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The Anomalies of the Increase in Viscosity in Binary Polymer Systems

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The literature data on the anomalies in the rheological properties of binary polymer systems, expressed as the increase in their viscosity characteristics, are examined and surveyed in the present review. The known hypotheses and theories of the anomalous changes in viscosity are analysed and an attempt is made to relate the concentration and temperature variations of the viscosities of binary polymer blends to their phase organisation.
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I. INTRODUCTION

The deviation of the characteristic features of the flow of solutions and melts from the behaviour of Newtonian liquids has come to be called an anomaly in viscosity.[1] However, according to Frenkel' [2] and Bartenev,[3] the natural manifestation in polymer systems of the strong intermolecular interaction, which determines the dependence of viscosity η on the stress τ and the rate of shear $\dot{\gamma}$, should hardly be classified as an anomalous phenomenon.

In the present review by "anomalies" we understand experimental manifestations of the viscosity-dependent properties which cannot be explained on the basis of the generally accepted theories of the flow of polymers and their blends.[1-13] From this point of view, the abrupt decrease or increase in the viscosity of polymers in the presence of low-molecular-weight, oligomeric, and polymeric additives should be classified as anomalies in the first place (see, for example, Refs.14-19). Cases where the viscosity of the mixture can prove to be lower or higher than the viscosity of the least or most viscous component of the system are of special interest.

The anomalous decrease in the viscosity of binary polymer systems† (BPS) has been discussed in detail in recent years in the review literature,[7,8,12,13] whereas virtually no attention has been devoted to the anomalous increase in viscosity (AIV). The illogicality of the phenomenon itself, namely the increase in the viscosity of the mixture after the introduction of a less viscous component,‡ and the absence of clear grounds for its theoretical justification have aroused a certain scepticism among investigators.

This review gives a systematic account of the experimental and theoretical results concerning the anomalous increase in the viscosity characteristics of BPS.

II. EXPERIMENTAL OBSERVATIONS OF THE ANOMALOUS INCREASE IN VISCOSITY

Publications concerning special studies of the AIV in BPS began to appear comparatively recently[14,15,17] although experimental observations of this phenomenon date back to studies as early as the 1960s.[16,18,20] The anomalies associated with the increase in the viscosity of the mixture compared with that of the highly viscous component itself are known not only for polymeric but also for low-molecular-weight organic[24,25] and metallic[26,27] liquids.

1. Mixtures of Low-molecular-weight Liquids

The increase in shear viscosity in a definite concentration range in a water-benzene mixture was observed as early as the beginning of the century. The dynamic properties[28-31] and anomalies in the viscosities[24,25] of a whole series of binary liquids systems have now been investigated. We may note two factors. Firstly, the increase in the viscosity of low-molecular-weight mixtures has usually been observed within a comparatively narrow range of compositions at temperatures close to the critical point. Secondly, the specific viscosity increments

$$\Delta\eta = \eta_m - \eta_v, \quad (1)$$

where η_m is the viscosity of the mixture and η_v the viscosity of the most viscous component, quoted in different studies, frequently do not agree since $\Delta\eta$ depends greatly on the experimental conditions.[30,31]

2. Mixtures of Metallic Liquids

The characteristic features of the dynamic properties of melts of metallic mixtures have been analysed in detail.[26] The extrema observed[26,27,32-36] on the viscosity isotherms for iron-nickel melts

† Unless specially stipulated, here and henceforth the binary polymer systems are understood as polymer-solvent mixtures, where the solvent can be a low-molecular-weight, oligomeric, or a high-molecular-weight compound.

‡ In terms of formal characteristics (but by no means in terms of the essential physical features), the effect discussed is close to the antiplasticisation phenomenon: the increase in the modulus and strength of polymers after the introduction of small amounts of plasticisers into the latter[21]—a phenomenon which aroused vigorous discussion in its time.[22,23]

as well as the anomalous effects consisting in the fact that, on heating in the temperature range from 1400° to 1800 °C, the viscosity η initially diminishes steadily as the temperature rises and then increases abruptly within a comparatively narrow temperature range (at 1500–1550 °C or at 1700–1750 °C [27,36]) only to fall again on raising the temperature still further are of greatest interest. According to Baum,[26] the previous history of the melt not only influences the intensity of the extrema but also determines the very fact of their existence.

3. Polymeric Liquids

The anomalous increase in viscosity has been observed in BPS of different types: mixtures of polymers with low-molecular-weight liquids[18,37] or with oligomers[15,38] and in blends of high-molecular-weight components.[5–8,14,16,17,39–42] In the last case the AIV effect has been observed for blends of two elastomers,[14,16,17,41] two plastics,[39,40,42] a plastic–raw rubber blend,[7,8,12,41] and also for block copolymers.[43,44] An extremum in the dependence of the viscosity on composition has been discovered both for binary polymer melts and for their solutions in a common solvent.[12]

The range of compositions in which AIV can be manifested is unusually broad. An increase in viscosity has been observed at both low concentrations (0.05–3%) of any of the components added to the system[7,11,12,15] and in the range of average compositions.[6,8,14,39] The range of concentrations in which the anomaly is manifested in the viscosity increment can be very narrow (fractions per cent) [15,18] or fairly broad (tens per cent).[14,39] Viscosity isotherms with a single extremum are characteristic of some systems,[12,16,38,39] while others have isotherms with two extrema[8,11,40] and in some instances there may be several extrema.[8]

It is so far impossible to compare quantitatively the published data on the AIV even for isotypical systems, since in most studies the viscosity parameters of the BPS have been determined on apparatus of different types and have been expressed in terms of different characteristics (effective viscosity, initial Newtonian viscosity, Mooney viscosity, torsional moment on the plastograph roller, the melt index, etc.).[12,14–17,37–42]

Analysis of the published experimental data shows that the sign of the extremum on the concentration variations of the viscosity, its absolute magnitude, and its position on the "viscosity–composition" curve depend on the molecular characteristics of the components, the temperature of the test,§ the deformation conditions ($\dot{\gamma}$ and τ), the method of preparation of the specimens, etc. A change in the parameters enumerated can lead not only to a displacement of the positions of the extrema or to a change in their absolute magnitude but can actually result in a transformation of a minimum into a maximum and conversely.

As an example, Fig.1 presents thermograms of the viscosity characteristic F (the force required to drive a melt through a capillary) obtained for a mixture of natural rubber (NR) and polybutadiene (PB) over the entire range of compositions at different shear velocities.[17] In the range of $\dot{\gamma}$ from 0.3 to 3 s^{-1}, the usual deviation of the viscosity[3,4,7] from additive values is observed but at higher shear velocities anomalies appear on the curves (the anomalies are shown shaded in the figure). In the given experiment, the character of the variation of F with mixture composition changes several times as $\dot{\gamma}$ is varied by five orders of magnitude.

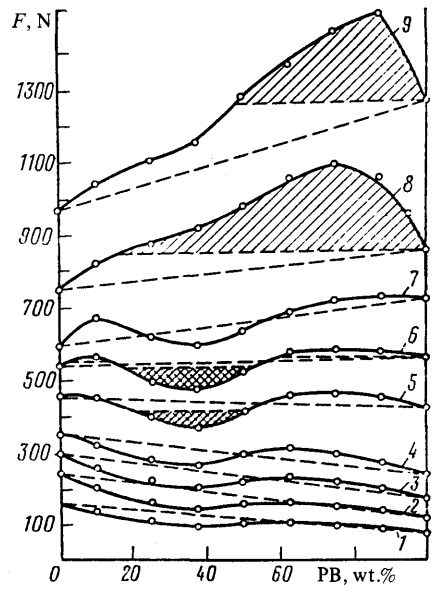


Figure 1. Dependence of the quantity F for the melt of a mixture of a natural rubber and PB on composition for different shear velocities ($\dot{\gamma}$, s^{-1}):[17] 1) 0.3; 2) 0.75; 3) 1.5; 4) 3.0; 5) 7.5; 6) 15; 7) 30; 8) 300; 9) 3000; T = 126 °C.

