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DEVELOPMENT AND RELAXATION OF INTERNAL STRESSES IN GRANULAR COMPOSITES WITH AN EPOXY MATRIX

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The development and relaxation of stresses in epoxy matrix–filler systems were studied experimentally under isotropic thermal and baric effects. Data on the nuclear quadrupole resonance of the filler crystals were analyzed using an empirical model for the relaxation processes in the matrix of the composite material. The effective stress-relaxation time was found to depend on the temperature, external pressure, and the magnitude and type of deformations of the polymer matrix.

Key words: *relaxation, granular composites, nuclear quadrupole resonance.*

1. FORMULATION OF THE PROBLEM

The production of articles from polymer composite materials usually involves the occurrence of internal stresses. The articles are subjected to annealing to relieve technological and shrinkage stresses. However, subsequent cooling leads to the development of significant stresses in the heterogeneous matrix–filler system [1, 2]. These stresses cannot be relieved by annealing or by different methods. They decrease only as a result of natural relaxation process due to molecular mobility in polymers.

The present paper gives results from a study of the relaxation of internal stresses in a granular composite with an epoxy matrix.

The experiments are performed with the use of nuclear quadrupole resonance (NQR). NQR is observed in crystalline substances containing atomic nuclei with a spin of $I \geqslant 1$. The NQR spectral parameters are highly sensitive to a change in the external conditions of the crystals. This allows the crystalline filler powder to be used as an indicator of internal stresses in the polymer matrix [3]. The pressure of the polymer matrix p_f on the surface of the indicator crystals leads to a proportional change in the NQR frequency ν_f:

$$\nu_f(p_f) = \nu_f(0) + \Big(\frac{\partial \nu}{\partial p}\Big)_T p_f.$$

Here $\nu_f(0)$ is the NQR frequency of the indicator crystals in the absence of pressure and p_f is the average contact pressure on the filler particles in the sample studied.

We studied samples of ÉD-10, ÉD-16, and ÉD-20 epoxy resins cured by polyethylene polyamine at a temperature $T = 413$ K. As the filler we used powdered Cu_2O copper oxide with a volumetric concentration $c_f = 0.10$–0.12. The samples had the shape of cylinders of diameter 8 mm and height 20 mm.

At $T = 293$ K and atmospheric pressure, the NQR frequency of the ^{63}Cu nuclei in the Cu_2O crystals is equal $\nu = 26{,}015$ KHz. Under uniform all-round compression of the crystals by a pressure p, the frequency increases at

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a constant rate $(\partial\nu/\partial p)_T = (369 \pm 2)$ Hz/MPa. The value of the coefficient $(\partial\nu/\partial p)_T$ is almost independent of temperature [2]. Another advantage of this indicator substance is the cubic structure of its crystal lattice, which allows Cu_2O particles to be considered as isotropic bodies under uniform all-round compression and heating.

In the range $T = 300$–400 K, the change in the NQR frequency of the copper nuclei is more than an order of magnitude higher than the frequency shift due to the pressure of the polymer matrix [4, 5]. Therefore, to compensate for the temperature dependence of the NQR frequency, we used a control sample (Cu_2O powder which was not introduced into the epoxy resin). Both samples were under identical conditions: at the same stabilized temperature T and the same external pressure p_e. We measured the frequency shift (frequency difference) of the NQR line ν_f in the examined sample with respect to the NQR line ν in the control sample [4]:

$$\Delta\nu = \nu_f(T, p_e) - \nu(T, p_e) = \Big(\frac{\partial\nu}{\partial p}\Big)_T (p_f - p_e). \qquad (1)$$

In the description of the results of the NQR experiments, the contact pressure is given in frequency units.

The experimental setup included a pulse Fourier NQR spectrometer, a high-pressure chamber filled with oil, and a temperature control system. An MT-600 press manometer was used to produce hydrostatic pressure in the chamber. The temperature was maintained constant to within 0.02 K. Using signal accumulation and some effects related to the detection of nonuniformly broadened lines, it was possible to reliably detect small shifts of the NQR frequency in the filler crystals and to determine the contact pressure with an error not exceeding 0.1 MPa.

