Some Analogies in the Mechanical
Behavior of Filled Polymers

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Synopsis

The temperature and frequency dependences of complex shear modulus and mechanical losses were studied for epoxy resin composition in the presence of different amounts of quartz and polystyrene fillers. The data obtained were analyzed by the use of the Williams-Landell-Ferry method. It was shown that in the mechanical behavior of filled polymers, except for the well-known temperature-time analogy there exist some lows connected with the presence of filler. The change in filler concentration leads to the same change in the real part of complex modulus as change in frequency (concentration–time analogy), and change in temperature is equivalent to concentration change (temperature–concentration analogy). The existence of these analogies is explained by a change in deformation conditions for polymeric matrix in the presence of different amount of filler, by the existence of surface layers of polymer at the interface with solid filler, and by peculiarities of the mechanical behavior of filler. It is also established that the thickness of surface layer which was determined from experimental data depends on temperature and has an extremum in the temperature region of the α-transition.

INTRODUCTION

Filled polymers are of great importance for modern technology. Incorporation of fillers in polymers allows to regulate mechanical and other properties of materials. Filled polymers are very complicated heterogeneous systems, and it is difficult to describe theoretically their mechanical behavior.[1] There is a great need in methods which allow to describe and predict the mechanical properties in a wide range of temperatures, frequencies, and filler concentration.

There are many experimental data[2-7] showing that the filler has a great influence on segmental mobility in surface layers of polymer at the interface with solid. In network polymers formed in the presence of filler,[8,9] as a result of adsorption interaction and conformation restrictions imposed by the surface there arose a great heterogeneity of network structure. We can therefore expect that relaxation behavior of polymer matrix will be changed in comparison with polymer in the absence of filler.[2]

Our main task here is to investigate the relaxation behavior of epoxy resin composition filled with quartz powder and polystyrene particles. The measurements were carried out in the range of temperatures near the

α-transition, which is connected with segmental motions. It has long been known that to describe the mechanical properties in this range, the method of Williams-Landell-Ferry is needed.[10] In some works, the application of the WLF method to filled polymers was described.[2,11,12]

EXPERIMENTAL

The study of the frequency and temperature dependence of complex shear modulus of specimens with different amounts of filler was carried out using a device the scheme of which is shown in Figure 1. Specimen 1, in the form of a right-angle parallelepiped of size $50 \times 10 \times 5$ mm, is fixed in the stationary clutch 2, whereas its middle part is connected to the movable clutch 3, which makes recurrence-translational movement according to harmonic law. The amplitude is determined by eccentric 4 and frequency by electromotor with reduction. Here, free parts of the specimen situated between the stationary and movable clutches are under action of forces which induce shear deformation. Their amplitude in our experiments was 0.02. The deformation measurements were made with the aid of tensoresistors which adhered to plane springs 5. The tension in the specimen was measured with tensodynamometer 6. The values of tension and deformation were registered automatically by an electron-recording potentiometer. The tangent of mechanical loss angle was determined from phase shift between tension and deformation. All experiments were carried out in the frequency range 0.004–0.4 cps and temperature range 70–140° ($\pm 0.05°$). For specimen preparation, needed amounts of resin, crosslinking agent, and filler were mixed in a vacuum
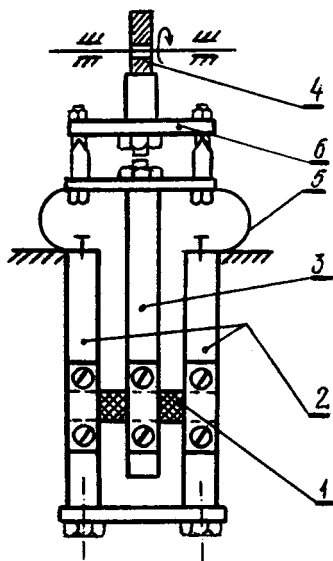

Fig. 1. Scheme of experimental device (see text).

mixer and then cast in Teflon form where the composition stayed for 24 hr at 20°. After this procedure, the specimens were annealed at 150° during 8 hr. The conversion degree was controlled by IR spectroscopy.

