On Shift and Resolution of Relaxation Maxima in Two-Phase Polymeric Systems

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Synopsis

The results of calculations of viscoelastic properties of filled polymers assuming "boundary layer" and the polymer matrix having their own and different glass transition temperatures are presented. The calculations have been made on the basis of the models in series and parallel coupling of viscoelastic bodies as well as Takayanagi's model. Using specified temperature, dependences of viscoelastic properties of the polymer and the "boundary layer" temperature dependences of the real part G' of the complex shear modulus and tan δ for such a two-phase system with varied differences in glass transition temperatures and concentration of the components were derived. The degree of maxima shift observed experimentally for the filled polymer owing to variation of properties of the "boundary layer" (its concentration and glass transition temperature) were evaluated. Conditions for the appearance of two maxima tan δ for the respective glass transition temperatures of the polymer and "boundary layer" on the curves tan $\delta = f(T)$ were determined.

INTRODUCTION

Study of viscoelastic and dielectric properties of filled polymers has shown that an increase in filler content usually results in a maximum shift toward higher temperatures, i.e., the glass transition temperature increases.[1,2] One of the reasons for this is a change in properties of the boundary layer between the polymer and the filler surfaces and a decrease in molecular mobility. In such a case the polymer between two filler particles consists of two parts: boundary layer with its own glass transition temperature, and unchanged polymer matrix. However, only one glass transition temperature for such systems was observed,[3] and the reason for the absence of maximum splitting was ambiguous.

The glass transition temperature of filled polymers linearly depends on the fraction of the polymer ν in the boundary layer:

$$T_{gf} = T_{g0} + \Delta T \nu$$

where T_{g0} is the glass transition temperature of the unfilled polymer, T_{gf} is the glass transition temperature for filled polymer, and ΔT is a constant corresponding to the increase in glass transition temperature for the system where all of the polymer is in the boundary layer ($\nu = 1$).[14] We can expect the appearance of two glass transition temperatures for such systems. If the reason for an increase in glass transition temperature of the filled polymer is the decrease of molecular mobility in the boundary layer, it is not clear why the splitting of maxima on experimental curves of temperature dependence of mechanical or dielectrical losses is not observed. The present study is intended to elucidate this question.

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Theoretical Calculation for Different Models of Filled Polymers

For a polymer filled with a mineral filler, the glass transition temperature (T_g) corresponding to maximum values for tan δ is unequivocally determined by T_g of the polymer between two filler particles. In this case, the position of T_g refers to the polymer as a mixture of two constituents—unchanged polymeric matrix with initial glass transition temperature and polymer in the boundary layer with properties changed by the action of the filler surface. The volume fraction of the boundary layer is usually a function of filler concentration and its nature.[1]

In real filled polymers the boundary layers and the unchanged polymer matrix are arranged randomly with regard to direction of deformation. This makes it difficult to describe the behavior of the system theoretically. However, the study of some simple models may be sufficient to determine the viscoelastic behavior of the system if we exclude the deformation of the filler. To elucidate the conditions of maxima resolution we have applied simple models with a polymer consisting of two regions or domains, each with different properties. These domains are thought to be coupled in parallel or in series with respect to the direction of deformation. We have also investigated the Takayanagi model.[5]

A simple equation enables us to estimate the main peculiarities in viscoelastic properties of the specimen made of two constituent parts. All the calculations were done using a computer. Typical curves of the temperature dependence of the real part of the shear modulus G' and tan δ were taken as initial data for calculations. For such curves the experimental data on the temperature dependence of G' and tan δ for an epoxy polymer in the region of transition from glassy to rubberlike states were chosen.[6]

These experimental dependences may be approximated as follows:

$$\log G' = A \operatorname{arccot} B(T - T_g) \tag{1}$$

$$\tan \delta = C e^{-D(T-T_g)^2} \tag{2}$$

The properties of the second component (boundary layer) were specified by shifting the experimental curves along the temperature axis in either direction, which simulated the decrease or increase of the glass transition temperature of the polymer in the boundary layer. The temperature dependence G' and tan δ for two-component systems were distinguished from those for the first component by value of T_g in eqs. (1) and (2).

