THE EFFECT OF INTERPHASE ON THE ELASTIC MODULUS OF PARTICULATE COMPOSITES USING TWO MODELS: i) OF SIX, AND ii) OF SEVEN COMPONENTS

By

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Abstract

In this paper the elastic modulus of particulate composites is evaluated by using two models: i) a six-component square-into-square model and ii) a seven-component cube-within-cube model. The R.V.E.s (representative volume elements) take into consideration the existence of the interphase between matrix and filler, which is a third phase in the composite whose thermomechanical properties vary between those of the inclusion and those of the matrix. The theoretical results are compared with those resulting by existing equations in the literature, as well as with tensile experimental results and ultrasonic measurements in epoxy / iron particulate composites.

Introduction

Among the theoretical models that have been appeared in the literature and concern the evaluation of the elastic modulus, only a few take into consideration the existence of an intermediate layer, developed during the preparation of the composite material, which, as it has been shown in Refs [1~8], plays an important role in the overall thermomechanical behavior of the composite.

In this layer (third phase) complex interactions develop around the inclusions. Phenomena as: areas of imperfect bonding, permanent stresses due to shrinkage of polymer phase during the curing period, high stress gradients, stress singularities due to rough surface of the inclusions, voids, microcracks, etc., show that there do not develop conditions of perfect adhesion between matrix and filler.

The interaction between the polymer matrix and the surface of the solid inclusion during curing, restricts the free segmental and molecular mobility of the matrix and thus creates the constrained (the boundary interface) with different mechanical and physical properties from those of the inclusion or the matrix, which play a major role in the properties of the composite. In particular, the large differences between the elastic properties of the matrix and the inclusion have to be bridged through the interface. Consequently it results that an understanding of the behavior of the composite depends upon the knowledge of the effect of the properties of this layer, on the overall performance of the system and the grasp of the fundamental filler – matrix interactions which determine these properties. The effect of the filler – matrix adhesion on the mechanical behavior of composites has been discussed in a series of models presented in refs [1~13] and [16].

In the present investigation the effect of the interface on the elastic modulus of the particulate composites has been studied by introducing i) a six component model and ii) a seven component model, which consider the existence of a third phase surrounding the inclusions and having different thermomechanical properties than those of the two main phases. The thermomechanical properties of this intermediate layer were further considered as varying between the properties of the filler and those of the matrix. For simplicity the variation of the properties of the intermediate layer was assumed to be linear.

The Interphase Model

Consider the models presented in Figs 1 and 2. It is clear that the composite consists of three different materials, namely the filler, the interphase and the matrix. The filler is surrounded by the interphase, which in turn is surrounded by the matrix.

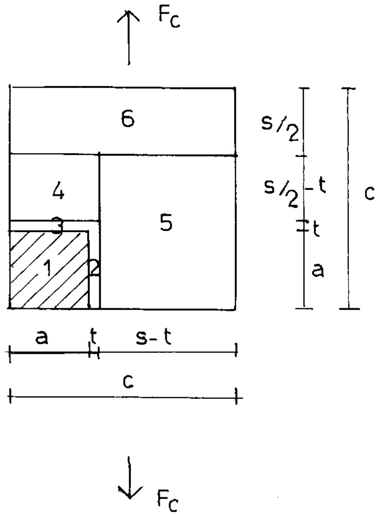

Fig. 1. A Schematic representation of the square-into-square model taking into account the interface. Model 1.

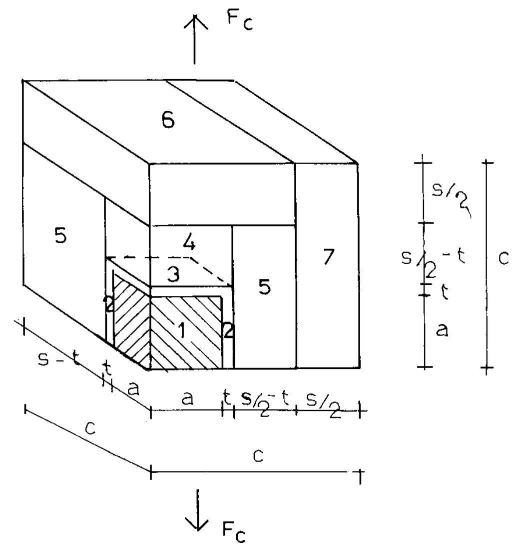

Fig. 2. A Schematic representation of the cube-within-cube model taking into account the interface. Model 2.

