

Thermal Expansion Properties of Particulates Based on the Concept of Mesophase

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Synopsis

The determination of the cubic thermal expansion coefficient of a two-phase particulate is presented in this paper. The model described is based on the well-known Kerner's model and takes into account the existence of mesophase, which constitutes a boundary layer between inclusions and the matrix in the composite. This layer is assumed as created by the substance of matrix during the preparation procedure of the composite, and it includes areas of imperfections around and near the inclusions. The influence of this layer on the effective properties of the composite has been proved to be significant. In order to take into consideration the influence of mesophase a spherical shell with the average properties of this layer is interposed between the spherical inclusion and the matrix. The evaluation of the average elastic and thermoelastic properties and also of the extent of mesophase is succeeded by considering the two-term unfolding model, introduced previously, for describing the change of the elastic modulus of the mesophase layer of fiber-reinforced and particulate composites. The two-term unfolding model was, in this paper, extended to incorporate the mode of variation of the thermal expansion coefficient and the bulk modulus in the mesophase. The model was applied to a polyurethane rubber filled with particles of sodium chloride, and its predictions were found to be in good agreement with the experimental data.

INTRODUCTION

The exact determination of stresses and strains in a particulate under the influence of external forces is a rather impossible task. However, when the volume fraction of the dispersed phase is not too large, an average problem can be constructed, for the determination of the average state of stress and strain near and inside an inclusion. There are many models presenting various average problems and all of them have as function the calculation of the effective properties of the composite materials. A usual supposition is that the composites may be described adequately by an elastic, homogeneous, and isotropic matrix with known moduli, in which inclusions of another elastic, homogeneous, and isotropic material are embedded, whose moduli are also given. The distribution of the inclusions is also considered uniform.

Hashin^{1,2} assumed the composite as a collection of small volume elements of various sizes and shapes, filling densely the volume of the composite. The solution of the problem was achieved by introducing a further condition. He also considered the particulates, as conglomerations of spherical inclusions and spherical shells, surrounding the inclusions, with the properties of the matrix. In every volume element the volume fraction of the inclusion was equal to the total volume fraction of the dispersed phase in the com-

posite. Wang and Kwei³ have used Hashin's model to calculate the thermal expansion coefficients of particulates. The same loading mode, applied to the representative volume element (RVE), was considered acting on another spherical, homogeneous and isotropic element, having the same size as the RVE, but the average properties of the composite and the distribution of stresses and displacements in it were used for the calculation of the state of stress in the RVE.

Van der Poel⁴ and Kerner⁵ followed a different way when they constructed their respective average problems. They considered a RVE consisting of the filler, the shell of the matrix, and around them a third substance, having such properties, so that the average state of stress and strain to be closer to the real situation in the composite. The differences between these two models are related to the different properties holding in this third phase.

Indeed, Van der Poel has considered two spheres of the same radius R ($R \gg 1$). The substance of one sphere had the effective properties of the composite, whereas the substance of the second sphere had also the effective properties of the composite, except in a small concentric spherical inclusion of radius equal to unity, which consisted of a sphere of radius a ($a < 1$) with the properties of the filler and a spherical shell with the properties of the matrix.

For the evaluation of a property of the particulate Van der Poel considered as acting the same external forces on the external spherical surfaces of both spheres. He solved completely the problem of the first sphere and then determined the respective property by using the solution of the second problem with the help of the following conditions:

- (i) Same displacements at the external surface of the two spheres ($r = R$).
- (ii) Continuity of stresses and displacements at the interfaces of radii $r = a$ and $r = 1$.

On the other hand, Kerner⁵ has placed an intermediate layer between the shell of the matrix and the composite, having properties changing continuously from those of the matrix to those of the composite. This change of properties, as well as the volume where this transition takes place were unknown. To avoid arbitrary assumptions about the mode of variation of these properties and the extent of this inhomogeneous layer, Kerner has considered average behaviors of the materials of the filler, the matrix, and the composite. From this description it is obvious that, in this model, a continuity of stresses and displacements is assured between the shell of the matrix and the external layer of the model. Then, it may be concluded that Kerner's model is closer to the real situation in a composite, since the microstructure of the composite material cannot be ignored at the vicinity of the inclusion.

It should be also mentioned that, in spite of the differences existing between the models of Hashin, Van der Poel, and Kerner, all these models yield the same expression for the effective bulk modulus of the composite. Since the determination of the thermal expansion coefficient is closely related to the evaluation of the bulk modulus, it is expected that all the above models yield also the same expression for the thermal expansion coefficient of the particulate.

On the other hand, all the above-sketched models assume perfect mathematical surfaces for their interfaces, as well as perfect adhesion between the matrix and the fillers. In reality, as has already been reported in previous articles,⁶⁻⁸ around an inclusion a complex situation develops. Areas of imperfect bonding, permanent stresses, due to shrinkage of the polymer phase during the curing period, high stress gradients, stress singularities, due to the rough surfaces of the inclusions, voids, microcracks, etc., make the above conditions far away from reality. Also the interaction of the matrix polymer during its curing period with the surface of the solid inclusion restricts the free segmental and molecular mobility of the polymeric matrix and thus creates a constrained layer with presumably different mechanical and physical properties.

