

## Effect of Filler on the Relaxation Time Spectra of Filled Polymers

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### Synopsis

The temperature and frequency dependences of the complex shear modulus  $G^*$  and  $\tan \delta$  of mechanical losses of epoxy compositions with various fillers were studied. The method of Nino-miya-Ferry applied to the reduced curves of frequency dependence of the effective part of the shear modulus was used to draw up relaxation time spectra for specimens with various concentrations of the filler. Regularities in the change of type and position of the spectral curves with increase in filler concentration were indicated. The findings make it possible to draw conclusions about the effect of the filler on the properties of the polymer matrix in the boundary layer and about changes in the conditions of the deformation of the polymer interlayers between the filler particles as compared with the deformations in bulk specimens.

### INTRODUCTION

It is an established fact that the surface of the filler has a noticeable effect on the molecular and segmental mobility of the filled polymer<sup>2</sup> and on the increase of imperfectness of the polymer network formed in the presence of the filler.<sup>3</sup> For this reason, many properties of the polymer in the boundary layers, including the mechanical properties and relaxation spectra, may change.<sup>4</sup> The expansion of the relaxation time spectra, in the filled polymer systems, was estimated by the parameter value obtained from the dielectric relaxation data.<sup>6</sup> There is information indicating an increase of the average relaxation time in the layer of the polymer which is on the surface of solid particles.<sup>1,5,6</sup> The increase of the average relaxation time and the expansion of the relaxation spectra are associated with changes in the structure of the surface layers<sup>6</sup> and with adsorption interaction which restricts the molecular mobility<sup>2</sup> and affects molecular packing. From this point of view, it could have been expected that with increase of the total surface area or filler concentration (i.e., with decrease in the thickness of the polymer layer between particles), a systematic decrease in the molecular mobility and increase of the average relaxation time will take place. This effect proceeds up to the point at which adjacent particles are in intimate contact and all the polymer segments will be powerful bounded by the surface. In this case, all relaxation processes with high relaxation times will be excluded and, as a result, some drop in the average relaxation time may be possible, as is observed during elastomer vulcanization.

The equivalence of the action of the filler to the increase of frequency or decrease in temperature was previously<sup>1</sup> made the basis of the superpositions "deformation frequency–filler concentration" and "temperature–filler concentration." Using epoxy compositions with quartz and polystyrene fillers, we have shown that the dynamic mechanical properties of filled polymers could be satisfactorily described and predicted within the framework of those superpositions. The above concentration superpositions are based on the conformity in the change of the average relaxation time with increase in the filler concentration. Yet, as follows from the above, some changes in the position and shape of the relaxation spectrum can be expected as well as filler concentration is changed. Since this problem has not been treated specially until now, with the aim of testing this theory we have conducted the study of viscoelastic properties of the filler epoxy resin compositions on the basis of which we have calculated the relaxation time spectra.

### EXPERIMENTAL

The temperature and frequency dependences of the complex shear modulus  $G^*$  and  $\tan \delta$  were examined by the use of a frequency relaxometer described in detail in reference 7. The specimens were epoxy resin-based compositions with 10% poly(ethyleneamine) as the crosslinking agent. Quartz powder with particles sized 2–3  $\mu$  and hardened resin powder with particle sized from 3 to 10  $\mu$  were used as a filler.

The viscoelastic properties were studied in the epoxy resin matrix transitional temperature  $\alpha$ -region (70–140°C) within the frequency range of 0.004 to 0.4 Hz with 0.01 deformation amplitude. The specimen preparation technique is explained in reference 1. The present work does not contain the direct experimental dependences  $\log G' = f(\omega)$  and the generalized dependences  $\log G' = f(\log \omega a_T)$  since they can be found in references 1 and 7. However, it is appropriate to mention here that all the generalized viscoelastic functions used to evaluate the spectra were constructed according to the WLF method.