The theoretical analysis is based on the following assumptions:

i) The matrix, the interphase and the filler are elastic isotropic and homogeneous.

ii) The filler particles are perfect cubes in shape.

iii) There are many filler particles and their distribution is uniform, so that the composite may be regarded as a quasi – homogeneous isotropic material.

iv) The volume fraction of filler is sufficiently small so that the interaction between filler particles can be neglected.

For the model square-into-square shown in Fig. 1, called model 1, the volume fractions can be written as

$$\upsilon_f = \frac{a^2}{c^2} \qquad \upsilon_i = \frac{2at}{c^2} \qquad \upsilon_m = \frac{c^2 - a^2 - 2at}{c^2} \tag{1}$$

Similarly for the model cube-within-cube shown in Fig. 2 and called model 2, the volume fractions can be written as

$$\upsilon_f = \frac{a^3}{c^3} \qquad \upsilon_i = \frac{3a^2 t}{c^3} \qquad \upsilon_m = \frac{c^3 - a^3 - 3a^2 t}{c^3} \tag{2}$$

In eqns (1) and (2) υ is the volume fraction and the indexes f, i and m correspond to the filler, the interphase and the matrix respectively.

Moreover as the filler volume fraction increases the proportion of the macromolecules characterized by a reduced mobility also increases. This is equivalent to an increase of the interphase volume fraction and supports the empirical conclusion of ref [14] which states that the extend of the interphase, expressed by its thickness Δx, is the cause of the variation of the amplitudes of the heat capacity jumps appearing at the glass transition zones of the matrix material and the composites with various filler volume fractions. Furthermore the size of these heat capacity jumps in unfilled and filled materials is directly related to Δx by an empirical relationship given in ref [14], which was verified in ref [15].

This relationship is expressed by

$$\left(\frac{a+t}{a}\right)^3 - 1 = \frac{\lambda \upsilon_f}{1-\upsilon_f} \tag{3}$$

where

$$\upsilon_i = \frac{2t\upsilon_f}{a} \tag{4}$$

for model 1, and

$$\upsilon_i = \frac{3t\upsilon_f}{a} \tag{5}$$

for model 2. The parameter λ is given by

$$\lambda = 1 - \frac{\Delta c_p^f}{\Delta c_p^o} \tag{6}$$

in which Δc_p^f and Δc_p^o are the sudden changes of the heat capacity of the filler and unfilled polymer respectively.

The problem under consideration is to determine a law governing the variation of the mechanical properties of the mesophase material as a function of the distance measured from the inclusion boundary. It is assumed that the variation of the elastic modulus and Poisson's ratio is linear. Then $E_i(x)$ and $\nu_i(x)$ can be written as

$$E_i(x) = P + Q\,x \tag{7}$$

$$\nu_i(x) = R + S\,x \tag{8}$$

where $\frac{a}{2} \le x < \frac{a+t}{2}$

and P, Q, R and S are functions of the moduli (or the Poisson's ratio), the side of inclusion a, and the thickness t of the mesophase. In order to evaluate them, use is made of the following boundary conditions:

at $x=\frac{a}{2}$, $E\left(\frac{a}{2}\right)=E_f$ and $\nu_i=\nu_f$

at $x=\frac{a+t}{2}$, $E\left(\frac{a+t}{2}\right)=E_m$ and $\nu_c=\nu_m$

Substituting in equs (7) and (8) one obtains

$$E_i(x)=\frac{E_f(a+t)-E_m a}{t}-\frac{E_f-E_m}{t}2x \tag{9}$$

$$\nu_i(x)=\frac{\nu_f(a+t)-\nu_m a}{t}-\frac{\nu_f-\nu_m}{t}2x \tag{10}$$

The mean values of $E_i(x)$ and $V_i(x)$ are obtained setting $x=\frac{a}{2}+\frac{t}{4}$