In the study quoted, it is emphasised that other measured viscosity parameters (for example, the Mooney viscosity at 100 °C and the twisting moment on the roller of the Brabender plastograph at 94 °C) do not exhibit significant anomalous deviations. Nevertheless, it follows from two investigations[14,16] that the AIV effect is not associated with any specific way of measuring viscosity.¶ Indeed, the viscosity maximum has been observed for the same mixture of NR and PB in a study[16] of the dependence of the parameter of the

§ In this case we are concerned not with the trivial influence of temperature, whose alteration can lead to fusion, devitrification, and the corresponding abrupt alteration of the properties of the system (such cases have been examined[45]), but with more complex mechanism of the effect of temperature on viscosity.

¶ Cases are known[6] where a change in the method of specifying the shear deformation or the design of the capillary in the rheological apparatus leads to the degeneration of the maximum to a minimum on the viscosity–concentration curve. As will be clear from the subsequent exposition, if the AIV is an objective property of a given system, then, regardless of the apparatus used, this effect can be observed by selecting the necessary experimental conditions for this purpose. Furthermore, the experimentally observed increase in viscosity can be a result of hydrodynamic flow effects determined by the design of the apparatus.

twisting moment on mixture composition. However, it is noteworthy that the experimental conditions in the study by Hess et al.[16] were different from those used by Folt and Smith.[17]

Using a capillary viscometer for the study of blends of polyethylene (HPPE) and polystyrene (PS), Han and Kim[14] observed, in particular, that, although at all the temperatures investigated (200°, 220°, and 240 °C) the viscosity thermograms have the form of curves with an extremum, nevertheless anomalies (in the sense adopted in the present review) are manifested at different temperatures and for different shear stresses in different ways.

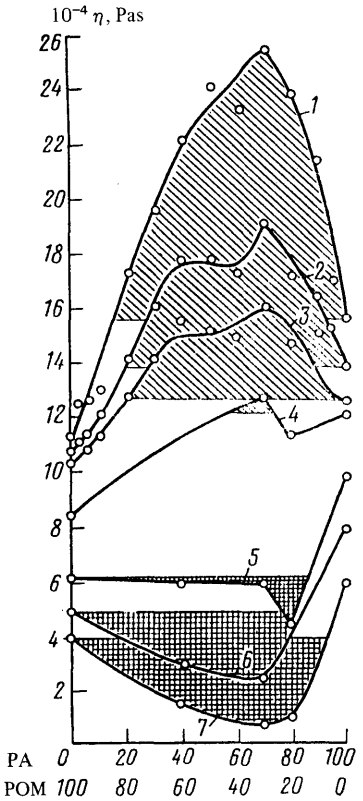


Figure 2. Dependence of the viscosities of POM–PA melts on composition at 190 °C and different shear stresses (10^4 τ, Pa):[47] 1) 1.27; 2) 3.93; 3) 5.44; 4) 6.30; 5) 12.59; 6) 19.25; 7) 31.62.

The influence of the shear stess on the AIV was also observed by Vinogradov and co-workers[39,40,46,47] in a study of the rheological properties of blends of polyoxymethylene (POM) and polyamide (PA) at 190 °C (Fig.2). With increase in τ from 0.6 to 3.5 × 10^4 Pa, Δη gradually diminishes in the range of compositions where a viscosity increment is manifested. Furthermore, after the attainment of a specific value of τ, the increase in η is replaced by its anomalous decrease, which progresses with increasing shear stress.

The examples presented show that the very fact of the anomalous variation of the viscosity of polymer blends compared with the viscosities of the components and the sign of this variation depend on the deformation conditions. The influence of the temperature of the test is just as complex. Apart from the study already mentioned,[14] this is indicated also by Lipatov's experimental data.[8] From the latter, it follows, in particular, that, when the composition of the polyethylene (HPPE)–polypropylene (PP) blend is altered, the viscosity of the melts, measured at 190–210 °C, passes twice through a maximum. An increase in the temperature of the test to 230–270 °C results in the disappearance of these maxima. In contrast to the case considered, in the cellulose acetobutyrate (CAB)–POM system (Ref.8, p.250) the AIV disappears on reducing the temperature and not on raising it.

In discussing the influence of temperature on the AIV, one should note several further unusual examples of an extremum in the variation of the viscosity.[7,12,13,16,18,21,41,42,45–50] A maximum has been observed[18] on the curve characterising the temperature variation of the viscosity of a solution of polystyrene in cyclohexane. This maximum can be recorded experimentally only when the temperature is varied in steps not greater than 0.2 K.

Data have been presented in a monograph[13] from which it follows that, after a monotonic decrease of the relative viscosity of an aqueous methylcellulose solution with increase in temperature, there is an abrupt increase in the range 50–55 °C.

It was shown in a recently published study[50] that η of a poly(vinyl chloride) (PVC)–trioxyethylene dimethacrylate mixture increases by a factor of two when the temperature is raised from 60° to 100 °C and then falls, reaching its initial value at 140 °C.

The maximum in the concentration variation of the effective activation energy for the viscous flow of BPS has been noted in several studies.[7,22,48,49]

Many investigators point out the role of the previous history of the system, which determines in many instances the character of the viscosity-dependent properties of BPS.[5–8,22,23,40,41,46] It has been specially emphasised[40] that, when POM is blended with PA in an alcoholic suspension (with subsequent removal of alcohol), there are two maxima on the "viscosity–composition" curve, but after the "dry blending" of the powders there is only maximum.

It has been shown[41] that a specimen prepared from PB–polyisoprene (PI) solutions is characterised by a viscosity maximum, which is converted into a minimum if the specimens are obtained by blending these raw rubbers on rollers.

The role of the previous history of the system as regards temperature has been noted.[7] If a mixture of PI and PS solutions is prepared and tested at a constant temperature (20 °C), then there is a viscosity maximum on the "property–composition" curve, but, when the system is first heated to 80 °C and then cooled to the temperature of the test (20 °C), a viscosity minimum is observed in the same composition range. This difference in behaviour is characteristic only of systems with a narrow molecular weight distribution (MWD) of the components. If the polymers constituting the blend were polydisperse, only a viscosity minimum was observed experimentally regardless of the previous heat treatment.

Some of the results discussed above indicate indirectly the kinetic nature of the anomalies discussed, but the communications quoted present facts indicating the thermodynamic nature of the anomalous

properties. Naturally, the hydrodynamic flow effects, associated with the structure of the blend, the design of the apparatus, and the deformation conditions, may mask or, on the contrary, can reveal anomalies which are objectively characteristic of specific systems.

4. Raw Rubber–Oligomer Mixtures

In the study of raw rubber oligoacrylate ester (OAE) systems,[15,28,51-58] the AIV was observed only in the range of low concentrations of the oligomers. It follows from the inspection of the flow curves for polydisperse SKI-3 raw rubber and its blends with two types of OAE—linear and branched[53]—that the AIV is manifested only in BPS with microamounts (< 0.5%) of the added linear oligomer. An increase in the OAE concentration to 1% restricts the range of τ values in which the anomalous effect is manifested and, on further increase in the oligomer content, the anomalies disappear over the entire range of τ.

It has been shown[51-53] that the AIV in binary raw rubber–OAE blends is not associated with the methodological characteristic features of the experiment and the chemical interaction of the components but is determined by the very structure of these systems, which depends on the nature of the components and their ratio.