### RESULTS AND DISCUSSION

The relaxation time spectra were calculated by numerical differentiation according to the Ninomia-Ferry method<sup>11</sup> the use of which requires the knowledge of the real part of the complex shear modulus for several frequency values equidistant on the logarithmic scale and found above and below the  $W = 1/\tau$  frequency corresponding to the relaxation time  $\tau$  for which  $H$  is being evaluated. The frequency values are taken equal to  $\omega/a^2$ ,  $\omega/a$ ,  $\omega a$ , and  $\omega a^2$  with an appropriate magnitude of  $a$ :

$$H(\tau) = \left( \frac{G'(a\omega) - G'(\omega/a)}{2 \ln a} - \frac{a^2}{(a^2 - 1)^2} \right) \times \frac{G'(a\omega) - G'(\omega/a^2) - 2G'(a\omega) + 2G'(\omega/a)}{2 \ln a}$$

The selected value for  $a = 0.2$  is considered optimum. The calculations were carried out with the aid of punched cards quoted in reference 12.

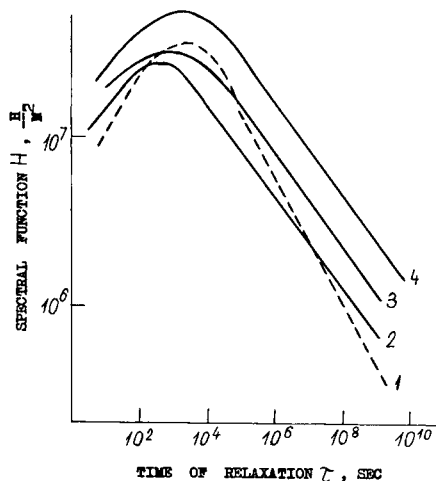


Fig. 1. Relaxation time spectra of polyepoxy resin filled with quartz powder at  $T = 80^{\circ}\text{C}$ : (1) specimen without filler; (2)  $\varphi = 0.04$ ; (3)  $\varphi = 0.31$ ; (4)  $\varphi = 0.44$ .

Figure 1 illustrates curves of the spectral function of  $H$  for relaxation times exceeding 10 sec versus various concentrations of the quartz filler. As is evident from the diagram, with a small concentration of the filler ( $\varphi = 0.04$  of the volume), the relaxation time spectrum of the filled polymer little differs from the spectrum of the unfilled  $\Delta$ -5 and undergoes perceptible changes only within the low-period region, somewhat shifting toward the reduced relaxation time.

An increase in the filler concentration (see curves 2 and 3 in Fig. 1), in addition to an expansion in the low-time region, also expands the spectrum and shift it toward larger periods. Besides, the value of the spectral function  $H$  increases with increase in the concentration of the filler and the slope of the linear portion of the spectrum in the filled specimens is less than in the unfilled specimens.

In view of the fact that the spectrum of the quartz relaxation time is not overlapped by the polymer spectrum, the indicated changes in the spectra can perhaps be associated with changes in the properties of the polymer matrix stipulated by the influence of the filler surface, and with changes in the conditions of its deformation due to the effect of the volume of the high-molecular filler.

Now let us analyze changes in the conditions of polymer deformation in the presence of the filler. In the first place, it should be noted that a high-modulus filler undergoes virtually no deformation during the deformation of the filled specimen, since its modulus is  $10^3$  to  $10^4$  times more than that of the polymer. For this reason, the deformation of the filled specimen occurs entirely at the expense of the polymer deformation. The presence of a sufficiently large amount of particles of the nondeformed filler results in that the relative deformation of the polymer between the filler particles may exceed many times the total deformation of the filled specimen.<sup>8,9</sup> Due to this, stresses in the polymer have an appreciably higher amplitude. In accordance with Gurevich,<sup>10</sup> the increase in the stresses leads to a reduction in the average time of relaxation, which may explain the initial shift of the spectrum