$$E_i=\frac{E_f+E_m}{2}, \quad \nu_i=\frac{\nu_f+\nu_m}{2} \qquad (11), (12)$$

This mean value of E_i can be obtained as follows

$$E_i=\frac{1}{V_i}\int_V E_i(x)dV \tag{13}$$

where $V_i=(a+t)^2\ {}^{t}\!/_{2}$ is the volume of the plane zone of the interphase of thickness ${}^{t}\!/_{2}$, and $dV=(a+t)^2dx$ is the elementary volume of a plane zone of interphase of thickness dx.

Introducing equ(9) into equ(13) and using the above equations for V_i and dV one obtains

$$E_i=\frac{E_f+E_m}{2} \tag{11}$$

Similarly

$$\nu_i=\frac{\nu_f+\nu_m}{2} \tag{12}$$

From this procedure it becomes clear that when $E_i(x)$ and $\nu_i(x)$ are not linear functions, then E_i and ν_i are not given by equs (11) and (12).

The elastic moduli of the composites consisting of the inclusions and the interface, presented in Figs 1. and 2., are given respectively by

$$E_{fi}^{(1)} = E_i \left(1 + \frac{2\upsilon_f (k-1)}{2\upsilon_f + \upsilon_i (k+1)} \right) \quad (14)$$

and

$$E_{fi}^{(2)} = E_i \left(1 + \frac{3\upsilon_f (k-1)}{3\upsilon_f + \upsilon_i (k+2)} \right) \quad (15)$$

where the superscripts 1 and 2 correspond to models 1 and 2 respectively, while the inexes i and f correspond to the interface and the filler respectively.

According to the principle of superposition, the elastic modulus of the model presented in Fig. 1 is given by

$$E_c^{(1)} = E_m \left(1 + \frac{\upsilon_f^{1/2} + \upsilon_f + \upsilon_i \upsilon_f^{-1/2} + \upsilon_i}{\frac{2m - 1 + \upsilon_f^{-1/2}}{m-1} - (2\upsilon_f^{1/2} + 2\upsilon_i \upsilon_f^{-1/2} - \upsilon_i \upsilon_f^{-1})} \right) \quad (16)$$

where $m = E_{fi}^{(1)} / E_m$.

In the model presented in Fig. 2 the superposition principle is also applied. The elastic modulus E_a of the composite consisting of the components (1)~(5) is given by

$$E_a^{(2)} = E_m \left(1 + \frac{12(\upsilon_f + \upsilon_i)}{\frac{3n(1 - \upsilon_f^{1/3}) + 6(\upsilon_f^{2/3} + \upsilon_f^{1/3})}{n-1} - 2\upsilon_i (\upsilon_f^{-1/3} + \upsilon_f^{-2/3})} \right) \quad (17)$$

where $n = E_{fi}^{(2)} / E_m$.

Considering now the whole composite, the elastic modulus is given by

$$E_c^{(2)} = E_m \left(1 + \frac{1 + 2\upsilon_f^{1/3} + \upsilon_f^{2/3}}{\frac{2(q+1)}{q-1} - 2\upsilon_f^{1/3}} \right) \quad (18)$$

where $q = E_a^{(2)} / E_m$.

All the above expressions where derived using the governing stress and strain equations of the model under consideration, in combination with the constitutive equations given by Hooke's law, as they are referred in refs [17, 18].

Results and Discussion

The presented square-into-square model consisting of four components without the interphase, may be considered as hybridic because it is formed from geometrical combinations of the three-component square-into-square R.V.E.'s.

Similarly the cube-within-cube model consisting of five components without the interface may also be considered as hybridic because it is formed from geometrical combinations of the three-component cube-within-cube R.V.E.'s.

If the interphase is taken into account the presented models consist i) of six and ii) of seven components respectively. When the interface is taken into account, to simplify the computations for the evaluation of the elastic modulus, the superposition principle is applied.

As it is pointed out in refs [17, 18], the three-component models, in both the above formations, give the upper and lower bound of the elastic modulus as it is predicted by models which belong to each formation.

