Adhesion Quality and Extent of Mesophase in Particulates along the Whole Viscoelastic Spectrum

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Synopsis

The extent of mesophase, which constitutes the boundary layer between the filler and the matrix of a composite, was defined in this paper along the whole viscoelastic spectrum of the polymeric substance constituting the matrix. The already established *two-term unfolding model*[1-3] was based on thermodynamic measurements of the heat capacity jumps at the glass transition regions of the filled and unfilled substances in order to define the extent of mesophase. In this paper we dispense ourselves with these delicate measurements, based on Lipatov's theory, and we use values taken from the storage and loss compliances of the composite and its constituents, along the whole viscoelastic spectrum of the composite. It was shown that the extent of the mesophase, necessary to sustain the shearing loading between phases, appearing at the glass transition zone, where the loss-compliances presented their characteristic peaks of resonance, remained constant and almost independent of the respective values of mechanical properties at this critical region. It was shown that any set of values of the mechanical characteristic quantities, defining the composite and its constituents along the whole viscoelastic spectrum, is sufficient to evaluate the extent of the mesophase, and this boundary layer undergoes only negligible variations. Experimental evidence with typical E-glass polystyrene and other particulates, at various volume fractions of the filler, yielded a satisfactory coincidence with the results derived by using Lipatov's theory and a constancy of the mesophase thickness along the whole temperature range.

INTRODUCTION

There are a number of theories which formulate the behavior of the elastic modulus of filled polymer systems. However, a satisfactory examination of the strength laws of rigid-particulate composites requires some further consideration.

Analytic solutions for various mathematical models are based on variational principles of mechanics and yield upper and lower bounds of approximations for the effective moduli of the composites. These solutions are valid only for rather low filler contents, since they ignore, for reasons of efficiency, all mechanical interactions between neighboring fillers, as well as physicochemical influences on either phase from the other one. A great number of empirical and semiempirical expressions for the effective moduli exist, expressing some kind of *law of mixtures*, or trying to match theoretical expressions to experimental data by appropriately defining the existing constants in these expressions. In all these models *perfect adhesion* is assumed holding between phases.[4-6]

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Another type of model is referred to multiphase particulates. It assumes three consecutive phases as concentric spheres and the external one is extended to infinity. The spherical filler is surrounded by a concentric spherical layer having the properties of the matrix, which in turn is embedded in the infinite medium with the properties of the composite. The model was introduced by Kerner.[7] Van der Poel[8] used a model similar to the Kerner model, but in different boundary conditions. Finally, Maurer, in his dissertation, used extensively the Van der Poel model and derived interesting results.[9]

Although the Kerner and Van der Poel models may be adapted for the study of the *mesophase* phenomena developed at the boundary layers between phases, only Lipatov[10] considered extensively the phenomenon of creation of the mesophase between main phases in particulates and gave relations interconnecting the heat-capacity jumps at the glass transition temperatures of the matrix polymer and the composites with the thickness of this boundary layer:

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

where Δr is the thickness of the mesophase, r_f is the radius of the filler particles, v_f is the volume fraction of the filler and λ is a weighing factor defining the influence of the state of mesophase to its extent and its dependence on the filler volume fraction. This factor is given by the empirical relationship

$$\lambda = 1 - \frac{\Delta C_p^f}{\Delta C_p^0} \tag{2}$$

where ΔC_p^f and ΔC_p^0 are the jumps of the heat capacity of the filled composite and the unfilled polymer, respectively, for particulate composites.

Moreover, the extent of mesophase may be calculated by dynamic measurements of the storage moduli and the loss factors at the vicinity of T_g's of the matrix and the composites.[11]

In all these models the boundaries of the phases were idealized as smooth surfaces described by exact mathematical expressions. In reality, around an inclusion a complex physical state develops by the creation of a boundary layer whose thickness and properties depend on the eventual imperfect bonding, on permanent stresses, due to shrinkage of the polymer phases during the curing period and the change of the thermal conditions there, on the high stress gradients and stress singularities, due to complicated geometry of the interfaces, on the voids, on impurities and microcracks, appearing at the vicinity of these boundaries, and, finally and most important, on the chemically adsorbed parts of the molecules of the one phase coming in contact with the other phase.

Some attempts have been made up to now to derive, in a simplified manner, the expression for the elastic modulus E_c of a particulate composite by taking into consideration the existence of the mesophase. One of these is the expression given by Lipatov,[12] based on a simple model given by Sagalaev and Simonov-Emeljanov.[13] In this model it was assumed that when the composite attains its critical filler content, the matrix phase of the Kerner model is thinned out and becomes the mesophase, whereas the uniform composite material outside it takes the properties of the matrix. In this case the compliance of the composite is expressed by the sum of compliances of the constituent phases, multiplied by their respective volume contents.

