The Transverse Elastic Modulus of Fiber-Reinforced Composites as Defined by the Concept of Interphase

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SYNOPSIS

A theoretical expression for the prediction of the transverse elastic modulus in fiber-reinforced composites was developed. The concept of interphase between fibers and matrix was used for the development of the model. This model considers that the composite material consists of three phases, that is, the fiber, the matrix, and the interphase. The latter is the part of the polymer matrix lying at the close vicinity of the fiber surface. In the present investigation it was assumed that the interphase is inhomogeneous in nature with continuously varying mechanical properties. Different laws of variation of its elastic modulus and Poisson ratio were taken into account in order to define the overall modulus of the composite. Thermal analysis method was used for the estimation of the thickness of the interphase. The results obtained were compared with the respective values of other models as well as with experimental data. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

A unidirectional fiber-reinforced composite can be considered as a basic element from which composite structures are constructed and also the simplest one from the geometrical point of view. From the mechanical point of view the simplest kind of fiber reinforced material is an elastic one, which is composed of linear elastic fibers and matrix. The study of the elastic properties of uniaxially fiber-reinforced materials on the basis of constituent elastic properties and the prediction of the elastic moduli is one of the main engineering problems.

A large number of theoretical models have been appeared in the literature. Paul[1] used the principles of minimum energy and minimum complementary energy to define the bounds on the elastic modulus of a macroscopically isotropic, two-phase composite with arbitrary phase geometry.

Hill[2] derived these same bounds using a different approach. Hashin and Rosen,[3] attempted to tighten Paul's bounds to obtain more useful estimates of moduli for isotropic heterogeneous materials. They have considered an idealized model of random array of parallel hollow or solid fibers embedded in a matrix. This model of a fiber-reinforced material is referred to a composite cylinder assemblage. Closed-form expressions for elastic moduli and bounds for a fifth modulus of such an assemblage were obtained.

Whitney and Riley[4] presented a work somewhat analogous to that of Hashin and Rosen, but less rigorous mathematically and written to appeal to the engineer rather, than to the mathematician.

The fiber arrays have been extensively studied by Adams and Tsai.[5] They found that the hexagonal array analysis agree better with experiments than do results of the square array analysis.

Problems of determining exact solutions to various cases of elastic inclusions in an elastic matrix were treated by Muskhelishvili,[6] who used complex variable mapping techniques. In addition, numerical solution techniques such as finite difference and finite elements have been used extensively.

In contrast to the simple geometric model discussed previously, there is a somewhat more complicated model known as the self-consistent model. In this, the average stress and strain in each phase are determined by the solution of separate problems in the case of multi-phase media. The material outside the inclusion is assumed to be that of the un-

known "effectively" macroscopic properties. The self-consistent model was introduced by Hershey[7] and Kröner.[8] Other self-consistent models include those by Hermans[9] and Hill[10] which have been discussed by Chamis and Sendeckyj.[11]

A third major type of model is that of three-phase model introduced by Kerner.[12] This model involves taking the inclusion to be surrounded by an annulus of matrix material which in turn is embedded in an infinite medium of the unknown effective macroscopic properties.

Tsai[13] and Halpin-Tsai[14] by using the models mentioned above developed simplified expressions for the moduli, in which different factors such as contiguity, fiber geometry, packing geometry and loading conditions have been taken into account.

Among a large number of theoretical models appeared in the literature, only some of them take into account the existence of an intermediate phase, developed during the preparation of the composite material and which plays an important role on the overall thermomechanical behavior of the composite.

In a model developed by Theocaris et al.,[15,16] this intermediate phase has been considered initially as being a homogeneous and isotropic material. In a better approximation[17] a more complex model has been introduced, according to which the fiber was surrounded by a series of successive cylinders, each one of them having a different elastic modulus in a step-function variation with the polar radius.

In ref. 18 the longitudinal elastic modulus E_L and Poisson's ratio ν_{LT} of a fiber-composite were determined by assuming that the cylinder composite (fiber–interphase matrix) had well-defined material properties for the fiber and matrix cylinders whereas the mechanical properties of the intermediate hollow cylinder of the interphase were variable along its radius. The thickness of the interphase was determined by thermal measurements of the heat capacity jump at the glass transition temperature of the filled and unfilled materials.

Another consideration of the variable modulus interphase is the so-called unfolding model,[19] which is based on the fact that the interphase constitutes a transition zone between fibers with high moduli and matrix with rather low moduli. By defining the thickness of the interphase with the help of accurate thermodynamic measurements of the heat capacity jump at T_g of the filled and unfilled substances and using the E_c value of the composite defines completely the variation of the $E_i(r)$ modulus.

In the present investigation we have studied the quality of adhesion between fibers and the matrix by the three-phase model which considers the existence of a third phase surrounding the fibers and having different mechanical properties than the respective properties of the two main phases which were considered as varying between the properties of fiber to those of the matrix. The laws of variation were assumed arbitrary to be simple ones, expressed by typical first-degree or second-degree curves.

THEORETICAL FORMULAE USED FOR COMPARISON

Paul's[1] Lower Bound

$$\frac{1}{E_T} = \frac{v_f}{E_f} + \frac{v_m}{E_m} \tag{1}$$

where E_T is the transverse elastic modulus and E_f, v_f and E_m, v_m are the elastic modulus and fiber volume fraction of fiber and matrix, respectively.

Whitney-Riley[4] Equation

$$E_T = \frac{[2K_c(1 - \nu_{TT})E_L]}{E_L + 4K_c\nu_{LT}^2} \tag{2}$$

where K_c is the bulk modulus and ν_{LT} and ν_{TT} are the longitudinal and transverse Poisson ratios of the composite respectively. The bulk modulus is given as:

$$K_c = \frac{[(k_f + G_m)k_m - (k_f - k_m)G_m v_f]}{[(k_f + G_m) - (K_f - k_m)v_f]} \tag{3}$$

where G_f, G_m are the shear moduli of the two phases and $k_f = E_f/2(1 - \nu_f - 2\nu_f^2)$, $k_m = E_m/2(1 - \nu_m - 2\nu_m^2)$

Tsai[13] Equation

For the elasticity approach in which the contiguity is considered, Tsai[13] obtained for the transverse modulus the following expression:

$$E_T = 2[1 - \nu_f + (\nu_f - \nu_m)v_m]$$

$$\times \left\{ (1 - c)\,\frac{K_f(2K_m + G_m) - G_m(K_f - K_m)v_m}{(2K_m + G_m) + 2(K_f - K_m)v_m} \right.$$

$$\left. + c\,\frac{K_f(2K_m + G_f) + G_f(K_m - K_f)v_m}{(2K_m + G_f) - 2(K_m - K_f)v_m} \right\} \tag{4}$$

with $K_f = E_f/2(1 - \nu_f)$ and $K_m = E_m/2(1 - \nu_m)$ where c denotes the degree of contiguity. The value $c = 0$ corresponds to no contiguity (isolated fibers) and $c = 1$ to perfect contiguity (all fibers in contact).