In Fig. 3 the elastic modulus is plotted versus the filler volume fraction. When the interface is taken into consideration the presented models correspond to the curves (c) and (f) respectively. When the interface is not taken into consideration the curves (a) and (d) correspond to the presented models (1 and 2 respectively). It is observed that the values of E_c evaluated by the presented models approximate better the experimental results when the interface is taken into account. Especially the results of model 2 almost coincide with the experimental results. We can explain this fact considering the increasing rate of the elastic modulus with the filler volume fraction.

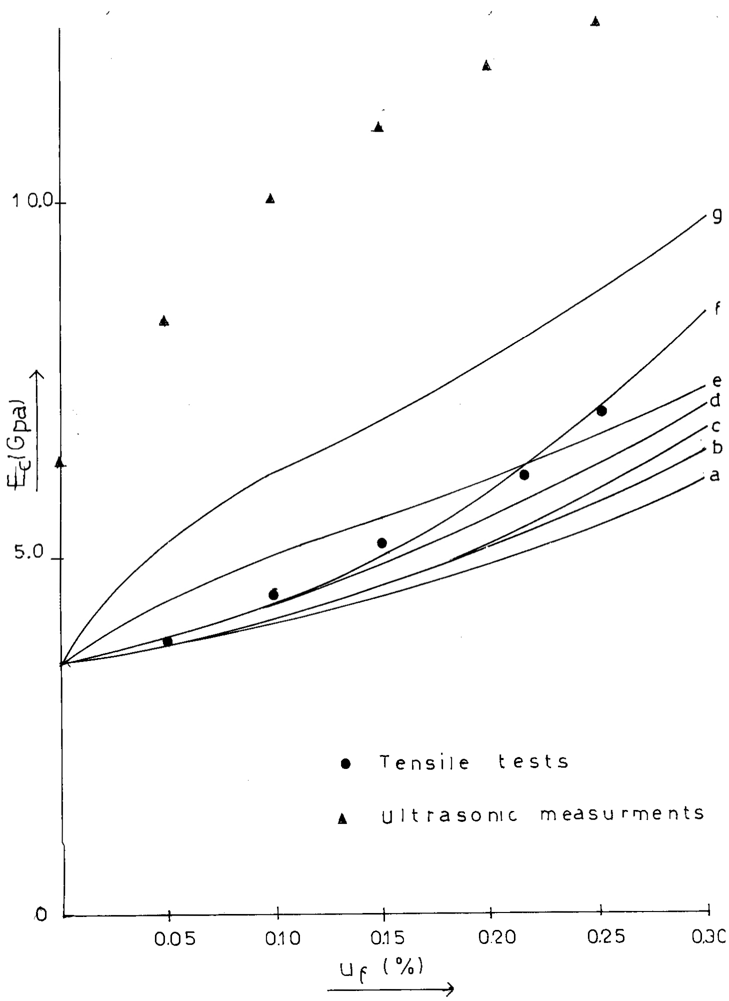

Fig. 3. The elastic modulus E_c versus filler volume fraction in epoxy/iron particulate composites
(a): Model 1 ($\upsilon_i = 0$), (b): Ishai-Cohen, (c): Model 1 ($\upsilon_i \neq 0$),
(d): Model 2 ($\upsilon_i = 0$), (e): Counto, (f): Model 2 ($\upsilon_i \neq 0$), (g): Paul

It is observed that when the interphase is ignored the models with low filler contents approximate satisfactorily the experimental results. But it is known that the rate of increase of the elastic modulus for low filler content is low, even when the interphase is taken into account. Consequently, when the filler content is low, the presented models in which the interphase is taken into account continue to approximate satisfactorily the experimental results. It is also observed that the models with high filler content in which the interphase is not taken into account provide values of E_c lower than the experimental ones.

But it is known that the rate of increase of E_c for high filler content is high when the interphase is taken into account. Consequently when the filler content is high, the presented models in which the interphase is taken into account approximate satisfactorily the experimental results. The above results are in agreement with those of ref [16] in sphere-within-sphere models. It is obvious that when the models of the presented formations give values close to or higher than the experimental results without consideration of the interphase, they give even higher values when the interphase is taken into account.