The calculations of G' and tan δ for the two-component system with parallel deformation was performed according to eqs. (3) and (4):

$$G' = \rho_1 G_1' + \rho_2 G_2' \tag{3}$$

$$\tan \delta = \frac{\rho_1 G_1' \tan \delta_1 + \rho_2 G_2' \tan \delta_2}{\rho_1 G_1' + \rho_2 G_2'} \tag{4}$$

where ρ_1 and ρ_2 are volume fractions of the components; and G_1', G_2', tan δ_1, and tan δ_2 are values of viscoelastic characteristics at any arbitrary temperature.

For the case of series model, eqs. (5) and (6) were used:

$$G' = \frac{G_1' G_2'}{\rho_1 G_2' + \rho_2 G_1'} \tag{5}$$

$$\tan \delta = \left(\frac{\rho_1}{G_1'} + \frac{\rho_2}{G_2'}\right)\left(\frac{\rho_1}{G_1' \tan \delta_1} + \frac{\rho_2}{G_2' \tan \delta_2}\right)^{-1} \tag{6}$$

Substituting the functions of temperature dependence of each component we obtain values for the temperature dependence of G' and $\tan \delta$ of the two-component specimen.

To determine T_g of the two-component system an analytical expression is needed for the first derivative of $\tan \delta$, and then it is equated with zero at various ratios of the components. However, we have used numerical integration to calculate the values G' and $\tan \delta$ of the system for different temperatures using eqs. (5) and (6) and varying volume fractions and glass transition temperatures of the components.

Figure 1 shows theoretical temperature dependence of $\tan \delta$ for the two-component system at various ratios of polymer–boundary layer and for arbitrarily chosen differences in their T_g. One of the components has a constant $T_g = 125°C$, whereas in the second one with $\rho_2 = \rho_l$ the T_g value varied in the temperature range of 90–160°C. Hence, the model includes both an increase and a decrease of T_g in the boundary layers under the influence of the filler surface.

With increasing fraction of the boundary layer, regular shift occurs, broadening and then splitting the mechanical losses into two maxima (Fig. 1). Analogous calculations were performed for other values of ΔT_g. As generalized characteristics of the curves of the type presented in Figure 1, temperatures of maximum of T_g and its value and $\tan \delta$ were taken.

Let us now consider the concentration dependences of T_g and $\tan \delta$ for two cases.
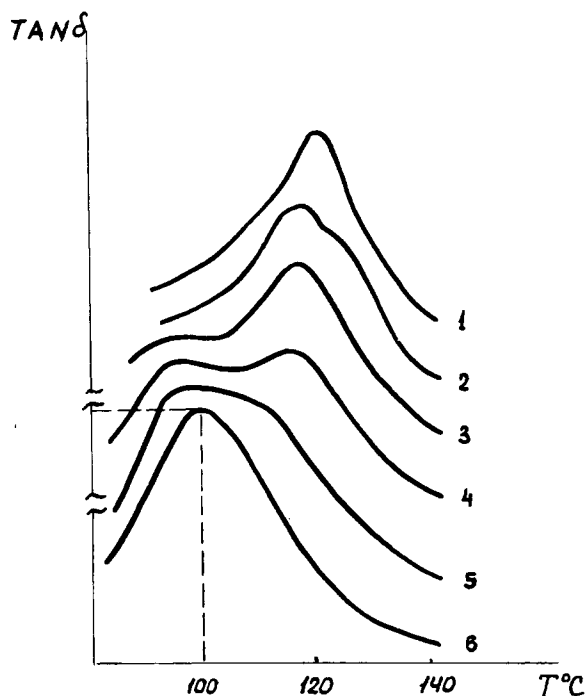

