THEORETICAL EVALUATION OF THE ELASTIC MODULUS OF PARTICULATE COMPOSITES BY THE CONCEPT OF INTERPHASE AND COMPARISON WITH DESTRUCTIVE AND NON-DESTRUCTIVE EXPERIMENTAL RESULTS

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ABSTRACT

In this work the elastic modulus of particulate composites is evaluated by taking into consideration the existence of an interphase between matrix and filler.

For this purpose basic models as cube-within-cube and square-into-square formations are used. It has been found that by considering the interphase as a third phase, consisting of a zone between matrix and filler with mechanical properties varying between those of filler and matrix, the elastic modulus value increases. The theoretical values are compared with tensile experimental results and ultrasonic measurements as well as with those derived from existing formulae in the literature. Although the elastic modulus values increases by considering the influence of an interphase, however remain close to the tensile experimental results that are situated well below the values derived from ultrasonic measurements.

INTRODUCTION

As known composite materials are among the materials which have recently undergone a marked degree of technological development and their use has increased in recent years. Their complete characterization has not been achieved entirely to date; that is due to complex material properties such as chemical compatibility, wettability, absorption characteristics and stress development owing to differences in expansion.

Many theoretical analyses, which define the elastic properties of composites and which give equations for predicting the elastic modulus, have been reported in the literature [1]. Among the theoretical models that have appeared in the literature only some take into account the existence of an intermediate layer, developed during the preparation of the composite material which, as it has been shown in Refs. [2] to [6], plays an important role in the overall thermomechanical behaviour of the composite.

This third phase extends between the two main phases of the composite and is the result of physico-chemical effects taking place at the interphase of the two main phases. It is the restricted zone where impurities and air bubbles are concentrated and microcracks are developed, because of the difference in the thermal expansion coefficient between matrix and filler. Moreover, high concentrations in stresses due to shrinkage and in some places, stress singularities are engendered in this layer, and other defects may be localized there [7].

In a model developed in Refs [8] and [9] the interphase has been considered initially as being a homogeneous and isotropic material. Thermal capacity measurements were performed [10] in order to determine the thickness and the volume fraction of the interphase. These values were used to calculate the elastic modulus, fracture strain and stress in a model consisting of six layers.

The concept of a variable modulus interphase was developed in Refs [11] and [12]. According to this model the mesophase constitutes a transition zone between inclusion and matrix and its modulus, fracture strain and stress vary with the coordinates as a power of the distance at $a+t$, where a is the side of cube or square and t the width of interphase.

In the present investigation the effect of the interphase between particulate fillers and their matrix on the elastic modulus has been studied by introducing five layer models in square-into-square [13,14,15] and cube-within-cube formations [16,17] which consider the existence of a third phase surrounding the inclusions and having different thermomechanical properties from the respective properties of the two main phases. The thermomechanical properties of this intermediate layer were further considered as varying between the properties of the fillers and the matrix. The law of variation was assumed to be a simple one, expressed by typical first-degree line.

THEORETICAL CONSIDERATIONS

The theoretical analysis will be based on the following assumptions.

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

ii) The interphase is elastic, anisotropic and homogeneous.

iii) There is perfect adhesion between the different phases.

iv) The deformations applied to the composite are small to maintain linearity of stress-strain relations.

From Figs (1a) and (1b) the models filler content is given by:

$$u_f = a^2/c^2 \qquad (1)$$

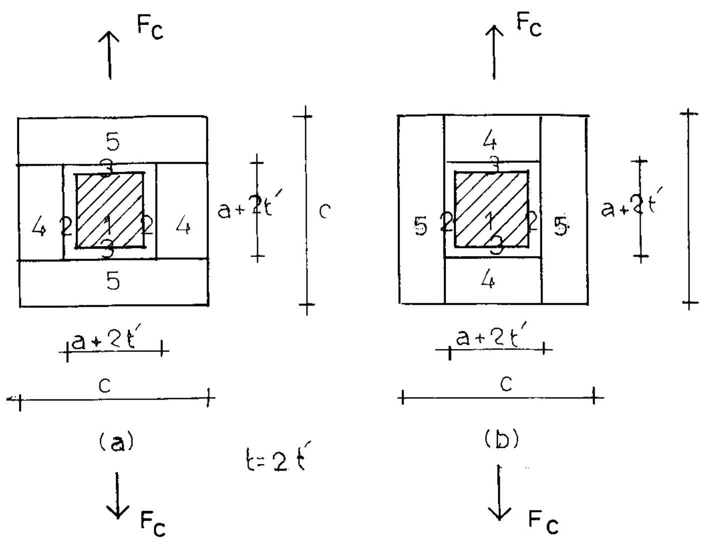

Fig (1) A schematic representation of the square- into- square models taking into account the intesphace, (a): model 1, (b): model 2.

