

The Unfolding Model for the Representation of the Mesophase Layer in Composites

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Synopsis

The adhesion between matrix and inclusions (fibers or particulates) in a composite material is one of principal factors characterizing the mechanical and physical behavior 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 unfold* from those of the hard-core fibers to those of the softer matrix. Thus, a multicylinder model was assumed, improving the classical two-cylinder 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, but they are considerably improved, in order to take into consideration, in a realistic manner, the physical phenomena developed in fiber-reinforced composites.

INTRODUCTION

In all theoretical models introduced in the literature for explaining the mechanical behavior 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, dispersed irregularly on the interfaces. Moreover, the geometry of inclusions, especially in the fiber-reinforced composites causes the development of corners, reentrant notches, microcracks, and microprotrusions, which have the deleterious effect of developing stress singularities in their neighborhood. 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 in 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 ladderlike molecules. All these types of chemisorbed elements on inclusions lead to rapid variations of the properties and mechanical strength of the interface 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 conditions 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 behavior 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 discontinuities of the surfaces of inclusions, to the concentration of voids and to the impurities, microcracks, and other anomalies.²⁻⁶

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 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 behavior of particulates and fiber composites. This layer was assumed as developed entirely on the side of the softer polymeric matrix, and the harder inclusion is considered as neutral. In the models the mesophase was assumed as an independent pseudophase 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 composites.

MODELS FOR COMPOSITES

The models introduced by Hashin⁸ for the particulates and by Hashin and Rosen⁷ for the fiber composites are of general acceptance. They assume in both cases representative volume elements (RVE) 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 behavior 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 Budiansky⁹ 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 in turn is embedded in an infinite medium with the unknown macroscopic properties of the composite.

However, following Nielsen,¹² we may state that there is practically no good theory for the evaluation of the moduli in particulates except the cases where the fillers are soft rubbers. This explains also the great number of models introduced in the literature, which is increasing continuously.

From all these models those introduced by Kerner¹¹ and Van der Poel¹³ give satisfactory results and allow for their extension to multiphase models.

The Kerner model considers the problem as an *average elastic problem* and finds the conditions between moduli and volume contents between phases in a generic spherical grain of the body without giving explicitly the states of stresses and strains in the composite, a fact which is extremely difficult to be explicitly defined. On the other hand, Van der Poel encounters the same problem by applying the solution introduced by Goodier¹⁴ and Fröhlich and Sack¹⁵ for a spherical cavity submitted either to a hydrostatic loading or to a pure shear loading to the case of the RVE of a typical particulate.

While the initial van der Poel model was valid for hard fillers and incompressible matrices, this model has been extended by Schwarzl and Eikhoff¹⁶ to incorporate the description of particulates along a wide temperature range. A further use of the van der Poel model and the Schwarzl and Eikhoff ideas were made by Maurer in his interesting dissertation.¹⁷

Similar attempts to study three-phase particulate composites were made by Sagalaev and Simonov-Emiljanov¹⁸ in the Kerner-Kerner model, where the classical Kerner model was used twice to cover successively by pairs the phases of a three-phase composite,¹¹ by Kudykina and Pervak,¹⁹ by Takano and Sakanishi,¹⁷ and finally by Spathis, Sideridis, and Theocaris.²⁰ All these models yield the moduli of the particulate composites in terms of the moduli and respective volume fractions of three constituent phases of

the composite, without considering, except the last one, that the middle phase is a product derived from the interaction of the two main phases and depends on their degree of adhesion. All these models have been compared previously in Ref. 21.

Finally, the Takayanagi model²² should be mentioned, where the influence of the filler modulus E_f is taken into account for the evaluation of the respective modulus of the composite, E_c . In this model the filler volume fraction, $v_f = \lambda\varphi$, was combined with a part $(1 - \varphi)\lambda v_m$ of the matrix volume fraction, v_m , which had a different influence on E_c than the rest of the matrix volume fraction $(1 - \lambda)v_m$.

A convenient combination of these three elements, that is, the filler volume fraction $v_f = \lambda\varphi$ (represented as an orthogonal of sides λ and φ , quantities which represent the state of mixing), the part of the matrix connected to v_f , $(1 - \varphi)\lambda v_m$, and the rest of the matrix, $(1 - \lambda)v_m$, were arranged in a convenient combination, either the v_f and $(1 - \varphi)\lambda v_m$ in parallel and then the $(1 - \lambda)v_m$ element in series (model A) or the v_f and $(1 - \varphi)\lambda v_m$ in series and the $(1 - \lambda)v_m$ in parallel with the previous unit (model B) gave satisfactory approximations either for the composite compliance D_c of a particulate (model A) or for the composite modulus E_c of a fiber composite (model B).

While the Takayanagi model was designed mainly for two-phase materials, it could be extended to incorporate the influence of mesophase.²³ It seems that a further extension of the concept of using mixed-mode connections, that is, in series and in parallel, for the elements contained in the model representing the mechanical properties of the particulate, is very promising, since it yields high flexibility in the model, so that it can be adapted to the real behavior of the substance. A first attempt towards this direction was made by Kraus and Rollmann,²⁴ who have introduced a modification in Takayanagi's model suitable for describing the idea of interpenetrating networks in polyblends.

