

ΦΥΣΙΚΟΧΗΜΕΙΑ.— **The Unfolding Model for the Representation of the mesophase Layer in Fiber - Composites**, by *P. S. Theocaris**, ὑπὸ τοῦ Ἀκαδημαϊκοῦ κ. Π. Σ. Θεοχάρη.

A B S T R A C T

The adhesion between matrix and inclusions (fibers or particulates) in a composite material is one of principal factors characterizing the mechanical and physical behaviour of the modern composite materials. All theoretical models describing these substances neglect to consider the influence of the boundary layer developed between phases during the preparation of the composite.

In this paper two versions of a theoretical model were introduced for the evaluation of this mesophase layer. It had been shown that this thin layer influences considerably the physical properties of the composite. It was assumed that the physical properties of the *mesophase* «unfolds» from those of the hard-core fillers to those of the softer matrix. Thus, a multilayer model was assumed, improving the classical two-layered model introduced by Hashin and Rosen for the representative volume element of the composite.

Based on thermodynamic phenomena appearing at the glass transition temperatures of the composite and concerning the positions and the sizes of the heat-capacity jumps there, as well as on the experimental values of the longitudinal elastic modulus of the composite, the extent of the mesophase and the mechanical properties of the composite may be accurately evaluated.

These versions of model are based on a previous one concerning a multilayer model, which is then considerably improved, in order to take into consideration, in a realistic manner, the physical phenomena developed in fiber-reinforced composites.

I N T R O D U C T I O N

In all theoretical models introduced in the literature for explaining the mechanical behaviour of composites, the surfaces of phases are considered as perfect mathematical surfaces, whereas in reality they constitute rough surfaces with corners, cavities, protrusions and other irregularities, creating thin anomalous layers, instead of perfect surfaces. Although these irregularities are generally infinitesimal, they are capable to create material – and stress – concentrations, scattered irregularly on the interfaces. Moreover, the geometry of inclusions, especially in the fiber-reinforced composites causes

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the development of corners, re-entrant notches, microcracks and microprotrusions, which have the deleterious effect of developing stress singularities in their neighbourhood. All these anomalies are not predicted by any mathematical model introduced in the literature [1].

The polymeric matrix, cast on the surfaces of such inclusions, created phenomena of physical and chemical adsorption. *Physisorbed* layers of the matrix contribute, in general, to weak mesophases. However, the physical interpenetration of the boundary layer of the matrix in cavities and other rough regions of the surfaces of solid inclusions, interrelated with the biased development of the molecular structure of the polymeric chains there, and any other structural variations of the adjacent layers, create an intermixing and interpenetrating phenomenon, which influences considerably the molecular structure of the mesophase, thus resulting to variations of its mechanical strength. Thus, the mechanical properties of the matrix films and layers close to the interfaces, which are functions of the initial structure of the matrix, are strongly depending on the physical situation of this boundary layer.

On the other hand, *chemisorbed* (chemically adsorbed) molecules on the interfaces create structural variations, by developing beaded structures of caged molecules or ladder-like molecules. All these types of chemisorbed elements on inclusions lead to rapid variations of the properties and mechanical strength of the mesophase layer, close to the surfaces of inclusions.

Chemical bonding at the interface is generally considered to be a major reinforcement mechanism of coupling aging functioning. Chemical reactivities of these boundary layers determine to a considerable extent the configurations of the mesophase, by implying conformations to the molecules much different than those of the bulk, and variable from place to place. Random, block and graft copolymers may be yielded by these reactivities, depending on the local combinations of the materials there and their condition of reaction.

Then, around each inclusion (fiber or particulate) a complex state is developed, which consists of an intermediate boundary layer of variable thickness along the inclusions, where all these anomalies are concentrated and influence the physical behaviour of this layer. This zone is extended beyond the thin layer including the phenomena of *physisorption* and *chemisorption*, and it incorporates the zones of imperfect bonding and shrinkage stresses, the high stress gradients, or even stress singularities, due to geometric dis-

continuities of the surfaces of inclusions, to the concentration of voids and to the impurities, microcracks and other anomalies [2 to 6].

It has been proved that the thickness of this boundary layer is intimately correlated with the cohesion energy of the matrix polymer, the free surface energy of the solid inclusions and on the flexibility of the polymeric structure of the matrix [4].

In this paper the existence of the boundary layer, constituting the *mesophase*, and developed between the two main phases of a two-phase composite was taken into account for the development of a convenient model describing the thermomechanical behaviour of unidirectional fiber composites. This layer was assumed as developed entirely on the side of the softer polymeric matrix and the hard inclusion is considered as neutral. In the models the mesophase was assumed as an independent pseudo-phase of variable properties, matching those of the inclusion on the one side and the matrix on the other. The models are based on the same basic ideas as the Hashin-Rosen model [7]. The evaluation of the characteristic properties of the mesophase was achieved by introducing two variations of an improved law of mixtures between phases and measuring the glass transition temperatures and specific-heat jumps of the matrix and the composite. These unfolding models proved to be adaptable to the real situation in the composite, yielding satisfactory values for the mechanical properties of fiber composites.

MODELS FOR COMPOSITES

For the study of the overall behaviour of a composite it is necessary to average its microscale properties and geometry, in order to obtain its macroscale properties. The models introduced by Hashin [8] for the particulates and by Hashin and Rosen [7] for the fiber composites are of general acceptance. They assume in both cases representative volume elements of the materials consisting of a gradation of sizes of cells, corresponding to the volume filling configuration existing in the particular material studied. Moreover, a fixed ratio of radii between the spheres or the cylinders of the inclusions (r_f) and the respective quantities for the matrix (r_m) are assumed, in order to have the analysis of a single representative volume element (RVE), representing the behaviour of the entire composite.

Besides these simple geometric models, other types of models include

the so-called *self-consistent model*, according to which the average values for stresses and strains in either phase are determined by solving two separate problems, whose superposition yields the final configuration of the model. The solution of the two individual problems allows the evaluation of the average properties of the composite, by knowing the respective properties of either phase. The self-consistent model was applied to composites by Budiansky [9] and separately by Hill [10].

An important variation of the self-consistent model is the *three-phase model* introduced by Kerner [11]. In this model the inclusion is enveloped by a matrix layer, which is turn is embedded in an infinite medium with the unknown macroscopic properties of the composite.

A better approach for the Rosen-Hashin models is to adopt models, whose representative volume element consists of three phases, which are either concentric spheres for the particulates, or co-axial cylinders for the fiber-composites, with each phase maintaining its constant volume fraction [4].

The novel element in these models is the introduction of a third phase in the Hashin-Rosen model, which lies between the two main phases (inclusions and matrix) and contributes to the progressive unfolding of the properties of the inclusions to those of the matrix, without discontinuities. Then, these models incorporate all transition properties of a thin boundary-layer of the matrix near the inclusions. Thus, this pseudo-phase characterizes the effectiveness of the bond between phases and defines a adhesion factor of the composite.

These models are improvements of a similar model [1], where the third phase was assumed with constant mechanical properties lying in-between the two main-phases and defined by considering the limiting values of the thermo-mechanical properties of the composite in terms of the properties of its constituents. Fig. 1 presents principal sections of the models by Hashin and Rosen and the respective improvements by our models both for particulates and fiber-reinforced composites.

