

Heterogeneous Polymer-Polymer Composites. III. Viscoelastic Properties of Acrylic Polyblends

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Synopsis

The physical properties of heterogeneous polymer-polymer composites such as rubber-modified plastics depend not only on the properties of the constituent polymers, but also on structural characteristics such as phase geometry and morphology. The dependence of the viscoelastic properties of particulate composites on phase morphology and composition has been treated in a previous paper. This analysis is further modified and applied to dynamic Young's modulus (E^*) data on several types of heterogeneous acrylic polyblends prepared in this laboratory. By taking into account interparticle interactions, copolymerization effects, and phase inversion, a nearly quantitative representation of E^* is obtained. Deviations from calculated behavior can be explained by assuming more complicated models of phase structure and composition and by postulating higher-order and temperature-dependent interaction effects.

INTRODUCTION

The effects of changes in composition and morphology on the dynamic Young's modulus of polymer-polymer composites have been explored in a previous paper¹ in terms of an approximate theoretical calculation. A subsequent paper² described the preparation and physical properties of several types of heterogeneous acrylic polyblends; elastic modulus and thermal expansion coefficient data were found to be in generally good agreement with theoretical predictions. Adequate representation of modulus data was found to require introduction of an interaction parameter which was interpreted as a maximum packing fraction. In this paper, an analysis is given of isochronal dynamic Young's modulus data obtained on these materials. Interparticle interactions and partial phase inversion are explicitly accounted for. The effect of a copolymer of intermediate composition on dynamic properties is also discussed.

THEORETICAL

Theoretical calculations of the viscoelastic properties of multiphase media have been reviewed previously.¹ Major attention was devoted to an equation first derived by Kerner³ for elastic shear modulus. This expression was applied to the viscoelastic case and written in terms of the dynamic Young's modulus E^* . It was found that the dynamic Poisson's

ratio could be replaced by its elastic counterpart without significant change in computed values of E^* . It was further assumed that the Poisson's ratio of the composite (ν) was approximately equal to that of the matrix phase (ν_m) [the assumption takes the form $(1 + \nu)/(1 + \nu_m) = 1$] to arrive at the expression

$$\frac{E^*}{E_m^*} = \frac{(1 - \nu)E_m^* + \beta(\alpha + \nu)E_i^*}{(1 + \alpha\nu)E_m^* + \alpha\beta(1 - \nu)E_i^*} \quad (1)$$

where

$$\alpha = 2(4 - 5\nu_m)/(7 - 5\nu_m)$$

and

$$\beta = (1 + \nu_m)/(1 + \nu_i).$$

E^* is dynamic Young's modulus ($E^* = E' + iE''$, where E' is the in-phase component of E^* , or storage modulus, and E'' is the out-of-phase component of E^* , or loss modulus; also, $E''/E' = \tan \delta$, the loss tangent); η is elastic Poisson's ratio; v is volume fraction of inclusions; subscript m denotes a property of the continuous or matrix phase; and subscript i denotes a property of the dispersed or inclusion phase.

In the treatment of elastic modulus data on real systems, the elastic form of eq. (1) is found to be applicable only at low concentrations. In a previous paper² it was reported that the effects of interactions between inclusions at high-volume loadings of filler could be approximately accounted for by replacing v with ψv , where ψ is given by

$$\psi = 1 + v(1 - \nu_m)/\nu_m^2 \quad (2)$$

where ν_m is interpreted as a maximum packing fraction, but may more generally be regarded as an interaction parameter.

In real systems, there is often a partial inversion of phase structure.^{4,5} The prediction of the moduli of such systems has been treated⁶ in terms of a geometrical average of the moduli of the two possible simple phase arrangements, simple inclusions of A in B and simple inclusions of B in A. A model more easily related to microscopically observed phase structure assumes that the inclusions themselves can be treated as composite structures, that is, that a partially phase-inverted composite of A and B can be treated as a material comprising either (1) a matrix of A with composite inclusions in which B is the continuous phase and A is the dispersed phase, or (2) a matrix of B with composite inclusions in which A is the continuous phase and B is the dispersed phase. The consequences of assuming such a model for a system comprising polymers of widely separated transition temperatures were explored previously.¹ It was found that (1) E' depends essentially only on the volume fraction of inclusions, not on the composition or internal morphology of the inclusions; (2) the temperature dependence of E' reflects primarily the temperature dependence of the continuous phase; and (3) E'' and $\tan \delta$ are sensitive to composition and

inclusion morphology as well as to overall volume fraction. The introduction of v_m into eq. (1) through eq. (2) compresses the concentration scale but does not alter these conclusions.

EXPERIMENTAL

Materials

The methods of preparation and detailed compositions of the materials used in this study have been described elsewhere.² Brief descriptions are given below.

Physical Blends. Physical blends were prepared by coagulation of latex mixtures. The constituents used were a poly(methyl methacrylate) (PMMA) latex and a crosslinked rubbery acrylic copolymer latex (95 mole-% butyl acrylate and 5 mole-% 1,3-butylene dimethacrylate).

