Effect of Filler on Rheologic and Thermodynamic Characteristics of Binary Polymeric Mixture Melts

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SYNOPSIS

Rheologic, thermodynamic, and mechanical loss tangent properties of a binary polymeric mixture were studied. The system was a mixture of poly(vinyl acetate) (PVA) with ethylene-vinyl acetate copolymer (EVC) with varying concentrations of the polymer components and filler. A correlation between the above characteristics of the PVA/EVC two-phase mixture was found. This mixture was thermodynamically unstable (positive values of the interaction parameter, χ) practically over the entire range of compositions at temperatures of rheologic studies. The presence of a disperse filler raised the thermodynamic stability, that is, parameter χ decreased. Reversal of the sign of the temperature dependence of χ of a mixture with increasing concentration of filler was found. The variations of viscosity with the composition, temperature, and shear for the PVA/EVC mixture are ascribed to different levels of heterogeneity occurring in the process of the shear straining in the working unit of the rheometer. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Some of us had earlier [see e.g.,[1-3] ascertained an interrelation between viscoelastic (rheologic) properties of polymeric mixtures and the thermodynamic state of the system, determined in the same temperature range. The interrelationship manifests itself in that a positive or zero departure of the viscosity–composition relationship from the logarithmic additivity rule corresponds to the thermodynamic stability concentration region, while a negative departure from the additivity corresponds to the thermodynamic instability region. At the same time some authors[4-6] who investigated the effect of fillers of varying natures on the thermodynamic stability of two-phase polymer–polymer systems, found both an increase and a decrease of the thermodynamic stability of the systems in the presence of fillers. They ascribed the complex dependence of the thermodynamic interaction parameter on the mixture composition to a selective adsorption of one of the mixture components on the filler surface. The behavior of filled polymer–polymer systems at their

flow has not been studied so far from this standpoint. A change in the thermodynamic state under the effect of a disperse filler with varying composition of the polymeric mixture and filler concentration should also affect the rheologic properties in view of the interrelationship between these parameters.[1-3]

An investigation into the rheologic and thermodynamic (thermodynamic interaction parameter, χ_{23}) properties of a binary polymer mixture was conducted by way of example of a mixture of polyvinyl acetate with ethylene-vinyl acetate copolymer with varying concentrations of the polymeric components and disperse filler. The temperature dependence of the tangent of mechanical loss angle was studied as well to judge the phase state of the compositions.

EXPERIMENTAL

Selected as the objects of investigation were commercial polyvinyl acetate (PVA), whose viscosity-average molecular weight $\bar{M}_\eta = 1.74 \cdot 10^5$ was determined from the Mark–Houwink equation (η) $= = 1.74 \cdot 10^{-5} \cdot M^{0.7}$ (m^3/kg) [$(\eta) = 0.081$ m^3/kg, PVA solution in acetone at 20°C],[7] and ethylene-

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vinyl acetate copolymer (EVC) Levapren 45 (Bayer, with rated 45% content of vinyl acetate) having $\bar{M}_n$ = 3.77·10^4, $\bar{M}_w$ = 2.56·10^5, M_w/M_n = 5.16.[8]

PVA/EVC mixtures of compositions (by mass) 1/9, 3/7, 5/5, 7/3, and 9/1 were prepared by mixing the components in a rotary-plunger-type micromixer (minimum charge, 4·10^{-3} kg) at a temperature of 403 K. The mixing lasted 30 s on the average. Filled PVA, EVC, and EVC/PVA 5/5 and 1/9 mixtures were prepared in the same manner. Used as the filler was aerosil with a specific surface of 300·10^3 $m^2/$ kg. The filler contents were of 1, 2.5, and 10% (mass). For rheologic measurements, 3.2-cm diameter, 0.07-cm thick disks were pressed of the mixtures and of EVC and PVA on a hydraulic press. The disks were also used to cut the plates for measuring the tangent of mechanical loss angle.

The shear viscosity and the first normal stress difference of EVC, PVA, and their mixtures with and without filler were measured on a PIRSP-03 rheometer[9] with a cone-plane working unit. The shear rate was calculated from the equation:

$$\dot{\gamma} = 6.28n/\tan \alpha,$$

where n is the cone rotation frequency and α the cone angle.

The shear stress τ and the first difference of normal stresses σ were calculated from the equations:

$$\tau = 3M/2\pi R^3,$$

$$\sigma = 2F/\pi R^2,$$

where M is the torque, F the normal force, and R the cone radius. A cone with R = 0.02 m and α = 0.035 rad was used.

Parameters of the thermodynamic interaction between polymeric components of the mixture, X_{23}, were estimated by inverse gas chromatography (details of the procedure can be found in ref. 6)[9]

Temperature dependences of the tangent of mechanical loss angle, $\tan \delta = f(T)$, were obtained on a dynamic spectrometer (10) at a forced sine-wave oscillation frequency of 100 Hz within a temperature range of 223–348 K.