Another model initiating the mesophase layer was introduced by Spathis, Sideridis, and Theocaris.[14] Here the elastic modulus of the composite is expressed as the sum of the filler, mesophase, and matrix moduli, multiplied with their respective volume fractions. The term expressing the contribution of the filler modulus was further multiplied by a corrective factor K, depending on the quality of adhesion. This factor was derived from the experimental determination of the mesophase volume fraction v_i and its modulus, by measuring the E_c values for different volume contents, which suffice for the evaluation of the factor K. Several tests were needed at different v_f's and different temperature levels to find the most appropriate average value of K. This model gave a lower bound for the composite modulus E_c.

Similar models considering the mesophase layer are the Kerner–Kerner model,[17] where the classical Kerner model was used twice, once for the filler-mesophase material, and for the second time for the internal heterogeneous material and the matrix, and the model introduced by Kudykina and Pervak,[15] which expresses the shear modulus G_c of the particulate.

The unfolding model, introduced by Theocaris,[1,2] relates the composite compliance to the compliances of the matrix, mesophase, and filler. It is based on principles of physics and mechanics between phases and it combines, in a harmonious way, the properties of the main phases together with the experimentally defined properties of the composite. Moreover, the model presents a high degree of flexibility and may be adapted easily to real situations.

As a byproduct of the unfolding models the thickness of the mesophase was calculated by using continuity considerations between phases[16] and without making recourse to Lipatov's formula.[10] Using as an additional condition the continuity of tangents at the mesophase-matrix interface, it was possible to evaluate the extent of mesophase and its mechanical properties.

Moreover, in Ref. 11 a preliminary study was undertaken where the boundary layer between reinforcements and matrices in fibrous composites was studied by using dynamic measurements of the composite and its matrix. It was shown there that the values of storage and loss moduli and their relative characteristics in the viscoelastic spectrum are sufficient for completely determining the mesophase.

In the present paper the thickness of mesophase was evaluated by using the composite, matrix, and filler compliances measured at various temperatures of the viscoelastic spectrum without using Lipatov's theory along the whole viscoelastic spectrum of the composite and its constituents. The results proved that the thickness of this boundary layer is constant along the whole visco-

elastic spectrum. Furthermore, the adhesion coefficient between phases can be determined which characterizes the adhesion quality of the phases.

THE UNFOLDING MODEL FOR PARTICULATES

The model, which has been introduced in Ref. 1, has a representative volume element (RVE), consisting of three concentric spheres. Each one of them represents the filler, the mesophase, and the matrix, respectively (radii r_f, r_i, and r_m). It is obvious that, for the RVE of a particulate composite, the following relations hold:

$$v_f = \left(\frac{r_f^3}{r_m^3} \right), \qquad v_i = \left(\frac{r_i^3 - r_f^3}{r_m^3} \right),$$

$$v_m = \left(\frac{r_m^3 - r_i^3}{r_m^3} \right), \qquad v_f + v_i + v_m = 1 \tag{3}$$

The appropriate boundary conditions between the internal sphere and any number of spherical layers surrounding it in the RVE must assure a continuity of radial stresses and displacements. Assuming these conditions, a relation interconnecting the moduli of the phases and the composite may be established. For a hydrostatic pressure P_m applied on the outer boundary of the matrix sphere, it can be found, by applying the energy balance principle between phases, that the following relation holds for spherical particulates[1]:

$$\frac{3(1 - 2\nu_c)}{E_c} = \frac{3(1 - 2\nu_f)v_f}{E_f} \left(\frac{\lambda_{fi}}{\lambda_{im}} \right)^2 + \frac{3(1 + \nu_i)v_f^2}{2BE_i v_i} \left(\frac{1 - \lambda_{fi}}{\lambda_{im}} \right)^2$$

$$+ \frac{3v_f^2(1 - 2\nu_i)}{E_i v_i} \left(\frac{\lambda_{fi}}{\lambda_{im}} - \frac{1}{B\lambda_{im}} \right)^2 + \frac{3v_f(1 + \nu_m)}{2BE_m v_m} \left(1 - \frac{1}{\lambda_{im}} \right)^2$$

$$+ \frac{3(1 - 2\nu_m)}{E_m v_m} \left(\frac{v_f}{B\lambda_{im}} - 1 \right)^2 \tag{4}$$