Heterogeneous Latex Particles. Heterogeneous latex particles were prepared by a two-stage emulsion polymerization. Materials prepared by polymerizing methyl methacrylate (MMA) on an acrylic rubber seed latex are designated HLP1. One set of HLP1 was prepared using a crosslinked acrylic copolymer seed latex of the same composition as that used in the preparation of physical blends; a second set was prepared using a seed latex from which the crosslinking comonomer was omitted. Materials prepared by reversing the order of polymerization are designated HLP2. One set of HLP2 was prepared from a crosslinked PMMA latex (95 mole-% MMA, 5 mole-% 1,3-butylene dimethacrylate); no crosslinking comonomer was used in the second-stage polymerization. A second set of HLP2 was prepared in which crosslinking comonomer was used in the second-stage polymerization, but not in the first.

Comparison Materials. Comparison materials included PMMA; a crosslinked rubbery acrylic copolymer (95 mole % butyl acrylate and 5 mole % 1,3-butylene dimethylacrylate); a similar acrylic rubber from which the crosslinking comonomer was omitted (i.e., polybutyl acrylate); and a series of random copolymers of the same composition as the above described heterogeneous materials (crosslinking comonomers were omitted).

Dynamic Measurements

Dynamic Young's modulus measurements were performed using a Vibron Model DDV-II direct-reading dynamic viscoelastometer (manufactured by Toyo Measuring Instruments Co., Tokyo, Japan). All measurements were performed at 110 Hz; the temperature range covered was generally -100°C to 170°C . Temperature measurements were made using a copper-Constantan thermocouple with a West Model 9B Pyrotest potentiometer. The rate of temperature change was generally $3^{\circ}\text{C}/\text{min}$ or less. No significant differences were observed between measurements taken during complementary heating and cooling cycles.

Specimens were cut from compression-molded films. Three specimens were usually required to encompass the entire temperature range while

conforming to Vibron specifications for sample size. Although loss tangent values are determined directly in the operation of the Vibron, calculation of the modulus requires measurements on a second set of specimens, so that a total of six specimens were needed for each material. Agreement between values obtained on different specimens was, with the exceptions noted later, excellent. Failure to observe sample size specifications was found to result in erroneous values of modulus and spurious loss tangent maxima.

RESULTS AND DISCUSSION

The materials studied are conveniently divided into four groups for purposes of discussion. Data are presented for PMMA and several other reference materials in Figures 1, 2, and 3; for three HLP1's in Figures 4, 5, and 6; for three physical blends, in Figures 7, 8, and 9; and for four HLP2's, in Figures 10, 11, 12, and 13. The theoretical calculations included in Figures 4 through 13, discussed in detail in the remainder of this section, are based on the curves of Figure 1 (extrapolated as indicated by the dotted lines) or (for copolymers) on interpolated values of E' and $\tan \delta$ from Figures 2 and 3. (Except for the high-temperature portion of those calculations which assume a continuous rubber phase, the extrapolations indicated in Figure 1 have very little effect on calculated values of E' and $\tan \delta$.)

Results on the HLP1's (Figs. 4, 5, and 6) are considered first. The experimentally observed values of moduli are lower than might be expected

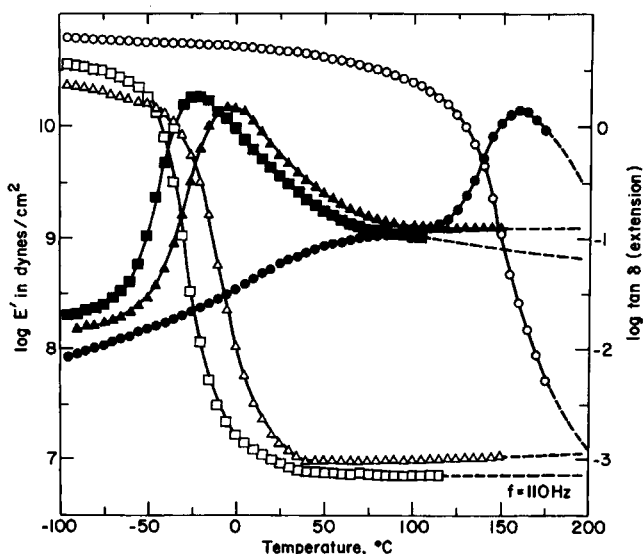


Fig. 1. Dynamic properties of PMMA (circles), poly(butyl acrylate) (squares), and a 95 mole-% butyl acrylate-5 mole-% 1,3-butylene dimethacrylate copolymer (triangles). In this and subsequent figures, open symbols are used for E' data, filled symbols, for $\tan \delta$ data.