For the models in Figs. (2a) and (2b) the filler content is given by:

$$u_f = \frac{a^3}{c^3} \qquad (2)$$

For the models in Figs. (1a) and (1b) called model 1 and model 2 respectively the interphase volume fraction is given by:

$$u_i = \frac{2at}{c^2} \qquad (3)$$

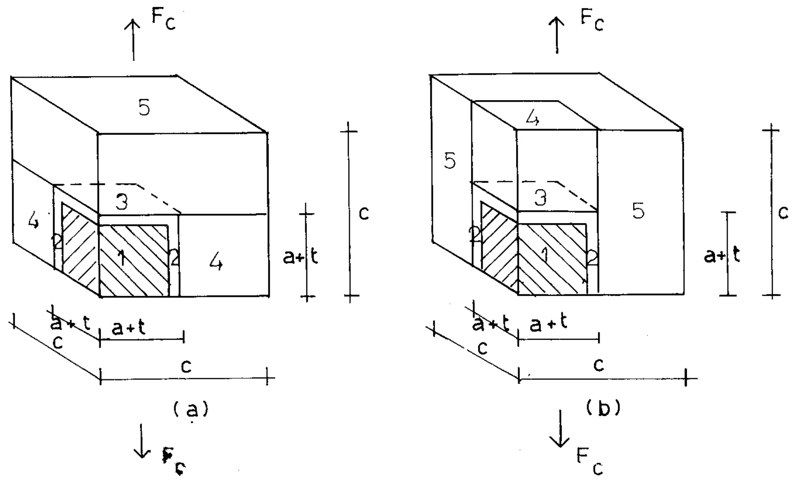

Fig (2) A schematic representation of the cube – within – cube models taking into account the interphace, (a): model 3, (b): model 4.

Similarly for the models in figs (2a) and (2b) called model 3 and model 4 respectively the interphase volume fraction is given by:

$$u_i = \frac{3a^2 t}{c^3} \tag{4}$$

The width t of interphase of particulate composites can be evaluated as in Ref. [12], from the following relationship

$$\left(\frac{a+t}{a}\right)^3 - 1 = \frac{\lambda u_f}{1-u_f} \tag{5}$$

where the coefficient λ is given by [18]

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

where ΔC_p^f and ΔC_p^o sudden jumps in heat capacity occurring in the region of glass transition temperature for the composite and matrix respectively.

For the models 1 and 2 for the composite (fi) consisting of the filler and interphase it is obtained

$$E_{fi}^{1,2} = E_i\left(1+\frac{2u_f(k-1)}{ku_i+2u_f+u_i}\right) \tag{7}$$

where $k = E_f / E_i$

The indices f and i correspond to the filler and interphase respectively.

The elastic modulus E_i by assuming a linear variation into the interphase thickness is obtained as a mean value of E_f and E_m.

Similarly for the models 3 and 4 for the composite consisting of filler and interphase it is found that:

$$E_{fi}^{3,4} = E_i\left(1+\frac{3u_f(k-1)}{3u_f+u_i(k+2)}\right) \tag{8}$$

By applying the superposition principle we obtain the following expressions for the elastic modulus of the composite

$$E_c^{(1)} = E_m\left(1+\frac{2(u_f+u_i)}{\frac{2}{m-1}+2\left(u_f^{1/2}-u_f-u_i\right)+u_iu_f^{-1/2}}\right) \tag{9}$$

$$E_c^{(2)} = E_m\left(1+\frac{2(u_f+u_i)}{\frac{2m}{m-1}-2u_f^{1/2}-u_iu_f^{-1/2}}\right) \tag{10}$$

where $m = E_{fi}^{1,2} / E_m$

and

$$E_c^{(3)} = E_m\left(1+\frac{3(u_f+u_i)}{\frac{3}{n-1}+3\left(u_f^{2/3}-u_f-u_i\right)+2u_iu_f^{-1/3}}\right) \tag{11}$$

$$E_c^{(4)} = E_m \left(1 + \frac{3(u_f + u_i)}{\frac{3n}{n-1} - 3u_f^{\,1/3} - u_i u_f^{\,-2/3}} \right) \tag{12}$$

where $n = E_{fi}^{3,4} \big/ E_m$

where the indices 1,2,3 and 4 correspond to models 1,2,3 and 4 respectively.