THE UNFOLDING MODELS

A decisive factor for the physical behaviour of a composite is the adhesion efficiency at the boundaries between phases. In all theoretical models this adhesion is considered as perfect, assuming that the interfaces

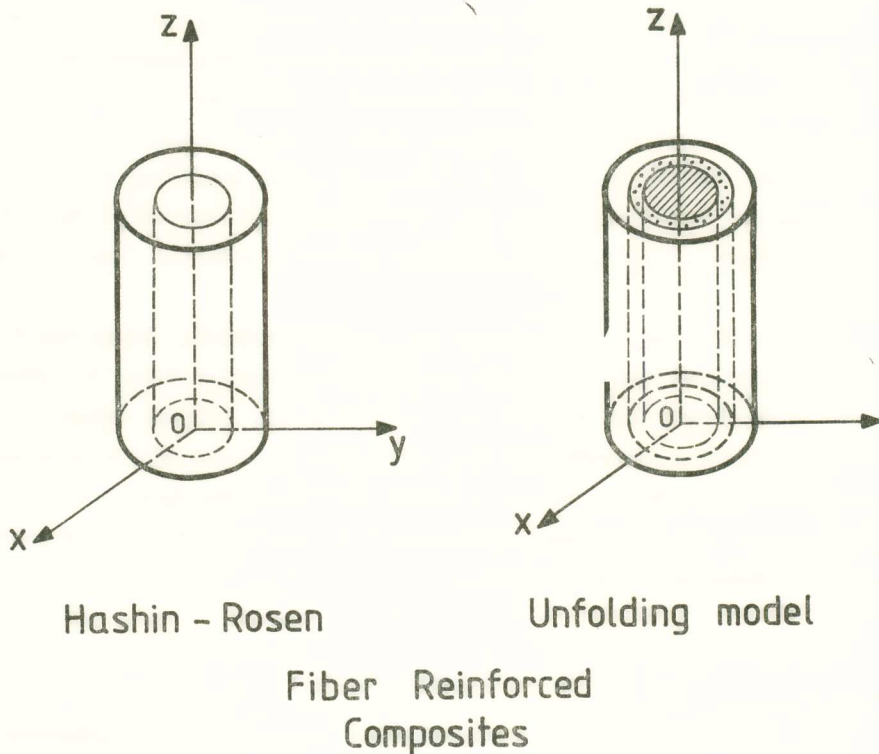
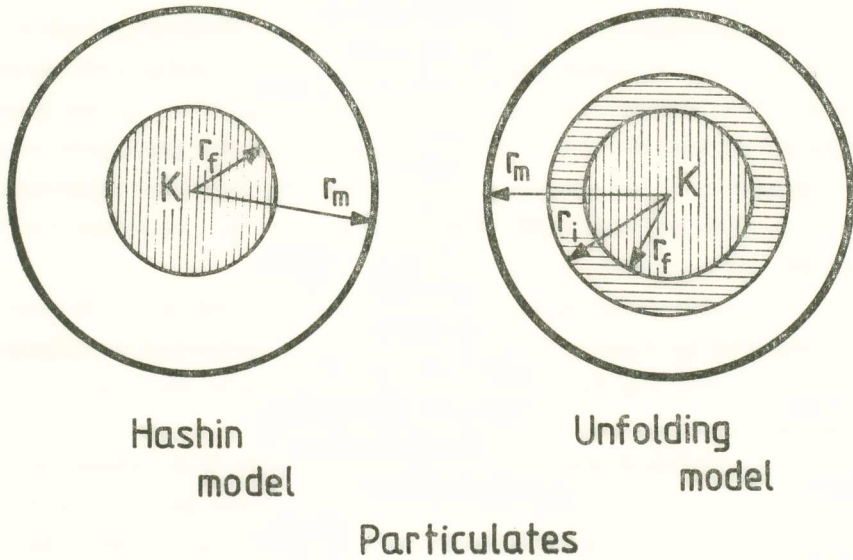


Fig. 1. Principal sections and axonometric vues of the Hashin-Rosen two-phase models and their respective three-layer unfolding models.

ensure continuity of stresses and displacements between phases, which should be different because of the proper nature of the constituents of composites. However, such conditions are hardly fulfilled in reality, leading to imperfect bonding between phases and variable adhesion between them. The introduction of the mesophase layer has as function to reconcile, in a smooth way, the differences on both sides of interfaces.

Thus, in the three-layer model, with the intermediate layer having variable physical properties (and perhaps also chemical), subscripts f, i, m and c denote quantities corresponding to the filler, mesophase, matrix and composite respectively. It is easy to establish for the representative volume element of a unidirectional fiber reinforced composite, consisting of a cluster of three co-axial cylinders of the same height, equal to unity, that the following relations hold:

$$\nu_f = \left(\frac{r_f^2}{r_m^2} \right), \quad \nu_i = \left(\frac{r_i^2 - r_f^2}{r_m^2} \right) \quad \text{and} \quad \nu_m = \left(\frac{r_m^2 - r_i^2}{r_m^2} \right) \quad (1)$$

Assuming the appropriate boundary conditions between the internal cylinder and any number of annuli surrounding it in the RVE of the composite, which assure continuity of radial stresses and displacements, according to the loading case considered we may establish readily, by an energy balance between phases, the well-known law of mixtures, valid for the longitudinal modulus $E_{CL} = E_c$ of the composite:

$$E_c = E_f \left(\frac{r_f^2}{r_m^2} \right) + E_i \left(\frac{r_i^2 - r_f^2}{r_m^2} \right) + E_m \left(\frac{r_m^2 - r_i^2}{r_m^2} \right) \quad (2)$$

This relation may be extended to any desired number n of coaxial cylinders.

If we assume further that the mesophase annulus consists of a material having progressively variable mechanical properties, in order to match the respective properties of the two main phases including the mesophase, we can define a variable elastic-modulus for the mesophase, which, for reasons of symmetry, depends only on the polar distance from the fiber-interface. In other words, we assume that the mesophase annulus consists of a series of elementary annuli, whose constant mechanical properties differ to each other by a quantity (small enough) defined by the law of variation of $E_i(r)$.

THE THREE-TERM VERSION OF THE UNFOLDING MODEL

In order to make compatible the variation of the $E_i(r)$ -modulus with its neighbour phases, this modulus should be expressed by three terms i.e.

i) a constant one and equal to the E_m -modulus.

ii) a variable one, depending on the modulus of the inclusion, E_f , which should be added to the first one, and

iii) a third variable-one, which should depend on the E_m -modulus of the matrix and which should be antagonistic to the second term.

The two variable terms should yield very abrupt variations in the $E_i(r)$ -modulus, since the generally large differences between the moduli of the inclusions and the matrix must be accommodated in very thin annuli for the mesophases. The appropriate functions for such steep variations are power functions of r with large exponents. Then, the $E_i(r)$ -modulus may be expressed by:

$$E_i(r) = E_m + E_f \left(\frac{r_f}{r} \right)^{\eta_1} - E_m \left(\frac{r_f}{r} \right)^{\eta_2} \quad (3)$$

Expression (3) may be interpreted by the fact that the variable $E_i(r)$ -modulus, which connects two phases with highly different mechanical properties and elastic moduli, must interconnect and span these differences. Indeed, for hard-core composites it is valid that $E_f \gg E_m$, whereas for rubber reinforcements we have the opposite relation $E_m \gg E_f$. However, never happens that $E_f \approx E_m$.

If we assume that the longitudinal displacements along each of the three phases (fiber-mesophase-matrix) are, in an average, equal and if we neglect transversal effects we can reason that, since longitudinal displacements and strains are equal, the stresses developed in these phases should be proportional to their respective moduli. It has been established that, for singular regions in elastic stress fields, singular distributions may be approximated by negative powers of the radial distances from the singular points. Then, it is reasonable to accept as appropriate functions, expressing the transfer of moduli from fibers to matrix, forms described by the terms of relation (3).

In relation (3) the second right-hand term expresses the contribution of the E_f -modulus to the variation of $E_i(r)$ -modulus, whereas the third right-hand term defines the counterbalancing contribution of the E_m -modulus, to

correct the contribution of the E_r -modulus, and insert the influence of the matrix to the outer layers of the mesophase-annulus.

From the compatibility conditions for the moduli at the fiber-mesophase and mesophase-matrix boundaries it may be derived that:

i) For $r = r_f$ we have:

$$E_i (r_f) = E_r \quad (4)$$

which indicates the automatic satisfaction of the boundary condition for this interface, and

ii) for $r = r_i$ we have:

$$E_i (r_i) = E_m + E_r \left(\frac{r_f}{r_i} \right)^{\eta_1} - E_m \left(\frac{r_f}{r_i} \right)^{\eta_2} = E_m \quad (5)$$

Relation (5) yields that:

$$\frac{E_r}{E_m} = \left(\frac{r_i}{r_f} \right)^{\eta_1 - \eta_2} \quad (6)$$

or:

$$(\eta_1 - \eta_2) = \log \left(\frac{E_r}{E_m} \right) : \text{Log} \left(\frac{r_i}{r_f} \right) \quad (7)$$

Putting:

$$A = \frac{\log (E_r/E_m)}{\log (r_i/r_f)} \quad (8)$$

we have:

$$\eta_1 = (\eta_2 + A) \quad (9)$$

where A is a real constant, depending on the ratio of the moduli of the two phases and the ratio of the radii of the fiber and the mesophase.