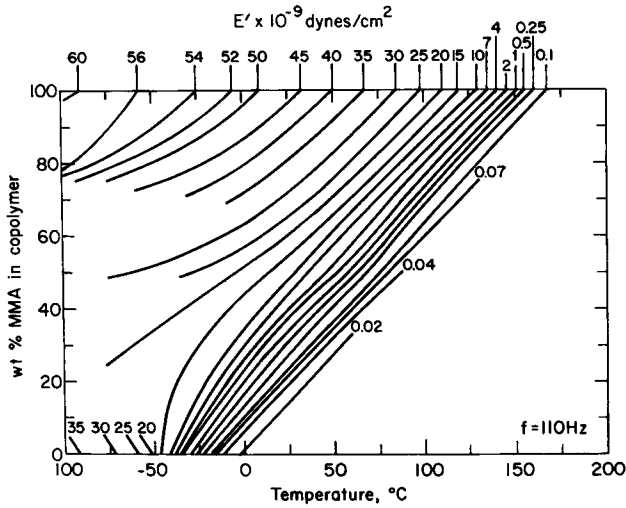


Fig. 2. Composition and temperature dependence of E' for MMA-BA copolymers.

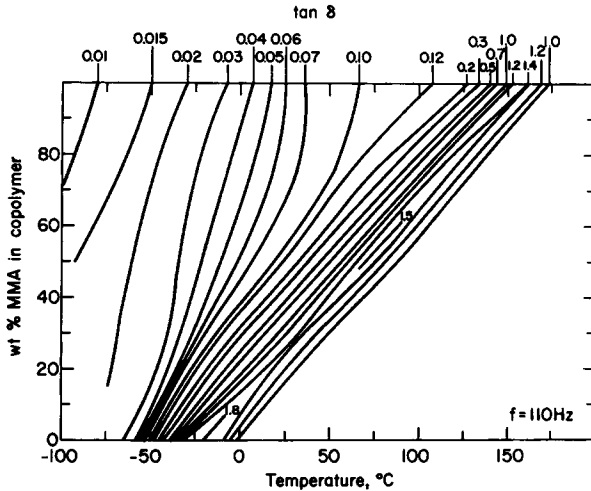


Fig. 3. Composition and temperature dependence of $\tan \delta$ for MMA-BA copolymers

from inspection of the computed curves displayed in Figure 6 of reference 1; also, the high-temperature loss maxima are shifted to lower temperatures than expected. In the quantitative application of the Kerner equation to data on hard particulate fillers, the need to consider interparticle interactions has been recognized for some time. From the data presented here and in reference 2, and from data on rubber-modified polystyrene,⁵ it is evident that a similar consideration is necessary for soft particles as well. The approach we have taken is an empirical one and can be regarded as replacing the volume fraction of filler by an *effective* volume fraction. In a previous discussion² of the dependence of elastic modulus on com-

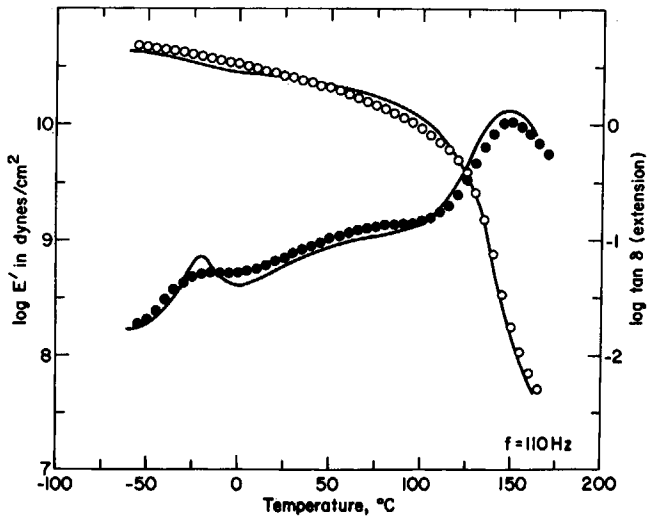


Fig. 4. Dynamic properties of an HLP1 based on a crosslinked rubber seed latex. MMA content, 75 wt-%. In this and subsequent figures, points are experimental, curves are calculated as described in the text.

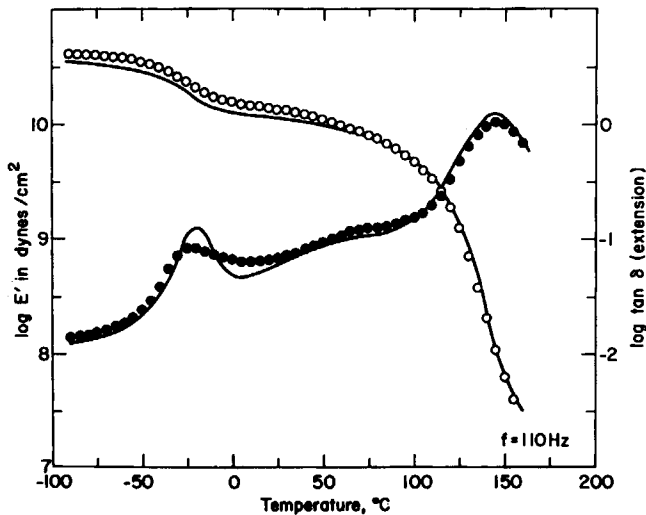


Fig. 5. Dynamic properties of an HLP1 based on a crosslinked rubber seed latex. MMA content, 50 wt-%.

