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# RHEOKINETIC AND MORPHOLOGICAL FEATURES OF THE REACTION FORMATION OF A POLYMER COMPOSITE MATERIAL BASED ON IMPACT-RESISTANT POLY(METHYL METHACRYLATE). MODEL AND APPLIED ASPECTS

*The authors dedicate this article to the memory of their teacher, Academician of the National Academy of Sciences of Ukraine Yuri Sergeevich Lipatov, whose constant interest and attention stimulated the formulation of this work, contributed to its implementation and understanding of the results*

*Based on the experimental data on the rheology of dispersions of hydrophobic aerosil ($A_m$) in a low molecular weight hydrocarbon medium, the possibility of using a «micellar» mechanism for the formation of a bulk structure for such dispersions is considered. A model of such a structure before, during and after shear deformation is proposed, which makes it possible to interpret experimental data on the rheology of dispersed systems. The results of the study of rheokinetics are presented in a new visio – from the point of view of self-organization under the influence of the shear field. The PMMA–PU–$A_m$ system was considered as a polymer composite (PC), in which the matrix is the poly(methyl methacrylate) (PMMA) being modified, and the dispersed phase is a mixture of polyurethane (PU) with $A_m$. It has been shown that during the reaction formation of this composition, the conditions of shear deformation of the system correspond to those at which self-organization and fixation of the coagulation rheopex structure of the nanofiller in PC is possible at the moment of reaching very high viscosity values (gel-point), when diffusion processes will be practically frozen. Two concentration regions of $A_m$ were predicted (before and after the percolation threshold), where an enhancement of the mechanical characteristics of PMMA can be expected. The relationship between the rheokinetics of the formation of a linear PMMA–crosslinked PU mixture in the presence of different amounts of oligomeric azo-initiator containing fragments of the polyurethane chain and*

*groups capable of initiating radical polymerization of methyl methacrylate and the process of phase separation, morphology and mechanical properties of the final products has been established. It was shown that the time of phase separation and gelation are interrelated and there is in a simple dependence on the concentration of the azo-initiator. Such an initiator affects the structural-rheological transitions in the system and leads to the formation of morphology with smaller domains. The most stable system with the best dispersion of polyurethane in polymethyl methacrylate is a mixture containing 0.002 mol/L of azo-initiator, which has improved mechanical properties and increased impact viscosity.*

**Key words:** *rheokinetics, viscosity, structure formation,  shear deformation, rheopexy, gelation.*

## Introduction

It is generally known that nanocomposites based on polymer matrices, which are polymers filled with nanoparticles of various natures, are currently attracting the attention of researchers as sources of new materials with a unique set of structural and functional properties. There is information about a significant enhancement of polymers upon the introduction of nanoparticles [1]. At the same time, the main attention was paid to characterization and, in some cases, modification of the surface of nanoparticles, methods of combining particles with polymer matrices, and, of course, the structure and properties of finished nanocomposites. The use of nanoparticles as fillers for polymers makes it possible to obtain a number of materials with improved mechanical and often new functional properties on the same polymer matrix [2]. Apparently, this is a result of the action of main factors: the adsorption of macromolecules on highly developed interfacial surfaces, effective distribution of nanoparticles in the polymer matrix, and the introduction of solid nanosized particles with certain mechanical and functional characteristics into the system. As a result, one can expect a change in the structure of the polymer matrix, and, consequently, in the strength characteristics, heat and chemical resistance of the finished composites. According to some researchers [1, 2], filler particles play the role of tracers that reveal the texture relief.

Currently, there is an increased interest in the appearance of regular structures (self-organization) during deformation of melts or solutions of polymers and colloidal systems. Numerous experimental data reveal the analogy and commonality of the phenomena observed in colloidal systems and polymer melts and solutions, when shear deformation is the driving force of structurization. However, we would consider it appropriate to refer to earlier works (see, for example, [3]) devoted to revealing the specific role of shear deformation (or superimposed shear stresses) in the phase state of polymer systems. In [3], a systematic consideration of numerous experimental studies of phase transitions under conditions of superimposed mechanical fields is presented, and the known results are generalized in order to establish the place, boundaries and causes of the discussed shear field effect in the set of general physicochemical regularities of the behavior of polymer systems. It was shown that mechanical action (shear or extension) can lead to a change in the phase state of both one- and multicomponent polymer systems, primarily melts and polymer solutions. In this case, deformation can play a double role. On the one hand, mechanical stresses affect the kinetics of the phase transition, which is most typical for the crystallization of the melt; on the other hand, the deformation effect leads to a shift in the equilibrium temperature of the phase transition (both amorphous and crystalline separation), i.e. plays the role of a thermodynamic factor. In [3], the main aspects of the influence of shear deformation are formulated:

*The thermodynamic role of deformation*, i.e. the answer to the question of how shear deformations affect the displacement of the equilibrium temperatures of phase transitions (crystallization temperature and phase separation temperature).

*The kinetic role of deformation*, i.e. elucidation of how shear deformations affect the rate of formation of a new phase. Both aspects are related, since it is well known that the phase transition rate, among other things, depends on the distance from the equilibrium temperature of this transition.

*The morphological role of deformation*, i.e. understanding how the structure (mutual arrangement and configurational order of macromolecules) of a polymer system, which obviously depends on the conditions of deformation, is fixed in the final state and determines the properties of the resulting material. It was noted that an important effect of shear deformation is the orientation of macromolecules in the flow,

which leads to a change in the intermolecular interaction, especially when it comes to polar macromolecules. As a result, structure formation occurs up to the formation of colloidal particles, which are released in the form of a new phase. The formation of structure induced with shearing in incompatible polymer mixtures was reported by the authors of works [4–6]. The effect of shear deformation on the equilibrium temperature of amorphous phase separation (i.e., taking into account the thermodynamic and kinetic role of deformation) of a polymer mixture was studied in [7]. There, for the first time, the results of a study of the effect of nanofillers on the phase separation of such systems are presented.

The review [8] considered various cases and physical reasons for self-organization (formation of ordered structures) caused by shear flow of polymer and colloidal systems, which are characterized by complex rheological behavior. This review also discusses various theoretical approaches that have been proposed to describe the instability and structural organization in polymer and colloidal systems. A possible consequence of structure formation in many cases may be the ambiguity of the flow curves with the existence of a region in which the stress decreases with an increase in the shear rate. However, in micellar and polymer systems capable of elastic deformations, it is elasticity that is the dominant cause of instability. Moreover, such systems can coexist (or behave) in two structural forms – fluid and elastic (highly elastic).

## The influence of the shear field on structurization in the model system

In series of our works [9–16], initiated by our teacher, academician of NAS Yu. S. Lipatov, reaction formation of PMMA–PU–A$_{\mathrm{m}}$ composition under conditions of shear deformation was investigated. It was suggested that under these conditions, in such a complex rheological system, self-organization and fixation of the coagulation rheopex structure of the nanofiller in the PMMA–PU matrix is possible at the moment it reaches very high viscosity values (gel-point), when the diffusion processes are practically frozen. To understand the mechanism of the formation of these structures, it was necessary to study the effect of the nanofiller and the shear field on them

for simple model systems. It should immediately be noted here that: *"A model is a phenomenological description that connects the most important or characteristic elements of a phenomenon and at the same time neglects factors that, when building this model, seem to be less significant. The balance between the most significant and seemingly not-so-important factors is a matter of the art of choice, which is always ambiguous, imprecise and possibly wrong. The more facts the proposed model describes, the more accurate and "better" it is, but at the same time it turns out to be more complex. Moreover, there can always be such an unaccounted factor that, in certain circumstances, will become decisive and lead to events that in no way correspond to the chosen model"* [17]. When studying the process of structure formation in a model system in a shear field, we would like to use a fairly simple model, but one that would take into account as many factors as possible that affect the complex rheological behavior of real systems. The general basis for this consideration is that, as a general rule, micellar systems behave in many respects like polymer solutions. It should be borne in mind that heterogeneous systems (incompatible mixtures of polymers, emulsions, suspensions, micellar systems, etc.), when considering their behavior at the nanoscale, behave similarly, regardless of the molecular weight of the dispersion medium, the nature of the interaction between the components of the system and external factors.