A more realistic examination of the behaviour of composite materials can be done by considering the mesophase as a spherical shell between the filler and the matrix. This is the main thought in Ref. 7, in which the properties and the extent of mesophase are calculated by the respective properties of the filler, the matrix, and the composite, as well as by their volume fractions. In this article the mesophase was considered homogeneous.

The consideration of the mesophase layer is also used in Ref. 9, where the thermoelastic behavior of this layer is investigated. The experimental data, which were used in the last two articles, were obtained by an experimental procedure, which is described in Ref. 10.

As the mesophase accommodates the differences between the properties of the matrix and the filler, it is obvious that the average properties of mesophase are somewhere in-between those of the matrix and those of the filler. Also, as the mesophase is created mainly by the macromolecules of the matrix polymer for hard-core composites, it is expected that the average properties of mesophase are closer to those of matrix.

The satisfaction of the above ideas and the accommodation of the different properties of the inclusions and the matrix may be succeeded by a continuous change of the properties of the mesophase from those of the filler to those of the matrix. This idea was developed in Ref. 8, where an approximation was introduced assuming that the mesophase is extended to infinity, penetrating into the matrix. Moreover, in some layers of the mesophase its properties were not lying always between their bounds of the filler and the matrix. All these approximations and disadvantages were corrected by the construction of the three-term and two-term unfolding models,^{6,11} the second being more simple and presumably more stable.

In this paper a model, suitable for the determination of the cubic thermal expansion coefficient of a particulate, will be presented by considering as known the properties of matrix, filler, and mesophase. The model is based on the conceptions of Kerner's model and the properties and the extent of mesophase are calculated by using the two-term unfolding model.

THE MODEL FOR THE THERMAL EXPANSION COEFFICIENT OF PARTICULATES

For the determination of the cubic thermal expansion coefficient of a particulate an average problem was constructed, whose solution describes

the average state of stress and strain, around and inside an inclusion. The model used is an extension of Kerner's model, and it is presented analytically here.

In the following, subscripts $f, i, m,$ and c correspond to filler, mesophase, matrix, and composite material, respectively. The model is presented in Figure 1. At first, there is a sphere of radius $r = r_f$, made of substance with the properties of the dispersed phase. This inclusion is surrounded by a spherical shell, being extended from $r = r_f$ to $r = r_b$, with the variable properties of the mesophase. A second spherical shell extending from $r = r_i$ to $r = r_m$, enveloping the previous layers, consists of a material with the properties of the matrix. The sizes of radii r_f, r_b and r_m are compatible with the average volume fractions of each phase in the composite. In this model, the volume fraction of the mesophase is assumed as known, and it will be evaluated in the next paragraph.

Sufficiently far beyond the matrix layer it is the average medium, but, in between, there is an intermediate zone having properties changing continuously from those of the matrix to the effective properties of the composite.

In this model all the materials are considered elastic, homogeneous, and isotropic, except the mesophase and the intermediate zone, which are inhomogeneous, because of their continuously changing properties with the radial distance. But, for the evaluation of the thermal expansion coefficient, the mesophase may be initially assumed as homogeneous having its average properties, which will be determined by applying the two-term unfolding model.

For the evaluation of the thermal expansion coefficient γ_c of the composite, a uniform heating of all phases is assumed raising the temperature of the RVE T degrees above the temperature, where the material is considered as released from any stress. Because of the existing spherical symmetry in the model, we may use spherical coordinates for the solution of

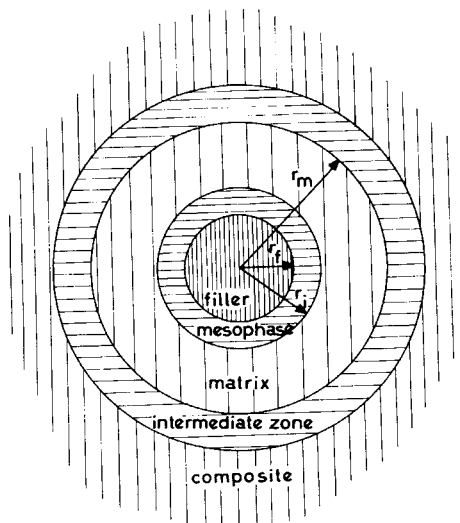


Fig. 1. Kerner's model extended by the introduction of the mesophase.

the problem. It is obvious that there are only normal components of stresses and radial displacements expressed in the following forms^{12,13}:

$$u = \frac{1}{3}\gamma Tr + Ar + Br^{-2} \quad (1)$$

$$\sigma_{rr} = 3KA - 4GBr^{-3} \quad (2)$$

$$\sigma_{\vartheta\vartheta} = \sigma_{\varphi\varphi} = 3KA + 2GBr^{-3} \quad (3)$$

where A and B are integration constants.