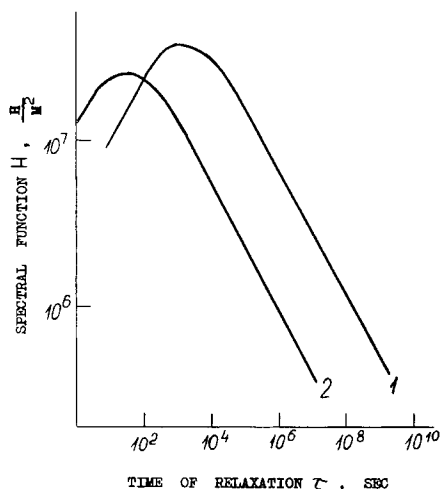


Fig. 2. Relaxation time spectra at various deformation amplitudes at  $T = 80^{\circ}\text{C}$ : (1)  $\epsilon = 0.01$ ; (2)  $\epsilon = 0.05$ .

toward smaller time. There are also more direct indications of changes in the position of the spectra on the scale with the increases of stresses. As is seen from the work of Schwarzl,<sup>14</sup> with higher stresses the spectral curves shift toward the smaller time region without changes in the shape of the curves.

To confirm this, an additional experiment was conducted in which the amplitude of deformation of the specimen was increased several times.

The relaxation time spectra versus various amplitudes of deformation are shown in Figure 2. Comparing the position of the spectral curves, one can see that indeed the increase in the amplitude of deformation substantially shifts the spectrum toward the smaller time region, virtually without changing the curve shape. It means that the presence of quartz filler would have to shift the spectral curves to the left, and the shift would have to increase with increase in filler concentration. However, as follows from Figure 1, such a shift does not occur. Moreover, with the increase in the concentration of the filler, the spectra shift to the right, expand, and the slope of the linear portion of the spectral curves changes. On the strength of these data, one can suggest that with the increase of the filler concentration, the filler surface action on the segmental mobility plays a predominant role, shifting the spectra toward greater periods. This surface effect not only compensates for the expected curve shift to the left induced by the incompressibility of the filler, but, on the contrary, shifts the spectral curves to the right. Particularly salient are the shifts in the larger relaxation time region. This means that the greatest influence of the filler surface is exercised on the restriction of mobility of the longest structural components which leads to an increase in the average relaxation time. This is confirmed by the data on bulk relaxation as given in the work of Lipatov and Geller.<sup>5</sup> A slight expansion of the spectra toward smaller relaxation periods can be interpreted as a result of a higher defectiveness of the polymer network in the presence of filler,<sup>3</sup> as well as a result of loosening of molecular packing in the polymer layer onto solid surface.

In filled polymer systems, a selective sorption of one of the components of the initial composition before hardening may occur on the filler surface.<sup>2</sup> In

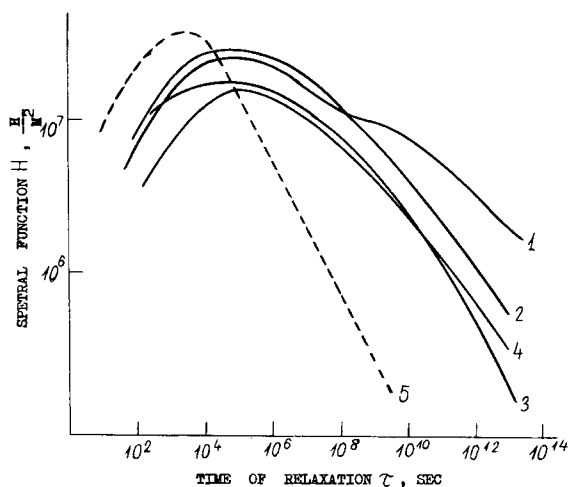


Fig. 3. Relaxation time spectra of specimen with polyepoxy filler at  $T = 80^{\circ}\text{C}$ : (1)  $\varphi = 0.05$ ; (2)  $\varphi = 0.010$ ; (3)  $\varphi = 0.25$ ; (4)  $\varphi = 0.40$ ; (5) filler relaxation time spectra.

this case, the surplus of the other component may act as a plasticizer which causes a reduction of elastic moduli and a change in the relaxation behavior of the filled system. We demonstrated this effect in the epoxy resin-poly(ethyleneamine) system, varying the hardener concentration. Having calculated the relaxation time spectra for such specimens (Fig. 3), we found that an excess of any component caused a perceptible shift of the spectra toward smaller periods. This result indicates that the shift of the spectral curves toward larger periods due to the introduction of the filler is not associated with the selective sorption of one of the composition components on the filler surface.