where

$$B = \frac{v_f}{v_f + v_i} \tag{5}$$

In these relations λ_{fi} and λ_{im} are the hydrosratic pressure ratios at the filler–mesophase and mesophase–matrix boundaries, respectively, because of the applied hydrostatic pressure P_m. The expressions for the λ_{fi} and λ_{im} are given by[1]

$$\lambda_{fi} = \frac{3(1 - \nu_i)(v_f + v_i)E_f}{2v_i E_i(1 - 2\nu_f) + \left[3v_f(1 - \nu_f) + v_i(1 + \nu_i) \right] E_f} \tag{6}$$

and

$$\lambda_{im} = 1 - \frac{2v_m(1 - 2\nu_m)}{3(1 - \nu_m)} - \frac{E_m v_m}{3E_i}\frac{(1 + \nu_i)}{(1 - \nu_m)} \tag{7}$$

Equation (4) yields the elastic modulus E_c of the composite in terms of the moduli and Poisson's ratios of the phases.

Since the mesophase is derived from the matrix material, it is reasonable to accept that

$$\nu_i \simeq \nu_m \tag{8}$$

Since, until now, the unfolding model has not been extended to the transition phenomena of Poisson's ratio in the mesophase, this quantity, ν_c, may be derived by using the following approximate relation, which, at the moment, yields satisfactory results[17]:

$$\frac{1}{\nu_c} = \frac{v_f}{\nu_f} + \frac{v_i}{\nu_i} + \frac{v_m}{\nu_m} \tag{9}$$

Indeed, the mesophase material is characterized by its varying chemical and mechanical properties. This happens mainly because of the different packing densities of the polymer macromolecules near the interface with the reinforcement, from those of the polymers lying at remote regions from the solid–polymer interaction zone.

Then, in order to describe this degradation of the mechanical and other physical properties of the mesophase material, from those of the filler to those of the polymeric matrix, a model was proposed in Refs. 1 and 2. According to this model, the complicated physicochemical phenomena occurring in the mesophase zone were simulated by a macromechanical model, which assumes that the elastic modulus of the mesophase $E_i(r)$ varies with the polar distance according to an inverse power law. This law was established on physical grounds; based on similar laws of variations of stresses near singularities in homogeneous and isotropic elastic stress fields.[2] The elastic modulus of the mesophase is then unfolding between two limits, that is, from the E_f to E_m modulus.

According to Ref. 2, the $E_i(r)$ modulus may be expressed by (two-term version)

$$E_i(r) = E_f\left(\frac{r_f}{r}\right)^{2n} + \left[E_m - E_f\left(\frac{r_f}{r_i}\right)^{2n}\right]\frac{(r - r_f)}{(r_i - r_f)} \tag{10}$$

For $r = r_f$, eq. (10) yields $E_i(r) = E_f$ and, for $r = r_i$, $E_i(r) = E_m$.

It should be emphasized that the exponent $2n$ in relation (10) is not a material characteristic constant, but its magnitude is only interpreted as good or bad adhesion because it is intimately related to the extent of the mesophase. An increase of $2n$ makes the slope of the $E_i(r)$ curve more steep, and this influences the thickness of the mesophase.

Then, the whole modeling tries to describe qualitatively the situation on the mesophase zone, and only the thickness of this layer has to be considered as a dimension having a physical meaning.

THE THICKNESS OF THE MESOPHASE AND THE EVALUATION OF THE MESOPHASE PARAMETER

It is valid for the mesophase layer that

$$E_i v_i = \frac{1}{r_m^3} \int_{r_f}^{r_i} E_i(r) \left[(r + dr)^3 - r^3 \right] \tag{11}$$

which leads to

$$E_i v_i = \frac{E_f v_f}{(2n/3 - 1)} \left[1 - B^{2n/3-1} \right] - \frac{v_f}{4} \left(E_m - E_f B^{2n/3} \right)$$

$$\times \left(1 + B^{-1/3} + B^{-2/3} - 3B^{-1} \right) \tag{12}$$

and after a truncated Taylor series expansion we find out that

$$\frac{1}{E_i v_i} = -16 \frac{D_m^2 E_f}{v_f (2n/3 - 1)} - \frac{4 D_m}{v_f} \left[1 - (B^{-1/3} + B^{-2/3} - 3B^{-1}) \right] \tag{13}$$

where terms of higher power of B have not been considered, as having very small contribution, and $D_m = 1/E_m$ the complex dynamic compliance of matrix.

