed, by means of which effective complex moduli of viscoelastic composites can be determined on the basis on analytical expressions for the effective elastic moduli of composites.

Studies of the effects of the presence of fillers on the dynamic behavior on glassy and semicrystalline thermoplastics were carried out by Nielsen [2] and Bohme [3], who investigated the effect of filler in polyethylene. Other studies, among them those by Hirai and Kline [4], Kardos et al [5], and Lewis and Nielsen [6], have addressed the problem of explaining the behavior of filled composites to the research of the deviations from the expected behavior. It may be concluded from these studies that the dynamic behavior of filled polymers is not only dependent upon the nature of the polymer and filler, but is often strongly influenced by the character of the polymer-filler interface. In order to investigate interface effects, different kinds of coupling in the polyethylene/ $CaCo_3$ systems were studied by Chako et al [7].

Experiments for the determination of the dynamic properties of metal filled epoxy composites have been reported [8]. Storage moduli and loss factors of a large number of composites were evaluated and the effects of filler volume fraction and particle size were examined, particularly for specimens exhibiting imperfect interfacial adhesion between matrix and filler. In refs [9,10] dynamic experiments in epoxy / iron particulate composites have been reported as well as analytical expressions for the dynamic moduli by using the correspondence principle in sphere-within- sphere formation. In ref [11] the longitudinal and transverse dynamic moduli are examined in epoxy/glass continuous fiber composites.

In this paper the dynamic moduli of particulate composites are evaluated using three-component models in cube-within-cube formation [12,13]. The correspondence principle is applied in the existing equation of the static elastic moduli E_c of particulate composites, as they are given by these two models. The theoretical results are compared with existing formulae in the literature, which are referred in Appendix, as well as with existing dynamic experimental results in epoxy/iron particulate composites. Since dynamic data and ultrasonic measurements have the frequency as a common parameter, the experimental dynamic curves of storage moduli $E_c^{'}$ are extrapolated up to the values of $E_c^{'}$ predicted by ultrasonic measurements in epoxy/iron particulate composites.

Theoretical Considerations

The theoretical analysis is based on the following assumptions:

1) The particles are perfectly cubic.
2) The volume fraction of the particles is sufficiently low, so that there is no interaction between the stress fields around neighboring particles.
3) The particles are uniformly distributed in the matrix, so that homogeneity can be assumed.
4) Both the matrix and the inclusions are prepared from perfectly homogeneous, elastic and isotropic materials of known mechanical properties,
5) There is perfect adhesion between matrix and filler.

From Fig. 1 for the filler content one has

$$u_f = a^3 / c^3 \tag{1}$$

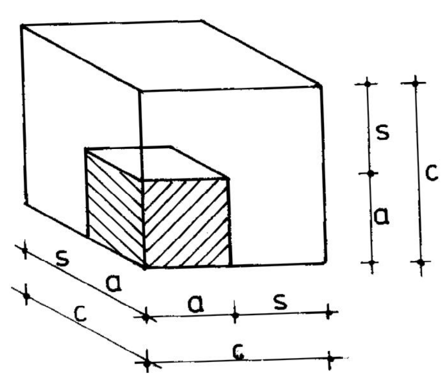

Fig. 1 A Schematic representation of cube-within-cube model.

The elastic moduli for models 1 and 2, Fig. 2 (a), (b), are given respectively by [12,13]

$$E_c = E_m \left[\frac{1+(m-1)u_f^{2/3}}{1+(m-1)(u_f^{2/3}-u_f)} \right] \tag{2}$$

and

$$E_c = E_m \left[1 + \frac{u_f}{\frac{m}{m-1} - u_f^{1/3}} \right] \tag{3}$$

where $m = E_f / E_m$ and the indexes m, f and c correspond to the matrix, the filler and the composite, respectively.