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 coaxial 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 pseudophase characterizes the effectiveness of the bonding between phases and defines an *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 thermomechanical properties of the composite in terms of the properties of its constituents. Figure 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. In the Hashin-Rosen models the

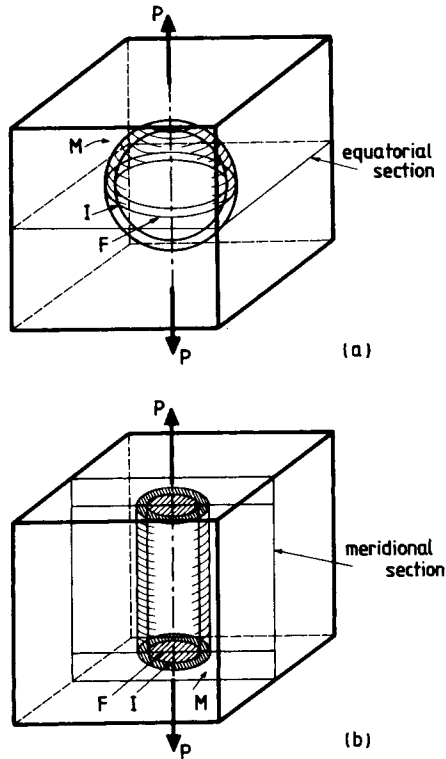


Fig. 1. Configurations of the representative volume elements for (a) particulates and (b) fiber-reinforced composites.

matrix phases (M) are concentric spheres or cylinders and the respective mesophases (I) disappear.

These models for particulates and fiber-reinforced composites have been introduced previously, and they have been described in Refs. 21 and 25. However, a brief description of both models is worthwhile here.

For the particulate composites the component phases are interconnected through consecutive spherical interfaces of the filler, mesophase, and matrix. The dominant transverse interconnection through shear, holding for the fiber composites, is in this case insignificant; the adhesion is now achieved by a continuously varying combination of shear and normal forces at the interfaces. Thus, variable components of the hydrostatic and shearing loading was developed between these surfaces. Then, it is closer to the real situation of force distribution to assume that the contributions of phases are done by superposed in series layers of the phases, lying the one on the top of the other in the direction of the application of the external load.

In this case, the compliances, instead of the moduli, should be added to derive the compliance of the composite, since now the capacitances of the respective electrical analogy, corresponding to the moduli of the elements, are connected in series. This argumentation explains the necessity of adding in this case the compliances of phases, instead of moduli.

However, since the approximation of superposed flat layers is again far away from reality, because of the average sphericity of the layers, the

expressions for the bulk compliance of the composite should be expected to be given by complicated expressions of the constituent compliances.

For the case of a unidirectional fiber composite a simple improved law of mixtures, where the contribution of the mesophase is taken into account, may be considered as satisfactory. This law is expressed by

$$E_c = E_f v_f + E_i v_i + E_m v_m \quad (1)$$

where the subscripts $c, f, i,$ and m denote the composite, the filler, the mesophase, and the matrix, respectively, and the v 's are expressing their respective volume fractions.

Relation (1) may be considered as satisfactory for fiber-reinforced composites because the individual moduli of phases in the RVE should cooperate through their interfaces, which are assumed parallel to the direction of application of the external load, this cooperation being achieved by the lateral surfaces of cylinders developing shears between phases. Thus, this model necessitates an addition of the moduli of the phases multiplied by weight factors, which are simply their respective volume contents. In an electrical analogy scheme, then, the weighted moduli constitute capacitances connected in parallel, which explains the validity of relation (1). This relationship was found to yield satisfactory results in the applications.¹⁻⁴

In order to determine the E_c modulus of a particulate, we consider that the representative volume element consists of three concentric spheres, having radii $r_f, r_i,$ and $r_m,$ respectively. The external radius of the RVE was taken such that this model corresponds to the average properties of the respective particulate. All quantities are normalized to the volume of the outer sphere $\frac{4}{3}\pi r_m^3$ to be equal to unity.

We assume further that all phases are elastic, homogeneous, and isotropic, with the exception of the mesophase layer, which has a variable modulus, changing with the polar distance between the values of E_f and E_m at its boundaries. However, this layer is also averaged, so that E_i corresponds to its E_i^a mean value. Besides, it is assumed that the fillers are perfect spheres, their distribution is uniform, and their intercenter distance large enough to ascertain a negligible interaction between neighboring fillers. Finally, we assumed that the RVE is submitted to a radial pressure of magnitude $p_m,$ so that, at the other boundaries, equal radial pressures of magnitudes p_i and p_f are exerted, which exhibit the interaction between successive phases.

Because of the spherical symmetry of the problem we introduce spherical (r, θ, φ) coordinates with the simplification that, from all the components of the spherical displacement vector, the u_r -radial displacements are different than zero, because of the nature of geometry and loading of the problem.

The solution of the problem may be derived by the stress functions $\Phi_j = f(r)$ (with $j = f, i, m$ for the filler, mesophase, and matrix, respectively), which are expressed by

$$\Phi_j = A_j r^{-1} + B_j r^2$$

with the constants A_j and B_j defined by the boundary conditions between phases, and $A_f = 0$ for finiteness of stresses at $r = 0$.

The components of displacements are given by

$$u_{rj} = (-A_j r^{-2} + 2B_j r)/2G_j \quad (2)$$

with the other components

$$u_{\theta j} = u_{\phi j} = 0 \quad (3)$$

The component u_{rf} is expressed by

$$u_{rf} = \frac{B_f r}{G_f} \quad (4)$$

since $A_f = 0$.