Given that $D_c = 1/E_c$, eq. (4) transforms to

$$D_c^{*3}(1 - 2\nu_c) = \frac{3(1 - 2\nu_f)v_f}{E_f} \left(\frac{\lambda_{fi}}{\lambda_{im}} \right)^2$$

$$+ \frac{3 D_m^*}{v_m} \left[\frac{v_f(1 + \nu_m)}{2B} \left(1 - \frac{1}{\lambda_{im}} \right)^2 + (1 - 2\nu_m) \left(\frac{v_f}{B \lambda_{im}} - 1 \right)^2 \right]$$

$$- \left[\frac{48 v_f E_f}{(2n/3 - 1)} D_m^{*2} + 12 D_m^* v_f \right.$$

$$\times \left. \left(1 - (B^{-1/3} + B^{-2/3} - 3B^{-1}) \right) \right]$$

$$\times \left[\frac{(1 + \nu_i)}{2B} \left(\frac{1 - \lambda_{fi}}{\lambda_{im}} \right)^2 + (1 - 2\nu_i) \left(\frac{\lambda_{fi}}{\lambda_{im}} - \frac{1}{B \lambda_{im}} \right)^2 \right] \tag{14}$$

where

$$D_c^*(\omega) = D_c'(\omega) - i D_c''(\omega) \tag{15a}$$

$$D_m^*(\omega) = D_m'(\omega) - i D_m''(\omega) \tag{15b}$$

In these relations the filler was considered as purely elastic, as it is the case with most composites. Separating real from imaginary parts of eq. (14), we obtain:

$$D_c'^3(1 - 2\nu_c) = \frac{3(1 - 2\nu_f)\nu_f}{E_f}\left(\frac{\lambda_{fi}}{\lambda_{im}}\right)^2$$

$$+ \frac{3D_m'}{\nu_m}\left[\frac{\nu_f(1 + \nu_m)}{2B}\left(1 - \frac{1}{\lambda_{im}}\right)^2 + (1 - 2\nu_m)\left(\frac{\nu_f}{B\lambda_{im}} - 1\right)^2\right]$$

$$- \left[\frac{48\nu_f E_f\left(D_m'^2 - D_m''^2\right)}{(2n/3 - 1)}\right.$$

$$\left. + 12D_m'\nu_f\left(1 - B^{-1/3} - B^{-2/3} + 3B^{-1}\right)\right]$$

$$\times \left[\frac{(1 + \nu_i)}{2B}\left(\frac{1 - \lambda_{fi}}{\lambda_{im}}\right)^2 + (1 - 2\nu_i)\left(\frac{\lambda_{fi}}{\lambda_{im}} - \frac{1}{B\lambda_{im}}\right)^2\right] \quad (16)$$

$$D_c''^3(1 - 2\nu_c) = \frac{3D_m''}{\nu_m}\left[\frac{\nu_f(1 + \nu_m)}{2B}\left(1 - \frac{1}{\lambda_{im}}\right)^2 + (1 - 2\nu_m)\left(\frac{\nu_f}{B\lambda_{im}} - 1\right)^2\right]$$

$$- \left[\frac{96\nu_f E_f D_m' D_m''}{(2n/3 - 1)} + 12D_m''\nu_f\left(1 - B^{-1/3} - B^{-2/3} + 3B^{-1}\right)\right]$$

$$\times \left[\frac{(1 + \nu_i)}{2B}\left(\frac{1 - \lambda_{fi}}{\lambda_{im}}\right)^2 + (1 - 2\nu_i)\left(\frac{\lambda_{fi}}{\lambda_{im}} - \frac{1}{B\lambda_{im}}\right)^2\right] \quad (17)$$

On the other hand and using the model of ref. 16, we can derive an obvious boundary condition holding at the interface between mesophase and matrix. This condition of continuity of tangents of the $E_i(r_i)$ and E_m moduli is given by

$$\text{For } r = r_i, \quad \frac{dE_i(r)}{dr} = 0 \quad (18)$$

which yields after some algebra that

$$\left(\frac{1}{r_i - r_f}\right)\left[\frac{E_m}{E_f}\left(\frac{r_i}{r_f}\right)^{2n} - 1\right] = \frac{2n}{r_i} \quad (19)$$

Combinations of the eqs. (16), (17), and (19) by two provide obviously three systems, each one of two equations with the two unknown quantities $2n$ and r_i. So it is possible to determine these unknowns $2n$ and r_i, either from the

experimental values of the dynamic moduli of the composite and the matrix or from one dynamic equation (16) or (17) and the boundary condition (19).