RESULTS AND DISCUSSION

Temperature–Time Analogy

It is known that the temperature–time analogy consists of equivalence of action of temperature increase and decrease in deformation frequency. From experimental data obtained in narrow diapason of frequencies, this allows to calculate by extrapolation values for a wide range of variables. Figure 2 represents the typical dependence of the real part of complex shear modulus G' at different temperatures on frequency in the transition region at filler concentration $\psi = 0.11$. It is seen that the curves have a typical shape, and therefore the WLF method can be applied.

Figure 3 shows the master curves $\lg G' = f(\lg \omega\, a_T)$ for specimens with different amount of filler at 80°C. There is a good coincidence between the theoretical curve and experimental points. Another argument showing the applicability of the WLF method is the shape of curve $\lg a_T = f(T - T_s)$ (Fig. 4).

It seemed interesting to evaluate the influence of filler concentration on the average relaxation time of polymer matrix in filled material. For this purpose, the dependence of the generalized tangent of mechanical loss on deformation frequency was calculated (Fig. 5). It can be seen that with increase in filler concentration, the maximum of mechanical loss shifts to the lower frequencies. Having used the dependence tg $\delta = f(\omega)$ and taking into account that $\tau = 1/\omega_m$ (ω_m = frequency at maximum loss), the relaxation times were calculated. It was shown that the dependence $\lg \tau = f(\varphi)$ (Fig. 6, curve 1) is nearly linear, which means that the relaxation times depend exponentially on filler concentration.
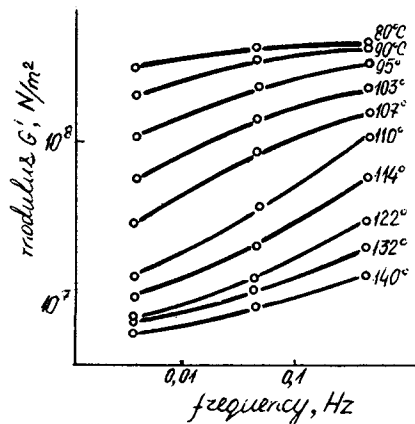

Fig. 2. Frequency dependence of real part of modulus of filled epoxy composition (filler-quartz powder, $\varphi = 0.11$) in the α-transition temperature region (φ-volume fraction).
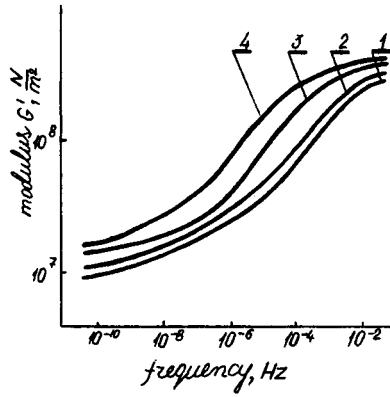
Fig. 3. Master curves for epoxy composition with quartz filler at 80°; (1) $\varphi = 0.045$; (2) 0.11; (3) 0.31; (4) 0.44.
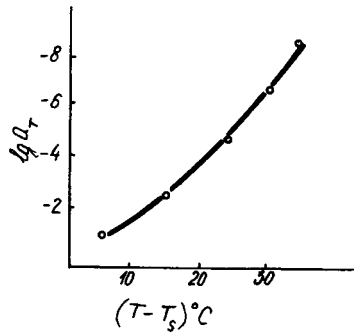

Fig. 4. Temperature dependence of shift factor a_T for composition with $\varphi = 0.11$.
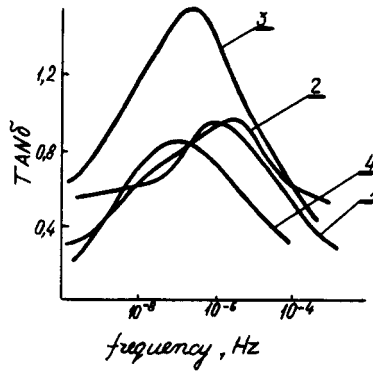