Thus, the experiments with the quartz filler and the modeling of some aspects of the effect of the filler on the viscoelastic properties of the matrix have shown that the shift of the  $H$  spectral function in polymers filled with a high-modulus filler is probably the result of the action of at least two causes, one of which, viz., a change of deformation conditions in the presence of the filler particles, shifts the spectrum to the left, and the other, viz., the effect of filler surface on the properties and structure of the polymer matrix, shifts it to the right. However, as follows from the general shift of the spectral curves to the right, the role of the second factor is much more significant.

We deemed it expedient to carry out further studies, excluding the effect of one of the factors. It appeared suitable to exclude the changes in the conditions of deformation of the polymer matrix by way of selecting a filler close in its mechanical properties to the binder. Most convenient in this respect was the powder of the same hardened epoxy resin was used as the binder.

The relaxation time spectra of specimens with such filler of various concentrations are shown in Figure 4. For the sake of comparison, there is also given a spectral curve of the specimen from which the filler was made. In analyzing the results of this experiment, the attention is drawn to the significant shift of the spectral curves toward larger relaxation periods as compared with the spectrum of the resin hardened without the filler. Also taking place

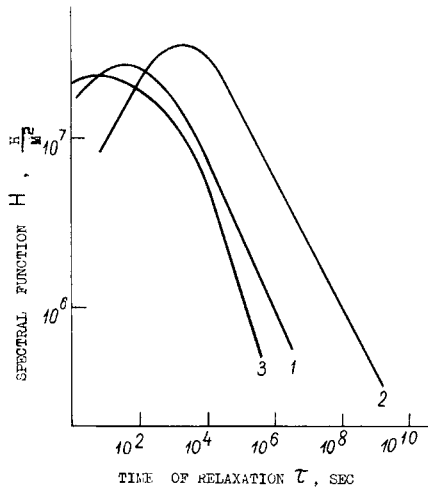


Fig. 4. Relaxation time spectra of specimen with various concentrations of crosslinking agent: (1)  $\varphi = 6\%$ ; (2)  $\varphi = 10\%$ ; (3)  $\varphi = 20\%$ .

in the presence of the filler is an expansion of the spectral curves and a change in their slope. It is significant that the shift and expansion of the spectra in this case is more conspicuous than for the quartz-filled specimens. It is obviously connected with the exclusion of the factor of nondeformability of the filler, due to which the effect of the filler surface on the change of properties of the surface layer of the polymer hardened on this surface is manifested in a purer form.

From the point of view of an increased share of the surface layers in the total volume of the matrix with an increase in filler concentration, a regular arrangement of the spectral curves would have been expected. Indeed, such regularity is traced in Figure 4, but it appeared more complex than could have been expected. It is seen directly from Figure 4 that, as the filler concentration increases, the right-hand parts of the spectrum shift toward smaller periods, i.e., approach the spectrum of the filler polymer. It indicates that the left-hand part of the spectrum is connected with the spectrum of the filler relaxation time, while the right-hand part is connected with the matrix spectrum. As the concentration of the filler increases the spectrum would have to narrow on one side and to shift to the left, since the share of the matrix decreases; but, on the other hand, the share of the surface layers of the polymer

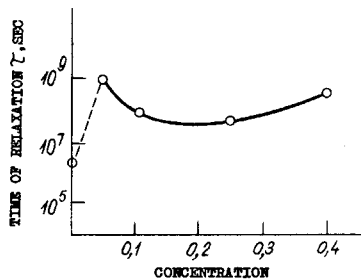


Fig. 5. Average relaxation time of filled specimens vs. concentration of polyepoxy filler at  $T = 80^\circ\text{C}$ .