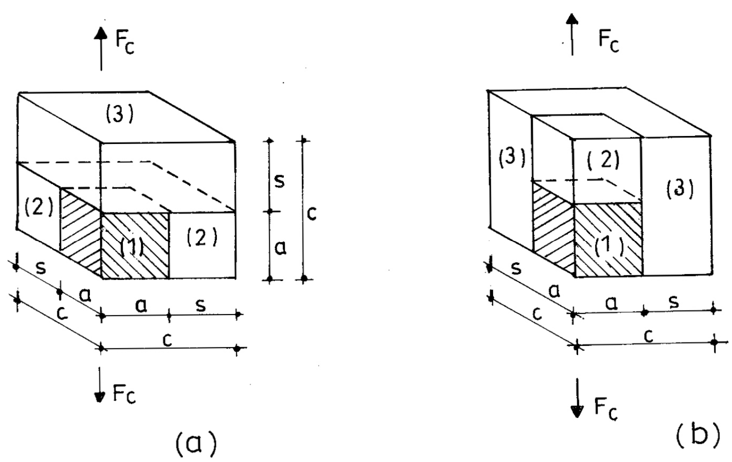

Fig. 2 The two cube-within-cube models each one consisting of three components, (a) Paul's model, model 1, (b) Ishay – Cohen's model, model 2

According to the correspondence principle, if one substitutes E_M^*, E_f^* and E_c^*, where

$$E_m^* = E_m^{'} + i\,E_m^{''} \tag{4}$$

$$E_f^* = E_f^{'} \tag{5}$$

$$E_c^* = E_c^{'} + i\,E_c^{''} \tag{6}$$

for E_m, $\mathrm{E_f}$ and E_c respectively in the above equations (2) and (3), they are still valid. In the above eqns (4)–(6) $E_c^{'}, E_f^{'}, E_m^{'}$ are the storage moduli, and $E_c^{"}$, $E_m^{"}$ are the loss moduli.

Substituting in eqns (2) and (3) it comes out that

$$E_c^{'} + i\,E_c^{"} = \frac{E_m^{'} E_f^2 R_j Q_j + E_f E_m^{'2} Q_j T_j + 2iE_m^{'} E_m^{"} E_f Q_j T_j + iE_m^{"} E_f^2 Q_j R_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j^2} +$$

$$+ \frac{-E_m^{"2} E_f Q_j T_j + E_m^{'2} E_f R_j S_j + E_m^{'3} T_j S_j + iE_m^{'2} E_m^{"} T_j S_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j^2} + \quad (7)$$

$$+ \frac{E_m^{"2} E_f R_j S_j + E_m^{'} E_m^{"} T_j S_j + iE_m^{"3} T_j S_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j^2}$$

The real part of (7) is

$$E_c^{'} = \frac{E_m^{'} E_f^2 R_j Q_j + E_f E_m^{'2} Q_j T_j - E_m^{"2} E_f Q_j T_j + E_m^{'2} E_f R_j S_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j} +$$

$$+ \frac{E_m^{'3} T_j S_j + E_m^{'} E_m^{"2} T_j S_j + E_m^{"2} E_f R_j S_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j} \quad (8)$$

and the imaginary part is

$$E_c^{"} = \frac{2E_m^{'} E_m^{"} E_f Q_j T_j + E_m^{"} E_f^2 Q_j R_j + E_m^{'2} E_m^{"} T_j S_j + E_m^{"3} T_j S_j}{(E_f Q_j + E_m^{'} S_j)^2 + E_m^{"2} S_j} \quad (9)$$

where

$$R_1 = u_f^{2/3}$$

$$T_1 = 1 - u_f^{1/3} \quad (10)$$

$$Q_1 = u_f^{2/3} - u_f$$

$$S_1 = 1 - u_f^{1/3} + u_f$$

and

$$R_2 = 1 - u_f^{1/3} + u_f$$

$$T_2 = u_f^{1/3} - u_f \qquad (11)$$

$$Q_2 = 1 - u_f^{1/3}$$

$$S_2 = u_f^{1/3}$$

Results and Discussion

By means of the eqns (8) and (9) two general expressions for the dynamic storage and loss moduli predicted by the above two cube-within-cube models are obtained. For these two models the general expression of the static elastic modulus has the form

$$E_c = E_m \frac{E_f R_j + E_m T_j}{E_f Q_j + E_m S_j}$$

and the relation among the filler volume fraction functions R_j, J_j, Q_j, S_j is given by

$$R_j - Q_j = S_j - T_j$$

From these two equations it is seen that the added reinforcing of the inclusion to the nominator is subtracted from the matrix in the denominator.