2. TECHNIQUE AND RESULTS OF EXPERIMENTS WITH EPOXY SAMPLES

2.1. Temperature Dependence of the Internal Stresses in the Epoxy Matrix. The samples were annealed at $T = 413$ K and then cooled to $T = 293$ K at atmospheric pressure. Immediately after the cooling, the stresses that arose in the matrix near the surface of the filler crystals reached $\sigma_{rr} = 12$–23 MPa, depending on the resin grade and the degree of filling.

To study the development of internal stresses, we placed the samples in the thermostat oil bath. The oil temperature was varied stepwise by 5 or 10 K at intervals of 30 min. The curves of $p_f(T) = \Delta\nu(T)/(\partial\nu/\partial p)_T$ for sample cooling (curves 1 in Fig. 1) almost coincide with the curves of $p_f(T)$ obtained for sample heating. These curves have two linear segments, which correspond to the glassy and highly elastic states of the matrix. The temperature range in which inflection of the curves is observed corresponds to the range of glass-transition temperatures. Below the glass-transition range, the contact pressure increases linearly, indicating a nonequilibrium state of the matrix–filler system. The average values of the glass-transition temperature are found to be $T_g = 356$ K for ÉD-10 samples, $T_g = 376$ K for ÉD-16 samples, and $T_g = 383$ K for ÉD-20 samples. The difference between the glass-transition temperatures measured using a dilatometric method and NQR does not exceed the experimental error.

2.2. Effect of External Hydrostatic Pressure on the Relaxation of Internal Stresses. The examined and control samples were placed in a high-pressure chamber filled with oil. The chamber had a water jacket connected to the outer contour of the ultrathermostat.

The all-round compression of the sample by external pressure causes a shift in the temperature curve of the contact pressure on the filler particles toward high temperatures. Curve 3 in Fig. 1 was obtained for sample cooling under a pressure $p_e = 49.1$ MPa. Its shift relative to curve 1 indicates an increase in the stress-relaxation time due to a reduction in molecular mobility in the material under compression. For ÉD-10 resin, the glass-transition temperature increases at a rate $\partial T_g/\partial p_e = 0.24$ K/MPa.

The exposure of the glassy samples to external hydrostatic pressure produces additional stresses in the matrix near the surface of the filler particles. Thus, compression of a ÉD-10 sample ($c_f = 0.12$) by a pressure $p_e = 49.1$ MPa at $T = 293$ K results in an increase in the contact pressure from $p_f = 18.7$ MPa to $p_f = 81.1$ MPa ($\Delta p_f = 62.4$ MPa). Curve 4 in Fig. 1 shows the variation in the contact pressure during heating of the loaded sample. The oil pressure in the chamber was kept at a level $p_e = 49.1$ MPa. The nonlinearity of the temperature dependence of the contact pressure indicates the presence of a relaxation process in the stressed matrix. With approach to the glass-transition temperature, the steepness of curve 4 increases, but at $T = T_g = 356$ K, the resin