In this way we dispose three different systems of equations, all of them based on mechanical properties of the composite and its constituents, as well as on the continuity of tangents of these moduli along the interface $r = r_i$, and these three systems may yield independently the values of the mesophase thickness $\Delta r_i = (r_i - r_f)$ and the *mesophase parameter* $2n$.[1] Thus, not only reliable results, based on dynamic mechanical tests of the composite and its constituents, are expectable, but also these results may be mutually checked along the whole viscoelastic spectrum of the composite.

However, the system of equations (17) and (19) consisting of the loss modulus vs. temperature equation and the continuity of tangents at the r_i interface is obviously less reliable and its results play only a secondary role for checking the values of $2n$ and r_i.

RESULTS AND DISCUSSION

In order to check the validity of the theory developed previously, experimental values of the G_c composite, the G_f filler, and the G_m matrix shear moduli of three typical particulate composites along the whole temperature spectrum were used.[9] These particulates were the following:

(i) A E-glass–polystyrene composite with $v_f = 10, 20,$ and 30% and Poisson's ratio of the matrix varying between 0.40 and 0.44.

(ii) A E-glass–polyethylene composite with $v_f = 12, 20,$ and 28% and Poisson's ratio of the matrix approximately equal to $\nu_m = 0.40$.

(iii) A E-glass–polypropylene composite with $v_f = 10, 20,$ and 30% and Poisson's ratio of the matrix approximately equal to $\nu_m = 0.40$.

The elastic modulus and the Poisson ratio of the E-glass were $E_f = 7 \times 10^{10}$ Nm^{-2} and $\nu_f = 0.25$, respectively.

TABLE I

The Values of the Characteristic Parameters of E-Glass–Polystyrene Particulates for Various Temperatures for Filler–Volume Fractions $v_f = 10, 20, 30\%$, Respectively

	$v_f = 10\%$				$v_f = 20\%$				$v_f = 30\%$			
	Eqs. (A, B)		Eqs. (A, C)		Eqs. (A, B)		Eqs. (A, C)		Eqs. (A, B)		Eqs. (A, C)	
T_c^0	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$
50	1.012	207	1.017	421	1.037	57	1.042	176	1.058	31	1.065	114
60	1.012	210	1.017	423	1.037	59	1.042	178	1.058	31	1.065	115
70	1.012	212	1.017	426	1.037	58	1.042	179	1.058	31	1.065	116
80	1.013	211	1.017	432	1.038	57	1.042	181	1.058	72	1.065	117
90	1.013	220	1.018	419	1.040	56	1.043	181	1.059	120	1.066	118
100	1.013	282	1.019	520	1.033	82	1.043	238	1.061	132	1.068	150
110	1.013	303	1.020	703	1.034	82	1.043	339	1.062	160	1.070	211
120	1.013	304	1.020	782	1.034	82	1.043	377	1.063	160	1.071	231
130	1.014	304	1.020	823	1.035	82	1.044	387	1.065	160	1.071	243
140	1.014	304	1.022	801	1.036	82	1.044	396	1.068	160	1.072	245
150	1.014	304	1.022	821	1.036	82	1.044	406	1.068	160	1.072	251

TABLE II
The Values of the Characteristic Parameters of E-Glass–Polyethylene Particulates
for Various Temperatures for Filler–Volume Fractions v_f = 12, 20, 28%, Respectively

| T_c^0 | $v_f = 12\%$ | | | | $v_f = 20\%$ | | | | $v_f = 28\%$ | | | |
| | Eqs. (A, B) | | Eqs. (A, C) | | Eqs. (A, B) | | Eqs. (A, C) | | Eqs. (A, B) | | Eqs. (A, C) | |
	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$
−150	1.017	118	1.023	178	1.045	40	1.050	80	1.080	16	1.087	47
−140	1.018	116	1.024	178	1.047	42	1.055	77	1.082	16	1.089	48
−130	1.018	116	1.025	172	1.049	35	1.055	78	1.082	16	1.091	48
−120	1.019	114	1.026	171	1.050	35	1.056	79	1.083	16	1.091	50
−110	1.020	114	1.026	180	1.054	34	1.059	79	1.086	16	1.091	52
−100	1.020	118	1.029	164	1.055	33	1.059	81	1.086	17	1.092	65
−90	1.020	124	1.030	160	1.055	34	1.061	80	1.087	17	1.093	53
−80	1.020	129	1.030	162	1.056	33	1.061	81	1.087	18	1.094	53

