NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

Influence of polymerization factors on the relaxation behavior of statistical acrylate polymers

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Experimental data obtained using the method of dynamic mechanical relaxation spectroscopy and internal friction spectroscopy in obtaining temperature-frequency dependences of the vibrational process in statistical latex polyacrylates in comparison with polyacrylates of free-radical type are analysed. The results of studies of relaxation behaviour of latex acrylate polymers used as a binder in composite coatings on surfaces of different chemical nature, structure and pattern are summarized in order to elucidate the temperature regions of their elastic and inelastic (dissipative) properties at temperatures from -150 to +200oC. The prospects of using the method to describe physical and mechanical properties of acrylate copolymers of different monomeric composition are shown.

Keywords: relaxation behaviour; structure; internal friction spectrum; temperature-frequency dependence; dynamic relaxation spectroscopy; latex polyacrylate; latex polyacrylate

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INTRODUCTION.

GENERAL IDEAS ABOUT THE METHOD OF DYNAMIC MECHANICAL RELAXATION SPECTROSCOPY OF DISSIPATIVE PROCESSES IN POLYMERS.

The method of dynamic relaxation spectroscopy of dissipative phenomena based on the reaction of structural elements of the material under study to external mechanical action is based on the processing of parameters of transient processes from a thermodynamically and mechanically nonequilibrium state to an equilibrium state [1, 2].

The type of transient process depends on the type of external influence that takes the material structure out of equilibrium. For statistical methods, kinetic dependencies of stress or strain are used as the transition function of the process. With dynamic periodic sinusoidal influences, the dependence of the logarithmic decrement of the oscillatory process on temperature or on the frequency of external influence is analyzed, followed by recalculation of the latter into the tangent of the mechanical loss angle and construction of the internal friction spectrum [3].

The study of dissipative phenomena through the analysis of internal friction spectra in materials of different chemical compositions shows that the temperature dependence of the tangent of the mechanical loss angle can exhibit both a monotonically increasing background of dissipative losses (with increasing temperature) and loss peaks appearing on the increasing background.

For polymeric glass-forming materials in the temperature range of transition from solid to highly elastic state (i.e., at temperatures above the glass transition temperature), not an increasing background of internal friction is observed, but a loss peak. The increasing background in this case is observed at temperatures lying in the region above the glass transition temperature and below the temperature of transition of the material from the highly elastic state of the glass-forming system to the viscous-flow state.

For high-molecular polymeric materials in the glass transition temperature region, a decrease in the elastic modulus value to the elastic modulus value of the highly elastic state is also observed, which is reflected in its temperature dependence as a kink. This kink corresponds to the difference between the elastic moduli of the solid aggregate and highly elastic states. Further temperature increase to the transition temperature to the viscous-flow state leads to a second temperature zone of intensive decrease in the elastic modulus.

The mobility of some structural elements of the system relative to others is a dissipative process, i.e., it is accompanied by the dissipation of part of the external impact energy in the given system. Therefore, it can be used as a characteristic of the dissipative process. For condensed systems, the most intensive dissipative processes are those observed in temperature ranges where the system transitions from one aggregate state to another, and their main characteristic is time. For relaxation processes, this is the relaxation time.

The methodology of dynamic relaxation spectroscopy of dissipative phenomena when manifestation of reactions of structural elements of the studied polymeric material is highly informative, as it allows tracking the relaxation behavior of macrochains and macrolinks to external mechanical influence of various factors [1].

This part of the review presents the perspective of using the dynamic relaxation spectroscopy methodology to analyze the relaxation structure and morphology of latex polymers obtained using homogeneous (statistical) emulsion polymerization, based on the study of dissipative processes in a wide temperature range from –150 to +100 °C.

Interest in latex polymers is due to the fact that latexes are widely used for preparing water-dispersion polymer coatings for various purposes, in which the polymer acts as a polymeric binding component of the composite material (including pigments, fillers, modifiers, functional additives). The main advantage of water-

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[1] It should be noted that the application of dynamic mechanical relaxation spectroscopy method, used by the authors for polymer systems, is also highly informative for studying the structure of solids and their surface layers [see e.g. 37]

dispersion polymer coatings is the absence of organic solvents, which ensures non-toxicity, explosion and fire safety of their preparation and application processes, and relatively low cost. Common latex polymer binders used in water-dispersion polymer coatings are copolymers of alkyl(meth)acrylates with styrene, methacrylic acid, and other monomers [4-7].

The main indicator characterizing the application area of a latex polymer is the minimum film formation temperature (MFFT). Below the MFFT, latex does not form monolithic films. An aqueous polymer dispersion with such a latex polymer does not form coatings with high hardness, adhesion, and wear resistance. Although latex films and coatings are formed at a minimum film-forming temperature of ~5 C, dispersions with a higher MFFT are used to obtain water-dispersion latex coatings [4-7].

The required characteristics of films and coatings determine the range of pigments, modifiers, and functional additives used in the preparation of water-dispersion polymer coatings. In this regard, this review presents data on the changes in the relaxation behavior of latex polymers when modified with various compounds, including water-soluble phthalocyanines, dyes, low-molecular-weight polyacrylates, solid metal powders, as well as under the influence of radiation.

1. STRUCTURAL FEATURES OF LATEX POLYMERS OBTAINED BY EMULSION POLYMERIZATION.

The morphology and structure of polymer particles (50-500 nm) are formed during latex polymerization, when the resulting macromolecules are mobile due to the presence of monomer, whose concentration is determined by thermodynamic equilibrium conditions and monomer content in the reaction system. The phase interface, where macromolecules form in particles, and then the particles themselves, is an important factor for the conformation of polymer molecules, their packing, and topographic distribution under the influence of forces acting at this interface (dispersive, polar, chemical).