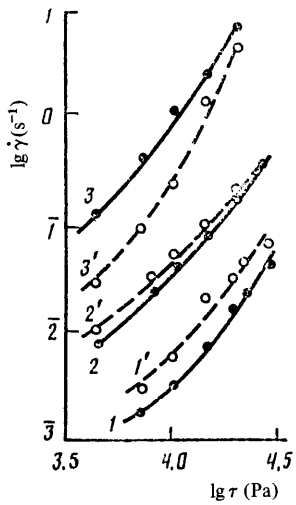


Figure 3. Flow curves for *cis*-polyisoprenes with MW = 6.2 × 10^5, 2.7 × 10^5, and 5 × 10^4 (curves 1–3 respectively) and their mixtures with 0.1 wt.% of TGM-3 (curves 1′–3′) at 70 °C.[54]

The relation between the anomalies in the viscosity-dependent properties of BPS on the molecular characteristics of the polymer component has been investigated.[54] Fig.3 presents the flow curves for *cis*-polyisoprene specimens differing in the molecular weight (MW) and their blends with trioxyethylene α ω-dimethacrylate (TGM-3), while Fig.4 presents the dependence of $\Delta \lg \eta$ for these blends on the MW of the polymer at different temperatures and shear stresses. It follows from these data that under the conditions selected for the test, the AIV effect is manifested only for blends of the low-molecular-weight raw rubber and OAE. With increase in the MW of the raw rubber, the relative magnitude of this effect diminishes and OAE has only a plasticising effect on high-molecular-weight raw rubbers.

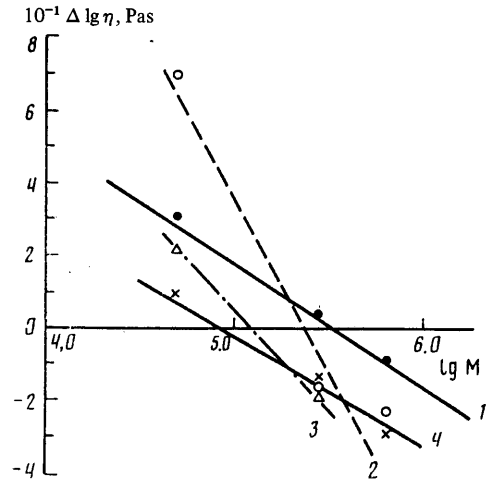


Figure 4. Dependence of $\Delta \lg \eta$ on the MW of *cis*-polyisoprene and its mixture with 0.1% of TGM-3 at 50 °C (curves 1, 3, and 4) and 70 °C (curve 2); lg τ (Pa): 1) and 2) 4.0; 3) 3 and 6; 4) 4.26.[54]

It has been shown[54] that the influence of the shear stress in experiments with a low-molecular-weight raw rubber is analogous to that observed[52] for blends of industrial high-molecular-weight raw rubbers with OAE: an increase in τ lowers the relative magnitude of the viscosity increment. On the other hand, the effect of temperature proved to be different. In contrast to experiments with industrial SKI-3 and SKD raw rubbers,[38,51,52] where the viscosity increment was totally eliminated with increase in temperature, in the given instance the relative magnitude of the AIV effect depends not only on the tendency towards a change in temperature and τ but also on their ratio: for some shear stresses, $\Delta\eta$ increases with increase in temperature whilst for others it diminishes. Nor can a distinct $\Delta\eta = f(c)$ relation be traced for blends of low-molecular-weight raw rubbers with OAE. It has been shown[54] that this is a consequence of the random variation of the MWD of raw rubbers in different syntheses.

An analogous conclusion has also been reached in a study[59] where it was shown in relation to blends of two polydisperse polymers (HPPE and POM) that the AIV depends in many respects on the MWD of the components and that the extremum is gradually abolished as the low-molecular-weight fractions are removed.

In the analysis of the influence of the polymeric component on the character of the manifestation of viscosity anomalies in raw rubber–OAE systems, attention should be drawn to two factors. (1) The viscosity anomaly is manifested most clearly and logically only in BPS based on polydisperse raw rubbers;[52] (2) even a slight difference between the MW and MWD of industrial batches of raw

rubbers may result in a situation where the AIV, which is consistently reproduced in specimens prepared from the same batch of raw rubber, cannot be observed in specimens obtained from another batch.[51-54]

The ambiguity of the entire set of experimental observations of the anomalous variation of the viscosity of BPS of different types considered above indicates the existence of parameters of the system (the actual system and not its components) which were not taken into account by the investigators and which can in fact be responsible for the extrema on plots reflecting the dependence of the viscosity of the BPS on concentration and temperature.

III. HYPOTHESES AND THEORIES OF THE ANOMALOUS CHANGES IN VISCOSITY

1. Low-molecular-weight Liquids

Ostwald[60] was apparently the first to suggest a relation between the increase in viscosity through an extremum and the phase transition in the vicinity of the critical point. This hypothesis was based on the modelling of the structure of the system in the critical state by "particles" constituting small-scale inhomogeneities, which led to an analogy with highly disperse colloids whose viscosity is higher than that of the solutions. This "colloidal" model was used for a comparatively long time to interpret many experimental observations at a qualitative level (see, for example, Refs.24, 25, and 28–31).

Quantitative schemes relating the shear viscosities of liquid systems to the appearance of large-scale fluctuations near the critical point began to appear in the 1960s. A theoretical justification of the anomalous variation of viscosity and other transport coefficients in mixtures of low-molecular-weight liquids in the critical state was initially provided by Fixman's studies,[61,62] concerned with the hydrodynamic description of the macroscopic properties of these mixtures within the framework of the approximation of interacting modes, and later by studies[63-65] in which this idea was examined within the framework of the decoupled-mode and the dynamic renorm group approximation.

The physical significance of all these approaches is that, when the system exists in the critical range of compositions and temperatures (c_{cr} and T_{cr}), then part of the mechanical energy (for example, in the deformation of the mixture) is dissipated on long-wavelength concentration fluctuations at a consequence of the interaction of the latter with the velocity gradient and their diffusion-dependent dissipation. Hence it follows naturally that the viscosity of the mixture in the critical state should increase, because in this case the entire shear energy is not consumed on the displacement of the molecules.

Thus, for systems in the vicinity of the critical point, the experimental viscosity η_m consists of the regular ("non critical") component η_r, which has been identified with the viscosity of the homogeneous solution, and the excess ("critical") correction ($\Delta\eta_{cr}$), whose value depends on the closeness of the experimental conditions to the critical conditions for the given system:

$$\eta_m = \eta_r + \Delta\eta_{cr}, \quad (2)$$

$$\Delta\eta_{cr} = f(r^{\Phi}), \quad (3)$$

where $r = (T - T_{cr})/T_{cr}$ is the critical parameter of the shear viscosity.

Solutions of the hydrodynamic equations within the framework of the approximations mentioned above yield in some cases[61-63] identical values of the parameter Φ, whilst in others[63-66] they lead to non-concordant results.

The ideology of large-scale fluctuations is applicable to systems which are both at the critical point and in the region of metastable states near the spinodal curve. The long-wavelength fluctuations arising under these conditions have the same influence on the shear viscosity.

Comparison of the experimental and calculated (within the framework of dynamic scaling) data[67,68] shows that Φ varies within broad limits: from −0.37 to 0.5 not only for different systems but even for isotypical systems.

2. Metallic Liquids

Virtually all the explanations of the concentration-dependent anomalies in the viscosities of metallic liquids are based on the use of the cybotactic model of the structure of liquids.[26,27]

Two versions of the possible explanation have been considered.[26] In one of them, it is assumed that the introduction of an additive or an increase in temperature lead to the decomposition of the initial large cybotaxes and to the formation of new ones having a smaller store of internal energy than the initial ones, which in fact causes an increase in the viscosity of the system. In the other version, the rearrangement of the structure of the cybotaxes is associated with the change in composition or temperature regarded as an activated process with a transition state, whose appearance requires an expenditure of additional energy. The entropy of the transition state is higher than that of the initial or final state and the change in the entropy of activation for viscous flow in the transition state accordingly proves to be smaller, while the activation energy and the viscosity are higher.