position and morphology, it was found that the elastic form of eq. (1), with v replaced by ψv , represented data on the HLP1 quite well. Each material was assumed to comprise simple rubbery inclusions in a glassy matrix; v_m was estimated to be between 0.8 and 0.83. A correction to account for copolymerization of unreacted first-stage monomer with second-stage monomer was also introduced. As discussed in reference 2, it was assumed that (1) for the HLP1, all unreacted first-stage monomer (BA) polymerizes

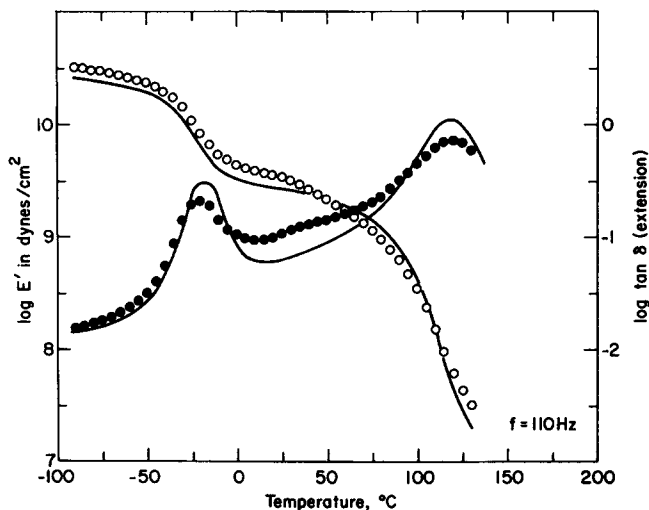


Fig. 6. Dynamic properties of an HLP1 based on a crosslinked rubber seed latex. MMA content, 25 wt-%.

uniformly and randomly with second-stage monomer (MMA), and (2) for the HLP2, the first-stage monomer (MMA) polymerizes to completion as the homopolymer. These assumptions resulted in corrections to the volume fraction of inclusions and to the matrix modulus for the HLP1. The amount of unreacted first-stage monomer was determined by comparison of calculated and measured latex solids content at the end of the first-stage polymerization. The volume fraction of inclusions and composition of the matrix were then computed assuming volume additivity.

Dynamic data on HLP1 can be reasonably well represented by making similar assumptions for the viscoelastic calculation. The parameter v_m has been taken as 0.83, independent of temperature and composition. Other parameters are summarized in Table I. The location of loss maxima and the level of E' are now approximately correctly given. However, loss tangent maxima are broader than predicted, and calculated values of E' at low temperatures are consistently below experimental results. Additional results, obtained on HLP1 based on an uncrosslinked rubber latex, are entirely comparable and have been omitted from this paper.

Although this treatment results in a reasonable representation of dynamic data, it cannot be correct in detail. Thus, the parameter v_m is assumed to be independent of temperature—and hence implicitly of matrix/filler modulus ratio. However, it is intuitively obvious that v_m (interpreted as an interaction parameter rather than simply as a geometrical maximum packing fraction) must approach unity as the moduli of filler and matrix become equal. There is some evidence for this in the present data; at temperatures at which the filler and matrix moduli are comparable, a much closer approximation to the experimental data can be obtained by assuming that $v_m = 1$.

TABLE I
Summary of Parameters for Theoretical Calculations

Composition, wt-% MMA	Disperse (inclusion) phase		Fig.	Curve		
	Continuous phase	Type			Description	
HLP1						
75	94.4 wt-% MMA copolymer	simple	22.5	crosslinked acrylic rubber	4	solid
50	93.8 wt-% MMA copolymer	simple	49.6	crosslinked acrylic rubber	5	solid
25	81.2 wt-% MMA copolymer	simple	71.7	crosslinked acrylic rubber	6	solid
Physical Blends						
75	PMMA	composite	30	9.0 vol-% PMMA in crosslinked rubber	7	solid
50	PMMA	composite	61	14.4 vol-% PMMA in crosslinked rubber	8	solid
25	PMMA	composite	82.1	6.0 vol-% PMMA in crosslinked rubber	9	solid
25	crosslinked acrylic rubber	composite	56	59.2 vol-% crosslinked rubber in PMMA	9	dashed
HLP2						
75	PMMA	composite	35	22 vol-% PMMA in crosslinked rubber	10	solid
50	PMMA	composite	82	35.4 vol-% PMMA in crosslinked rubber	11	dashed
50	crosslinked acrylic rubber	composite	58	19.0 vol-% crosslinked rubber in PMMA	11	solid
25	PMMA	composite	82.5	6.4 vol-% PMMA in crosslinked rubber	13	dashed
25	crosslinked acrylic rubber	composite	39	44 vol-% crosslinked rubber in PMMA	13	solid
25	uncrosslinked acrylic rubber	simple	22.8	crosslinked PMMA	12	solid

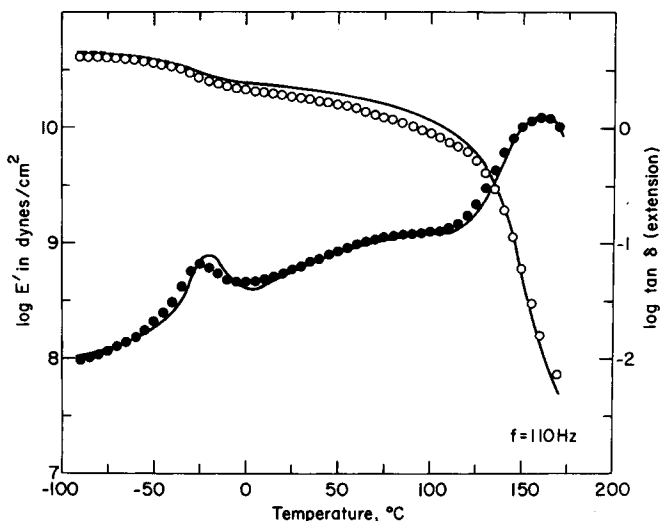


Fig. 7. Dynamic properties of a physical blend containing 75 wt-% PMMA.

