Viscoelastic Properties of the Model System: Epoxy Resin–Glass Beads–Poly(buthylmethacrylate)

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Synopsis

Temperature dependences of viscoelastic characteristics for a model system epoxy resin–glass beads covered with poly(buthylmethacrylate) were studied. The formation of interphase region was established with its own relaxation maximum. The structure of this region is supposed to be a kind of semi-interpenetrating network formed by crosslinked and linear polymers. Using the Gordon–Taylor equation, the volume fractions of both polymeric components in the interphase region were calculated. An experimental evidence in favor of theoretical calculations has been obtained showing some increase in the glass transition temperature of a two-phase polymeric system by introducing small amounts of the component with a lower glass temperature as compared with this temperature for the main component.

INTRODUCTION

It is well known that most polymeric systems are heterogeneous. The specific feature of the heterogeneity of the two-phase system is the existence of two maxima on temperature dependence of mechanical losses at any composition. At the same time the appearance of only one maximum is often explained as a sign of restricted compatibility of the components. However, theoretical calculations show[1] that, to strictly prove this statement, some definite conditions are necessary, the main condition being the great difference in glass transition temperatures T_g of the components. That means the lack of overlapping of two main relaxation transitions. It is also essential by discussing temperature dependences for two-component systems to take into account the shift of maxima on the temperature scale.[2–7] This shift may be connected both with pure phenomenological reasons and some structure transformations (the formation of interphase layers, migration of low molecular weight homologues into the interphase region, etc.). In Ref. 1 the case where the splitting maxima doesn't take place some increase was theoretically predicted in the glass transition temperature of the two-phase system in the region of small concentrations of the component with lower glass temperature.

To check experimentally some effects predicted theoretically in Ref. 1 we have investigated temperature dependences of tangent of mechanical loss angle and complex shear modulus for the model system: epoxy resin, filled by glass beads covered with a thin layer of poly(buthylmethacrylate). The choice of given model was conditioned by the great difference in the glass temperature of two polymers (about 80°C). At the same time, using a filler, we could have introduced into the system a small amount of the uniformly distributed second component with low T_g. In accordance with Ref. 1, we would expect some shift of the main maximum to higher temperatures.

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It was interesting also to compare such an experimental result with data[2] for fillers treated by low molecular weight substance (dimethyldichlorosylane), where independence of molecular mobility on chemical nature of filler surface was established. Such a comparison is of importance for understanding the mechanism of the reinforcing action of fillers and the role of surface treatment.

EXPERIMENTAL

Commercial epoxy resin ED-20 was taken as a binder for glass beads treated with poly(buthylmethacrylate) (PBMA).

The glass beads were covered with PBMA by immersing them into PBMA solutions of different concentration and drying in vacuum at 60°C. Epoxy resin with filler treated as mentioned above was cured by poly(ethylene polyamine) (10% by weight). The composite has been formed in Teflon press form and hardened at 20°C for 20 h and then in vacuum at 150°C for 8 h. Epoxy resin was preliminary dried in vacuum at 40° for 8 h. The average size of the glass beads was 5 μm. The thickness of the surface layers were calculated from the beads' weight change after immersing into solution and drying, these thickness being 0.015 μm and 0.8 μm.

The dynamic mechanical measurements have been done at frequency 0.5 Hz using equipment described in Ref. 3 at 0–150°C. Filler concentration was varied in the range 0–40 volume parts. The compositions and some characteristics of samples under investigation are given in Table I.

RESULTS AND DISCUSSION

For sure interpretation of experimental results, as a first step we have studied the influence of the mineral filler on the mechanical properties of each component separately. Figure 1 shows temperature dependence of the mechanical loss maximum for both epoxy resin and PBMA filled with glass beads. As was expected, introducing filler into epoxy resin shifts the transition temperature to higher values (curves 1–4). This shift is accompanied by decrease in absolute value of maximum. The same results were observed earlier for epoxy resin filled with quartz powder.[4] For PBMA there is no change in the temperature position

TABLE I

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
ED-20 weight part	100	100	100	100	100	100	100	100	100	100	—	—	—	—
PEPA weight part	10	10	10	10	10	10	10	10	10	10	—	—	—	—
Glass beads, volume part	—	8	16	40	8	16	40	8	16	40	—	8	16	40
T_g ED-20 (°C)	112	119	125	126	123	119	112	104	104	115	—	—	—	—
PBMA	—	—	—	—	0.015	0.015	0.015	0.08	0.08	0.8	100	100	100	100
T_g PBMA (°C)	—	—	—	—	40	33	40	33	42	40	29	29	29	31
T_g of interphase layer (°C)	—	—	—	—	—	82	90	62	59	—	—	—	—	—
Volume fraction PBMA in the interphase region	—	—	—	—	—	0.36	0.3	0.6	0.64	—	—	—	—	—

