

Relaxation properties of organo-mineral composites

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Abstract. The relaxation properties of hybrid organic-mineral composite materials based on liquid sodium glass, 2,4-toluendiisocyanate and the polyisocyanate, modified epoxy resin have been investigated. The aim of this work is to produce building materials, combining the properties of organic polymers and inorganic materials. Obtaining such materials in one stage creates the preconditions for energy savings and obtaining high quality materials. Curing in the mild conditions at temperatures of 60-70°C leads to the formation of network structures of the polymers. Methods: To characterize the mechanical properties used method stress relaxation. For polymers, the relaxation properties are not less important than the ultimate mechanical properties (strength and deformability). At constant strain, the stress relaxes intensively, resulting in loss of mechanical efficiency of the material. Measurement of stress relaxation at various temperatures gave the opportunity of creating master curves of relaxation and prediction of mechanical behavior for a long time. To study the chemical structure of the produced materials we used the method of IR spectroscopy. The outcome of the following: Spectral studies and related calculations using the computer program "Cascade" (INEOS RAS) indicate the complex nature of the chemical transformations during thermal exposure in preparing monolithic samples. Modification of the initial mixtures with epoxy resin results in a more homogeneous fine-grained structure of the composites and improving their mechanical properties. The study of the process of stress relaxation at various temperatures in the range 20-100°C were provided and the physical parameters of the memory functions were found. The initial relaxation modulus reached values of 1000 MPa at 20°C, and 540 MPa at 100°C. For free of non-modified epoxide starting materials of the relaxation module was 730 MPa at 20°C and at 100°C to 520. The master curves were drawn to predict relaxation behavior for large durations of the course of process. The greatest relaxation module has material containing an increased amount of a polyisocyanate. Conclusions: the resulting structures can serve as the basis of decorating and construction building materials. They are easily painted in different color, have moderate stress relaxation and high relaxation modules.

Keywords: relaxation properties, organo-mineral composite materials, liquid sodium glass, 2,4-toluendiisocyanate, polyisocyanate.

1. Introduction

The promising direction of improvement of technological, physical-mechanical, thermophysical and other properties of composite materials is the development and use of complex binders, among which



of particular interest are hybrid organic-mineral compositions [1-3]. Representatives of such compositions are hybrid organic-inorganic binders that allow to obtain composite materials having properties inherent to organic polymers and inorganic materials [4-5]. The other way of looking at the problem is addition into polymer matrix of inorganic particles with the surface modified by the grafted organic molecules [6-7]. This allows to obtain nanocomposites with unusual combination of properties.

Structure and properties of metal-polymer composites are described in [8]. In the review article [9] analyzed the structure and properties of polymer nanocomposites, in which matrix polymers have different chemical structure. Among them polymer-layered silicates, as well as composites in which the dispersed phase is nanodiamond. Considered hybrid materials based on liquid crystal polymers. The authors devote considerable attention to chemical modification of nanoparticles and intermolecular interactions between the nanoparticles and the matrix polymer. In the other review article [10] presented the results of studying structural and functional properties of hybrid nanomaterials. Discussed methods of modification of nanoparticles and their dispersion in the polymer matrix, the role of interactions between polymer matrix and fillers and the morphology of the nanoparticles are discussed.

The series of works [11-15] on preparing and research of properties of hybrid materials, the modification of organic silicon compounds polyurethanes [11-13] and polyetherurethanes [14-15] were published.

In these papers an attempt is made to simplify the process of producing hybrid materials for use as the inorganic component of the aqueous solution of silicates of alkali metals. In this regard, as modifiers to the silicate compositions used isocyanatobenzene compound (ICC), which possesses a high reactivity towards water. In the case of using aqueous solutions of silicates of alkali metals in combination with ICC a chemical interaction between the components with the formation of covalent bonds takes place.

It should also be noted that the relaxation properties of hybrid materials have not been practically studied, while for polymer composites, they are fundamental.

