

On Shift and Resolubility of Relaxation Maxima with Change in Properties of the Boundary Polymer Layer in Composite Materials

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Synopsis

Temperature dependencies of viscoelastic functions of the three-component models of composite materials in the transition state temperature range of polymer binder have been studied. On the basis of theoretical calculations for the models, a conclusion has been made about the conditions for shift of the relaxation maxima along the temperature axis. Also conditions for their resolubility on $\tan \delta$ curves were determined for materials such as filled polymers as well as anisotropic laminated and reinforced plastics with deformation of the components in series. These effects are due to the change in properties of the boundary layer of the polymer. They are entirely dependent on the concentration ratio between the boundary layer and the bulk of the binder polymer and on the difference in their glass temperatures T_g . Concentration of the high-modulus filler affects T_g of the composition. This is due to the change in the ratio of concentrations of the polymer in the boundary layer and in the bulk. With parallel deformation of the components of the three-component model, resolubility and shift of the relaxation maxima depend not only on the above factors, but also on the reinforcing filler concentration.

Introduction

In a previous theoretical study,¹ we have considered the viscoelastic behavior of composite polymeric materials in the range of transition temperatures. Changes in properties of polymer layers of finite thickness at the interphase with high-modulus fillers were analyzed under the assumption that composite materials consist of three components: filler, surface layer, and bulk polymer. Mechanical losses tangent $\tan \delta$ of this three-component system should have its maximum at a temperature equivalent to the temperature of maximum $\tan \delta$ for the two-component system: boundary layer–bulk polymer.

Thus, neglecting contribution to the losses by the high-modulus nonrelaxing filler, the question of calculation of the shift and finding conditions for the resolubility of the relaxation maxima in a three-component composite was confined to a study of conditions for shift and resolubility of maxima on $\tan \delta = f(T)$ curves for the two-component system.¹

Closer approximation to filled and reinforced polymers would be a three-component model, since mineral filler, though showing no temperature dependence of viscoelastic properties in the polymer transition temperature range, still substantially increases the complex modulus G' , which may change shape of the $\tan \delta = f(T)$ curves of a composite, since $\tan \delta = G''/G'$ where G'' is the imaginary part of the complex modulus.

Besides, presence of the filler changes concentration ratios of the boundary layer φ_l and the bulk polymer φ_f . This can result in a change of resolution and

shift conditions of the relaxation maxima on the $\tan \delta = f(T)$ curves for a composite material.

Therefore, more precise calculations and analysis of viscoelastic behavior of composite polymeric materials in the transition temperature range have been made for three-component models comprising: high-modulus filler f , boundary polymer layer l , and bulk polymer b (see Fig. 1).

We shall first deal with the simplest models for fiber-reinforced and laminated plastics with unidirectional arrangement of the reinforcing elements. For the case of deformation of such compositions normal to the arrangement of reinforcing fibers or normal to the plane of layers of the reinforcing elements (in the case of laminated plastics), the model is Figure 1(a). If deformation direction coincides with the direction of reinforcing elements, then the model is Figure 1(b).

MODEL WITH PARALLEL DIRECTION OF DEFORMATION

Consider the composite materials formed by reinforcing fibers and polymer. Considering our three-element model, assume the fibers are always separated by the boundary layer which surrounds them.

In the case of parallel deformation of all three elements—the polymer, its boundary layer, and the reinforcing element—the complex shear modulus G^* of the composite can be expressed using the complex modulus of the components² as follows:

$$G^* = \varphi_f G_f^* + \varphi_b G_b^* + \varphi_l G_l^* \quad (1)$$

where G_f^* is the complex modulus of the reinforcing material, G_b^* is the complex modulus of the polymer; G_l^* is the complex modulus of the boundary polymer layer; and φ_f , φ_b and φ_l are relative volumes for each of the components, respectively.