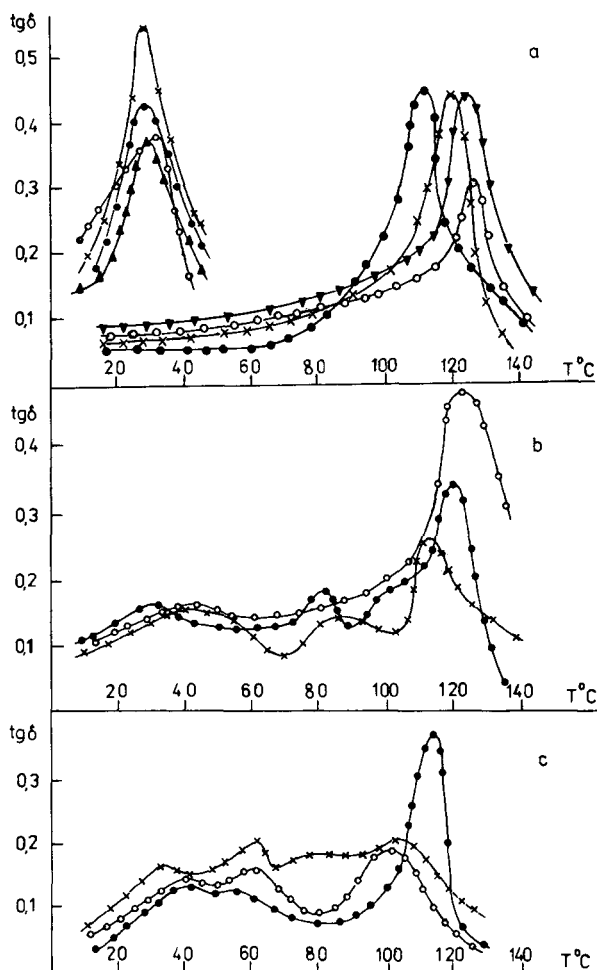Fig. 1. Temperature dependences of mechanical losses tan in the system: epoxy resin–glass beads covered by polybuthylmethacrylate. Compositions corresponding to the curves are given in Table I. Curve numbers: (a) Left curves: (×) 11; (●) 12; (▲) 13; (○) 14; right curves: (●) 1; (×) 2; (▼) 3; (○) 4. (b) (○) 5; (●) 6; (×) 7; (c) (×) 8; (○) 9; (●) 10.

of the main maximum, considerable decreasing of its value and some broadening being distinctly observed (curves 11–14). The influence of the mineral filler on the glass temperatures of filled polymers was the subject of many discussions (see, for example, Refs. 5, 6) and was explained by diminishing molecular mobility in the surface layer of polymer onto filler particles. Our results are in fairly good agreement with data for many filled polymers published earlier.[5] In such a way, in the model system chosen, the difference between temperature positions of the main maxima is $\Delta T_g = 80°$C, this excluding the overlapping of maxima for both polymers. This fact is of importance for interpretation of some intermediate maxima appearing at various compositions of model system.

Now let us discuss the results for epoxy resin filled with PBMA covered filler particles (layer thickness 0.015 μm) [Fig. 1(b)]. Increasing filler concentration from 8 up to 40 volume parts leads to shifting tan δ maximum to lower temperatures. On curve 5 there may be detected a weak maximum corresponding to

glass transition of PBMA. With increasing filler concentration this maximum manifests itself more markedly with some shift to higher temperatures (curves 6, 7). At the same time maximum for epoxy resin shifts to lower temperatures. Such effect of mutual influence of two components on their transition temperature was described earlier.[5] Of interest are two intermediate maxima tan δ at 82°C and 90°C (curves 6, 7). Their appearance shows the existence of an interphase layer at the interface between epoxy resin and PBMA. The structure formation of composites under investigation takes place initially at room temperature close to T_g for PBMA. The high mobility of PBMA segments in this temperature range promotes to diffusion of reaction mixture (epoxy resin + curing agents) into PBMA phase. This may lead to the formation of an interphase region having its own tanδ maximum (curves 6–9). This interphase region is supposed to be a kind of semi-interpenetrating polymeric network (IPN) consisting of network polymer (epoxy resin) and linear one (PBMA).[7] The maximum positions for the interphase region on the temperature scale are dependent on the number of crosslinks in epoxy resin which are in entanglement with linear PBMA macromolecules. It is clear that increasing content of PBMA should shift glass temperature of interphase region to lower temperatures (82°C—curve 6, 62°C—curve 8, 59°C—curve 9).

There was observed considerable change in the shape and position of maximum tanδ for layer with thickness 0.8 μm (Fig. 1). Curves 8 and 9 allows to suppose the formation of continuous network of glass beads covered with PBMA. The absolute values of losses for PBMA and epoxy resin (curves 8, 9) are approximately equal, this being according to Refs. 8, 9 a sign of continuity of both phases. It is remarkable that there are intermediate maxima on curves 8 and 9 at 62°C and 59°C. The temperature difference observed in position of tanδ maxima for layers of different thickness may be explained if we suppose enrichment of the interphase region with epoxy resin (thickness 0.015 μm) and with PBMA (thickness 0.8 μ).