Latex polymerization begins with the nucleation of polymer-monomer particles in the aqueous phase, usually in an emulsion of monomer in water with monomer content in the reaction mass of 15-30%. The nucleation zones can be emulsifier micelles [7]; molecular solution of monomer in water [8, 9]; monomer microdroplets [10]. This depends on the molecular solubility of the monomer, its ratio to the colloidal solubility in emulsifier micelles, the type of emulsifier and initiator, and the intensity of hydrodynamic effects on the reaction system. As polymer-monomer particles grow, depending on the nature of the monomer, formulation, and process method, various physicochemical changes may occur in them in the orientation of macromolecules; phase separation and inversion, formation of transition layers between them, flocculation of primary particles, heteroflocculation, coalescence. As a result of such changes, the structure of the final latex particles is formed.

The formation of primary dispersion particles depends on the hydrophilic-hydrophobic properties of the monomer/polymer. These issues are especially relevant in the case of alkyl(meth)acrylic monomers, which are characterized by relative solubility in the aqueous phase, which determines the nucleation of polymer-monomer particles in the aqueous phase and the mechanism of the polymerization process depending on its magnitude. Thus, the solubility of one of the common acrylic monomers (methyl methacrylate) is 1.5%, while acrylates such as (meth)acrylic acids are completely soluble in warm water.

The process of emulsion polymerization of acrylic monomers in the aqueous phase is carried out by the formation of polymer particles during the addition of monomer molecules to the radical molecule of a water-soluble process initiator at the first stage and then to the radical end of the macrochain in the aqueous phase or already with participation in the volume of the polymer particle.

To increase the stability of monomer emulsions, surfactants are added to them. Since water serves as the reaction medium, water-soluble initiators are used. The concentration of initiator and surfactants used in the polymerization process determines the particle size on the one hand, and on the other hand, the stability of the forming polymer latex particles.

Quantitative description of latex polymerization based on the Smith-Ewart theory [39] refers to the "post-micellar" stage, when there are no inactive micelles in the system anymore, and the content of polymer-monomer particles is constant. The main principle of the theory is that only one macroradical can form in a polymer-monomer particle. A second radical penetrating the particle immediately or after attaching a small number of monomer molecules interacts with the macroradical, leading to chain termination. Polymerization in the particle resumes after the next free radical enters it. This polymerization mechanism determines the fulfillment of a specific requirement for the hydrophilicity of the monomer participating in the latex process in the aqueous phase. Highly hydrophilic monomers include alkyl(meth)acrylates in combination with other comonomers, which can provide a variety of properties for the polymer based on them.

In accordance with the radical mechanism of emulsion (including emulsifier-free) polymerization carried out in the presence of a radical initiator [8-10], the synthesized latex copolymers are characterized by high molecular weight ($\sim 10^{6}$). Taking into account the radical mechanism of polymerization of alkyl(meth)acrylates in the presence of persulfate initiator without the participation of any crosslinking agents, based on the chemical structure of the polymer chain, it is possible to predict and analyze physical relaxation transitions in a linear polymer.

The structure of the polymer is determined by the reactivity of the selected monomers and their relative solubility in water [11, 12]. Typically, the emulsion polymerization method leads to the formation of a statistical copolymer. However, using the peculiarity of the process of macromolecule formation in latex systems, it is possible to regulate the polymer structure and particle morphology and, thus, influence the properties of latex films without changing the composition of the original components. This can be achieved by varying the sequence of introducing monomers or their combinations into the reaction, one of which is the polymerization of monomers on already formed particles of seed latex, the so-called seed method of emulsion polymerization.

Large surface areas and a higher surface-to-volume ratio, which is characteristic of polymerization involving latex particles, usually increase the process rate due to a larger reaction surface, and also lead to a significant influence of surface properties on their structure [7-10]. The dispersity of materials is a key factor for surface effects [2].

The effect of the monomer composition of latex polymer determines its film formation temperature and the size of latex particles during their formation process. Increased interest in alkyl(meth)acrylic latexes is caused by their low film formation temperatures. Compositions consisting of several monomers are used to obtain latexes. The composition determines the physicochemical, adhesive, performance, and decorative properties of latex polymers.

2. RELAXATION BEHAVIOR OF LATEX POLYMERS AND THEORETICAL DESCRIPTION OF ELASTICITY: DISSIPATIVE PROCESSES IN THE GLASS TRANSITION TEMPERATURE REGION.

The consideration of the relaxation behavior of polymers, particularly latex polyacrylates, is based on general concepts about the relaxation structure of the polymer.

It is known that the structural feature of a polymer is due to the presence of two types of structural elements (chain units and the chains themselves), which differ significantly in mobility. In the case of highly elastic polymers, which include polyacrylates, this manifests in the rearrangement of units, i.e., changes in chain conformation with temperature changes. Analysis of the relaxation mobility of chain

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[2] Surface effects related to polymerization on surfaces of different composition and structure (for example, during film formation on a metallic substrate) also have a significant influence on the structure and properties of latex polymer [34-36].

units and/or the chains themselves using the method of relaxation spectroscopy, based on the analysis of the response of individual structural-kinetic elements of polymer systems to external influences that take them or the entire system out of a state of mechanical and thermodynamic equilibrium [14-16], can provide insight into the structure of the forming particles and polymer. Due to their large size, the mobility of polymer chains is low. Therefore, temperature changes in highly elastic polymers mainly cause rearrangement of units, i.e., changes in chain conformation. It follows that the introduction of ingredients active to the functional groups of the polymer in a composite system can cause changes in the conformation of polymer chains.

Figure 1 presents the analysis of internal friction spectra λ (a, c) and temperature dependence of frequency ν (b, d) of the oscillatory process excited in statistical copolymers of styrene St-methylmethacrylate MMA - butylacrylate BA - methacrylic acid MAA with glass transition temperatures of 5 and 15 ^{0}C (hereinafter referred to as AK1 $_5$ and AK2 $_{15}$ respectively). The experimental data were obtained using the DMRT method [14, 16-19].