Taking into account that $G^* = G' + iG''$ and $\tan \delta = G''/G'$, it can be shown that

$$G = \varphi_f G_f' + \varphi_b G_b' + \varphi_l G_l' \quad (2)$$

$$G'' = \varphi_f G_f'' + \varphi_b G_b'' + \varphi_l G_l'' \quad (3)$$

$$\tan \delta = \frac{\varphi_f G_f' \tan \delta_f + \varphi_b G_b' \tan \delta_b + \varphi_l G_l' \tan \delta_l}{\varphi_f G_f' + \varphi_b G_b' + \varphi_l G_l'} \quad (4)$$

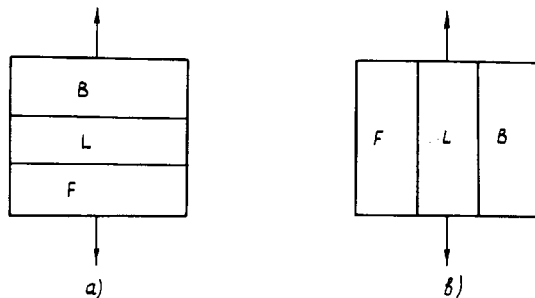


Fig. 1. Models of composite materials with unidirectional arrangement of fibers in presence of the polymer interphase layer: A, deformation direction normal to the fiber axis; B, deformation direction parallel to the fiber axis. Arrows indicate deformation direction.

In calculations according to formulas (2) and (3), the following assumptions have been made: Reinforcing elements are cylindrical fibers (radius r) with shear modulus and losses $G'_f = 10^5 \text{ kg/cm}^2$; $\tan \delta_f = 10^{-3}$; these values are constant in the studied temperature range. Experimental values for temperature dependencies G'_b and $\tan \delta_b$ for an epoxy polymer on the basis of the epoxy diamine resin and polyethylene polyamine³ were used as mechanical characteristics of the polymer binder. Thickness of the boundary layer d was independent of the filler concentration.

In calculations, it was also assumed that curves of the temperature dependence G'_l and $\tan \delta_l$ are similar to the curves $G'_b = f(T)$ and $\tan \delta_b = f(T)$, but are shifted arbitrarily along the temperature axis to lower or higher temperatures. Equation (4) is correct only in the cases when boundary layers do not overlap. At $d/r = 0.2$ for hexagonal packing of fibers at $\varphi_f > 0.60$, the boundary layers begin to overlap and at $\varphi_f > 0.70$ all the binder moves into the boundary layers. In this case, the system becomes two-phase and $\varphi_b = 0$. For $\varphi_f > 0.7$, $\varphi_b = 1 - \varphi_f$. In the interval $0.60 > \varphi_f > 0.70$, the determination of φ_b [eq. (4)] becomes incorrect. For materials with cylindrical reinforced fibers, there is one more restriction. Even if we suppose only point contacts between fibers and no boundary layer at all, φ_f cannot be more than 0.907. Therefore, the calculations have been made only up to $\varphi_f = 0.69$, because for greater values φ_f , they are theoretically meaningless for accepted assumption as for fiber radius, boundary layer thickness, etc.

With a parallel, unidirectional arrangement of the cylindrical reinforcing elements, the concentration of the boundary layer φ_l will be a linear function of the filler concentration φ_f .

On this basis, for any specified φ_f value the respective φ_l and $\varphi_b = 1 - \varphi_l - \varphi_f$ have been substituted into eq. (3). Fig. 2 shows temperature dependencies

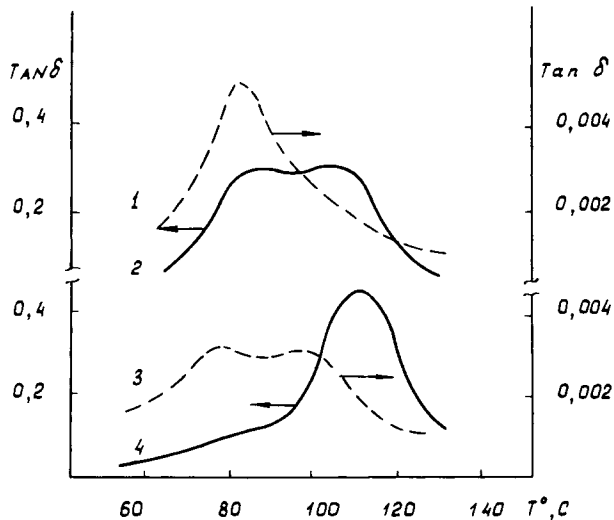


Fig. 2. Dependencies $\tan \delta = f(T)$ of the two-component model polymer boundary layer (curves 2 and 4) and of the three-component models of type B on the basis of these binders (curves 1 and 3) at different volumes fractions of the components for $T_{gl} = 92^\circ\text{C}$ and $T_{gb} = 117^\circ\text{C}$: 1. $\varphi_f = 0.5$; $\varphi_l = 0.45$; $\varphi_b = 0.05$. 2. $\varphi_l = 0.9$; $\varphi_b = 0.1$. 3. $\varphi_f = 0.5$; $\varphi_l = 0.25$; $\varphi_b = 0.25$. 4. $\varphi_l = 0.5$; $\varphi_b = 0.5$.