The rheological characteristics of a model dispersion of hydrophobized aerosil in a hydrocarbon medium were investigated in [18]. The rheopex effect was studied during the flow of dispersions at low stresses. When using the entire shear rate range, the ascending and descending sections of the flow curves coincide above a certain shear rate. As the shear rate increases, there is a Newtonian section in the low velocity range on the flow curve, while plastic deformation (yielding) was observed on the downward curve. The yield limits of dispersions with different filler contents are determined in three ways. In one case, steady-state experiments were carried out over the entire range of stepwise decrease in shear rates. The obtained flow curves clearly showed the existence of the yield point of dispersions at a volumetric concentration of the filler $\varphi \geq 1.39$ vol. %. The Herschel – Bulkley's model was used to determine the yield points. In the second case, the vibration

amplitude was changed at three frequencies, and the "dynamic yield stress" was defined as the stress at which there was a deviation from linearity. It was found that the dynamic yield stress depends on the frequency, and therefore should not be considered as a property of a material that has any physical meaning. At a given frequency, the dynamic yield stress does not correlate with the yield stress obtained from the flow curves. The dependences of the loss modulus on frequency also indicated the existence of the yield stress for the studied dispersions (third case). The percolation threshold for the investigated dispersions was determined: $\varphi^* = 1.35 \pm 0.03$ vol. %.

When discussing the experimental results of work [18], such as the appearance of the yield stress due to the formation of rheopex structures, thixotropy, percolation threshold, etc., we postulated the formation of a «structural network of nanosized filler particles» in an oligomeric hydrocarbon medium. The question arises: what is the mechanism for the formation of such a network and what is the role of the medium in its formation? Moreover, this question is complicated by the fact that this mechanism will probably be characteristic only for a particular dispersed system. We propose to discuss the possibility of using the «micellar» mechanism for the formation of a bulk structure for the dispersion of hydrophobic aerosil in oligodiethylene glycol adipate. This mechanism is well developed for colloidal systems. It is now known [19] that the yield point, i.e. the minimum shear stress ($\sigma_Y$), above which the flow of the material begins (in fact, $\sigma_Y$ characterizes the strength of the structural framework of the filler), for filled polymer systems does not depend on the molecular weight of the polymer matrix, its nature, and temperature. At the same time, the role of the medium and its nature in the formation of the filler structure has not been described. Earlier, in works [20, 21] on the rheology of dispersions of pyrogenetic aerosil in mineral oil and polypropylene glycol, general ideas about the formation of the structural network of the filler and the effect of preliminary sinusoidal shear deformation on the destruction–restoration of the filler structure were given. In such dispersions, adjacent aggregates can interact via silanol–silanol hydrogen bonds, leading to the formation of large structures called floccules. At high concentrations (5–10 wt %.) of aerosil, a three-dimensional volumetric floccular network (the so-called "infinite cluster") is formed. This suspension is a "physical gel". The flocculated microstructure thus has several levels: aggregate can be considered as the primary structure of aerosil, floccules are formed by interconnected aggregates, and a three-dimensional network is formed by floccules [20, 21].

In contrast to the formation of regular dynamic structures in the flow of low-molecular-weight liquids, when the viscosity of the liquid plays a decisive role, in the case of complex rheological media, structurization is associated with the elasticity of the medium and/or the existence of various structural forms of the material. They arise due to shear deformation and have different rheological properties, which leads, in particular, to the ambiguity of the flow curves of the medium. In situations associated with the flow of colloidal systems, one should think about thixotropic phenomena, although in colloidal systems effects are possible due to the elasticity of the system. The difference lies in the kinetics - in polymers, the transition between different relaxation (physical) states is clearly not related to the time factor, while the destruction and formation of structures in colloidal systems is thixotropic, i.e. stretched out in time. As a general fact, the orientation of micelles in the direction of flow was also noted [22, 23].

One and the same material can exhibit either thixotropic or anti-thixotropic (rheopex) properties, and the transition between two cases of rheological behavior can depend on seemingly insignificant details of the system. For example, as shown in [19], for aqueous solutions of lycithin forming polymer-like micelles (PPMs), a slight change in composition makes it possible to transfer from a thixotropic (with decreasing viscosity) to rheopex (with increasing viscosity) colloidal system. The described effect (rheopexy) is explained by the growth, rearrangement of PPMs and the network formed by them. It should be noted that rheopexy is kinetic in nature, i.e. depends and develops over time. The authors of [19] believe that it is more reasonable to apply a quasi-chemical approach to the study and description of thixotropy–rheopexy phenomena, as it was developed for micellar systems [24].

Before proceeding to review structure formation in a suspension of hydrophobic aerosil in oligodiethylene glycol adipate, let us first
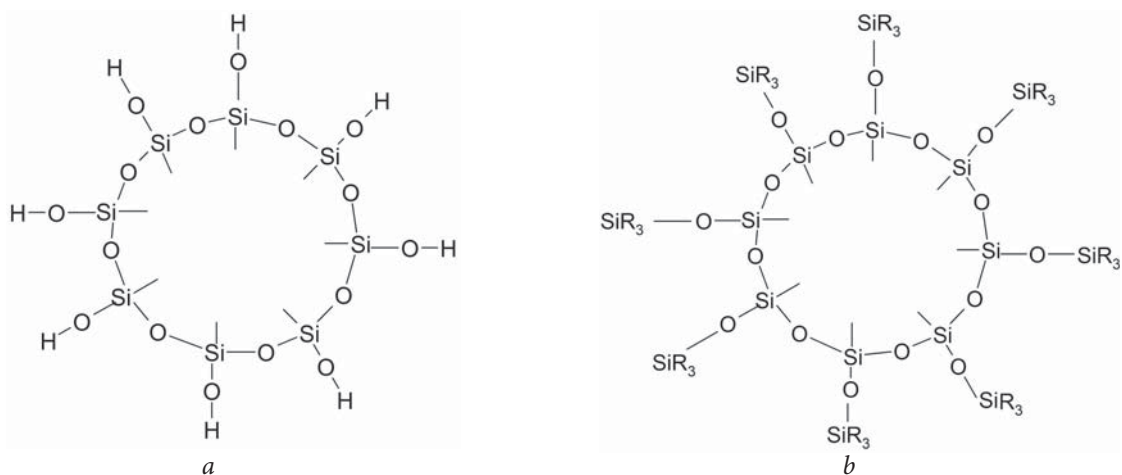
*a*



*b*

**Fig. 1.** Structure of particles of hydrophilic (*a*) and hydrophobic (*b*) aerosol

consider the structure of particles of pyrogenic aerosil (initial aerosil) and then its hydrophobized analogue. Silanol groups are usually located on the surface of silicon dioxide particles, while the $\equiv$ Si – O – Si $\equiv$ bonds are localized inside the particles (Fig. 1a).

The formation of silanol groups in the process of obtaining silicon dioxide prevents the particles from sticking together during their growth. The presence of silanol groups on the surface of neighboring particles promotes the formation of hydrogen bonds between them. In this case, the appearance of a three-dimensional lattice structure consisting of particles of silicon dioxide leads to an increase in the viscosity of liquid systems when colloidal silicon dioxide is introduced into them. When low shear stresses are applied, relatively weak hydrogen bonds are destroyed. In addition to increasing the viscosity and thixotropic effect, the presence of silanol groups on the surface of silicon dioxide particles determines the possibility of its chemical modification. In particular, the treatment of silicon dioxide particles with organochlorine silanes containing long hydrocarbon chains promotes hydrophobization of their surface due to the formation of organic functional groups on it. A scheme of a hydrophobic aerosil particle is shown in Fig. 1b (here R is an alkylaromatic radical). The particle size of pyrogenic silicon dioxide is 3–10 nm [25].