RESULTS AND DISCUSSION

Thermodynamic Interaction Parameter

The concentration dependence of the parameter X_{23} at various temperatures is shown in Figure 1 (solid
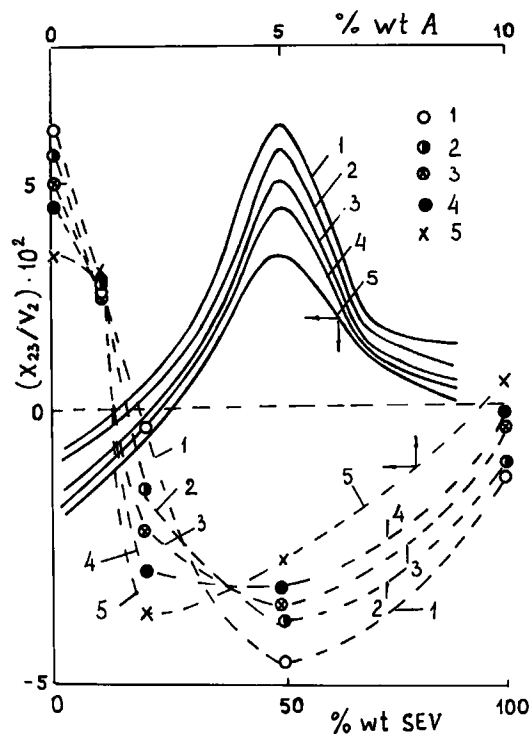

Figure 1 Thermodynamic interaction parameter X_{23} in PVA/EVC mixture as a function of composition (solid lines) and in PVA/EVC = 5/5 mixture as a function of aerosil mass fraction (dashed lines) at various temperatures, K: 392 (1); 400 (2); 408 (3); 417 (4); 425 (5).

lines), where it can be seen that within a temperature range of 392–425 K, the PVA/EVC mixture is thermodynamically unstable ($X_{23} > 0$) practically over the entire range of compositions, except for PVA/EVC = 9/1 (small negative X_{23}). As the temperature increases, the system becomes less unstable, since positive X_{23} decreases in the absolute value. The same figure shows the dependence of the parameter X_{23} of the PVA/EVC = 5/5 mixture on the aerosil concentration in the same temperature range (dashed lines). These data evidence that the presence of the disperse filler in the polymeric mixture shifts it into the region of a stable thermodynamic state, beginning from an aerosil concentration of 2%. As noted previously, such an effect of a disperse filler on the thermodynamic stability of binary polymeric mixtures has been demonstrated.[4-6] A new effect, found in our study, is reversal of the sign of the temperature dependence of X_{23} of a filled mixture with increasing concentration of a disperse filler. As is well seen from the presented figure, beginning from an aerosil concentration of 5%, X_{23} rises with the temperature. Such a result appears to be caused by formation of a coagulation structure of the filler.

It is interesting to note that extrapolation of the concentration dependence of the parameter X_{23} toward higher (over 10%) aerosil concentrations (Fig. 1) leads to positive X_{23} values. At any case, $X_{23} > 0$ already at a filler concentration of 10% and a temperature of 425 K; that is, under these conditions a filled polymeric mixture again becomes thermodynamically unstable.

Thus, the addition of a filler to a binary polymeric mixture reduces the parameter X_{23}, that is, increases the thermodynamic stability of the system. In a certain region of the filler concentrations the parameter acquires a negative value. This kind of effect had been studied in detail earlier[4-6] and was attributed to a change in the conditions of interaction of mixture components in the boundary layer because of a selective[b] adsorption of one of them and to a redistribution of components between the boundary layer and the bulk of the matrix, not affected by the filler surface action. The parameter X_{23} of the matrix is known to depend on the mixture composition. Increasing the filler content to concentrations at which it forms a continuous coagulation structure can be assumed to result in a progressively greater depletion of the matrix, predominantly in the component interacting with the surface. According to concepts of the effect of the filler on phase equilibriums in binary polymeric systems,[11] a great change in the composition is tantamount to the proceeding of the phase separation process, that, however, is in this case initiated not by a change of the temperature near the phase equilibrium curve, but by adsorbing action of the filler. It follows that the latter acts as a phase-forming agent. A decline in the thermodynamic stability of the system, that is, an increase of the parameter X_{23} corresponds to this region of filler contents.[11]

We judged the concentration region of formation of a structural network of aerosil in PVA, EVC, and their mixtures, proceeding from rheologic properties of filled systems (see following).

Temperature Dependence of the Tangent of Mechanical Loss Angle

Existence of one or two vitrification temperatures is one of the symptoms of homogeneity or heterogeneity (two-phaseness) of polymeric mixtures. Data on vitrification temperatures for investigated

mixtures from results of dynamic mechanical tests are presented. Figure 2 shows temperature dependences of tan δ for PVA, EVC, and their mixtures as well as for a filled PVA/EVC = 5/5 mixture (aerosil content, 1 and 5%). As can be seen, the PVA/EVC mixture is characterized by two maxima of the mechanical loss, corresponding to vitrification of the components, the tan δ maxima being closer to each other and the vitrification regions being extended as compared with pure PVA and EVC. Simultaneous extension of the vitrification temperature range, increase of the lower T_g and decrease of the higher T_g of components of a two-phase polymeric mixture, as this occurs in our case, indicates that the system is in a state very close to compatibility of components,[12] that is, this pair of components (PVA and EVC) can be classed with "partly compatible" polymers,[12-16] which is also substantiated by the vitrification temperature dependence on the mixture composition [Fig. 2(b)].