Table 1. (Filler and interphase content)

u_f	u_i
0,05	0,0013
0,10	0,004
0,15	0,013
0,20	0,028
0,25	0,050

RESULTS AND DISCUSSION

In the cube within cube formation the Paul model (eqn (11)) constitutes the upper bound for E_c, while the Issay-Cohen model (eqn (12)) the lower bound. In the square-into-sphere model the Counto model (eqn (9)) constitutes the upper bound while the model 2 or Ref [15] the lower bound (eqn (10)).

In fig. (3) the elastic modulus E_c of particulate composites is plotted versus filler content. The theoretical results predicted by the above models and illustrated by the aid of the curves (c, f, l, k) respectively are compared with tensile experimental results and ultrasonic measurements in iron/epoxy particulate composites.

In the same figure the theoretical results predicted by eqn (A1) and (A2) of the literature , and illustrated by the aid of the curves (e) ~ (f) respectively, are also traced. From this figure it is observed that eqns (12), (A2) and (9) approximate better the experimental results,

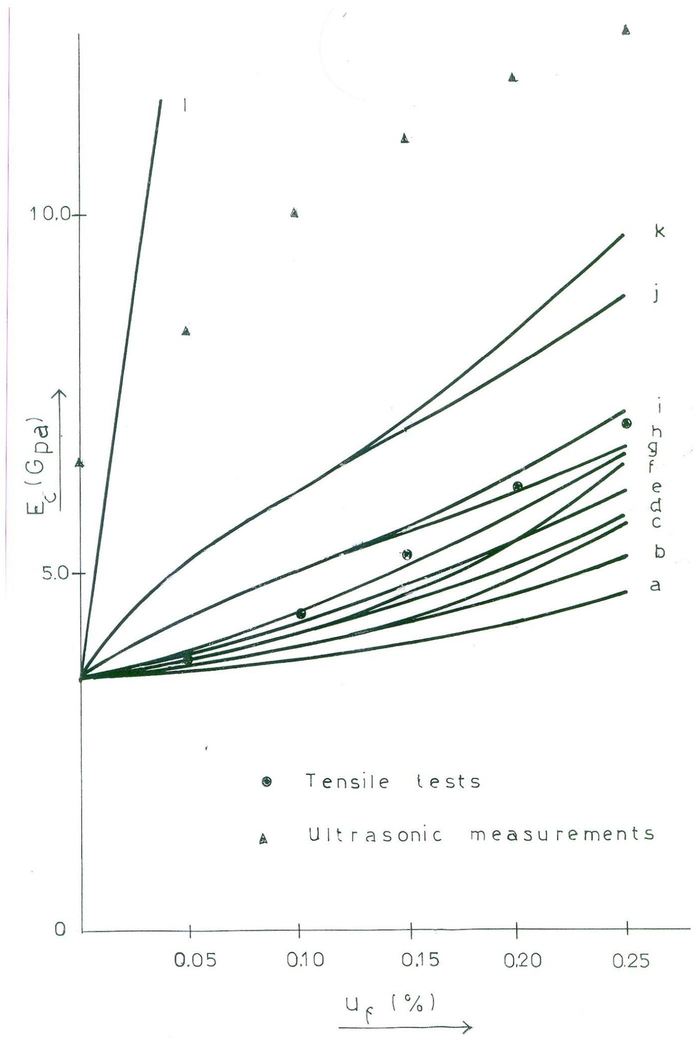

Fig (3) The elastic modulus E_c versus filler volume fraction in epoxy / iron pasticulute composites.
(a) : Inverse law of mixtures, (b) : model 2 $(u_i = 0)$,
(c) : model 2 $(u_i \neq 0)$, (d) : model 4 $(u_i = 0)$,
(e) : sphere – within shere $(u_i \neq 0)$, (f) : model 4 $(u_i \neq 0)$,
(g) : sphere – within sphere $(u_i \neq 0)$, (h) : model 1 $(u_i = 0)$,
(i) : model 1 $(u_i \neq 0)$, (j) : model 3 $(u_i = 0)$,
(k) : model 3 $(u_i \neq 0)$, (l) : low of mixtures