The dispersion medium was oligodiethylene glycol adipate with a molecular weight of 1500 (ODA-1500), which we used as a flexible-chain block in the synthesis of polyurethane (see below). Based on the structural formula of this oligoester,
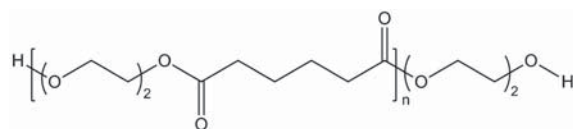


it can be assumed that ODA-1500 is a hydrophobic dispersion medium in the suspension under discussion (hydrophilic end groups can be neglected due to their low concentration). Due to the high surface energy of nanosized aerosil particles and the similarity of the chemical composition of the surface of hydrophobic aerosil particles and ODA-1500 molecules, it is highly probable that an adsorbed layer of oligomer molecules will form on the surface of such particles. The minimum thickness of such a layer is determined by the transverse dimension of the elongated oligomeric molecule, i.e. it is ~ 1 nm.

Based on the definition of micelles, we propose to call the particles of hydrophobic aerosil as micelle-like particles consisting of a very small core insoluble in this medium (Fig. 1b) surrounded by a stabilizing shell of adsorbed oligomer ODA-1500 molecules. The critical volumetric concentration $\varphi^*$ of such a filler (percolation threshold), at which a volumetric structural network is formed from its particles, is 1.35 vol. % [18]. Due to the smallness of $\varphi^*$, it can be assumed that such a structure is formed from the initial aggregates in the form of chains (fragments of the structural network, Fig. 2).
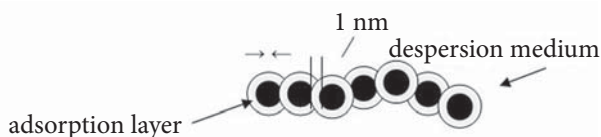
**Fig. 2.** Fragment of the structural network of hydrophobic aerosol–worm-like micelle
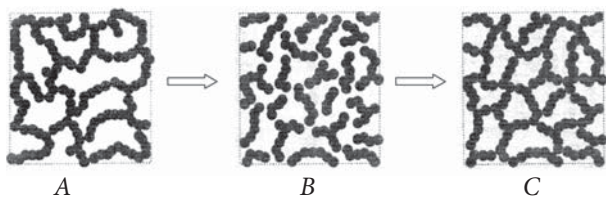


**Fig. 3.** Schematic representation of the microstructure of a suspension of hydrophobic aerosil during and after shear deformation. *A* – original network; *B* – micelle-like structure at shear; *C* – a structural network formed from micelle-like fragments after the end of reverse shear deformation (with decreasing stress)

In this case, between the particles interacting with each other, there is a thin layer of a liquid medium with a thickness no more than 1 nm. This implies the definition of such a structure as coagulation structure (such structures arise in colloidal systems). Since such structures are dynamic, one cannot exclude the possibility of the existence in the suspension aggregates of aerosil particles, the

shape of which can be described by a sphere. In addition, small size premicellar aggregates can be present in a dispersion medium [24, 26].

In dispersions, adjacent aggregates can enter into interparticle hydrophobic van der Waals interactions, leading to the formation of large structures called polymer-like or worm-like micelles. At high concentrations of aerosil, a three-dimensional volumetric coagulation network (the so-called "infinite cluster") is formed. This suspension is a "physical gel". Thus, the micelle-like microstructure has several levels: aggregate can be considered as the primary structure of aerosil, micelle-like aggregates are formed by interconnected initial aggregates, then forming a three-dimensional network. A model of such a structure before, during and after shear deformation is shown in Fig. 3 (by analogy with work [21]).

The influence of the shear field on structure formation can also be indirectly illustrated by comparing the data shown in Fig. 4, which shows the dependence of viscosity on shear stress σ, when the experiment was carried out at first with an increase of the stress (open circles), and then with its decrease (darkened circles). In the first case, there is a Newtonian section (I) (the viscosity does not depend on the stress), in the region of low shear stresses σ on the flow curves. It corresponds
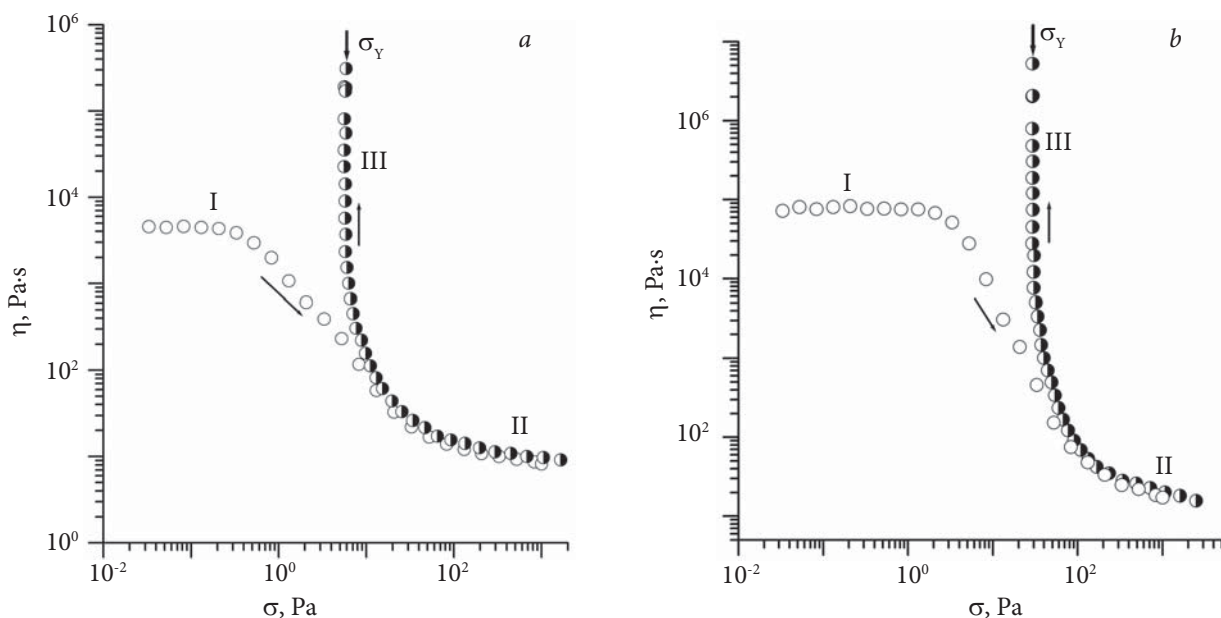


**Fig. 4.** Rheological behavior of dispersions as a function of shear stress at filler concentrations 2,34 (*a*), 3,31 vol. % (*b*). I – Newtonian viscosity of the material with the original unbroken structure; II – effective viscosity of a material with a completely destroyed structure; III – yield stress of a material with a rheopex structure

to the flow of a suspension with the not destroyed structure. Then, starting from a certain value of σ, the viscosity begins to decrease with increasing stress, which indicates the destruction of the network and the orientation of the resulting network fragments in the direction of the flow. And finally, in the region of high shear stresses, a quasi-Newtonian (weak dependence of viscosity on σ) region (II) is observed on the curves, which indicates the flow of a system with a destroyed structure. The most interesting thing happens when, without stopping the flow, the suspension begins to deform with decreasing stress. In this case, at first (in the region of high stresses), the flow curves coincide, and then, at a certain stress, depending on the volumetric content of the filler, the viscosity of the suspension begins to increase noticeably with decrease σ. This leads, in the end, to a catastrophic increase in viscosity (it tends to infinity, section III) at a critical shear stress $\sigma_Y$ (yield stress).

This phenomenon gives us grounds to assert that with this method of shear deformation, a new self-organizing denser (in contrast to the initial structure) rheopex coagulation structure of hydrophobic aerosil is formed in the suspension. Unfortunately, a method for stabilizing ("freezing") such structures has not yet been developed. This problem is relevant due to the fact that the transition from the self-organizing structure (C), formed by micelle-like fragments of the network (B) and induced by the reverse calm and continuous flow, to the initial structure (A) occurs very quickly. This fact was noted earlier for suspensions with a high content of nanofillers in [21] and for highly concentrated emulsions in [27]. We point out that in the recent past, an attempt was made to stabilize similar (micellar) structures by polymerization of monomeric surfactants [28]. Another approach to solving this problem is possible (see below).