In Fig. 3 the static elastic modulus is plotted versus filler content in epoxy/iron particulate composites. It is observed that the experimental results are bounded by the theoretical values of E_c predicted by model 1, curve (d) and model 2, curve (b). Because the curves predicted by these two models do not coincide with the experimental results, one could expect a similar behavior between the dynamic moduli predicted by egns (8) and (9) and the dynamic experimental results. In Fig 3. the curves (a),(c),(e) and (f) show the theoretical results obtained by eqns (A1),(A3),(A2) and (A4) respectively. In this figure one can observe that the experimental results are bounded by the theoretical results predicted by the above equations. In Fig. 4 the storage modulus $E_c^{'}$ is plotted against the filler volume

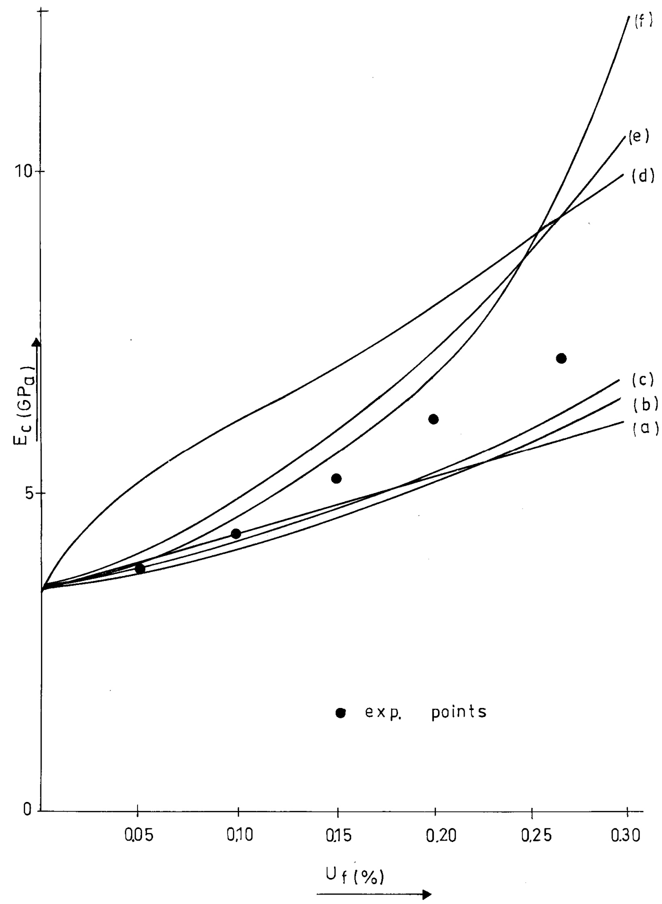

Fig. 3 The static elastic modulus E_c versus filler content in epoxy/iron particulate composites, (a) Einstein, (b) model 2, (c) Kerner, (d) model 1, (e) Guth and Smulwood, (f) Mooney

fraction, for frequency $f = 0{,}1\,Hz$, in epoxy/iron particulate composites. By comparing Fig's 3 and 4 one can observe that there exist small differences between the reinforcing coefficients in the static and the dynamic theoretical results as well as that the predicted dynamic curves of $E_c^{'}$ have the same form as in the curve of static elastic modulus E_c.

In Fig. 4 also one can see that the experimental results for $E_c^{'}$ are close to the values predicted by egns (A1), (A3), as well as close to the values obtained by model 2. One can also observe that the experimental results coincide to the theoretical results predicted by model 2 by means of eqn (8). From the form of eqns (A1)-(A4) one can conclude that the reinforcing coefficients of the storage, the loss and the static elastic

