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Title: On the diffusion nature of α-relaxation in the amorphous polymer T20-60

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The temperature dependences of internal friction $Q^{-1}(T)$ for the T20-60 epoxy polymer hardened at room temperature and deposited on a glass-ceramic substrate were studied. The $Q^{-1}(T)$ dependence of the polymer structure in the region of the α-relaxation process has a maximum associated with the diffusion of vacancy-like oxygen defects of the end groups of the epoxy resin. In the α-relaxation region, three straight sections with different slope angles are observed in the $\ln Q^{-1}(1/T)$ dependence for the mboxT20-60 polymerized at room temperature. Based on the $\ln Q^{-1}(1/T)$ experimental dependences, the migration energy and formation energy of vacancy-like oxygen defects of epoxy groups for the polymer under study were estimated. In the pre-hardened T20-60 polymer, in the α-relaxation region on the $\ln Q^{-1}(1/T)$ dependence for the low-temperature branch of the Q^{-1} maximum, two straight sections with different slope angles are observed, associated with the migration of vacancy-like oxygen defects entering the polymer network. The migration energy and formation energy of vacancy-like oxygen defects in the main polymer network were estimated, which turned out to be $E_{m2} = 0.88 \pm 0.09$ eV and $E_{v2} = 0.91 \pm 0.09$ eV. The $\ln Q^{-1}(1/T)$ dependence for the high-temperature branch of the Q^{-1} maximum has one straight section. The assessment of the activation energy on this branch showed higher values than on the low-temperature branch of the Q^{-1} maximum, which indicates the diffusion nature of the α-relaxation process of the T20-60epoxy binder.

Keywords: internal friction, epoxy polymer, α-relaxation, glass transition temperature.

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Introduction

Currently, there is an increased interest in the amorphous state of matter which is attributable to intensive studies of physical, thermodynamic and other properties of various glasses [1–3]. Nevertheless, the physical nature of structural organization and relaxation behavior of non-crystalline solids remains a topic of much discussion despite the advances in understanding the short-range order in them [4–6]. The heat treatment of amorphous solids leads to relaxation of their atomic structure since the amorphous state of matter is nonequilibrium. Mechanical spectroscopy is broadly used to study relaxation transitions in amorphous solids (metallic, inorganic, chalcogenide glasses, polymers) due to the universality of the effect of mechanical fields on the structural elements of matter [7–9]. A large amount of experimental material has been obtained to date on the study of relaxation phenomena in various glasses and polymers, in which several local peaks of dissipative losses are detected using the spectra of internal friction [10,11]. Several relaxation loss peaks have been established in glassy materials, two of which are typical for almost all types of glasses [12,13]: primary α-relaxation near the glass transition temperature T_g, associated with high joint mobility of atoms leading to irreversible viscous flow, and secondary β-relaxation below T_g, characterizing local atomic rearrangements of the amorphous structure [14,15].

The most intense relaxation transition detected in these spectra is the α-transition, which is a response of the segmental structural subsystem of a glassy material to an external periodic force action [16,17]. It should be noted that an exponential increase of internal friction Q^{-1} in the region of α-relaxation is observed in all classes of non-crystalline solids: in inorganic glasses with covalent bonds [17], in metallic glasses [18,19], bulk metallic glasses [20,21], chalcogenide glasses [22,23], thin-film oxides [24], in polymers [25,26]. The authors of scientific papers propose various attenuation mechanisms to explain the experimental dependencies, but there is no generally accepted point of view on this problem yet. For example, while α-transition is associated with the defrosting of segmental mobility in amorphous polymers [27,28], then the vitrification of inorganic glasses is associated with the chemical relaxation process [29]. At the same time, the authors associate α-process with the breaking (switching) of Si$-$O bonds in inorganic glasses and believe that movement of the „bulky" oxygen atom takes place [29].

When studying internal friction in amorphous polymers and inorganic glasses, the Q^{-1} analysis is usually conducted in the region of α-relaxation using temperature-frequency dependencies in $\ln\omega = f(1/T)$ coordinates, which are curved, indicating the dependence of these processes on temperature [30,31]. The main condition of the maximum $\tau\omega = 1$ is replaced by the Deborah correlation under such consideration [32]:

$$\omega\tau = c, \tag{1}$$

where the dimensionless coefficient c introduces a certain ambiguity [31]. Certain provisions of the relaxation spectrometry theory associate the value of this coefficient with relaxation process scale: the value of this coefficient for large-scale processes can be equal to 10, while for small-scale processes it can be equal to one [33]. Analyzing experimental studies of relaxation processes in glasses and polymers, the authors of Ref. [33] came to the conclusion that the activation energy of the glass transition process consists of two components:

$$U_\alpha = U_1 + U_2(T), \tag{2}$$

where U_1 and $U_2(T)$ are activation energies of the first and second stages of the mechanical relaxation process, respectively. The first component U_1 characterizes the potential barrier of transition to the activated state. The second component $U_2(T)$ is associated with the energy required for the formation of a free volume and the transition of the kinetic unit to the neighboring position [34].

On the other hand, the authors of this paper, without denying the association of α-relaxation in inorganic glasses with the breaking (switching) of Me$-$O bonds (where Me are metal atoms), believe that it is not the oxygen atoms themselves that diffuse, but vacancy-like defects (dangling bonds) of the amorphous structure. The authors use the internal friction method [24,35] to estimate the migration energy and the energy of formation of vacancy-like defects in various amorphous materials, and Q^{-1} analysis in the region of α-relaxation is carried out in the maximum form. Thus, any relaxation process manifested as a peak of dissipative losses on the spectrum of internal friction can be described by the following equation of a standard linear body from the standpoint of the phenomenological theory of inelasticity [36]:

$$\operatorname{tg}\phi = Q^{-1} = \Delta\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{3}$$

where $\Delta = (M_n - M_r)/M_n$ — relaxation degree or modulus defect, ω — circular frequency, M_n and M_r — nonrelaxed and relaxed elastic moduli, respectively, τ — relaxation time changing under the Arrhenius law

$$\tau = \tau_0 \exp\left(\frac{E}{kT}\right), \tag{4}$$

where τ_0 — the pre-exponential factor, E — activation energy, k —the Boltzmann constant, T — absolute temperature.

Then it results from formulas (3) and (4) for the low-temperature leg of the peak ($\omega\tau \gg 1$) that

$$Q^{-1} \propto \exp\left(-\frac{E}{kT}\right), \tag{5}$$

and for the high-temperature leg of the peak ($\omega\tau \ll 1$)

$$Q^{-1} \propto \exp\left(\frac{E}{kT}\right). \tag{6}$$

The peak on the dependence $Q^{-1}(1/T)$ is symmetric in the case of the relaxation process caused by the reorientation of elastic dipoles, therefore, the activation energies of the relaxation process are determined along the left (below the temperature of Q^{-1} peak) and right (above the temperature of Q^{-1} peak) legs of the peak should have the same values. However, in many glasses, the peak on the $Q^{-1}(1/T)$ dependence in the α-relaxation region is asymmetric. It is assumed that this is attributable to the diffusion of vacancy-like defects in the amorphous structure under the action of alternating mechanical stresses [37].