As soon as the radius of the extent of mesophase is defined, the constant A is immediately defined and fixes the constant difference between the exponents η_1 and η_2 . The constant A is called the *adhesion parameter*, since it defines the influence of the moduli of the two main phases on the adhesion quality of the composite and its dependence on the ratio of the mesophase and fiber-radii.

Higher values of A indicate better adhesion for a particular composite, because they imply small differences in the values of r_i and r_f . For hard-core materials, where $E_r \gg E_m$, the radius r_i must be always larger than r_f .

and $E_f \gg E_m$, therefore the logarithm of the ratio r_i/r_f is a positive number and since $\log(E_f/E_m) > 0$ the values of Λ are always positive. This means for a hard-core composite it is always valid that $\eta_1 > \eta_2$. On the contrary, for rubber-core composites $\log(E_f/E_m)$ is then negative and therefore it is valid that $\eta_1 < \eta_2$.

THE TWO-TERM VERSION OF THE UNFOLDING MODEL

Since the third term of the right-hand side of Eq. (3) takes care of the influence of the matrix modulus E_m to the variation of $E_i(r)$ -modulus and since always for strong-core composites this contribution is secondary, relation (3) may be somehow relaxed by assuming that this third term varies linearly with the radius r along the mesophase. This means, in other words, that the exponent η_2 is assumed equal to unity without losing generality and imposing to the first right-hand side term to take care of the totality of the change of slope of the $E_i(r)$ -modulus.

Then, relation (3) may be written as follows:

$$E_i(r) = E_f \left(\frac{r_f}{r} \right)^{2\eta} + \left\{ E_m - E_f \left(\frac{r_f}{r_i} \right)^{2\eta} \right\} \frac{(r - r_f)}{(r_i - r_f)} \quad (10)$$

Now, relation (10) contains only two terms in its right-hand side, since the contribution of the E_m -constant term in the Eq. (3) is now incorporated into the second linear right-hand side term of Eq. (10).

It is easy to show that the boundary conditions for this equation are automatically satisfied. Indeed, for $r = r_f$ we have the second right-hand term of Eq. (10) equal to zero and the first term equal to the E_f -modulus, as it should be.

Moreover for $r = r_i$ equation (10) yields automatically $E_i(r) = E_m$ and this satisfies the exterior boundary condition.

In this way both boundaries of the mesophase layer with the fiber and the matrix are automatically satisfied and, therefore, equation (10) is a convenient relationship yielding the variable $E_i(r)$ -modulus accommodating, in a natural way, the smooth transition from a large E_f -modulus to a reduced E_m -modulus for the matrix and vice versa.

Relation (10) has the advantage to contain only one unknown exponent and therefore simplifies considerably the evaluation of the unknown quantities in the definition of the variable $E_i(r)$ -modulus.

Moreover, it was established during the numerical evaluation of the unknown quantities in relations (3) and (10) that the definition of the two exponents η_1 and η_2 in relation (3) is rather unstable, depending frailly on small variations of the value of the E_c -modulus. On the contrary, the single unknown 2η -exponent, defining relation (10), yields rather stable and reliable results.

Then, in this two-term unfolding model remains to define this exponent 2η , since all other quantities and especially the r_f -radius are either given, or evaluated from the thermodynamic equilibrium relations. Then, in this model the 2η -exponent is the characteristic parameter defining the quality of adhesion and therefore it may be called the *adhesion coefficient*. This exponent depends solely on the ratios of the main-phase moduli (E_f/E_m), as well as on the ratio of the radii of the fiber and the mesophase.

DEFINITION OF THE MESOPHASE THICKNESS

It had been observed that, for the same volume fraction v_f of the filler, an increase of T_g indicates an increase of the total surface of the filler [12]. 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 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 mesophase, and this results forcibly to an increase in T_g . A considerable amount of experimental work indicates an increase of T_g in composites with an increase of the filler content [13]. The degree, however, of this variation and the character of its change

may differ from composite to composite and, also, for the same composite, is depending on the method used for its measurement [14, 15].

Moreover, in many cases, a shift of T_g to lower values of temperature has been detected, but in these cases the quality of adhesion between phases may be the main reason for the reversing of this attitude [13, 16]. 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 neighbourhood. 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 mesophase 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 surface of the solid inclusions.

It was shown [17, 18] that, as the filler-volume fraction is increased, the proportion of macromolecules participating in this boundary layers with reduced mobilities is also increased, so that the number of macromolecules participating in the T_g -process is reduced. This is equivalent to a relative increase of v_i .

Lipatov [13] has indicated that the following relation holds between a weight constant λ , defining the mesophase volume-fraction v_i , and the jumps of the heat capacity ΔC_p^f of the filled-composite and ΔC_p^0 of the unfilled polymer for particulate composites:

$$\lambda = 1 - \frac{\Delta C_p^f}{\Delta C_p^0} \quad (11)$$

where λ is a real constant, which multiplies the fiber volume fraction v_f , in order to take into consideration the contribution of the mesophase volume fraction v_i to the mechanical behaviour of the composite.

In order to define the volume-fraction v_i of the mesophase for the particular composite studied, which was a E-glass-epoxy unidirectional fiber composite, a series of dilatometric measurements were executed in a differential scanning calorimeter, over a range of temperatures including the glass tran-

sition of a pure epoxy polymer used as matrix, and seven samples of composites containing different amounts of E-glass fibers varying between $v_i = 10$ percent to $v_f = 70$ percent.

The graphs of all the data, which were similar to the heat-capacity graphs for iron-epoxy particulates, shown in ref. [16], presented shapes, which were qualitatively similar to one another. They consisted of two linearly increasing regions separated by the glass transition zone. While the glassy linear regions presented a positive and significant slope, the rubbery linear regions were, all of them, almost horizontal.

The ΔC_p 's were calculated by ignoring the smooth protrusions B'BC appearing in the $C_p = f(T)$ curves (see Fig. 2) and measuring the distance of the intersection A of the tangents AA' of the glassy curve and AB of the transition curve from the horizontal tangent CC' of the rubbery part of the curve $\Delta C_p = f(T)$. The values of ΔC_p 's for the different composites are indicated, among others, in Table I.

In order now to define the radius r_i of the cylindrical layer corresponding to the mesophase, we express it as $r_i = (r_f + \Delta r)$ and we modify the respective relation given by Lipatov [13] for particulates to the appropriate relation for cylindrical inclusions. For the cases of unidirectional fiber-reinforced composite it was shown that the following relation holds [4]:

$$\frac{(r_f + \Delta r)^2}{r_f^2} - 1 = \frac{\lambda v_f}{1 - v_f} \quad (12)$$

Relation (12) may be written as:

$$\frac{v_f + v_i}{v_f} - 1 = \frac{\lambda v}{1 - v_f}$$

which yields:

$$B = \frac{v_f}{v_f + v_i} = \frac{v_f}{1 - v_m} = \frac{1 - v_f}{1 - v_f(1 - \lambda)} \quad (13)$$

The real constant B depends only on the fiber-volume fraction and the coefficient λ and it is critical for evaluating the exponents η_1 and η_2 . Introducing the values of λ from Table I we can define the values of Δr for the various fiber-volume contents v_f for a composite with E-glass fibers having a radius $r_f = 6 \mu\text{m}$. Then, it is easy to evaluate the volume fraction v_i for the mesophase layer. It can be readily derived from Fig. 3, where the ΔC_p 's and Δr 's