Because of symmetry the displacements are zero at the center of the spherical inclusion. So, it is easy to derive that

$$B_f = 0 \quad (4)$$

The dilatation of a phase takes the following value:

$$\frac{\Delta V}{V} = e = \epsilon_{rr} + \epsilon_{\varphi\varphi} + \epsilon_{\vartheta\vartheta} = \frac{\partial u}{\partial r} + 2\frac{u}{r} = \gamma T + 3A \quad (5)$$

$$\frac{\Delta V}{V} = e = \frac{p}{K} + \gamma T \quad (6)$$

so that it is valid that

$$p = 3AK \quad (7)$$

where p is hydrostatic pressure on the phase considered.

As mentioned above, no external force is acting on the composite. Therefore, the hydrostatic pressure far away from the inclusion, where the stresses are eliminated, must be equal to zero. Then, it is valid that

$$p_c = 3A_c K_c = 0 \quad (8)$$

and

$$A_c = 0 \quad (9)$$

Considering now the above equation, it is easy to observe that everywhere in the composite material the hydrostatic pressure is zero.

The state of stresses and displacements is described by the following equations:

$$[u]_f = \frac{1}{3}\gamma_f Tr + A_f r \quad (10)$$

$$[u]_i = \frac{1}{3}\gamma_i Tr + A_i r + B_i r^{-2} \quad (11)$$

$$[u]_m = \frac{1}{3}\gamma_m Tr + A_m r + B_m r^{-2} \quad (12)$$

$$[u]_c = \frac{1}{3} \gamma_c Tr + B_c r^{-2} \quad (13)$$

$$[\sigma_{rr}]_f = 3K_f A_f \quad (14)$$

$$[\sigma_{rr}]_i = 3K_i A_i - 4G_i B_i r^{-3} \quad (15)$$

$$[\sigma_{rr}]_m = 3K_m A_m - 4G_m B_m r^{-3} \quad (16)$$

$$[\sigma_{rr}]_c = -4G_c B_c r^{-3} \quad (17)$$

$$[\sigma_{\vartheta\vartheta}]_f = [\sigma_{\varphi\varphi}]_f = 3K_f A_f \quad (18)$$

$$[\sigma_{\vartheta\vartheta}]_i = [\sigma_{\varphi\varphi}]_i = 3K_i A_i + 2G_i B_i r^{-3} \quad (19)$$

$$[\sigma_{\vartheta\vartheta}]_m = [\sigma_{\varphi\varphi}]_m = 3K_m A_m + 2G_m B_m r^{-3} \quad (20)$$

$$[\sigma_{\vartheta\vartheta}]_c = [\sigma_{\varphi\varphi}]_c = 2G_c B_c r^{-3} \quad (21)$$

Since stresses and displacements must be continuous at the two interfaces, between inclusion and mesophase, and also between mesophase and matrix, the following boundary conditions are valid:

$$[u(r_f)]_f = [u(r_f)]_i \quad (22)$$

$$[u(r_i)]_i = [u(r_i)]_m \quad (23)$$

$$[\sigma_{rr}(r_f)]_f = [\sigma_{rr}(r_f)]_i \quad (24)$$

$$[\sigma_{rr}(r_i)]_i = [\sigma_{rr}(r_i)]_m \quad (25)$$

Stresses and displacements are also continuous at the spherical surface of radius r_m because of the assumed continuous mode of variation of the properties in the intermediate zone. Because of the unknown way that these properties change, as well as because of the unknown extent of the intermediate zone, it is necessary to consider the average behavior of the component materials. Then, the dilatation of the particulate must be the sum of the dilatations of the component materials multiplied each one by its respective volume fraction. Then, we have the following relation:

$$\int e_c dV_c = \sum_j \int e_j dV_j \quad j = f, i, m \quad (26)$$

or

$$\bar{e}_c = \bar{e}_f v_f + \bar{e}_i v_i + \bar{e}_m v_m \quad (27)$$

where $v_j = V_j/V_c$ and $\sum_j v_j = 1$ ($j = f, i, m$).

For any plane surface drawn in the composite it is valid that the mean normal force across it, is the sum of the mean normal forces across its parts, which lie in the inclusion, the mesophase and the matrix. Then, we have

$$\int p_c dS_c = \sum_j \int p_j dS_j \quad j = f, i, m \quad (28)$$

where S_j is the surface of a component material, or

$$\bar{p}_c = \bar{p}_f v_f + \bar{p}_i v_i + \bar{p}_m v_m \tag{29}$$

where

$$v_j = V_j / V_c = S_j / S_c \tag{29'}$$

This last expression for the volume fraction v_j is correct, because the inclusions are uniformly dispersed in the composite and their size is too small compared with that of the composite.