The noted broadening of the transitions probably indicates a somewhat more complicated particle structure than assumed. (However, this broadening probably does *not* imply a “phase-within-a-phase-within-a-phase” structure; as discussed in reference 1, such a change in structure at constant composition *or* constant dispersed-phase volume fraction increases the magnitude of the dispersed-phase loss maximum with little change in shape.) The copolymerization correction included in the treatment of the HLP1 data assumes a single inclusion species dispersed in a copolymer matrix of uniform composition. If a shell-core model of latex particle growth^{8,9} is accepted, then a more realistic model of HLP1 particle structure might assume a gradation of composition, i.e., a rubbery core surrounded by a copolymer shell which becomes increasingly rich in second-stage monomer with increasing distance from the core. Qualitatively, such a structure would appear to have a temperature-dependent volume fraction of inclusions, the net effect of which would be a broadening of transition regions. Experimentally, it is found that increasing the amount of random copolymer formed in the synthesis of an HLP1 containing 75 wt-% MMA (by adding an appropriate monomer mixture between the normal first and second stages of polymerization) completely obliterates the low-temperature loss maximum (compare Figs. 4 and 14). The level of E' and the location of the high-temperature loss maximum are essentially unchanged although the high-temperature loss maximum is broadened somewhat by increasing the amount of random copolymer.

Results on the physical blends are considered next (Figs. 7, 8, 9). As indicated in Figure 9 of reference 2, modulus values for the physical blends are lower than those of HLP1 at comparable volume fractions of rubber. This behavior can be attributed either to a change in v_m relative to the

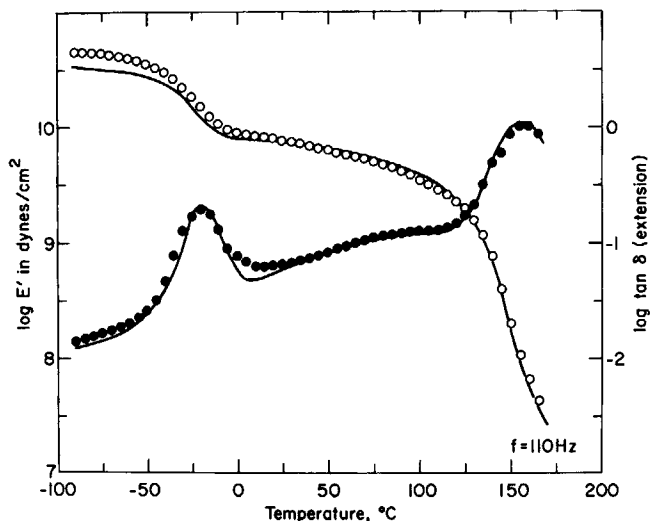


Fig. 8. Dynamic properties of a physical blend containing 50 wt-% PMMA.

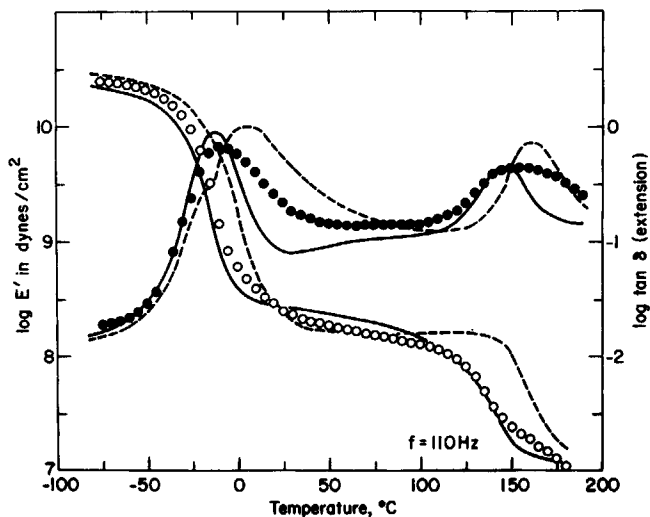


Fig. 9. Dynamic properties of a physical blend containing 25 wt-% PMMA.

HLP1 or to partial phase inversion. Although differentiation between these effects should be possible, it is found that either approach can provide a satisfactory representation of the physical blend data. Model calculations¹ indicate that, for a given level of E' in the temperature range between the constituent polymer transition regions, the height (and shape) of the low-temperature loss maximum depends on inclusion composition. On the other hand, if v_m is regarded as an adjustable parameter used to fit E' data, there is a unique corresponding value for the height of the low-temperature loss maximum. Comparison of these two approaches to representation of

E' data might allow a choice to be made on the basis of the corresponding representation of low-temperature loss tangent behavior. However, at low degrees of phase inversion, the differences between the two calculations are negligibly small.