TABLE III
The Values of the Characteristic Parameters of E-Glass–Polypropylene Particulates
for Various Temperatures for Filler–Volume Fractions v_f = 10, 20, 30%, Respectively

| T_c^0 | $v_f = 10\%$ | | | | $v_f = 20\%$ | | | | $v_f = 30\%$ | | | |
| | Eqs. (A, B) | | Eqs. (A, C) | | Eqs. (A, B) | | Eqs. (A, C) | | Eqs. (A, B) | | Eqs. (A, C) | |
	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$	r_i/r_f	$2n$
−40	1.018	141	1.021	208	1.052	34	1.055	83	1.085	16	1.091	51
−30	1.004	106	1.008	559	1.049	59	1.055	84	1.086	16	1.093	50
−20	1.014	100	1.016	284	1.054	34	1.057	82	1.086	15	1.093	51
−10	1.008	103	1.011	437	1.056	33	1.061	82	1.088	17	1.094	53
0	1.015	101	1.019	268	1.061	30	1.063	84	1.091	15	1.095	56
10	1.024	114	1.030	188	1.047	45	1.054	105	1.092	16	1.098	59
20	1.016	100	1.020	285	1.047	46	1.053	112	1.093	16	1.099	61
30	1.025	118	1.030	203	1.048	47	1.054	114	1.093	17	1.100	63

Moreover, the following relations for the complex moduli and compliances as well as for their components were used:

$$G^* = E^*/2(1 + \nu^*) \tag{20}$$

$$D' = E'/(E'^2 + E''^2) \tag{21}$$

$$D'' = E''/(E'^2 + E''^2) \tag{22}$$

Using as input data in either of the systems developed in this paper, that is the sets of equations (16), (17) (named as A, B, for brevity) and (16), (19) (named A, C) have been solved numerically giving the respective values for r_i and $2n$.

As can be seen from Tables I–III, the values of the ratio r_i/r_f are stable and independent of the temperature along the whole temperature spectrum for any fixed value of the filler-volume content for each particulate. Moreover, an increase in the filler-volume content v_f leads to an increase of r_i. If can be
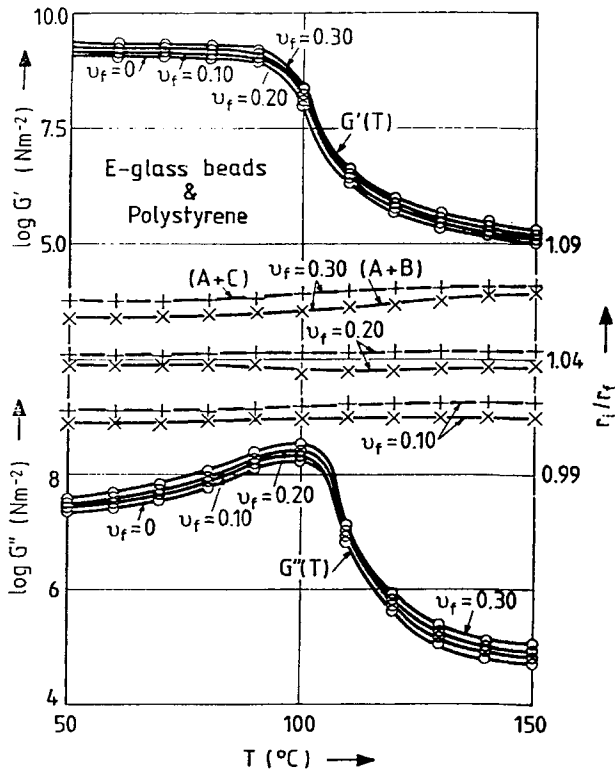
Fig. 1.   The variations of the ratio (r_i/r_f), G_c', and G_c'' vs. their respective temperatures for various filler (v_f) volume fractions for E-glass–polystyrene particulates.

noticed that the values of r_i given by the set of equations (A, B) are a little smaller than the values given by the system (A, C).

Figures 1–3 show the variation of ratio r_i/r_f vs. temperature for all three particulate composites for which measurements of dynamic moduli are available.

The exponent $2n$ is called the mesophase parameter and constitutes a means for defining the adhesion between the main phases of the composite. Since adhesion between solid phases is a complicated phenomenon, any model characterizing this quantity should take into consideration this parameter. An increase of the filler volume content v_f reduces $2n$ since it extends the mesophase layer due to the interaction of the neighbor fillers. Since simultaneously the v_m content is decreased, the percentage reinforcement of the matrix is significantly increased.

The extent of mesophases as shown in Figures 1–3 when the layers have been derived from dynamic mechanical tests, was almost the same as the extent expected by applying Lipatov's theory and calorimetric measurements in DSC. This extent was of the order of $\Delta r_i = 0.01 r_f$ up to $0.10 r_f$ approximately.