The nature of point defects in the amorphous structure of all glasses is widely discussed in the literature. Defects of a solid body are usually divided in the general case according to their cause into doped, induced and thermal defects [38]. Thermal defects that occur because of the energy fluctuations during the thermal motion of atoms are of interest in our case. Defects in densely packed structures, such as metallic glasses, are associated with the presence of local areas of reduced density, called free volumes [39–42]. The dangling bond is the simplest defect for covalent bonded glasses [43]. The ideas of point defects in the amorphous structure were developed by Spaepen [44,45] and other researchers [46,47]. In other words, the excess free volume characteristic of the amorphous state is distributed in the amorphous structure in the form of defects, which affect the physical properties of various amorphous solids [48,49]. By analogy with crystalline vacancies, where free volume is localized, we call such defects with an amorphous structure vacancy-like defects [49].

Using the method of determining the activation energy of the relaxation process in the region of α-relaxation according to the dependence form $Q^{-1}(T)$, the authors of the article established that the dependence of the left leg $Q^{-1}(T)$ for various glasses: metallic [50,51], bulk metallic [52], chalcogenide [22], oxide [24], and polymers [35,53] exhibit exponential regions with different activation energies on both sides of T_g. The energy of migration of vacancy-like defects was estimated for the low-temperature region of exponential growth of internal friction to T_g (for the left leg of the peak of α-relaxation), and for the high-temperature region (after the glass transition temperature) — the formation energy.

The nature of α-relaxation of the amorphous structure is found in this paper by setting the task of estimation of the values of the activation energy of the relaxation peak along the left and right legs using experimental dependences $Q^{-1}(T)$ in one of the amorphous samples. If the obtained estimates of the activation energy turn out to be the same, then this will speak in favor of the relaxation point of view. If the shape of the peak of α-relaxation turns out to be asymmetric (i.e., the activation energy calculated from the right leg turns out to be greater), then the result will be evidence in favor of the diffusive nature.

Metallic and chalcogenide glasses crystallize earlier than the of condition the peak $\omega\tau = 1$ is reached, and inorganic glass is technologically less suitable for the preparation of experimental samples. Therefore, the epoxy compound T20-60 (produced by „ITEKMA“ LLC) was chosen for the study as its behavior is closer to the behavior of inorganic glasses than to the behavior of linear polymers, since it forms a rigid polymer grid in the polymerized state [28]. It should be noted that α-transition is associated in amorphous polymers with unfreezing of the segmental mobility of segments, chain links, or simply small-scale defects, as well as their structural change with the increase of the temperature, suggesting a relaxation nature [27,28].

Studies of internal friction in the selected binder are also of great practical importance for the following reason. For example, we studied in Ref. [35] the internal friction in the region of α-relaxation in fiberglass with an epoxy polymer matrix of the commercial grade T-107. Two rectilinear regions with a king point temperature corresponding to the glass transition temperature were observed on dependence $\ln Q^{-1}(1/T)$, which made it possible to associate the growth of Q^{-1} in the region of α-relaxation with the diffusion of vacancy-like defects in the amorphous structure (broken bonds of oxygen, which is part of the end group of the epoxy resin). The authors assumed that oxygen atoms involved in the relaxation process did not interact with the radicals of the hardener since the energy of defect formation turned out to be twice as high as the energy of migration. It should be noted that the amount of hardener in the binder T-107 relative to the resin component itself was below 10 mass % (as a result of which the authors assumed the presence of unbound oxygen in the cured polymer). Considering the above, a commercially available epoxy binder T20-60 (manufactured by „ITEKMA“ LLC) was selected, which has a different ratio of components mixed in a mass ratio of 100 : 31.6 [54]. It was assumed that a large amount of the hardener involved in the polymerization process should lead to the full completion of the polymerization process. Thin-film samples were selected for the studies in this paper since the peak Q^{-1} was not reached in previous experiments because of the high attenuation level.

1. Samples and measurement procedure

Samples of epoxy binder T20-60 [54] deposited on a polycrystalline glass substrate were used to measure internal friction. The epoxy binder was made by mixing the components at room temperature A and B in a mass ratio of 100 : 31.6 until a homogeneous mixture is obtained. Next, the resulting mixture was applied to the largest surfaces of a rectangular-shaped polycrystalline glass substrate with geometric dimensions $30 \times 2.5 \times 0.54$ mm and was kept at room temperature for 24 h. The thickness of the epoxy binder layers was $\approx 30\,\mu$m.

The structure of the obtained films was studied by X-ray diffraction using Bruker D2 Phaser diffractometer ($\lambda_{\mathrm{Cu}K\alpha 1} = 1.54$ Å) with DIFFRAC.EVA 3.0 software and ICDD PDF Release 2012 database jcite55.

Differential scanning calorimetry (DSC) was performed using Netzsch STA 449 F3 instrument in a flowing atmosphere N_2 (99.999%).

The internal friction was measured by the method of freely damped bending vibrations of the sample [56] in the temperature range from 20 to 160°C at infra-low frequencies. The sample was heated at a rate of 1°C/min by a thermoradiative heater made of nichrome wire and its temperature was maintained using temperature controller Thermodat-14E5. The sample temperature was controlled using a chromel−alumel differential thermocouple with an error of less than ±0.5°C.

The amount of internal friction was determined by the formula

$$Q^{-1} = \frac{1}{\pi N} \ln \frac{A_1}{A_N}, \tag{7}$$

where N is the number of vibrations of the sample when the oscillation amplitude changes from A_1 to A_N.

The internal friction of the epoxy binder film Q_f^{-1} was calculated according to the equation [57]:

$$Q_f^{-1} = Q_C^{-1} - Q_S^{-1}, \tag{8}$$

where Q_C^{-1} is the internal friction of the experimental sample (film with substrate), Q_S^{-1} — is the internal friction of the substrate.

The setup is configured to measure Q^{-1} with a relative strain amplitude from 10^{-5} to 10^{-6}. The relative measurement error Q^{-1} did not exceed 3%.

The modulus of elasticity of the deposited polymer sample film was calculated using the formula [57]:

$$E_f = E_s \frac{\Phi - 1}{(1+\delta)^3 - 1}, \tag{9}$$

where E_S — elastic modulus of the substrate, $\Phi = \frac{f_c^2 l_c^4}{f_s^2 l_s^4}\left(1 + \frac{\rho_f}{\rho_s}\delta\right)$ — coefficient, f_s — resonant frequency of the substrate, l_s — substrate length, ρ_s — substrate density, f_c — resonant frequency of the film substrate, l_c — length of the film substrate, ρ_f — film density, $\delta = d_f/d_s$, d_s — substrate thickness, d_f — film thickness.