Fig. 1. Transformation of curve $\tan \delta = f(T)$ with variation of concentration of components: 1, $\rho_l = 0.6$; 2, 0.7; 3, 0.8; 4, 0.9; 5, 0.95; 6, 0.99; $T_{g0} = 125°C$, $T_{gl} = 100°C$.
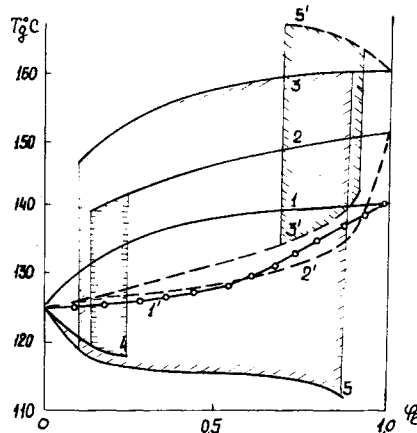
Fig. 2 Dependence of T_g of the two-component model on volume fraction ($T_{gl} > T_{g0}$). Curves 1–5 for deformation in parallel and 1'–5' for deformation series. T_{gl}: (1,1') 140°C, (2.2', 4) 150°C, (3,3',5,5') 160°C, T_{g0} = 125°C. Regions ρ_l with two maxima tan δ are shaded.

Case 1

The boundary layer has a higher glass transition temperature as compared to that for the polymer in bulk, i.e., the layer is more "rigid." Figures 2 and 3 give dependences T_g and tan δ calculated for the model with parallel deformation of the components. If T_{g0} exceeds T_{gl} by less than ΔT_g = 15°C, some shift of the maximum occurs toward higher temperatures without appearance of the second maximum at any concentration of the polymer in the boundary layers (curves 1 and 1', Fig. 2). Here, the value of the maximum passes over the minimum in the range of small concentrations of the polymer in the boundary layer (see curve 1, Fig. 3).

For the series model, the minimum tan δ lies in the range of rather high concentrations, ρ_l = 0.8–0.9. The method of coupling the components strongly influences the concentration dependence of T_g.

For parallel coupling of the components, a comparatively small increase in ρ_l leads to the essential growth of T_g (see curve 1, Fig. 2), whereas for series coupling the marked growth of T_g may appear only at high ρ_l (see curve 1; Fig. 2).

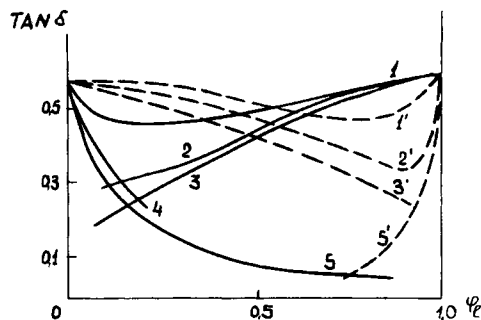In parallel coupling, the second maximum of losses which characterizes the

Fig. 3. Dependence of tan δ of the two-component model on the "rigid" component. For designations, see Fig. 2.

properties of the boundary layer becomes more marked at a small concentration of the layer (curves 2 and 3, Fig. 3). At the same time, for the second model this second maximum shows itself only at very high concentrations of the boundary layer (curve 5, Fig. 3). It is also peculiar that for resolution of maxima for the model with series coupling a much higher difference in glass temperature between polymer matrix and boundary layer is required. For parallel coupling, the resolution of maxima is possible at $\Delta T_g = 25°C$ (curve 2, Fig. 2), while for the series coupling the resolution manifests itself only at $\Delta T_g = 35°C$ (curve 5, Figs. 2 and 3).