tan δ of three component specimens (curves 1 and 3) calculated by the above method. From these curves, temperature T_g for maximum tan δ with various values of T_{gl} and φ_f have been derived. Values obtained in this way are generalized in dependencies of T_g vs. concentration φ_f of fibers with various properties of the boundary layer, specified by T_{gl} value (Fig. 3). Figure 3 shows that the presence of the boundary layer of set thickness in a three-component model considerably affects T_g of the composition only at rather high filler concentrations. If T_{gl} in particular is higher or lower than T_{gb} by more than 20°C, the second loss maximum appears on the curves tan $\delta = f(T)$ at temperatures which are much lower than T_{gl} . Further increases of φ_f and transition into the boundary layer of large amounts of the binder leads to the presence of only one maximum on the tan $\delta = f(T)$ curves due to the properties of the boundary layer; but T_g for this maximum is substantially lower than T_{gl} chosen in calculations. If T_{gl} differs from T_{gb} by not more than 20°C, only one maximum remains on tan $\delta = f(T)$ curves in the entire φ_f range. At rather high φ_f , the maximum is shifted towards higher or lower temperatures depending on properties of the boundary layer, and T_g remains substantially lower than T_{gl} assumed in the calculations. The reason for the substantial decrease of T_g of the model as compared with T_g of the binder in this case is due to the inclusion of the elastic high-modulus element into the model which substantially increases the value of G' . Increase in G' decreases the mean relaxation time τ of the model since $\tau = \eta/G'$ where η is the internal friction coefficient. $\tau = f(T)$, tan δ values reach a maximum at a temperature where the τ value becomes comparable to the model deformation period. Thus, decrease in τ values due to the increase of G' should result in equality of τ and a cyclical deformation period which occurs at lower temperatures, where a maximum of tan δ is observed.

Another important peculiarity of the three-component model, with parallel deformation of the components, is the change in the temperature dependence of tan δ as compared to the tan $\delta = f(T)$ curve of a two-component binder included into the three-component model (1). Curves 2 and 3 of Figure 2 illustrate this phenomenon, showing temperature dependencies tan δ_b of the binder, on whose basis the three-component models and curves 1 and 3 of Figure 2 were

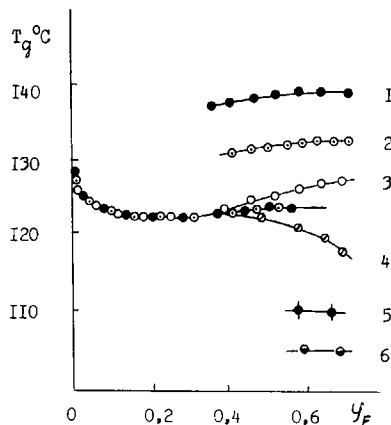


Fig. 3. Dependencies $T_g = f(\varphi_f)$ for type B model at $T_{gf} = 117^\circ\text{C}$ for boundary layers with different T_{gl} : 1. $T_{gl} = 152^\circ\text{C}$; 2. 142°C ; 3. 132°C ; 4. 102°C ; 5. 92°C ; 6. 82°C .