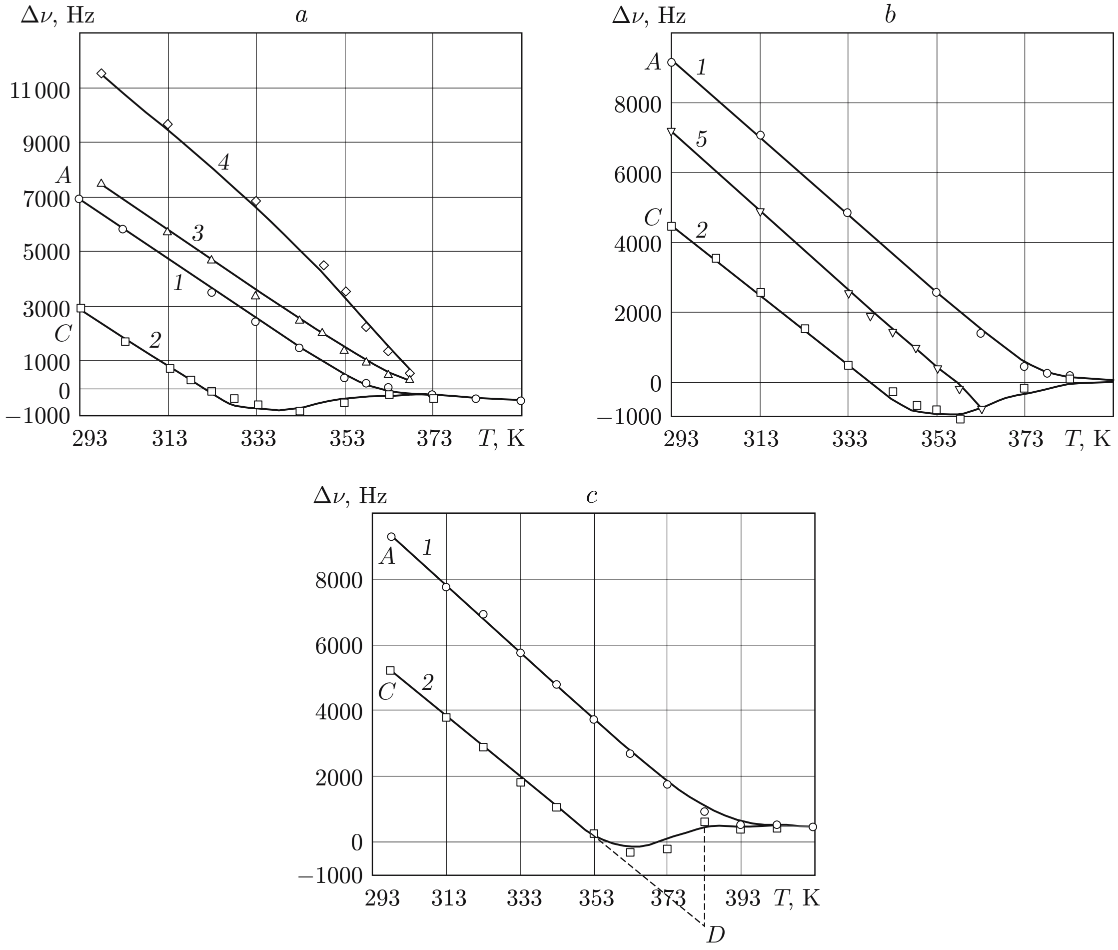

Fig. 1. NQR frequency shift in the filler versus temperature in ÉD-10 (a), ÉD-16 (b), and ÉD-20 samples (c): 1) sample cooling after annealing; 2) sample heating after precooling under pressure; 3) cooling of the sample under external pressure; 4) sample heating under external pressure; 5) sample cooling after heating to $T > T_g$.

does not enter a highly elastic state, as is indicted by the presence of a contact pressure exceeding the external pressure by 8 MPa. In Fig. 1, the ordinates $\Delta\nu = (\partial\nu/\partial p)(p_f - p_e)$ of the points on curves 3 and 4 correspond to values of the contact pressure p_f ignoring the external hydrostatic pressure p_e applied to the sample.

2.3. Glass Transition of the Matrix under External Pressure. Slowly relaxing stresses were found to form in the matrix–filler system at temperatures exceeding the glass transition temperature (Fig. 2). A stepwise increase in the hydrostatic pressure p_e on the ÉD-10 sample ($c_f = 0.12$) by 4.91 MPa every 30 min at a temperature exceeding the glass-transition temperature by 7 K (curve 1 in Fig. 2) and 12 K (curve 2) leads to the occurrence of a contact pressure $p_f = p_e + \Delta\nu/(\partial\nu/\partial p)$ that exceeds the external pressure.

The slope of the curves of $\partial(p_f - p_e)/\partial p_e \leqslant 0.08$ is much smaller than that in the case of pressure application on the sample at room temperature [5]: $\partial(p_f - p_e)/\partial p_e = 0.27$. Consequently, stress relaxation proceeds simultaneously with stress growth, and the relaxation time increases from 10 to 10^3 sec during the compression of the sample. The response to all-round compression can be treated as transition of the matrix to a nonequilibrium (glassy) state due to a decrease in the “free volume” required for conformational motion of the polymer chains.