T A B L E 1

| ν_f | ν_i | ν_m | ΔC_p | λ | r_i | E_{CL} | E_i^a | η_1 | η_2 | A | 2η |
|---------|---------|---------|--------------|-----------|---------|----------------|----------------|----------|----------|-------|---------|
| | Percent | | Cal/g, °C | | μm | $10^9 Nm^{-2}$ | $10^9 Nm^{-2}$ | | | | |
| 0 | 0 | 100.00 | 0.081 | 0.1220 | 6.000 | 3.445 | — | — | — | — | — |
| 40 | 0.123 | 89.877 | 0.072 | 0.1110 | 6.036 | 10.32 | 21.70 | 629 | 121 | 0.19 | 436 |
| 20 | 0.492 | 79.508 | 0.073 | 0.0984 | 6.071 | 17.23 | 19.97 | 350 | 87 | 0.25 | 220 |
| 40 | 1.960 | 58.040 | 0.075 | 0.0735 | 6.145 | 31.12 | 16.60 | 203 | 76 | 0.375 | 114 |
| 50 | 3.075 | 46.925 | 0.076 | 0.0615 | 6.182 | 38.11 | 16.37 | 166 | 65 | 0.39 | 96 |
| 60 | 4.428 | 35.572 | 0.077 | 0.0492 | 6.217 | 45.12 | 15.70 | 144 | 60 | 0.41 | 78 |
| 65 | 5.200 | 29.800 | 0.0775 | 0.0431 | 6.235 | 48.62 | 15.40 | 135 | 58 | 0.43 | 72 |
| 70 | 6.030 | 23.970 | 0.078 | 0.0369 | 6.254 | 52.15 | 15.40 | 128 | 55 | 0.43 | 68 |

are plotted for various values of v_r , that as v_r is increasing the ΔC_p 's are increasing slightly with v_r and the mesophase volume-fraction v_i are progressively increasing. This behaviour is in accordance with similar measurements

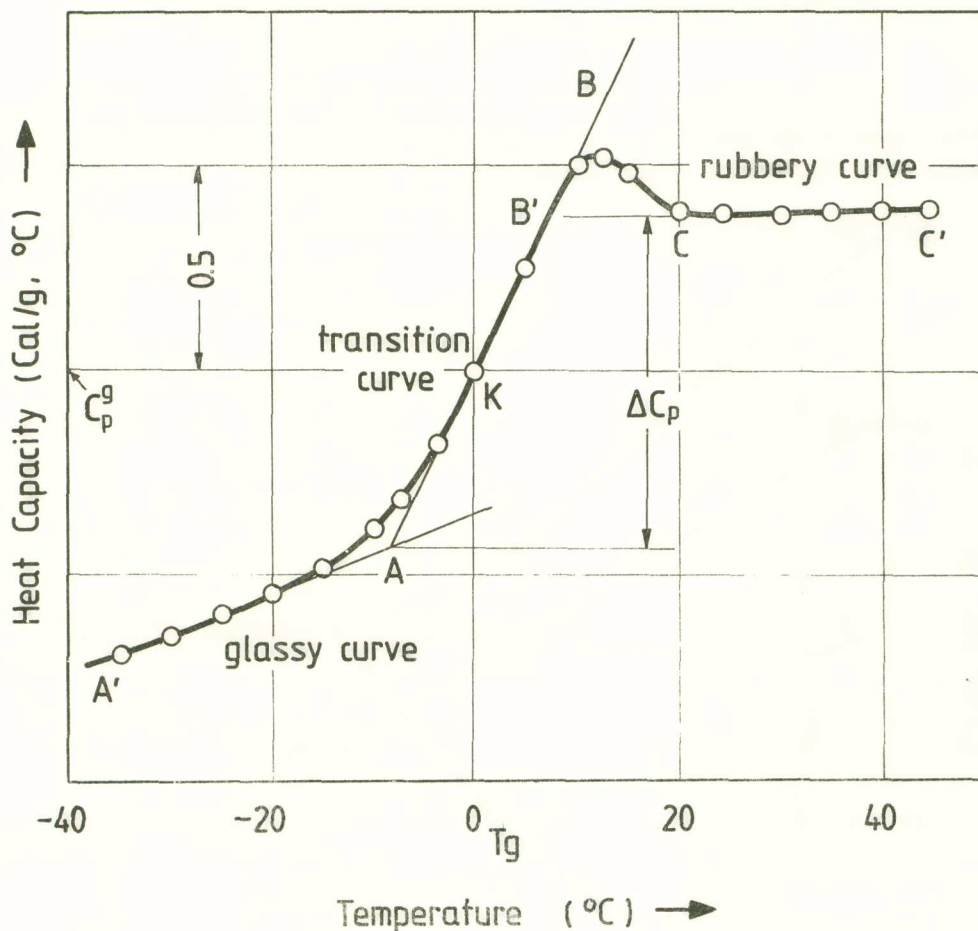


Fig. 2. Typical DSC traces for the specific-heat jumps at the glass-transition regions of E-glass fiber-epoxy resin composites and the mode of evaluation of ΔC_p 's.

of composites, although measurements of ΔC_p in crosslinked polymers are still sparse.

Fig. 3 presents the variation of the heat capacity jumps ΔC_p^f at the glass-transition temperature of the various composites together with the variation of the coefficient λ and the volume fractions for the mesophase and

matrix versus the volume fraction of the filler, as they have been derived from the Lipatov law.

EVALUATION OF THE ADHESION PARAMETER A AND THE ADHESION COEFFICIENTS $\eta_{1,2}$ FOR THE THREE-TERM MODEL

As soon as the Δr 's were determined and the values of r_i 's are found, the values of the adhesion parameter A may be readily defined by using relation (8). The values of A's for the different fiber-volume contents studied

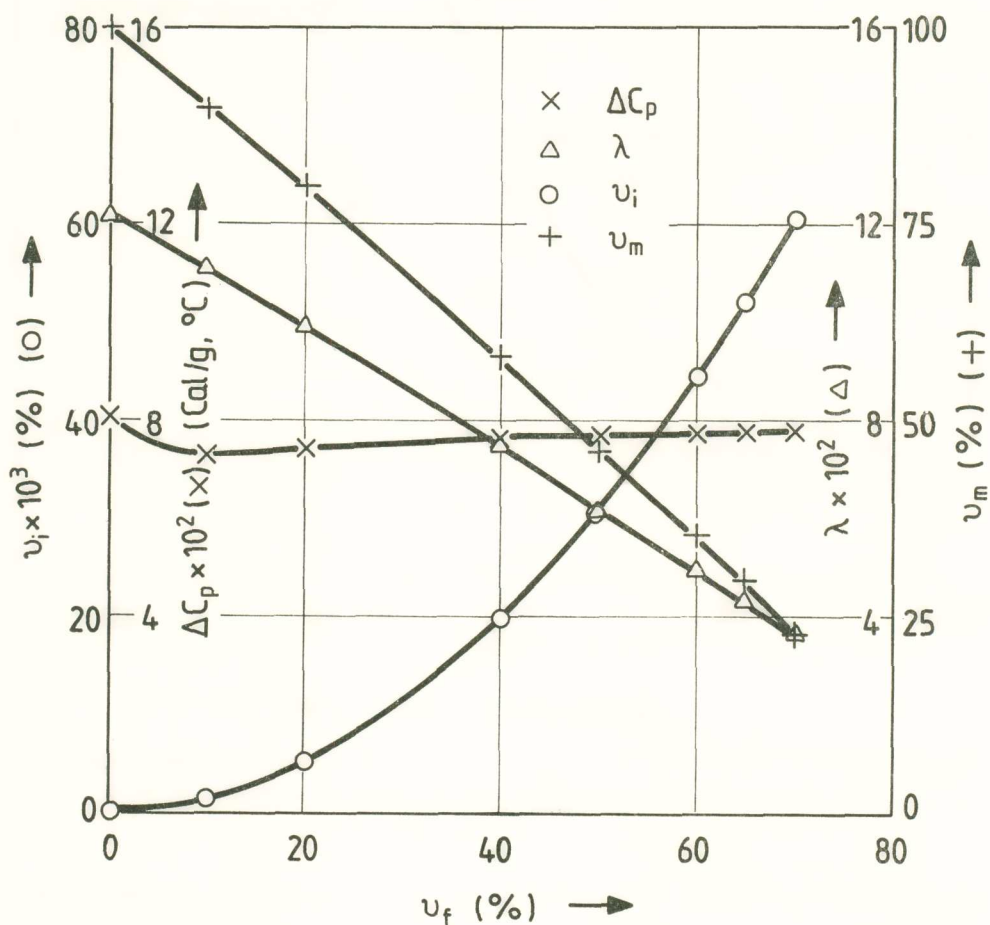


Fig. 3. The variation of the specific heat jumps at glass-transition temperatures of glass-epoxy composites versus the fiber volume content v_f . The values for the factor λ , the mesophase (v_i)- and the matrix (v_m)-volume fractions versus v_f , as derived from the values of the respective ΔC_p 's are also plotted.

are given in Table I for E-glass fiber-epoxy resin composites with different amounts of fillers, up to 70 percent [19].