## Rheokinetics, morphology and mechanical properties of the PMMA–PU–A$_m$ system

So, we have considered some problems of the structure formation of a nanofiller in a medium (matrix), which is a homogeneous, unstructured viscous oligomeric liquid. A more complicated situation occurs when the matrix is a heterogeneous viscoelastic polymer medium, the components of
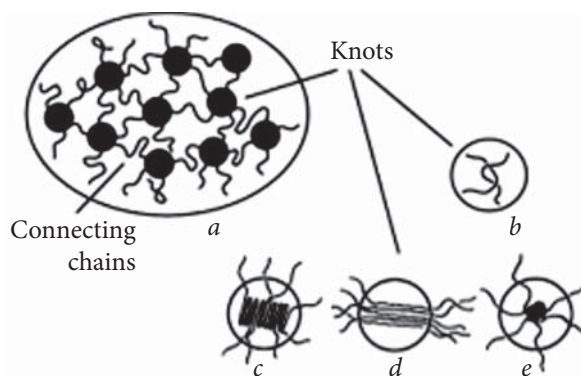


**Fig. 5.** Scheme of the structure of the Ieha's amorphous polymer

which are thermodynamically incompatible. In this case, in rheokinetic research, the structuring processes are determined by several factors, namely, chemical reaction and temperature, phase separation, gelation, dispersed nanofiller, molecular weight of the flexible polyurethane fragment, and shear field. At the same time, little attention is usually paid to the effect of shear deformation on the PC structure formation.

Since in our case the components of the composition obtained by the method of reaction formation were amorphous polymers PMMA and PU, it seems appropriate to present the modern concept of the structure of these polymers.

Based on the Ieha's model [36], an amorphous polymer is a set of blocks (domains, clusters) with a diameter of 4–10 nm, in the center of which there are the most ordered regions (2–4 nm); border regions with a length of 1–2 nm contain the ends of polymer chains, folds and loops.

The space between the domains (1–5 nm) is filled with connecting chains (sections of macromolecules belonging to two or more domains simultaneously) and coils of macromolecules. That is an in accordance with Ieha's model, the main reason for the structural organization of amorphous polymers is the presence of ordered regions alternating with regions of disorder and the small size of ordered regions.

Thus at present, the concepts of the physical structure of amorphous polymers are as follows. First, short-range order in the arrangement of fragments of macromolecules is characteristic of amorphous polymers. The size of the short-range order regions is comparable to the size of segments of flexible-chain polymers and lies

within ten nanometers. Second, the physical structure of amorphous polymers is interpreted from the standpoint of a fluctuation network of entanglements. The knots of the physical network are the entanglements of macromolecules (Fig. 5b), as well as ordered clusters (λ-structures) built from segments of macromolecules in a folded (Fig. 5c), straightened (Fig. 5d) or globular (Fig. 5e) conformation. These λ-structures form a fluctuation network, and as a result of thermal motion, their continuous formation and disintegration occurs. Each macromolecule participates in the formation of several clusters or, in other words, passes through several clusters. Thus, the fluctuation network is a kinetically rather than thermodynamically stable system: the cluster lifetime decreases with increasing temperature.

Now let us dwell in more detail on one of the main rheokinetic characteristics – viscosity and its dependence on the molecular mass and structure of amorphous polymers. In rheokinetic studies, the range of the shear rate variation is $10^{-3} \div 10^{3}$ s$^{-1}$ (respectively, viscosity is $10^{5} \div 10^{-3}$ Pa·s). In the region of shear rate $10^{-3} \div 10^{0}$ s$^{-1}$, rheopex thixotropic structures (viscosity $\eta \to \infty$) are formed. In the region of moderate shear rates $10^{0} \div 10^{2}$ s$^{-1}$, the structure induced by shear deformation begins to destroy (effective or structural viscosity). And finally, in the region of strong flow (shear rate more than $10^{2}$ s$^{-1}$) the induced structure is destroyed and the formation of dilatant (antithixotropic) structures is possible.

Based on a large volume of experimental data relating to polymers with different chemical structures, it was found [19] that the dependence of the highest Newtonian viscosity on the molecular mass $\eta_0$ (M) consists of two regions: at low M this dependence is almost linear, and in the high molecular mass region this dependence is a power law with a universal "scaling" exponent close to 3.4. Thus:

$$\eta_0 = \begin{cases} K_1 M^{\alpha} & \text{at } M < M_c; \\ K_2 M^{b} & \text{at } M > M_c, \end{cases} \qquad (1)$$

where: $K_1$, $K_2$ – empirical constants; the exponent $\alpha$ is close to 1, and $b \approx 3.4$.

Critical molecular weight $M_c$ in essence is the border between low molecular weight substances and polymers. The value of $M_c$ corresponds to

chains that are long enough so that their parts ("*segments*") can move independently of the others, generate entanglements and form a network. This value is a measure and reflection of the rigidity of the macromolecular chain [19].

Segmental movement is conditioned by the flexibility of the polymer chain, due to which one part of the macromolecule can move independently of the movement of other parts of the chain. Macromolecules, being in a melt or in a concentrated solution, come into contact with each other, forming a network *of* movable entanglements. You can enter a certain average length of the chain fragment between two adjacent engagements. This fragment of the chain consists of several segments if the macromolecule has sufficient flexibility. The knots of engagements are characterized by a certain lifetime, which is reflected in the corresponding relaxation times. If the deformation occurs slower than these relaxation times, then the chain moves "without noticing" these knots, i.e. the chains slide over each other, which mean that the polymer is flowing. If the deformation is faster compared to the relaxation times, then there is not enough time for the knots to decay. In this case, the polymer behaves like a crosslinked elastomer, and physical engagement is like stable chemical bonds, that is, the polymer cannot flow and goes into a forced high-elasticity (rubbery) physical (or relaxation) state. It should be borne in mind that the lifetime of an engagement is not a constant, but on the contrary, the lifetimes and the corresponding relaxation times are distributed over a wide time range [19].

With the formation of chemical bonds between chains, the distance between adjacent links decreases. This occurs during the crosslinking of the elastomer. Chemical bonds can be interpreted as engagements with an infinitely long lifetime [19]. The formation of permanent chemical bonds prevents from the flow because the chemically bonded chains cannot slide relative to each other. Moreover, the shorter the distance between adjacent bonds, the more rigid the material becomes, for example: weakly cross-linked rubber is a soft material, and strongly cross-linked rubber is hard ebonite.

To reveal the relationship between the processes taking place in the system (chemical reactions, phase separation) and the properties of the systems
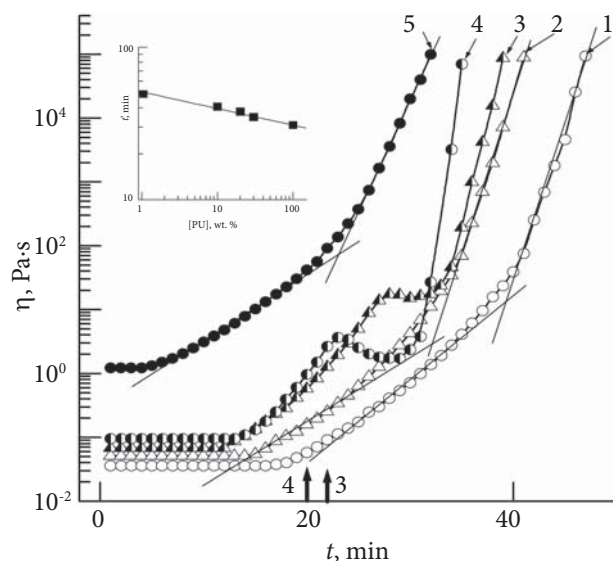
**Fig. 6.** Viscosity vs. time of reaction for PMMA (*1*), PMMA–PU blends of the compositions 90:10 (*2*), 80:20 (*3*), 70:30 wt. % (*4*) and PU (*5*). The inset shows the dependence of the time of gelation on PU concentration. $T = 80\,°C$, $\sigma = 130$ Pa

under study, rheokinetic studies of their formation were carried out.