2.4. Stress Relaxation at Temperatures Close to the Glass-Transition Temperature. In the cured epoxy resins at room temperature, the stress-relaxation time is very large; therefore, it is expedient to perform the study at a temperature close to the temperature of transition of the resin to the highly elastic state T_g. However, as T_g is approached, the temperature stresses in the matrix–filler system tend to zero (curves 1 in Fig. 1). To produce stresses in the matrix at $T \approx T_g$, we heated the samples to a temperature $T = 423$ K and then cooled them under a hydrostatic pressure $p_e = 49.1$ MPa to room temperature (curve 3 in Fig. 1).

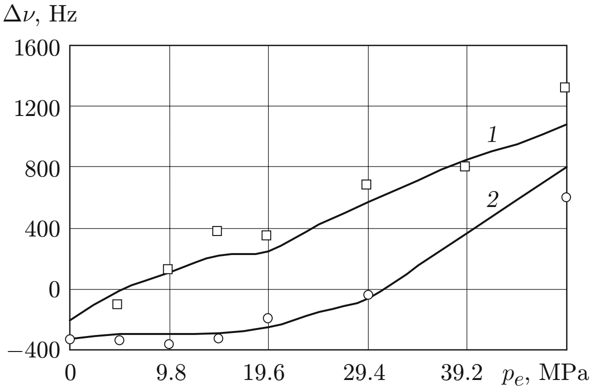

Fig. 2. The development of stresses in the matrix–filler system caused by a stepwise increase in the hydrostatic pressure for $T = 363$ (1) and 368 K (2).

All-round compression of the sample by the external pressure at $T > T_g$ causes volume and shear stresses in the matrix layers adjoining the filler particles. Cooling of the sample under a pressure leads to "freezing" of the stresses. After removal of the external pressure at room temperature, the internal stresses turn out to be lower (the points C on curves 2 in Fig. 1) than those in the samples cooled without exposure to the external pressure (the points A on curves 1).

The samples that undergone glass transition under the pressure were heated in the thermostat oil bath at $p_e = 0$. It was expected that the contact pressure on the filler particles would vary linearly to the glass-transition temperature T_g (the curve CD on Fig. 1c). It was found that stress relaxation occurs at temperatures well below the glass-transition temperatures (curves 2 in Fig. 1). Thus, the relaxation processes become significant at $T = 328$ K for ÉD-10 samples, at $T = 343$ K for ÉD-16 samples, and at $T = 358$ K for ÉD-20 samples. At these temperatures, the contact pressure changes sign, which indicates the occurrence of tensile stress in the matrix layers adjoining the surface of the filler particles. The tensile deformation is accompanied by volume expansion since the Poisson coefficient for glass epoxy is smaller than 0.5. The considerable reduction in the relaxation times is a consequence of an increase in the "free volume."

The temperature dependences of the contact pressure are similar in shape for all samples that undergo glass transition under pressure. It was verified whether the matrix is separated from the filler crystals when tensile stresses occur. At a temperature that has not reached the glass-transition temperature, the heating of the sample was stopped and cooling began; in this case, the contact pressure immediately began to increase linearly (curve 5 in Fig. 1).

In the case of slow heating of the samples with "frozen" strains, the stresses in the matrix–filler system relax almost completely at a temperature below the glass-transition temperature. To study the relaxation process at a temperature close to T_g, we performed sample heating as rapidly as possible. Before the experiment, the oil bath was heated to the chosen temperature T. After the attainment of the temperature, we placed the sample in the bath and examined the variation in the NQR signal frequency of the filler.

Relaxation curves for each sample were obtained at several temperature values below the glass-transition temperature. One of the relaxation curves is given in Fig. 3. As the glass transition temperature is approached, the stress-relaxation time is considerably reduced. The observed relaxation process has an exponential nature.