Some features are, however, observed as the concentration of components is varied. Attention is drawn by a strongly smeared vitrification region, a small height of the peak of the EVC component right up to its high contents in the mixture ($\leq 60\%$), and a full absence of the EVC vitrification region in the mixture of a composition PVA/EVC = 9/1. The latter experimental fact might serve as the grounds for assuming the mixture to be homogeneous (one vitrification peak), the more so because the thermodynamic interaction parameter X_{23} in this composition region is negative (Fig. 1) and the resolving power of the dynamic mechanical method makes it possible to estimate the vitrification region at such contents of a component in fully incompatible mixtures. Such a conclusion, however, would be premature. The point is that identification of a component whose content in the mixture is lower is difficult when the two components are close to compatibility and, accordingly, a shift of vitrification temperatures and broadening of the vitrification temperature range are observed. There exist sufficient grounds to believe that mixing of shorter macromolecules of the two components in the interphase region occurs in such mixtures, because the thermodynamic force of compatibility of such macromolecules is the greatest. The composition and length of interphase layers vary over broad ranges,[17,18] with the result that their vitrification occurs in a broad temperature range and presents as broadening of the maxima of tan δ of one or both components and growth of the background of loss between their vitrification temperatures. Therefore at low contents of one the of components, when the

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[b] In our case there exists a predominant interaction (hydrogen bond) between hydrogen of hydroxyl groups on the aerosil surface and unsaturated carbonyl oxygen of the PVA component, since its concentration in the copolymer is about half that in PVA.
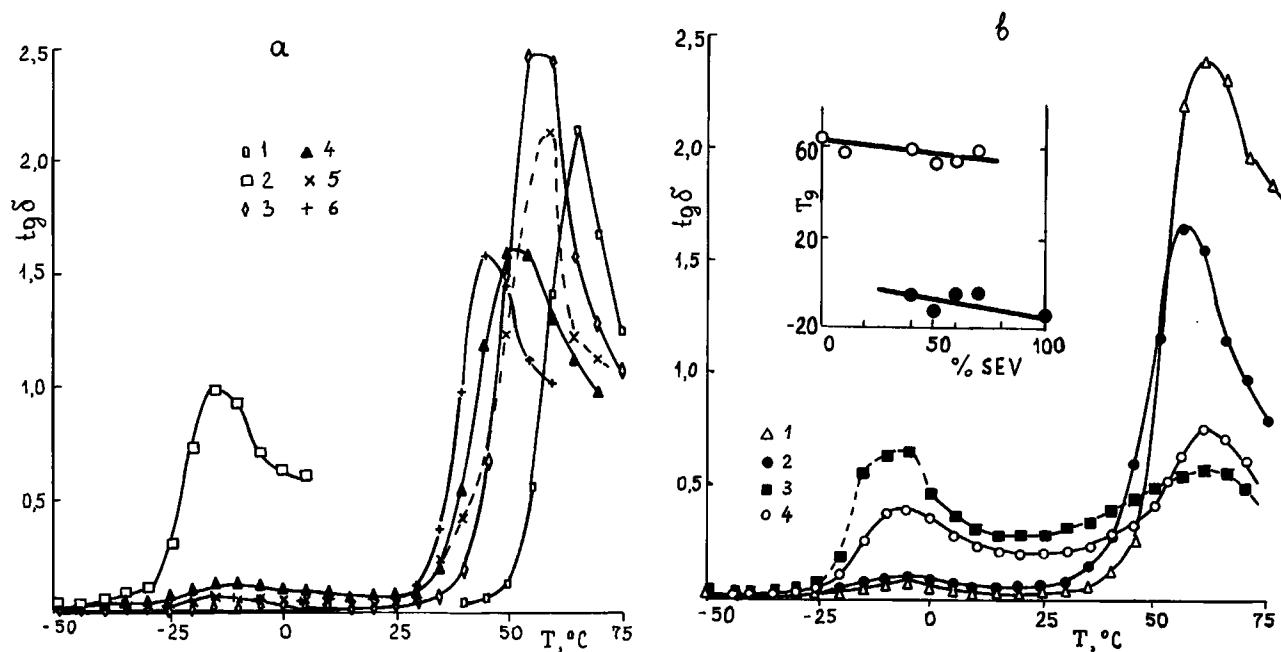
Figure 2 Temperature dependence of tan δ for PVA, EVC, and PVA/EVC mixtures of various compositions as well as for PVA/EVC = 5/5 mixture at various aerosil mass fractions (a, b). Concentration dependence of vitrification temperatures for the same mixtures (b). Explanations are given in text. (a) 1—PVA; 2—EVC; 3—PVA/EVC = 9/1; 4—PVA/EVC = 5/5; 5—PVA/EVC = 5/5 + 1%A; 6—PVA/EVC = 5/% + 5%A. (b) 1—PVA/EVC = 6/4; 2—PVA/EVC = 4/6; 3,4—PVA/EVC = 3/7.
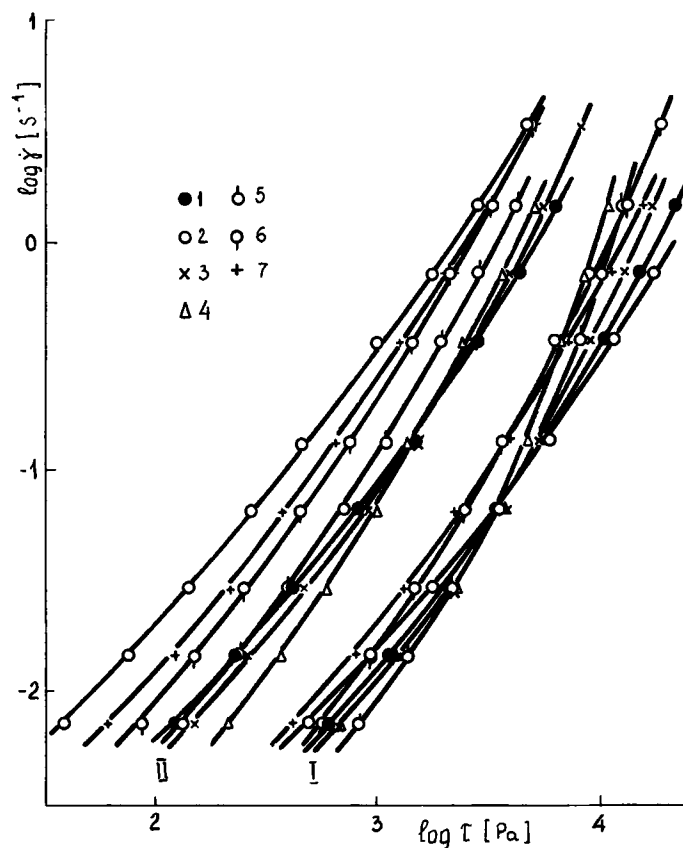