It is therefore a clear indication, since the differences in the extent of mesophases as defined by either method are minimal, that both types of measurements of the mesophase yield correct and reliable results. Then this
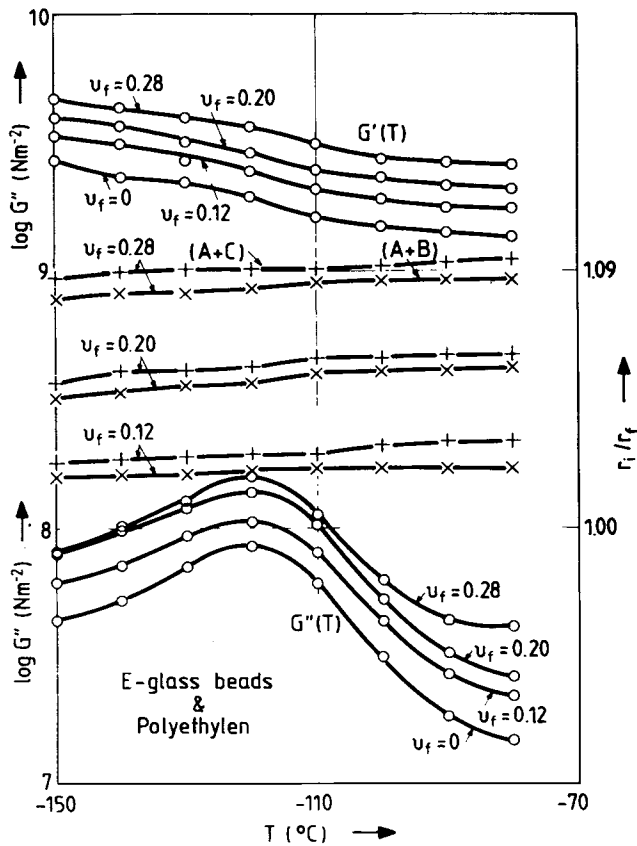
Fig. 2. The variations of the ratio (r_i/r_f), G_c', and G_c'' vs. their respective temperatures for various filler (v_f) volume fractions for E-glass–polyethylene particulates.

coincidence constitutes also a solid proof that the evaluation of the extent of mesophase by Lipatov's theory is a sound one and in conformity with the results of dynamic mechanical measurements. Therefore, any skepticism about the use either of the empirical formula of Lipatov or the results based on measurements at T_g is totally groundless.

Finally, the fact that all over the temperature spectrum the extent of mesophase (defined by r_i) remains essentially constant indicates the soundness of the method.

CONCLUSIONS

An analytical method for evaluating the thickness of the mesophase in particulate composites was established in this paper, which was based exclusively on data taken from mechanical tests. Up to now the thickness of this layer was evaluated only experimentally by means of the heat-capacity jumps of samples in DSC tests applying the method developed by Lipatov.[10] According to this method, calorimetric measurements of the existing jumps in heat capacity, ΔC_p, at the glass-transition temperatures, T_g's, of the polymeric composite and the matrix were sufficient to determine by an empirical formula
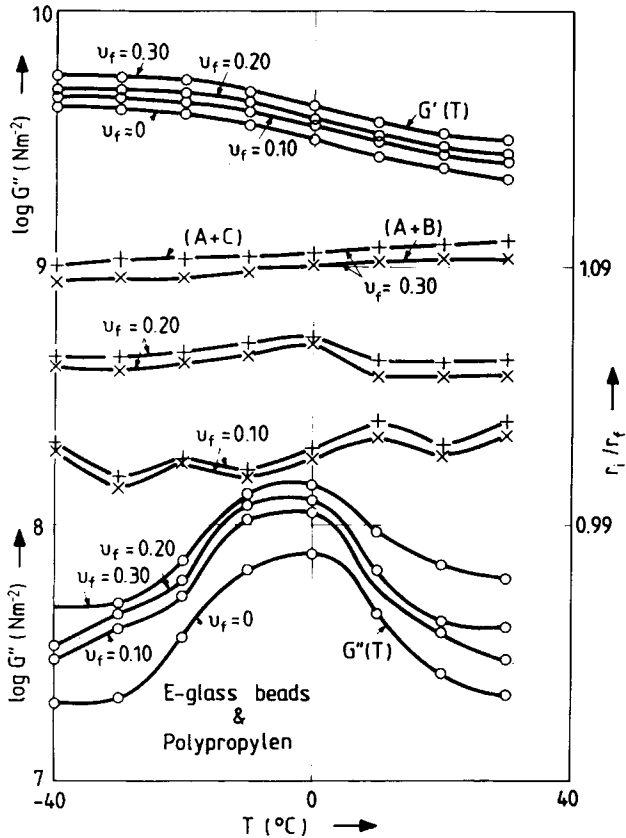
Fig. 3. The variations of the ratio (r_i/r_f), G'_c, and G''_c vs. their respective temperatures for various filler (v_f) volume fractions for E-glass–polypropylene particulates.

the extent of mesophase. The reason that this measurement was made in T_g is that at this temperature there is a strong manifestation of the mobility of the segments of the polymer chains and the adsorption and adhesion interaction is more pronounced there than at any other temperature level.