The components of stresses are given by

$$\sigma_{rj} = \frac{2A_j}{r^3} + \frac{2(1 + \nu_j)}{(1 - 2\nu_j)} B_j, \quad \sigma_{\theta j} = \sigma_{\phi j} = -A_j r^{-3} + \frac{2(1 + \nu_j)}{(1 - 2\nu_j)} B_j \quad (5)$$

The boundary conditions yield:

$$\begin{aligned} (i) \text{ At } r = r_f, \quad \sigma_{rf} = \sigma_{ri} = -p_f \\ (ii) \text{ At } r = r_b, \quad \sigma_{ri} = \sigma_{rm} = -p_i \\ (iii) \text{ At } r = r_m, \quad \sigma_{rm} = -p_m \end{aligned} \quad (6)$$

The solution of the system derived from the boundary conditions (6) yields the values of the constants A_j and B_j :

$$A_j = \frac{(p_j - p_{j-1})r_j^3 r_{j-1}^3}{2(r_j^3 - r_{j-1}^3)}, \quad B_j = -\frac{(r_j^3 p_j - r_{j-1}^3 p_{j-1})(1 - 2\nu_j)}{2(r_j^3 - r_{j-1}^3)(1 + \nu_j)} \quad (7)$$

where the index $j + 1$ means the next layer of the layer j considered, with a succession from the filler outwards, so that $j = 1$ corresponds to the filler, $j = 2$ to the mesophase, and $j = 3$ to the matrix of the particulate, and $r_0 = r_{j-1} = 0$ for $j = 1$, $r_j = r_m, r_b, r_f$ for $j = 1, 2, 3$, respectively.

The respective relations for the radial displacements and the components of strains follow readily from the above relations, and they are given in detail in Ref. 21.

The boundary conditions, which imply continuity of displacements between phases and normal tractions at the interfaces, yield some further relations, sufficient for the solution of the respective elasticity problem, provided that a relationship between the elastic modulus E_c of the composite and the stresses and strains of the constituent phases is established by using the theorem of elastic strain-energy balance on the representative volume element.

The balance of strain energies in the RVE yields

$$\begin{aligned} \frac{1}{K_c} = & \frac{\nu_f (\lambda_{fi})^2}{K_f (\lambda_{im})} + \frac{3\nu_f^2 (1 - \lambda_{fi})^2}{4BG_i \nu_i (\lambda_{im})} + \frac{\nu_f^2 (\lambda_{fi} - \frac{1}{B\lambda_{im}})^2}{K_i \nu_i (\lambda_{im})} \\ & + \frac{3\nu_f}{4BG_m \nu_m} \left(1 - \frac{1}{\lambda_{im}}\right)^2 + \frac{1}{K_m \nu_m} \left(\frac{\nu_f}{B\lambda_{im}} - 1\right)^2 \end{aligned} \quad (8)$$

where

$$\lambda_{fi} = \frac{p_f}{p_i}, \quad \lambda_{im} = \frac{p_m}{p_i}, \quad \text{and} \quad \frac{p_f}{p_m} = \frac{\lambda_{fi}}{\lambda_{im}} \quad (9)$$

and

$$\frac{r_i^3}{r_m^3} = \nu_f + \nu_i, \quad \frac{r_f^3}{r_m^3} = \nu_f \quad (10)$$

and

$$\frac{r_i^3}{r_f^3} = \frac{\nu_f + \nu_i}{\nu_f} = \frac{1}{B} \quad (11)$$

Equation (8) yields the bulk modulus K_c of the composite in terms of the bulk and shear moduli of the phases and the stress ratios λ_{fi} and λ_{im} which, on the other hand, depend on the elastic moduli and Poisson's ratios of the phases. These stress ratios are expressed by²¹

$$\lambda_{fi} = \frac{3(1 - \nu_i)(\nu_f + \nu_i)E_f}{2\nu_i E_i (1 - 2\nu_f) + [3\nu_f(1 - \nu_i) + \nu_i(1 + \nu_i)]E_f} \quad (12)$$

and:

$$\lambda_{im} = \frac{3(1 - \nu_m) - 2\nu_m(1 - 2\nu_m)}{3(1 - \nu_m)} - \frac{E_m \nu_m}{E_i} \frac{(1 + \nu_i)}{3(1 - \nu_m)} \quad (13)$$

For the complete solution of the problem, a relation between the Poisson ratios of the composite and its constituent phases is needed. Since the mesophase is derived from the matrix material, it is reasonable to accept that

$$\nu_i \simeq \nu_m \quad (14)$$

whereas for the Poisson ratio ν_c of the composite we use a modification of relationship given by Ref. 26, interconnecting the values of Poisson's ratios. This relationship was found satisfactory for our purposes and is given by

$$\frac{1}{\nu_c} = \frac{\nu_f}{\nu_f} + \frac{\nu_i}{\nu_i} + \frac{\nu_m}{\nu_m} \quad (15)$$

The last equation completes the number of relationships, necessary for evaluating the characteristic properties of the particulate.

The model expressed by relations (8) and (15) yields accurate results if the constituent phases of the particulate composite are accurately defined. However, it should be mentioned that its validity holds only in the purely elastic behavior of the composite, since viscoelastic effects have not been encountered in this model. To this aspect the model is similar to all other models and especially the most sophisticated Kerner-Kerner, Krauss, Takayanagi, van der Poel, and Maurer models. Furthermore, it contains an additional advantage that it, alone, incorporates the influence of the mesophase developed between phases, which depends on the adhesion quality of their bonding, and in some regions it plays an important and regulating role to the mechanical behavior of the composite.

Indeed, in all previous models the boundaries of their phases were visualized as smooth surfaces. In reality, around an inclusion a complex state develops, which consists of areas of imperfect bonding, permanent stresses, due to shrinkage of the polymer phases, during the curing and after-curing periods, and the change of the thermal conditions there, high stress gradients and stress singularities, due to the complicated geometry of the interfaces, voids, impurities, and microcracks, appearing at the vicinity of these boundaries.