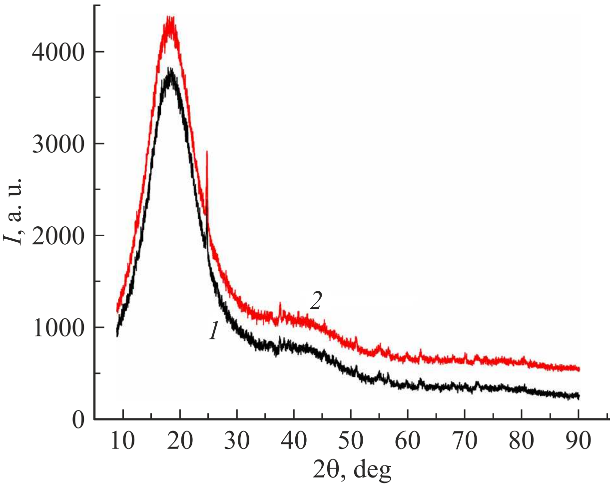

Figure 1. Diffraction patterns of synthesized samples after polymerization at room temperature (curve *1*) and after heat treatment at $T = 150°$C (curve *2*).

2. Experimental results and discussion

2.1. Experiment

Analysis of the diffraction patterns of the synthesized samples showed that the structure of the binder T20-60 polymerized at room temperature (curve *1* in Fig. 1) and heat-treated at $T = 150°$C (curve *2* in Fig. 1), is amorphous.

Curve *1* in Fig. 2,*a* shows the dependence $Q^{-1}(T)$ of the studied polymer T20-60 on a substrate exhibiting a wide peak $Q^{-1}_{\max}$ at $T \approx 90°$C, and the dependence $Q^{-1}(T)$ of the studied polymer (after deducting the contribution of the substrate), determined by expression (8) is shown in Fig. 2, it b. The peak at $T \approx 90°$C has been identified as a process of α-relaxation observed near T_g for many amorphous polymers and composites based on them [25,26]. $Q^{-1}_{\max}$ shifts to a higher temperature ($T \approx 130°$C) (curve *2* in Fig. 2) after heating the sample to $T = 140°$C, cooling and subsequent heating of the sample. The behavior of $Q^{-1}(T)$ and the position of $Q^{-1}_{\max}$ change slightly after subsequent heating and cooling of the sample (curve *3* in Fig. 2).

The temperature dependences of the elastic modulus $E_f(T)$ for the studied samples are shown in Fig. 3. E_f behaves in a complex way in case of heating for the first time: first it decreases to a temperature of 50° C, then it increases, reaching a peak at $T = 60°$C, and then decreases again when the temperature changes to 120°C (curve *1* in Fig. 3). E_f decreases to about $T \approx 93°$C during the second heating, then a sharp decrease is observed, reaching a minimum value at $T = 140°$C (curve *2* in Fig. 3). The value of E_f after subsequent heating and cooling of the sample changes slightly to about 100°C, after which a strong decrease is observed (curve *3* in Fig. 3).

Fig. 4 shows the results of measuring the DSC of the studied polymer, cured at room temperature (curve *1*) and after heating to 140°C (curve *2*). An exothermic peak is observed on the DSC curve of the studied polymer cured at room temperature (curve *1* in Fig. 4), which correlates with the maximum modulus of elasticity (curve *1* in Fig. 3). There is no peak on the heat-treated sample, which indicates the completion of the polymerization process of the sample. The glass transition temperature T_g in the studied sample could not be determined by the DSC method due to the low mass of the sample.

2.2. Discussion of the results

The observed wide peak of Q^{-1} at temperature $T \approx 90°$C of the polymer cured at room temperature (curve *1* in Fig. 2) can be associated with the process of α-relaxation in the polymer binder T20-60, since its glass transition temperature ($T_g \approx 87°$C) [54] is in the region of the relaxation process. The region of initial growth of Q^{-1} correlates with a sharp increase of the modulus of elasticity (curve *1* in Fig. 3) and the exothermic peak of DSC (curve *1* in Fig. 4). This reflects the high diffusion mobility of the polymer chain atoms, as well as the „secondary“ polymerization of the binderT20-60, since this temperature range corresponds to the post-curing temperature (50−80°C for 3−6 h) [54]. Relaxation processes in the region of α-relaxation are observed at $T > 100°$C (curve *2* in Fig. 2) after the completion of the polymerization process and formation of a three-dimensional grid and shift to higher temperatures after heat treatment at temperatures of the order of 140°C (curve *3* in Fig. 2).

The activation energy of the relaxation process can be determined based on the shape of the left (or right) leg of the peak taking into account (5) and (6). If we reconstruct the dependence $Q^{-1}(T)$ near the peak in coordinates $\ln Q^{-1}(1/T)$, then the activation energy of the relaxation process can be estimated from the slope of the rectilinear region. Three rectilinear regions with intersection points at $T_1 = 316$ K and $T_2 = 326$ K were found on the left leg of the dependence $\ln Q^{-1}(1/T)$ for a polymer cured at room temperature (Fig. 5). The evaluation of the activation energy in different regions gave the following values: $E_{B1} = 0.35 \pm 0.06$ eV, $E_{B2} = 1.75 \pm 0.06$ eV, $E_{B3} = 0.39 \pm 0.06$ eV. The analysis of the high-temperature leg of the peak of Q^{-1} will be discussed below.

Only two linear sections with intersection points are observed for polymer post-cured by heating to 140°C on the left leg of the dependence $\ln Q^{-1}(1/T)$ at $T_1 = 354$ K after the first heating (Fig. 6,*a*) and at $T_1 = 358$ K after the second heating (Fig. 6,*b*). The evaluation of the activation energy in different sections of the left leg of the internal friction peak gave the values $E_{B1} = 0.42 \pm 0.06$ eV, $E_{B2} = 1.27 \pm 0.06$ eV after the first heating and $E_{B1} = 0.44 \pm 0.06$ eV, $E_{B2} = 1.35 \pm 0.06$ eV after second heating (Fig. 6).

We associate the initial area of internal friction growth of the studied polymer T20-60 (Fig. 5), as in Ref. [35] with the diffusion of vacancy-like defects in the amorphous

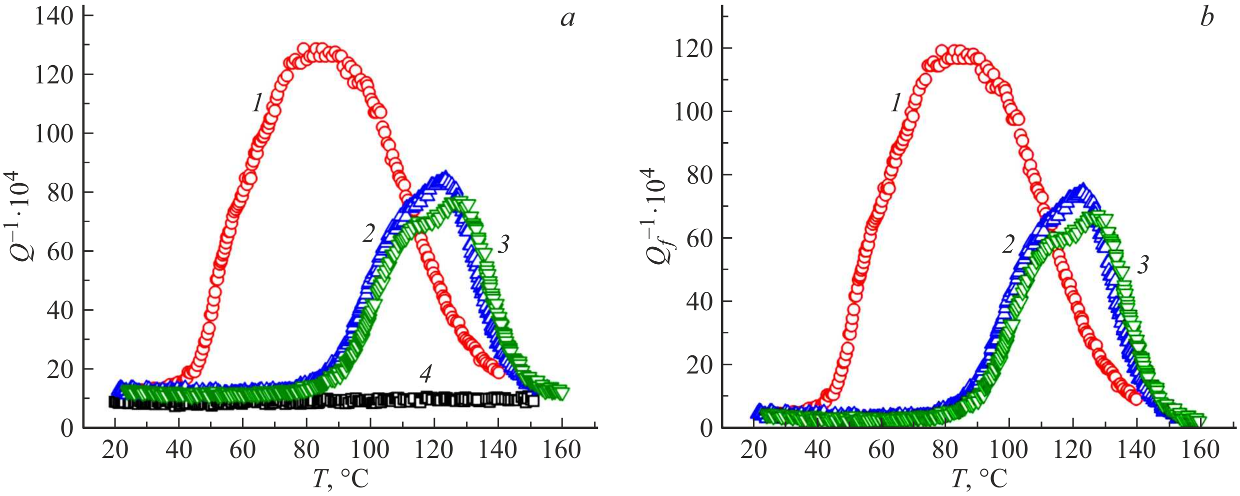

Figure 2. Temperature dependences of the internal friction of the polymer sample T20-60 with substrate (a) and after deducting the contribution of the substrate (b) cured at room temperature (curve 1), after heating to 140°C (curve 2) and after reheating to 140°C (curve 3), as well as the dependence $Q^{-1}(T)$ of a polycrystalline glass substrate (curve 4).