Then, this procedure presents two main weaknesses: (i) The definition of the thickness of the mesophase at the glass transition temperature of the composite may yield excessive values for this thickness and (ii) there is no physical explanation about the validity of the arbitrary empirical relationship introduced by Lipatov,[10] in determining the factor λ from the heat capacity jumps, from which the thickness r_i of the mesophase is evaluated.

Another further disadvantage of this method is the difficulty with which ΔC_p values can be measured by small samples convenient for the differential scanning calorimeter. Finally, there is always large discrepancies in the definition of T_g of polymers by mechanical and thermodynamic tests. This discrepancy influences also considerably the absolute values of the quantities yielding the thickness r_i.

On the other hand, the method introduced in this paper gives the values of $2n$ and r_i based only on the mechanical properties of the composite and its constituents. Therefore, any set of values of the mechanical characteristic

quantities which is sufficient to evaluate the thickness of the mesophase based on mechanical measurements is always preferable.[18]

By using measurements of the dynamic storage and loss compliances of the composite and its constituents, as well as the boundary condition at the interface between mesophase and matrix of the continuity of tangents of their moduli we could establish three combinations of two-equation systems which yielded the values of the mesophase parameter $2n$ and the thickness of mesophase $\Delta r_i = (r_i - r_r)$. It was shown that the results derived from any one of the systems were reliable and conformal to each other and they were in good agreement with the expected results, derived from Lipatov's theory. Moreover, and most important, it was established that these quantities remained constant along the whole viscoelastic spectrum of the composite.

This constancy and coincidence of the results from the mechanical and thermodynamic measurements constitutes a further strong proof of their validity.

References

1. P. S. Theocaris, *J. Reinf. Plast. Compos.*, **3**, 204–231 (1984).
2. P. S. Theocaris, *Adv. Polym. Sci.*, **66**, 149–187 (1985).
3. P. S. Theocaris, *Colloid Polym. Sci.*, **262**(12), 929–938 (1984).
4. P. S. Theocaris and E. Sideridis, *J. Appl. Polym. Sci.*, **29**(10), 2997–3011 (1984).
5. K. Takahashi, M. Ikeda, K. Harakawa, K. Tanaka, and T. Sakai, *J. Polym. Sci.*, **16**, 415–425 (1978).
6. M. Takayanagi, H. Harima, and Y. Iwata, *J. Soc. Mater. Sci.*, (*Jpn.*) **12**, 129–134 (1963).
7. E. H. Kerner, *Proc. Phys. Soc. Lond.*, **B69**(2), 808–813 (1956).
8. C. Van der Poel, *Rheol. Acta*, **1**(2–3), 198–205 (1958).
9. F. Maurer, Ph.D. thesis, University of Duisburg, Federal Republic of Germany (1983).
10. Yu. Lipatov, *Physical Chemistry of Filled Polymers*, Engl. Transl. By R. J. Moseley, Int. Polym. Sci. Techn., Monograph No. 2 (1977).
11. P. S. Theocaris, B. Kefalas, and G. Spathis, *J.Appl. Polym. Sci.*, **28**(12), 3641–3649 (1983).
12. Yu. Lipatov, *Adv. Polym. Sci.* **22**, 1–59 (1977).
13. G. Sagalaev and I. Simonov-Emeljanov, *Plast. Massy*, **2**, 48–52 (1973).
14. G. Spathis, E. Sideridis, and P. S. Theocaris, *Int. J. Adhes. Adhes.*, **1**, 195–201 (1981).
15. I. G. Pervak and T. A. Kudykina, *Plast. Massy*, **8**, 19–21 (1977).
16. P. S. Theocaris and T. P. Philippidis, *J. Reinf. Plast. Compos.*, **4**(2), 173–185 (1985).
17. R. Jones, *Mechanics of Composite Materials*, McGraw-Hill, New York, (1975).
18. P. S. Theocaris *Colloid Polym. Sci.*, **263**(11), 863–872 (1985).