Halpin-Tsai[14] Equation

Halpin and Tsai[14] in order to avoid complicated equations developed an interpolation procedure that is an approximate representation of more complicated micromechanics results. The essence of the procedure is that they shaved that Herman's[9] solution generalizing Hill's self-consistent model[10] can be reduced to the approximate form:

$$E_T = E_m \frac{1 + \xi \eta v_f}{1 - \eta v_f} \tag{5}$$

with

$$\eta = \frac{(E_f/E_m) - 1}{(E_f/E_m) + \xi}$$

where ξ is a measure of fiber reinforcement of the composite that depends on fiber geometry, packing geometry and loading conditions.

Ekvall's[20] Equation

Ekvall[20] obtained a modification of the above lower bound (Eq. 1) in which the triaxial stress state in the matrix due to fibre restrained is accounted for:

$$E_T = \frac{E_f E'_m}{v_f E'_m + v_m E_f (1 - \nu_m^2)} \tag{6}$$

where

$$E'_m = \frac{E_m}{1 - 2\nu_m^2}$$

For lamina thicknesses of one-filament diameter and square or rectangular filaments, Ekvall uses the simple assumption but attempts to eliminate the unequal longitudinal Poisson deformation by applying additional longitudinal stresses such that

$$\sigma_{ml} A_m + \sigma_{fl} A_l = 0$$

This results in a biaxial state of stress, and he obtains

$$\frac{1}{E_T} = \frac{v_m}{E_m} + \frac{v_f}{E_f} - \frac{v_f}{E_f} \frac{[(E_f \nu_m/E_m) - \nu_f]^2}{E_f [(v_f E_f/v_m E_m) + 1]} \tag{7}$$

for the transverse modulus.

THEORETICAL CONSIDERATIONS

The model introduced here is based on the mechanical behavior of the fiber-reinforced composite materials. First of all it should be clarified that the composite material was treated as a three phase material in which the three phases are as follows: The first is the polymeric matrix which is characterized by its elastic modulus E_m and Poisson's ratio ν_m. The second is the fibre which constitutes the filler and has elastic modulus E_f and Poisson's ratio ν_f.

The intermediate phase, or interphase is considered as consisting of an inhomogeneous and transversely isotropic (isotropy at the xy plane) material of finite thickness with elastic modulus $E_i(r)$ and Poisson's ratio $\nu_i(r)$. (see Fig. 1). Both of them are supposed to vary with distance from fiber surface. The representative volume element [Fig. 1(a)] of this model consists of three separate regions (i.e., the fiber, the interphase, and the matrix). If we denote by r_f, r_i, r_m the outer radii of them, respectively, then the volume fractions of each material will be given by:

$$v_f = \frac{r_f^2}{r_m^2}, \quad v_i = \frac{r_i^2 - r_f^2}{r_m^2}, \quad v_m = \frac{r_m^2 - r_i^2}{r_m^2} \tag{8}$$

where $v_m = 1 - v_f - v_i$.

It has been observed that, for the same volume fraction v_f of the filler, an increase of the glass transition temperature T_g indicates an increase of the total surface of the filler.[21] This is because an increase in T_g may be interpreted as a further formation of molecular bonds and grafting between secondary chains of molecules of the matrix and the solid surface of inclusions, thus restricting significantly the mobility of neighbour chains. This increase leads to a change of the overall viscoelastic behaviour of the composite, by increasing the volume fraction of the strong phase of inclusions.

This variation in the properties of polymers along their interfaces with inclusions is extended to layers of a sometimes significant thickness. This follows from the fact that, if only a thin surface-layer of the polymer was affected by its contact with the other phase, then the change in T_g should be insignificant, since the level of the glass transition temperature
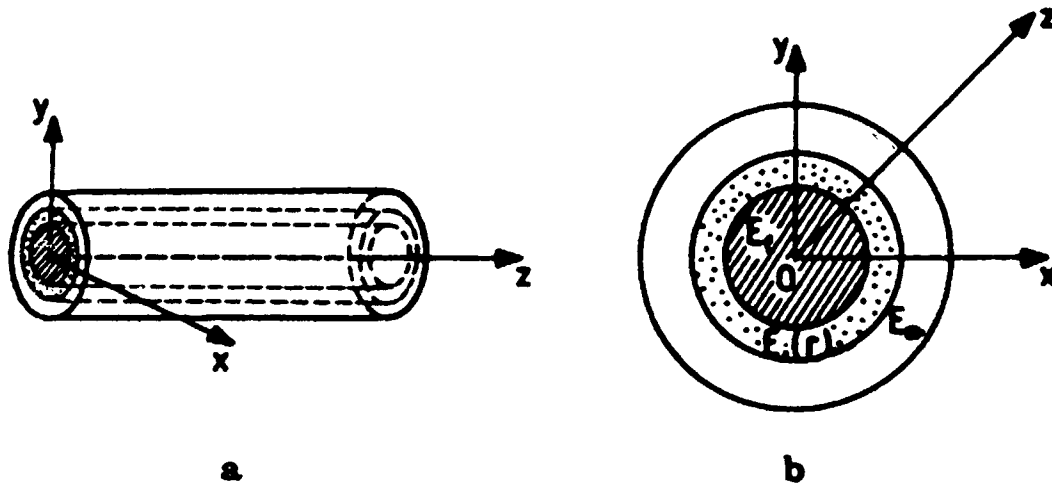
Figure 1 (a) Schematic representation of the model used for the representative volume element of a unidirectional fiber composite, (b) Cross-sectional area.

is associated with the bulk of the polymer, or, at least, with a large portion of it.

The same phenomena appear when the volume fraction of the strong inclusions is increased. In this case, if the adhesion of the main phases is satisfactory, an increase of v_f means an automatic increase of the strong boundary layer (stronger than the matrix) forming the interphases and this results forcibly to an increase in T_g.