The mean values introduced by eqs. (27) and (29) are those which can be determined by solving the average problem, described above.

Using eqs. (22)–(25), as well as (27) and (29) after some algebra, we may obtain the following relationship for the thermal expansion coefficient γ_c of the composite:

$$\gamma_c = \frac{P_f}{P_c} \gamma_f + \frac{P_i}{P_c} \gamma_i + \frac{P_m}{P_c} \gamma_m \tag{30}$$

where

$$P_f = \frac{4}{3} G_i O_{11} - \frac{4}{3} (G_m - G_i) K_m v_m B O_{12} + K_m v_f O_{13} \tag{31}$$

$$P_i = -\frac{4}{3} G_i O_{11} - \frac{4}{3} G_m K_m v_m O_{12} + \frac{4}{3} (G_m - G_i) K_m v_m B O_{12} + K_m v_i O_{13} \tag{32}$$

$$P_m = \frac{4}{3} G_m K_m v_m O_{12} + K_m v_m O_{13} \tag{33}$$

$$P_c = K_m O_{13} \tag{34}$$

$$O_{11} = A_1 A_4 - A_2 A_3 \tag{35}$$

$$O_{12} = A_5 A_4 - A_6 A_3 \tag{36}$$

$$O_{13} = A_5 A_2 - A_6 A_1 \tag{37}$$

$$A_1 = (3K_f K_m + 4G_m K_f) v_f + 4(G_m - G_i) K_m v_m B \tag{38}$$

$$A_2 = (3K_i K_m + 4G_m K_m) v_m + (3K_i K_m + 4G_m K_i) v_i - 4(G_m - G_i) K_m v_m B \tag{39}$$

$$A_3 = 3(K_m - K_f) v_f \tag{40}$$

$$A_4 = 3(K_m - K_i) v_i \tag{41}$$

$$A_5 = 3K_f + 4G_i \tag{42}$$

$$A_6 = -3K_i - 4G_i \tag{43}$$

$$B = (r_f / r_i)^3 = v_f / (v_f + v_i) \tag{44}$$

Supposing now that $G_m = G_i$ and $K_m = K_i$ or $G_f = G_i$ and $K_f = K_i$,

Kerner's equation for the thermal expansion coefficient of the composite may be derived. This was expected because, by assuming these equalities valid, the mesophase is annulled.

Also, by using the equations $v_f = 0$, $v_i + v_m = 1$, $K_m = K_i$, and $G_m = G_i$ or $v_m = 0$, $v_f + v_i = 1$, $K_f = K_i$, and $G_f = G_i$ in the relation (30), we may find the following values for the thermal expansion coefficient of the composite respectively:

$$\gamma_c = \gamma_m$$

and

$$\gamma_c = \gamma_f$$

THE EXTENT AND THE AVERAGE BULK- AND ELASTIC-MODULI AND THE THERMAL EXPANSION COEFFICIENT OF THE MESOPHASE

Mesophase, in our model, accommodates the differences, which exist between the properties of the filler and the matrix. In all other models the accommodation of the above differences is succeeded abruptly by supposing only that the stresses and the displacements are continuous at ideally smooth and mathematically described interfaces. This assumption, however, is far from reality. In actual particulates the smoothing of differences is always obtained by an intermediate zone, which has continuously varying properties, as is assumed by the mesophase in our model. This is the reason why Kerner's model may be considered more satisfactory than any similar model, because in Kerner's model the differences between the matrix and the composite are accommodated, by introducing the intermediate zone between them, imitating nature by this zone.

The variation of the properties of the mesophase satisfies the following conditions:

(i) The properties of the mesophase must be identical with those of the inclusion at the spherical surface of radius $r = r_f$.

(ii) The properties of the mesophase must be identical with those of the matrix at the interface between mesophase and matrix.

The mesophase is assumed to be created by the macromolecules of the matrix during the preparation of the composite material, and has small thickness for a good quality of adhesion of the composite. Because of the above considerations we may introduce two more boundary conditions:

(iii) The tangent of the curve, which represents the change of a property in the mesophase, at the interface $r = r_i$ must coincide with the line corresponding to the constant value of the respective property of matrix and so satisfying the tangent continuity assumption between mesophase and matrix.¹⁴ This condition is a result of the composition of the mesophase.

(iv) The curve must be steep, but always smooth. This condition is a result of the composition and the thickness of the mesophase.

The two models, that were developed in Ref. 11 satisfy rigorously the conditions (i), (ii), and (iv), whereas the satisfaction of the third condition

is achieved by a suitable choice of the parameters, expressing the variation of the properties of the mesophase. The two-term unfolding model¹¹ will not be extended to satisfy rigorously the third also condition for the case of the elastic¹⁴ and bulk moduli and the thermal expansion coefficient.

Because of the radial symmetry, which holds in the problem, it is obvious that all the properties of the mesophase depend only on the distance from the center of the inclusion, r .