In fig. 6 in semilogarithmic coordinates for PMMA, PU, and PMMA–PU mixtures of different compositions, the dependence of the viscosity $\eta$ on the reaction time $t$ is shown. As seen from this figure, under the selected reaction conditions for PMMA, PU, and a PMMA–PU mixture of the composition 90:10 wt. % on the dependence $\log \eta(t)$ after a certain induction period (longer for PMMA), two regions can be distinguished where the viscosity of the reaction system changes according to a relatively simple law [29]:

$$\eta = \eta_o \exp(k_\eta t), \qquad (2)$$

where: $\eta_o$ is the viscosity of the reaction mixture at the initial moment of time; $k_\eta$ is the rheokinetic constant characterizing the "viscometric" reaction rate.

At the same time, the total process of viscosity change during the formation of PMMA–PU mixtures of compositions 80:20 and 70:30 wt. % is extreme. In these systems, a fluctuation of the viscosity takes place: after a certain increase in the viscosity, it drops to a minimum (in the region presumably corresponding to the phase separation of the mixture), and then it rapidly increases up to the gel-point (Fig. 6, curves *3* and *4*). Such a course of the curves is in good agreement with

the literature data [10, 12, 29–31], where it is indicated that in the region of the amorphous phase transition as mixtures of polymers [30] and the forming two-component polymer system [10, 12, 29, 31], the dependences of viscosity on composition, time, or degree of conversion are extreme. The authors of [30] associate this effect with the achievement of the solubility limit of one polymer in another, i.e. with the beginning of the phase separation process.

The extreme dependence $\eta = f(t)$ or $\eta = f(\beta)$ ($\beta$ is conversion) for the PMMA–PU blends (80:20 and 70:30 wt. %) may be apparently explained by the reaction induced phase separation occurring in the blends of noncritical compositions for which these PMMA–PU blends are typical representatives. As was shown in [32], in these systems, phase separation begins at the early stages of reactions and occurs via two stages. The first stage occurs via the nucleation mechanism, while the second stage proceeds via the spinodal mechanism; subsequently, spinodal structures decompose to give rise to droplets, because these processes occur long before gelation. The maxima on the time dependences of viscosity probably correspond to the onset of phase separation occurring via the nucleation and growth mechanism, when the system transforms into the metastable state and a new phase appears in the form of spherical globules, whose concentration and sizes increase during the reaction. In this case, viscosity of the dispersion medium will be lower than viscosity of the homogeneous reaction mass at the time of its separation (in the region of maxima on the curves from Fig. 6); as a result, viscosity declines. Then, the system enters into the region of instable states and the second stage of phase separation begins via the spinodal mechanism to give rise to interrelated periodic structures; as a consequence, viscosity increases (a minimum on the time dependence of viscosity). Later on, the formed structures are fixed as a result of gelation.

The times of the onset of phase separation, as estimated via light scattering, are shown by arrows in Fig. 6. These times are smaller than the times of the onset of phase separation that were estimated through the rheological method. In other words, miscibility of the reaction mass improves during the application of a shear field. One of the possible causes of this effect may be related to destruction of nuclei of a new phase in the mechanical field.

Stability of the volume of new phase particles is determined by the ratio between interfacial surface energy and deformation energy [3]. In our case, under the chosen shear conditions ($\sigma$ = 130 Pa and $T$ = 80 °C) of the reaction blend PMMA–PU, destruction of the formed particles during amorphous separation is possible only at very low values of interfacial surface energy (probably lower than $\alpha \sim 10^{-3}$ N/m for the PMMA–PS blend; e.g., [33]). In this case, the destruction of aggregates composed of particles of the dispersed phase, that is, a decrease in the sizes of these structures, cannot be excluded. In addition, this circumstance should facilitate a shift in the time of the onset of phase separation to longer times. Note that, for the PMMA–PU blend (90:10 wt. %), no phase separation is observed by method of light scattering and there is no extremum on the time dependence of viscosity for this composition (Fig. 6, curve 2).

The inset in Fig. 6 presents the dependence of the time of gelation on the composition of the PMMA–PU blend, which may be described by the equation:

$$\log t^* = 1{,}724 - 0{,}112 \log c, \tag{3}$$

in which $t^*$ is the time of gelation (min) and $c$ is the concentration of PU (wt. fractions).

As a rule, homogeneous polymer blends obey the rule of logarithmic additivity of viscosity (geometric mean approximation) [34]:

$$\log (\eta) = \Sigma\, c_i \log (\eta_i), \tag{4}$$

where $\eta_i$ is the viscosity of components (Pa·s) and $c_i$ is the concentration of components (wt fractions).

Viscosities of the initial MMA–PU blends obey this rule (Fig. 7, curve 1). During the reaction, viscosities deviate from additivity (curves 2, 3). In the first case, the positive deviation may be associated with increases in the molecular masses of blend components (curve 2), while in the second case; S-shaped curve 3 characterizes now the heterogeneous (two phase) system.

Figure 8 shows the dependences of viscosity on the conversions of components, $\beta_{MMA}$ and $\beta_{PU}$. These dependences were plotted based on the kinetic data obtained for reactions of formation of every blend component [32].

Before proceeding to consideration of the experimental data on the dependences of viscosity on the conversions of components shown in Fig. 8, it is suitable to express our views about the origin of the gel effect observed in the polymerization of
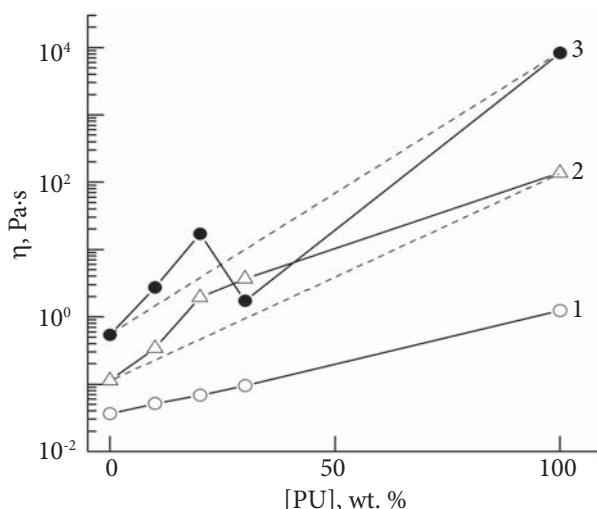


**Fig. 7.** Dependence of the viscosity of the reaction mixture on PU concentration at reaction times of 0 (*1*), 23 (*2*), 29 min (*3*)

MMA and the reaction of polyaddition giving rise to the crosslinked PU as well as in the formation of the PMMA–PU blend.

In the free-radical polymerization, in accordance with its idealized model, the molecular mass of the growing polymer remains invariable during the process and polymerization consists in the formation of new macromolecules of the same length, so that the concentration of the polymer in the reaction medium increases [19].