Evidence for particle agglomeration (which would be expected to result in partial phase inversion) has been presented elsewhere.² On this basis, and in light of the fact that the rubber latex particles used to prepare the physical blends are essentially the same as those used as seed particles for the HLP1 syntheses, it has been assumed that v_m is 0.83 and that a small amount of phase inversion has taken place. Since calculated values of E' depend essentially only on v and not on the detailed structure of the inclusions,¹ the composition of the postulated composite inclusions can be estimated from Figure 9 to reference 2 by noting the horizontal displacement of the experimental relative modulus from expected simple inclusion behavior. The solid curves of Figures 7, 8, and 9 have been calculated assuming that each material comprises a glassy continuous phase with composite rubbery inclusions. The inclusion compositions assumed are indicated in Table I. Inclusion properties have been calculated using eq. (1) with v replaced by ψv and v_m taken to be 0.6.

A different representation is obtained if it is assumed that the material comprises a rubbery continuous phase with composite glassy inclusions. For data shown in Figures 7 and 8, such a representation proves completely unrealistic and is not presented or considered further. For the data of Figure 9, the results of the alternate representation are indicated by dashed lines. The assumed inclusion composition is given in Table I. Inclusion properties have been calculated from eq. (1) with v replaced by ψv and v_m assumed to be 0.83. For the second stage of the calculation, v_m is assumed to be 0.6.

All three physical blends can be reasonably well represented as materials having a continuous glassy phase with composite rubbery inclusions. This phase morphology probably reflects the substantial structural integrity, even under molding conditions, of the crosslinked rubber latex particles used to prepare these blends. The experimental loss tangent maxima are somewhat broader than predicted, especially at the highest rubber content (Fig. 9). In the latter case, the loss tangent behavior lies between the glass continuous and the rubber continuous-phase predictions; however, the glass continuous-phase calculation gives a better representation of E' .

The broadening of transitions relative to computed values may reflect interparticle interactions too complex to be accounted for in the simple way postulated here. It should also be noted, however, that the model assumes a single species of composite inclusion. If phase inversion occurs by occlusion of a portion of matrix polymer by aggregates of rubbery particles, there may be local variations in phase structure and composition resulting in broadened transitions.

Although there is some ambiguity in the selection of model and parameters, and hence also in detailed interpretation, a good representation of

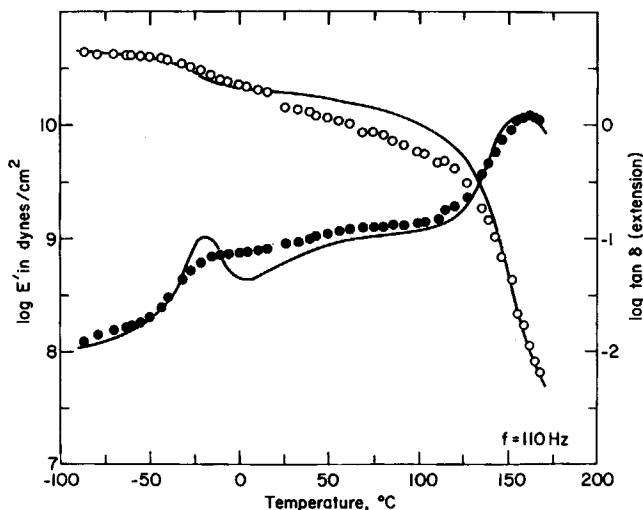


Fig. 10. Dynamic properties of an HLP2 based on an uncrosslinked PMMA latex. MMA content, 75 wt-%.

dynamic data is obtained. It is especially interesting that the locations of the low-temperature loss maxima (shifted by 15° or 20°C relative to the value for the rubbery constituent polymer) are correctly predicted.

Finally, results on HLP2 are considered (Figs. 10 through 13). Greater experimental difficulties were encountered with the HLP2's than with the other materials studied. A continuous film could not be prepared from a 75 wt-% PMMA HLP2 based on a crosslinked seed latex. This is not unexpected. The volume fraction of PMMA particles is probably higher than v_m (estimated to be 0.6), but since the particles are crosslinked, phase inversion and subsequent fusion is unlikely. For some of the other HLP2's, mechanical properties were found to depend on molding conditions.

Data are presented in Figure 10 for a 75 wt-% PMMA HLP2 based on an uncrosslinked PMMA seed latex. It appears that almost complete phase inversion has taken place (compare with the rubber continuous-phase and glass continuous-phase curves of Figures 5 and 6, reference 1). The calculated curves of Figure 10 assume a glassy continuous phase with composite rubbery inclusions. Minor differences in the properties of films molded at different times were noted, probably caused by minor variations in phase morphology. These differences appear in Figure 10 as a slight mismatch in E' values for different specimens (e.g., between 15° and 25°C and a 112°C).