Moreover, the interaction of the matrix polymer, during its after-curing period, with the surface of the solid inclusion is always a complicated procedure. Indeed, the presence of the filler restricts the free segmental and molecular mobility of the polymeric matrix, as adsorption interaction between phases occurs. This phenomenon influences considerably the quality of adhesion between phases, contributing to the development of a hybrid phase between main phases, which is called *interphase*, or, better, *mesophase*.

The existence of mesophase was proved experimentally and its extent was evaluated by a theory developed by Lipatov.²⁷ Similar evaluations of the extent of mesophase were executed by calculating, through dynamic measurements of the storage moduli and the loss factors at the vicinity of T_g 's of the matrix and the composites the differences of these quantities for the composite and the matrix materials.²⁸ Finally, the mesophase volume fraction ν_i may be evaluated by executing measurements of the strain magnification factor for the unfilled and filled polymer, as has been nicely advanced by Ziegel and co-workers,^{29,30} on a theory based on the concept of line fraction introduced by Bueche.³¹

Although the extent of mesophase may be determined from thermodynamic measurements, the influence of this pseudophase to the mechanical behavior of the composite was not extensively studied.

For the case of fiber-reinforced and particulate composites a multilayer model was introduced in Ref. 1, in which the influence of the mesophase

on the properties of the composite was studied. Another model was afterwards presented, where the variable with polar distance elastic modulus of the mesophase was expressed as sum of a constant term and two variable terms, expressed as modifications of the moduli of the filler and the matrix by negative power laws.^{4,32} The two-term improvement of the previous model,²⁵ where the variable mesophase modulus was expressed by a negative power term of variation of the E_f modulus and a linear term for the variation of the E_m modulus, gave better and much more stable results.³³

THE UNFOLDING MODELS FOR THE MESOPHASE

A decisive factor for the physical behavior 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 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 a 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.

The model for the representative volume element of a particulate consists of a unit of three concentric spheres with respective radii r_f , r_i , and r_m , whose volume contents are expressed by

$$v_f = \left(\frac{r_f^3}{r_m^3} \right), \quad v_i = \left(\frac{r_i^3 - r_f^3}{r_m^3} \right), \quad \text{and} \quad v_m = \left(\frac{r_m^3 - r_i^3}{r_m^3} \right) \quad (16)$$

Assuming the appropriate boundary conditions between the internal sphere and any number of layers surrounding it, in the RVE of the composite, which assure continuity of radial stresses and displacements, we may establish, by an energy balance between phases, a relationship, interconnecting the compliances, or the moduli between phases and composite. Such a relationship is given by eq. (8). In this relation the quantity E_i corresponds to the average value of the modulus of the mesophase and, in the following, it will be denoted as E_i^e . However, this *effective* or *average value* of the *mesophase modulus*, necessary for introducing the contribution of the mesophase to the value of the modulus of the composite, does not really exist, except in a very thin spherical layer.

It is easy to establish the respective model for the representative volume element of a unidirectional fiber reinforced composite, consisting of a cluster of three coaxial cylinders of the same height equal to unity, for which the following relations hold:

$$v_f = \left(\frac{r_f^2}{r_m^2} \right), \quad v_i = \left(\frac{r_i^2 - r_f^2}{r_m^2} \right), \quad \text{and} \quad v_m = \left(\frac{r_m^2 - r_i^2}{r_m^2} \right) \quad (17)$$

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 $E_{cl} \equiv E_c$ of the composite:

$$E_c = E_f \left(\frac{r_f^2}{r_m^2} \right) + E_i \left(\frac{r_i^2 - r_f^2}{r_m^2} \right) + E_m \left(\frac{r_m^2 - r_i^2}{r_m} \right) \quad (18)$$

This relation may be extended to any described 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 bounding the mesophase, we can define a variable elastic modulus for the mesophase, $E_i(r)$, which, for reasons of symmetry, depends only on the polar distance from the fiber-mesophase surface. In other words, we assume that the mesophase layer consists of a series of elementary layers, whose constant mechanical properties differ with 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 OF THE MESOPHASE

In order to make compatible the variation of the $E_i(r)$ modulus with its neighbor 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 in 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 layers of the mesophases. The appropriate functions for such steep variations are power functions of r with large negative exponents. Then, the $E_i(r)$ modulus may be expressed by

$$E_i(r) = E_m + E_f \left(\frac{r_f}{r} \right)^{m_1} - E_m \left(\frac{r_f}{r} \right)^{m_2} \quad (19)$$

Expression (19) 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 (filler–mesophase–matrix) are, on the 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 in this case also as appropriate functions, expressing the transfer of moduli from fillers to matrix, forms described by the terms of relation (19).

The second right-hand term in eq. (19) 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_f modulus, and insert the influence of the matrix to the outer layers of the mesophase layer.

From the compatibility conditions for the moduli at the filler–mesophase and mesophase–matrix boundaries, it may be derived that:

(i) For $r = r_f$ we have

$$E_i(r_f) = E_f \quad (20)$$

which indicates the automatic satisfaction of the boundary condition for this interface.

(ii) For $r = r_i$ we have

$$E_i(r_i) = E_m + E_f \left(\frac{r_f}{r_i} \right)^{\eta_1} - E_m \left(\frac{r_f}{r_i} \right)^{\eta_2} = E_m \quad (21)$$

Relation (21) yields that

$$\frac{E_f}{E_m} = \left(\frac{r_i}{r_f} \right)^{\eta_1 - \eta_2} \quad (22)$$

or

$$(\eta_1 - \eta_2) = \log \left(\frac{E_f}{E_m} \right) : \log \left(\frac{r_i}{r_f} \right) \quad (23)$$

Putting

$$A = \frac{\log(E_f/E_m)}{\log(r_i/r_f)} \quad (24)$$

we have

$$\eta_1 = (\eta_2 + A) \quad (25)$$

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 filler 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 .