The gel effect in radical polymerization implies a sharp acceleration of the process once a certain conversion is attained. This phenomenon is
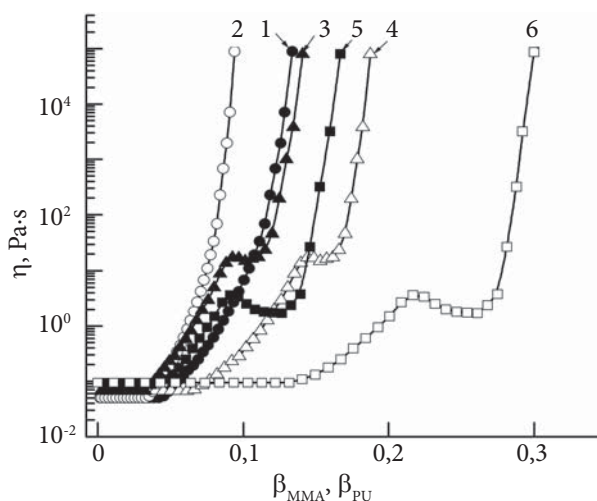


**Fig. 8.** Viscosity values of the PMMA–PU blends of the compositions 90:10 (*1, 2*), 80:20 (*3, 4*), 70:30 wt. % (*5, 6*) vs. conversions of MMA (*1, 3, 5*) and PU (*2, 4, 6*)

associated with structural rearrangement of the homogenous polymerizable system related to the formation of the network of fluctuation entanglements, when the critical concentration of the polymer and the corresponding change in the relaxation properties of the system (solution) are achieved [29]. In other words, in fact, this is the relaxation transition from the viscous flow state to the rubbery state. This gelation is commonly supposed to be physical [35], as opposed to the chemical gelation typical for obtainment of the network PU via the polycondensation mechanism. In this case, the polymer is formed via joining of ends of growing chains, so that its concentration remains equal to unity while the molecular mass of macromolecules changes. The process of gelation may be divided into two stages. At the first stage, the degrees of branching of macromolecules increase, but there is no common network covering the entire volume of the material. At the second stage, this network is formed. A similar analysis of the rheokinetics of network PU synthesis was described in [29].

The gel-point corresponds to the conversion calculated from a concentration of reactive groups close to $\beta^* = 0.71$. This estimate corresponds to the value of $\beta^*$ in terms of the Flory classical statistical theory of gelation. According to this theory, at this $\beta^*$ value, a continuous network of chemical bonds should be formed and the system loses flowability. In [36], a level of viscosity of $10^5$ Pa s was taken as the gel-point, with the corresponding value of $\beta^*$ being to 0.707. In our case, the conversion of PU at the gel point was close to the value of $\beta^*$ and amounted to 0.7, in accordance with the Flory theory, as opposed to the $\beta$ value, which was as low as 0.12 [10].

Thus, the gel point in the chemically crosslinked system is unambiguously determined by the time at which molecular mass tends toward infinity and viscosity increases unrestrictedly. As a result, the liquid–solid transition occurs in the crosslinked polymer.

Different mechanisms of formation of PMMA and PU and, accordingly, of their gelation processes have an effect on the gelation in the PMMA–PU blends on the whole. As follows from Fig. 8, conversion of the components at the gel-point increases with an increase in the concentration of PU in the blend. If there is a small difference in the values of $\beta^*_{PMMA}$ in the blends and that of the individual PMMA (0.12), then the values of $\beta^*_{PU}$ in the blends are much smaller than that for the individual PU (0.7). In addition, for the PMMA–PU blends (70:30 and 20:80 wt. %), the value of $\beta^*_{PU} > \beta^*_{PMMA}$, while for the PMMA–PU blends (90:10 wt. %), $\beta^*_{PMMA} > \beta^*_{PU}$. The position of curves $\eta(\beta)$ for the blends (Fig. 8) is fully determined by



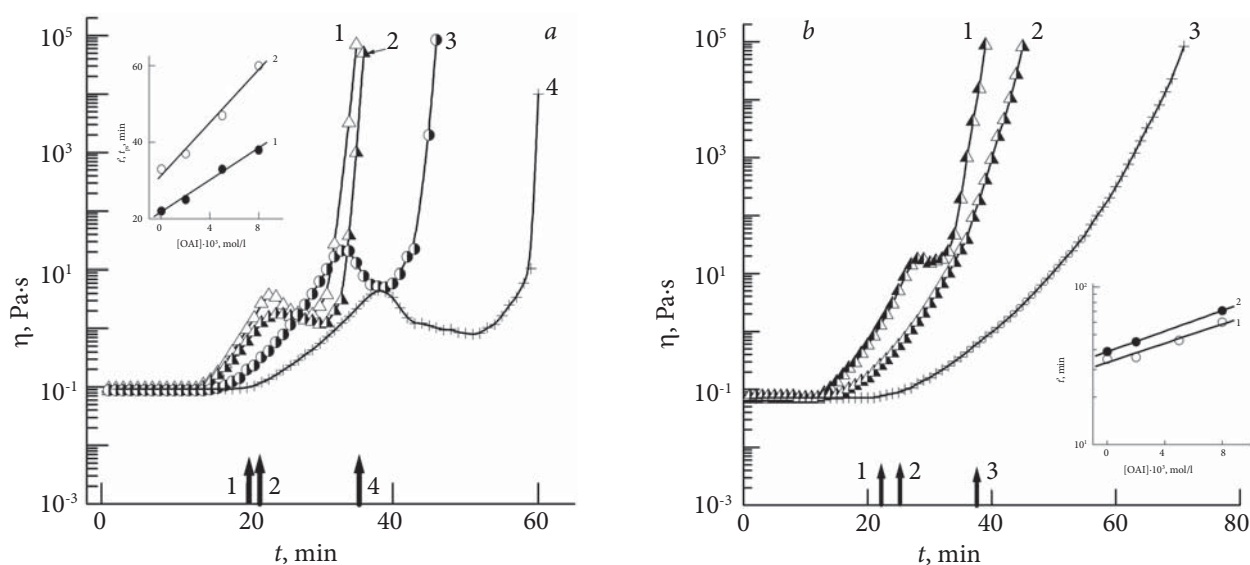**Fig. 9.** Viscosity versus reaction time for PMMA–PU mixtures of composition 70:30 (*a*) and 80:20 wt. % (*b*). *a*: [OAI] = 0 (*1*), 0.002 (*2*), 0.005 (*3*) and 0.008 mol/l (*4*), the inset shows the dependence of the time of the onset of phase separation (*1*) and gelation (*2*) on the concentration of OAI; *b*: [OAI] = 0 (*1*), 0.002 (*2*) and 0.008 mol/l (*3*), the inset shows dependence of the gelation time on the concentration of the OAI for the PMMA–PU blends of the compositions 80:20 (*1*) and 70:30 wt. % (*2*)

the kinetics of formation reactions of PMMA–PU blend components [32].

The observed tendency toward a gain in the conversion of MMA at the gel point relative to that of the individual MMA (12–17%) may be explained by a change in the critical concentration, at which the net-work of PMMA entanglements appears in its own monomer. The effect of PU particles on the critical concentration of PMMA is related to a change in the molecular mass of PMMA in the blends relative to the molecular mass of the individual PMMA [9]. In addition, PU particles may be regarded as a semi-IPN, where PU serves a dispersion medium and a certain amount of PMMA occurring in this phase serves as a dispersed phase. A decrease in the conversion of PU at the gel point from 70% for the individual PU to 7–30% in the blends may be rationalized by topological constraints of the structural network of PMMA particles included in the PU phase.

The effect of of oligomeric azo-initiator (OAI) on the rheokinetic behavior of blends of various compositions is shown in Fig. 9. When the OAI is introduced into the PMMA–PU blend (70:30 wt. %) and its amount increases, the time of gelation $t^*$, and the time of the onset of the phase separation $t_{ph.s}$, increase (Fig. 9a, curves *2–4*). In this figure $t_{ph.s}$ are shown by arrows (as in Fig. 6).