Fig. 5. Dependence of tg δ on frequency; (1) $\varphi = 0.045$; (2) 0.11; (3) 0.31; (4) 0.44.
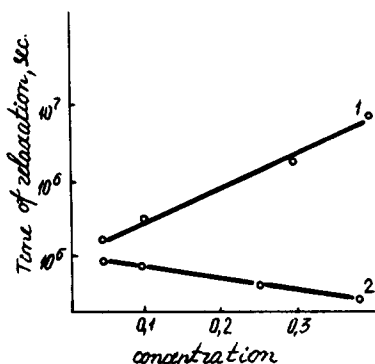
Fig. 6. Dependence of log of relaxation time on filler concentration; (1) for quartz filler; (2) for polystyrene filler.

Concentration–Time Analogy

The exponential dependence of relaxation times on temperature is the premise for the existence of temperature-time analogy. The linear dependence of log τ on filler concentration allows the conclusion to be drawn that in filled polymers the concentration–time analogy can exist. Having analyzed the frequency dependences of the real part of complex modulus for specimens with different filler concentration at constant temperature, we discovered the characteristic shape and position of curves lg $G' = f(\lg \omega)$ at φ = variable (Fig. 7) which allow the WLF method to be applied.

Having made the reduction to lowest filler concentration and introducing concentration shift factor $a\varphi$, the master curve lg $G' = f(\lg \omega \, a\varphi)$ was constructed (Fig. 8). The curve lg $a\varphi = f(\varphi)$ is smooth enough (Fig. 9). Thus, in this case the WLF method can also be applied. It is evident that shift factor $a\varphi$ represents the ratio of the average relaxation times of specimens with different filler amount,

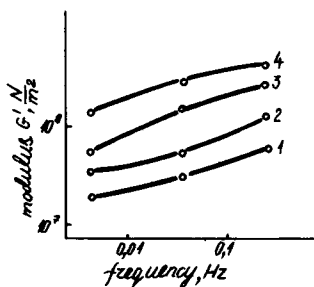$$a\varphi = \frac{\tau\varphi_1}{\tau\varphi_2}.$$

Fig. 7. Frequency dependence of real part of modulus at 114° for epoxy composition filled with quartz: (1) 0.045; (2) 0.11; (3) 0.31; (4) 0.44.
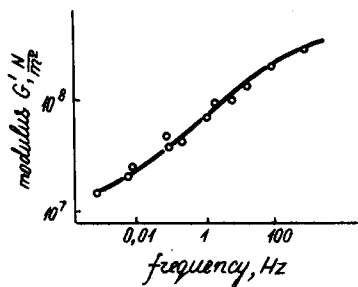
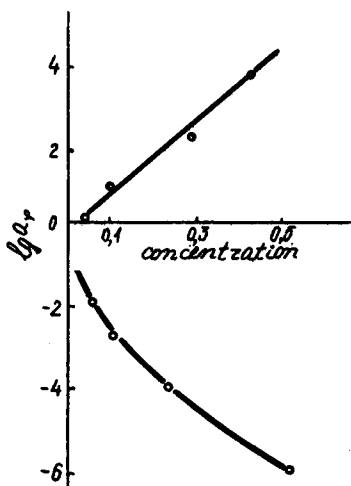Fig. 8. Master curve constructed from data on Fig. 7 for $\varphi = 0.045$ and 114°.

Fig. 9. Concentration dependence of shift factor a_φ at 114° for quartz filler (curve 1) and for polystyrene filler at 110° (curve 2).

Having in mind that a_φ characterizes the shift of curve lg $G' = f(\omega)$ on the frequency scale and having compared the increase lg G' with increase in frequency and increase in filler concentration, we have concluded that in polymers filled with hard filler, the concentration–time analogy exists. It may be expressed in the following way: The increase in filler concentration leads to an increase in the real part of complex shear modulus in the same way as increase in deformation frequency. It is worth noting that the established analogy allows not only to investigate the filler influence of polymer matrix but to broaden essentially the frequency diapason for prognosis of the mechanical properties of filled polymers.