3. DISCUSSION OF EXPERIMENTAL RESULTS

3.1. Phenomenological Model for the Relaxation Processes in the Matrix–Filler System of Solid Composites. The model of a cross-linked amorphous polymer material with a granular filler is based on the assumption of macroscopic uniformity of the system consisting of an viscoelastic disperse medium with uniformly distributed elastic dispersed particles. A compound body containing one particle of the filler is used as the representative volume (Fig. 4). The stress on the external boundaries of all compound bodies are identical and

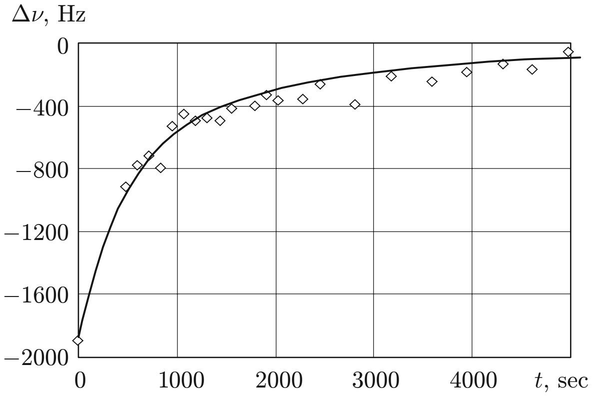

Fig. 3. Stress relaxation in the matrix–filler system in a ÉD-16 sample at $T = 358$ K.

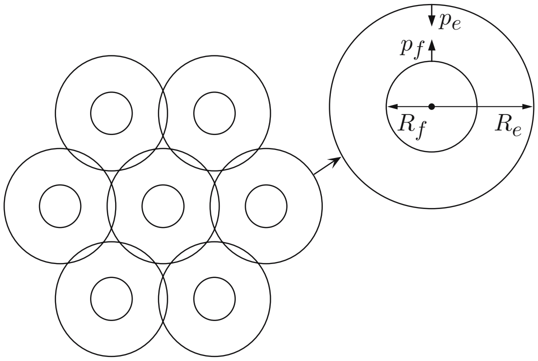

Fig. 4. Structural model for a material with spherical inclusions.

equal to the stresses on the external boundary of the medium. The initial unstrained state is taken to be the state of the compound body at a temperature T_g (the glass-transition temperature of the matrix) and the external pressure $p_e = 0$. In spherical coordinates with origin at the center of the compound body, the stress tensor components in the matrix near the surface of the filler particle have the form [4, 5]

$$\sigma_{rr} = -s + c_f s - p_e, \qquad \sigma_{\theta\theta} = \sigma_{\varphi\varphi} = s/2 + c_f s - p_e. \tag{2}$$

The expression for the stress tensor deviator

$$s = 4\mu\,\frac{(\alpha - \alpha_f)(T_g - T) + (\chi - \chi_f)p_e}{3 + 4\mu[\chi c_f + \chi_f(1 - c_f)]} \tag{3}$$

includes the elastic and thermal characteristics of the matrix: the volume thermal-expansion coefficient α, the volume compressibility χ, the shear modulus μ, the volume thermal-expansion coefficient α_f and volumetric compressibility χ_f of the filler particle, and the volume concentration of the filler $c_f = (R_f/R_e)^3$.

In the model considered, the contact pressure p_f on all filler particles is the same and is numerically equal to the matrix stress component normal to the particle surface [4]:

$$p_f = -\sigma_{rr}. \tag{4}$$

From expressions (1), (2), and (4), it follows that the quantity s can be found experimentally from the NQR frequency shift in the filler:

$$s = \frac{\Delta\nu}{(1 - c_f)(\partial\nu/\partial p)}. \tag{5}$$

Relations (2) and (3) do not take into account the viscoelastic properties of the polymer matrix. These relations describe the temperature and pressure dependences of the stresses if conformal transformations of the polymer chains do not occur throughout the experiment. In Fig. 1, this case corresponds to the linear segments of curves 1 and 3 at temperatures below the glass-transition temperature. The observed nonlinearity of the temperature dependences of the NQR frequencies for the filler (curves 2 and 4 in Fig. 1) indicates relaxation processes in the stressed matrix of the samples at temperatures below the glass-transition temperature.