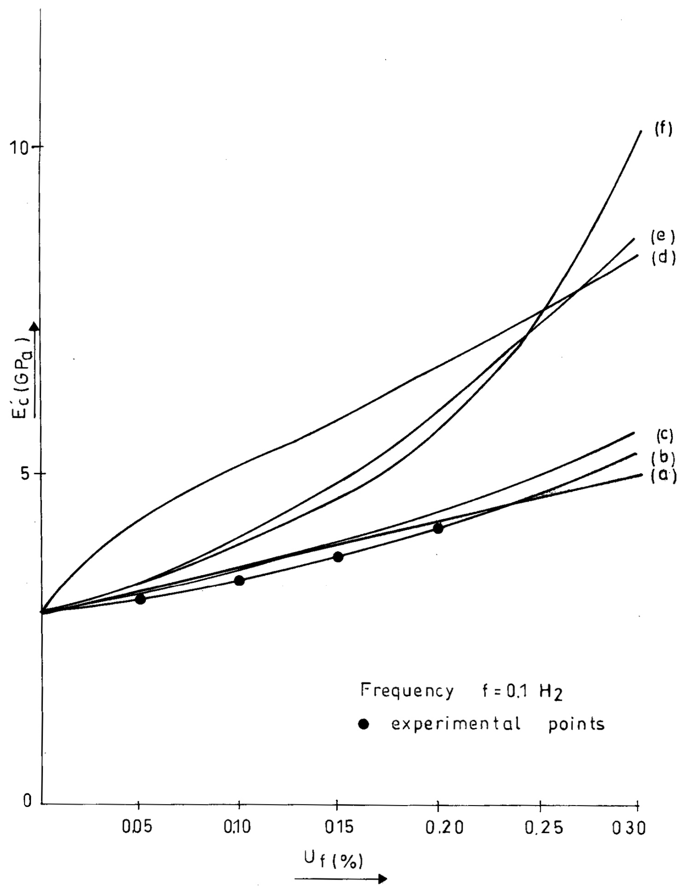

Fig. 4 The storage modulus $E_c^{'}$ versus filler volume fraction in epoxy/iron particulate composites, for frequency $f = 0{,}1\,\text{Hz}$, (a) Einstein, (b) model 2, (c) Kerner, (d) Model 1, (e) Guth and Smulwood, (f) Mooney

moduli are the same. However in more complicated equations as eqns (2) and (3) discrepancies between the reinforcing coefficients appear which yet are small. The reinforcing coefficient obtained by the static and dynamic theoretical results of the presented models 1 and 2 are almost the same. the higher discrepancies appear in $E_c^{''}$ of model 1 and give difference of the order of 0,1.

In Fig. 5 the loss modulus $E_c^{''}$ versus the filler content is plotted, for frequency $f = 0{,}1\,Hz$ in epoxy/iron particulate composites. Similar remarks can be done as for the storage modulus $E_c^{'}$ of Fig. 4. Again the reinforcing coefficients are close to those predicted by the static elastic modulus.

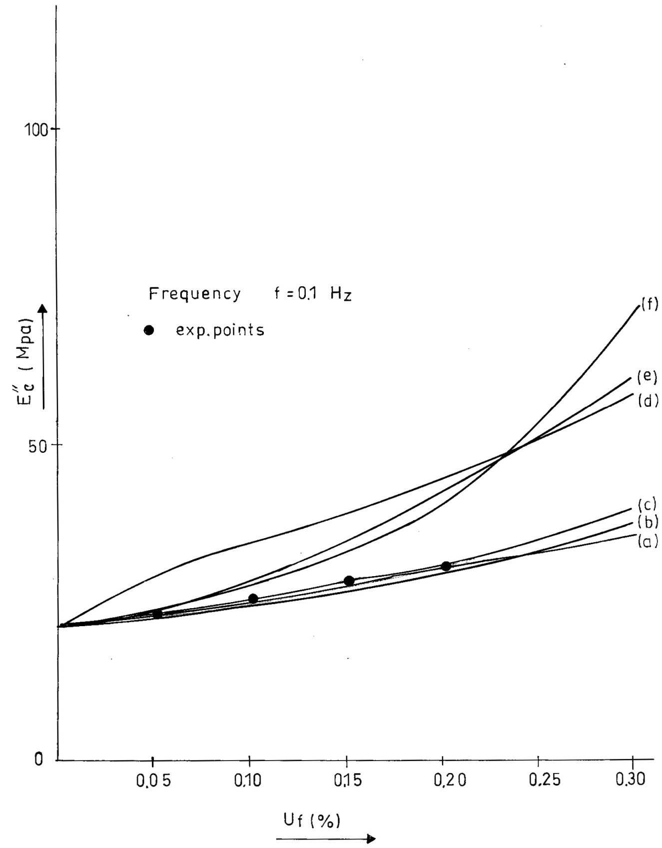

Fig. 5 The loss modulus $E_m^{''}$ against filler content in epoxy/iron particulate composites, for frequency $f = 0{,}1\,\text{Hz}$, (a) Einstein, (b) model 2, (c) Kerner, (d) model 1, (e) Guth and Smulwood, (f) Mooney

In Fig. 6 the storage modulus $E_c^{'}$ is plotted versus the frequency f for different values of the filler content u_f. In this figure the experimental results of $E_c^{'}$ in epoxy/iron particulate composites are presented. These dynamic curves are extrapolated up to the values of $E_c^{'}$ which were predicted by ultrasonic measurements for frequency $f = 10^6\,Hz$ in the above composites. Using this extrapolation, the value of the static modulus E_c, to which the values of the storage modulus $E_c^{'}$ of the dynamic experiments, for $f \approx 10^3\,Hz$, tend, is overcome. This can be explained by the fact that as the frequency f increases, different dynamic spectra, derived by different molecular, intermolecular and atomic oscillations appear. Besides the above