Fig. 1

The dependencies λ = *f* (T) and ν = *f* (T) indicate significant structural microheterogeneity of the elastomer AK1 $_5$ in comparison with similar dependencies for the elastomer AK2 $_{15}$ (Fig. 1). The subscript in the polymer designation corresponds to its glass transition temperature.

Each peak of local dissipative losses ($\lambda_{i\,max}$), identified on the spectra λ = *f* (T), characterizes the temperature range of local freedom of displacement of a particular structural element near the position of local mechanical and thermodynamic equilibrium without breaking the main chemical bond of the structure as a whole.

The spectrum λ = *f* (T) of the elastomer AK1 $_5$ represents a combination of two local dissipative processes: α– and β–processes.

Simultaneously, the temperature dependence of frequency ν = *f* (T) of free damping oscillations of external dynamic impact becomes more complex, which displaces structural elements of all structural-kinetic subsystems forming the system from the state of mechanical and thermodynamic equilibrium.

Table 1 presents the physical-mechanical and physical-chemical characteristics of systems AK1 $_5$ and AK2 $_{15}$ respectively.

Table 1

The obtained experimental results show that the intensity of the α–dissipative process in the AK2 $_{15}$ system is significantly higher than in the AK1 $_5$ system.

In the elastomeric system AK1 $_5$ a β–dissipative process is observed. This process has a different internal friction mechanism from the α–process, which follows from the theoretical analysis of the temperature dependence of frequency.

In addition, in the AK1 $_5$ system, a weakly expressed μ-dissipative process is observed at negative temperatures.

The elastomeric system AK2 $_{15}$ is more structurally homogeneous and is characterized by only one dissipative α-process and an extremely weakly expressed μ-process in the temperature range of ~ -150 ^{0}C.

Figure 1 shows a significant difference in the intensity of the α-relaxation process of AK1 $_5$ and AK2 $_{15}$, which correlates with their glass transition temperature, and the decline of the frequency dependence responsible for their modulus defect and elastic properties of the polymers. Also, the spectrum of AK1 $_5$ has a temperature range from -12 to -4 ^{0}C, responsible for the β-relaxation process, which characterizes the mobility of the polymer macrochain units.

From the nature of the temperature dependencies of the frequency ν = *f* (T) of free damped oscillations of external dynamic action, which take the structural elements of all structural-kinetic subsystems forming the system out of mechanical and thermodynamic equilibrium (Fig.1 b, d), follows the relaxation mechanism of dissipative processes occurring in AK1 $_5$ and AK2 $_{15}$.

In the article [21, 22], a theoretical approach is proposed for describing the dissipative processes occurring in polyacrylates under dynamic mechanical load excitation depending on temperature, which is based on the following consideration.

According to works [21, 22], the comparison of continuous relaxation time spectra in latex polymers is based on the selection of a phenomenological model of a standard linear body to confirm experimental data on the modulus defect, corresponding to the manifestations of dissipative losses on the spectra of their temperature dependence and characterizing the inelastic properties of the polymer material. The presence of a modulus defect manifests as a sharp, abrupt decrease in the elastic modulus with increasing temperature of the studied latex polymer system.

In the temperature domain of the internal friction spectrum under free damped oscillations, a peak of α-relaxation losses is observed, and on the corresponding temperature-frequency dependence, there is a sharp decrease in the frequency of free oscillations ν_i,: from $\nu_{\mathrm{i\,max}}$ to $\nu_{i\,min}$.

For the relaxation process described using the model representations of the standard linear solid [14], the modulus defect ΔG is presented as:

$$\Delta G = (G_{T1} - G_{T2}) / G_{T1} \qquad (1),$$

where G_{T1} and G_{T2} - the value of the shear modulus at temperature, respectively. The inequality $G_{T2} < G_{T1}$, is maintained since $T_2 > T_1$.

It is known from the literature [23, 24] that in a polymer, considered as a solid condensed system, two types of mechanical stress waves can propagate: longitudinal C_p and transverse C_s, where $C_p > C_s$.

Both types of waves are related to the shear modulus. Their relationship with the frequency of the oscillatory process ν is the same, which allows us to consider the frequency dependence of the modulus defect ΔG using the example of a transverse shear wave, where

$$C_s = \sqrt{G/\rho} \quad \Rightarrow G = \rho\, C_s^2 \qquad (2),$$

where G – shear modulus, ρ - density of the system under study.

For linear waves, there is a relationship:

$$\nu = C_s / l \qquad (3),$$

where l -wavelength and internal $\lambda = \upsilon\Theta = \upsilon/f = 2\pi\, \upsilon/\omega$; Θ – period of the process oscillations, υ – linear velocity, ω - angular velocity .

Taking into account equations (1-3), we get:

$$\nu\, l = \sqrt{}G/\rho \Rightarrow G = \rho\, \nu^2 l^2 \qquad (4).$$

Considering that in the temperature range where the α-relaxation process occurs, we can neglect insignificant changes in ρ and λ , then from equation 4 it follows:

$$\Delta G = (G_{T1} - G_{T2}) / G_{T1} \approx \rho\, l^2 (\nu_{T1} v\, \nu_{T2}) / \rho\, l^2 \nu_{T1} = (\nu_{T1} v\, \nu_{T2}) / \nu_{T1} \qquad (5).$$

Based on relation (5), the authors conclude that the modulus defect, which characterizes relaxation phenomena in the polymer and its elastic properties, can be described by a change in the frequency of the oscillatory process, which is experimentally controlled in the method of dynamic mechanical relaxation spectroscopy (DMRS).

Taking into account the relationship between the elastic modulus of the material and the oscillation frequency of the damping process of the system returning to equilibrium [14, 17-19], the correlation dependence "elastic modulus - oscillatory process frequency" is used for theoretical analysis of the width of the continuous relaxation time spectrum.

The theoretical modulus defect of internal friction is calculated as the difference in frequencies at the intersection points of tangents to the linear sections of the experimentally established temperature dependencies of the oscillatory process frequency.