in the matrix increases, and this has to shift the spectrum toward larger periods. Just this simultaneous action of the factors causes such a complex behavior of the spectrum. This is revealed particularly clearly in the analysis of the concentration dependence of the average relaxation time. The diagram of the average relaxation time versus filler concentration is shown in Figure 5. As is seen, the dependence is of a nonmonotonic character with a minimum in the 15–25% filler concentration region. Along with the reasons explained at the beginning of this report, such character of the curve may be due to the fact that an increase of the share of the filler in the system decreases the total average system relaxation time, since the average time of relaxation of the filler itself is less than the average time of relaxation of the binder solidified in the presence of the filler. At the same time, the share of the boundary layers also increases with the increase of the filler concentration. But the increase in concentration of the boundary layers with a greater relaxation time increases the average system relaxation time. As a result of the opposite action of those two factors, the average relaxation time of the specimen filled with a polymer filler is a nonmonotonic function of the filler concentration. The noted nonmonotonic character of the change in viscoelastic systems may be also associated with a nonmonotonic character of the change in the structure of polymer surface layers of different thickness.<sup>15</sup>

In connection with the above, the authors deem it appropriate to revert to the question of the “concentration–time” and “concentration–temperature” superpositions in the viscoelastic behavior of filled polymer systems stated in references 1 and 13. It was shown that for filled polymers in which the average relaxation time is a monotonic function of the filler concentration, the “concentration–time” and “concentration–temperature” superpositions take place. The existence of the nonmonotonic dependence  $\tau_{\text{aver}} = \chi(\varphi)$  in the heterogeneous system epoxy matrix–epoxy filler narrows the range of superposition application to filler concentrations in which the dependence  $\tau_{\text{aver}} = \chi(\varphi)$  is of a monotonic character.

## CONCLUSIONS

The findings give evidence of the fact that the filler has a noticeable and complex effect on the relaxation time spectra of filled polymer systems. It has been indicated that the principal reasons for the alteration in the type and position of the spectral curves are changes in the conditions of deformation of the polymer between solid particles and the restriction in the molecular mobility due to adsorption interaction in polymer surface layers onto filler particles.

## References

1. Yu. S. Lipatov, V. F. Babich, and V. F. Rosovizky, *J. Appl. Polym. Sci.*, **18**, 1213 (1974).
2. Yu. S. Lipatov and L. M. Sergeeva, *Adsorption of Polymer*, New York, 1974.
3. Yu. S. Lipatov, *Plaste Kautschuk*, **10**, 738 (1973).
4. Yu. S. Lipatov and V. F. Babich, *Vysokomol. Soedin.*, **B10**, 848 (1968).
5. Yu. S. Lipatov and T. E. Geller, *Vysokomol. Soedin.*, **8**, 592 (1966).
6. Yu. S. Lipatov and F. G. Fabulyak, *J. Appl. Polym. Sci.*, **16**, 2131 (1972).
7. Yu. S. Lipatov, V. F. Rosovizky, and V. F. Babich, in *New Methods in the Study of Polymers* (Russ.), Naukova Dumka, Kiev, 1975.

8. K. D. Ziegel, H. K. Frensdorff, and A. W. Fogel, *J. Appl. Polym. Sci.*, **13**, 867 (1969).
9. V. E. Zgaevsky, S. Y. Frenkel, and Yu. V. Zelenev, in *Structure and Properties of Polymer Surface Layers* (Russ.), Naukova Dumka, Kiev, 1972.
10. G. I. Gurevich, *Deformability of Media and Propagation of Seismic Waves* (Russ.), Nauka, Moscow, 1974.
11. Ninomiya and J. D. Ferry, *J. Colloid Sci.*, **14**, 36 (1959).
12. J. D. Ferry, *Viscoelastic Properties of Polymers*, New York, 1961.
13. Yu. S. Lipatov, V. F. Rosovizky, and V. F. Babich, *Vysokomol. Soedin.*, **B16**, 512 (1974).
14. F. Schwarzl, *Kolloid-Z.*, **165**, 861 (1959).
15. Yu. S. Lipatov, E. G. Moysya, and G. M. Semenovich, *Polymer*, **16**, 582 (1975).

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