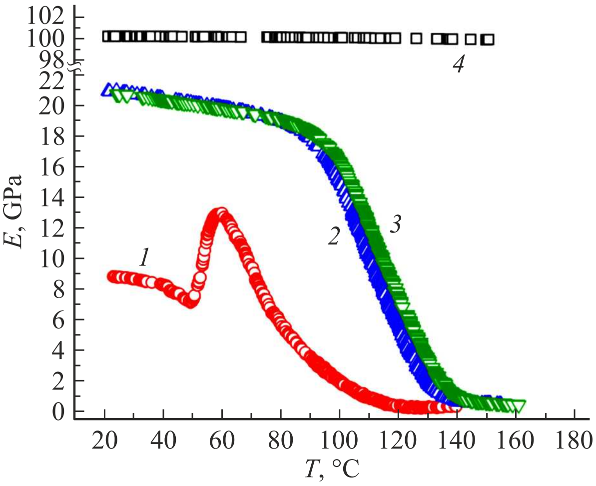

Figure 3. Temperature dependences of the modulus of elasticity $E_f(T)$ of a polymer sample T20-60 cured at room temperature (curve 1), after heating to 140°C (curve 2) and after the second heating to 140°C (curve 3), as well as the dependence of $E_s(T)$ of the polycrystalline glass substrate (curve 4).

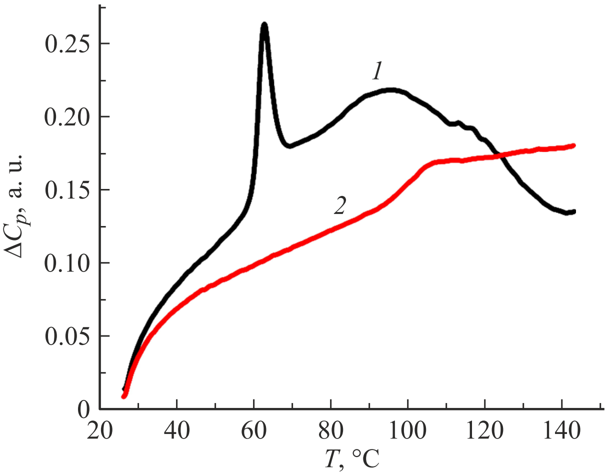

Figure 4. Temperature dependences of DSC polymer sample T20-60 cured at room temperature (curve 1) and after heating to 140°C (curve 2).

structure, representing the excess free volume frozen during glass transition [58,59]. Such simplest defects in systems with covalent bonds, to which the studied polymer belongs, include one dangling chemical bond [43,60]. The defective atom is the oxygen atom in our case, which is part of the epoxy groups that have not yet reacted with the hardener [35]. With an increase of temperature, when the energy of thermal vibrations of the polymer grid, attributed to the defective oxygen atom, becomes equal to the energy of atom delocalization ($T = 303\,\mathrm{K}$ in Fig. 5), the latter ceases to be bound to the polymer grid and the defect of the amorphous structure (dangling bond) begins to diffuse under the impact of thermal vibrations. Such a process can be represented as switching a dangling chemical bond from one atom of the polymer grid to another, and the migration energy during such a switch can be equated to the energy of the chemical bond of oxygen with the atoms of the epoxy group. The application of alternating stresses results in the directed diffusion of the defect from the region of tension to the region of compression, which is accompanied by the appearance of a low-temperature leg in the region of α-relaxation (Fig. 5). The oxygen atom in this case passes from the bound state to the delocalized state according to Sanditov's terminology [61]. From a physical point of view, the value of Q^{-1} in this case is proportional to the concentration of defects frozen during quenching n and the

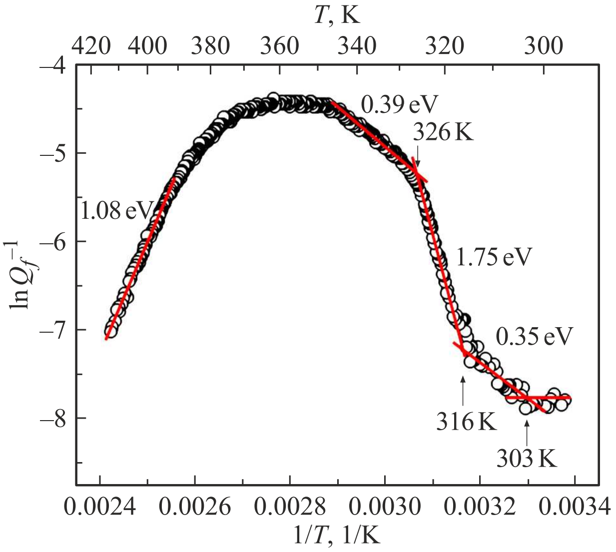

Figure 5. Temperature dependence of the internal friction of the binder T20-60 in coordinates $\ln Q^{-1}(1/T)$ after deducting the contribution of the substrate for a sample cured at room temperature.

average length of their diffusion L, i.e. [51]:

$$Q^{-1} \propto nL \propto n\sqrt{Dt} \propto \frac{n}{\omega^{1/2}} \exp\left(-\frac{E_m}{2kT}\right), \tag{10}$$

where D — defect diffusion coefficient, t — time, k — Boltzmann constant, E_m — activation energy of defect migration. We will assume in this case that the concentration of defects in the amorphous structure n is determined according to Ref. [62], as

$$n = \begin{cases} n_0, & T < T_g \\ A\exp\left(-\frac{E_v}{kT}\right), & T > T_g. \end{cases} \tag{11}$$

Here n_0 and A — constants, E_v — the energy of formation of vacancy-like defects in the amorphous matrix associated with a delocalized oxygen atom at temperatures above T_g.

Thus, the low-temperature region of growth of Q^{-1} (up to $T_g \approx 316$ K in Fig. 5) of the polymer T20-60 cured at room temperature can be associated with the migration of nonequilibrium defects (broken oxygen bonds of epoxy groups). An increase of temperature above $T_g = 316$ K (Fig. 5) results in the formation of new equilibrium defects in the amorphous matrix that are caused by the breakage of chemical bonds of the epoxy groups of the polymer grid, which is reflected by an increase of the angle of inclination in the second region of α-relaxation (above $T_g = 316$ K in Fig. 5). In this case, the amount of internal friction in the first and second sections of the dependence $\ln Q^{-1}(1/T)$, respectively, can be described using the following formulas [62]:

$$Q^{-1} = Q_0^{-1} \exp\left(-\frac{E_m}{2kT}\right), \tag{12}$$

$$Q^{-1} = Q_0^{-1} \exp\left(-\frac{E_m/2 + E_v}{kT}\right), \tag{13}$$

where E_m is the activation energy of migration of a mobile defect, E_v is the energy of formation of defects in an amorphous structure.