Figure 3 Stress as a function of shear rate for PVA, EVC, and their mixtures at various concentrations and temperatures: EVC (1); PVA (2); PVA/EVC = 1/9 (3); PVA/EVC = 3/7 (4); PVA/EVC = 5/5 (5); PVA/EVC = 7/3 (6); PVA/EVC = 9/1 (7). Temperatures, K: 393 (I); 433 (II).

proportion of interphase layers is comparable with the concentration, it is difficult to identify the process of vitrification of such a component.

The method of preparation of polymeric mixtures is known to affect substantially their structure and properties. One of the samples [Curve 3, Fig. 2(B)] was subjected to a prolonged annealing (60 min) at 433 K and then to a rapid cooling with the aim of freezing the structure, differing from that obtained with the previously described preparation method. It turned out that the EVC maximum height increased, while the PVA one decreased and, moreover, the mechanical loss background rose. Vitrification temperatures of components did not change, but the vitrification regions broadened [Fig. 2(a)]. These facts indicate that annealing improves interaction between components, but this predominantly occurs at the interface. It should be noted that samples in the working unit of the rheometer in rheologic measurements were subjected to the same prolonged holding in a temperature region of 393–433 K, that is, it is reasonable to assume that phase structures frozen for measuring the temperature dependence of tan δ and those in the measurement of rheologic characteristics are identical.

Presence of the disperse filler in the mixture in an amount sufficient for formation of its structural network (5%) shifts the region of the main relaxational transition of the PVA component toward lower temperatures [the shift, as compared with individual PVA, amounts to $\sim$ 20°, Fig. 2(a)]. This correlates well with the variation of the parameter

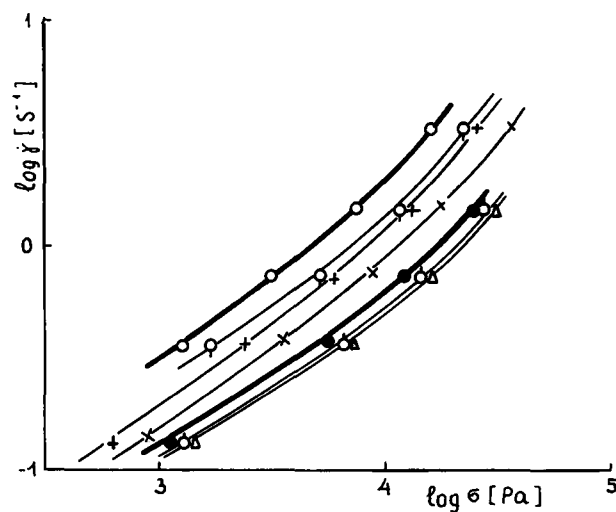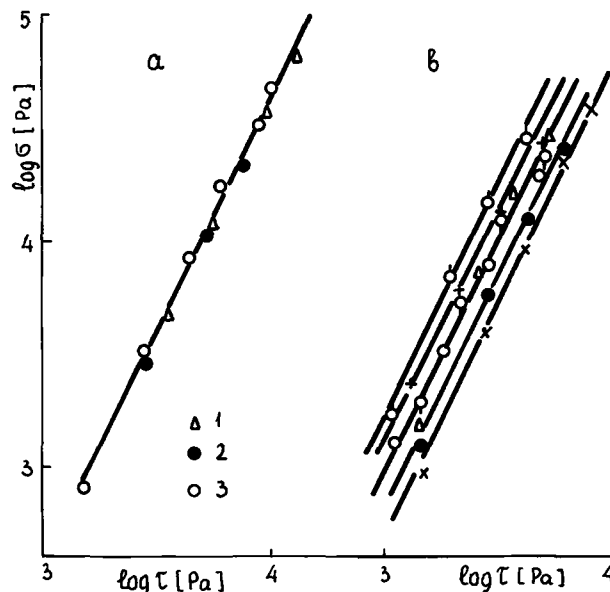**Figure 5** Normal stresses as a function of shear stress for PVA/EVC = = 1/9 mixture at various temperatures (a) and for PVA, EVC, and their mixtures at 433 K (b). Temperatures, K: 393 (1); 413 (2); 433 (3). Designations for Figure 5(b) are the same as for Figure 3.

X_{23} at filling (Fig. 1), that is, under such conditions the thermodynamic parameters of mixing shift toward compatability of PVA and EVC.