obtained. At a certain ratio of components (Fig. 2) and variations in their properties, addition of reinforcing elements promote loss maxima resolubility on curves $\tan \delta = f(T)$ of the boundary layer and of the bulk of the binder (see curves 3 and 4), but worsening of the resolubility is also possible (compare curves 2 and 1). Curves $T_g = f[\varphi_l/(\varphi_b + \varphi_l)]$ were obtained on the basis of calculations of $\tan \delta = f(T)$ curves by variation of relative concentration of boundary layer in binder polymer for various constant values φ_f . Curve 1 of Figure 4 characterizes the temperature of maximum $\tan \delta$ in the absence of an elastic component, i.e., $\varphi_f = 0$. An increase in relative concentration of the component with T_{gl} , which is 15° lower than T_{gb} , shifts maximum $\tan \delta$ to lower temperatures, and at high "soft" component content the second maximum appears (curve 1'). Simultaneously, two maxima on curves $\tan \delta = f(T)$ are observed only in a very narrow interval of changes in $\varphi_l/(\varphi_l + \varphi_b)$ (from 0.8 to 0.9). The presence of the third (elastic) reinforcing element markedly changes this interval. For example, at $\varphi_f = 0.05$, the second maximum appears at lower φ_l (see curves 2 and 2'), and the simultaneous existence of two maxima is seen in a broader interval (0.5 – 0.75) of $\varphi_l/(\varphi_l + \varphi_b)$.

For $\varphi_f = 0.2$, the concentrations range $\varphi_l/(\varphi_l + \varphi_f)$ (see curves 3, 3', 4, and 4', Fig. 4) for the simultaneous existence of both maxima becomes still wider and shifts toward lower values φ_l . A change in $T_g = f[\varphi_l/(\varphi_l + \varphi_f)]$ dependence also occurs with addition of the elastic element. In the presence of the elastic element, (filler), T_g of the model is significantly less dependent on $\varphi_l/(\varphi_l + \varphi_f)$ within a wide concentration range than in the absence of the elastic element.

These peculiarities may explain the results of the study of viscoelastic properties of anisotropic composite materials in the transition region temperature and aid in obtaining data on properties of polymer boundary layers in such compositions.

MODELS WITH SERIES DEFORMATION OF THE COMPONENTS

For series deformation of the components, dynamic viscoelastic properties of the system are calculated by²

$$\frac{1}{G^*} = \frac{\varphi_f}{G_f^*} + \frac{\varphi_b}{G_b^*} + \frac{\varphi_l}{G_l^*} \quad (5)$$

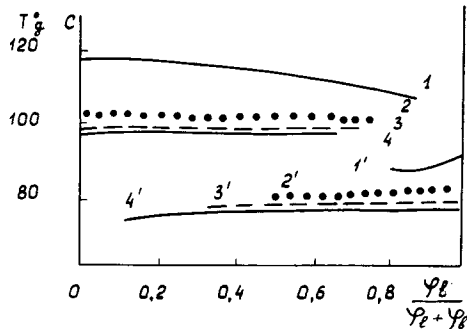


Fig. 4. Dependence T_g vs. φ_l for three-component model with deformation of the components in parallel at different concentrations φ_f of the reinforcing elements: 1, 1'. without reinforcing elements, $\varphi_f = 0$. 2, 2'. $\varphi_f = 0.05$. 3, 3'. $\varphi_f = 0.2$. 4, 4'. $\varphi_f = 0.6$.

The complex modulus can be expressed in terms of the real and the imaginary part. However, calculation of $\tan \delta$ in this case would be very complicated; and, therefore, it was preferred to use the equation for the two-component series deformation model²:

$$G' = \frac{x}{x^2 + y^2} \quad G'' = \frac{y}{x^2 + y^2} \quad \tan \delta = \frac{G''}{G'} = \frac{y}{x} \quad (6)$$

$$x = \frac{\varphi_c G'_c}{(G'_c)^2 + (G''_c)^2} + \frac{\varphi_f G'_f}{(G'_f)^2 + (G''_f)^2} \quad (7)$$

$$y = \frac{\varphi_c G''_c}{(G'_c)^2 + (G''_c)^2} + \frac{\varphi_f G''_f}{(G'_f)^2 + (G''_f)^2} \quad (7')$$

where G'_f and G''_f are the real and imaginary parts of the complex shift modulus of the reinforcing elements.