In the work [20], the assessment of the modulus defect characterizing the inelasticity of the polymeric material was carried out based on the analysis of temperature-frequency dependence in the temperature range from -100 to +100 °C in the mode of free damping torsional oscillations at a frequency ν on a horizontal torsional pendulum

A sharp decrease in the shear modulus in both cases indicates the destruction of the cross-linking of the relaxation structure and a significant change in the modulus defect $\varDelta G$, which is estimated by the segment cut off by tangents to the curve of the temperature dependence of the oscillatory process frequency. The value ΔG is proportional to the ratio $(\nu_2 - \nu_1)/(T_2 \mathrm{T}\ T_1) = \varDelta \nu / \varDelta T$, where ν_1, ν_2 are the values of the oscillatory process frequency corresponding to the end and beginning of the curve decline at temperatures T_1 and T_2 [14, 20].

Based on experimental data on internal friction spectra in polyacrylates (Fig. 1 a, c), the activation energy of dissipative α-, β-, μ-processes was calculated, leading to conclusions about the dissipation mechanism and their structural nature (table).

Taking into account the presented theoretical concepts and experimental curves of temperature-frequency dependencies (Fig. 2 b, d), the values of the polymers' modulus defect corresponding to local dissipative processes were calculated (Table 1).

Based on the above, the authors [14, 20] conclude that the data obtained using the DMTA method provides sufficiently complete information about the relaxation structure of polymers.

Taking into account this theoretical approach, it is possible to describe the relaxation behavior of polyacrylates and its changes under the influence of various factors.

It was of interest to compare the structural-morphological characteristics of the studied statistical latex polyacrylates with statistical polyacrylate obtained by free-radical homogeneous polymerization. As the latter, the most well-known polymer polymethyl methacrylate (PMMA) was chosen, studies of which showed its amorphous and domain structure related to the conformations of its macromolecular chains [23].

Fig. 2a shows the internal friction spectrum $\lambda = f\left(T\right)$ of statistical free-radical type PMMA, which indicates the manifestation of three most pronounced local peaks of dissipative losses in the temperature range from -200 to +200 ^{0}C [19, 23, 24].

Fig. 2

The most intense of all relaxation transitions detected in the PMMA spectrum is the α -transition, which represents the response of segmental mobility of its structural subsystem to external periodic force, which correlates with the internal friction spectra data of latex polyacrylates AK1 $_5$and AK2 $_{15}$in Fig. 1a.

It is evident that the glass transition temperature region of highly elastic latex polymers lies in a much lower temperature range, while the glass transition temperature region corresponds to the generally accepted PMMA glass transition temperature of ~100 ^{0} °C. At the same time, a much higher intensity of the dissipative process is detected, indicating much higher segmental mobility of the PMMA structural subsystem compared to highly elastic latex polymers.

Unlike latex polymers, the PMMA spectra (along with the α -maximum) show another well-defined maximum of mechanical losses β of the dissipative process. In works [19, 24], this maximum is associated with local mobility of monomer units in the macromolecule chain, however, the chemical nature of this unit is significantly more complex, as it includes two structural groups: the group $-CH_2$ (β_{CH_2} -process) and the group consisting of methyl and ester structural components ($C(CH_3)COOCH_3$ γ γ -process): i.e. $\beta = \beta_{CH_2} + \gamma$.

Based on the results of theoretical calculation of continuous relaxation time spectra and PMMA macromolecule structure, the authors of work [24] explain the rather large temperature interval of the β dissipative process manifestation in its spectrum $\lambda = f(T)$ by including five additive components of dissipative processes: γ_1; γ_2; γ_3; $\gamma_\text{э}$; $\beta_{\mathrm{CH_2}}$ (where γ_1 – mobility of the methyl group CH_3 in the ester side group; γ_2 – mobility of the methyl side group CH_3 in the macromolecule chain; γ_3 – mobility of the group OCH_3 ; $\gamma_\text{э}$ – mobility of the ester group $COOCH_3$; i.e. $\beta_{\mathrm{CH_2}}$ mobility of methylene groups $\mathrm{CH_2}$ in the macromolecule chain). The calculation results are presented in Fig. 2c.

As shown in Fig. 1a, the spectrum of $\lambda = f(T)$ latex polymers reveals an extremely weakly expressed and practically unnoticeable maximum of mechanical losses on the ascending branch of the curves β of the dissipative process, corresponding to the local mobility of monomer units in the macromolecular chains of latex polymers, which is associated with their high elasticity.

Fig. 2b shows the temperature dependence of the frequency of free-damping oscillatory process of PMMA, which exhibits a sharp break in the curves in the glass transition temperature region at ~100 ^{0}C, indicating high elasticity of the polymer synthesized during free-radical polymerization. When comparing this dependence with the temperature-frequency dependence of the damping oscillatory process occurring in latex polymers (Fig. 1b), lower frequency values of the damping oscillatory process can be noted in the latter, which also indicates much lower segmental mobility of chains in latex polymers.

Thus, when comparing the internal friction spectra and temperature dependence of the damping oscillatory process frequency, obtained using the DMTA method in the study of statistical polymers of latex polyacrylate and free-radical type polymethyl methacrylate, a fairly similar pattern can be found in the form of dependencies manifestation. However, when comparing the intensity of dissipative processes occurring in them, a significant difference in the segmental mobility of macrochains in polymers of different inelasticity is revealed.

In works [19, 24], the activation energy of all dissipative processes occurring in PMMA was calculated, taking into account less intense dissipative processes (including β dissipative process), presented in Table 2.

Table 2

As shown in Tables 1 and 2, the activation energy value of the most intensive dissipative process α -relaxation, presented for latex acrylate polymers with glass transition temperatures of 5 and 15 ^{0}C and free-radical type polymethyl methacrylate with glass transition temperature of ~100 ^{0}C, is 54 and 43 ^{0}C in latex systems and 92 ^{0}C for PMMA. This theoretically confirms much higher intensity of segmental mobility of the polymer with greater elasticity.