Unfortunately all the treatments of the anomalies in the viscosity-dependent properties of metallic melts are qualitative.

3. Polymeric Liquids

The AIV effect has been hardly considered in the reviews published in recent years on studies of the viscosities of dilute and concentrated solutions of polymers and polymer melts.[69,70] In the original studies the most varied ideas and approaches have been invoked to account for the anomalous variation of the viscosity-dependent properties of BPS, but all of them (with some exceptions—for example in Refs.5, 40, and 56) had as their aim the explanation of the causes of the abrupt decrease in viscosity. Ideas involving structural plasticisation,[23,46,71] a change in the free volume of the system after the introduction of the second component,[4,8,42] a decrease in the energy of the intermolecular interaction in the presence of the additive,[7,12] the separation into layers comprising different phases,[5-8] critical[7] and metastable[8,11] states of the system, etc. were invoked for this purpose. The development of these ideas has been reflected in reviews and monographs[7,8,11,12] and they will therefore not be considered in the present communication. We shall only mention that, from our point of view, the approaches based on the search for correlations between the anomalies in the rheological properties and the system thermodynamics proved most fruitful and most general.[7,8]

Judging from the number and wide variety of the experimental facts (see Section II), the AIV effect in BPS is a fairly common phenomenon. However, a reasonable explanation, providing for a single treatment of all the characteristics of its manifestation, has not so far been found. In many instances the causes of the increase in the viscosity of BPS are so evident that the absence of this effect would have to be regarded as anomalous and not its experimental manifestation. Thus, the increase in the viscosity of the blend of powdered PVC with liquid OAE mentioned above[50] with increase in temperature must inevitably occur as a consequence of the conversion of the mixture into a monolithic form and the transition from the flow of a dispersion to the flow of a plastisol. Gel formation in a solution of methylcellulose, occurring at a specific concentration of the solution in a specific temperature range, should also entail an increase in viscosity, which has in fact been observed in the experiment discussed above.[13] On the other hand, the disappearance of one of the two viscosity maxima, noted in a study[40] of the POM–PA system on raising the temperature, should have occurred without the fusion of the crystallising component.

It is just as evident that the phase transitions in BPS causing the transformation of the flow of single-phase solutions into the flow of dispersions can lead to an increase in viscosity, for example, in conformity with the familiar Einstein equation:†

$$\eta_m = \eta_0(1+2{,}5\varphi), \qquad (4)$$

where η_0 is the viscosity of the dispersion medium and φ the volume fraction of the disperse phase. However, from this it does not follow by any means that the viscosity of the mixture must be higher than the viscosity of the disperse phase.

(a) Single-phase BPS

A large group of studies,[2,4,7,13,73] devoted to the characteristics of the flow of polymer solutions, were confined to the elucidation of the possible causes of the deviation of the viscosities of the BPS from additivity without concentrating attention on the anomalously high values of these deviations. For this purpose, the idea that the free volume of the system changes (increases or decreases) on mixing the initial components were resorted to; the idea of a fluctuating network of entanglements, which can be more or less stable in BPS than the initial polymers, has also been used. In some cases, the concept of the supermolecular structure of polymers in solutions has likewise been employed.[4]

Virtually all the experimental features observed for polymer solutions can be ultimately accounted for qualitatively within the framework of the kinetic theory of Frenkel' or its modifications.[10]

Application of the scaling hypothesis to the analysis of the dynamic properties of polymer solutions made it possible to[74,75] impart to the idea of entanglements the form of quantitative relations. In particular, the viscosity of solutions of flexible-chain polymers is described by the expression[74]

$$\eta_m \simeq \eta_s N_e^{-2} N^3 \varphi^{\frac{3}{3\nu-1}} = \eta_s N_e N^3 \varphi^{11/4}, \qquad (5)$$

where η_s is the viscosity of the solvent, N the number of monomer units in the polymer chain, N_e the average length of the chain between entanglements in the polymer melt, φ the volume fraction of the polymer, and $\nu = 3/5$ the swelling index of the coils in semidilute solutions.

This approach is being vigorously developed at the present time. For example, different scaling expressions have been obtained recently[76] for the viscosities of systems of polymer solutions in each of the six regions of a dynamic phase diagram (Fig.5) as a function of the solution concentration φ, the length of the polymer chain N, and its flexibility P.

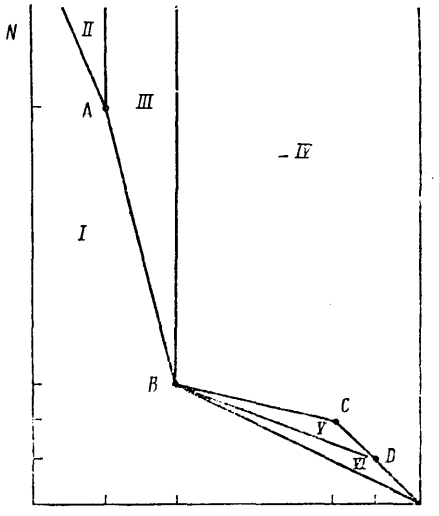


Figure 5. Dynamic phase diagram for a BPS solution;[76] φ = volume fraction of the polymer; points A, B, C, and D correspond to P^3, P, $P^{3/4}$ and $P^{1/2}$ respectively.

In region I, the entanglements between the macromolecular coils are insignificant and the viscosities of the solution in the solvent are identical. With increase in φ, the swollen coils begin to overlap and the system passes to region II, and there is a corresponding change in the laws governing viscous flow. The subsequent differentiation of the regions in the diagram is associated with allowance for N and P. For example, if $P = 1$, then the differences between the properties of the solutions corresponding to regions II–VI disappear, these regions "merge", and only two zones remain on the diagram—with overlapping and non-overlapping coils. On the other hand, if $P = 1$, then (and this is important for the problem discussed here) in each of the differentiated regions of the diagram the viscosity depends in different ways on φ. For example, at high dilutions ($\varphi_m \simeq \varphi^{3.8}$), the power exponent increases to 6 in the region of semidilute solutions and on passing to region V it diminishes to 1.4. This makes it possible to explain the presence of extrema on the $\eta_{sol} = f(\varphi)$ curves. Furthermore, the different power relations beween η_m and P, noted[76] for different regions of the diagram, and the temperature dependence of the flexibility of the molecule explain the non-linearity of η_m as a function of T. Analysis of the expressions quoted[76] shows that in region II the viscosity of the solution

† Subject to the condition that this equation, which was derived for dispersions of hard spheres, is applicable to BPS.[72]

should diminish on heating, while in region IV it should increase. Consequently, depending on the BPS concentration, an increase in temperature can lead to both an increase and a decrease in viscosity.

(b) Two-phase BPS

In order to account for viscosity-dependent properties of BPS known to be heterogeneous, two approaches are mainly used. In one of them the viscosity of the BPS is considered from the standpoint of the flow of colloidal dispersions for which the increase in viscosity with increasing fraction of the disperse phase is reasonable, and this is why a number of workers[5,7,11,22,23] have been surprised by the appearance of minima and not maxima on the $\eta_m = f(\varphi)$ curves.

For heterogeneous BPS, which can be regarded as dispersions with particles deformed under the influence of a load applied to the system (i.e. the shape of the particle is a function of τ and $\dot{\gamma}$), the applicability of Eqn.(4) is problematic (see the preceding footnote). There is as yet no universal theory of the flow of dispersions, although there are many empirical equations and models taking into account the influence of individual factors (the nature and shape of the particles, the state of aggregation of the disperse and dispersion phases, etc.). We may note, for example, the equation proposed by Lipatov,[11] which takes into account the molecular weight of the polymer, and the Schowalter–Taylor model[79] in which the viscosity of the mixture is related to the viscosity of each phase.