Therefore, the activation energy of defect migration for a sample cured at room temperature can be estimated from the tangent of the slope angle of the dependence $\ln Q^{-1}(1/T)$ to the glass transition temperature. The activation energy of migration of the point defect $E_m = 0.70 \pm 0.09$ eV, is estimated based on expression (12), which, within the margin of error, coincides with the estimates for the epoxy polymer T-107 [35].

The energy of formation of a vacancy-like defect of $E_v = 1.75 - 0.35 = 1.40 \pm 0.09$ eV was estimated in the second region of growth of Q^{-1}, taking into account the first region. The obtained value within the error range coincides with a value twice as high as the value of the activation energy of defect migration for the amorphous structure of a polymer cured at room temperature. It should be noted that the formation energy of metallic glasses within the margin of error coincides with the energy of migration of vacancy-like defects of the amorphous structure [62]. The observed difference of the energy of migration and the energy of formation of new dangling bonds (E_v is twice as high as E_m) was attributed by the authors of Ref. [35] to the breakage of two chemical bonds of oxygen atoms, which are part of the epoxy groups of the polymer grid of polymer T-107, resulting in the formation of free oxygen ions. The results of studies of the epoxy binder T20-60, in which the structure of the hardener differs from the structure of hardener of polymer T-107, showed the same values of the energy of migration and formation, which indicates the reliability of the conclusions reached.

Since not all epoxy groups reacted with the hardener molecules during polymerization at room temperature, the high diffusion mobility of oxygen ions in this temperature range is accompanied by the process of secondary polymerization, which is reflected by an increase in the modulus of elasticity in this temperature range (Fig. 3) and a peak on the DSC curve (Fig. 4). All oxygen atoms of the epoxy groups, interacting with the radicals of the hardener, are embedded in the main bulk polymer grid after the full completion of the polymerization process ($T = 326$ K Fig. 5) [28]. As a result, a third rectilinear region is observed on the dependence $\ln Q^{-1}(1/T)$ (Fig. 5), which already reflects the migration process of broken chemical bonds (having the weakest chemical bonds) formed at the post-curing stage of the polymer grid. In this case, the energy of the broken chemical bond of the formed polymer grid increases (as evidenced by a different angle of inclination of the 3rd rectilinear region compared to the first one) to the value $E_m = 0.39 \cdot 2 = 0.78 \pm 0.09$ eV. It should be noted that all oxygen atoms for this sample in this temperature range have broken chemical bonds and the diffusion process takes place without the formation of

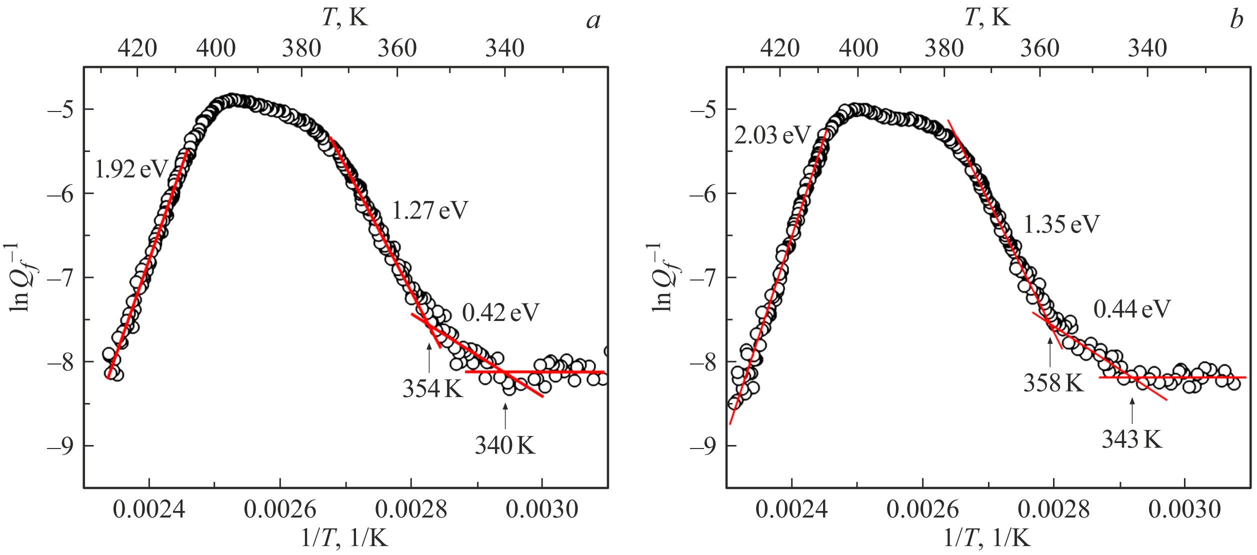

Figure 6. Temperature dependences of the internal friction of the binder T20-60 in coordinates $\ln Q^{-1}(1/T)$ after deducting the contribution of the substrate for polymer after the first (a) and second (b) heating.

new vacancy-like defects in the polymer grid. Consequently, the diffusion process at the third region of growth of Q^{-1} (Fig. 5) proceeds with a constant concentration of broken bonds embedded in the basic polymer grid.

It should be emphasized that the pattern of interaction of all end epoxy groups with the hardener and the second region of dependence $\ln Q^{-1}(1/T)$, where the energy of defect formation, twice the energy of defect migration, ceases to exist after post-curing of the binder T20-60, which is of great practical importance for the control of polymerization process by the internal friction method.

The determination of the physical nature of the process of α-relaxation requires an analysis of the curves $Q^{-1}(T)$ after heating above T_g, when the polymerization processes are completed and do not affect the mechanical relaxation of the amorphous structure. Therefore, we will devote further consideration only to samples that have undergone polymerization and were cooled to room temperature (Fig. 2, curves *2* and *3*). Thus, only two rectilinear regions are observed on the dependence $\ln Q^{-1}(1/T)$ of the left leg of Q^{-1} peak (Fig. 6). Moreover, the estimation of the migration energy of defects in a low-temperature region gives the value $E_{m1} = 0.84 \pm 0.09$ eV after the first heating and $E_{m2} = 0.88 \pm 0.09$ eV after the second heating. These values slightly increased relative to estimates of the migration energy of broken oxygen bonds in the third region of dependence $\ln Q^{-1}(1/T)$ for a polymer cured at room temperature. The values of the energy of defect formation are $E_{v1} = 1.27 - 0.42 = 0.85 \pm 0.09$ eV and $E_{v2} = 1.35 - 0.44 = 0.91 \pm 0.09$ eV, respectively, which, within the error range, coincides with estimates of migration energy after heat treatment. Most of the defects in the main polymer grid regained their chemical bonds after heating to 140°C and subsequent cooling to room temperature, and some of the broken bonds were frozen in the glass transition region. Therefore, only two rectilinear regions and not three, as in Fig. 5 are observed on dependence $\ln Q^{-1}(1/T)$ for the polymer T20-60 when measuring Q^{-1} after heating to a temperature of 140°C (Fig. 6). Heat treatments that facilitate the completion of polymerization process also led to an increase of the glass transition temperature from $T_g = 316$ K for the sample cured at room temperature (Fig. 5), to $T_g = 354$ K after the first heating and $T_g = 358$ K after the second heating (Fig. 6). The completion of the polymerization process after heat treatment resulted in a greater thermal stability of the polymer, which is confirmed by the higher temperature of the onset of internal friction growth: $T = 340$ K after the first heating and $T = 343$ K after the second heating (Fig. 6) vs. $T = 303$ K (Fig. 5).