Due to the capabilities of the DMTA method, the review (part 1.2.) will examine the results of studies on the relaxation behavior of polyacrylates depending on their preparation method using homogeneous (statistical) or microheterogeneous (seed) emulsion polymerization.

To illustrate the differences in relaxation and morphological behavior of latex polyacrylate polymers, articles [20, 25, 26, 38] present research results in modified and filled latex polyacrylates considering the effect of modifiers and fillers.

3. RELAXATION BEHAVIOR OF LATEX POLYMERS: LOCAL DISSIPATIVE PROCESSES AT NEGATIVE TEMPERATURES

In works [27, 28], mathematical processing of internal friction spectra curves of latex acrylate copolymers St-MM-BA-MAA (hereinafter referred to as AK1$_{5}$and AK2$_{15}$), as well as temperature-frequency dependencies of the dissipation process was carried out using differential apparatus to obtain a detailed understanding of these processes. Mathematical processing of spectral curves allowed the authors to gain a clearer understanding of local dissipative processes occurring in polyacrylates at negative temperatures.

The data in Fig. 1 provide only a general idea of the nature of changes in the internal friction spectrum in polymers at negative temperatures. It can only be said that local processes at negative temperatures are weakly expressed.

Analysis of dissipative processes occurring in various polymers was based on differential processing of internal friction spectra across the entire temperature range from -150 to +50 $^{\circ}$C.

Fig. 3 shows the differential image of internal friction spectra in polymers with different glass transition temperatures, clearly demonstrating the significant difference in the relaxation behavior of elastomers.

The data in Fig. 3 (a) also show that in the glass transition temperature region, the intensity of the α-relaxation process significantly depends on the value of T_g of the polymer, which increases in the case of polymer AK2 $_{15}$. The intensity of dissipative processes occurring in polymer AK1 $_5$ is much lower than in AK2 $_{15}$, and is explained by the low glass transition temperature, which determines the high adhesive properties of the polymer [1, 2].

Fig. 3

Considering the data in Fig. 1 b regarding the negative temperature region, where it is impossible to identify any effects, the differential analysis of internal friction spectra for these conditions is of particular interest (Fig. 3 b).

There are studies indicating the relationship between the manifestation of local dissipative μ-relaxation processes and the formation of various forms of water during temperature reduction to -150 °C [29-31].

Fig. 3 b shows the differential image of internal friction spectra of polymers in the negative temperature region, which provides information about the temperature intervals of local dissipative processes at negative temperatures.

The occurrence of these dissipative processes may be related to the presence of a certain amount of bound molecular water in the latex polymer structure [29-31].

The lowest-temperature process has weak loss intensity of μ_c-process and manifests in the temperature range from -140 to -120 °C. This local dissipative μ_c-process corresponds to an increase in the frequency of the oscillatory process ν excited in the polymer (Fig. 1 b, d).

In the temperature range from -110 to -80 °C on the spectrum $\lambda = f(T)$, another small-scale dissipative μ_{LDA}- process is observed, which also corresponds to an increase in frequency ν of free damped torsional oscillations excited in the studied system and transferring the system from equilibrium state to non-equilibrium mechanical and thermodynamic state.

Further temperature increase leads to the appearance of a local dissipative μ λ= f(T) in the temperature range from -80 to -50 $_{\mathrm{h}}$-process on the internal friction spectrum °C, which also corresponds to an increase in frequency v.

The presence of water in the structure of various polymers is confirmed by optical and dielectric loss data, as well as IR spectra studies of water at normal pressure [28, 29].

Investigation of possible water cluster forms showed that at temperatures below 273K, water can be present in the polymer structure in several forms: hexagonal crystalline form J_{h}; cubic crystalline form J_{c} and amorphous or glassy phase J_{LDA}.

According to the conclusions of work [30], only the crystalline cluster J_{h}-form is a relatively thermostable water system. Systems J_{c} and J_{LDA} are characterized by thermodynamic instability. At reduced temperatures, their transformation into a more thermodynamically stable phase is kinetically hindered. Cubic ice J_{c} forms at temperatures from -140 to -120 °C and when temperature increases to the range from -120 to -70 °C, J_{c}-phase transforms into hexagonal crystalline J_{h}-phase. Besides J_{c}-phase, the amorphous J_{h}-phase in the temperature range from -120 to -110 $_{\mathrm{LDA}}$-phase also transforms into J °C.

All three local dissipative processes are characterized by a positive modulus defect, i.e. G_{Jc}>0; G_{Jh}>0; $G_{\mathrm{J-LDA}}$>0 [31], which defines the mechanism of dissipative losses as phase-related, associated with specific crystalline structural-kinetic subsystems, whose elements' mobility determines the appearance of the loss peak in the internal friction spectrum.

As the authors of [27] indicate, based on differential processing of internal friction spectra, mobility regions can be identified at negative temperatures.

As follows from 3b, the values of *df/dT* indicate a significant difference in the manifestation of local dissipative processes in the studied polyacrylates with different elastic properties, which is confirmed by the temperature localization of maxima in Fig. 2 (a, c), as well as the differential representation in Fig. 3a. It can be seen that in the temperature range from -110 to -40 °C in polymer AK1$_5$ two local relaxation maxima appear, while in the less elastic polymer AK2$_{15}$ there is only one broad peak. This difference can be attributed to the higher hydrophilicity of AK1$_5$ compared to AK2$_{15}$, due to which AK1$_{15}$ contains an increased amount of water. Therefore, its freezing at negative temperatures has a greater effect on the destruction of the relaxation structure.

This approach demonstrates the possibility of conducting detailed analysis of dissipative processes in latex acrylic polymers, both in the glass transition temperature region and at negative temperatures based on differential processing of internal friction spectra.