2. Materials and methods

As objects of study used polyisocyanate (PIC, brand MELLIONATE MR-200), 2,4-TDI, epoxy oligomer (technical brand ED-20), and liquid glass (LG). As a source of silica particles was used an aqueous solution of sodium silicate. Mixing the initial components: the PIC with a LG, ED-20, 2,4-TDI, and catalyst was performed using laboratory vane-type stirrer at a speed of 950 rpm for 2-3 min at room temperature. The time interval between subsequent additions of the starting components in the reaction mixture amounted to 10-15 min. Process thermo-curing of binder was carried out to 65-70°C.

To evaluate the heat resistance of the prepared compositions was determined by thermo-mechanical curves on the instrument TMA Q400 (TA Instruments).

Holding micro-photographing was performed using the polarizing microscope POLAM-312P. Compression curves were determined on samples of size 4×4×6 mm at a deformation rate of $4.68 \cdot 10^{-2}$ mm/min. The measurements were performed at different temperatures up to 100°C. The moduli of elasticity E and yield stresses σ_y were evaluated. IR spectra were measured on a Fourier transform infrared spectrometer Tensor 37 (Bruker) with a resolution of 2 cm^{-1} . The investigated composition was placed between the windows of KBr. FTIR spectra with a resolution of 4 cm^{-1} measured on Fourier spectrometer Vertex 70v with an attachment for FTIR GladiATR with diamond work item. Correction of FTIR spectra was performed using OMNIC programs. The stepwise monitoring of the process was provided.

3. The results of the study

Holding microphotographing (polarization microscope POLAM-312P) showed that the sample prepared free of 2,4-TDI and catalyst possessed a distinct phase separation (Figure

1a). The samples containing 2,4-TDI and the catalyst were more uniform operating at high temperatures (Figure 1b).

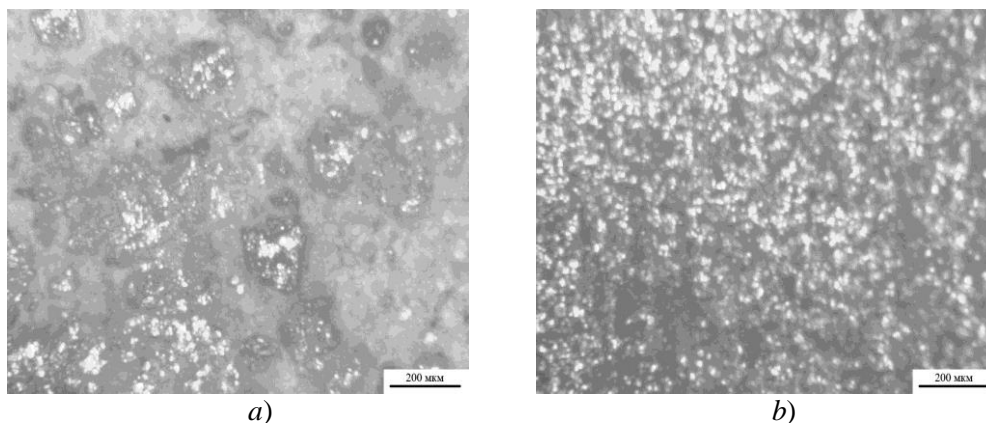


Figure 1. Micrograph of the composite containing LG (40 %) and PIC (60 %) (a), 2,4-TDI, and catalyst+ED (5% of the total amount of 2,4-TDI and PIC) (b).

Thermo-mechanical curves are shown in Figure 2. The development of large deformation when heating occurs at several different temperatures depending on the composition. The same figure contains the curve for the control sample that does not contain 2,4-TDI and catalyst; thus, this sample contains only LG and PIC. The highest softening temperature is observed for the sample containing 3 % TDI and 5% of the catalyst. The maximum softening temperature reaches 265°C.