Concentration–Temperature Analogy

From the results mentioned above it is seen that filler concentration influences relaxation time. It was interesting to examine the filler influence on temperature dependence of the relaxation time. For this purpose, we analyzed the temperature dependence of the real part of the complex
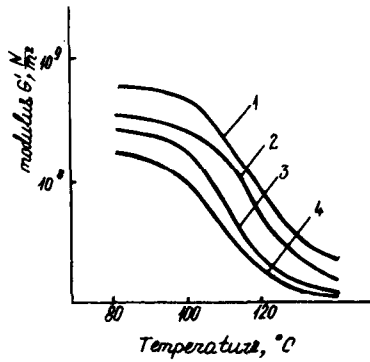
Fig. 10. Temperature dependence of real part of modulus filled with quartz composition at (1) 0.44; (2) 0.31; (3) 0.11; (4) 0.045.
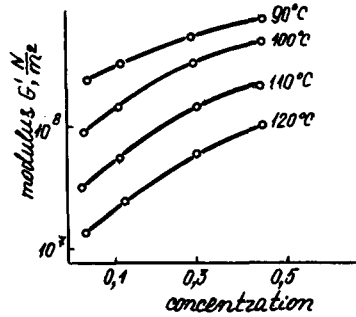

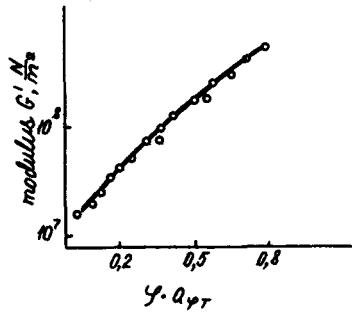Fig. 11. Concentration dependence of real part of modulus in the α-region.

Fig. 12. Master curve for composition, constructed from the data given in Fig. 11 for 120°

modulus at various filler concentrations (Fig. 10). It is seen that with increase in filler concentration, curves $\lg G' = f(T)$ are situated higher and shifted to higher temperatures. Without considering the reason for this, let us discuss the dependence of these effects on filler concentration.

From the data given in Figure 10 we can construct the concentration dependence of the real part of modulus on temperature (Fig. 11). It is evident that curves $\lg G' = f(\varphi)$ have a characteristic shape and equidistant
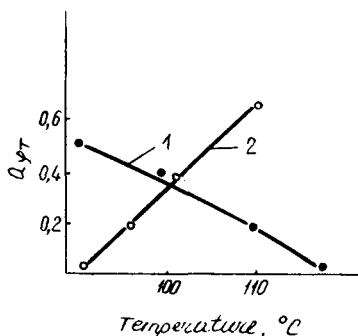
Fig. 13. Temperature dependence of shift factor $a_{T,\varphi}$: (1) for composition with quartz filler; (2) for polystyrene filler.

arrangement, which allows to apply the WLF method. The master curve, reduced to 120°, is given in Figure 12. The dependence $\lg a_{T,\varphi} = f(T)$ is nearly linear (Fig. 13, curve). Thus, we can conclude that in the discussed case the in crease in filler concentration leads to the same increase in the real part of modulus as the decrease in temperature. This may be described as concentration–temperature analogy. This analogy may be of great interest for broadening the possibilities to predict the influence of fillers on the mechanical properties of polymers.