G'_c , G''_c , and φ_c have similar characteristics for the binder, which, in turn, can be calculated from the equations:

$$G'_c = \frac{Z}{Z^2 + K^2} \quad G''_c = \frac{K}{Z^2 + K^2} \quad \tan \delta_c = \frac{G''_c}{G'_c} = \frac{K}{Z} \quad (8)$$

where

$$Z = \frac{\varphi_l G'_l}{(G'_l)^2 + (G''_l)^2} + \frac{\varphi_b G'_b}{(G'_b)^2 + (G''_b)^2} \quad (9)$$

$$K = \frac{\varphi_l G''_l}{(G'_l)^2 + (G''_l)^2} + \frac{\varphi_b G''_b}{(G'_b)^2 + (G''_b)^2} \quad (10)$$

Thus, using eqs. (8), (9), and (10), the characteristics of the two-component binder are first calculated and then these are used to calculate characteristics of the reinforcing elements–two-component binder system by the eqs. (5), (6), (7). Properties of the boundary layer and of the bulk of the polymer have already been specified. To avoid difficulties connected with nonuniformity of deformation of the binder at the same deformation direction, plate reinforcing elements were used ($r = 10$ mcm) instead of the cylindrical ones. As in the previous case, φ_l can be expressed through φ_f using eq. (4). The change of cylindrical reinforcing elements for thin plate by series deformation makes the model more crude; however, its physical meaning does not change (the components are deformed in series) and, qualitatively, the trend for change in $T_g = f(\varphi_f)$ will be the same. For plate reinforcing elements, their concentration may be close to 1. As for the given value $2d/r = 0.2$ at $\varphi_f \geq 0.85$, all the polymer in the bulk transforms in the state of boundary layer. The system becomes a two-component one, and φ_l should be determined as $\varphi_l = 1 - \varphi_f$.

Calculations yielded data on T_g of compositions with different concentrations of the reinforcing filler at different T_{gl} . These data are generalized in Figure 5 as concentration dependencies T_g of compositions with varying T_{gl} . Figure 5 shows decreasing T_g of the polymer under the action of the filler surface. In such a composite, there occurs a shift of the loss maximum to lower temperature if difference between glass transition temperatures $\Delta T_g = T_{gb} - T_{gl}$ of the boundary layer and that of the bulk of the binder does not exceed 20°C (curves 5 and 6). If $\Delta T_g > 20^\circ\text{C}$, then with certain content in reinforcing elements the filler (in our case $\varphi_f = 0.2$), there appears the second loss maximum (curve 7).

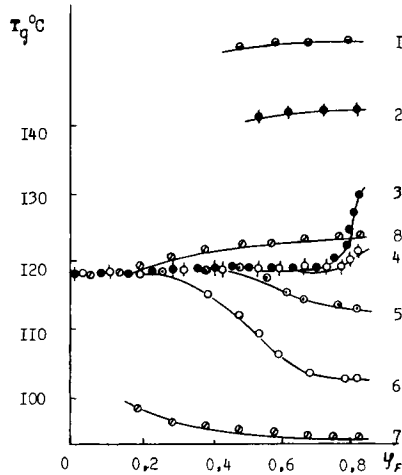


Fig. 5. Dependence $T_g = f(\varphi_f)$ for type A models having $T_{gb} = 117^\circ\text{C}$ and different T_{gl} : 1. $T_{gl} = 152^\circ\text{C}$. 2. 142°C . 3. 132°C . 4. 122°C . 5. 112°C . 6. 102°C . 7, 8. 92°C .

Its position on the temperature scale is close to T_g and shifts toward lower temperatures with growing concentration of the reinforcing elements. The first maximum in this case is shifted toward higher temperatures (see curve 8, Fig. 5). In case T_{gl} of the boundary layer increases under the influence of the filler surface, T_g of the composition is significantly increased only at very high filler concentrations (see curves 3 and 4, Fig. 5) when actually the entire polymer has properties of the boundary layer. In this case, when $\Delta T_g > 20^\circ\text{C}$, second maximum appearance is also observed, but at higher filler concentration than in the case of "soft" boundary layer (see curves 1 and 2, Fig. 5).

The studied model shows a loss maximum shift toward higher temperatures with growing φ_f and T_g of the boundary layer is more than 20°C as compared with T_g of the bulk of the polymer (see curve 8, Fig. 5). In this case, the increase in T_g of the composition with increase in φ_f occurs more smoothly than in the case of the "rigid" boundary layer. "Rigid" boundary layer sharply increases the T_g of the composition, but only at high filler concentrations (see curves 3 and 8, Fig. 5).