The mode of variation of the elastic modulus in the mesophase was presented in Refs. 6 and 11 by the following expression:

$$E_i(r) = E_f \left(\frac{r_f}{r} \right)^{2\eta_E} + \left[E_m - E_f \left(\frac{r_f}{r_i} \right)^{2\eta_E} \right] \frac{(r - r_f)}{(r_i - r_f)} \tag{45}$$

Conditions (i) and (ii) are automatically satisfied. The third condition is satisfied by the next equation:

$$E_m - E_f B^{2\eta_E/3} = 2\eta_E E_f B^{2\eta_E/3} (1 - B^{1/3}) \tag{46}$$

which is derived by zeroing the derivative of $E_i(r)$ at $r = r_i$. Subscript E denotes that the exponent 2η corresponds to the elastic modulus.

The average elastic modulus of the mesophase E_i , which is indispensable for the determination of r_i , as will be presented below, may be determined by integrating from $r = r_f$ to $r = r_i$. So we have

$$E_i v_i = \frac{1}{r_m^3} \int_{r_f}^{r_i} E_i(r) [(r + dr)^3 - r^3] \tag{47}$$

or

$$E_i v_i = \frac{3E_f v_f}{(2\eta_E - 3)} (1 - B^{2\eta_E/3-1}) - \frac{v_f}{4} (E_m - E_f B^{2\eta_E/3}) \tag{48}$$

$$\times (1 + B^{-1/3} + B^{-2/3} - 3B^{-1})$$

Since the bulk modulus of the mesophase has an analogous mode of variation as the elastic modulus, it is obvious that, in this case, expressions similar to (45), (46), and (48) will hold. Then, we have

$$K_i(r) = K_f \left(\frac{r_f}{r} \right)^{2\eta_b} + \left[K_m - K_f \left(\frac{r_f}{r_i} \right)^{2\eta_b} \right] \frac{(r - r_f)}{(r_i - r_f)} \tag{49}$$

$$K_m - K_f B^{2\eta_b/3} = 2\eta_b K_f B^{2\eta_b/3} (1 - B^{1/3}) \tag{50}$$

$$K_i v_i = \frac{3K_f v_f}{(2\eta_b - 3)} (1 - B^{2\eta_b/3-1}) - \frac{v_f}{4} (K_m - K_f B^{2\eta_b/3}) \tag{51}$$

$$\times (1 + B^{-1/3} + B^{-2/3} - 3B^{-1})$$

where K_i is the average bulk modulus of the mesophase. Subscript b denotes that the exponent 2η corresponds to the bulk modulus.

The bulk modulus of a particulate was determined in Ref. 11, by using the properties of the filler, the mesophase, and the matrix, and the following relations were found:

$$\begin{aligned} \frac{1}{K_c} = & \frac{v_f (\lambda_{fi})^2}{K_f (\lambda_{im})^2} + \frac{3v_f^2 (1 - \lambda_{fi})^2}{4BG_i v_i (\lambda_{im})^2} + \frac{v_f^2 (\lambda_{fi} - \frac{1}{B\lambda_{im}})^2}{K_i v_i \lambda_{im}} \\ & + \frac{3v_f (1 - \frac{1}{\lambda_{im}})^2}{4BG_m v_m} + \frac{1}{K_m v_m} \left(\frac{v_f}{B\lambda_{im}} - 1 \right)^2 \end{aligned} \tag{52}$$

where

$$\lambda_{fi} = \frac{3(1 - \nu_i) (v_f + v_i) E_f}{2v_i E_i (1 - 2\nu_f) + [3v_f(1 - \nu_i) + v_i(1 + \nu_i)] E_f} \tag{53}$$

$$\begin{aligned} \lambda_{im} = & \frac{3(1 - \nu_m) - 2(1 - 2\nu_m)v_m}{3(1 - \nu_m)} - \frac{E_m v_m}{E_i} \frac{1}{3(1 - \nu_m)} \\ & \times [3(1 - \nu_i) \frac{v_f}{v_i} (\lambda_{fi} - 1) - 2(1 - 2\nu_i)] \end{aligned} \tag{54}$$

The precise value of λ_{im} can be found by the relation (54) while the respective one presented in Ref. 11 may be derived from (54) by considering $v_i^2 = 0$. This last consideration is avoided in this paper because the value of v_i is not always small enough.

The values of ν_i and G_i in eqs. (52)–(54) can be found easily by the well-known relations:

$$\nu_i = \frac{3K_i - E_i}{6K_i} \tag{55}$$

$$G_i = \frac{E_i}{2(1 + \nu_i)} \tag{56}$$

Relations (46), (48), (50), (51), and (52) form a system of five equations with five unknowns, that is, the quantities, E_b , $2\eta_E$, K_b , $2\eta_b$, r_b which can be found by solving the above system. The value of the bulk modulus of the particulate, K_c , is considered as known and can be found by experiments. It is important to say that the experimental value of K_c is necessary for the evaluation of r_b because the extent of the mesophase greatly depends on the procedure of the preparation of the composite. We also must note that only the value of K_c is necessary and not of the elastic modulus E_c , because we don't have any expression for the elastic modulus of the composite, or for its Poisson's ratio.