Peculiarities of Mechanical Behavior in Polymer–Polymeric Filler Systems

From the point of view of the analogies considered above, we can now discuss the results of study of relaxation properties in the system epoxy resin–polystyrene as filler. The experimental data on dependences $\lg G' = f(\omega)$ at temperatures in the range of the α-transition and application of the WLF method have shown that in the system polymer–polymeric filler the temperature–frequency analogy takes place, too. From generalized curves tg δ for different concentrations of polystyrene filler φ, the dependence of the average relaxation time τ on φ was calculated (curve 2, Fig. 6). It is seen that increase in filler concentration diminishes the relaxation time in filled specimens. However, in this case the character of the analogy is different. Actually, from Figure 14 it is seen that increase in filler concentration leads to a shift of dependence $\lg G' = f(\omega)$ to higher frequencies and diminishes the real part of the complex modulus. As a result, for reducing to lowest filler concentration and for master curve construction, we must make the shift of curves to the lower frequencies, as the value of shift factor a_φ has an opposite sign (see Fig. 9, curve 2). Therefore, in reference to the system epoxy resin–polystyrene filler, the frequency–concentration analogy consists in equivalency of increase in filler concentration to decrease in deformation frequency. From the data on dependences $\lg G' = f(\varphi)$ at different temperatures in the transition region, we can conclude that it is reasonable to reduce the data to lower
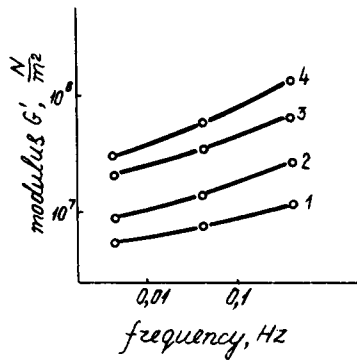
Fig. 14. Frequency dependence of real part of modulus for composition with polystyrene filler at 110°: (1) $\varphi = 0.5$; (2) 0.25; (3) 0.1; (4) 0.05.
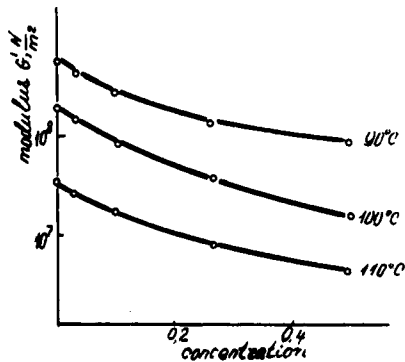

Fig. 15. Concentration dependence of real part of modulus for composition with polystyrene filler in the α-transition region.

temperatures, as in the opposite case we should shift the curves to negative concentrations, which has no physical meaning (Fig. 15). This circumstance allows us to speak about an opposite sign of $a\varphi$ for the system under consideration (Fig. 13, curve 2). Therefore in reference to the system epoxy resin–polystyrene filler, the concentration–temperature analogy means that the increase in filler concentration leads to the diminishing of the real part of modulus as the temperature increases.

GENERAL DISCUSSION

Now let us consider the main reasons for the existence of some analogies in the viscoelastic properties of filled polymers. The temperature–time analogy in filled polymers is caused by the same factors as in unfilled polymers.[10] It is based on the exponential dependence of viscoelastic properties on reverse temperature and logarithmic dependence on deformation rate. The frequency–concentration analogy is based on the exponential dependence of the viscoelastic properties on filler concentration and log-
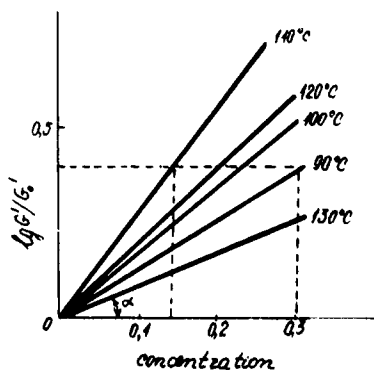
Fig. 16. Concentration dependence of relative modulus for composition with quartz filler.

arithmic dependence on deformation rate. Therefore, the ascertaining of the factors which cause the analogies mentioned above consists in determining the causes of change in shear modulus with increase in filler concentration.

For quartz filler, we can select some phenomenon of physicochemical character connected with high modulus of filler. Here, filler practically cannot be deformed, and this influences deformation condition and mechanical behavior of polymer matrix. In filled specimens, the deformation amplitude of matrix increases essentially with increase in filler concentration at constant deformation of specimen, and this increases the tension and the modulus.[13,15] The increase in matrix deformation amplitude leads to growth of its deformation rate, which in turn increases modulus, too.

As an essential cause of increase in modulus with filler concentration can be named the increase in polymer part in a form of surface layers at the interface with solid (between filler particles). In such thin films, the polymer is subjected to bulk deformation. It is known that bulk modulus is much higher then shear modulus, and therefore the increase in polymer fraction in surface layers leads to a general increase in modulus of the filled system. It was shown[5-7] that in surface layers the molecular mobility of chains and segments is diminished as a result of conformation restrictions. The existence of such a hard layer may be considered as another cause of modulus increase as a result of apparent increase in particles size. At constant filler amount, it is equivalent to an increase in filler concentration.