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 $E_f \gg E_m$, 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 A 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 also 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. (19) takes care of the influence of the matrix modulus E_m to the variation of $E_i(r)$ modulus and since for strong-core composites this contribution is always secondary, relation (19) 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 may be assumed equal to unity, without losing generality, and requiring 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 (19) may be written as follows:

$$E_i(r) = E_f \left(\frac{r_f}{r} \right)^{2\eta} + \left[E_m - E_f \left(\frac{r_f}{r_i} \right)^{2\eta} \right] \frac{(r - r_f)}{(r_i - r_f)} \quad (26)$$

Now relation (26) contains only two terms in its right-hand side, since the contribution of the E_m constant term in the eq. (19) is now incorporated into the second linear right-hand side term of eq. (26).

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. (26) equal to zero and the first term equal to the E_f modulus, as it should be.

Moreover, for $r = r_i$ eq. (26) 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 filler and the matrix are automatically satisfied and, therefore, eq. (26) is a convenient relationship, yielding a 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 (26) has the advantage of containing 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 (19) and (26) that the definition of the two

exponents η_1 and η_2 in relation (19) is rather unstable, depending fraily on small variations of the value of the E_c modulus. On the contrary, the single unknown 2η exponent, defining relation (26), 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_i 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 filler and the mesophase.

DEFINITION OF THE THICKNESS OF THE MESOPHASE

It has 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.³⁴ 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 neighbor chains. This increase leads to a change of the overall viscoelastic behavior of the composite, by increasing the volume fraction of the strong phase of inclusions.

The variation of 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 mesophases, 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.²⁷ 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.^{35,36,41}

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.^{27,37} If calorimetric measurements are executed in the neighborhood 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 pertaining to the mesophase layers are totally or partly excluded from participating in the cooperative process taking place in the glass-transition zone, due to their interactions with the surfaces of the solid inclusions.

It was shown^{38,39} 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 .

Lipatov²⁷ 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:

$$\lambda = 1 - \frac{\Delta C_p^f}{\Delta C_p^0} \quad (27)$$

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

In order to define the volume fraction v_i of the mesophase for the particular composite studied, a series of dilatometric measurements were executed in a differential scanning calorimeter, over a range of temperatures including the glass transition of the matrix and the composites containing different amounts of fillers. The variation of the heat capacity C_p of the samples per mole vs. temperature was plotted automatically in a differential scanning calorimetry. All $C_p = f(T)$ curves plotted for pure polymers and composites presented a typical jump ΔC_p in heat capacity at the glass transition zone. Figure 2 presents schematically the variation of C_p at this zone versus temperature.

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 $\Delta C_p = f(T)$.

In order now to define the radius r_i of the layer corresponding to the mesophase, we express it as $r_i = (r_f + \Delta r)$ and we introduce this value into the relation (16) holding for particulates, or into relation (17) valid for cylindrical inclusions. For unidirectional fiber-reinforced composites, which will be used in the applications of the method, use will be made of a modification of Lipatov's formula, valid for particulates.²⁷ This relation for fiber-reinforced composites takes the form:

$$\frac{(r_f + \Delta r)^2}{r_f^2} - 1 = \frac{\lambda v_f}{1 - v_f} \quad (28)$$

Relation (28) may be written as

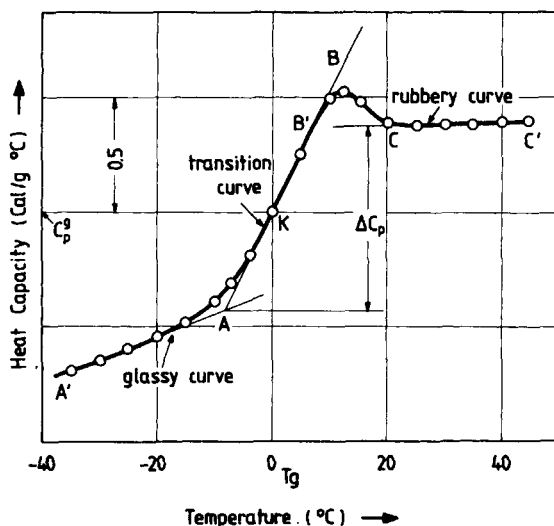


Fig. 2. Typical DSC traces for the specific-heat jumps at the glass-transition regions of E-glass fiber-epoxy resin composites and the mode of evaluation of ΔC_p 's.

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

which yields

$$B = \frac{v_f}{v_f + v_i} = \frac{v_f}{1 - v_m} = \frac{1 - v_f}{1 - v_f(1 - \lambda)} \quad (29)$$

The real constant B depends only on the filler volume fraction and the coefficient λ , and it is critical for evaluating the exponents η_1 and η_2 . Introducing the values of λ defined from relation (27), we can define the values of Δr for the various filler volume contents v_f for a composite with various volume contents v_f of 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 Figure 3, where the ΔC_p 's and Δr 's are plotted for various values of v_f , that, as v_f is increasing, the ΔC_p 's are increasing slightly with v_f and the mesophase volume fractions v_i are progressively increasing. This behavior is in accordance with similar measurements of composites, although measurements of ΔC_p in crosslinked polymers are still sparse.

The graphs of all the data for the heat capacity, which were similar to the heat-capacity graphs for iron-epoxy particulates, shown in Ref. 37, 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 almost horizontal.