Differing from the parallel deformation case, deformation curves $\tan \delta = f(T)$ of the three-component composition with high-modulus interlayers are nearly the same shape as that for the pure polymer. Maxima are observed at the same temperature as for the polymer. Therefore, shift and resolubility of the maxima in a three-component system of type A occur similarly as in a two-component polymeric system with series deformation of the components.¹ The volume concentration of filler in this case is insignificant.

MODEL OF THE COMPOSITE MATERIAL WITH A DISPERSE FILLER

In composite materials with a disperse filler, some part of the polymer interlayers in the binder is getting deformed in series with the filler particles, while the other part is deformed in parallel. To simplify calculations, assume that filler particles are cube-shaped with edge a . Filler particles are arranged in the

filler regularly as a simple cubic lattice with distance b between filler particles centers and thickness of boundary layer d . An elementary cell of such a material is represented in Figure 6(a). To determine ratio of the volume fractions of the components with varying filler concentrations, consider the equivalent plain model. The phenomenological model of the filled polymer [Fig. 6(b)] with changed properties of the polymer at the interface looks more complex than the Takayanagi model.⁴ The model of Figure 6(b) can be considered as consisting of two models, deformed in series: one of them being the Takayanagi model, formed of the boundary layer 2' and the binder 3'; the other being that with deformation of the filler 1, boundary layer 2 and polymer 3 in parallel, Figure 1(b).

Figures 6(a) and 6(b) illustrate that the λ and ϕ parameters of the Takayanagi model formed of the boundary layer 2' and some part of the binder 3 can be expressed as

$$\varphi_f = a^3/b^3:$$

$$\phi = \frac{d}{\frac{b}{2} - \frac{a}{2}} = \frac{2d}{a} \frac{\sqrt[3]{\varphi_f}}{(1 - \sqrt[3]{\varphi_f})} \quad (11)$$

$$\lambda = \frac{\left(\frac{a}{2} + d\right)^2}{\left(\frac{b}{2}\right)^2} = \frac{(a + 2d)^2}{a^2} \sqrt[3]{\varphi_f^2} = \left(1 + \frac{4d}{a} + \frac{4d^2}{a^2}\right) \sqrt[3]{\varphi_f^2} \quad (12)$$

Similarly, for parallel deformation of components 1, 2, and 3, the model volume fraction of the filler ρ_1 , can be expressed in terms of the volume fraction of the filler φ_f

$$\rho_1 = \frac{a}{b} = \sqrt[3]{\varphi_f} \quad (13)$$

and volume fraction of the boundary layer ρ_2 in the same volume element

$$\rho_2 = \frac{d \cdot a}{(b/2)^2} = \frac{4ad}{b^2} = \frac{4d}{a} \sqrt[3]{\varphi_f^2} \quad (14)$$

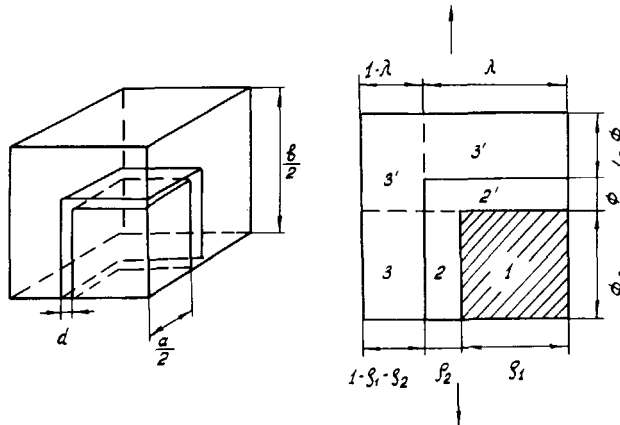


Fig. 6. Elementary cell of filled polymer A and its plain model B.