Rheologic Properties

Let us now consider flow characteristics of the two-phase PVA/EVC mixture at absence and presence of a disperse filler. Dependences of shear stresses and first difference of normal stresses on the shear rate at temperatures of 393, 413, and 433 K for PVA, EVC, and their mixtures were obtained; their examples are shown in Figures 3 and 4. Figure 5(a) shows, as an example, σ as a function of τ at various temperatures for a PVA/EVC = 1/9 mixture. As can be seen, the relation between these rheologic characteristics is temperature independent. The quadratic relation between σ and τ, following from equations $\tau = \eta_0 \dot{\gamma}$ and $\sigma = \xi_0 \dot{\gamma}^2$, and characteristic for a linear region of the rheologic behavior, that is, at $\dot{\gamma} \to 0$ (or $\tau \to 0$), is also retained at finite $\dot{\gamma}$ or τ values. A temperature-independent correlation between σ and τ takes place both for PVA and for EVC as well as for their mixtures at a constant composition.

At the same time no common temperature–concentration dependence between normal and tangential stresses is observed. This is well seen from Figure

Figure 4 Normal stresses as a function of shear rate for PVA, EVC, and their mixtures at 433 K. Designations are the same as in Figure 3.

5(b), showing the $\sigma - \tau$ dependence for all the studied mixtures at a constant temperature (433 K). Rheologic studies of a number of polymeric mixtures[19] demonstrated the occurrence of various types of relations between normal and tangential stresses, depending on whether the system is homogenous or heterogenous. If the polymeric mixture is truly compatible at the molecular level and homogenous, then the relation between σ and τ is independent of the mixture composition. This is characteristic for mixtures of polymers of one and the same homologous series (e.g., for mixtures of LDPE of different molecular weights.[19] It should be recalled that the shear stress can be interpreted as the measure of the dissipative energy and σ as the measure of the energy stored by macromolecules in the process of the shear strain; and therefore, as long as the molecular structure remains unchanged, the ra-
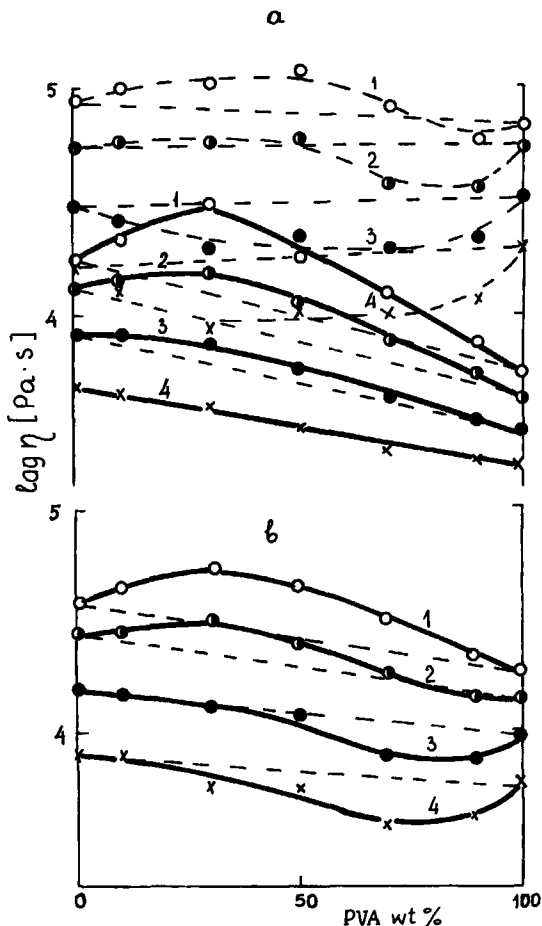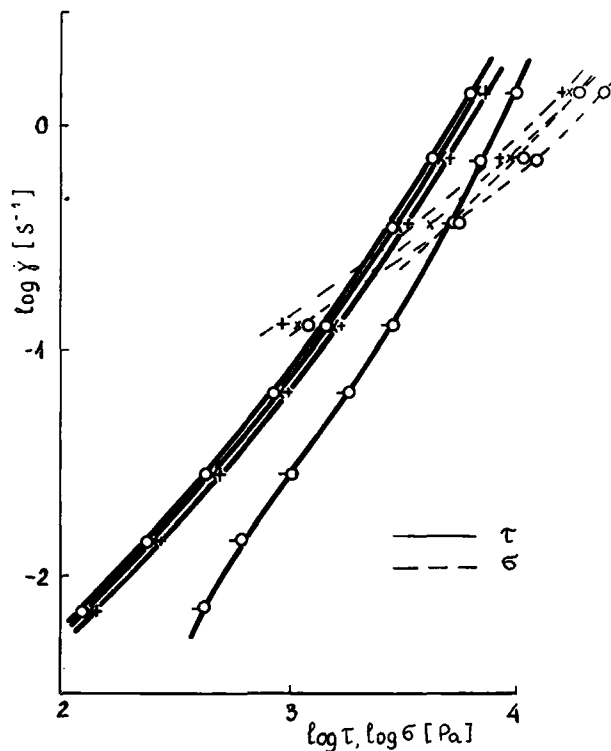

Figure 7 Tangential and normal stresses as functions of shear rate for PVA at 433 K and various aerosil mass fractions, %: 0 (1); 1 (2); 2 (3); 5 (4); 10 (5).

tio of the energy stored and the energy dissipated in the process of the shear strain should not depend on the composition. The dependence of the relation between σ and τ for the PVA/EVC mixture on its composition serves as an indirect proof of existence of various types of the disperse state, determined by the mixture composition and straining conditions, at various concentrations. This is characteristic for heterogenous (two-phase) polymeric mixtures, and therefore it can be believed that the PVA/EVC mixture is two-phase at the temperatures of rheologic studies, the existing heterogeneity level being transferred also to the solid state, which can be judged from the results of measurements of the temperature dependence of the tangent of mechanical loss angle. That the studied mixture is two-phase at temperatures of 393–433 K is also directly evidenced by positive values of the thermodynamic interaction parameter. It follows that a well-defined correlation between the results of measurements of mechanical, rheologic, and thermodynamic characteristics takes place.