Based on the mathematical processing of internal friction spectra, it is possible to establish and compare relaxation activity regions in a wide temperature range from -150 to +50 °C.

Based on differential processing of spectra at negative temperatures, dissipative processes corresponding to μ-relaxation have been discovered.

For systems of different chemical composition and structures, including latex systems, the phenomenological mechanism of local dissipative losses is well described by the nature of the temperature-frequency dependence of the oscillatory process. The negative slope of this dependence curve characterizes the dissipative process as relaxational, while the positive slope indicates a phase process. In this regard, the observed experimental data in Fig. 3 indicate that the local dissipative processes μ_c, μ_{LDA}, μ_h are characterized by a phase mechanism of internal friction.

The processes μ_c, μ_{LDA}, μ_h correspond to the formation of various forms of ice during polymer freezing at temperatures from -150 to 0 °C, which is accompanied by the destruction of the polymer structure and manifests as local dissipative μ-processes [32, 33].

The differential representation of internal friction spectra in acrylic polymers with different glass transition temperatures shows that even with relatively similar chemical composition, it is possible to detect differences in the manifestation of dissipative processes both at T_{g1} and at negative temperatures. In this case, the difference is due to the adhesive properties of the highly elastic polymer at positive temperatures. At negative temperatures, the difference in the manifestation of local dissipative μ-processes can also be attributed to the greater hydrophilicity of the highly elastic polymer and, consequently, to its increased water content. Therefore, its freezing at negative temperatures shows a greater effect on the destruction of the relaxation structure.

CONCLUSION

This article (Part 1.1) summarizes the results of studies conducted using the DMTA method on the relaxation behavior of latex acrylate polymers obtained through homogeneous (statistical) emulsion polymerization processes.

Based on internal friction spectra, the temperature regions of greatest segmental mobility of polyacrylate macrochainsw ere established, both at low negative temperatures (from -150 to 0 °C) and in the glass transition temperature range (from 0 to 50 °C).

The segmental mobility of macrochains at the glass transition temperature is a consequence of the monomer composition of the copolymer, corresponding to the manifestation of minimum film formation temperature and local dissipative processes in the temperature range T_g.

Local dissipative processes at negative temperatures can be detected through mathematical differential processing of spectral curves. Their manifestation may be a consequence of the effect of water traces in hydrophilic polyacrylates experiencing dynamic load at negative temperatures.

Based on the study of temperature-frequency dependencies of the oscillatory process, the possibility of evaluating the elastic properties of acrylate polymers through mathematical graphical processing of temperature-frequency dependence of the damped oscillatory process is shown.

As a result of analyzing studies conducted using the DMTA method, significant differences in the relaxation structure of statistical polymers of various elasticity were found, both in the glass transition temperature range and at negative temperatures.

When comparing statistical polymers obtained by latex and free-radical polymerization, using the DMTA method to describe the segmental mobility of macrochains, most pronounced in the case of elastic polymethyl methacrylate.

It has been established and theoretically substantiated that continuous relaxation time spectra differ significantly for polymers of different chemical structure, as evidenced by the occurrence of local dissipative processes in different temperature regions.

Announcing the next section of the review (section 1.2.), dedicated to comparing the chemical and relaxation structure of polyacrylates synthesized using methods of statistical (homogeneous) and seed (microheterogeneous) emulsion copolymerization, in their glass transition temperature range and at negative temperatures from -150 to 0 ^{0}C, the following can be noted. To clarify the difference in relaxation structures of both polymers in these regions, the effect of water-soluble modifier on the main and local dissipative processes occurring in its presence is considered.

The relaxation microheterogeneity of statistical and seed polymers was determined, also taking into account the modifier's influence on internal friction spectra of latex polymers with different polymerization structures. A theoretical approach is proposed for evaluating the relaxation microheterogeneity of latex polymers with homogeneous and microheterogeneous chemical structures, based on selecting a function to describe dissipative processes occurring in latex polymers and its correlation with experimental data.

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Table 1. Physical-mechanical and physical-chemical characteristics of elastomers $AK1_5$ and $AK2_{15}$ [14, 20]

Polymer	Process	λ_{max}	T_{max}, (^{0}C)	U, kJ/mol	ΔG	Mechanism of dissipation	Structural nature of the process
$AK1_5$	α	0.23	5	54	0.30	Relaxational	Segment mobility
	β	0.09	-20	39	0.38		Mobility of macromolecular chain units
	C	0.10	-12	0.06	0.06	Phase	Mobility of locally ordered structure elements
	μ	0.05	-120	24	-0.1		Decomposition and transformation of crystalline local formations of molecular water forms
$AK2_{15}$	α	0.58	7	43	0.90	Relaxational	Segment mobility
	μ	0.07	0	-	-	Phase	Decomposition and transformation of crystalline local formations of molecular water forms

Table 2. Physical-mechanical and physical-chemical characteristics of free-radical PMMA [23]

Process	$T_{i_{\max}}$, °C	U_i, кДжмол	Kinetic unit responsible for process
$\square$	140	92	segment
$\square_1$	-188	7.1	Methyl group CH_3 in ester side group
$\square_2$	-109	22	Methyl side group CH_3 in main chain
$\square_3$	-17	57	Group OCH_3
$\square_{э}$	20	50	Ester group $COOCH_3$
$\square$	115	69	Polymer chain unit $CH_3 \square C \square COOCH_3$
$\square_{CH_2}$	-142	30	Methylene group CH_2 in main chain
$\square_*$	-80	48	Hydrogen bond (adsorbed water)
$\square_*$	~190	~110	Dipole-dipole physical junction of molecular network
$\square_{1^*}$	250	80	Microvolume physical junctions of molecular network
$\square_{2^*}$	250	80	Microvolume physical junctions of molecular network
$\square_{3^*}$	335	80	Microvolume physical junctions of molecular network

*) Dissipative $\square$ -, $\square$ -, $\square_1$-, $_2$- and $_3$- processes corresponding to the kinetic unit responsible for the process (hydrogen bond; dipole-dipole physical junction of molecular network: adsorbed water; microvolume physical junctions of molecular network) are not shown in Fig. 2 but are mentioned in [19, 24].