The elastic modulus varies in the mesophase from a value E_f to a smaller one E_m , when the radius r is increased. But, in the case of the thermal expansion coefficient, $\gamma_i(r)$ is increased from γ_f to γ_m with the distance from

the interface between the inclusion and the mesophase. This difference makes it necessary to adapt the form of relation (45):

$$\gamma_i(r) = \gamma_f \left[1 - \frac{\Gamma}{\Gamma_i} \right] + \gamma_m \left[1 - \left(\frac{1}{1 + \Gamma} \right)^{2\eta_T} + \left(\frac{1}{1 + \Gamma_i} \right)^{2\eta_T} \frac{\Gamma}{\Gamma_i} \right] \quad (57)$$

where

$$\Gamma = \frac{r - r_f}{r_f} \quad (58)$$

$$\Gamma_i = \frac{r_i - r_f}{r_f} \quad (59)$$

Conditions (i) and (ii) are automatically satisfied. The third condition in this case it is obtained by the following relations:

$$\gamma_f - \gamma_m B^{2\eta_T/3} = 2\eta_T \gamma_m B^{2\eta_T/3} (1 - B^{1/3}) \quad (60)$$

where the subscript *T* denotes that the exponent 2η corresponds to the thermal expansion coefficient.

The quantity γ_i in relation (30) expresses the average value of the thermal expansion coefficient of the mesophase and is given by

$$\gamma_i v_i = \frac{1}{(r_m)^3} \int_{r_f}^{r_i} \gamma_i(r) [(r + dr)^3 - r^3] \quad (61)$$

or

$$\begin{aligned} \gamma_i v_i = & (\gamma_f + \gamma_m) v_f (B^{-1} - 1) + \frac{\gamma_m v_f}{(2\eta_T/3 - 1)} (B^{2\eta_T/3 - 1} - 1) \\ & + (\gamma_f - \gamma_m B^{2\eta_T/3}) \frac{v_f}{4} (1 + B^{-1/3} + B^{-2/3} - 3B^{-1}) \end{aligned} \quad (62)$$

The calculation of the values of $2\eta_T$ and γ_i is succeeded by the solution of the system of eqs. (60) and (62).

The three exponents $2\eta_B$, $2\eta_b$, and $2\eta_T$ express the quality of adhesion between matrix and filler. Large absolute values of the exponents express good quality of the adhesion, while a decrease of their values corresponds to a deterioration of the quality of the adhesion.

The value of r_i can also be calculated by solving the system of the eqs. (30), (60), (62), (46), (48), (50), and (51), considering the value of γ_c as given by experimental data. The two values of r_b , which can be calculated by assuming the values of K_c or γ_c as known, respectively, must be the same.

APPLICATION AND DISCUSSION

As already noted, the knowledge of experimental data for the bulk modulus of the composite is indispensable for the calculation of the extent of

the mesophase, by using the elastic properties of the composite material. This is the reason why the experimental results of van der Wal, Bree, and Schwarzl¹⁵ were used for the investigation of the behavior of our model. The composite material, which was examined by the above-mentioned scientists, was polyurethane rubber, filled with particles of sodium chloride. The elastic and thermoelastic properties of these materials at 20°C are presented in Table I. The experimental values of the volume expansivity, γ_c , and of the bulk modulus, K_c , of the particulate are presented in the third columns of the Tables II and III, respectively, and they were measured by using specimens containing inclusions having a size of 90–105 μm .

The size of the inclusion surrounded by the mesophase, corresponding to the quantity d_b , was calculated by assuming the experimental value, at first, of the thermal expansion coefficient, and secondly of the bulk modulus of the composite as known. Subscripts T and b were used respectively to distinguish the two values of d_i that were calculated by the above-mentioned methods. The results, which are presented in the fifth columns of the Tables II and III, were calculated by assuming that the average particle size is equal to 98 μm . The differences between the values of d_{iT} and d_{ib} , presented in the last column of the Table II, are small. The greatest difference, as we can see, is equal to 6.12%, while the average difference for all the other cases is equal to 2.5%.

All the above remarks permit to predict the value of the thermal expansion coefficient of the particulate. We can consider that the extent of the mesophase is calculated by using the experimental value of the bulk modulus of the composite and follow the inverse way for the case of the volume expansivity. The calculated values of γ_c , as well as their discrepancies from the experimental ones are presented in Table III. The greatest discrepancy is equal to 2.04% and corresponds to a volume fraction of sodium chloride equal to 0.414.

It must be noted that when the extent of the mesophase is increased, its influence to the effective properties of the particulate is also increased. So, the mesophase extending to a volume fraction equal to 3.6%, and corresponding to a volume fraction of the filler equal to 41.4%, influences significantly the respective value of the thermal expansion coefficient of the particulate. Thus, the discrepancy of the value derived from Kerner's model, which ignores the existence of mesophase, is the double of the discrepancy derived from the mesophase model for this type of composite.