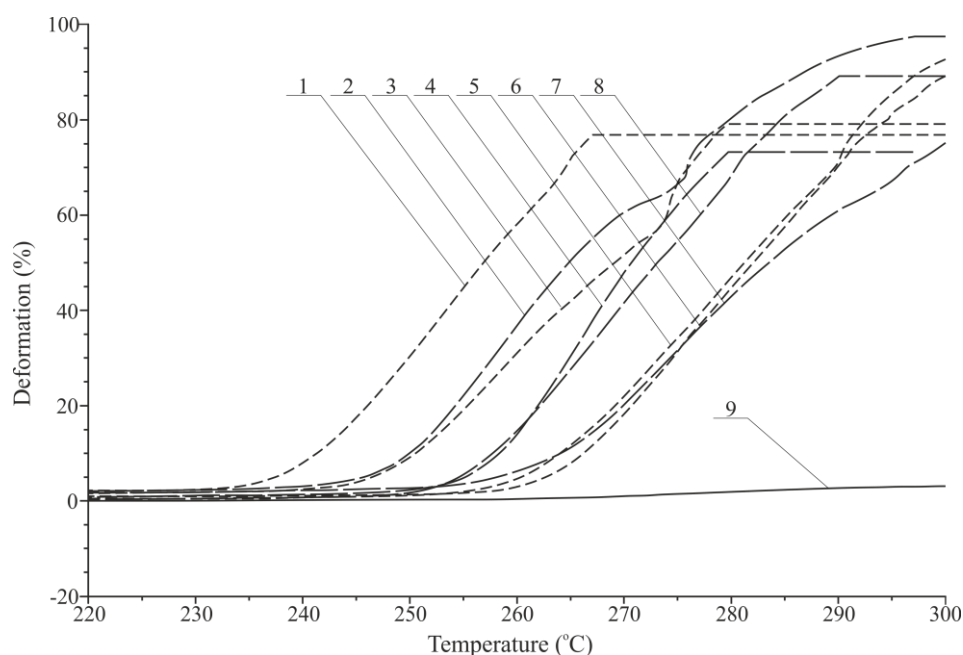


Figure 2. Thermo-mechanical curves of hybrid organic polymers depending on the quantitative ratio of the starting components. In parentheses are shown the formulations of the compositions: (LG %: 2,4-TDI %: the catalyst %). 1 – (40:0:5), 2 – (40:0:10), 3 – (40:1:5), 4 – (40:3:10), 5 – (40:5:5), 6 – (40:3:5), 7 – (40:5:10), 8 – (40:1:10), 9 – (40:0:0).

Monitoring of chemical transformations mix the components under heating was carried out meth-IR spectroscopy. In Figure 3 (upper curve) presents the IR spectrum of the initial composition of the

PIC with liquid glass and also the spectra of the original components (Figure 3.). The figure shows that the upper range is fully consistent with the sum of the spectra of the original components.

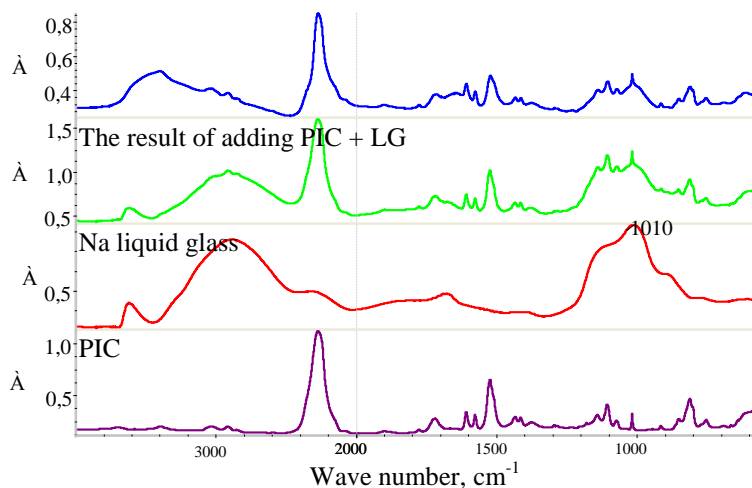


Figure 3. IR spectra: 1 – initial mixture PIC + LG, 2 – PIC, 3 – LG, 4 is the result of adding 2 and 3.

In the next stage of monitoring to the original mixture added ED-20 and measured the IR spectrum (Figure 4, upper curve). Characteristic bands of epoxides in the IR spectrum (lower curve) were 1511, 1248, 830 cm^{-1} . On the middle spectrum shows the result of computer addition spectra of the original components, which well coincides with the experimental spectrum.