In order to define the η_1 - and η_2 -exponents it is necessary to dispose a second equation, besides relation (12), for the evaluation of r_i -radius and relation (8) for the definition of the difference ($\eta_1 - \eta_2$). For this purpose we used the values of the composite moduli in the direction of the fibers taken for various fiber-volume contents in a particular case of E-glass-epoxy composites, whereas the mesophase volume fractions v_i were determined from the experimental values of these quantities for certain values of v_f 's, by applying the approximate multilayer model introduced by ref. [4]. These values fitted excellently a parabola, expressed by relation $v_i = Cv_f^2$ with $C = 0.123$. The values for v_i 's, together with the respective values for the moduli of the composites evaluated experimentally, were introduced in the adequate models, expressing the mechanical properties of the composites in terms of their constituents, and gave excellent coincidence with their experimental values based on the parabolic variation of v_i with v_f . The values of the characteristic quantities for the three-term unfolding model, as derived from the above-described procedure, are all included in Table I.

In order to evaluate the exponent η_1 we make recourse to the law of mixtures, given by relation (2), which expresses the longitudinal elastic modulus of the composite in terms of the moduli and the radii (or volume fractions) of the constituent phases. This relation may be written as:

$$E_c = E_f v_f + \frac{1}{r_m^2} \int_{r_f}^{r_i} E_i(r) [(r + dr)^2 - r^2] + E_m v_m \quad (14)$$

The second right-hand term of relation (14) expresses the contribution of the mesophase, with volume fraction v_i , to the E_c -modulus.

If the integral in relation (14) is approximated by:

$$I_1 \approx \frac{2}{r_m^2} \int_{r_f}^{r_i} E_i(r) r dr = \frac{2}{r_m^2} \int_{r_f}^{r_i} \left[E_m + E_f \left(\frac{r_f}{r} \right)^{\eta_1} - E_m \left(\frac{r_f}{r} \right)^{\eta_2} \right] r dr \quad (15)$$

relation (14) becomes:

$$(E_c - E_m) - (E_f - E_m) \nu_f = \nu_f \left\{ \frac{E_f}{\left(\frac{\eta_1}{2} - 1\right)} \left[1 - B \left(\frac{\eta_1}{2} - 1\right) \right] - \frac{E_m}{\left(\frac{\eta_2}{2} - 1\right)} \left[1 - B \left(\frac{\eta_2}{2} - 1\right) \right] \right\} \quad (16)$$

in which the quantity B is given by Eq. (13) and the only unknown is the exponent η_1 , which can be readily calculated numerically.

Fig. 4 presents the variation of the adhesion parameter A versus the

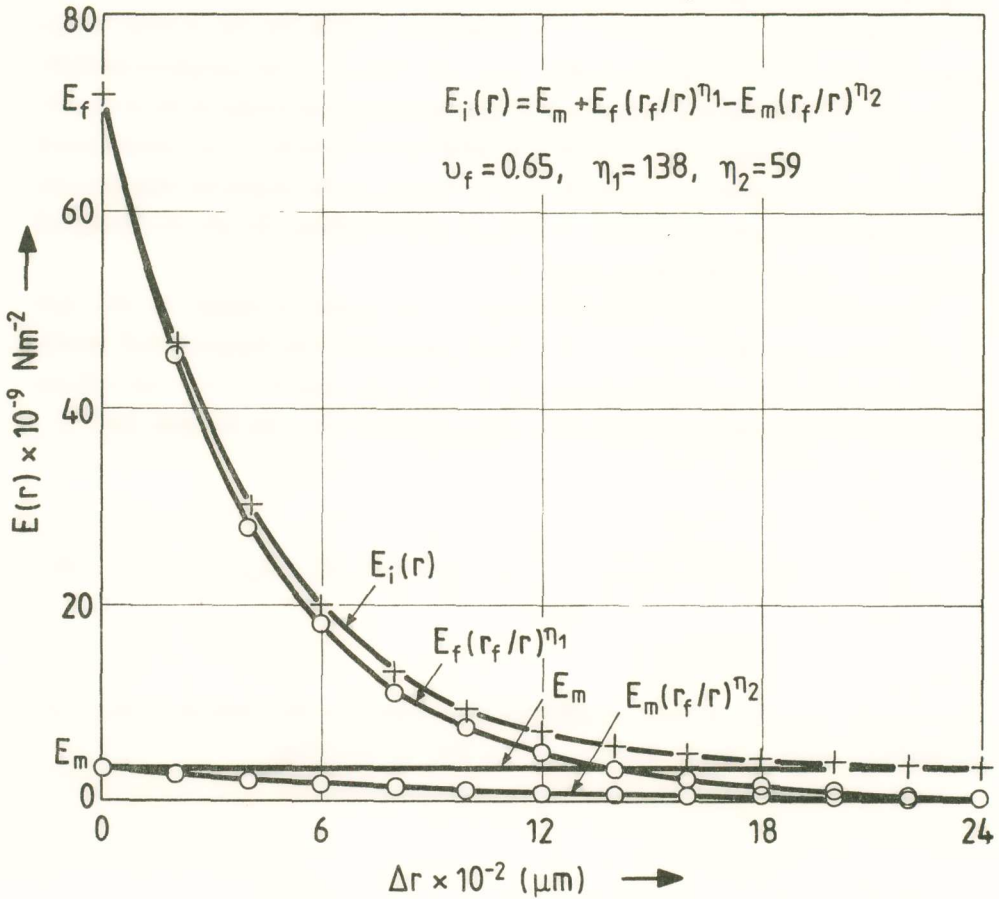


Fig. 4. The mode of evolution of the variable terms $E_f(r/r)^{\eta_1}$ and $E_m(r/r)^{\eta_2}$, contributing to the definition of the mesophase modulus, versus the polar distance r from the fiber boundary for a 65% E-glass fiber-epoxy resin composite.

filler-volume content v_f of a series of E-glass-epoxy resin composites, whose mechanical properties are given in ref. [19] for values of the filler-volume fraction varying between $v_f = 0$ and $v_f = 0.70$.

Equations (9) and (16) form a system of two equations and two unknowns, which can be solved and yields the values of the exponents η_1 and η_2 and their ratio $\alpha = \eta_2/\eta_1$, which expresses the quality of adhesion and it is called the *adhesion coefficient*. The values of the exponents η_1 and η_2 , as well as of their ratio $\alpha = \eta_2/\eta_1$ were given in Table I and plotted in Fig. 4 for the E glass-fiber-epoxy composites studied, together with the values of A's.

Fig. 5 presents the variation of the terms $E_f (r_f/r)^{\eta_1}$ and $E_m (r_f/r)^{\eta_1}$ in the mesophase layer for a 65 percent E-glass -fiber-reinforced epoxy resin, as they have been derived from Eq. (16). It is worthwhile indicating the smooth transition of the E_i -modulus to the E_m -modulus at the region $r \approx r_f$. Similar behaviours present all other compositions.

It is interesting plotting the variation of the $E_i(r)$ -modulus versus polar distance around a typical fiber. Fig. 6 presents this transition of the moduli from the fibers to the matrices, exemplifying the important role played by the mesophase layer to the overall mechanical behaviour of the composite.

Fig. 7 presents the variation of the various moduli of the composite and its constituents for various volume fractions of the series of E-glass-epoxy fiber composites. It is interesting to point out the small variation of the average value of the variable $E_i(r)$ -modulus of the mesophase which reflects the uniformity of the adhesion quality of these series of composites which is also indicated by the almost linear variation of the longitudinal composite modulus versus the volume content.