while the results from eqn (A2) are in good agreement with experimental results. But given that for every formation the limits have been traced, then the mean value of the cube-in-cube formation approaches the experiment whereas the mean value of the square-into-square formation is found lower than the experiment. In this figure the values derived from the present models namely the curves with the consideration of interphase and without it were traced.

By considering that the elastic modulus in the interphase varies linearly into the width of that zone from the elastic modulus of the filler to the matrix elastic modulus a mean elastic modulus of the interphase equal to the mean value of the elastic modulus of the two phases can be found. Although the bounds in the two formations shift upwards by the consideration of the interphase, however the relative increase of the elastic modulus is small, as to the values derived by the method of ultrasonics. From this shift of the bounds, in any case, we can observe that the upper bounds move away from the experimental values (exception is the Counto model) whereas the lower bounds approach them. By generalizing this principle we can say that through the interphase, the “strong” models go away from the experiments whereas “weak” models approach them.

A remarkable fact is the way by which the bounds shift. There are not, that is to say, parallel shifts, however the modulus increases more as the filler content increases. Thus, for models that in low filler volume fractions approach the experiment whereas in higher volume fractions yield lower values than the experimental ones, it is expected that by the consideration of the interphase they will approach the experiment better.

On the contrary, models that approach the experiment in high filler volume fractions and yield higher values than the experimental ones for low filler contents by the consideration of the interphase they will go away more from the curve of experimental values. In any case, although the present models are considered as simple relatively to complicated models of the literature, however from them it results a satisfactory approach of the experimental curve. Here, it is worth mentioning that the interphase constitutes only one of the parameters that influences the mechanical properties of a composite material. Other parameters such as the size, the shape, the homogeneity, the existence of aggregations, air bubbles in the matrix, the shape factor, the orientation of the inclusions in the case that they are not spherical, the stress concentrations, permanent stresses in the composite because of contraction of the matrix during curing, poor adhesion normally should be correlated for the final theoretical value of the elastic modulus.

In the illustration of Fig.(4), they are given the values of the reinforcement coefficients of the composite as they result from the examined model with and without interphase and ultrasonic measurements where it is observed a good approach to the values of ultrasounds by the Counto model and by the mean value of the bounds of the cube-in-cube formation with or without interphase.