In this case, the rheokinetic curves follow the extremum pattern that is related to fluctuations of viscosity. The dependences of $t^*$ and $t_{ph.s}$ on the concentration of the OAI for the given system are shown in the inset in Fig. 9a. It is seen that these dependences are satisfactorily described by simple linear functions and may be shown by the following analytical expressions:

$$t_{ph.s} = t_{ph.s0} + b_1 c_{OAI} \qquad (5)$$
$$t^* = t^*_0 + b_2 c_{OAI}, \qquad (6)$$

where: $t_{ph.s}0 = 22.4$ min and $t = 31.6$ min are the time of the onset of phase separation and the time of gelation of the initial PMMA–PU blend (70:30 wt. %), respectively; $c_{OAI}$ is the concentration of the OAI (mol/L); and $b_1 = 2.01$ and $b_2 = 3.32$ min L/mol are coefficients that are probably related to the achievement of a certain critical length of the growing chain and/or the concentration of the polymer being formed. As follows from the above data, such parameters of the in situ formation of the binary matrix PMMA–PU and the time of phase separation and the time of gelation are interrelated and depend on the concentration of

azo-initiator in a simple manner. This finding is likewise valid for temperature dependences of the mentioned parameters obtained with the use of nanofiller as a compatibilizer [12]. However, in the latter case, there was not extremum change in viscosity of the blend formed in situ. Fig. 4b shows the time dependence of viscosity for the formation of the PMMA–PU blend (80:20 wt. %) containing different amounts of the OAI. For this system, viscosity fluctuations occur only in the case of the initial blend (curve *1*). When various amounts of the OAI are used, this effect does not manifest itself on rheokinetic curves (curves *2*, *3*), a result unlike that attained for the blend containing a higher amount of PU (Fig. 9a). In this case, determination of the time corresponding to the onset of phase separation in the PMMA–PU blends (80:20 wt. %) containing the OAI via the rheological method becomes a problem. At the same time, as was noted above, for the PMMA–PU blends (70:30 wt. %) without the OAI and with the OAI, the plot η = f(t) shows a well-defined extremum pattern (Fig. 9a) and the dependence of the time of the onset of phase separation, as estimated from these curves, on the concentration of the OAI may be described by Eq. (5). Possible causes of this behavior of PMMA–PU blends will the subject of further studies.

The inset in Fig. 9b shows the dependence of the time of gelation on the amount of the OAI for the PMMA–PU blends of various compositions. It is seen that the dependences are symbate. This finding implies that the effects of the oligomeric
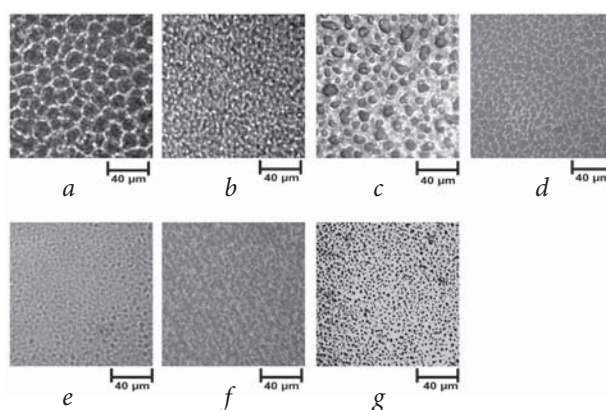


***Fig. 10.*** Micrographs of in situ formed PMMA–PU blends of the compositions 70:30 (*a–c*), 80:20 (*d–f*), and 90:10 wt. % (*g*) taken at concentrations of the OAI of 0 (*a, d, g*); 0.002 (*b, e*); and 0.008 mol/l (*c, f*)
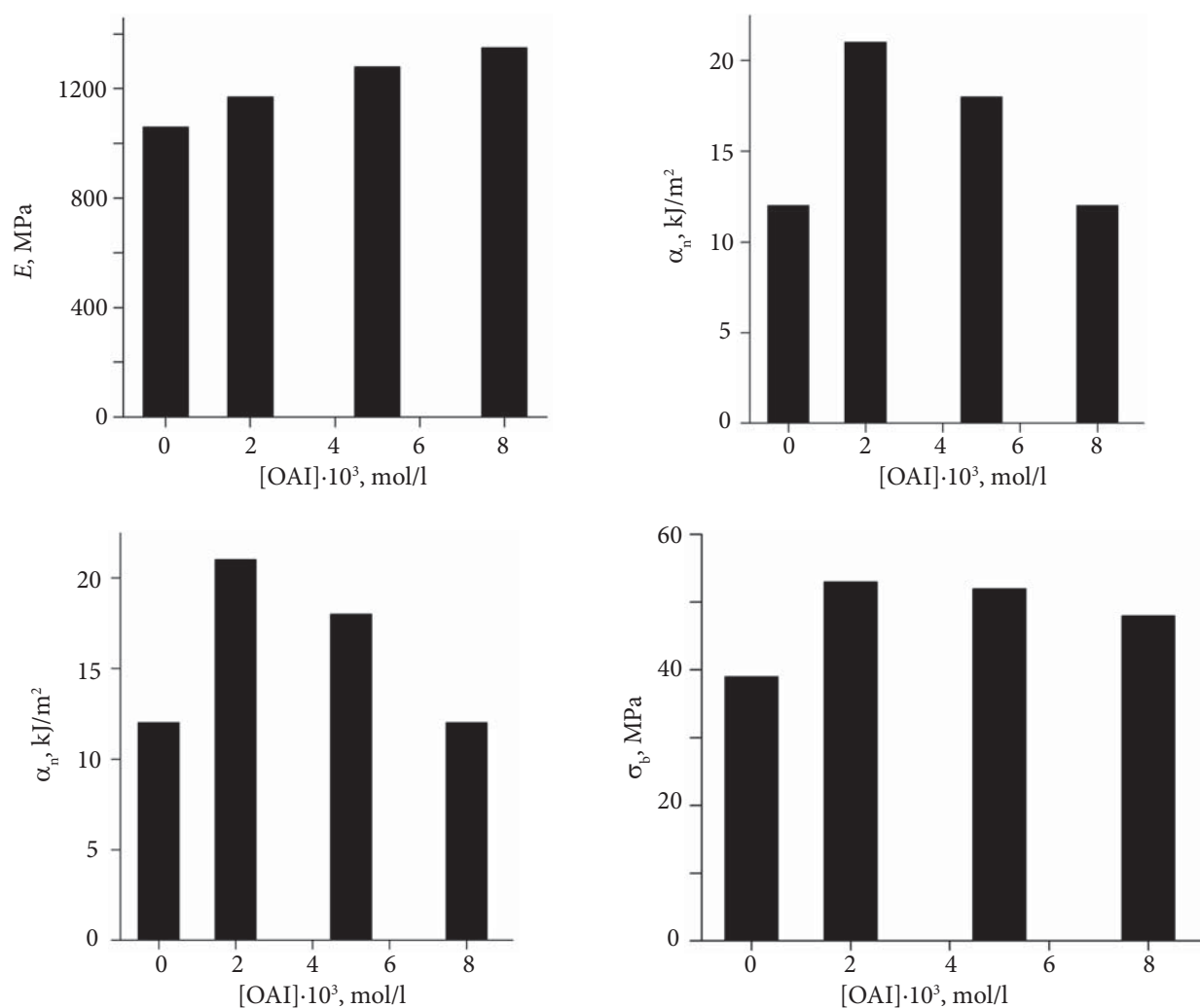
***Fig. 11.*** Elastic modulus (*a*), impact strength (Izod's notched test) (*b*), ultimate strain (*c*), and ultimate strength (*d*) of the PMMA–PU blend with a composition of 70:30 wt. %) vs. concentration of the OAI

azo-initiator on the formation of PMMA–PU blends of the studied compositions follow a common mechanism.

The introduction of the OAI into the initial reaction mixture causes marked changes in the morphologies of the formed systems, which are shown in Fig. 10 [32]. In each case, the domain structure of the blend is observed; for the blends with a higher amount of PU (30 wt. %), the sizes of domains are larger than those for the blends with a smaller amount of PU (20 wt. %), regardless of the presence or absence of the OAI. This effect may be due to a higher rate of phase separation for the blend containing a higher amount of PU [32], as a result of higher rates of both reactions (polymerization and urethane formation). The morphology presented in Fig. 10 for the PMMA–PU

blends (70:30 and 80:20 wt. %) without the OAI and in the presence of 0.008 mol/L OAI is typical for systems in which phase separation is completed at intermediate stages of spinodal decomposition [38]. This domain structure in the studied systems is related to the fact that phase separation in them proceeds prior to gelation and that decomposition of interrelated spinodal structures accompanied by the formation of droplets may occur [39, 40]. The final structures of the blends of both compositions with a concentration of the OAI 0.002 mol/L are similar to those that are formed in blends at the final stages of phase separation, where the growth of spinodal structures occurs without the transition to coalescence and nucleation [39, 41]. As a result, a finer final structure containing domains of smaller sizes is formed than those in the blends

without the OAI and at a higher content of the OAI (Fig. 10). Different morphological structures of the blends containing different amounts of the OAI are related to the carrying out conditions of the chemical reactions of blend component formation and the phase separation induced by these reactions [32].