The range of the stress-relaxation times for polymers is very wide because of the difference in the mobility of kinetic units from individual chain links to supermolecular structures [6]. However, without considering details of the mechanism of these motions, it is possible to introduce a certain effective energy of their activation U and to describe the temperature dependence of the relaxation time τ using the Arrhenius relation [7]

$$\tau(T) = \tau_0 \exp\left(U/(RT)\right). \tag{6}$$

Here $R = 8.31$ J/(mole $\cdot$ K) is the universal gas constant; the preexponent τ_0 is set to be equal to the period of fluctuations of the free kinetic segment: $\tau_0 = 10^{-12}$ sec [7].

It is necessary to choose a function $U(p, T)$ such that relation (6) describes relaxation processes in both the highly elastic and glassy states of the matrix, including the transition region.

Transition from the highly elastic to the glassy state occurs in a narrow temperature range $T_g - \delta T \leqslant T \leqslant T_g + \delta T$. In the range δT, the volume in which molecular segments can move decreases to such an extent that individual segments cannot perform correlated motion [8]. The degree of cooperativeness in molecular motion can be put in correspondence to the increment in the effective activation energy:

$$U = U_E\Bigl(1 + g\,\frac{1}{1 + \exp\left[(T - T_g)/\delta T\right]}\Bigr) \tag{7}$$

(U_E is the effective activation energy for relaxation processes in the matrix in a highly elastic state).

From the experiments performed, it follows that external pressure and internal stresses in the material influence the relaxation rate. As a measure of the increase in the effective activation energy for the compression of the material, we use the change in the specific potential energy of elastic deformation:

$$\Delta F = \chi p_e^2/2.$$

In the model of the network of intermolecular bonds [9, 10], the internal stresses in the material are mainly the stresses of physical intermolecular bonds. The strength of the bonds decreases as the stresses increase. Assuming that segmentary motion of molecules becomes possible only in the case of rupture of physical bonds, we supplement Eq. (7) by a term that characterizes the variation in the effective activation energy due to internal stresses in the matrix:

$$\Delta F = -3s^2/(8\mu).$$

Thus, the equation for the effective activation energy becomes

$$U = U_E\Bigl(1 + g\,\frac{1}{1 + \exp\left[(T - T_g)/\delta T\right]}\Bigr) - V\Bigl(\frac{3}{8\mu}\,s^2 - \frac{\chi}{2}\,p_e^2\Bigr), \tag{8}$$

where V is the molar volume [2].

Experiments were performed with a stepwise change in the parameters of external action on the tested material sample; therefore, to describe the stress development and relaxation in the matrix using Eqs. (3), (6), and (8), we constructed the recursive relation

$$\begin{gathered} s_k = \Bigl(s_{k-1} + \frac{\partial s}{\partial T}\,\Delta T_k + \frac{\partial s}{\partial p}\,\Delta p_k\Bigr) \exp\Bigl(-\frac{\Delta t_k}{\tau_k}\Bigr), \qquad \tau_k = \tau_0 \exp\Bigl(\frac{U_k}{RT_k}\Bigr), \\ U_k = U_E\Bigl(1 + g\,\frac{1}{1 + \exp\left[(T_k - T_g)/\delta T\right]}\Bigr) - \frac{3}{8\mu}\,V s_{k-1}^2 + \frac{\chi}{6}\,V p_k^2, \end{gathered} \tag{9}$$

where ΔT_k and Δp_k are the changes in the temperature and external pressure at the kth step; Δt_k is the step duration (i.e., the time during which the sample is at specified T_k and p_k); U_k is the effective activation energy, which determines the temperature dependence of the relaxation time; and the coefficients $\partial s/\partial T$ and $\partial s/\partial p$ are determined by the instantaneously elastic characteristics χ, μ, and α of the matrix (3).

TABLE 1

Degree of Slope of Linear Segments of Temperature Dependences of NQR Frequency Shift for Filler (see Fig. 1)

Epoxy	T_g, K	$\partial\Delta\nu/\partial T$, Hz/K	
		for curve 1	for curve 2
ÉD-10 + PEPA	356	−110	−103
ÉD-16 + PEPA	376	−112	−100
ÉD-20 + PEPA	383	−103	−91

Note. PEPA is a polyethylene polyamine.