Thus the increase in viscosity is inherent in the very nature of the flow of colloidally disperse systems, although none of the known models lead to the conclusion that η_m should be greater than the viscosity of the most viscous component.

The second approach is based on the ideas concerning the structural transformations introduced by the BPS flow process itself, for example, the formation of a vibrous structure of the stream as a result of one of the components being stretched in the direction of the deformation or as a result of the formation of alternating annular layers when emulsions flow in a capillary,[7,14,39,40,77,78] etc. When the composition of the initial mixture, the deformation conditions, or the design of the apparatus are altered, the diameter of the fibres, the radius of curvature of the layers, the order in which they alternate, etc. can change. As a result of hydrodynamic effects, this can induce in its turn a decrease of an increase in the translational mobility of the macroscopic system as a whole.

(c) Binary Polymer Systems with Limited Compatibility of the Components

For systems of this type, the change in the character of the flow and all the non-linear effects in the concentration and temperature dependences of the viscosity are attributed to phase transitions, while anomalous deviations are usually attributed to the characteristic features of the structures formed under these conditions.

Thus the increase in viscosity has been explained[80] by the possibility of the formation of "strongly interlinked mosaic-like structures" during spinodal separation. In other studies,[51–55] the anomalous variations of the viscosity-dependent properties of rubber–oligomer systems are interpreted by analogy with the antiplasticisation effect.

Having compared the experimental $\eta = f(\varphi)$ curves with phase diagrams, Lipatov[8] proposed a modified Mooney's equation with a description of the viscosity of BPS in the region of a homogeneous state (before the attainment of the binodal curve):

$$\eta_m = K(1-\varphi_1)^{\alpha} M^{3,4}, \tag{6}$$

where K and α are empirical constants and φ_1 is the concentration of one of the polymers; in the region of the two-phase state (within the spinodal curve), Einstein's Equation (4) holds, while the viscosity of the system in the metastable zone (between the binodal and spinodal curves) can be calculated by means of the equation

$$\eta_m = K(1-\varphi_1')M^{3,4}(1+2{,}5\varphi_1''), \tag{7}$$

where $\varphi_1' + \varphi_1'' = \varphi_1$ represents the concentrations of the added polymer in the continuous and disperse phases and its overall content in the system.

Thus the section corresponding to a decrease in the viscosity on the $\eta = f(\varphi)$ curve is described by Eqn.(6), while the increase in viscosity is described initially by Eqn.(4) and then, after the interaction with the spinodal curve, by Eqn.(7).

Although the scheme considered does not yield quantitative agreement with experiment (as was pointed out by the author himself), nevertheless it permits a qualitative explanation of the possibility of the appearance of a viscosity minimum on the $\eta_m = f(\alpha)$ curves and the subsequent increase in viscosity. However, a whole series of other experimental facts (in particular the multiplicity of extrema) can in no way be accounted for by this scheme.

(d) Theory of the Viscosity of BPS in the Critical State

The work of Manevich and co-workers[81] is based on the fundamental idea of the approximation of interacting modes. However, in contrast to earlier studies,[61,62] they took into account additionally the non-Newtonian character of the flow of polymeric liquids and the asymmetry of the phase diagrams of polymer blends. As a result, the following expression was obtained for positive critical corrections to the viscosity:

$$\Delta\eta_{cr} = ac_2^2 \frac{1}{q} M^3 \left(1 + \frac{b}{q^4}\right), \tag{8}$$

where $q \simeq [(T - T_{cr})/T_{cr}]^{1/2}$, c_2 is the concentration of the polymer, M its molecular weight, and a and b are numerical coefficients. The parameter q is related in its turn to the chemical potential of the system μ_1 by the expression

$$\frac{4\pi a}{q^2} = \frac{V_1}{c_2}\left[KT\Big/\left(\frac{\partial\mu_1}{\partial c_2}\right)_{P,T} + m\right], \tag{9}$$

where $m = V_2/V_1$ is the ratio of the molecular volumes of the components. The change in the chemical potential is calculated here in accordance with the Flory–Huggins theory.

It follows from the theory of the viscosity of BPS in the critical state, that, in order to record the increase in viscosity, it is necessary to select the temperature-concentration conditions in such a way that the temperature and concentration are either identical or approach T_{cr} and c_{cr}.

Unfortunately in the form presented by Manevich et al.,[81] this theory does not establish quantitative criteria which would make it possible to estimate the difference between the experimental parameters of state and the critical values for which the contribution of the critical corrections is comparable to the experimental accuracy. It is

qualitatively clear that, if $\Delta c = c_{cr} - c \to 0$ and $\Delta T = T_{cr} - T \to 0$, then $\eta_{cr} \to$ max. But for each specific polymer–solvent pair, the Δc and ΔT for which $\Delta\eta_{cr}$ is comparable to η_m apparently have values characteristic of the given system. This apparently also explains the finding that, in the study mentioned above,[18] the AIV could be observed only under conditions where the temperature was varied in steps $\Delta T \leqslant 0.2$ K.

We emphasise that, if the current values of c and T are less than the critical values, then their increase brings the system closer to the consolute temperature (CT), whereupon $\Delta\eta_{cr}$ increases, which means that η_m will also increase. On the other hand, if c and T are greater than the critical values, then the subsequent increase in these parameters will entail a decrease in $\Delta\eta_{cr}$. As already mentioned in the previous Section, significant changes in the character of the concentration and temperature dependence of the viscosity have indeed been observed for BPS investigated under different conditions. It also follows from the theory examined that, with increase in the shear stress, the large-scale concentration fluctuations, which determine the increase in viscosity, are gradually disrupted‡ with a corresponding decrease also in $\Delta\eta_{cr}$.

(e) Theory of the Viscosity of BPS Near the Limit of Thermodynamic Stability

The character of the variation of the viscosity of BPS as the spinodal curve is approached, where large-scale concentration fluctuations also arise spontaneously, has been examined.[82,83] When a shear deformation is superimposed, part of the energy of the hydrodynamic flow is dissipated at these fluctuations which in fact entails an increase in the viscosity of the blend. The addition ("spinodal") correction to the viscosity has the form

$$\Delta\eta_{sp} = \frac{3\sqrt{2}\pi^3}{20}\frac{\rho f^2 k_B T\,(N_A(1-c)\,\tau_M^A + N_B c\tau_M^B\,(N_A N_B)^{1/2}}{N_e[N_A c + N_B(1-c) - 2\chi c\,(1-c)\,N_A N_B]^{1/2}}, \qquad (10)$$

where c is the concentration of component A expressed in terms of the number of monomer units, N_A and N_B are the degrees of polymerisation of the components, τ_M^A and τ_M^B are the microscopic relaxation times of the components, N_e is the number of monomers between entanglements in the reptation diffusion model along the "tube" formed by the entanglements, f is the Onsager coefficient characterising the degree of the intermode relation between the viscous and diffusion modes, k_B is the Boltzmann constant, and χ is the Huggins constant.

Eqn.(10) reflects the dependence of $\Delta\eta_{sp}$ on the length of the molecular chains of the components, their relaxation characteristics, the degree of the intermode relation, and the composition, temperature, and density of the mixture. However, the applicability of this formula is limited to monodisperse systems. In order to account for the polydispersity of the macromolecules, an additional function of the distribution density with respect to the degrees of polymerisation of each component (Π_A and Π_B) was introduced[82] into Eqn.(10).

Analysis of the integral form of the expression for $\Delta\eta_{sp}$ with allowance for Π_A and Π_B shows that, for a specified mixture composition and the total number of molecules in the system $N_A c + N_B(1-c)$, only those molecules contribute to $\Delta\eta_{sp}$ whose N_A and N_B for specified c and χ fall within the region adjoining the thermodynamic stability limit of the BPS. The same A and B molecules (for example, molecules with low degrees of polymerisation) which for a given T form true solutions with one another and those (for example, molecules with large N_A and N_B) which form heterogeneous mixtures under these conditions do not contribute to $\Delta\eta_{sp}$ and influence the macroscopic viscosity of the system only additively or in accordance with other laws.