The average properties of the mesophase, as well as the three exponents,

TABLE I
Elastic and Thermoelastic Properties of Polyurethane Rubber and Sodium-Chloride at 20°C

Material	Volume expansivity γ ($10^{-4} \text{ }^\circ\text{C}^{-1}$)	Shear modulus G (N m^{-2})	Elastic modulus E (N m^{-2})	Bulk modulus K (N m^{-2})	Poisson's ratio ν
Sodium chloride	1.134	1.28×10^{10}	4.43×10^{10}	2.53×10^{10}	0.208
Polyurethane rubber	7.23	1.32×10^6	3.96×10^6	1.97×10^9	0.500

TABLE II
 Values of the Characteristic Quantities of the Composite Calculated by Using the Experimental Values
 of the Thermal Expansion Coefficient of the Composite γ_c

v_f	Particle size d_f (μm)	γ_c ($10^{-4} \text{ }^\circ\text{C}^{-1}$) experimental	v_i	d_{ir} (μm)	γ_i ($10^{-4} \text{ }^\circ\text{C}^{-1}$)	$2\eta_T$	K_i (10^9 N m^{-2})	$2\eta_b$	E_i (10^9 N m^{-2})	$2\eta_E$	$\frac{d_{ir} - d_{ib}}{d_f} \times 100$
0.104	98	6.49	0.036	108.208	5.176	-9.982	9.85	-10.303	15.00	-10.600	5.53-6.12
0.207	98	5.86	0.034	103.096	5.114	-19.021	10.08	-19.649	15.44	-20.230	2.99-3.59
0.311	98	5.32	0.036	103.380	5.118	-18.067	10.07	-18.663	15.42	-19.214	
			0.003	98.314	5.054	-293.826	10.32	-303.778	15.88	-312.988	1.77-2.19
			0.005	98.522	5.056	-177.057	10.31	-183.047	15.86	-188.590	
0.414	98	4.50	0.066	102.953	5.113	-19.541	10.09	-20.187	15.46	-20.785	2.24-2.38
			0.068	103.096	5.114	-19.021	10.08	-19.649	15.44	-20.230	

* The upper and lower bounds, for all calculated quantities, depend on the respective values of v_i , and they are given, only when these values differ by amounts larger than 0.002.

TABLE III
 Values of the Characteristic Quantities of the Composite Calculated by Using the Experimental Values of the Bulk Modulus of the Composite K_c

v_f	Particle size d_f (μm)	K_c experimental (10^9 N m^{-2})	d_b (μm)	K_c (10^9 N m^{-2})	$2\eta_b$	E_i (10^9 N m^{-2})	$2\eta_E$	γ_c ($10^{-4} \text{ }^\circ\text{C}^{-1}$) calculated	γ_c ($10^{-4} \text{ }^\circ\text{C}^{-1}$) experimental	$2\eta_T$	$\frac{\gamma_{\text{cal}} - \gamma_{\text{exp}}}{\gamma_{\text{exp}}} \times 100$
0.104	98	2.21	102.214	10.13	-23.557	15.52	-24.257	6.552	5.103	-22.801	0.86-0.96
			102.788	10.10	-20.850	15.47	-21.468	6.546	5.110	-20.182	
0.207	98	2.47	99.858	10.24	-52.167	15.74	-53.736	5.929	5.074	-50.472	1.08-1.18
			100.161	10.23	-44.990	15.71	-46.341	5.923	5.077	-43.530	
0.311	98	2.84	100.258	10.22	-43.089	15.70	-44.392	5.264	5.079	-41.701	1.05-1.18
			100.459	10.21	-39.668	15.68	-40.857	5.257	5.081	-38.383	
0.414	98	3.35	100.762	10.20	-35.420	15.65	-36.480	4.592	5.085	-34.274	2.04

^a The upper and lower bounds, for all calculated quantities, depend on the respective values of v_b and they are given only when these values differ by amounts larger than 0.002.

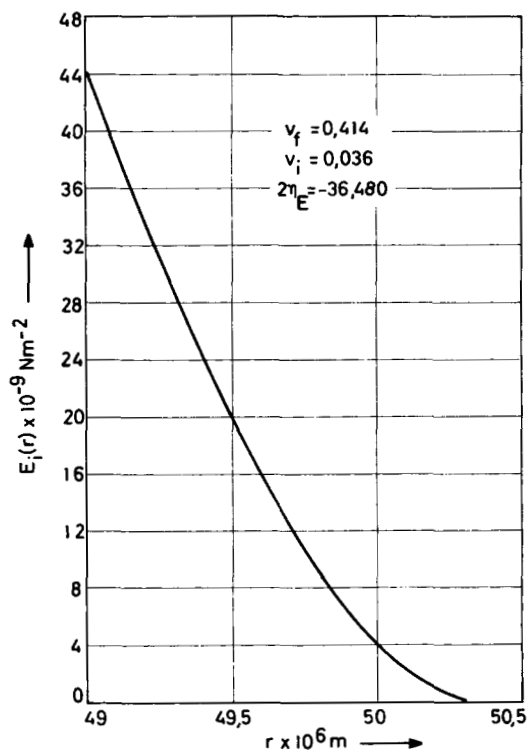


Fig. 2. The variation of the elastic modulus of the mesophase vs. the polar distance r from the center of the inclusion.