The recursive relation (9) includes five adjusting parameters: the effective activation for the relaxation process in the highly elastic matrix U_E, the molar volume of the kinetic segment of the macromolecule V, the range of the glass-transition temperatures $(T_g - \delta T, T_g + \delta T)$, and the relative increase in the activation energy in the transition region g.

3.2. Stress Development and Relaxation in the Epoxy Matrix. We transform relation (9) to a convenient form to describe the experimental NQR data. The glass-transition temperature T_g included in (9) should be determined as the temperature at which the relaxation time of the examined type of stresses becomes comparable to the characteristic time of the experiment (the step duration for the external-action parameters). Its value obtained from the relaxation dependences can coincide with the value of T_g determined by a dilatometric method only in the case of stress-relaxation temperature. To avoid ambiguity, we eliminate T_g from the recursive relation (9).

Using relations (3) and (5), we replace the quantities s and $T - T_g$ by the corresponding NQR frequency shifts in the filler ignoring the quantities α_f, χ_f, and c_f because of their smallness. The recursive relation becomes

$$\Delta\nu_k = \Big(\Delta\nu_{k-1} + \frac{\partial\Delta\nu}{\partial T}\,\Delta T_k + \frac{\partial\Delta\nu}{\partial p_e}\,\Delta p_k + A_k\Big)\exp\Big(-\frac{\Delta t_k}{\tau_k}\Big) - A_k,$$

$$\tau_k = \tau_0 \exp\Big(\frac{U_k}{RT_k}\Big), \qquad (10)$$

$$U_k = U_E\Big(1 + \frac{g}{1 + \exp\left[-b(\Delta\nu_{k-1} + A_{k-1})/(\alpha\delta T)\right]}\Big) - V\Big(\frac{2\mu}{3}\,b^2(\Delta\nu_{k-1} + A_{k-1})^2 - \frac{\chi}{2}\,p_k^2\Big),$$

where $b = 3/[4\mu(1 - c_f)(\partial\nu/\partial p)]$.

The instantaneously elastic characteristics of the matrix χ, μ, and α, included in expression (10) are set equal to the corresponding characteristics of this matrix in the glassy state. For example, for ÉD-10 epoxy cured by polyethylene polyamine, they have the following values [5]: $\alpha = 2.5\cdot 10^{-4}$ K^{-1}; $\chi = 0.253$ GPa^{-1}; and $\mu = 1.05$ GPa. Taking into account that the elastic characteristics of the epoxy resins cured by the same hardener have close values [11], we use the above values α, χ, and μ for all samples tested.

For the highly elastic state of the matrix, the measured NQR frequency shifts for the filler (curves 1 and 2 in Fig. 1) are different from zero, and these differences exceed the experiment error. Obviously, these differences result from the stresses in the matrix layer with reduced molecular mobility near the surface of the filler crystals [12]. Their effect on the recorded frequency shift is taken into account in relation (10) by introducing the corrections $A_k = B - CT_k$, where B and C are constants that describe the elastic properties the subsurface layer of the matrix. Their values are found by linearizing the segments of the dependences $\Delta\nu(T)$ corresponding to the highly elastic state of the matrix.

The values of the coefficients $\partial\Delta\nu/\partial T$ in relation (10) are determined by linearizing the low-temperature segments of the dependences $\Delta\nu(T)$ corresponding to the glassy state of the matrix (curves 1 and 2 in Fig. 1) and are given in Table 1. The values of the adjusting parameters U_E, g, δT, and V are found by minimization of the sum of the squares of the differences of the calculated curves $\Delta\nu_k(T_k)$ from experimental points and are given in Table 2.