A considerable amount of experimental work indicates a variation of T_g in composites with an increase of the filler. The degree, however, of this variation and the character of its change may differ from composite to composite and also, for the same composite, depending on the method used for its measurement.[21]

Moreover, if calorimetric measurements are executed in the neighbourhood of the glass transition zone, it is easy to show that jumps of energies appear in this neighborhood. These jumps are very sensitive to the amount of filler added to the matrix polymer and they were used for the evaluation of the boundary layers developed around fillers.

The experimental data show that the magnitude of the heat capacity (or similarly of the specific heat) under adiabatic conditions decreases regularly with the increase of filler content. This phenomenon was explained by the fact that the macromolecules, appertaining to the interphase layers, are totally or partly excluded to participate in the cooperative process, taking place in the glass-transition zone, due to their interactions with the surfaces of the solid inclusions.

Moreover the increment of the fiber volume fraction increases the proportion of macromolecules

which are in contact with fiber surface and are characterized by a reduced mobility. This is equivalent with an increase in interphase volume fraction and leads to the conclusion reported in ref. 21, stating that a relation holds between ΔC_p, which expresses the sudden change in the heat capacity at the glass transition region, and the interphase volume fraction v_i. This relation is expressed by:

$$\left(\frac{r_f + \Delta r_i}{r_f}\right)^2 - 1 = \frac{\lambda}{1 - v_f} \qquad (9)$$

where Δr_i is the thickness of the interphase and the parameter λ is given by:

$$\lambda = 1 - \frac{\Delta C_p^f}{\Delta C_p^o} \qquad (10)$$

in which ΔC_p^f and ΔC_p^o are the sudden changes of the heat capacity for the filled and the unfilled polymer respectively.

Let us consider the cylindrical model of a cross-section as described in Figure 1(b). In order to find the elastic transverse modulus a radial pressure p_1 is applied to the surface of the composite cylinder such that:

$$p_1 = \frac{(\sigma_{xx} + \sigma_{yy})}{2} \qquad (11)$$

Let us also assume that an axial stress is applied to it such that the axial strain is zero. This particular problem is an axisymmetric one, so that the displacements strains and stresses depend only on the

r-coordinate and they are independent of the polar angle θ. Then by using the Airy stress-function, Φ the compatibility equation can be expressed by:

$$\nabla^4\Phi = \frac{d^4\Phi}{dr^4} + \frac{2}{r}\frac{d^3\Phi}{dr^3} - \frac{1}{r^2}\frac{d^2\Phi}{dr^2} + \frac{1}{r^3}\frac{d\Phi}{dr} = 0 \quad (12)$$

This equation has the form of an Euler differential equation whose solution is given by:

$$\Phi = C_1\ln r + C_2 r^2\ln r + C_3 r^2 + C_4 \quad (13)$$

Each one of the constituents of the composite material is characterized by a corresponding stress function. Thus the expressions for the stresses in each one of the phases is expressed by:

$$\sigma_{r,f} = \frac{1}{r}\frac{d\Phi_f}{dr} = \frac{A}{r^2} + B(1 + 2\ln r) + 2C \quad (14)$$

$$\sigma_{\theta,f} = \frac{d^2\Phi_f}{dr^2} = -\frac{A}{r^2} + B(3 + 2\ln r) + 2C \quad (15)$$

$$\sigma_{r,m} = \frac{1}{r}\frac{d\Phi_m}{dr} = \frac{F}{r^2} + G(1 + 2\ln r) + 2H \quad (16)$$

$$\sigma_{\theta,m} = \frac{d^2\Phi_m}{dr^2} = -\frac{F}{r^2} + G(3 + 2\ln r) + 2H \quad (17)$$

$$\sigma_{r,i} = \frac{1}{r}\frac{d\Phi_i}{dr} = \frac{K}{r^2} + L(1 + 2\ln r) + 2M \quad (18)$$

$$\sigma_{\theta,i} = \frac{d^2\Phi_i}{dr^2} = -\frac{K}{r^2} + (3 + 2\ln r) + 2M \quad (19)$$

In order to avoid infinite stresses at $r = 0$ the constants A and B take the values $A = B = 0$. Thus it is valid that:

$$\sigma_{r,f} = \sigma_{\theta,f} = 2C \quad (20)$$

For the matrix and interphase materials it can be shown by taking into consideration the strain conditions that: $G = L = 0$. Thus it may be obtained that

$$\sigma_{r,m} = \frac{F}{r^2} + 2H \qquad \sigma_{\theta,m} = -\frac{F}{r^2} + 2H \quad (21)$$

$$\sigma_{r,i} = \frac{K}{r^2} + 2M \qquad \sigma_{\theta,i} = -\frac{K}{r^2} + 2M \quad (22)$$

The condition that the axial strain be zero gives:

$$\epsilon_{z,f} = \frac{1}{E_f}[\sigma_{z,f} - \nu_f(\sigma_{r,f} + \sigma_{\theta,f})] = 0$$

$$\epsilon_{z,m} = \frac{1}{E_m}[\sigma_{z,m} - \nu_m(\sigma_{r,m} + \sigma_{\theta,m})] = 0$$

$$\epsilon_{z,i} = \frac{1}{E_i}[\sigma_{z,i} - \nu_i(\sigma_{r,i} + \sigma_{\theta,i})] = 0$$

Substituting the stresses from eqs (20), (21), and (22) and solving for the axial stresses we find:

$$\sigma_{z,f} = 4C\nu_f, \quad \sigma_{z,m} = 4H\nu_m, \quad \sigma_{z,i} = 4M\nu_i \quad (23)$$

The radial displacements are given as:

$$u_{r,f} = r\epsilon_{\theta,f} = \frac{2C}{E_f}(1 - \nu_f - 2\nu_f^2)r \quad (24)$$

$$u_{r,m} = r\epsilon_{\theta,m}$$
$$= \frac{r}{E_m}\left[-\frac{F}{r^2}(1 + \nu_m) + 2H(1 - \nu_m - 2\nu_m^2)\right] \quad (25)$$

$$u_{r,i} = r\epsilon_{\theta,i}$$
$$= \frac{r}{E_i}\left[-\frac{K}{r^2}(1 + \nu_i) + 2M(1 - \nu_i - 2\nu_i^2)\right] \quad (26)$$