When the relaxation maximum temperature is reached, all defects in the amorphous structure (broken chemical bonds) will reach the sample boundary (diffuse to the sample thickness) and the maximum condition (by analogy with thermoelastic attenuation) can be written as follows [37]:

$$\tau^{-1} = \pi^2 D/h^2, \tag{14}$$

where D is the diffusion coefficient of the amorphous structure defect, h is the thickness of the sample.

It follows from the condition of the maximum $\omega\tau = 1$ that Q^{-1} at temperatures above the temperature of the peak of α-relaxation can be described using the following formula [63]:

$$Q^{-1} = Q_0^{-1} \exp\left(\frac{E_m + E_v}{kT}\right). \tag{15}$$

Therefore, if we estimate the activation energy of the peak of α-relaxation based on its right leg, then higher energy values should be obtained for Q^{-1} of a diffusive

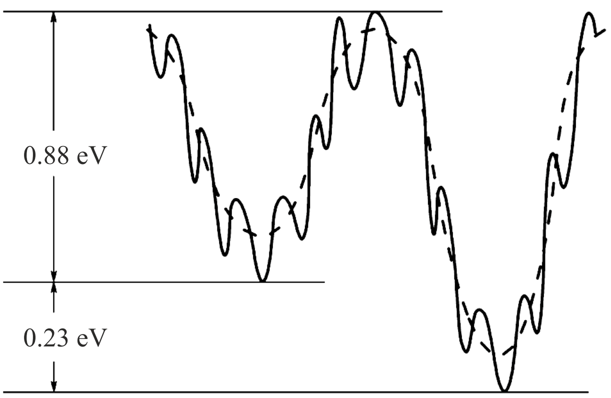

Figure 7. Energy barrier in the amorphous structure of polymer T20-60.

nature compared to the values determined on the left leg (see expression (13)). The activation energy estimates amounted to $E_{H1} = 1.08 \pm 0.09\,\text{eV}$ for the sample cured at room temperature (Fig. 5), $E_{H2} = 1.92 \pm 0.09\,\text{eV}$ after the first heating (Fig. 6, *a*) and $E_{H3} = 2.03 \pm 0.09\,\text{eV}$ after the second heating (Fig. 6, *b*). The activation energy of diffusion of vacancy-like defects E_D can be obtained by summing the formation energy E_v and the migration energy E_m. The diffusion activation energy was estimated as follows

$$E_{D1} = E_{m1} + E_{v1} = 0.84 + 0.85 = 1.69 \pm 0.09\,\text{eV}$$

after the first heating and

$$E_{D2} = E_{m2} + E_{v2} = 0.88 + 0.91 = 1.79 \pm 0.09\,\text{eV}$$

after the second heating. And the activation energy estimates made based on the high-temperature leg of the peak exceed the diffusion activation energy by

$$\Delta E_1 = E_{H2} - E_{D1} = 1.92 - 1.69 = 0.23 \pm 0.09\,\text{eV}$$

after the first heating and

$$\Delta E_2 = E_{H3} - E_{D2} = 2.03 - 1.79 = 0.24 \pm 0.09\,\text{eV}$$

after the second heating. The estimates of ΔE_1 and ΔE_2 correlate well with each other and reflect the contribution of two-level amorphous structure systems to mechanical relaxation (Fig. 7). The results obtained in this study indicate that the energy landscape of the amorphous polymer does not change even above T_g (at least in the region of α-relaxation), which is somewhat different from the results of Ref. [64]. The high joint mobility of atoms of the amorphous structure causes irreversible viscous flow and is associated with thermal activation of the free volume with an increase in temperature.

Thus, the results obtained above confirm the diffusive nature of the peak of α-relaxation. The activation energy values determined from the right and left legs should be equal for a relaxation peak of a non-diffusive nature. An additional confirmation of the diffusive nature of the peak of α-relaxation of the polymer T20-60 is the presence of a kink on the dependence $Q^{-1}(T)$ in the peak region (curve *3* in Fig. 2), which can be associated with different thicknesses of polymer layers the material deposited during the preparation of the sample. The maximum condition in this case is realized earlier in the thinner layer than in the thicker one, which results in the occurrence of a kink on the experimental curve (curves *2* and *3* in Fig. 3). It should be noted that control measurements of the polymer deposited on one side of the polycrystalline glass did not show „bifurcation" of a maximum in the region of α-relaxation.

Relaxation transitions in epoxy polymer T20-60 in the region of α-relaxation

Sample	T_m, K	τ_0, s	E_i, eV
Initial state	363	$6.24 \cdot 10^{8}$	$E_{B3} = 0.39$
After the 1st heating	403	$9.06 \cdot 10^{-8}$ $3.8 \cdot 10^{-13}$	$E_{B1} = 0.42$ $E_v = 0.85$
After the 2nd heating	408	$5.95 \cdot 10^{-8}$ $9.3 \cdot 10^{-14}$	$E_{B1} = 0.44$ $E_v = 0.91$

Knowing the activation energy E of the maximum of the internal friction and the frequency of mechanical vibrations f, we determine the pre-exponential factor τ_0 in the formula (4) of the relaxation process according to the formula [36]:

$$\tau_0 = \frac{1}{2\pi f} \exp\left(-\frac{E}{kT}\right), \tag{16}$$

where f is the frequency of mechanical vibrations of the sample under resonance conditions (at $\omega\tau = 1$).

Let us estimate the pre-exponential factor τ_0 of the relaxation process for a polymer cured at room temperature, taking the activation energy values determined by the left leg of the maximum Q^{-1} ($E_{B3} = 0.39\,\text{eV}$), which corresponds to the process of migration of defects with a constant concentration. The obtained values of the pre-exponential factor (see table) are lower than the inverse frequency of atomic vibrations ($\sim 10^{-13}\,\text{s}$), which also confirms the diffusive nature of the peak of α-relaxation for a sample cured at room temperature (Fig. 2).

We obtain similar values of the frequency factor for samples that have undergone the post-curing process during heating to 140°C (Fig. 6) (see table). The first value in this case corresponds to the activation energy determined in the low-temperature region Q^{-1}, when the migration of frozen defects takes place. Let us take the formation energy to estimate the frequency factor responsible for the formation of point defects of the amorphous structure taking into account the fact that diffusion of equilibrium defects of the amorphous structure (broken oxygen bonds) formed above T_g as a result of thermal activation takes place in the high-temperature region. The obtained values of the frequency factor ($\sim 10^{-13}\,\text{s}$) indicate the thermally activated nature of their formation. If we take the total energy of the relaxation peak of α-relaxation of the studied epoxy polymer of $E_m + E_v \approx 1.8$ eV, we obtain values of the frequency factor $\tau_0 \sim 10^{-26}$ s, devoid of physical meaning, which indicates the course of two thermally activated processes (diffusion and formation of point defects).