Having used the Gordon–Taylor[10] equation for compatible components, the volume fractions of PBMA and ED-20 in the interphase region have been calculated;

$$T_{g12} = T_{g1} + K\left[\frac{\varphi_2(T_{g2} - T_{g12})}{\varphi_1}\right]$$

Here T_{g1} is the glass temperature for PBMA, T_{g2}, the same for epoxy resin, T_{g12}, the glass transition temperature of interphase region, φ_1 and φ_2 are volume fractions of PBMA and ED-20 in the interphase layer, and K is a constant for a given system.

Taking $K = 1$ and $\varphi_2 = 1 - \varphi_1$ and using experimentally found transition temperatures, the fraction of PBMA in the interphase was found for samples 6–9. Values φ_1 given in Table I confirm the suppositions made before as for redistribution of components in the interphase layer depending on its composition.

As is seen from Fig. 1, curve 10, there are present two sharp maxima for PBMA and epoxy resin, the intermediate maximum being less pronounced. It may be explained by the formation of some aggregates consisting of covered with PBMA glass beads at their high concentration 40 volume parts.[11] In this case the interphase area and fraction of interphase region in model system sharply decrease.

The comparison of peaks in maxima tanδ allows us to suppose epoxy resin to be a continuous phase. The greatest fraction of interphase region is present in curves 8, 9 as follows from the peak height of tanδ corresponding to glass transition. Such type of temperature dependences of tanδ have been often observed for partially compatible polymer mixtures, where both glass transition peaks of individual polymers and interphase region are present.[12]

Curves 2 and 5 (Fig. 1) show the influence of thin PBMA layers (0.015 mm) (glass bead concentration 8 v.p.) on glass transition temperature. For such composition, according to Ref. 1, a very small fraction of component with lower T_g should increase T_g of two-phase fraction of component with lower T_g should increase T_g of two-phase system. The maximum tanδ position shows that covering filler with a layer with lower T_g really increases glass temperature of epoxy resin, the maximum tanδ becoming broader.

In our opinion these results may be regarded as an experimental evidence in favor of theoretical prediction.[1]

Special attention should be paid to the question about long-range action of filler solid surface on properties of polymer in surface layer.

Increasing glass temperature in the system with PBMA (thickness 0.015 μm) shows that surface influence manifests itself through such a "soft" layer and leads to the increasing rigidity of epoxy resin, the PBMA layer diminishing at the same time inner stresses by curing.[5] At a thickness of 0.8 μm such an effect is absent and filler influences only on the soft layer. These data give some reasons to conclude that long-range action of solid surface is considerable and are of importance for improving properties of polymeric compositions.

CONCLUSIONS

The studying temperature dependences of viscoelastic properties of model system: epoxy–resin–glass beads covered with poly(buthylmethacrylate) allows the following conclusions to be drawn:

1. The interphase layers the epoxy resin—PBMA interphase have their own relaxation maximum, its position on temperature scale being a function of interphase layer composition.

2. The structure of the interphase region may be represented as semi-interpenetrating network consisting of crosslinked linear polymers.

3. Application of Gordon–Taylor equation for calculating fraction of components in the interphase region shows some changes in component ratio as a function of composition.

4. The experimental evidence of theoretical prediction was obtained showing some increase in glass temperature of the two-phase system of introducing into the system a small amount of component with lower glass transition temperature. It was shown also that the long-range action of solid surface extends up to at least 0.015 μm.

5. At the definite thickness of PBMA layer on glass surface there are observed three maxima of relaxation corresponding to individual components and the interphase region which may be the result of some compatibility of components in their mixture.

References

1. Yu. S. Lipatov et al., *J. Appl. Polym. Sci.*, **25**, 1029 (1980).

2. Yu. S. Lipatov, F. G. Fabulyak, V. V. Shifrin, *Vysokomol. Soed.* **A18**, 763 (1976).

3. Yu. S. Lipatov, V. F. Rosovizky, V. F. Babich, in *New Methods of Polymer Investigation* (in Russian), Kiev, 1975.

4. Yu. S. Lipatov, V. F. Rozovizky, V. F. Babich, *J. Appl. Polym. Sci.*, **18**, 1313 (1974).

5. Yu. S. Lipatov, *Physical Chemistry of Filled Polymers*, British Library, Lending Division, West Yorks, 1979.

6. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974, Vol. 1.

7. Yu. S. Lipatov and L. M. Sergeeva, *Interpenetrating Polymeric Networks* (in Russian), Kiev, 1979.

8. T. Miyamoto, K. Kodama, and K. Shibayama, *J. Appl. Polym. Sci. A2*, **8**, 2095 (1970).

9. P. Baner and J. Henning, *J. Angew. Macromol. Chem.*, **17**, 145 (1970).

10. *Polymer Encyclopedia* (in Russian) Moscow, 1977, Vol. 3, p. 495.

11. L. E. Nielsen, *J. Polymer Sci., Polym. Phys.* **17**, 1897 (1979).

12. *Multicomponent Polymer Systems*, R. F. Gould, Ed., Amer. Chem. Soc., Washington, D.C., 1971.

13. E. G. Moysya, G. M. Semenovitch, and Yu. S. Lipatov, *Vysokomol. Soed.* **A16**, 1337 (1974).

14. *Reinforcement of Elastomers*, G. Kraus, Ed., Interscience, New York, London, 1965.