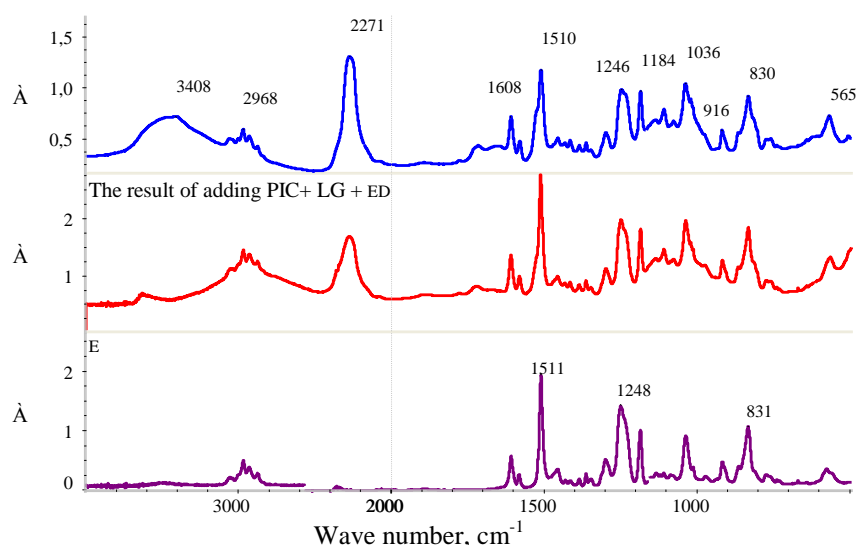


Figure 4. The IR spectrum of the mixture containing PIC, LG, and ED-20 is shown on upper curve. Range of ED-20 is depicted in the lower curve, and the result of adding the experimental spectra of PIC, GL and ED-20 are shown on the middle curve.

Upon further addition of 2,4-TDI the IR spectrum is not qualitatively changed, only observed an increase in the intensity of the band of stretching vibrations of isocyanate group at 2350 cm^{-1} . In the process of thermo-curing of binder from 25 to 65°C spectra were recorded every hour.

Analysis of curing process shows that the main changes are observed in the region of 4000 – 3000 cm^{-1} (Figure 5). From figure 5 it is seen that the intensity of the band of stretching vibrations $\nu(\text{OH})$ in the region 3500 cm^{-1} gradually decreases and in the final product disappears (lower curve); in the final product there remains only the band of stretching vibrations of $\nu(\text{NH})$ at 3337 cm^{-1} .

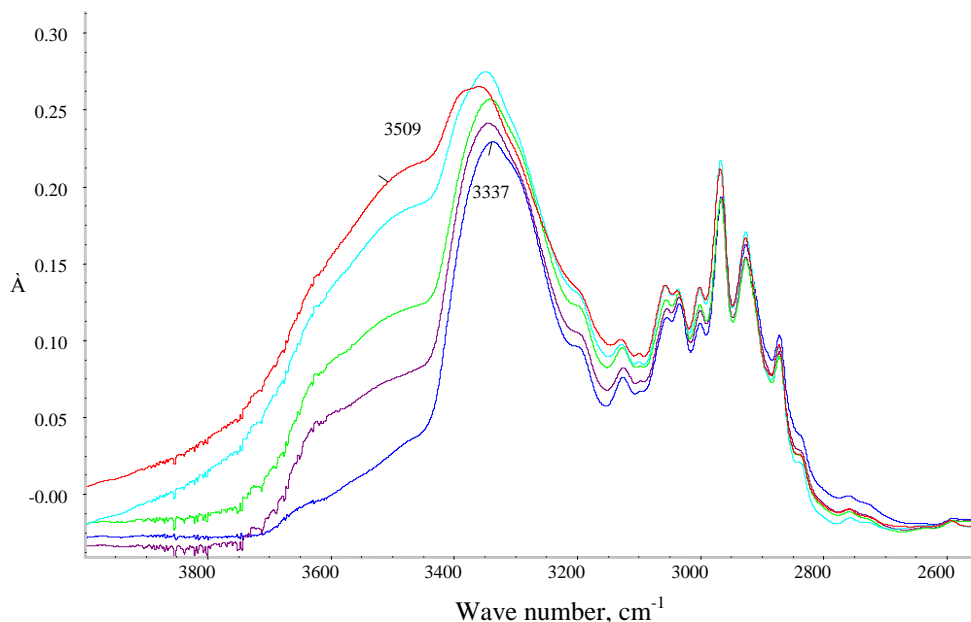
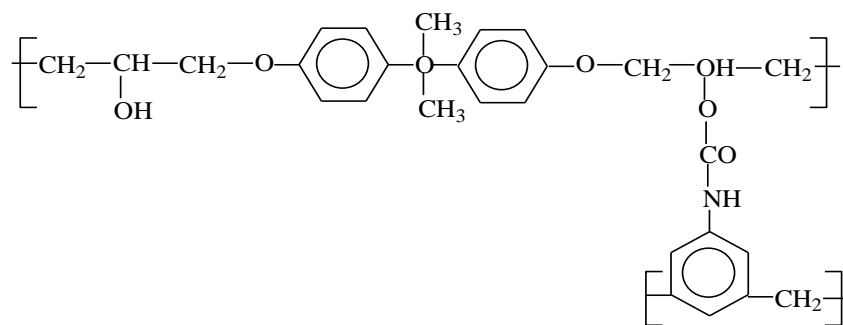