Thus, if a "polydisperse" system with specified experimental c and T falls within the region adjoining the spinodal curve, then and only then do some of the molecules participate in the formation of large-scale fluctuations and only that fraction of them determines the agreement between the experimental viscosity and the value calculated by Eqn.(10). The remaining molecules, for which the elementary flow steps take place in accordance with other laws, will mask the flow in accordance with Eqn.(10).

The reliability of the experimental observation of the AIV has also been estimated.[82] For $\Pi_A \to 0$ and $\Pi_B \to 0$, the possibility of observing the effect is determined by the relation

$$\delta\eta/\Delta\eta_{sp} = \delta T/2\Delta T, \qquad (11)$$

where $\delta\eta$ is the accuracy of the measurement of $\Delta\eta_{sp}$ and δT is the accuracy of the thermostatic temperature control. Hence it follows that the possibility of obtaining a reliable value of $\Delta\eta_{sp}$ appears only if $\Delta T \geqslant \delta T$. It was found that, for a monodisperse BPS characterised by $N_A = N_B \simeq 10^4$, $N_e \simeq 10^2$, $\tau_M^A = \tau_M^B = 10^{-9}$ s, $f \simeq 1$, and $\rho \simeq 1000$ kg m^{-3}, an increase in viscosity by a factor of 2 (i.e. when $\Delta\eta_{sp} = \eta_r$) can be observed near the spinodal curve for $\delta T \simeq 1$ K.

The "critical" and "spinodal" corrections to viscosity have been revised[83] in connection with allowance for osmotic forces whose interaction with viscous friction forces is believed[74] to determine in many respects the mechanism of the dynamics of polymer solutions and melts.

The inclusion of the osmotic pressure of components A and B in the rheological equation for BPS leads to an expression in which, apart from positive corrections inducing an increase in viscosity, there is also another correction $\Delta\eta_{os}$ whose sign is negative (reducing the viscosity). This is due to the fact that osmotic forces facilitate the "dissipation" of the concentration fluctuations themselves and hence less of the energy supplied to the system from outside is expended on this process.

Yet another important conclusion has been made,[83] namely that the more significant the difference beween N_A and N_B, the greater the contribution by the above negative correction to the overall $\Delta\eta$. In other words, the greater the difference between the MW of the components of the BPS, the greater the probability of a decrease and not an increase in viscosity.

IV. COMPARISON OF THEORY WITH EXPERIMENT

The above analysis of experimental and theoretical data indicates a wide variety of possible causes leading to the AIV and the absence of a single view concerning the mechanism of this phenomenon. However, it is evident that the increase in the viscosity of BPS is always associated with structural features characteristic of them as mixed systems.

‡ A qualitative dependence of the microstructure of the blend on the shear stress has been described[2,84] and it has been shown that, with increase in τ, the dimensions of the microparticles and the formations produced by association diminish. The influence on τ on the orientational effects of concentration fluctuations, which induces the anisotropy of the dynamic properties of BPS, has been noted.[85]

1. The Phase Diagram of BPS

Fig.6 presents a conventional phase diagram of BPS in terms of the variables $\varphi_A - T$, where φ_A is the concentration of the polymeric component. Regions have been differentiated in the diagram in which the laws governing flow are apparently different. The phase diagrams of BPS have been analysed in detail in a number of studies.[13,86–88] Here we shall note only the most general postulates necessary for further logical exposition. Fig.6 illustrates the θ-line for the solutions shown by a dashed curve. In the zone above the θ-line, only three regions are shown: with non-overlapping (V) and overlapping (V') coils as well as the region of swollen gels (V''), although in principle this zone can be differentiated in greater detail (as was done, for example, by Semenov[76]).

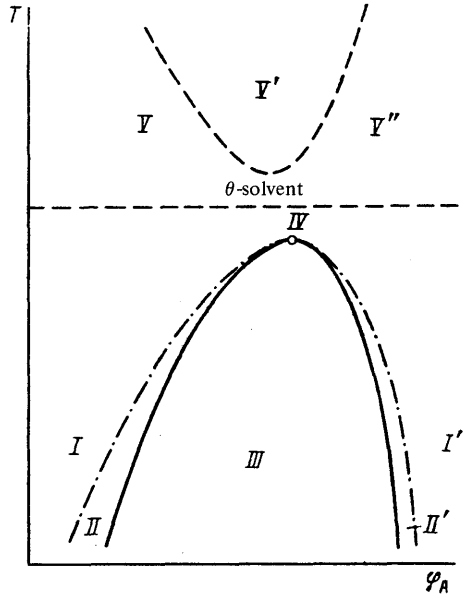


Figure 6. Conventional phase diagram for a BPS.[54]

In the zone of "poor" solvents (below the dashed line), six regions have been differentiated: two regions of true solutions—with an excess of the solvent (I) and with an excess of the polymer (I'); two regions of a metastable state (between the binodal and spinodal curves)—to the left (II) and to the right (II') of the spinodal curve; the region of two-phase states (III) located within the spinodal curve; the region of the critical state (IV) adjoining the upper consolute temperature (UCT).§ The positions of the branches of the binodal and spinodal curves depend on the affinity of the components (χ) and on their molecular-weight characteristics. For example, if N_B is large (the BPS consists of two polymers), then the branches are usually close to the coordinate axis and region (III) predominates in the diagram. If the MW of the solvent diminishes (transition to oligomeric and low-molecular-weight liquids), then the solution zone (especially to the left of the binodal curve as virtually all known phase diagrams of BPS are asymmetric) as a rule becomes broader.

Thus above the θ-line BPS form two solutions over the entire composition range regardless of temperature. Below the θ-line, two solutions are formed for any values of φ only at $T >$ UCT. On the other hand if $T <$ UCT, then BPS are by definition systems with limited compatibility, and when $\varphi < (\varphi'_A)_B$ (where the subscript B denotes the position of the point on the binodal curve) they form true solutions (region I) which correspond to traditional ideas about polymer solutions[4] whereas in the case where $\varphi > (\varphi''_A)_B$ they form solutions corresponding to molecularly plasticised systems.[22,23] Here $(\varphi'_A)_B$ and $(\varphi''_A)_B$ are the polymer concentrations along different branches of the binodal curve at a specified T.

Unfortunately few studies of the anomalies in the viscosity-dependent properties of systems with known phase diagrams have so far been published.[11,52,59,80] It is therefore difficult to compare experimental rheological data with thermodynamic features of the BPS. This is especially significant for systems with limited compatibility of the components for which the position of the CT and the regions of the metastable state are unknown in the vast majority of cases. As regards solutions and heterogeneous mixtures, there are usually sufficient indirect data confirming whether or not they belong to a particular phase organisation.

2. Solution Regions

The explanations of the causes of the non-linear effects of the AIV observed in polymer solutions and in single-phase BPS melts have not been adequately supported by arguments at the present time. The scaling approaches to the analysis of the dynamics of dilute and concentrated polymer solutions in "good" solvents (regions $V - V''$ in the diagram), which have been developing vigorously, undoubtedly contain new ideas capable of providing in the future a clear-cut physical interpretation of the entire set of effects which have been discovered. Examples of the fruitfulness of these approaches have been published.[74,76] However, in the present state of the development of these views, statistical physics has not yet provided a general picture of the relation between the viscosity and the parameters of state of BPS, the system thermodynamics, and the conditions of the rheological experiment. Nevertheless, it has yielded the very significant conclusion that the fundamental laws do not prohibit the possibility, in principle, of an increase in viscosity in polymer–solvent systems both in the region of dilute and semi-dilute solutions and in the region of polymer gels.

The scaling approaches being developed should undoubtedly influence also the development of the theory of polymer solutions in solvents with different thermodynamic affinities (regions I and I').