The boundary conditions are:

At $r = r_f$: $\sigma_{r,f} = \sigma_{r,i} \rightarrow 2C = \frac{K}{r_f^2} + 2M$ $\quad$ (27)

At $r = r_i$: $\sigma_{r,i} = \sigma_{r,m} \rightarrow \frac{K}{r^2} + 2M = \frac{F}{r^2} + 2H$ $\quad$ (28)

At $r = r_f$: $u_{r,f} = u_{r,i} \rightarrow$

$$2C(1 - \nu_f - 2\nu_f^2)E_i$$
$$= E_f\left[-\frac{K}{r_f^2}(1 + \nu_i) + 2M(1 - \nu_i - 2\nu_i^2)\right] \quad (29)$$

At $r = r_i$: $u_{r,i} = u_{r,m} \rightarrow$

$$E_m\left[2M(1 - \nu_i - 2\nu_i^2) - \frac{K}{r_i^2}(1 + \nu_i)\right]$$
$$= E_i\left[2H(1 - \nu_m - 2\nu_m^2) - \frac{F}{r_i^2}(1 + \nu_m)\right] \quad (30)$$

At $r = r_m$: $\sigma_{r,m} = -p_{22} \rightarrow \frac{F}{r_m^2} + 2H = -p_1$ $\quad$ (31)

In order to find the solutions of the eqs. (27) to (31) we shall try different laws of variation expressing $E_i(r)$ and $v_i(r)$ in the interphase zone, as assumed in the development of the model.

Linear Variation

The first approximation is the linear variation for $E_i(r)$ and $v_i(r)$. According to this variation these quantities are given as:

$$E_i(r) = P + Qr \quad \text{and}$$

$$v_i(r) = R + Sr \quad \text{with } r_f \leqslant r \leqslant r_i \quad (32\text{a,b})$$

where P, Q, R, S are functions of the moduli and the radii of the main phases of the composite. In order to evaluate them we consider the following boundary conditions:

$$\text{At } r = r_f : E_i = E_f \quad \text{and} \quad v_i = v_f$$

$$r = r_i : E_i = E_m \quad \text{and} \quad v_i = v_m$$

Substituting these values in Eq. (32a,b) we obtain:

$$E_i(r) = \frac{E_f r_i - E_m r_f}{r_i - r_f} - \frac{E_f - E_m}{r_i - r_f} r \quad (33)$$

and

$$v_i(r) = \frac{v_f r_i - v_m r_i}{r_i - r_f} + \frac{v_m v_f}{r_i - r_f} r \quad (34)$$

Hyperbolic Variation

For this variation we assume:

$$E_i(r) = P + \frac{Q}{r} \quad \text{and}$$

$$v_i(r) = R + \frac{S}{r} \quad \text{with } r_f < r < r_i \quad (35\text{a})$$

With the previous boundary conditions we have:

$$E_i(r) = \frac{E_m r_i - E_f r_f}{r_i - r_f} + \frac{(E_f - E_m) r_i r_f}{(r_i - r_f) r} \quad (36)$$

and

$$v_i(r) = \frac{v_m r_i - v_f r_f}{r_i - r_f} - \frac{(v_m - v_f) r_i r_f}{(r_i - r_f) r} \quad (37)$$

Parabolic Variation

For this variation we assume:

$$E_i(r) = Nr^2 + Pr + Q \quad \text{and}$$

$$v_i(r) = Rr^2 + Sr + T \text{ with } r_f \leqslant r \leqslant r_i \quad (38\text{a,b})$$

In addition to the previous boundary conditions we also assume that the parabolas representing these variations must have their minimum values for E_i and their maximum values for v_i at $r = r_i$. Thus:
At

$$r = r_i : \frac{dE_i}{dr} = 0 \quad \text{with } \frac{d^2 E_i}{dr} > 0 \quad \text{and}$$

$$\frac{dv_i}{dr} = 0 \quad \text{with } \frac{d^2 v_i}{dr^2} > 0$$

By applying all the boundary conditions we find:

$$E_i(r) = \frac{E_f - E_m}{(r_i - r_f)^2} r^2 - \frac{2(E_f - E_m) r_i}{(r_i - r_f)^2} r$$
$$+ \frac{E_f r_i^2 + E_m r_f^2 - 2 E_m r_f r_i}{(r_i - r_f)^2} \quad (39)$$

and

$$v_i(r) = \frac{v_f - v_m}{(r_i - r_f)^2} r^2 + \frac{2(v_m - v_f) r_i}{(r_i - r_f)^2}$$
$$+ \frac{v_f r_i^2 - v_m r_f^2 - 2 v_m r_f r_i}{(r_i - r_f)^2} \quad (40)$$

The solution of the system of eqs. (27) to (31) after the substitution of the expressions $E_i(r)$ and $v_i(r)$ for each variation yields the unknown constants C, F, H, K, and M.

The Transverse Elastic Modulus

The transverse elastic modulus E_T of the composite can be obtained by applying the energy balance to the composite cylindrical model. The strain energy of the system must be equal to the sum of the strain energies of the fiber, interphase, and matrix. Thus

$$\frac{1}{2} \int_{V_c} \frac{P_1^2}{K_c} dV_c$$

$$= \frac{1}{2} \int_{V_f} (\sigma_{r,f} \epsilon_{r,f} + \sigma_{\theta,f} \epsilon_{\theta,f} + \sigma_{z,f} \epsilon_{z,f}) dV_f$$

$$+ \frac{1}{2} \int_{V_i} (\sigma_{r,i}\epsilon_{r,i} + \sigma_{\theta,i}\epsilon_{\theta,i} + \sigma_{z,i}\epsilon_{z,i}) \, dV_i \quad (41)$$

$$+ \frac{1}{2} \int_{V_i} (\sigma_{r,i}\epsilon_{r,i} + \sigma_{\theta,i}\epsilon_{\theta,i} + \sigma_{z,i}\epsilon_{z,i}) \, dV_i$$