EVALUATION OF THE ADHESION COEFFICIENT 2η FOR THE TWO-TERM UNFOLDING MODEL

For the case of the two-term unfolding model we have to replace the second right-hand term in relation (2) by introducing, instead of integral I_1 , the new integral I_2 derived from relation (10) and expressed by

$$I_2 = \frac{2}{r_m^2} \int_{r_f}^{r_i} E_i(r) r dr = \frac{2}{r_m^2} \int_{r_f}^{r_i} \left\{ E_f \left(\frac{r_f}{r} \right)^{2\eta} + \left[E_m - E_f \left(\frac{r_f}{r_i} \right)^{2\eta} \right] \left(\frac{r-r_f}{r_i-r_f} \right) \right\} r dr \quad (17)$$

This integral, after some algebra, yields:

$$I_2 = \frac{E_f v_f}{(\eta-1)} \{1 - B^{\eta-1}\} + \frac{v_i}{3} \left\{ E_m - E_f B^\eta \right\} \quad (18)$$

Introducing this integral into relation (14) we obtain

$$E_c = \frac{\eta}{(\eta-1)} E_f v_f \left[1 - \frac{B^{\eta-1}}{\eta} \right] - \frac{E v_i B^\eta}{3} + E_m [1 - v_f - 2 v_i/3] \quad (19)$$

In this relation the only unknown is the exponent 2η , which may be

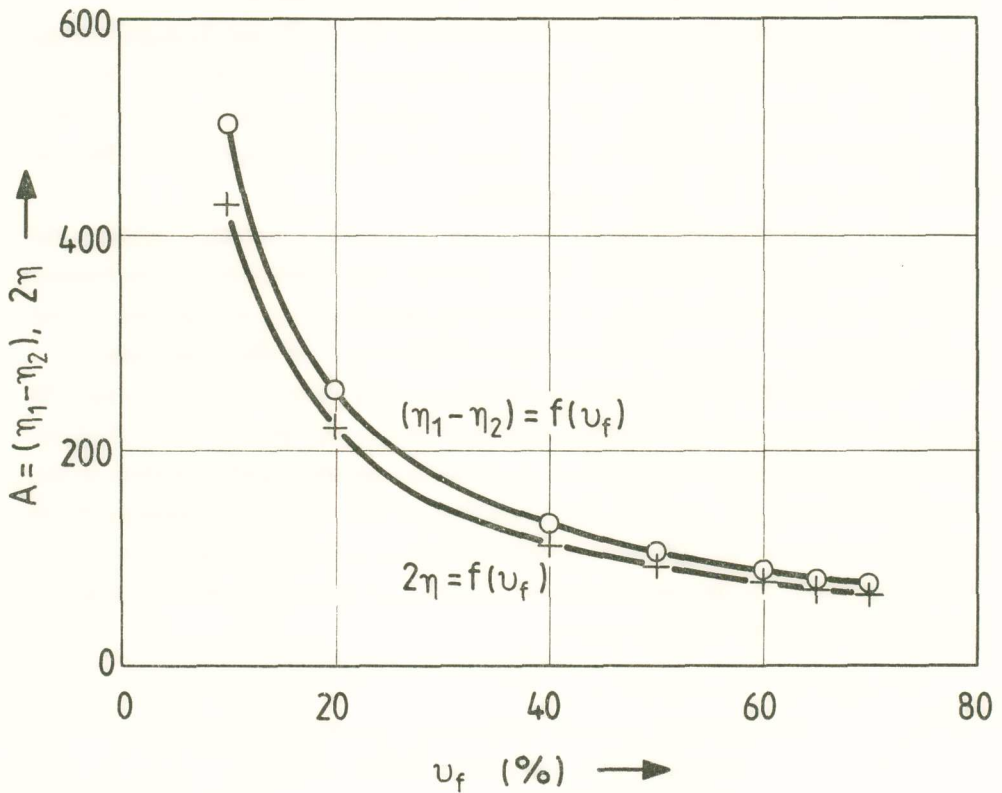


Fig. 5. The variation of the adhesion parameter A for the three-term unfolding model and the adhesion exponent 2η for the two-term mode versus the filler volume fraction v_f .

calculated by introducing the appropriate values for all known quantities corresponding to each fiber volume content.

The values of the exponent 2η are included in Table I and they are plotted in Fig. 4. A comparison between the corresponding adhesion param-

ters A and 2η for the two versions of the unfolding model shows the equivalence of the two cases.

Fig. 8 presents the variation of the mesophase moduli $E_i(r)$ for the various fiber volume fractions versus the extent of the mesophase Δr , normalized

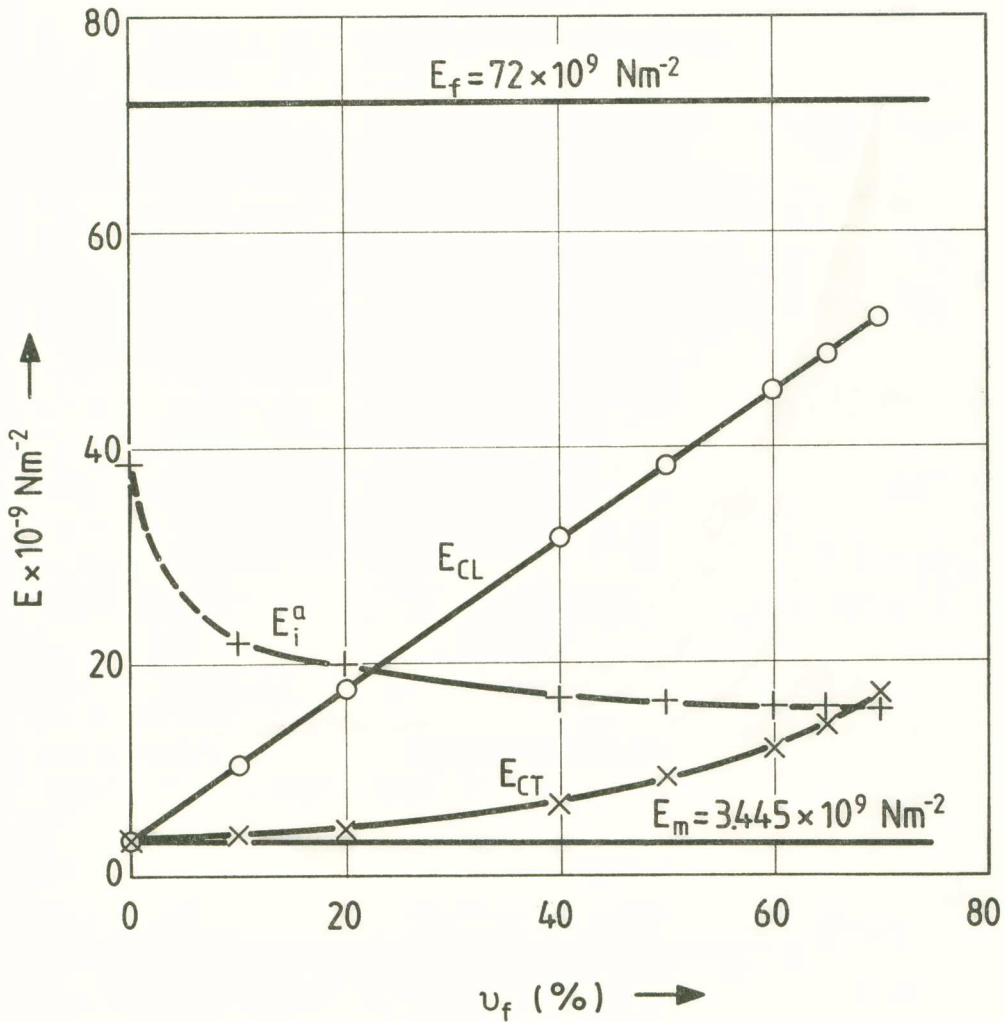


Fig. 6. The variation of the longitudinal and transverse moduli for the composite (E_{CL} , E_{CT}) versus the filler-volume fraction, v_f , and the mode of variation of the average mesophase modulus, E_i^a , as derived from the models.

to the highest fiber-volume fraction of 70 percent. This was done in order to show the similarity of variation of the E_i -modulus for the various values of v_f in this series of composites, possessing the same adhesion properties bet-

ween them. These normalized patterns are equivalent with those presented in Fig. 6 for the three-term unfolding model, since the differences between corresponding values of the two versions of the model are insignificant.