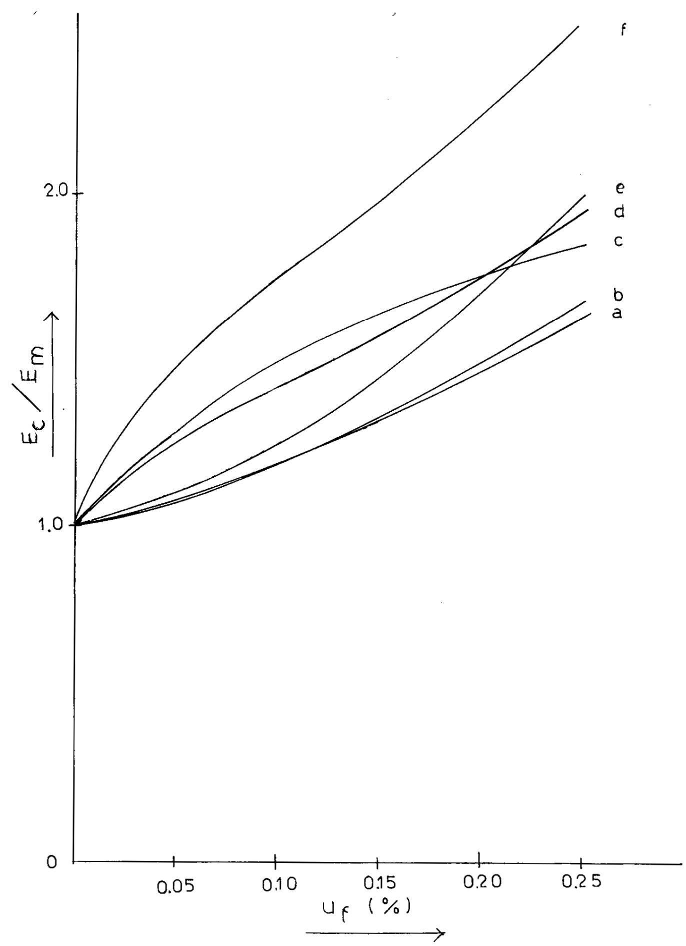

Fig. 4. (a): Ishai-Cohen, (b): Model 2 ($\upsilon_i \neq 0$), (c): ultrasonic measurements, (d): Counto, (e): Model 2 ($\upsilon_i \neq 0$), (f): Paul

In Fig. 4, the reinforcing coefficients predicted by the above models are compared to those predicted by ultrasonic measurements. One can observe that there is a satisfactory agreement between the presented models and ultrasonic measurements.

Finally according to refs [5 and 8] the thickness of the interphase of the particulate composites is obtained higher than that of the fiber composites. Therefore the thickness of the interphase of model 1, if it is determined by means of fiber composites, is expected to be lower than that evaluated by the present procedure

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

$$E_m = 3{,}5\,GPa \qquad E_f = 210\,GPa$$

$$\nu_m = 0{,}36 \qquad \nu_f = 0{,}29$$

Conclusions

When the interphase is taken into account the values of E_c predicted by model 1 approach the experimental results, while the values of E_c predicted by model 2 almost coincide with the experimental results.

Also when the interphase is taken into account the relative increase of E_c is greater in model 2 than in model 1.

By determining the thickness of the interphase corresponding to model 1 using fiber composites instead of particulate composites, the relative increase of E_c predicted by model 1 is expected to arise smaller than that which has been evaluated by the present procedure.

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Appendix

The equations of the literature used for comparison are:

1. Paul's equation [19]

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

2. Ishai-Cohen's equation [20]

$$E_c = E_m \left(1 + \frac{\upsilon_f}{\frac{m}{m-1} - \upsilon_f^{1/3}} \right)$$

3. Counto's equation [21]

$$E_c = E_m \left(1 + \frac{\upsilon_f}{\frac{1}{m-1} + \upsilon_f^{1/2} - \upsilon_f} \right)$$