Figure 5. Monitoring the process of curing by the method of IR-spectroscopy in the region 4000-3000 cm^{-1} .

For the analysis of the complex composition of the reaction products we used the following technique. Written chemical formulas of the reaction products and conducted a computer analysis of the glass transition temperature of the mixtures containing these products. For one of the components chemical structure shown below.



For all the samples were calculated glass transition temperatures, and each sample was selected composition of the reaction products so that the experimental glass transition temperature T_g coincides with the calculated one. The calculated glass transition temperature of polymeric networks was evaluated by the equation [16-18]

$$T_g = \frac{\left(\sum_i \Delta V_i \right)_{\text{r.f.}}}{\left(\sum_i a_i \Delta V_i + \sum_j b_j \right)_{\text{l.ch.}} + \left(\sum_i K_i \Delta V_i \right)_{\text{crl.p.}}}, \quad (1)$$

where $\left(\sum_i \Delta V_i\right)_{\text{r.f.}}$ is the Van-der Waals volume of the repeating fragment of the network;
 $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_{\text{l.ch.}}$ is the set of atomic constants and increments for the linear chains that are involved in the structure of the repeating fragment of the network; $\left(\sum_i K_i \Delta V_i\right)_{\text{crlp.}}$ is the set of atomic constants for cross-linked point.

The cross-linked point represents a group of atoms, including the atom, from which there is branching of the chains, and next chemically related atoms with their substituents.

For mixtures of components (polymer networks) is valid the following relation [16-18]

$$T_g = \frac{\sum_{k=1}^{k=n} \alpha_k \left(\sum_i \Delta V_i\right)_k}{\sum_{k=1}^{k=n} \alpha_k \frac{\left(\sum_i \Delta V_i\right)_k}{T_{g,k}}} \quad (2)$$

where α_k is the mole fraction of the k -th component, $\left(\sum_i \Delta V_i\right)_k$ is the Van-der Waals volume of the k -th component, T_g is the glass transition temperature of the k -th component, n is the number of components.

The composition of the hybrid composites is implemented in table 1.

Table 1. The compositions of the hybrid composites.

Sample	The weight fraction, %			
	LG	PIC	ED-20	2.4-TDI
II-1	48.5	29.1	17.5	4.9
II-2	34.5	43.1	17.2	5.2
II-3	24.6	49.2	20.5	5.7
II-4	20.7	51.7	20.7	6.9

The highest glass transition temperature $T_g = 260^\circ\text{C}$ has a sample **II-2**. It contains a large number of reaction products in which there is a substantial amount of the polar aliphatic cycles, $-\text{NH}-\text{CO}-\text{O}-$, and OH -groups, leading to the formation of hydrogen bonds. The smallest glass transition temperature $T_g = 145^\circ\text{C}$ and $T_g = 150^\circ\text{C}$ have the samples of **II-4** and **II-1** that at the initial stage of curing does not contain SiO_2 .