Figure 3 presents the variation of the heat capacity jumps ΔC_p 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 vs. the volume fraction of the filler, as they have been derived

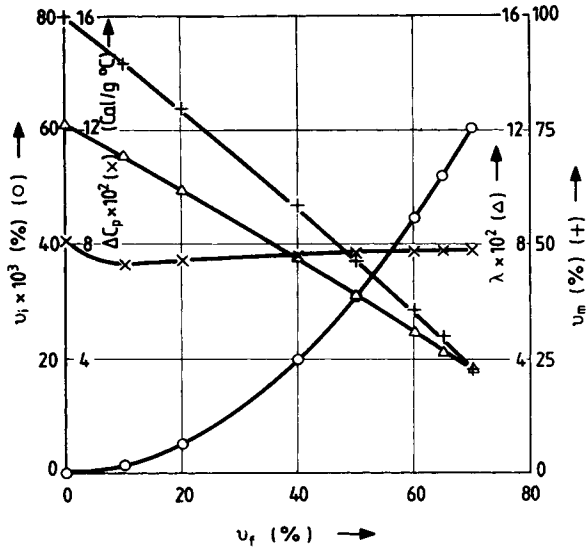


Fig. 3. The variation of the specific heat jumps at glass-transition temperatures of glass-epoxy composites vs. the fiber volume content v_f . The values for the factor λ (Δ) and the interphase (v_i) (O) and the matrix (v_m) (+) volume fractions vs. v_f as derived from the values of the respective ΔC_p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

from the Lipatov law. The filler volume fractions v_f were varied between $v_f = 0.10$ up to $v_f = 0.70$.

EVALUATION OF THE ADHESION EXPONENTS η_1 AND η_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 (24). This parameter defines the difference ($\eta_1 - \eta_2$) of the exponents and therefore constitutes a characteristic value for the adhesion quality of mesophase.

In order to evaluate the η_1 and η_2 exponents it is necessary to dispose a second equation, besides relation (28), for the evaluation of r_i radius and relation (24) for the definition of the difference $A = (\eta_1 - \eta_2)$. For this purpose we used the values of the composite moduli in the direction of the fibers, taken for various fiber volume contents in the 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 in 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 contained in Table I.

TABLE I
 Values of Characteristic Parameters of a Series of E-Glass Fiber-Epoxy Resin Unidirectional Composites for Various Fiber-Volume Contents v_f

v_f (%)	v_i (%)	v_m (%)	ΔC_p 10^{-5} J/Kg (°C)	λ	r_i (μm)	E_{cl} (10^9 Nm $^{-2}$)	E_y (10^9 Nm $^{-2}$)	η_1	η_2	α	2η
0	0	100.00	1.93	0.1220	6.000	3.445	—	—	—	—	—
10	0.123	89.877	1.72	0.1110	6.036	10.32	21.70	629	121	0.19	496
20	0.492	79.508	1.74	0.0984	6.071	17.23	19.97	350	87	0.25	220
40	1.960	58.040	1.79	0.0735	6.145	31.12	16.60	203	76	0.375	114
50	3.075	46.925	1.81	0.0615	6.182	38.11	16.37	166	65	0.39	96
60	4.428	35.572	1.84	0.0492	6.217	45.12	15.70	144	60	0.41	78
65	5.200	29.800	1.85	0.0431	6.235	48.62	15.40	135	58	0.43	72
70	6.080	23.970	1.86	0.0369	6.254	52.15	15.40	128	55	0.43	68

In order to evaluate the exponent η_1 , we make recourse to the law of mixtures, given by relation (18), 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 for fiber composites may be written as

$$E_c = E_f v_f + \frac{1}{r_m^2} \int_{r_f}^{r_i} E_i(r) [(r + dr)^2 - r^2] + E_m v_m \tag{30}$$

The second right-hand term of relation (30) expresses the contribution of the mesophase, with volume fraction v_i , to the E_c modulus.

If the integral in relation (30) is approximated by

$$I_1 \simeq \frac{2}{r_m^2} \int_{r_f}^{r_i} E_i(r) r dr = \frac{2}{r_m^2} \int_{r_f}^{r_i} \left[E_m + E_f \left(\frac{r_f}{r}\right)^{\eta_1} - E_m \left(\frac{r_f}{r}\right)^{\eta_2} \right] r dr \tag{31}$$

relation (30) becomes

$$(E_c - E_m) - (E_f - E_m)v_f = v_f \left\{ \frac{E_f}{(\eta_1/2 - 1)} [1 - B^{(\eta_1/2 - 1)}] - \frac{E_m}{(\eta_2/2 - 1)} [1 - B^{(\eta_2/2 - 1)}] \right\} \tag{32}$$

in which the quantity B is given by eq. (29) and the only unknown is the exponent η_1 , which can be readily calculated numerically.

Figure 4 presents the variation of the adhesion parameter A vs. the filler volume content v_f of a series of E-glass-epoxy resin composites, whose mechanical properties are given in Ref. 40 for values of the filler volume fraction varying between $v_f = 0$ and $v_f = 0.70$.