Figure 6 shows the viscosity as a function of the mixture composition at various shear rates and at temperatures of 393 (dashed lines), 433 [solid lines, Fig. 6(a)], and 413 K [Fig. 6(b)]. They illustrate

Figure 6 Variation of viscosity with composition for PVA/EVC mixture at various temperatures and shear rates. Temperatures, K: 393 (- - -, a); 433 (———, a); 413 (b). Shear rates, s^{-1}: 0.0073 (1); 0.066 (2); 0.37 (3); 1.46 (4).

a complex rheologic behavior of the PVA/EVC mixture with varying composition, temperature, and straining conditions. Thus, a positive departure of the viscosity from the logarithmic additivity law is observed at 433 K, the degree of the departure declining with increasing shear rate. At 393 K, S-shaped dependences of the viscosity on the composition take place at low $\dot{\gamma}$, while a negative departure of the viscosity from the logarithmic additivity rules is observed at high shear rates. When the composition of the mixture is changed, its viscosity decreases and becomes less than that for the starting components. At 413 K an intermediate case is observed.

Fundamentally important for the insight into such a complex transformation of the concentration dependence of viscosity with varying temperature and strain rate is the information on the thermodynamic state of the mixture composition at the stage of mixture preparation and measurement of rheologic characteristics in a certain temperature–concentration range. If polymers are mixed at temperatures at which they are thermodynamically

compatible, then, depending on the mixture preparation method (through a common solvent or in mixing devices), experimental viscosity values should either exceed those calculated with the logarithmic additivity law or follow the law at mixing at the molecular level.[3,20] If the system has been mixed not to the end, that is, to the molecular level, and is heterogenous (depending on the use in the mixing device of such variables as temperature, mixing time, speed-and-force parameters as well as on the relation between viscosities of the polymers mixed), then the system will be in a nonequilibrium state and its properties will be time independent. Therefore, different signs of departure of viscosity of the composition from additive values are possible in this case. Thus, Chung and Han[19] reported an example of a specific rheologic behavior of the PVDF/PMMA mixture, that is compatible (from results of measurements of the tangent of mechanical loss angle). For such a mixture the viscosity at 503 K was below the additive values and the values for the starting components even at low shear rates. Such a behavior is similar to that characteristic of
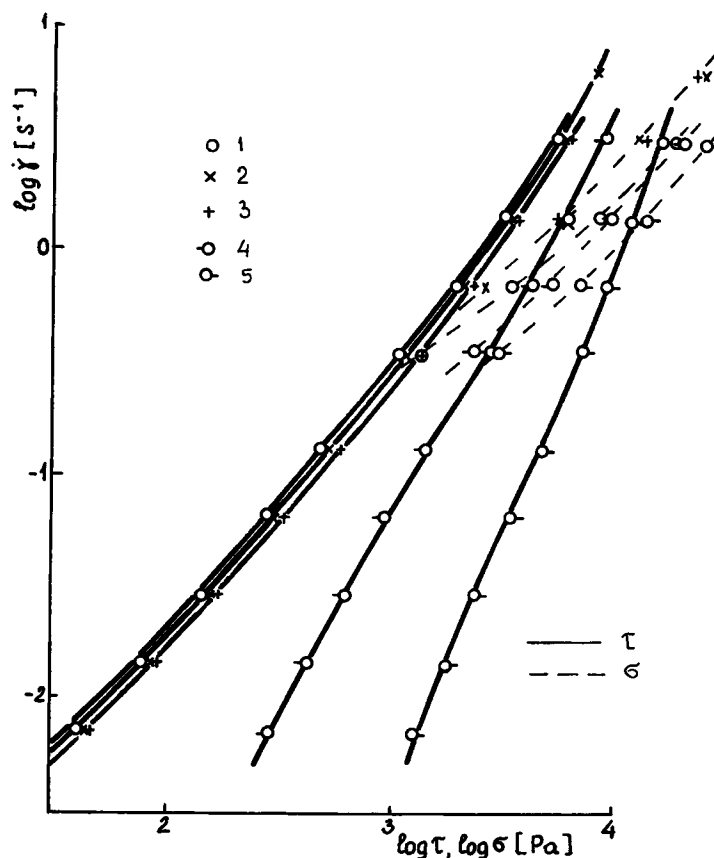

Figure 8 Tangential and normal stresses as functions of shear rate for EVC at 433 K and various aerosil mass fractions. Designations are the same as for Figure 7.
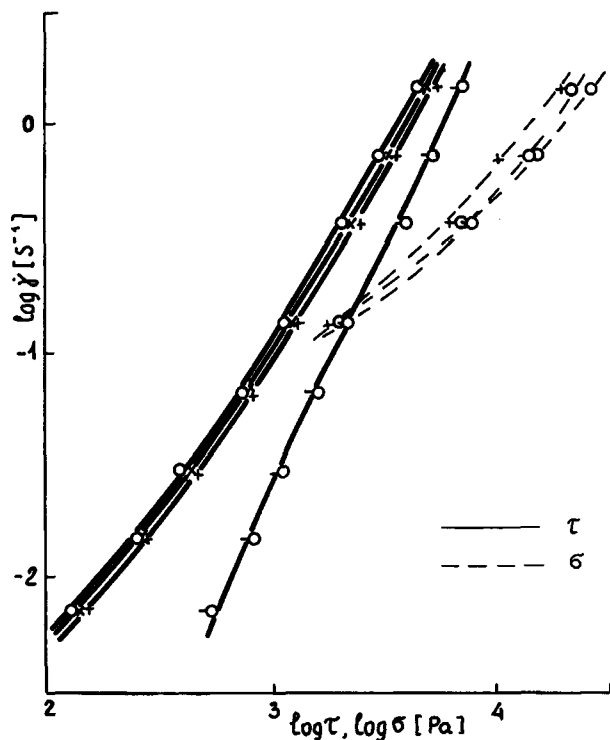
Figure 9 Tangential and normal stresses as functions of shear rate for PVA/EVC = 5/5 mixture at 433 K and various aerosil mass fractions. Designations are the same as for Figure 7.