In our view, the approach based on the cybotactic (by analogy with metallic liquids) or anisotropic (by analogy with liquid crystal systems) models is undoubtedly promising. However, virtually no examples of the interpretation of the experimentally observed anomalies in the viscosity-dependent properties of BPS from these standpoints are encountered in the literature.

§ For systems with a lower consolute temperature (LCT), the above reasoning does not change fundamentally.

3. The Region of Two-phase BPS

The heterophase nature of BPS is as a rule due to the following causes: (1) the components are entirely thermodynamically incompatible; (2) the compatibility of the components is limited but at the experimental temperature the compositions of the systems investigated correspond to the two-phase state; (3) the components are potentially miscible but, by virtue of kinetic causes, the system has not attained equilibrium by the beginning of the rheological experiments and is therefore characterised by a definite level of heterogeneity; (4) phase separation takes place during the flow process. We shall examine further two main groups of factors which can lead to an anomalous variation of the viscosity-dependent properties regardless of the cause which has induced the heterophase nature of the BPS. One of them is associated with the intrinsic heterogeneity of the initial mixtures, which determines the characteristic features of their flow as disperse systems. The other is associated with the morphology of the extruded materials, arising solely during the flow process, which can alter the mechanism of mass transfer during the rheological experiment. It is more accurate to say that the structural changes accompanying the flow of BPS can mask the manifestation of features characteristic of classical dispersions.

As mentioned above, there is as yet no universal theory of the flow of polymer dispersions and the Einstein, Goot, Wand, Andrade-de Gusman, Mooney, Schowalter–Taylor, etc. equations are used to account for the experimental observations (depending on the form of the particles of the disperse phase and the range of concentrations of the dispersions). Within the framework of these ideas, the increase in the viscosity of BPS as a function of concentration is evident. However, a satisfactory explanation of the anomalously high values of $\Delta\eta$ observed experimentally has not yet been found.

As regards the factors inducing the increase in viscosity (or diminishing it) as a consequence of the change in the structure of the extruded material during the flow of BPS, at the present time they are considered only at the qualitative level. Examples were quoted above (see, for example, Refs.7, 39, 40, 47, 80) in which typical approaches to the interpretation of the anomalies in the increase and decrease in viscosity as the morphology of the extruded material varies are described.

We may note that it is precisely in two-phase BPS that the influence of the design of rheological apparatus on the results of the rheological experiment is manifested to the greatest extent. This is apparently associated with the fact that the method used to establish a given shear deformation, the design of the capillary, and hence the flow regimes in many respects determine the structure of the BPS formed during the flow process. For example, the transformation of the viscosity minimum into a maximum on the $\eta = f(c)$ curves, which has been observed[6] for a heterogeneous system as the length of the capillary was varied, is apparently induced by the increase in the viscosity of the wall layer, which is caused in its turn by a change in the hydrodynamics of the flow.

4. The Regions of the Metastable and Critical States

A distinctive feature of BPS with limited compatibility of the components is the fact that the structure of these systems, arising in the metastable and critical states itself, induces the manifestation of anomalies in dynamic properties. The large-scale fluctuations arising spontaneously in the critical region and in the vicinity of the spinodal curve, dissipate "non-productively" part of the energy of the shear deformation of the system, which leads ultimately to an increase in the macroscopic viscosity of such BPS.

Manevich and co-workers[81–83] were able to impart (in relation to BPS) the form of mathematically complete physical series to the idea of the dissipation of energy by large-scale fluctuations. The viscosity η_m, manifested in regions II, II′, and IV (Fig.6), consists of the viscosity of the regular solution (η_r) and the additional positive corrections $\Delta\eta_{sp}$ (regions II and II′) and $\Delta\eta_{cr}$ (region IV). Furthermore, it follows from the study of Mitlin and Manevich[83] that the "osmotic" correction, whose sign is negative, contributes to η_m. Each correction is defined by the corresponding equations, relating its value to the molecular characteristics of the components, the thermodynamic parameters of the system, the state parameters, and the deformation regimes.

Comparison of the conclusions derived from these theories with experiment yields a satisfactory qualitative agreement in some cases,[8,59,80] whilst in others[51–55] it does not. The physical clarity of the theories of Manevich and co-workers[81–83] is so attractive that it has stimulated the desire to account (at least formally) for the causes of the disagreement between experiment and theory in the latter cases. If it is assumed that the increase in viscosity for BPS of the rubber–OAE type is indeed induced by large-scale concentration fluctuations, then in the most general case the above discrepancy may be caused by the molecular polydispersity of the polymer, which leads to the "smearing" of the limits of the thermodynamic stability of the BPS in the vicinity of which these fluctuations are in fact generated. Since this approach may prove useful in the analysis of the dynamic properties of any polydisperse systems,¶ we shall deal in greater detail with certain causes of the discrepancies between theory and experiment. The following fact may be regarded as established:

1. A polydisperse polymer is in fact a solution of fractions with different MW. It has been demonstrated[8,11,89–92] that, under certain conditions (the role of the MWD is of primary importance), there is even a possibility of microphase separation in mixtures of polymeric homologues.

2. The dissolution of a mixture of polymeric homologues in an organic solvent should lead to the establishment of equilibrium between the solutions of fractions with different MW.[13] One of the technological procedures for the fractionation of polymers is based on this precise factor. There is a possibility of at least two thermodynamically non-equivalent cases: (a) the solvent forms a molecular solution with all the fractions of the polymer; (b) for a specified composition and temperature, certain fractions of the polymer are insoluble.

3. Theoretical calculations[93] have shown that, when the blended polymers have similar MWD, then the CT for the blend is independent of composition; otherwise the CT shifts to the region of extreme compositions. Bearing in mind the previous conclusion, one may conclude that in a blend of two polydisperse polymers there is a range of CT determined by the CT of different fractions. The claim that there exists a region of consolute concentrations whose width should depend on the width of the MWD of the components is also valid.

¶ We may recall the anomalies in the viscoelastic properties of a series of other BPS have also been attributed[59] to the polydispersity of the components.

4. It follows from the study of Vinogradov and Malkin[1] that, in a flow of polydisperse polymers, the low-molecular-weight fractions can be regarded as plasticisers of the high-molecular-weight fractions. The converse claim that the high-molecular-weight fractions thicken the low-molecular-weight fractions should also be valid.

5. A decrease in the proportion of low-molecular-weight fractions in a polydisperse polymer should lead to an increase in the viscosity of the mixture.[1]

6. Allowance for the polydispersity of the components in the theory of the viscosity of BPS near the thermodynamic stability limit[82] leads to the conclusion that only some of the total number of molecules in the system participate in the generation of large-scale fluctuations. Consequently, only some of the molecules ensure the increase in the viscosity of the system. The laws governing the translational movement of the remaining BPS molecules determine their "entry" into a particular region of the phase diagram.

When applied to blends of a polydisperse rubber with OEA, the postulates formulated above mean that structural inhomogeneities should exist in such systems. The inhomogeneities are characterised by different local concentrations of the oligomer corresponding to the limits of its solubility in fractions with different MW: the low-molecular-weight fractions contain a relatively larger amount of the dissolved oligomer than the high-molecular-weight fractions; furthermore, the CT of the solutions of the low-molecular-weight fractions are lower than those of the high-molecular-weight fractions.