At 50 wt-% PMMA, HLP2 based on crosslinked and uncrosslinked seed latexes displayed essentially identical behavior, except that the phase structure of the former was apparently somewhat more stable than that of the latter. Only data on the latter are presented in Figure 11. No satisfactory representation for these data has been found. Two attempts, both involving partial phase inversion, are shown. The numerical parameters

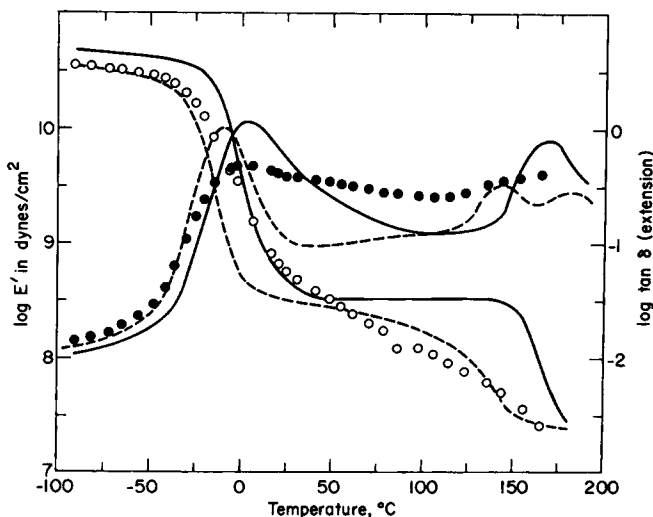


Fig. 11. Dynamic properties of an HLP2 based on an uncrosslinked PMMA latex. MMA content, 50 wt-%.

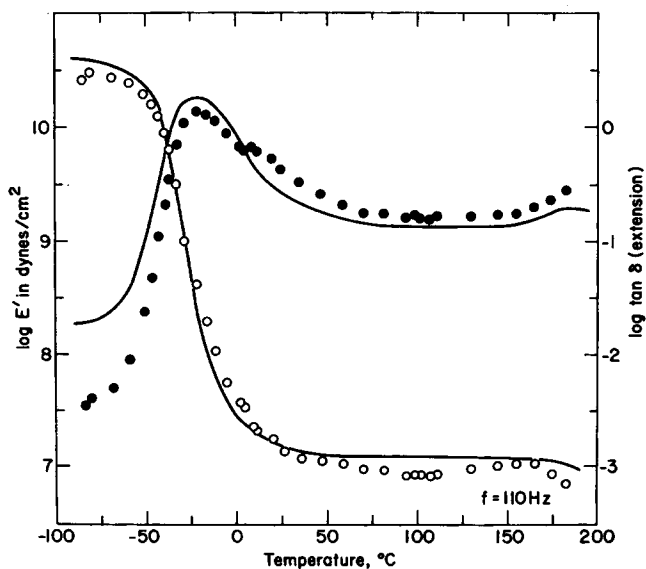


Fig. 12. Dynamic properties of an HLP2 based on a crosslinked PMMA latex. MMA content, 25 wt-%.

used are given in Table I. Data obtained on another specimen molded under conditions favoring phase inversion could best be represented by a model assuming a continuous glassy phase with composite inclusions. In terms of Figure 9 of reference 2, the modulus behavior shown in Figure 11 could be explained by assuming $v_m = 0.5$. However, the loss tangent behavior observed probably results from a complicated partially phase-

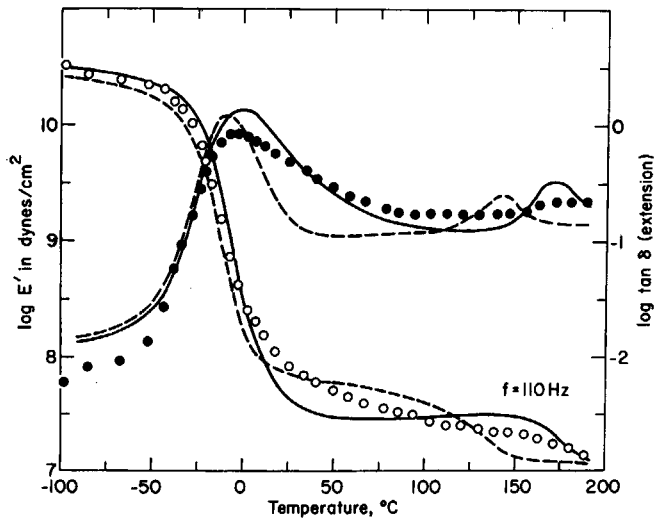


Fig. 13. Dynamic properties of an HLP2 based on an uncrosslinked PMMA latex. MMA content, 25 wt-%.