The observed morphology of the formed blends should affect the mechanical characteristics of the final materials. It was found that, when 30 wt. % PU was introduced into PMMA, the elastic modulus decreased from 2500 to 1060 MPa, ultimate strain increased from 2 to 16 %, impact strength increased from 8.8 to 12.0 kJ/m², and breaking strength decreased from 51 to 39 MPa. Figure 11 plots the mechanical characteristics as functions of the concentration of the OAI for the PMMA–PU blends (70:30 wt. %).

When the blend of this composition is formed in the presence of the OAI, the best mechanical behavior is featured by the blend containing 0.002 mol/L OAI. This composite material is



*Fig. 12.* Dependence of the viscosity of a suspension of hydrophobic aerosil ($A_m$) on the shear rate (or stress) and the viscosity of the PMMA–PU–$A_m$ on the reaction time (details in the text)

characterized by even higher ultimate strain (20 %), higher impact strength (21 kJ/m²), and a breaking strength of 53 MPa. However, although the elastic modulus insignificantly increases (to 1170 MPa), its remains lower than that for the individual PMMA (2500 MPa). Hence, the mechanical characteristics of the blends are in good agreement with the optical microscopy data, which indicate that the blend containing 0.002 mol/L OAI is a more stable system with the best dispersive ability of the components. It should be emphasized that the value of impact strength for this composite material (21 kJ/m²) is on the same order of magnitude as those in organic glasses based on a partially crosslinked MMA that are applied in aviation equipment under sea climate conditions (23–25 kJ/m²) [42].

Thus, our studies have shown that there is a relationship between the chemical kinetics, phase separation, and structural transformations, as registered by a change in viscosity of the reaction mass up to the gel-point, during the formation of the composite material. All these processes govern the morphology of the final products and their properties.

## Conclusions

To clarify this thesis, Fig. 12 compares the dependences of the viscosity of the dispersion of aerosil $A_m$ in an oligomeric medium on the shear rate (or stress, dotted line) (upper part of the figure) and viscosity of the PMMA–PU–$A_m$ blend on the reaction time at constant stress (lower part of the figure). For convenience of comparison, the arrows in the figure show the directions of decreasing the shear rate (or stress) and increasing the reaction time.

In the kinetic part of Fig. 12 the shear rate $\gamma = \sigma/\eta$ ($\eta$ is the effective viscosity) decreases in the direction of increasing viscosity and, when approaching the gel-point $t^*$, reaches very low values, since in the vicinity of $t^*$ $\eta \to \infty$. Consequently, during the reaction formation of the PMMA–PU–$A_m$ composition, the conditions of the shear deformation of the system correspond to those at which the self-organization and fixation of the coagulation rheopex structure of the nanofiller is possible in the PMMA–PU matrix at the moment when it reaches very high viscosity values (gel-point), and the diffusion processes will practically
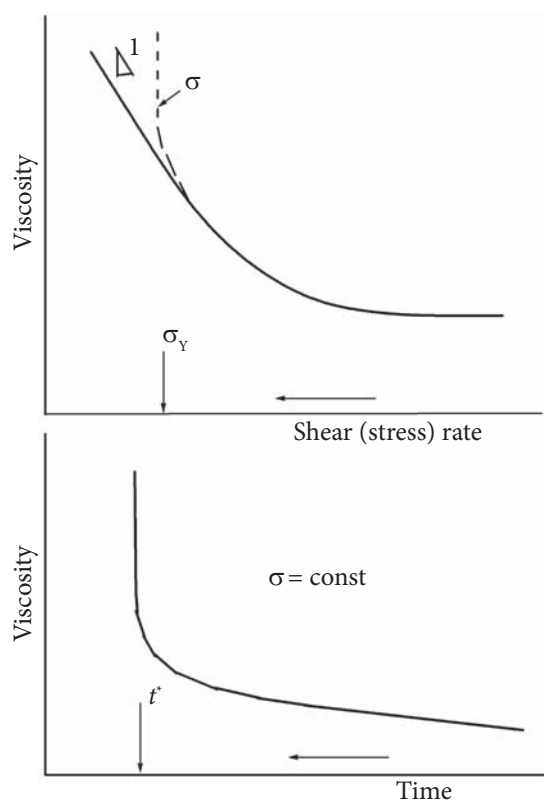
be frozen. The behavior of such a structure in a shear field is model and is indirectly illustrated in the upper part of Fig. 12. Whether this structure will be bulky (the so-called infinite cluster) or such a structure will be located in micron-sized clusters will depend on the concentration of the blend components and on the ratio of the reaction rates of both components of the mixture after their phase separation.

We have considered some problems of the structure formation of a nanofiller in a medium (matrix), which is a simple viscous oligomeric liquid. A more complicated situation occurs when the matrix is a two-component viscoelastic polymer medium, the components of which are thermodynamically incompatible and, thus, the matrix becomes actually three-component (the third component is a transitional diffuse interphase layer with properties different from the properties of both components). In this case, one of the important problems in modeling the structure formation will be the identification of the distribution of the nanofiller and its concentration in each component. Since it is in a loosened interfacial layer with a large specific free (unoccupied) volume that the formation of a coagulation rheopex structure of a nanofill initiated by an ultralow shear rate with a geometry determined by the geometry of the transition interfacial layer is more likely.

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РЕОКІНЕТИЧНІ ТА МОРФОЛОГІЧНІ ОСОБЛИВОСТІ РЕАКЦІЙНОГО ФОРМУВАННЯ ПОЛІМЕРНОГО КОМПОЗИТНОГО МАТЕРІАЛУ НА ОСНОВІ УДАРОМІЦНОГО ПОЛІМЕТИЛМЕТАКРИЛАТУ. МОДЕЛЬНІ ТА ПРИКЛАДНІ АСПЕКТИ

На підставі експериментальних даних із реології дисперсій гідрофобного аеросилу ($A_м$) у низькомолекулярному вуглеводневому середовищі розглянута можливість використання для таких дисперсій «міцелярного» механізму формування об'ємної структури. Запропоновано модель такої структури до, в процесі і після зсувного деформування, що дає змогу інтерпретувати експериментальні дані з реології дисперсних систем. Результати дослідження реокінетики подані по-новому – з погляду самоорганізації під впливом зсувного поля. Систему ПММА–ПУ–$A_м$ розглядали як полімерний композит (ПК), у якому матрицею є поліметилметакрилат (ПММА), що піддається модифікації, а дисперсною фазою – суміш поліуретану (ПУ) з $A_м$. Показано, що при реакційному формуванні композиції ПММА–ПУ–$A_м$ умови зсувного деформування системи відповідають таким, за яких можлива самоорганізація і фіксація коагуляційної реопексної структури нанонаповнювача в ПК у момент досягнення дуже високих значень в'язкості (гель-точки), коли дифузійні процеси практично будуть заморожені. Передбачені два концентраційні діапазони аеросилу $A_м$ (до і після порога перколяції), де можна очікувати посилення механічних характеристик ПК. Встановлено взаємозв'язок реокінетики формування *in situ* суміші лінійний ПММА–зшитий ПУ за наявності різної кількості олігомерного азоініціатора, що містить фрагменти поліуретанового ланцюга і групи, здатні ініціювати радикальну полімеризацію метилметакрилату, з процесом фазового поділу, морфологією і механічними властивостями кінцевих продуктів. Показано, що часи фазового поділу і гелеутворення взаємопов'язані й перебувають у простій залежності від концентрації азоініціатора. Такий ініціатор впливає на структурно-реологічні переходи в системі і призводить до утворення морфології з дрібнішими доменами. Найбільш стабільною системою з найкращим диспергуванням поліуретану в поліметилметакрилаті є суміш, яка містить 0.002 моль/л азоініціатора, і яка має покращені механічні властивості та підвищену ударну в'язкість.

*Ключові слова:* реокінетика, в'язкість, структуроутворення, зсувна деформація, реопексія, гелеутворення.