To discuss the problem from this point of view, let us consider the relative modulus which represents the ratio of modulus of filled specimen to unfilled one, G_1'/G_0'. Here, as G_0' we have taken the value obtained by extrapolation of G' to zero filler concentration. Some results are given in Figure 16, from which it is seen that the dependence of lg (G_1'/G_0') on filler concentration is nearly linear and the slope of the curves at different temperatures is not the same. Therefore, the same value of relative modulus at different temperatures corresponds to different values of filler
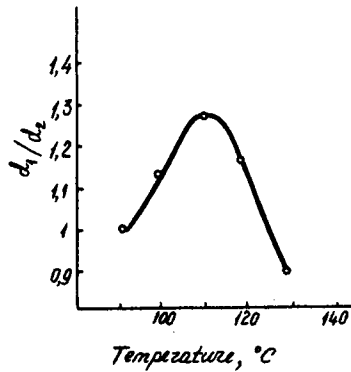
Fig. 17. Influence of temperature on change in surface layer thickness in composition with quartz filler.

concentration. For example, the value of lg $(G_1'/G_0') = 0.4$ at $110°$ corresponds to $\varphi = 0.12$ and at the same time at $90°$ for the same relative modulus $\varphi = 0.3$. If we attribute such a phenomenon to different thickness of surface layer of polymer at the interface, we can approximately calculate the change in surface layer thickness with temperature. Really, at a constant number of filler particles, their volume fraction in polymer is proportional to particle volume $V = d^3$ (d = diameter of particle) for spherical particles:

$$\frac{\varphi_1}{\varphi_2} = V_1 V_2 = d_1^3/d_2^3$$

where suffixes 1 and 2 are related to comparison temperatures. If we denote the slope of curves lg (G_1'/G_0') versus φ as α, we can show that

$$\text{tg } \alpha = \text{lg}(G'/G_0')/\varphi \tag{1}$$

and

$$d_1^3/d_2^3 = \varphi_1/\varphi_2 = \text{tg } \alpha_2/\text{tg } \alpha_1. \tag{2}$$

Therefore,

$$d_1/d_2 = \sqrt[3]{\frac{\text{tg } \alpha_2}{\text{tg } \alpha_1}}. \tag{3}$$

Having taken as base for comparison the particle size with surface layer at $90°$ we have calculated ratio (3) at different temperatures (Fig. 17). This dependence has a maximum in the same temperature range as for mechanical losses. Such a coincidence probably can be explained having in mind that at this temperature the experimental time is comparable to the average relaxation time of polymer matrix. We have already mentioned above that with increase in filler concentration the relaxation times increase, too. This allows the conclusion to be drawn that in surface layers the relaxation times are higher than at great distances from the

phase border.   It is evident that at the temperature which corresponds to the mechanical loss maximum, the relaxation time in the surface layer is higher than the experimental time, and surface layer cannot be essentially deformed.   At the same time, in more distant layers relaxation time is comparable to experimental time, and therefore the general deformation is determined by the deformation of these distant layers.   This statement confirms the dependence found earlier[14] of surface layer thickness on polymer properties and experimental conditions.

It was already mentioned that in the system polymer–polymeric filler, the temperature–concentration and concentration–time superpositions have a negative sign, as the average relaxation time and modulus diminish with increase in filler concentration.   The main reason for this is the essential decrease in polystyrene modulues with increase in temperature, especially in the transition region for epoxy matrix.   The increase in such a filler concentration diminishes the real part of complex modulus of filled specimen and relaxation times.

CONCLUSIONS

It is thus established that in filled polymers the concentration–time and temperature–concentration analogies exist in mechanical behavior and that change in filler concentration leads to the same change in modulus as changes in temperatures or deformation frequencies.   The laws established can be used to predict the filler influence on the mechanical behavior of filled polymers.

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