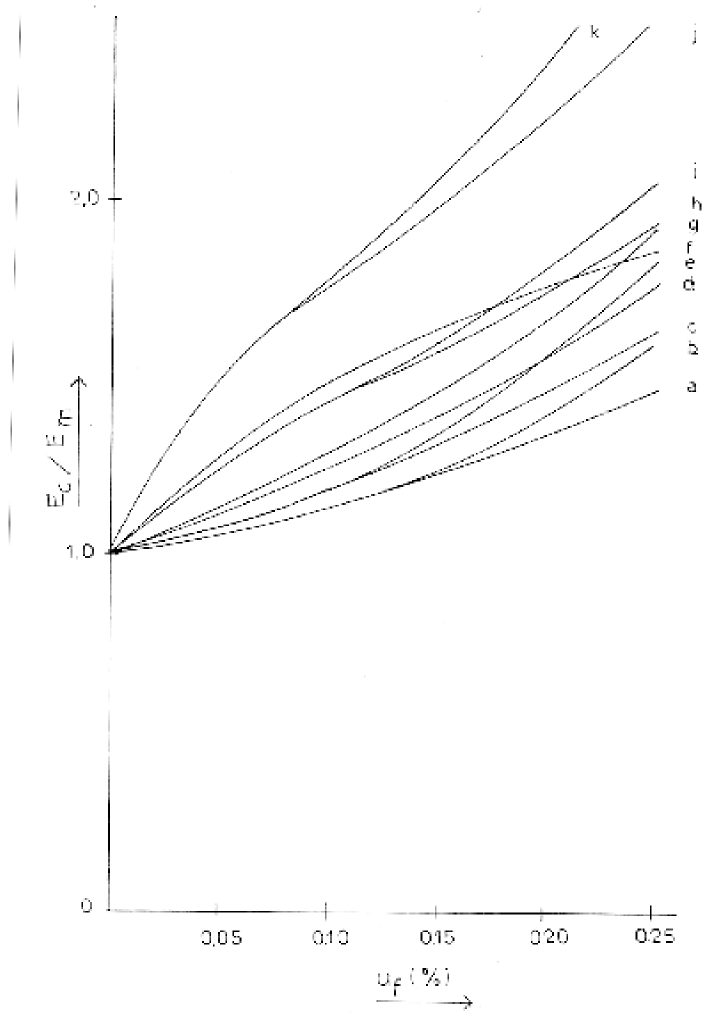

Fig (4) The reinforcing coefficients (E_c/E_m) versus filler volume fraction
(a) : model 2 $(u_i = 0)$, (b) : model 2 $(u_i \neq 0)$,
(c) : model 4 $(u_i = 0)$, (d) : sphere – within sphere $(u_i = 0)$,
(e) : model 4 $(u_i \neq 0)$, (f) : ultrasonic measurements,
(g) : sphere – within sphere , (h) : model 1 $(u_i = 0)$,
(i) : model 1 $(u_i \neq 0)$, (j) : model 3 $(u_i = 0)$,
(k) : model 3 $(u_i \neq 0)$.

Yet, it should be mentioned that the influence of the interphase zone seems stronger in the cube in cube models than that in square into square models. This fact is due to the geometry of the models. Also, the second type models are idealized models, for particulate composites as correspond to fibrous composites. The thickness of the interphase in this geometry is found smaller than that measured experimentally in particle reinforced composites [6,[19,20].

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:

$$E_m = 3{,}5\,Gpa \qquad E_f = 210\,Gpa$$
$$V_m = 0{,}36 \qquad V_f = 0{,}29$$

CONCLUSIONS

The shift models in both formations go away from the experimental results. The weak models in both formations approach the experimental results. Considering the interphase the modulus increases more as the filler content increases.

Taking into account the interphase the relative increase of the elastic modulus is small compared to the values derived by the menthol of ultrasonics.

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APPENDIX

1. The two phase model in sphere-within-sphere formation [16]. The elastic modulus E_c is given by

$$\frac{2(1-2v_c)}{\mathrm{E}_c}=\frac{2\lambda^2 u_f}{\mathrm{E}_f}+\frac{1}{\mathrm{E}_m}\left[\frac{u_f(1-\lambda)^2(1+v_m)+2(\lambda u_f-1)^2(1-2v_m)}{1-u_f}\right]$$

where $\frac{1}{v_c}=\frac{u_f}{v_f}+\frac{u_m}{v_m}$

and

$$\lambda=\frac{3(1-v_m)\mathrm{E}_f}{\left[2u_f(1-2v_m)+1+v_m\right]\mathrm{E}_f+2(1-2v_f)(1-u_f)\mathrm{E}_m}$$

2. The three phase model in sphere-within-sphere formation [20]. The interphase is considered to be the third phase. The elastic modulus E_c is given by

$$\frac{1-2v_c}{\mathrm{E}_c}=\frac{(1+v_f)^2(1-2v_m)^2}{(1+v_m)^2(1-2v_f)\mathrm{E}_f}u_f+\frac{(1-2v_m)}{\mathrm{E}_m}u_m$$
$$+\frac{3u_f(1-2v_m)^2}{(1+v_m)^2 r_f^3}\int_{r_f}^{r_m}\frac{[1+v_i(r)]^2}{[1-2v_i(r)\mathrm{E}(r)]}r^2dr$$

where

$$\frac{1}{v_c}=\frac{u_f}{v_f}+\frac{u_m}{v_m}+\frac{u_i}{v_i}$$
$$uf=\frac{r_f^3}{r_m^3}\ ,\ u_i=\frac{r_f^3-r_i^3}{r_m^3}\ ,\ u_m=\frac{r_m^3-r_i^3}{r_m^3}\quad \text{with}\quad u_f+u_m+u_i=1$$

and $\mathrm{E}_f(r)$ and $v_i(r)$ varying according to assumed laws of variation.