The models under discussion have an interesting peculiarity in the case of rather high values of $\Delta T_g \approx 25°C$, namely, at low content of the rigid boundary layer, the increase of its concentration leads to the shift of the maximum toward lower temperatures (see curves 4 and 5, Fig. 3); the height of the maximum diminishes rapidly. At comparatively small concentrations of the rigid layers, there appears the second maximum, its value increasing linearly with increase of ρ_l (curves 2 and 3, Fig. 3).

For coupling in series this effect is less pronounced and appears only in the range of very high concentrations of the rigid component, i.e., of the boundary layer (curve 5, Figs. 2 and 3).

Case 2

The boundary layer has a T_g lower than T_g of the initial polymer ("soft" layer). Data calculated for this case are presented in Figures 4 and 5. With difference in glass transition temperature ΔT_g not higher than 15–20°C, only one maximum is present on the curves, tan $\delta = f(T)$, since its location is shifted to lower temperatures (curves 1 and 1', Figs. 4 and 5). The height of the maximum depends on ρ_l passing over the minimum. The position of the minimum on the concentration axis and its value depend on the method of coupling of the deformed domains: for series deformation even low content of the soft component de-
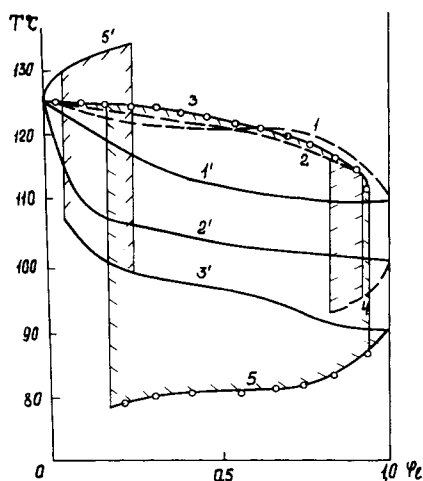

Fig. 4. Influence of the "soft" component content on T_g of the two-component model with parallel (1–5) and in series (1'–5') loading of the layers. T_{gl}: (1,1') 110°C, (2,2', and 4) 100°C, (3,3',5,5') 90°C, $T_{gl} < T_{g0}$.
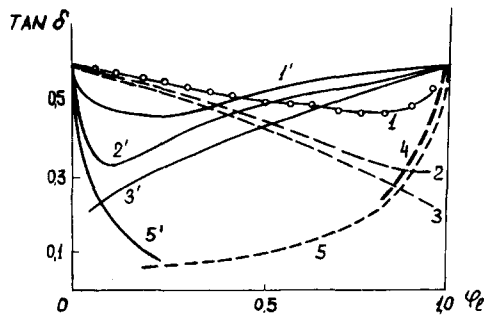
Fig. 5. Influence of "soft" component content on tan δ of the two-component model. For designations, see Fig. 4.

presses markedly T_g and tan δ (curve 1, Figs. 4 and 5). For parallel coupling, a decrease in T_g with increasing ρ_l is nearly linear and only slightly depends on ΔT_g, reaching noticeable values at $\rho_l > 0.8$–0.9, where nonlinear dependence, $T_g = f(\rho_l)$, appears (curves 1–3, Fig. 4).

The appearance of the second (low-temperature maximum) may be observed for the model with parallel coupling at comparatively high values of ρ_l and is followed by the shift toward high temperatures with increase in ρ_l (curves 4 and 5, Fig. 5).

Another paradoxical phenomenon of this case ($T_{gl} < T_{g0}$) is the increase in T_g of the specimen in coupled layers in the range of small ρ_l (see curve 5, Fig. 4). As in the case of $T_{gl} > T_{g0}$, this is observed at high enough ΔT_g and is evidently due to superposition of "tails" of the curves tan $\delta = f(T)$ of the initial component. The two models discussed above may occur in composite materials like laminated plastics and in anisotropic glass-fiber-reinforced plastics with transverse (unidirectional) arrangement of the fibers. In such systems the shift of the maxima of mechanical losses to higher or lower temperatures and conditions for their resolution depend on the properties of the boundary layer, its volume fraction, and arrangement of two constituent components with respect to the deformation direction.