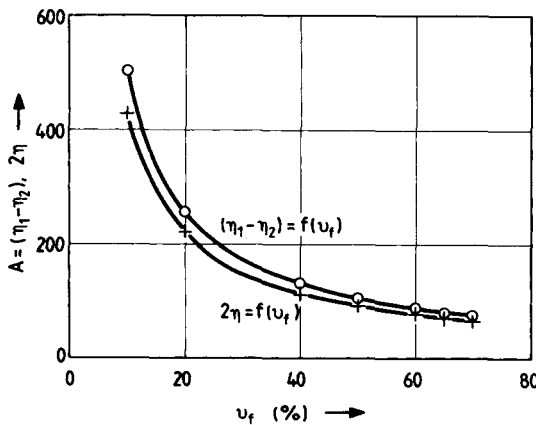


Fig. 4. The mode of evolution of the variable terms $E_f(r_f/r)^{\eta_1}$ and $E_m(r_f/r)^{\eta_2}$, contributing to the definition of the interphase modulus, vs. the polar distance r from the fiber boundary for a 65% E-glass fiber-epoxy resin composite.

Equations (25) and (32) 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. In Figure 4 the values of $A = (\eta_1 - \eta_2)$ vs. v_f were plotted for the E-glass-fiber-epoxy composites studied.

Figure 5 presents the variation of the terms $E_f(r_f/r)^{\eta_1}$ and $E_m(r_f/r)^{\eta_2}$ in the mesophase layer for a 65% E-glass-fiber-reinforced epoxy resin, as they have been derived from eq. (32). It is worthwhile indicating the smooth transition of the E_i modulus to the E_m modulus at the region $r \simeq r_i$. Similar behaviors are presented in all other compositions.

It is interesting plotting the variation of the $E_i(r)$ modulus vs. polar distance around a typical fiber. Figure 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 behavior of the composite.

Figure 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 vs. the volume content.

For the case of particulate composites relation (28) should be replaced by²⁷

$$\frac{(r_f + \Delta r)^3}{r_f^3} - 1 = \frac{\lambda v_f}{1 - v_f} \tag{33}$$

from which the radius of the mesophase $r_i = (r_f + \Delta r)$ can be determined.

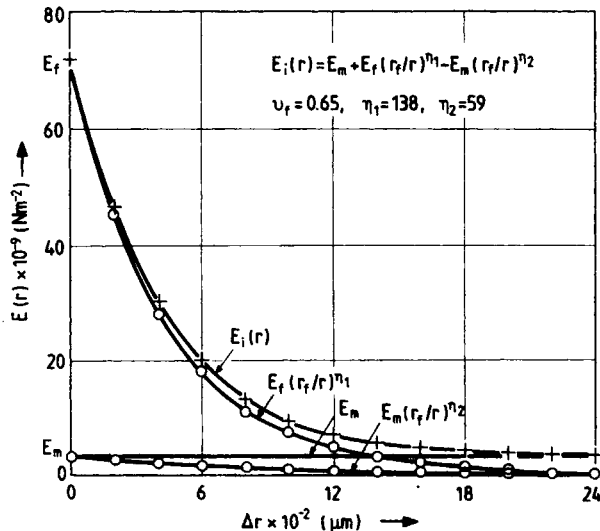


Fig. 5. The variation of the adhesion parameter A for the three-term unfolding model and the adhesion exponent 2η for the two-term mode vs. the filler volume fraction v_f .

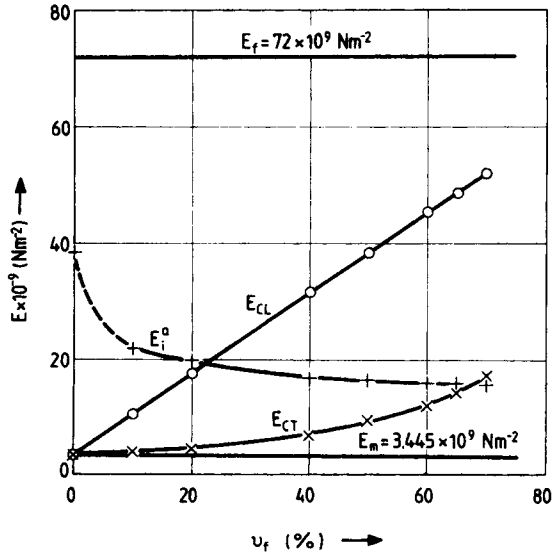


Fig. 6. The variation of the longitudinal and transverse moduli for the composite (E_{CL} , E_{CT}) vs. the filler-volume fraction v_f and the mode of variation of the average mesophase modulus, E_i^a , as derived from the models.

Furthermore, since for the particulates the simple law of mixtures, expressed by relation (1), does not hold and instead relation (8) interconnects the compliance D_c of the composite with the compliances and Poisson's ratios of the phases, it is not possible to directly use relation (30). In this case, it is necessary to define the average value of D_i^a from relation (8) and, then, to introduce its inverse E_i^a in relation (31), yielding the contribution of the mesophase.

For the rest, the calculation of the characteristic parameters of the mesophase for particulates follows the same procedure for fiber-reinforced composites.

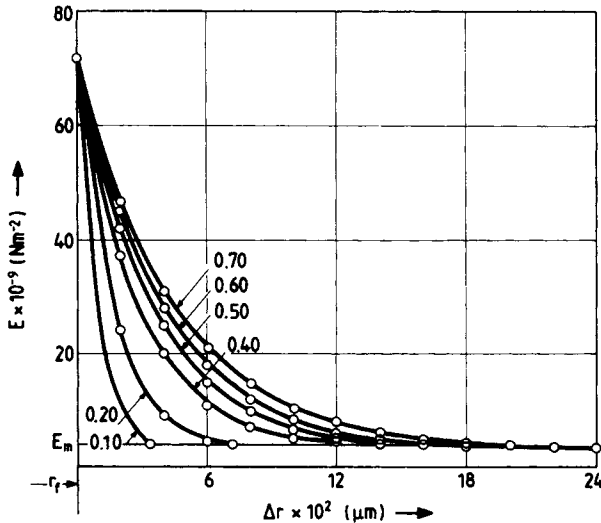


Fig. 7. The variation of the interphase moduli vs. polar distance r for different fiber-volume contents v_f for the three-term unfolding model.