TABLE 2

Values of Adjusting Coefficients in Recursive Relation (10)

Epoxy	U_E, kJ/mole	g, kJ/mole	δT, K	V, m^3
ÉD-10 + PEPA	96.0 ± 0.5	108.0 ± 0.5	2	0.02
ÉD-16 + PEPA	101.6 ± 0.5	113.4 ± 0.5	3	0.01
ÉD-20 + PEPA	103.5 ± 0.5	114.5 ± 0.5	5	0.01

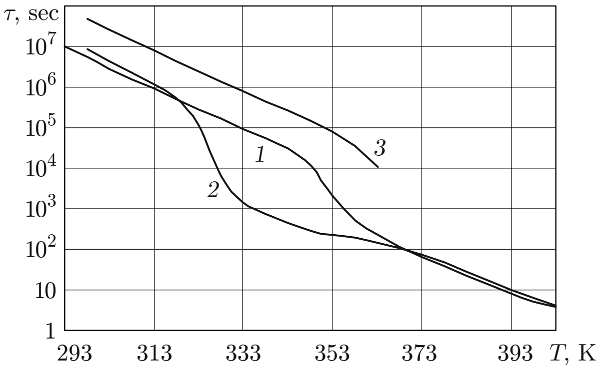

Fig. 5. Effective stress-relaxation time versus temperature in an ÉD-10 sample: 1) sample cooling without external pressure; 2) sample heating with “frozen” strains without pressure application; 3) sample cooling under pressure.

The calculated temperature curves of the NQR frequency shifts for the filler for sample heating (curves 2 and 4 in Fig. 1) and cooling (curves 1 and 3 in Fig. 1) are fitted to experimental points by using the same values of the adjusting parameters. We note that high stresses lead to acceleration of relaxation processes in the matrix (curves 2 and 4 in Fig. 1).

In samples with “frozen” strains at a fixed temperature, the stress-relaxation process is described by relation (10) in which the coefficients p_k, Δp_k, ΔT_k, and A_k are set equal to zero. The adjusting parameters (see Table 2) obtained by processing the temperature dependences $\Delta\nu(T)$ were used. One of the obtained relaxation curves is given in Fig. 3. The reduction in the internal stresses with time has a multiexponential nature.

From Figs. 1 and 3 it follows that the recursive relation (10) adequately describes stress relaxation in the matrix at a temperature below the glass-transition temperature.

For an adequate description of the pressure dependences of internal stresses obtained for the case of stepwise application of a pressure $\Delta p_k = 4.91$ MPa at a temperature higher than the glass-transition temperature (see Fig. 2), the adjusting parameter V was decreased to $V = 0.009$ m^3.

Temperature curves of the effective stress-relaxation time τ that correspond to the recursive relation (10) are given in Fig. 5. In the range of temperatures corresponding to transition to the glassy state, an increase in the degree of cooperativeness in the segmentary motion of the matrix macromolecules results in an increase in the effective activation energy of relaxation and a more than an order of magnitude change in the time τ (curve 1 in Fig. 5). The relaxation time depends not only on the temperature but also on the stress state of the matrix–filler system. In the case of compression of the material by an external pressure $p_e = 49.1$ MPa, the relaxation time increases (curve 3). The tensile stresses arising from heating of a sample with “frozen” strains lead to a decrease in τ at a temperature well below T_g (curve 2 in Fig. 5).

CONCLUSIONS

The effects of temperature and external pressure on internal stresses in granular composites with epoxy binders was studied experimentally. At temperatures higher than the glass-transition temperature of the binder, the stresses are close to zero. At room temperature, the stresses near the surface of the filler particles reach $\sigma_{rr} = 19$–27 MPa.

The all-round compression of the material by external pressure leads to an increase in the stress-relaxation time and the occurrence of slowly relaxing stresses at the temperatures corresponding to the highly elastic state of the matrix whereas an increase in the internal stresses leads to a reduction in the stress-relaxation time. The glass-transition temperature determined from the degree of activation of the relaxation processes depends on the external pressure, stresses, and strains.

The experimentally observed temperature and pressure dependences of the internal stresses are described by one phenomenological relation. Adjusting parameters were sought by joint processing of measured frequency shifts in all experiments performed. As a result, a set of adjusting parameters was obtained for each sample. The proposed calculated dependences are in good agreement with experimental data obtained for all samples tested.

Thus, use of NQR spectroscopy extends the capabilities of experimental studies of chemical processes in the system of a matrix and a solid composite filler.

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