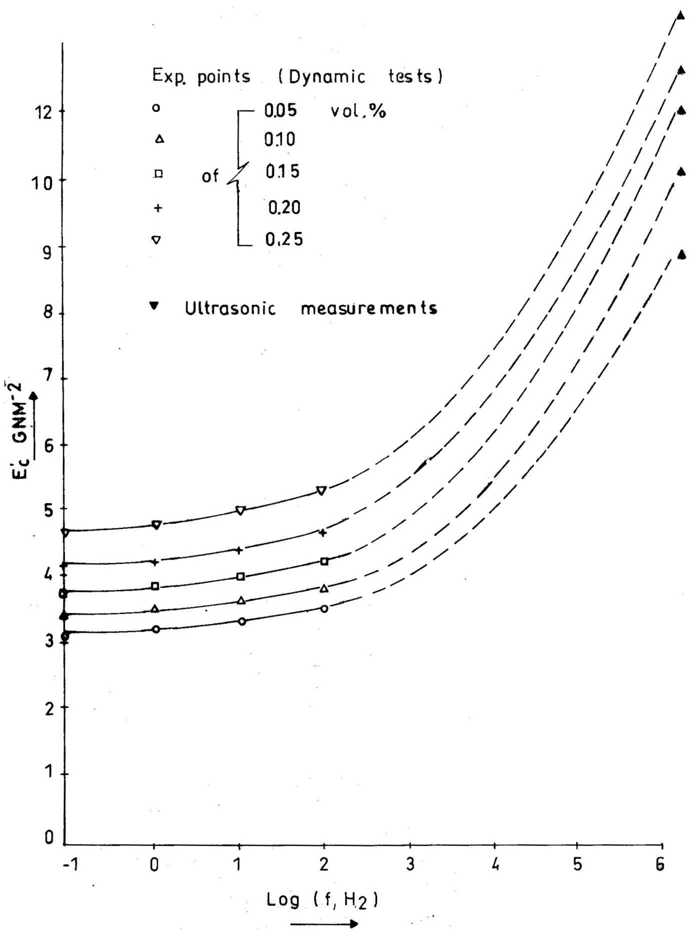

Fig. 6 The storage modulus $E_c^{'}$ versus frequency f for different filler contents. The dynamic curves are extrapolated up to the values of $E_c^{'}$ predicted by ultrasonic measurements.

explanation, one can additionally conclude that in high frequencies inertial phenomena influence the values of $E_c^{'}$.

The tensile experimental results and ultrasonic measurements have been carried out in our laboratory in epoxy/iron particulate composites.

The elastic constants of the used materials were:

$E_m = 3{,}5\,GPa$	$E_f = 210\,GPa$
$E_m^{'} = 2{,}92\,GPa$	$E_m^{''} = 20{,}4\,\mathrm{M}Pa$
$\nu_m = 0{,}36$	$\nu_f = 0{,}29$

Conclusions

1) The obtained differences between the reinforcing coefficients of the static and dynamic moduli predicted by the presented models are small. For this reason it can be assumed that the predicted curves of the static and dynamic moduli have the same form.
2) The reinforcing coefficients appearing in the dynamic experimental results are lower than those of the tensile exapriments.
3) The discrepancies of $E_c^{'}$ between the tensile experimental results and ultrasonic measurements can be explained by the fact that as the frequency f increases, different dynamic spectra derived by different molecular, intermolecular and atomic oscillations appear in combination to inertial phenomena.

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Appendix

The equations used for comparison are the following:

1. Einstein’s equation [14]

$$E_c = E_m (1 + 2{,}5\,\mathrm{u}_\mathrm{f}) \qquad \text{(A1)}$$

2. Guth and Smulwood equation [15,16]

$$E_c = E_m (1 + 2{,}5\,u_f + 14{,}1\,u_f^2) \qquad \text{(A2)}$$

3. Kerner equation [17]

$$\frac{E_c}{E_m} = 1 + \frac{u_f \cdot 15 \cdot (1 - v_m)}{u_m (8 - 10 v_m)} \qquad \text{(A3)}$$

4. Mooney equation [18]

$$E_c = E_m \exp\left(\frac{2{,}5\,u_f}{1 - s\,u_f}\right) \qquad \text{(A4)}$$

where $1 < s < 2$