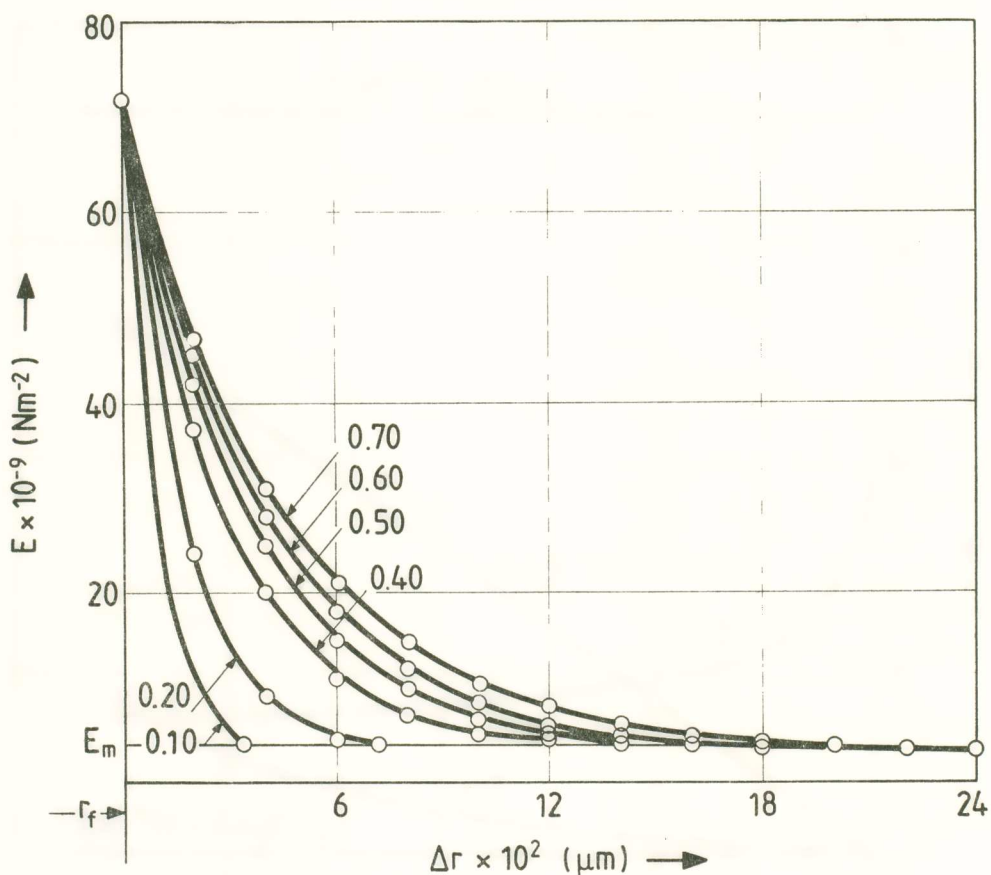


Fig. 7. The variation of the mesophase moduli versus polar distance r for different fiber-volume contents v_f for the three-term unfolding model.

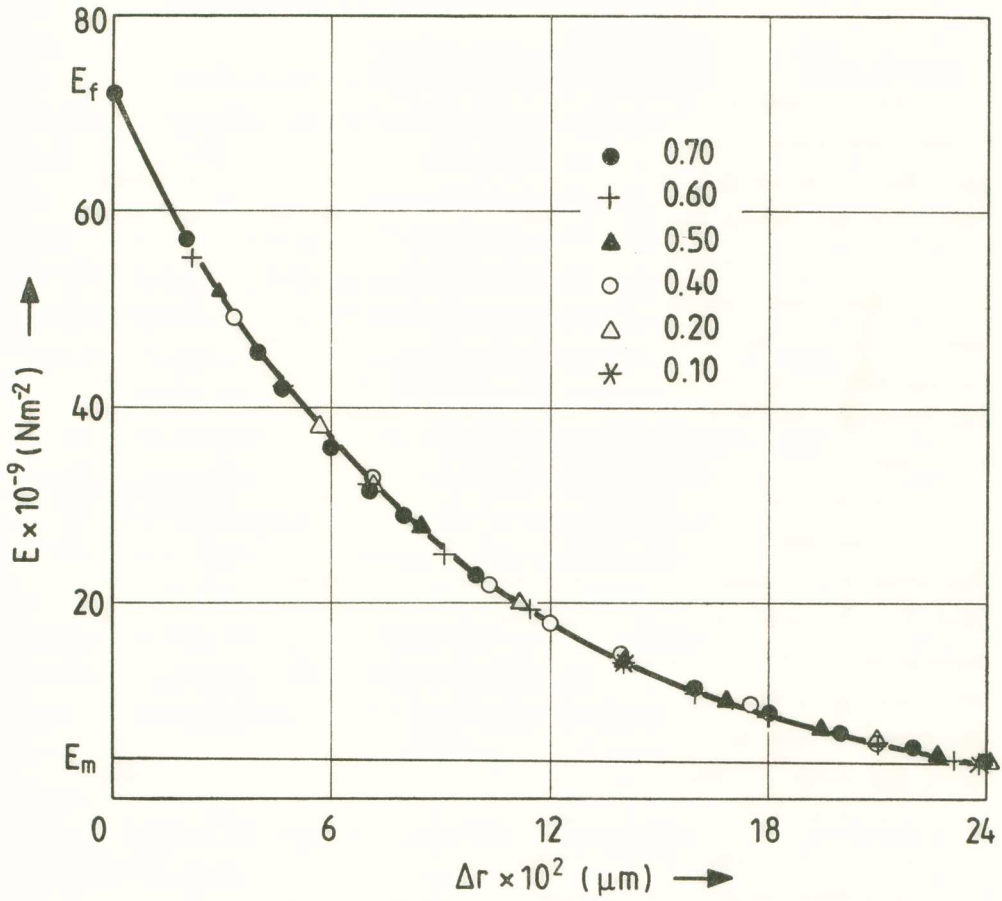


Fig. 8. The variation of the mesophase moduli, normalized to the mesophase thickness Δr for the 70 percent composite, versus polar distance r for the two-term unfolding model. Table I. The values of the characteristic parameters of a series of E-glass fiber, epoxy resin unidirectional composites for various fiber-volume contents v_f .

CONCLUSIONS

The multilayered model introduced in previous publications by the author has been shown to present a basic inconsistency, as it appeared in previous references [1 to 5]. This was its incompatibility with the assumption made for the model that the boundary layer, constituting the mesophase between fibers and matrix, should extend to a thickness well defined by thermodynamic measurements, yielding jumps in the heat capacity values at the glass-transition temperature region of the composites. By leaving this layer in the first models to extend freely and tend, in an asymptotic manner, to its limiting value of E_m , we allowed an extension of the mesophase layer several times larger than the annulus anticipated from thermodynamic measurements, fact which does not happen in the new versions.

In the new versions of the model this inconsistency was alleviated, by imposing at the mesophase-matrix boundary the agreement between $E_i(r_i)$ and E_m . The new versions of the model gave reasonable thicknesses for the mesophase layer in its proper sense. The first version of the model, on the contrary, gave the region influenced by the perturbation of the mesophase layer, which may be extended far beyond the real mesophase annulus. However, the mode of variation of the mesophase modulus in the annulus indicated the role of transition, played by this layer in adapting and smoothing out the large differences in the mechanical properties of phases.

A perfect cooperation between phases is the ideal for an optimum behaviour of the composite. A good indication of this cooperation is given either by the adhesion coefficient A , as defined by the first version of the unfolding model, or by the exponent 2η defined by its second version.

Between the two versions of the model the two-term version is preferable, since it depends on a much more stable procedure for evaluating the adhesion coefficient 2η and it is easier to handle.

Both models could readily be extended to describe the mesophase phenomena in particulates and impregnated composites.

ΠΕΡΙΛΗΨΙΣ

Ἡ πρόσφυσις μεταξὺ τῆς μήτρας καὶ τῶν ἐγκλεισμάτων (ἰνωδῶν ἢ σφαιρικῶν) εἰς σύνθετον ὕλικόν ἀποτελεῖ ἓνα ἐκ τῶν κυριωτέρων παραγόντων, οἱ ὁποῖοι

χαρκτηρίζουν τήν μηχανικήν καί φυσικήν συμπεριφοράν τῶν συγχρόνων αὐτῶν ὑλικῶν, τῶν χρησιμοποιουμένων εὐρύτατα εἰς τὰς κατασκευάς.