Case 3

This is represented by the Takayanagi model. In real filled polymers the arrangement of the boundary layers around the filler particles is random. Hence, some of them may be deformed in parallel with the polymer matrix and some may be deformed in series. Therefore, it is of interest to calculate the shift of T_g and conditions of maximum resolution for the Takayanagi model[5] applied to the structure of the polymer between filler particles wherein the combination of both cases occurs.

Choosing values of parameters of Takayanagi model λ and ϕ for describing two-component polymer binder in the filled polymers, we have made the following simplifications. Particles of the filler are considered to be cubic, edge length equal to c, and form simple cubical lattices. The boundary layer of the polymer has thickness d, which is constant for all filler concentrations. Owing to very high modulus of the filler, the latter is barely deformed. Therefore, the domains of the polymer loaded in parallel with the filler (shaded in Fig. 6) are
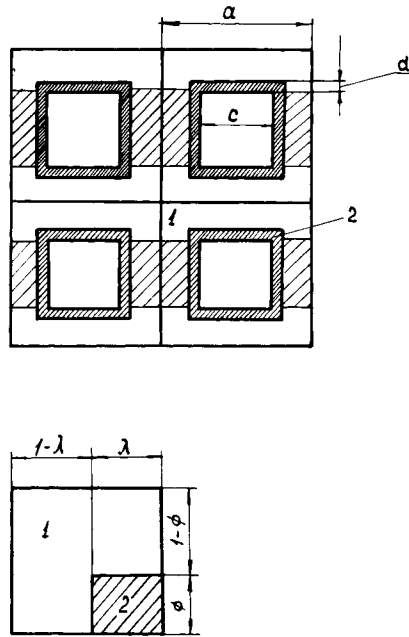
Fig. 6. Schematic drawing of arrangement of filler particles in the polymer matrix.

not deformed. Consequently, viscoelastic properties of a filled specimen depend only on the properties of the boundary layers that are deformed in series. With such simplifications the increase in volume fraction of the filler causes some diminishing of the edge length of the elementary unit consisting of filler particles and a boundary layer $(c + d)$ with changes in parameters λ and ϕ of the Takayanagi model in the following way. It may be shown that with regard to $\rho_f = c^3/a^3$,

$$\phi = \frac{d}{1/2(a - c)} = \frac{2d}{c} \frac{\rho_f^{1/3}}{1 - \rho_f^{1/3}}$$

$$\lambda = \frac{c + 2d}{a} = \frac{c + 2d}{c} \rho_f^{1/3}$$

Having calculated the values of these parameters for various volume fractions of the filler and assuming[6] $c = 10 \times 10^{-6}$ m and $d = 0.5 \times 10^{-6}$ m, we can obtain the following expressions:

$$G' = (1 - \lambda)G_1' + [\lambda X/(X^2 + Y^2)] \tag{7}$$

$$G'' = (1 - \lambda)G_2'' + [\lambda Y/(X^2 + Y^2)] \tag{8}$$

where

$$X = \frac{(1 - \phi)G_1'}{(G_1')^2 + (G_1'')^2} + \frac{\phi G_2'}{(G_2')^2 + (G_2'')^2}$$

$$Y = \frac{(1 - \phi)G_1''}{(G_1')^2 + (G_1'')^2} + \frac{\phi G_2''}{(G_2')^2 + (G_2'')^2}$$

The temperature dependence of G' and tan δ for "mixtures" of the boundary layer and the unchanged polymer matrix were calculated and T_g of mixtures at

various ρ_f were found.   Figure 7 shows the dependences T_g of the polymer and boundary layer on filler concentration at different glass transition temperatures of the constituent components.