The expressions for the strains of the three phases are obtained from the stress–strain relationships as follows:

$$\epsilon_{r,f} = \frac{2C}{E_f} (1 - \nu_f - 2\nu_f^2) \quad (42)$$

$$\epsilon_{\theta,f} = \frac{2C}{E_f} (1 - \nu_f - 2\nu_f^2) \quad (43)$$

$$\epsilon_{r,m} = \frac{1}{E_m} \left[-\frac{F}{r^2} (1 + \nu_m) \right.$$
$$\left. + 2H(1 - \nu_m - 2\nu_m^2) \right] \quad (44)$$

$$\epsilon_{\theta,m} = \frac{1}{E_m} \left[-\frac{F}{r^2} (1 + \nu_m) \right.$$
$$\left. + 2H(1 - \nu_m - 2\nu_m^2) \right] \quad (45)$$

$$\epsilon_{r,i} = \frac{1}{E_i} \left[-\frac{K}{r^2} (1 + \nu_i) + 2M(1 - \nu_i - 2\nu_i^2) \right] \quad (46)$$

$$\epsilon_{\theta,i} = \frac{1}{E_i} \left[-\frac{K}{r^2} (1 + \nu_i) + 2M(1 - \nu_i - 2\nu_i^2) \right] \quad (47)$$

Assuming the composite material to be macroscopically homogeneous and to obey Hooke's law, the following stress-strain relationships are applicable.

$$\epsilon_{xx} = \frac{1}{E_T} [\sigma_{xx} - \nu_{TT}\sigma_{yy}] - \left(\frac{\nu_{LT}}{E_L}\right)\sigma_{zz} \quad (48)$$

$$\epsilon_{yy} = \frac{1}{E_T} [\sigma_{yy} - \nu_{TT}\sigma_{xx}] - \left(\frac{\nu_{LT}}{E_L}\right)\sigma_{zz} \quad (49)$$

$$\epsilon_{zz} = \frac{1}{E_L} [\sigma_{zz} - \nu_{LT}(\sigma_{xx} + \sigma_{yy})] \quad (50)$$

In the relationships E_L, E_T denote the elastic longitudinal and transverse moduli of the composite and ν_{LT}, ν_{TT} the Poisson's ratios in longitudinal and transverse directions, respectively.

The bulk modulus K_c of the composite can be found by considering the change in volume caused by the applied pressure p_1.

$$1 + \Delta V = (1 + \epsilon_{xx})(1 + \epsilon_{yy})(1 + \epsilon_{zz}) \approx \epsilon_{xx} + \epsilon_{yy}$$

since $\epsilon_{zz} = 0$

This yields:

$$\sigma_{zz} = \nu_{LT}(\sigma_{xx} + \sigma_{yy})$$

Using the above stress-strain relationships $\Delta V/V$ can be found as:

$$\frac{\Delta V}{V} = 2p_1 \left[\frac{1 - \nu_{TT}}{E_T} - \frac{2\nu_{LT}^2}{E_L} \right] \quad (51)$$

The bulk modulus K_c will be:

$$K_c = \frac{P_1}{\Delta V/V} = \frac{1}{2\left[\dfrac{1 - \nu_{TT}}{E_T} - \dfrac{2\nu_{LT}^2}{E_L} \right]} \quad (52)$$

We introduce the stress relationships from eqs. (20)–(22) the strain relationships from eqs. (42)–(47), and the values of the constants in the right hand side; the value of the bulk modulus in the left-hand side of Eq. 41. Next, after some algebra the final expression for the elastic transverse modulus of the composite is obtained by using eqs. (8). We find for E_T:

$$\frac{1 - \nu_{TT}}{E_T} - \frac{2\nu_{LT}^2}{E_L} = \frac{1}{E_f} (1 - \nu_f - 2\nu_f^2)v_f$$

$$+ \frac{1}{E_m} (1 - \nu_m - 2\nu_m^2)v_m$$

$$+ \frac{2v_f}{r_f^2} \int_{r_f}^{r_i} \frac{(1 - \nu_i(r) - 2\nu_i^2(r))}{E_i(r)} r \, dr \quad (53)$$

Longitudinal Elastic Modulus E and Poisson's Ratio ν_{LT}

For the calculation of E_T from eq. (53) the longitudinal elastic modulus E_L and Poisson's ratio ν_{LT} of the composite are given in ref. 18 as follows:

$$E_L = E_f v_f + \left(\frac{1 - \nu_m - 2\nu_m^2}{E_m} + E_m \right)v_m$$

$$+ \tfrac{1}{3}\{ (E_f + 2E_m)(1 - v_m) - (2E_f + E_m)v_f$$

$$+ (E_f - E_m)[v_f(1 - v_m)]^{1/2}\} \quad (54)$$

and

$$\nu_{LT} = \nu_f v_f + \nu_m v_m + \tfrac{1}{3}\{ (\nu_f + 2\nu_m)(1 - v_m)$$

$$- (2\nu_f + \nu_m)v_f + (\nu_f - \nu_m)[v_f(1 - v_m)]^{1/2}\} \quad (55)$$

for linear variation.

$$E_L = E_f v_f + \left(\frac{1 - \nu_m - 2\nu_m^2}{E_m} + E_m\right) v_m$$

$$+ 2(E_f - E_m)[v_f^{1/2}(1 - v_m)^{1/2}] \quad (56)$$

$$+ [E_m(1 - v_m)^{1/2} - E_f v_f^{1/2}][(1 - v_m)^{1/2} + v_f^{1/2}]$$

and

$$\nu_{LT} = \nu_f v_f + \nu_m v_m + [\nu_m(1 - v_m)^{1/2} - \nu_f v_f^{1/2}]$$

$$\times [(1 - v_m)^{1/2} + v_f^{1/2}]$$

$$+ 2(\nu_f - \nu_m)[v_f(1 - v_m)]^{1/2} \quad (57)$$

for hyperbolic variations.

$$E_L = E_f v_f + \left(\frac{1 - \nu_m - 2\nu_m^2}{E_m} + E_m\right) v_m + \frac{3(E_f - E_m)[(1 - v_m)^{3/2} + v_f^{1/2}(1 - v_m) + v_f(1 - v_m)^{1/2} + v_f^{3/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]}$$

$$- \frac{8(E_f - E_m)(1 - v_m)^{1/2}[1 - v_m + v_f + [v_f(1 - v_m)]^{1/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]}$$

$$+ \frac{6\{E_f(1 - v_m) + E_m v_f - 2E_m[v_f(1 - v_m)]^{1/2}\}[(1 - v_m)^{1/2} + v_f^{1/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]} \quad (58)$$

and

$$\nu_{LT} = \nu_f v_f + \nu v_m + \frac{3(\nu_f - \nu_m)[(1 - v_m)^{3/2} + v_f^{1/2}(1 - v_m) + v_f(1 - \mu_m)^{1/2} + v_f^{3/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]}$$

$$- \frac{8(\nu_f - \nu_m)(1 - v_m)^{1/2}[1 - v_m + v_f + [v_f(1 - v_m)]^{1/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]}$$

$$+ \frac{6[\nu_f(1 - v_m) + \nu_m v_f - 2\nu_m[v_f(1 - v_m)]^{1/2}][(1 - v_m)^{1/2} + v_f^{1/2}]}{6[(1 - v_m)^{1/2} - v_f^{1/2}]} \quad (59)$$

for parabolic variation.