“Ὅλα τὰ θεωρητικά πρότυπα, τὰ ὅποια εἰσήχθησαν μέχρι σήμερον διὰ τήν περιγραφὴν τῶν νέων αὐτῶν ὑλικῶν, παραλείπουν νὰ λάβουν ὑπ’ ὄψιν τὴν ἐπίδρασιν τοῦ ἐπιφανειακοῦ στρώματος, τὸ ὁποῖον ἀναπτύσσεται μεταξύ τῶν φάσεων κατὰ τήν κατασκευὴν τῶν συνθέτων ὑλικῶν. Πράγματι, ὅλα τὰ πρότυπα αὐτὰ θεωροῦν τὰς διαχωριστικὰς ἐπιφανείας τῶν φάσεων ὡς τελείας μαθηματικὰς ἐπιφανείας. Εἰς τήν πραγματικότητα αἱ ἐπιφάνειαι αὐταὶ περιλαμβάνουν γωνίας, κοιλότητας, προεξοχὰς καὶ ἄλλας ἀνωμαλίας, αἱ ὅποια δημιουργοῦν λεπτὰ στρώματα διαφόρου πάχους, ἀντὶ τῶν θεωρουμένων τελείων μαθηματικῶν ἐπιφανειῶν. Ἄν καὶ αἱ ἀνωμαλίας αὐταὶ εἶναι γενικῶς ἀπειροελάχισται, εἶναι ἐν τούτοις ἱκαναὶ νὰ δημιουργήσουν τοπικὰς συγκεντρώσεις ὑλικοῦ καὶ συγκεντρώσεις τάσεων, διασκορπισμέναις ἀκανονίστως ἐπὶ τῶν διαχωριστικῶν αὐτῶν ἐπιφανειῶν.

Περαιτέρω, ἡ γεωμετρία τῶν ἐγκλεισμάτων, εἰδικῶς εἰς τὰ ἰνώδη ἐνισχυμένα σύνθετα ὑλικά, δημιουργεῖ τήν ἀνάπτυξιν γωνιῶν, εἰσερχομένων ἐγκοπῶν, μικρορωγμῶν καὶ μικροπροεξοχῶν, αἱ ὅποια ἔχουν τήν καταστρεπτικὴν ἐπίδρασιν νὰ δημιουργοῦν ἰδιομορφίας τάσεων εἰς τήν γειτονίαν των. “Ὅλαι αὐταὶ αἱ ἀνωμαλίας δὲν προβλέπονται ἀπὸ τὰ μαθηματικὰ πρότυπα τὰ ὑπάρχοντα μέχρι σήμερον εἰς τήν βιβλιογραφίαν.

Ἡ πολυμερὴς μήτρα, ἡ ἐγχυνομένη ἐπὶ τῶν ἐγκλεισμάτων αὐτῶν δημιουργεῖ φαινόμενα φυσικῆς καὶ χημικῆς προσροφήσεως. Ἡ φυσικὴ διείσδυσις τοῦ ἐπιφανειακοῦ στρώματος τῆς μήτρας εἰς τὰς κοιλότητας καὶ εἰς τὰς ἀνωμάλους προεξοχὰς τῶν ἐπιφανειῶν τῶν στερεῶν ἐγκλεισμάτων δημιουργεῖ φαινόμενα ἀλληλοαναμίξεως καὶ ἀλληλοεισδύσεως τῶν φάσεων, αἱ ὅποια ἐπιδροῦν σημαντικῶς ἐπὶ τῆς μοριακῆς δομῆς τῆς ἐνδιαμέσου φάσεως, μεταβάλλουσαι τὰς μηχανικὰς ιδιότητας τοῦ στρώματος αὐτοῦ.

Ἡ χημικὴ προσρόφησης τῶν μακρομορίων τῆς μήτρας ἐπὶ τῆς διαχωριστικῆς ἐπιφανείας δημιουργεῖ, ἐξ ἄλλου, μεταβολὰς τῆς δομῆς τοῦ ἐπιφανειακοῦ στρώματος, διὰ τῆς δημιουργίας ἀλυσωτῶν δομῶν τῶν μορίων τῶν ἐγκλεισμένων εἰς τὰς κοιλότητας.

“Ὅλαι αὐταὶ αἱ μορφαὶ τῶν στοιχείων, αἱ ὅποια διὰ τῆς χημικῆς προσροφήσεως προσκολῶνται ἐπὶ τῶν διαχωριστικῶν ἐπιφανειῶν τοῦ ὑλικοῦ, μεταβάλλουν τήν μηχανικὴν ἀντοχήν τοῦ ἐπιφανειακοῦ αὐτοῦ στρώματος.

Κατὰ συνέπειαν γύρω ἀπὸ κάθε ἐγκλεισμα δημιουργεῖται ἐνδιάμεσον στρώμα, μεταβλητοῦ πάχους, τὸ ὁποῖον περιβάλλει ὅλα τὰ ἐγκλείσματα, εἰς τὸ ὁποῖον συμπεριλαμβάνονται ὅλαι αἱ περιγραφεῖσαι μεταβολαὶ τῆς μορφῆς τῶν μορίων τῆς μήτρας.

Έχει αποδειχθεί ότι το πάχος του επιφανειακού αυτού στρώματος συνδέεται στενῶς με τὴν ἐνέργειαν προσφύσεως τοῦ πολυμεροῦς τῆς μήτρας, με τὴν ἐλευθέραν ἐπιφανειακὴν ἐνέργειαν τῶν στερεῶν ἐγκλεισμάτων, καθὼς ἐπίσης καὶ με τὴν εὐκαμψίαν τῆς δομῆς του.

Ἡ ὑπαρξίς τοῦ ἐπιφανειακοῦ αὐτοῦ στρώματος, τὸ ὁποῖον συνιστᾷ τὴν λεγομένην διάστρωσιν, καὶ τὸ ὁποῖον ἀναπτύσσεται μεταξὺ τῶν δύο φάσεων διαφασικοῦ συνθέτου ὑλικοῦ, λαμβάνεται ὑπ' ὄψιν, εἰς τὴν ἐργασίαν αὐτὴν, διὰ τὴν διαμόρφωσιν δύο παραλλαγῶν καταλλήλων προτύπων, τὰ ὁποῖα περιγράφουν τὴν θερμομηχανικὴν συμπεριφορὰν ἰνωδῶν συνθέτων ὑλικῶν. Τὸ στρώμα αὐτὸ θεωρεῖται ὅτι ἀναπτύσσεται ὀλοκληρωτικῶς εἰς τὴν πλευρὰν τῆς πολυμεροῦς μήτρας, ἐνῶ τὸ σκληρὸν ἐγκλεισμα παραμένει οὐδέτερον.

Εἰς τὰ δύο πρότυπα τὰ ὁποῖα περιγράφονται εἰς τὴν ἐργασίαν αὐτὴν ἢ διάστρωσις αὐτὴ θεωρεῖται ὡς ἀνεξάρτητος ψευδόφασις με μεταβλητὰς ιδιότητας, αἱ ὁποῖαι συμβιβάζονται, τόσον με τὸ ἐγκλεισμα ἀπὸ τὴν μίαν πλευρὰν των, ὅσον καὶ με τὴν μήτραν ἀπὸ τὴν ἄλλην. Τὰ πρότυπα αὐτὰ στηρίζονται ἐπὶ τῶν αὐτῶν βασικῶν ἰδεῶν, ὅπως τὸ πρότυπον Hashin-Rosen. Ἡ ἀποτίμησις τῶν χαρακτηριστικῶν ιδιοτήτων τῆς διαστρώσεως ἐπιτυγχάνεται δι' εἰσαγωγῆς βελτιώσεων εἰς τὸν νόμον τῶν μιγμάτων μεταξὺ φάσεων. Διὰ τῆς μετρήσεως τῶν μεταβατικῶν θερμοκρασιῶν ἀπὸ τὴν ὑαλώδη εἰς τὴν κομμιώδη κατάστασιν τοῦ πολυμεροῦς, καθὼς ἐπίσης καὶ τῶν ἀποτόμων μεταβολῶν τῆς εἰδικῆς θερμότητος τόσον τῆς μήτρας ὅσον καὶ τῶν συνθέτων ὑλικῶν εἰς τὴν περιοχὴν αὐτὴν, ἐπιτυγχάνεται ὁ καθορισμὸς τῶν ἀναγκαίων μεγεθῶν διὰ τὸν προσδιορισμὸν ὅλων τῶν στοιχείων τῶν προτύπων.

Τὰ ἐξελικτικὰ αὐτὰ πρότυπα ἀποδεικνύονται ὅτι προσαρμύζονται εἰς τὴν πραγματικὴν κατάστασιν τῶν συνθέτων ὑλικῶν, παρέχοντα ἱκανοποιητικὰς τιμὰς διὰ τὰς μηχανικὰς ιδιότητας τῶν ἰνωδῶν συνθέτων ὑλικῶν.

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