incompatible polymeric mixtures at high $\dot{\gamma}$.[21] It follows that mechanisms of viscosity reduction for compatible and incompatible mixtures are different. Chung and Han suggested that a mixture of polymers with different chemical structures, although mixed with each other at the molecular level, can have entanglements among macromolecules, which exert at the shear strain a lower resistance (or friction force) than do molecular entanglements in the starting polymers. This was subsequently substantiated by analysis of the entanglement density, based on the viscoelasticity of the PVDF/PMMA mixture.[22] Yet, in our opinion, it cannot be ruled out that such a behavior of the PVDF/PMMA mixture is related either to a nonequilibrium state of the system or to its two-phase state at the viscosity measurement temperature.

Mixture systems prepared at temperatures at which they are in a two-phase state (or in the compatibility region, but the viscosity is measured in the temperature–concentration region of a two-phase state) can also exhibit negative or positive departures of the viscosity–composition dependence from the additivity law, depending on the state of dispersion, size of disperse phase particles,[19,21,23] and nature of interaction at the interface; S-shaped vis-

cosity vs. composition curves can also occur in this case.

Therefore, the features of viscosity variation with the composition, temperature, and conditions of straining of the two-phase PVA/EVC mixture (Fig. 6) can be ascribed solely to different heterogeneity levels occurring not only at the mixture preparation stage, but also in the course of the shear straining in the rheometer's working unit. Positive departures of the viscosity of the studied mixture appear to stem from the state of dispersion, for which a strong interaction between dispersion components at the interface is characteristic. In the region of high shear rates, as before, there exists a distinct interrelation between rheologic and thermodynamic characteristics,[1-3] namely: negative departures of viscosity from additive values correspond to positive values of the thermodynamic interaction parameter X_{23}.

Let us consider now the rheologic data for a filled PVA/EVC mixture. Figures 7–10 show the $\tau(\dot{\gamma})$ and $\sigma(\dot{\gamma})$ dependences (solid and dashed lines, respectively) at various aerosil contents at 433 K for EVC, PVA, and PVA/ECV = 5/5 and 9/1 mixtures. As can be seen, the form of the $\tau(\dot{\gamma})$ dependence starts changing at a 5% aerosil content both in the starting components and in their mixtures, which is a consequence of formation of a structural network of the filler at this concentration. It is important to note here that the structure-forming capacity of aerosil rises in a series EVC → PVA/EVC = 5/5 → PVA/EVC = 9/1 → PVA. If the structure-forming capacity of aerosil is defined as the τ/τ_0 ratio (where τ is the shear stress for a filled, and τ_0, for an unfilled system), taken at $\dot{\gamma}$ = const, then, at $\dot{\gamma}$ = 7.3·10⁻³ s⁻², τ/τ_0 = 3.39 for EVC; 4.36 for PVA/EVC = 5/5; 5.75 for PVA/EVC = 9/1; and 7.08 for PVA. It follows that a stronger coagulation structural network of aerosil particles forms when the PVA melt (as compared with the EVC melt) is a continuous medium, and therefore a stronger particle–medium adhesion contact appears to take place in the filled PVA/aerosil system. This in turn causes the selectivity of aerosil–medium interaction in filled PVA/EVC mixtures. Hence, it can be assumed that addition to the PVA/EVC mixture of aerosil in amounts sufficient for exhibition of its structure-forming capability (in our case, 5%) should also affect thermodynamic parameters of the system (Fig. 1).