Overall, this implies that, when the polymeric component of the BPS has a fairly wide MW distribution, then the system always contains molecules "belonging" to different parts of the phase diagram. Consequently even insignificant changes in the MWD, the composition, or the temperature should entail a shift of the thermodynamic equilibrium established between solutions of different fractions and a redistribution of the molecules between different regions. This should inevitably lead to a change in the macroscopic viscosity of the system, which is made up of the viscosity of the regular solution and the corresponding corrections for the increase in viscosity due to the molecules "present" in regions II and IV (Fig.6). Furthermore yet another factor becomes significant: after the introduction of the oligomer, the molecules of the low-molecular-weight fractions of the polymer, which serve as plasticisers of the high-molecular-weight fractions in the absence of the solvent, cease to exert a plasticising effect and are therefore forced to enter a metastable or critical state participating in the generation of the large-scale fluctuations. The experimental "resultant" viscosity is in fact determined by the competition between all these factors.†

Thus the macroscopic viscosity of the mixture of a polydisperse polymer and the solvent can be represented as follows:

$$\eta_m = \eta_r + \Delta\eta_{cr}\varphi_{cr} + \Delta\eta_{sp}\varphi_{sp} + \Delta\eta_a\varphi_a - \Delta\eta_p\varphi_p, \qquad (12)$$

where η_r is the viscosity of the regular solution, $\Delta\eta_{cr}$ the positive "critical" correction taking into account the increase in the viscosity of the fraction of macromolecules (η_{cr}) in the critical region, $\Delta\eta_{sp}$ the positive (spinodal) correction determined by the appearance of large-scale fluctuations among the fraction of the macromolecules (φ_{sp}) near the spinodal curve, $\Delta\eta_a$ a positive correction (for "anti-plasticisation") determined by the fact that a proportion (φ_a) of the molecules of the low-molecular-weight fractions cease to plasticise the system, $\Delta\eta_p$ the correction (the "plasticising" correction) determined by the plasticising effect of the solvent and a proportion (φ_p) of the polymer molecules.

Evidently, $\Delta\eta_{cr}$, $\Delta\eta_{sp}$, and $\Delta\eta_a$ lead to an increase in the viscosity of the blend, while $\Delta\eta_p$ leads to its decrease. On this basis, a structural organisation of solutions of the individual fractions of the "polydisperse system" such that, according to Eqn.(12), the positive viscosity corrections predominate is presumably established under the experimental conditions selected[51-55] at low OAE concentrations. Other conditions being equal, an increase in the oligomer content increases φ_p and hence $\Delta\eta_p\varphi_p$ and therefore entails a decrease in η_m. After an increase in viscosity, its decrease is therefore observed on the "viscosity–composition" curve.

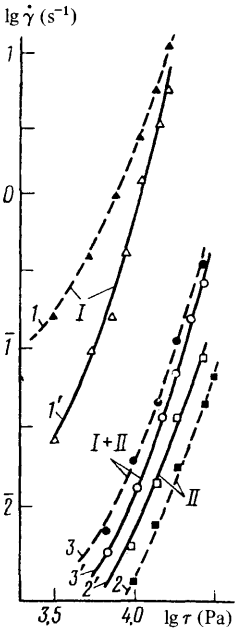


Figure 7. Flow curves for *cis*-polyisoprenes with MW = 5×10^4 (curves 1 and 1′) and 6.2×10^5 (curves 2 and 2′) and for their equimolar blend (curves 3 and 3′): 1)–3) without TGM-3; 1′)–3′) with 0.1 wt.% of TGM-3.[54]

† The contribution of the negative "osmotic" correction to the viscosity proposed by Mitlin and Manevich[83] is not taken into account below, because its quantitative relation with the "plasticising" viscosity correction ($\Delta\eta_p$) is not clear. It is suggested that the latter includes the "osmotic" correction.

The above schematic considerations make it possible to explain also why the position of the maximum on the experimental "viscosity–composition" curve is inconsistent with the theoretical prediction.[81-83] The cause of the discrepancy is the "diffuseness" of

the phase states of the individual fractions of the solutions of polydisperse BPS. This hypothesis has so far been confirmed only by indirect experiments.[54]

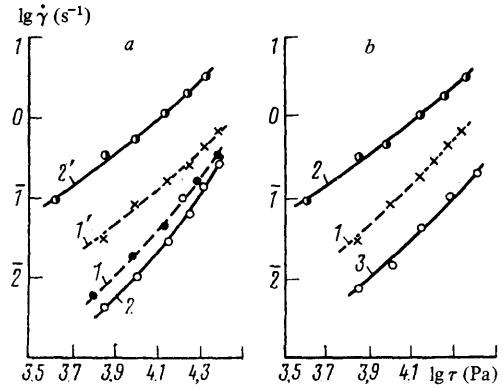


Figure 8. Flow curves for blends of *cis*-polyisoprenes with MW = 5×10^4 and 6.2×10^5: (a): 1) and 2) 1:1 concentration ratio; 1′) and 2′) 2:1 concentration ratio; 1) and 1′) without TGM-3; 2) and 2′) with 0.05 wt.% of TGM-3; (b): 1) without TGM-3; 2) with 0.05 wt.% of TGM-3; 3) with 0.05 wt.% of TGM-3; 2:1 concentration ratio.

It follows from Fig.7 that the increase in viscosity in the raw rubber–OAE system based on a high-molecular-weight raw rubber is manifested only when the system is "diluted" by the low-molecular-weight fraction of the same rubber. Since the relative increase in the viscosity is a maximum for BPS based on low-molecular-weight raw rubbers (Fig.3), it was to be expected that, in complex systems consisting of OAE and a blend of high- and low-molecular-weight raw rubbers, an increase in proportion of the low-molecular-weight fraction of the rubber component in the latter should increase the relative AIV. However, it follows from Fig.8 that, for the same OAE concentration, an increase in the proportion of the low-molecular-weight fraction in the raw rubber (the ratio of the low- and high-molecular-weight fractions is 2:1) not only does not intensify the effect but actually leads to a monotonic decrease in viscosity. This unexpected result is reasonable, provided that the hypothesis discussed above is valid. Indeed, the low-molecular-weight fraction is "responsible" not only for $\Delta\eta_{cr}$ and $\Delta\eta_{sp}$ but also for $\Delta\eta_p$. In the given instance, an increase in its concentration entails an increase in φ_p and an increase in the contribution to η_m by the negative viscosity correction. This results in a decrease in the experimental value.

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The anomalous dependence of the viscosity-dependent properties of BPS on concentration and temperature is a consequence of the characteristic features of their structural organisation for different parameters of state (in different regions of the phase diagram).

Although the true mechanism of the anomalous viscosity effect is still far from being understood, the studies in recent years have provided a physical foundation (the relation between the viscosity and the structural parameters of the BPS determined from its phase organisation) for the correct formulation of experimental and theoretical investigations of this phenomenon and have also extended the possibilities for its practical application.

The decrease in the viscosity of BPS (regardless of whether it is manifested in a traditional or anomalous manner) has a favourable effect on the processing of polymers and there are no fundamental problems as regards its practical use. The situation is much more complex with the practical application of the AIV. This is a many-sided problem. On the one hand, in many instances it is essential to increase the viscosity of compositions, for example, of paint and varnish systems, deposited on vertical and inclined surfaces. A fairly wide range of viscosities is inherent in the requirements which must be met by adhesive compositions, hermetic seals, etc. The regulation of viscosity (including its increase) is therefore an important technological procedure for the preparation of polymeric materials with specified properties. Another aspect of this problem consists in the fact that the understanding of the mechanisms of the increase in viscosity permits its prevention in those cases where it is undesirable.

As mentioned above, in BPS based on industrial polymers, which means polydisperse polymers, there are always microregions with a locally increased viscosity regardless of the macroscopic viscosity of the system as a whole. This property of BPS has made it possible to discover yet another application of the AIV phenomenon.[94] By increasing the viscosity in individual mixing stages, it has become possible to improve the dispersion of the filler in raw rubbers. The use of solvents with different solvent powers (the corresponding compositions with OEA) has made it possible to diminish simultaneously the energy expenditure on the processing.

The search for new practical applications of the increased viscosity effect is undoubtedly an interesting task in polymer materials science, but it can be solved successfully only if the true mechanisms of the rheological anomalies in binary polymer systems are clearly understood.

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