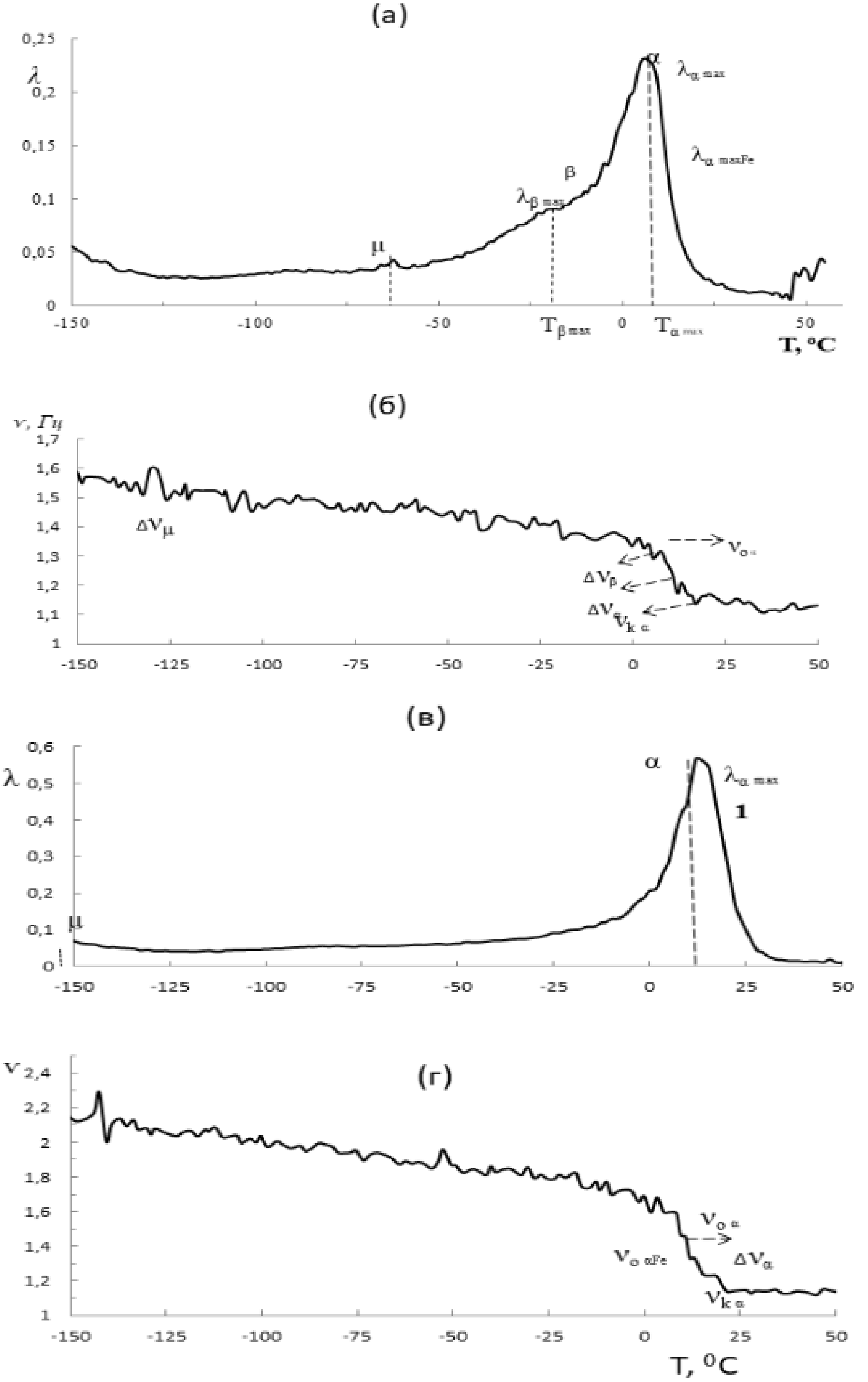

Fig. **1** . Internal friction spectra λ (a, c) and temperature dependence of frequency v (b, d) of the oscillatory process excited in elastomers AK1 (a, b) and AK2 (c, d) [20]