that is the quantities $2\eta_T$, $2\eta_b$, and $2\eta_E$, are presented in Tables II and III. Upper and lower bounds, for all calculated quantities, are presented in these tables because of the accuracy of the experimental results.

It is observed that the absolute values of the exponents decrease when the volume fraction of the mesophase increases, that is, when the adhesion becomes less and less effective.

The mode of variation of the elastic and bulk moduli and of the thermal expansion coefficient of the mesophase is plotted in Figures 2, 3, and 4, respectively, for the case where the volume fraction of the filler is equal to 0.414. A steep, but smooth, transition from the properties of the inclusion to those of the matrix is derived from this model.

CONCLUSIONS

The two-term unfolding model, which describes the mode of variation of the elastic modulus in the mesophase, was extended for the case of the bulk modulus, as well as of the thermal expansion coefficient of the mesophase. This model describes the accommodation of the differences between the properties of the inclusion and the matrix by a more realistic way than the previous models. These models considered a continuity of stresses and displacements at the interface, between the matrix and the inclusion, which is also supposed as a perfect, and mathematically described surface.

The assumption of the tangent continuity at the interface between the

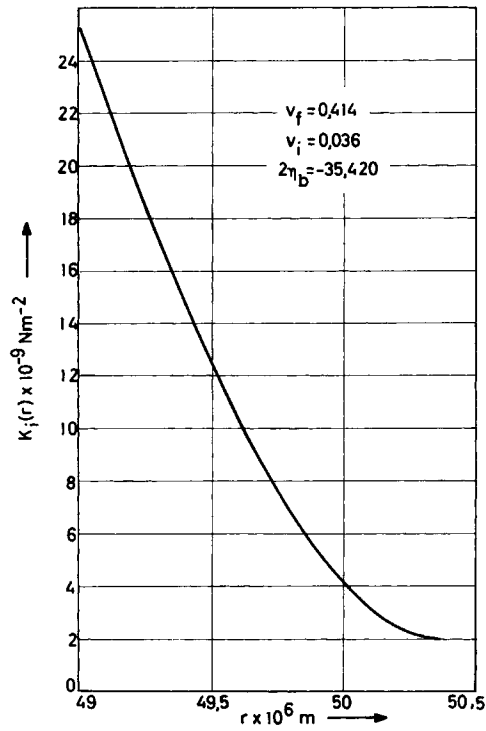


Fig. 3. The variation of the bulk modulus of the mesophase vs. the polar distance r from the center of the inclusion.

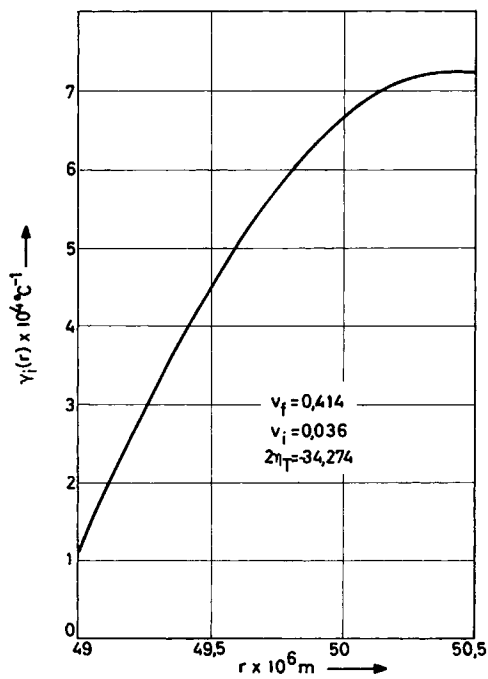


Fig. 4. The variation of the thermal expansion coefficient of the mesophase vs. the polar distance r from the center of the inclusion.

mesophase and the matrix improved the two-term unfolding model and added one more condition, which makes possible the determination of the extent of the mesophase by using the experimental value of the bulk modulus of the composite.

Then, an accurate prediction of the thermal expansion coefficient of the particulate is possible, with small discrepancies from the experimental values, by using the calculated value of r_i and the model for the volume expansivity, which was described in detail in this paper. This model, based on Kerner's model, presents a more satisfactory behaviour than all previous models, because of the introduction of the mesophase, which takes into account the quality of the adhesion. This mesophase, although of a small extent, exerts a great influence on the properties of the composite.

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