The volume fraction ϕ_f of the model with parallel deformation in the generalized model of the filled polymer, respectively, can be expressed as:

$$\phi_f = \frac{a^2}{b^2} = \sqrt[3]{\varphi_f^2} \quad (15)$$

Modeling properties of the boundary layer of the polymer and using eqs. (2)–(15), curves $\tan \delta = f(T)$ for various φ_f and T_g have been calculated. For these calculations we have taken $d/a = 0.1$. At $\varphi_f > 0.6$, all the polymer exists in the boundary layer. For $\varphi_f > 0.6$, the results of calculation of $T_g = f(\varphi_f)$ are not given. For the “rigid” boundary layer ($T_{gl} > T_{gb}$) (Fig. 7), a filler concentration increase would not necessarily result in $\tan \delta$ maximum; T_{gl} should be more than 20°C higher than T_{gb} . In this case, only at rather high φ_f concentration on $\tan \delta = f(T)$ curves a second maximum appears at a temperature close to T_{gl} .

For the “soft” boundary layer ($T_{gl} < T_{gb}$), a more complex behavior of the model is observed. When $\Delta T = T_{gb} - T_{gl} < 20^\circ\text{C}$ in particular, a φ_f increase displaces $\tan \delta$ maximum toward lower temperatures, but with $\Delta T > 20^\circ\text{C}$, or φ_f increase displaces $\tan \delta$ maximum toward higher temperatures. At rather high filler concentrations, the second maximum appears at a temperature close to T_{gl} .

Comparison of the results obtained with the data reported in Ref. 1 illustrates that in a three-component model of the filled polymer with changing properties of the polymer boundary layer, shift and resolubility maxima on $\tan \delta = f(T)$ curves occur similar to the two-component binder model, part of the three-component model.

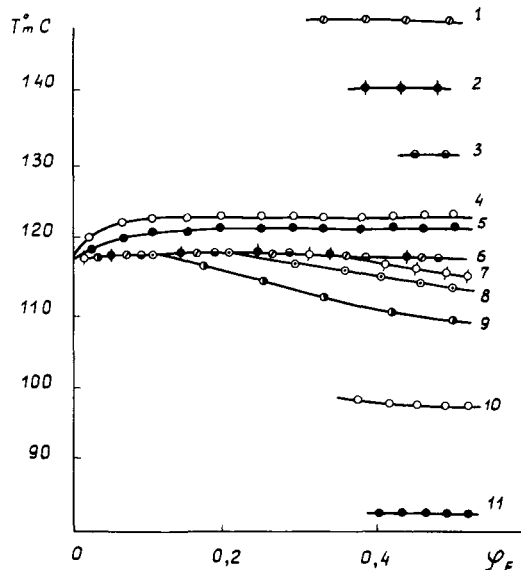


Fig. 7. Dependencies $T_g = f(\varphi_f)$ at $T_{gl} = 117^\circ\text{C}$ and T_{gl} : 1. $T_{gl} = 152^\circ\text{C}$. 2. 142°C . 3. 132°C . 4. 92°C . 5. 82°C . 6. 120 – 152°C . 7. 112°C . 8. 107°C . 9. 102°C . 10. 92°C . 11. 82°C .

CONCLUSIONS

Thus, quantitative analysis of viscoelastic behavior of the three-component models of composite materials in the range of the polymer transition state has shown that in materials such as laminated and reinforced plastics at deformation of the components of the composite materials in series, resolubility and shift of $\tan \delta$ maxima are due to the change in properties of the polymer boundary layer. These property changes are entirely dependent on the ratio of concentrations of the boundary layer, the bulk polymer, and difference in glass-transition temperatures. Concentration of the filler only affects T_g of the composition due to the change in concentrations of the boundary layer and the bulk of the binder.

For relatively simple models of the filled polymer and for the three-component models with deformation of the components in series,¹ the relaxation maxima $\tan \delta$ for three-component models of composite materials are located at temperatures where $\tan \delta$ maxima of the polymer constituent of the composite material are observed. In deformation of the components of the three-component model, maximum resolubility depends not only on the φ_l to φ_b ratio and ΔT_g , but on filler concentration φ_f as well.

Parallel deformed three-component models have an interesting peculiarity: in small concentration ranges for the high-modulus component, a sizable decrease in T_g of the composition is observed with increasing φ_f . In our previous report,¹ similar effects were obtained in calculations for the two-component model with increasing boundary layer concentration containing much higher T_{gl} as compared to T_g . However, for the models with a high-modulus filler, this effect is more essential.

The above analysis of temperature dependencies, the $\tan \delta$ of simple models of composite materials in the transition temperature range for the polymer can be useful for understanding experimental data for viscoelastic behavior of real composite materials.

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