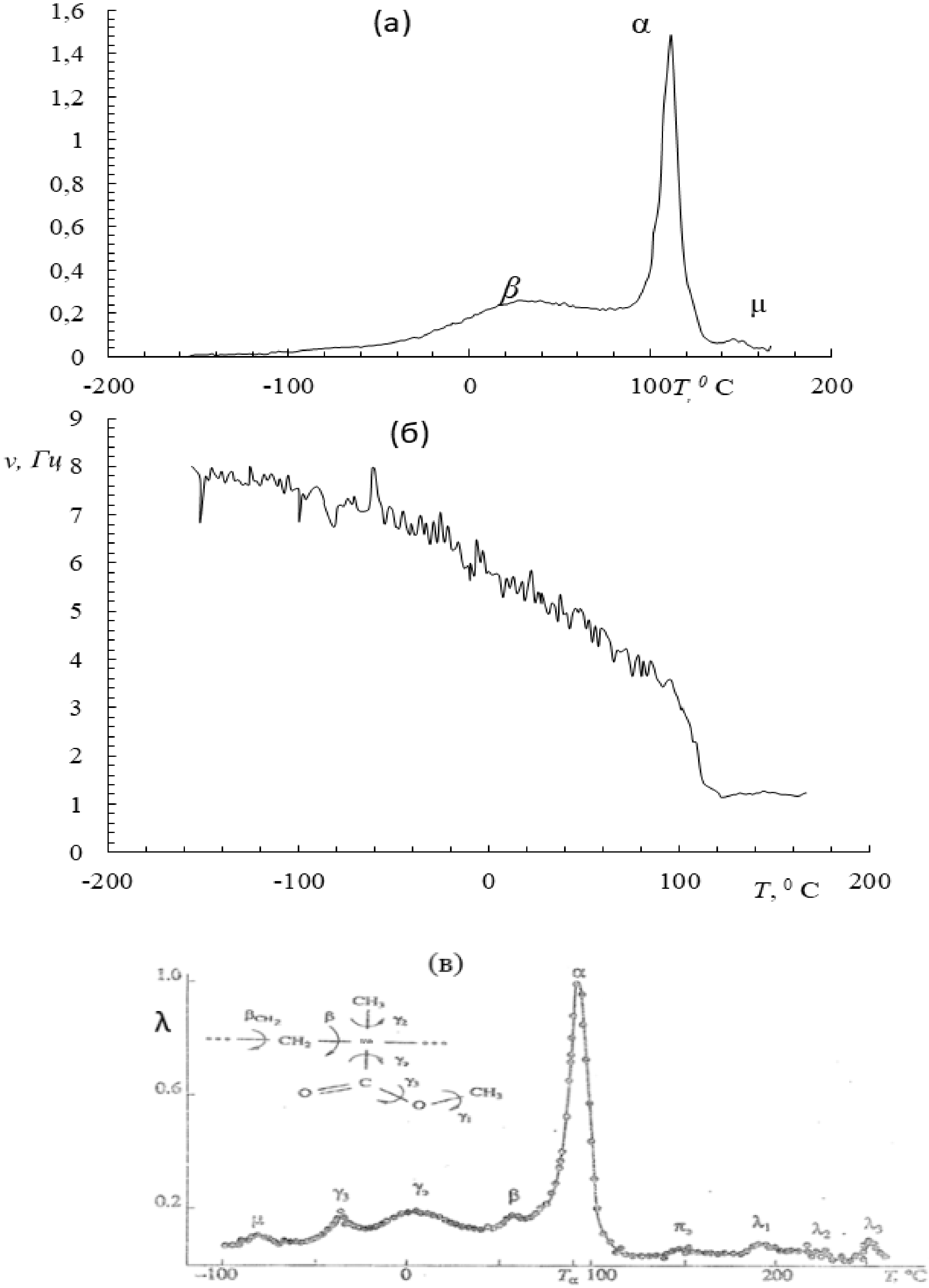

Fig. 2. Experimental data on internal friction spectrum (a) and temperature-frequency dependence of damped oscillatory process (b) for PMMA (MW=1.8.10 ^{5}) (a, b) [23];

theoretically calculated continuous relaxation time spectra of PMMA (MW=5.10^6) considering internal friction spectra (c) [19, 24]

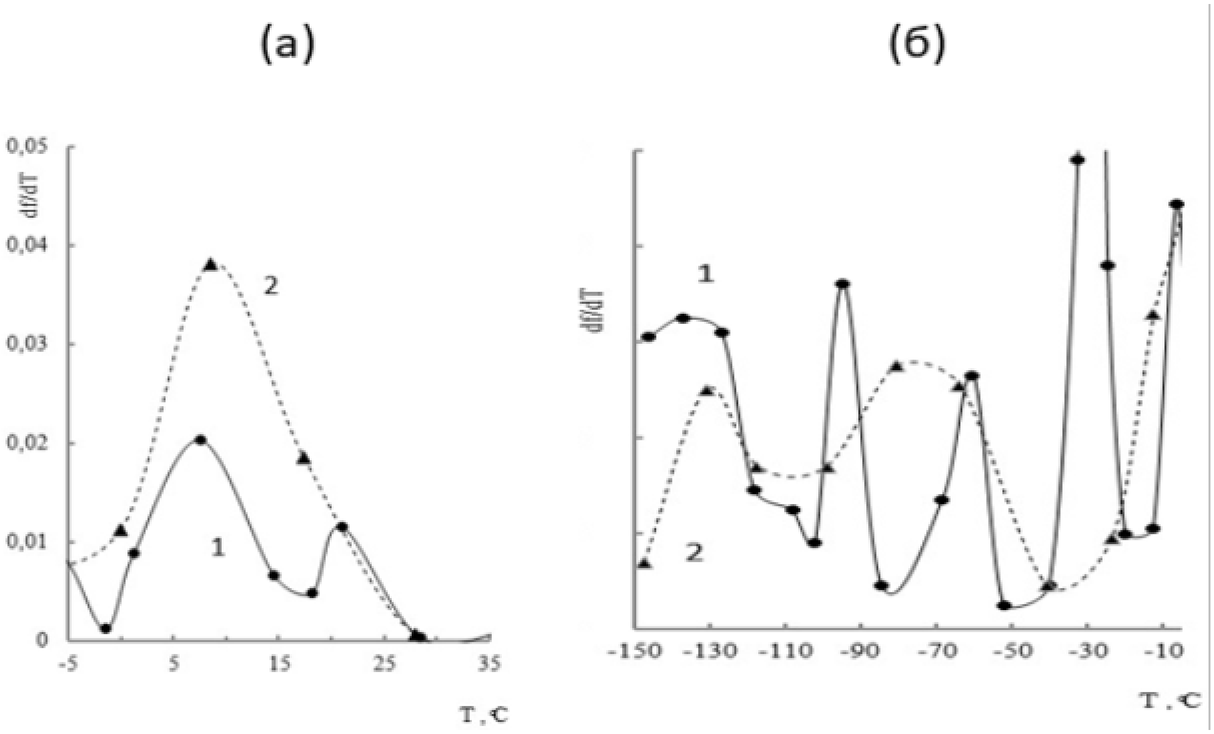

Fig. 3. Differential representation of internal friction spectra in the glass transition region (a) and at negative temperatures (b): *curves* 1 - AK1 $_5$; *curves* 2 - AK2 $_{15}$[27, 28]