Transverse Poisson's ratio ν_{TT}

The Poisson ratio ν_{TT} of the composite can be calculated by the law of mixtures eq. (22), modified in order to include the interphase.

$$\frac{1}{\nu_{TT}} = \frac{v_f}{\nu_f} + \frac{v_m}{\nu_m} + \frac{v_i}{\nu_i(r)}$$

which yields:

$$\frac{1}{\nu_{TT}} = \frac{v_f}{\nu_f} + \frac{v_m}{\nu_m} + \frac{r_i^2 - r_f^2}{r_m^2 \nu_i(r)}$$

Since $\nu_i(r)$ is assumed to be variable in the inter-

phase region, the relationship takes the following form in order to take into account this variation:

$$\frac{1}{\nu_{TT}} = \frac{v_f}{\nu_f} + \frac{v_m}{\nu_m} + \frac{2}{r_f^2} \int_{r_f}^{r_i} \frac{[(r + dr)^2 - r^2] \, dr}{\nu_i(r)}$$

which finally gives:

$$\frac{1}{\nu_{TT}} = \frac{v_f}{\nu_f} + \frac{v_m}{\nu_m} + \frac{2v_f}{r_f^2} \int_{r_f}^{r_i} \frac{r \, dr}{\nu_i(r)} \quad (60)$$

Thus, it enables the calculation of a theoretical value for the Poisson's ratio ν_{TT} by introducing the assumed law of variation of ν_i.
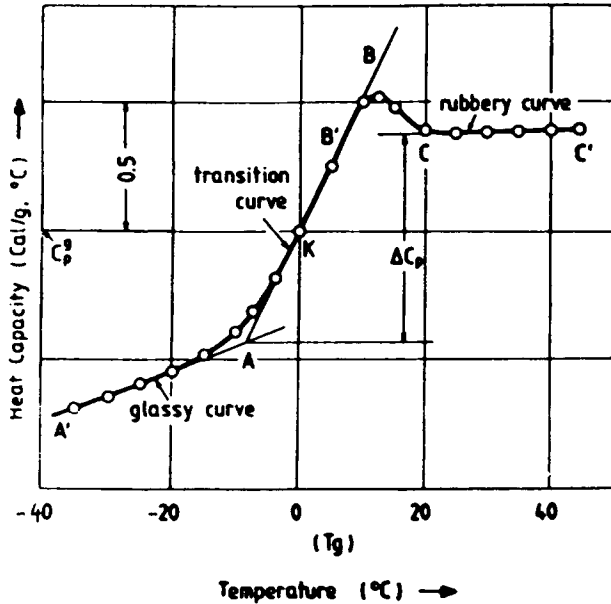
Figure 2 A typical DSC-trace for the specific heat jump ΔC_p at the glass-transition region of E-glass fiber epoxy composites and the mode of evaluation of ΔC_p's.

EXPERIMENTAL WORK

The unidirectional glass-fiber composites used in the present investigation consisted of an epoxy matrix (Permaglass XE5/1, Permali Ltd., U.K.) reinforced with long E-glass fibers. The matrix material was based on a diglycidyl ether of bisphenol A together with an aromatic amine hardener (Araldite MY 750/HT972, Ciba-Geigy, U.K.). The glass fibres had a diameter of 1.2×10^{-5} m and were contained at a volume fraction $v_f = 0.65$.

The volume fraction v_f was determined, as customary, by igniting samples of the composite and weighting the residue, which gave the weight fraction of glass as: $w_f = 79.6 \pm 0.28\%$. This and the measured values of the relative densities of permaglass ($\rho_f = 2.55$ gr/cm^3) and of the epoxy matrix ($\rho_m = 1.20$ gr/cm^3) gave the value $v_f = 0.65$. The experiments which have been carried out on five specimens gave for the transverse elastic modulus the mean value $E_T = 16.2 GN/m^2$ with crosshead speed 0.2 cm/min.

On the other hand, chip specimens with a 0.004 m diameter and thicknesses varying between 0.001 and 0.0015 m made either of the fiber composite of different v_f's, or of the matrix material, were tested on a differential scanning calorimetry (DSC) Thermal Analyzer at the zone of the glass transition temperature for each mixture, in order to determine the specific heat capacity values.

The values of the weight factor λ were derived from the values of ΔC_p^f and ΔC_p^0 measured on the $\Delta C_p = f(T)$ diagrams according to Fig. 2. The values of λ determined from these DSC tests allowed the evaluation of the thickness Δr_i of the interphase for each composite.

It has been shown that for unidirectional fiber-reinforced composites the simple relation between the volume fraction of interphase, v_i, and v_f holds:

$$v_i = C v_f^2$$

with the constant C for our case found to be[18]

$$C = 0.123$$

Table I gives the values of v_i and Δr_i's for the various fiber–volume contents, as they have been derived from our tests.

Figure 3 presents the variation of ΔC_p's at the glass transition temperature, the weight factor λ, as well as the values v_i and v_m, versus the fiber volume content v_f in the E-glass fiber-reinforced composites.

Introducing now the values for $r_i = r_f + \Delta r_i$ and v_i for the various fiber volume contents into eqs. (53) and (60), respectively, we may calculate the values for the transverse elastic modulus of the composite, E_T, corresponding to the three laws of variation of the E_i and ν_i moduli considered in the paper.

The calculations for the transverse elastic modulus E_T, were carried out with $E_f = 72$ GN/m^2 and $E_m = 3.5$ GN/m^2 for the fiber and matrix moduli, and $\nu_f = 0.20$ and $\nu_m = 0.35$ for their Poisson's ratios respectively.