EVALUATION OF THE ADHESION EXPONENT 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 (18) by introducing, instead of integral I_1 , the new integral I_2 , derived from relation (26), and expressed by

$$I_2 = \frac{2}{r_m^2} \int_{r_f}^{r_i} E_i(r)r dr = \frac{2}{r_m^2} \int_{r_f}^{r_i} \left\{ E_f \left(\frac{r_f}{r} \right)^{2\eta} + \left[E_m - E_f \left(\frac{r_f}{r_i} \right) \right] \left(\frac{r - r_f}{r_i - r_f} \right) \right\} r dr \quad (34)$$

This integral, after some algebra, yields

$$I_2 = \frac{E_f v_f}{(\eta - 1)} (1 - B^{\eta-1}) - \frac{v_f (E_m - E_f B^\eta)}{3} (1 + B^{-1/2} - 2B^{-1}) \quad (35)$$

Introducing this integral into relation (30), we obtain

$$\begin{aligned} & (E_c - E_m) - (E_f - E_m/3)v_f \\ &= \frac{E_f v_f}{(\eta - 1)} (1 - B^{\eta-1}) + \frac{E_f v_f B^\eta}{3} (1 + B^{-1/2} - 2B^{-1}) - \frac{E_m v_f}{3} (B^{-1} + B^{-1/2}) \quad (36) \end{aligned}$$

In this relation the only unknown is the exponent 2η , which may be calculated by introducing the appropriate values for all known quantities corresponding to each filler volume content.

The values of the exponent 2η are included in Table I and they are also plotted in Figure 4. A comparison between the corresponding adhesion parameters A and 2η for the two versions of the unfolding model shows the equivalence of the two cases.

Figure 8 presents the variation of the mesophase moduli $E_i(r)$ for the various fiber volume fractions vs. the extent of the mesophase Δr , normalized to the highest fiber volume fraction of 70%. This was done in order to show the similarity of variation of the E_i modulus for the various values of v_f for this series of composites, possessing the same adhesion properties between them. These normalized patterns are equivalent with those presented in Figure 6 for the three-term unfolding model, since the differences between corresponding values of the two versions of the model are insignificant.

The values of the radii r_i of the mesophase for this series of fiber composites varied between 3×10^{-8} m (300 Å) and 24×10^{-8} m (2400 Å) for the various filler volume contents v_f . The values of mesophase cited in the bibliography are varying between 100 and 300 Å. The higher values derived for the unfolding models may be justified as follows:

(i) The extent of mesophase derived by these models incorporates all perturbation phenomena, appearing and influencing the mesophase. These are due not only to the physical and chemical reactions taking place at the mesophase, but also to mechanical reactions because of shrinkage phenomena, stress concentrations at corners, and discontinuities of the phases and

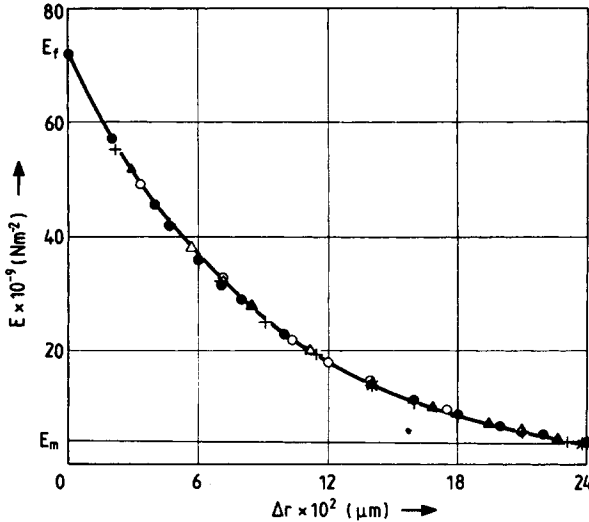


Fig. 8. The variation of the mesophase moduli, normalized to the mesophase thickness Δr for the 70% composite vs. polar distance r for the two-term unfolding model: (●) 0.70; (+) 0.60; (▲) 0.50; (○) 0.40; (△) 0.20; (*) 0.10.

stress singularities. They include also any interactions between neighboring fillers, since all these factors are contributing to the variation of the heat capacity jumps.

(ii) The mesophase was calculated at the glass transition temperatures of the matrix and the composite, where all the above phenomena are accentuated, thus leading to a maximum value for the thickness of the mesophase layer.

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.¹⁻⁵ This was its incompatibility with the assumption made for the model that the boundary layer, constituting the mesophase between fillers 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 layer anticipated from thermodynamic measurements, 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 $E_i(r)$ 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 layer. However, the mode of variation of the mesophase modulus in the layer indicated

the role of transition, played by this layer in adapting and smoothing out the large differences in the mechanical properties of phases.

The values of the radii r_i for the mesophase defined by the model may be judged as reasonable, extending to 2000 Å for the highest filler volume content, if one takes into account the fact that this layer was calculated at the critical zone of the glass transition of the composite, where a resonance of disparities between phases should occur; furthermore, this layer embraces all the factors contributing to its existence and not only just the physiorption and chemisorption phenomena of macromolecules at this zone as is the case of evaluation of such layers in other cases.²⁷

A perfect cooperation between phases is the ideal for an optimum behavior of the composite. A good indication of this cooperation is given either by the adhesion parameter 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 is easier to handle.

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

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