If T_g of the boundary layer is 15°C higher than T_g of the polymer matrix, then with specified assumptions the change in T_g of the filled polymer will not be observed even at high ρ_f (curve 3, Fig. 7), and the second loss maximum, if any, will manifest itself only in some broadening of the maximum and asymmetry of the descending part of the curve tan $\delta = f(T)$.   If the glass transition temperature of the boundary layer was 40°C higher than that for the polymer matrix, then the respective high-temperature maximum may appear at comparatively low content of the filler, but at a temperature 5°C higher than the accepted T_g of the boundary layer (curve 1, Fig. 7).   With the T_g of the boundary layer being lower than T_g of the polymer matrix, the boundary layer essentially influences the position and the value of the loss maximum.   Figure 7 shows that for a soft boundary layer the Takayanagi model predicts linear dependence of T_g on ρ_f, i.e., increase in ρ_f causes a shift of the maximum toward lower temperatures (curves 2, 4, and 6, Fig. 7).   A maximum corresponding to T_g of the soft boundary layer may be observed only at very high volume fraction of the filler and over 40°C (curve 6, Fig. 7).

It is obvious that in real systems parameters of the model depend on ρ_f in a different way, as the considered case excludes a great part of the boundary layer out of the deformation process.   Therefore, the results obtained for the Takayanagi model may be regarded only as qualitative regularities that show
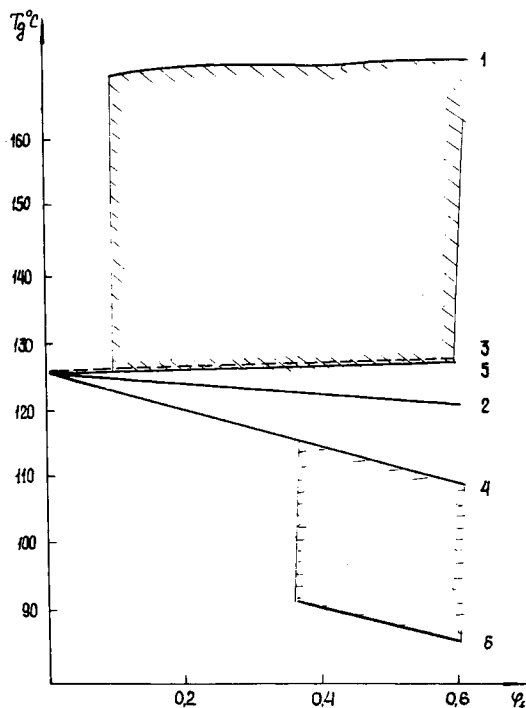

Fig. 7. Dependence of T_g of filled polymer on filler concentration in the case of "rigid" (curves 1, 3, and 5) and "soft" (curves 2, 4, and 6) boundary layer. T_{gl}:   (1,5) 165°C, (3) 140°C, (2) 110°C, (4) 85°C, and (6) 85°C.

that the rigid boundary layer (with higher T_g as compared with polymer matrix) increases the T_g of the filled polymer insignificantly, whereas the soft layer essentially decreases T_g.

CONCLUSIONS

The application of a two-phase model of the polymer between filler particles in the filled polymer to calculate its glass transition temperature shows that the shift in T_g of the whole polymer and the resolution of maxima on the curves $\tan \delta = f(T)$ depend on the ratio of the constituents and their glass transition peratures. On the basis of calculations which were done for different models, it was established that the appearance of the two maxima corresponding to the unchanged polymer matrix and boundary layer is possible if there exists an essential difference in their glass transition temperatures, namely, $T_g > 20$–$40°$C. This also depends on the boundary layer concentration (which is dependent on filler concentration) and on the conditions of the deformation.

The data obtained using some simple models correspond to the experimental results on the shift in T_g of various filled polymers. The calculations also show why only one changed glass transition temperature is observed in filled polymers and the conditions for the appearance of two glass transition temperatures, one of them corresponding to the boundary layer of polymer on filler surface.

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