Table I Values of Interphase Thickness ($\Delta r_i = r_i - r_f$) and Volume Fraction v_i Versus Fibre Volume Fraction v_f

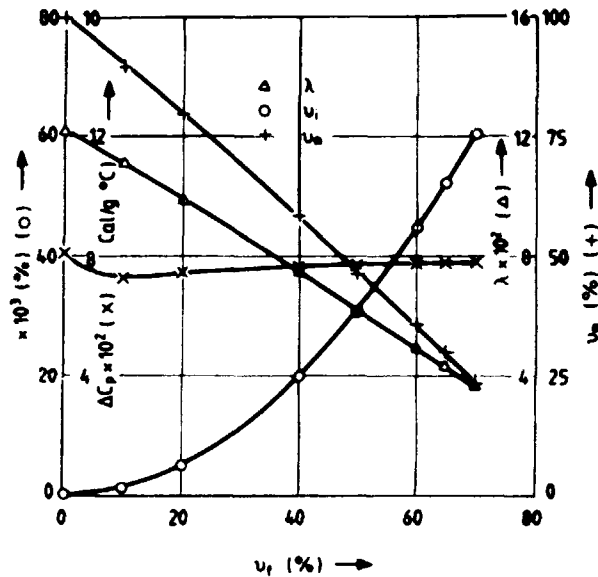| v_f	r_i (μm)	v_i
0.0	6.0	0.0
0.10	6.037	1.20×10^{-3}
0.20	6.073	4.92×10^{-3}
0.30	6.110	11.07×10^{-3}
0.40	6.146	19.68×10^{-3}
0.50	6.182	30.75×10^{-3}
0.60	6.217	44.28×10^{-3}
0.70	6.254	60.27×10^{-3}
0.80	6.288	78.22×10^{-3}

Figure 3 The variation of the specific heat jumps ΔC_p at glass transition temperature of E-glass fiber epoxy composites, versus the fiber volume content, v_f as well as the values of λ-factor, the interphase, volume and matrix contents v_i and v_m.

RESULTS AND DISCUSSION

The values of the interphase–volume fraction, as well as its thickness for various fiber–volume fractions are given in Table I. These results were evaluated from the experimentally obtained values of the sudden change in heat capacity in the transition region of filled and unfilled specimens and then introducing these values into eqs. (8)-(10).

From this table it is clear that Δr_i and v_i are increasing functions (at least up to a certain value) of the fiber volume fraction. This type of variation is consistent with the fact that, because of the existence of fibers, a part of macromolecules that are in the close vicinity of the fiber surface, that is within the interphase region are characterized by a reduced mobility. As a result of this type of behaviour of these macromolecules, the higher the fiber content, the larger fiber surface and, consequently, the higher amount of macromolecules with reducing mobility are developed in the matrix material.

In Figure 4 and in Table II the theoretical values of the transverse elastic modulus E_T calculated from eq. (53) are presented in respect of fiber content v_f. The theoretical values of the transverse Poisson's ratio ν_{TT} as calculated by the interphase model from eq. (60) and used in eq. (53) are given in Table III, together with other theoretical values from the literature. The predictions of E_T by the procedure described in previous section, were compared with the respective values given by eqs. (1), (2), and (4)-(7). This comparison reveals discrepancies. Any agreement between two predictions can be observed only for some fiber contents. However it can be seen that there is a good correlation between the values given by eq. (53) and those predicted by Halpin and Tsai[14] and given by eq. (7). The predictions of Whitney and Riley[8] given by eq. (2) are closer to those of Tsai[13] given by eq. (4) with $c = 0$. The values calculated by eq. (4) but with $c = 1$ are very high and differ very much from all others.

If we compare the theoretical predictions with the experimental values presented in the same figure,

Table II Theoretical Values of the Transverse Elastic Modulus E_T Given By the Interphase Model and Other Theories

	E_T(GN/m^2) Interphase Model (eq. 53)			Lower Bound[1] [eq. (1)]	Tsai[13] eq. (4)		Whitney Riley[4] eq. (2)	Halpin Tsai[14] eq. (5)	Ekvall[20] eq.		Sih[28]
v_f	Linear	Hyperbolic	Parabolic		$c = 0$	$c = 1$			(6)	(7)	
0.0	3.50	3.50	3.50	3.50	3.50	3.50	3.50	3.50	4.64	3.50	3.50
0.10	5.33	5.33	5.32	3.87	4.03	5.37	5.13	4.50	5.12	4.21	4.13
0.20	6.57	6.57	6.56	4.32	4.68	7.61	6.08	5.70	5.70	4.78	4.55
0.30	7.90	7.90	7.88	4.90	5.53	10.34	6.98	7.19	6.45	5.45	
0.40	9.52	9.52	9.48	5.65	6.62	13.69	8.02	9.08	7.41	6.31	
0.50	11.70	11.70	11.60	6.68	8.09	17.87	9.31	11.54	8.74	7.46	9.16
0.60	14.93	14.93	14.67	8.16	10.18	23.19	11.04	14.88	10.57	9.11	11.71
0.70	20.25	20.20	19.64	10.48	13.38	30.10	13.53	19.71	13.44	11.67	
0.80	30.93	30.81	29.22	14.65	18.91	39.41	17.48	27.27	18.43	16.20	

Theoretical curves

Eq. " (4, c=1)
" (53, hyp.)
" (53, par.)
" (5)

Experimental values "

∇ Authors
○ Gresczuk [29]
□ Ogorkiewicz-Weidman [25]
× Clements Moore [26]
+ Sih [28]
■ Ogorkiewicz [24]
△ Tsai [13]

E_T (GN/m²)