Finally, the question arises: what diffuses — oxygen atoms (as assumed for inorganic glasses in Ref. [29]) or point defects of the amorphous structure? The higher value of Q^{-1} peak (approximately two times) of the binder T20-60 after polymerization at room temperature (curve *1* in Fig. 2) compared with the height of the peaks after heat treatment, leading to the post-curing of the polymer, indicates the diffusion of point defects (broken chemical bonds). The diffusion process itself is similar to the conservative movement of the edge dislocation core in the crystal [65].

Thus, two rectilinear regions with different angles of inclination are observed in the epoxy polymer T20-60 in the region of α-relaxation on the left leg of the dependence $\ln Q^{-1}(1/T)$ which can be associated with the diffusion of vacancy-like defects in the three-dimensional polymer grid, which is consistent with the statement about unfreezing of segmental mobility of macromolecules of the polymer mesh, since the vacancy-like defect is an integral part of the grid [27,28], and the internal friction method itself can be recommended as a method for controlling the process of polymerization of epoxy polymers and determination of the glass transition temperature of amorphous solids.

Conclusion

The temperature dependences of internal friction $Q^{-1}(T)$ in the epoxy binder T20-60 deposited on a polycrystalline glass substrate have been studied. A peak associated with the process of α-relaxation was found near the glass transition temperature based on the dependence $Q^{-1}(T)$. Three linear sections with different angles of inclination are observed on the dependence $\ln Q^{-1}(1/T)$ for the left leg of Q^{-1} peak for the sample cured at room temperature. The migration energy $E_m = 0.70 \pm 0.09$ eV and the formation energy $E_v = 1.40 \pm 0.09$ eV were estimated which is associated with vacancy-like oxygen defects of the epoxy groups of the studied polymer.

Q^{-1} peak shifts towards higher temperatures after heat treatment, and two rectilinear regions with different angles of inclination are already observed on the dependence $\ln Q^{-1}(1/T)$ for the left leg of Q^{-1} peak. This behavior is associated with the migration of vacancy-like defects formed during the post-curing of the three-dimensional polymer grid. The migration energy $E_{m2} = 0.88 \pm 0.09$ eV, and formation energy $E_{v2} = 0.91 \pm 0.09$ eV of vacancy-like defects in the basic polymer grid is estimated. One straight section is observed on the dependence $\ln Q^{-1}(1/T)$ for the right leg of Q^{-1} peak. The evaluation of the activation energy on this leg showed higher values compared to the low-temperature leg, which indicates the diffusive nature of the process of α-relaxation of the epoxy binder T20-60.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] N.P. Kobelev, V.A. Khonik. UFN, **193** (7), 717 (2023) (in Russian). DOI: 10.3367/UFNr.2022.04.039173 [N.P. Kobelev, V.A. Khonik. Phys.-Usp., **66** (7), 690 (2023). DOI: 10.3367/UFNe.2022.04.039173]
[2] A.S. Arkhipin, A. Pisch, G.M. Zhomin, S.V. Kuzovchikov, A.V. Khvan, N.N. Smirnova, A.V. Markin, N.A. Kovalenko, I.A. Uspenskaya. J. Non-Cryst. Solids, **603**, 122098 (2023). DOI: 10.1016/j.jnoncrysol.2022.122098
[3] X. Liu, M.R. Abernathy, T.H. Metcalf, B. Jugdersuren, J.C. Culbertson, M. Molina-Ruiz, F. Hellman. J. Alloy. Compd., **855**, 157431 (2021). DOI: org/10.1016/j.jallcom.2020.157431
[4] W.H. Wang. Prog. Mater. Sci., **57**, 487 (2012).
[5] G.E. Abrosimova, D.V. Matveev, A.S. Aronin. Phys.-Usp., **65** (3), 227 (2022). DOI: 10.3367/UFNe.2021.04.038974
[6] E.V. Safonova, Yu.P. Mitrofanov, R.A. Konchakov, A.Yu. Vinogradov, N.P. Kobelev, V.A. Khonik. J. Phys.: Condens. Matter., **28**, 215401 (2016). DOI: 10.1088/0953-8984/28/21/215401
[7] A.D. Bereznera, V.A. Fedorov, M.Yu. Zadorozhnyy. J. Alloy. Compd., **923**, 166313 (2022). DOI: org/10.1016/j.jallcom.2022.166313
[8] Y.J. Duan, L.T. Zhang, J.C. Qiao, Y.J. Wang, Y. Yang, T. Wada, H. Kato, J.M. Pelletier, E. Pineda, D. Crespo. Phys. Rev. Lett., **129**, 175501 (2022). DOI: 10.1103/PhysRevLett.129.175501
[9] A.A. Valishin, A.A. Gorshkov, V.A. Lomovskoy. Mech. Solids, **46** (2), 299 (2011).
[10] Y.J. Duan, J.C. Qiao, T. Wada, H. Kato, Y.J. Wang, E. Pineda, D. Crespo. Scr. Mater., **194**, 113675 (2021). https://doi.org/10.1016/j.scriptamat.2020.113675
[11] V.S. Postnikov. Russ. Chem. Rev., **36** (10), 787 (1967).
[12] J.S. Harmon, M.D. Demetriou, W.L. Johnson, K. Samwer. Phys. Rev. Lett., **99**, 135502 (2007).
[13] J. Hachenberg, K. Samwer. J. Non-Cryst. Solids, **352**, 5110 (2006).
[14] H.B. Yu, W.H. Wang, K. Samwer. Mater. Today, **16**, 183 (2013).
[15] M. Atzmon, J.D. Ju. Phys. Rev. E, **90**, 042313 (2014).
[16] V.A. Lomovskoy, N.A. Abaturova, N.Yu. Lomovskaya, T.B. Galushko. Theor. Found. Chem. Eng., **55** (3), 457 (2021).

[17] S.V. Nemilov, Yu.S. Balashov. Glass Phys. Chem., **42** (2), 119 (2016). DOI: 10.1134/S1087659616020139

[18] N.P. Kobelev, I.G. Brodova, Ya.M. Soĭfer, A.N. Manukhin. Physics Solid State, **41** (4), 501 (1999). DOI: 10.1134/1.1130813

[19] V.A. Khonic. J. Phys. IV, **6** (8), 591 (1996).

[20] B. Cai, L.Y. Shang, P. Cui. Phys. Rev. B, **70**, 184208 (2004).

[21] L.T. Zhang, J.M. Pelletier, J.C. Qiao. J. Alloy. Compd., **869**, 159271 (2021). https://doi.org/10.1016/j.jallcom.2021.159271

[22] V.S. Bilanich, V.B. Onishchak, I.I. Makauz, V.M. Rizak. Physics Solid State, **52** (9), 1820 (2010). DOI: 10.1134/S1063783410090064

[23] A.N. Kabanskaya, V.A. Lomovskoy, A.A. Gorshkov, Z.I. Fomkina, E.V. Kopylova. Vestnik MITHT, **8** (5), 89 (2013) (in Russian).