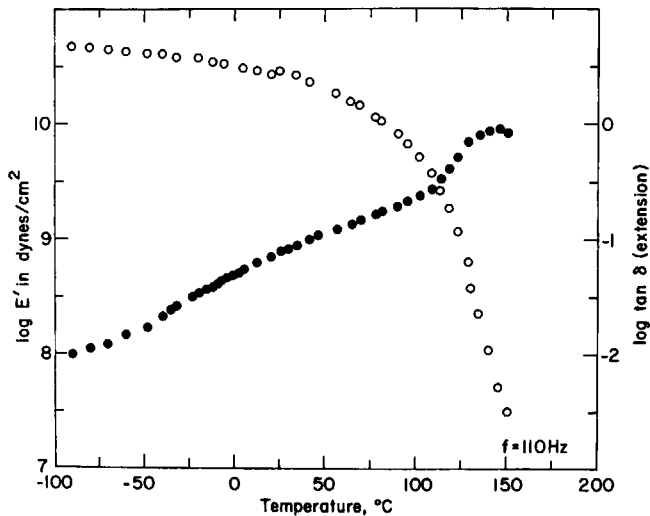


Fig. 14. Dynamic properties of an HLP1 of enhanced random copolymer content (see text). MMA content, 75 wt-%.

inverted structure, and therefore a somewhat higher value (0.6 has been assumed). This choice has relatively little effect on the calculated properties except for the 50 wt-% MMA HLP2 of Figure 11, but does give acceptable results for the two 25 wt-% MMA HLP2 (Figs. 12 and 13).

At 25 wt-% MMA, data on the HLP2 based on a crosslinked glassy seed latex (Fig. 12) can be represented assuming simple glassy inclusions in a continuous rubbery phase. (Data on uncrosslinked PMMA have been used for the calculation, as data on the appropriate crosslinked PMMA

were not obtained.) The similar HLP2 based on an uncrosslinked seed latex has apparently undergone some phase inversion (Fig. 13). Of the two representations given, the rubber continuous-phase calculation provides a slightly better approximation.

CONCLUSIONS

In this and the preceding two reports of this series, the viscoelastic properties of heterogeneous polymer-polymer composites have been examined both theoretically and experimentally. An approximate theoretical expression for elastic shear modulus, the well-known Kerner equation, has been adapted for representation of dynamic Young's modulus (E^*). The conclusions previously reached on the basis of model calculations—that the loss tangent depends on phase morphology as well as phase volume fraction, that the elastic modulus and the in-phase component of the complex modulus depend primarily on dispersed phase volume fraction, and that the temperature dependence of the complex modulus is dominated by the continuous phase except near the dispersed-phase transition region—are qualitatively substantiated by inspection of data on model systems presented in this report as well as by other data in the literature (e.g., references 4, 5, and 10).

In the analysis of data obtained on model systems, it is found that a reasonable representation of E^* can generally be obtained using the Kerner equation, provided that corrections for partial phase inversion, copolymerization, and interparticle interactions are introduced. In effect, the representations given for each material have been based on a comparison of the modulus at one intermediate temperature with theoretical predictions. The results on one group of materials, designated HLP1, which are assumed to have simple phase morphology comprising rubbery particles dispersed in a glassy matrix, are subjected to a correction, based on kinetic considerations, for copolymerization, and then are used to establish a value for an interaction parameter. Partial phase inversion is postulated to explain the behavior of a group of comparable physical blends. The composition of the assumed composite inclusions is deduced from the deviation of the experimentally observed modulus (at one temperature) from expected simple inclusion behavior. Similar procedures are applied to obtain representation of the dynamic properties of a third group of materials, designated HLP2. At high rubber content, these materials comprise a continuous rubbery phase with either simple or composite glassy inclusions. Discrepancies between calculated and observed values of E^* are attributed to higher-order and temperature-dependent interaction effects as well as to differences between actual and assumed phase morphology and composition.

It should be possible to apply the procedures developed in this report to estimate isochronal dynamic mechanical properties and composite phase structure of other systems of incompatible polymers of widely separated glass transition temperatures. It would be necessary to determine or

estimate at least one interaction parameter and the properties of the constituent polymers. Alternatively, the concepts developed in these reports should allow a fuller analysis of dynamic mechanical data on composite systems in terms of composition and phase morphology. Although the proposed model is a relatively simple one and cannot account for all details of dynamic behavior, it does provide a baseline against which the importance of factors otherwise ignored can be evaluated.

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References

1. R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 45 (1973).
2. R. A. Dickie, M. F. Cheung, and S. Newman, *J. Appl. Polym. Sci.*, **17**, 65 (1973).
3. E. H. Kerner, *Proc. Phys. Soc.*, **69B**, 808 (1956).
4. E. R. Wagner and L. M. Robeson, *Rubber Chem. Technol.*, **43**, 1129 (1970).
5. G. Cigna, *J. Appl. Polym. Sci.*, **14**, 1781 (1970).
6. L. Nielsen, *J. Appl. Phys.*, **41**, 4626 (1970).
7. T. B. Lewis and L. Nielsen, *J. Appl. Polym. Sci.*, **14**, 1448 (1970).
8. D. H. Napper, *J. Polym. Sci. A1*, **9**, 2089 (1971).
9. M. R. Grancio and D. J. Williams, *J. Polym. Sci. A1*, **8**, 2617 (1970); P. Keusch and D. J. Williams, *Polymer Preprints*, **12**, 464 (1971).
10. H. Keskkula, S. G. Turley, and R. F. Boyer, *J. Appl. Polym. Sci.*, **15**, 351 (1971).

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