CONCLUSIONS

Thus, the conducted studies ascertained a distinct correlation between the results of measurements of
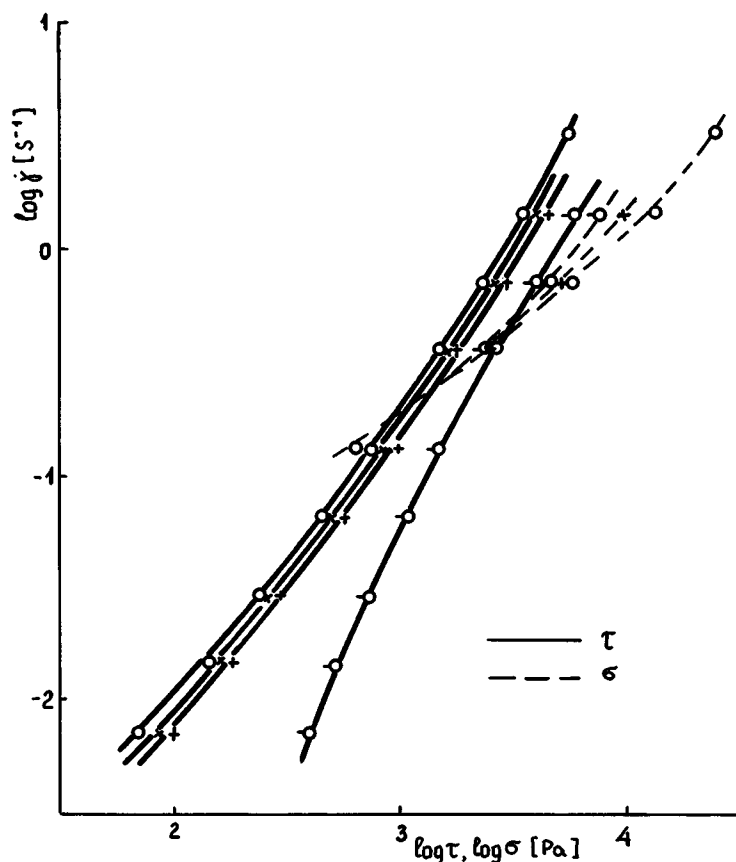
Figure 10   Tangential and normal stresses as functions of shear rate for PVA/EVC = 9/
1 mixture at 433 K and various aerosil mass fractions. Designations are the same as for
Figure 7.

mechanical, thermodynamic, and rheologic char-
acteristics of a two-phase polyvinyl acetate–ethyl-
ene-vinyl acetate copolymer mixture. Such a mixture
is thermodynamically unstable practically over the
entire composition range in the region of rheologic
measurement temperature. Presence of a disperse
filler in a polymeric mixture raises its thermody-
namic stability. The variations of viscosity with the
composition, temperature, and straining conditions,
characteristic for the studied mixture, are ascribed
to various levels of heterogeneity, occurring in the
course of shear straining in the rheometer's working
unit and to a strong interaction between dispersion
components at the interface. The interrelation be-
tween rheologic and thermodynamic characteristics,
established earlier, takes place in the region of high
shear rates.

REFERENCES

1. Yu. S. Lipatov, V. F. Shumsky, E. V. Lebedev, and
   A. E. Nesterov, *Dokl. AN SSSR,* **244,** 148–151 (1979).

2. Yu. S. Lipatov, A. E. Nesterov, and V. F. Shumsky,
   et al. *Eur. Polym. J.,* **18,** 981–986 (1982).

3. V. F. Shumsky, *Physico-Chemistry of Multicomponent
   Polymeric Systems,* Vol. 2, Chap. 9, Naukova Dumka,
   Kiev, 1986, pp. 279–317.

4. Yu. S. Lipatov, V. V. Shifrin, and O. I. Vasilenko,
   Vysokomolek. Soed., **29,** 1400–1405 (1987).

5. V. V. Shifrin, Yu. S. Lipatov, and O. I. Vasilenko,
   Dokl. AN USSR, Ser. B, 56–59 (1987).

6. V. V. Shifrin, Yu. S. Lipatov, and A. E. Nesterov,
   Vysokomolek. Soed., Ser. A., **27,** 369–373 (1985).

7. S. R. Rafikov, S. A. Pavlova, I. I. Tverdokhlebova et
   al., in *Methods for Determining Molecular Weights and
   Polydispersity of Molecular Compounds,* AN SSSR,
   Moscow, 1963.

8. J. S. Walsh, S. T. Higgins, and A. Rostani, *Macro-
   molecules,* **16,** 388–391 (1983).

9. G. V. Vinogradov, A. Ya. Malkin, E. P. Plotnikova et
   al. *Vysokomolek. Soed., Ser. A,* **20,** 226–230 (1978).

10. V. F. Rosovitsky and V. V. Shifrin, *Physical Methods
    for Study of Polymers,* Naukova Dumka, Kiev, 1981,
    pp. 85–93.

11. Yu. S. Lipatov, *Colloidal Chemistry of Polymers,* Nau-
    kova Dumka, Kiev, 1984.

12. W. J. Macknight, F. E. Karasz, and J. R. Fried, *Poly-*

mer Blends, Vol. 1, Chap. 5, Mir, Moscow, 1981, pp. 219–281.

13. A. R. Shultz and B. M. Gendron, *J. Macromol. Sci. Chem.,* **A8,** 175–189 (1974).

14. C. Elmgvist and J. Svanson, *Eur. Polym. J.,* **12,** 559–561 (1976).

15. R. Buchdahl and L. E. Nielsen, *J. Polym. Sci.,* **15,** 1–8 (1955).

16. V. F. Rosovitsky and Yu. S. Lipatov, *Physico-Chemistry of Multicomponent Polymeric Systems,* Vol. 2, Chap. 7, Naukova Dumka, Kiev, 1986, pp. 229–254.

17. E. V. Lebedev, Yu. S. Lipatov, and V. P. Privalko, *Vysokomolek. Soed., Ser. A,* **17,** 171–175 (1975).

18. J. Letz, *J. Polym. Sci., Phys. Ed.,* **7,** 1987–1994 (1969).

19. H. K. Chung and C. D. Han, *J. Appl. Polym. Sci.,* **29,** 2205–2209 (1984).

20. L. A. Utracki, *Polym. Eng. Sci.,* **23,** 602–609 (1983).

21. C. D. Han, *Rheology in Polymer Processing,* Khimiya, Moscow, 1979.

22. S. Wu, *J. Polym. Sci., Polym. Phys. Ed.,* **25,** 557–566 (1987).

23. H. P. Schreiber and A. Olguin, *Polym. Eng. Sci.,* **23,** 129–134 (1983).