[24] S.A. Gridnev, Yu.E. Kalinin, V.A. Dybov, I.I. Popov, M.A. Kashirin, N.A. Tolstykh. J. Alloy. Compd., **918**, 165610 (2022). https://doi.org/10.1016/j.jallcom.2022.165610

[25] T.R. Aslamazova, V.A. Kotenev, N.Y. Lomovskaya, V.A. Lomovskoi, A.Y. Tsivadze. Protection Metals and Physical Chemistry of Surfaces, **52** (6), 1012 (2016). DOI: 10.1134/S2070205116060071

[26] E.S. Zhavoronok, I.N. Senchikhin, O.A. Khlebnikova, N.Yu. Lomovskaya, V.A. Lomovskoi, V.I. Roldugin. Russ. J. Phys. Chem., **89** (4), 715 (2015). DOI: 10.1134/S0036024415040305

[27] G.M. Bartenev, S.YA. Frenkel *Fizika polimerov*. (Khimiya, L., 1990) (in Russian).

[28] V.I. Irzhak. *Epoksidnye polimery i nanokompozity* (Red.-izdat. otd. IPHF RAS, Chernogolovka, 2021) (in Russian).

[29] G.M. Bartenev, D.S. Sanditov. *Relaksatsionnye protsessy v stekloobraznykh sistemakh* (Nauka, Novosibirsk, 1986) (in Russian).

[30] G.M. Bartenev, V.A. Lomovskoi. Polym. Sci. Ser. A, **44** (8), 841 (2002).

[31] V.A. Lomovskoy. Tonkie khimicheskie tekhnologii, **10** (3), 5 (2015) (in Russian).

[32] M. Reiner. Phys. Today, **17** (1), 62 (1964). DOI: 10.1063/1.3051374

[33] G.M. Bartenev, A.G. Barteneva. *Relaksatsionnye svoistva polimerov* (Khimiya, M., 1992) (in Russian)

[34] G.M. Bartenev, V.A. Lomovskoi. Russ. J. Phys. Chem., **77** (12), 2045 (2003).

[35] Y.E. Kalinin, A.M. Kudrin, O.V. Ovdak, I.I. Popov. Polym. Sci. Ser. A, **64** (1), 1 (2022). DOI: 10.1134/S0965545X22010047

[36] A.S. Nowick, B.S. Berry. *Anelastic relaxation in crystalline solids.* (Academic Press, NY., London, 1972)

[37] B. Escaig. Acta Metal., **10**, 829 (1962).

[38] Yu.R. Zakis. *Defekty v stekloobraznom sostoyanii veshchestva* (Zinatne, Riga, 1984) (in Russian).

[39] A.K. Doolittle. J. Appl. Phys., **22**, 1471 (1951).

[40] D. Turnbull, M.H. Cohen. J. Chem. Phys., **34**, 120 (1961).

[41] D. Turnbull, M.H. Cohen. J. Chem. Phys., **52**, 3038 (1970).

[42] Ya.I. Frenkel. *Vvedeniye v teoriyu metallov* (Nauka, L., 1972) (in Russian).

[43] Yu.R. Zakis. *Fizika i himiya stekloobraznyh sistem* (LGU, Riga, 1980) (in Russian).

[44] F. Spaepen. J. Non-Crystal. Solids, **31** (1-2), 207 (1978).

[45] F. Spaepen. Scr. Mater., **54**, 363 (2006).

[46] C.A. Schuh, T.C. Hufnagel, U. Ramamurty. Acta Mater., **55**, 4067 (2007).

[47] A. Van den Beukel, J. Sietsma. Acta Metall. Mater., **38**, 383 (1990).

[48] G.V. Kozlov, V.U. Novikov. Phys.-Usp., **44** (7), 681 (2001). DOI: 10.1070/PU2001v044n07ABEH000832

[49] K.S. Gabriels, T.V. Dubovitskaya, Yu.E. Kalinin, M.A. Kashirin et. al. Thin Solid Films, **804**, 140504 (2024). https://doi.org/10.1016/j.tsf.2024.140504

[50] I.V. Zolotukhin, Y.E. Kalinin. Sov. Phys. Usp., **33** (9), 720 (1990). DOI: 10.1070/PU1990v033n09ABEH002628

[51] S.A. Gridnev, Y.E. Kalinin. Tech. Phys., **68** (3), 532 (2023). DOI: 10.1134/S1063784223900826

[52] N.P. Kobelev, E.L. Kolyvanov, V.A. Khonik. Physics Solid State, **45** (12), 2225 (2003). DOI: 10.1134/1.1635489

[53] Yu.E. Kalinin, A.T. Kosilov, O.V. Ovdak, A.M. Kudrin, O.A. Karaeva, M.A. Kashirin, D.Ya. Degtyarev. Tech. Phys., **64** (4), 535 (2019). DOI: 10.1134/S1063784219040121

[54] Electronic resource. *Epoxy binderT20-60* Available at: www.itecma.ru

[55] A.V. Sitnikov, V.A. Makagonov, Y.E. Kalinin, S.B. Kushchev, V.A. Foshin. Tech. Phys., **68** (11), 1542 (2023). DOI: 10.21883/0000000000

[56] S.A. Gridnev, I.I. Popov, M.A. Kashirin, A.I. Bocharov. J. Alloy. Compd., **889**, 161764 (2021). https://doi.org/10.1016/j.jallcom.2021.161764

[57] Z.S. Li, Q.F. Fang, S. Veprek, S.Z. Li. Mater. Sci. Eng. A, **370**, 186 (2004). https://doi.org/10.1016/j.msea.2003.09.048

[58] D.S. Sanditov, M.I. Ojovan. Phys.-Usp., **62** (2), 111 (2019). DOI: 10.3367/UFNe.2018.04.038319

[59] D.S. Sanditov. Dokl. Phys. Chem., **464** (2), 255 (2015). DOI: 10.1134/S0012501615100097

[60] I.V. Zolotukhin, YU.E. Kalinin, O.V. Stognej. *Novye napravleniya fizicheskogo materialovedeniya* (Izd-vo VGU, Voronezh, 2000) (in Russian).

[61] D.S. Sanditov, A.A. Mashanov. Polym. Sci. Ser. A, **61** (2), 119 (2019). DOI: 10.1134/S0965545X1902010X

[62] Y.E. Kalinin, B.M. Darinskii. Metal Sci. Heat Treatment, **54** (5-6), 221 (2012).

[63] V.S. Postnikov. *Vnutrenneye treniye v metallakh* (Metallurgiya, M., 1974) (in Russian).

[64] Z. Wang, B.A. Sun, H.Y. Bai, W.H. Wang. Nat. Commun., **5**, 5823 (2014).

[65] *Sovremennaya kristallografiya* (v chetyrekh tomakh). *Fizicheskie svojstva kristallov* L.A. Shuvalov, A.A. Urusovskaya, I.S. Zheludev i dr. (Nauka, M., 1981), t. 4. (in Russian).

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