Eq. (2)
" (6)
" (4, c=0)
" (7)
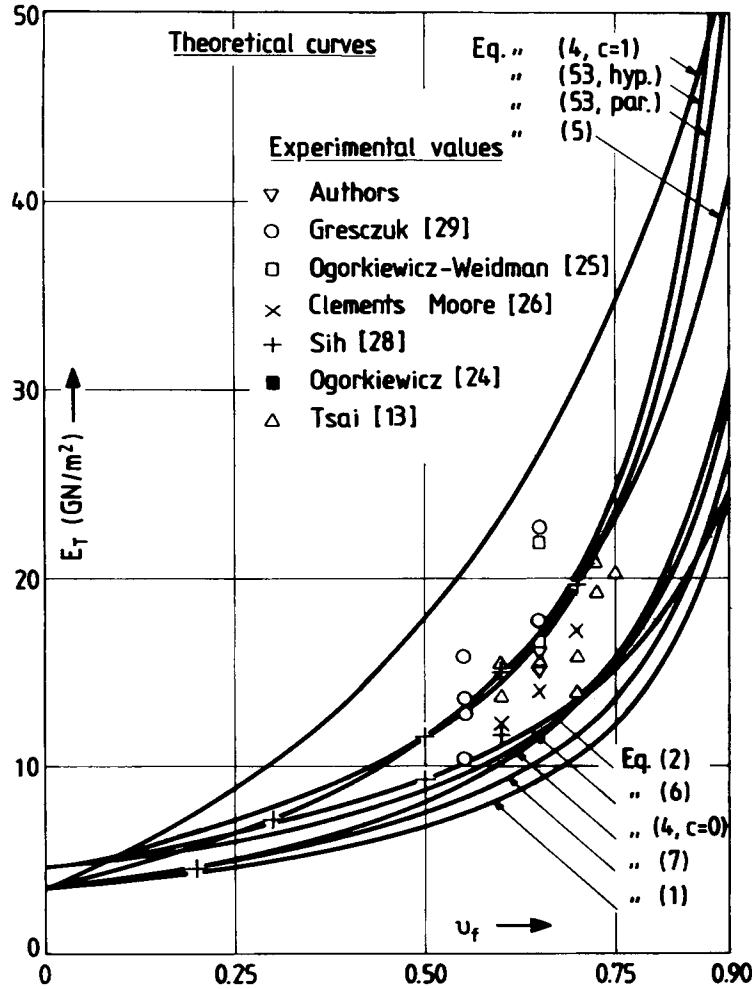" (1)

$v_f \longrightarrow$

Figure 4   Theoretical predictions of transverse elastic modulus E_T obtained by the interphase model, compared with those from other theories and with experimental values.

we may also observe discrepancies. Only the experimental value for $v_f = 0.65$ obtained by Ogorkiewicz and Weidman[25] is in perfect agreement with that obtained in this work. They are also in good agreement with the theoretical values obtained from eqs. (5) and (53). The experimental results given by Clements and Moore[27] are situated between the theoretical curves given by eqs. (53) and (5) in one part and eqs. (2) and (4) in the other part. For $v_f = 0.65$ there is an agreement with the experimental value given in ref. 27. Also we may observe that the experimental results obtained by Sih et al.[28] are closer to the theoretical curves given by eqs. (2) and (4) for $c = 0$. Finally the experimental value obtained by Ogorkiewicz[24] for $v_f = 0.65$, is superior to the theoretical values except those of Tsai[13] for $c = 1$.

A slight difference of the predictions given by eq. (53) with respect to the experimental results might

have been expected because of the alignment of the fibers which is very difficult to achieve during the preparation of the specimens.

In addition to the misalignment of the fibers, a great part of the discrepancies observed between theory and experiment can be attributed to the interaction between the fibers, that it is not taken into account in the theoretical development and to the adhesion efficiency between fibers and matrix. This latter may be incorporated in the extent of the interphase which in this way, takes into account any imperfections in the adhesion of the phases.

From the comparison of the selected laws of variation for both the elastic modulus $E_i(r)$ and Poisson's ratio $v_i(r)$, it becomes clear that there are no serious discrepancies between the values predicted by the various approximate expressions for the variation of $E_i(r)$ and $v_i(r)$. The linear and hyperbolic

**Table III   Theoretical Values of the Transverse Poisson's Ratio v_{TT}
as Calculated by the Interphase Model and Other Theories**

v_f	v_{TT} Interphase Model eq. (60)			Lower Bound[1]	Tsai[13] $c = 0$	Halpin Tsai[14]	Sih[28]
	Linear	Hyperbolic	Parabolic				
0.0	0.350	0.350	0.350	0.350	0.350	0.350	0.350
0.10	0.325	0.325	0.326	0.326	0.332	0.333	0.330
0.20	0.304	0.304	0.304	0.304	0.315	0.316	0.320
0.30	0.285	0.285	0.285	0.286	0.298	0.300	
0.40	0.268	0.268	0.268	0.269	0.283	0.284	
0.50	0.253	0.253	0.253	0.255	0.267	0.269	0.300
0.60	0.239	0.239	0.240	0.242	0.253	0.254	0.290
0.70	0.227	0.227	0.228	0.230	0.239	0.240	
0.80	0.216	0.216	0.217	0.219	0.225	0.226	

variation of the interphase properties give slightly greater values for E_T than the parabolic and this for $v_f > 0.5$. It seems that the choice of a specific law of variation is not crucial.

However, if we take into consideration the condition of a smooth variation of $E_i(r)$, i.e., $dE_i(r)dr|_{r=r_i} = 0$, then the parabolic variation, which satisfies approximately this condition, must be accepted as the best of all approximations.

CONCLUSIONS

The majority of theoretical models, describing the physical and mechanical properties of composites, consider the surfaces of inclusions as perfect mathematical surfaces. In this way, the transition of the mechanical properties from the one phase to the other is done by jumps in the characteristic properties of either phase. This fact introduces high-shear straining at the boundaries, which is an unrealistic fact.

In order to alleviate this singular and unrealistic situation, a model was presented in this study, in which a third phase, the interphase, was considered as developed along a thin boundary layer between phases, during the polymerization of the matrix, whose properties depend on the individual properties of the phases and the quality of adhesion between them.

This kind of interphase, which was also detected by experimental methods, possesses variable properties, accommodating the two extremes between inclusions and matrices.

In our work, by using Lipatov's theory interrelating the abrupt jumps in the specific heat of composites at the glass transition temperature with the

values of the extents of these boundary layers, the thickness of the interphase was calculated.

It was observed that the interphase which is created between the fibers and the polymeric matrix of the unidirectional fiber composites, influence the effective properties of the composites. In this paper a new relation for the transverse elastic modulus was derived, which takes into account the above mentioned interphase layer. This was succeeded by considering the contribution of interphase, which is an inhomogeneous phase between the fiber and the matrix in the concept of the well known Hashin–Rosen model.

The new relation yields satisfactory results when it is compared with existing experimental data and other theoretical formulae of the literature. The theoretical predictions of this relation are in better agreement with corresponding experimental results than other theoretical values which were derived from research works accepted as successful models for defining the transverse elastic modulus of unidirectional fiber composites.

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