Approximation curves of stress relaxation in the linear region of mechanical behavior were performed using the Boltzmann equation:

$$\sigma = \sigma_0 \left[1 - \int_0^t T(\tau) d\tau \right], \quad (3)$$

where σ_0 is the initial stress appearing in the output of the job “instantaneous” deformation; $T(\tau)$ is the memory function; τ – current time, which runs through values from 0 to t ; t is the finite time.

Used the memory function of $T_1(\tau)$, which is based on the analysis of the velocity of interaction relaxers:

$$T_1(\tau) = -\frac{S_0}{k_B m} \left[\frac{1}{(\alpha - \alpha_0) \ln(\alpha - \alpha_0) + (1 - \alpha + \alpha_0) \ln(1 - \alpha + \alpha_0)} - \frac{1}{\ln 0.5} \right], \quad (4)$$

where $m = m^* \int_0^\infty T^*(\tau) d\tau$; k_B is the Boltzmann constant; m^* is the total number of relaxers and non-relaxers per unit volume; α is the share relaxers of the total kinetic units, $T^*(\tau)$ is the variable part of the memory function; S_0 is the initial entropy of the sample,

$$\alpha = \frac{C}{C_0} = \frac{1}{(1 + k^* \tau / \beta)^\beta}, \quad (5)$$

where $k^* = k C_0^{n-1}$; $\beta = \frac{1}{n-1}$; n is the order of reaction, C_0 is the initial concentration of relaxers; $\alpha_0 = 10^{-10}$.

Approximation curves of the stress-relaxation was performed using a personal computer, into the software which was pre-recorded tabulated values of the variable parts of memory functions which are given in [16-18]. Automatically the selection of those parameter values for which the sum of squares of deviations of experimental values of the tension relaxing from the settlement was minimal and the correlation coefficient is maximum.

For all samples the curves of stress relaxation in uni-axial compression were measurement. The compositions of the samples are shown in table 1. The parameters of the memory function $T_1(\tau)$ are shown in table 2.

Table 2. The parameters of the memory function $T_1(\tau)$.

Sample	$T, ^\circ\text{C}$	Memory function $T_1(\tau)$					Experimental values	
		k, min^{-1}	Correlation coefficient, r	n	Initial stress, σ_0, MPa	Quasi-equilibrium stress $\sigma_\infty, \text{MPa}$	$\sigma_{\text{initial}}, \text{MPa}$	σ_{180}, MPa
II-4	20	0.0100	0.997	6.00	21.551	9.095	15.347	9.388
	50	0.0010	0.999	2.25	29.386	11.096	20.711	12.469
	85	0.1000	0.933	4.33	30.257	5.590	9.301	4.635
	100	0.0100	0.986	3.50	11.671	4.097	7.368	3.908
II-3	20	0.0100	0.999	6.00	40.461	20.145	30.071	20.435
	50	0.0100	0.998	6.00	37.277	15.753	26.408	16.249
	85	0.0100	0.998	6.00	27.525	6.207	16.743	6.728
	100	0.0100	0.994	6.00	24.491	7.292	16.089	7.746
II-2	20	0.0010	0.997	6.00	24.139	10.012	18.327	12.964
	50	0.0010	0.999	6.00	22.031	7.272	16.132	10.464
	85	0.0001	0.999	6.00	20.938	2.026	14.766	8.778
	100	0.0010	0.999	4.33	17.627	3.561	11.467	5.551
II-1	20	0.0000	0.999	6.00	10.897	1.024	7.833	4.737
	50	0.0100	0.996	6.00	7.700	3.726	5.74	3.850
	85	0.0100	0.996	4.33	5.632	2.561	3.865	2.499
	100	0.0100	0.996	6.00	4.554	1.796	3.199112	1.871

The obtained master curves for the samples, the compositions of which are given in table 3.

Table 3. The composition of the hybrid composites.

Sample	Weight fraction, %			
	LG	PIC	catalyst*	2.4-TDI
I-1	50	47	5	3
I-2	50	45	5	5
I-3	50	40	5	10
I-4	40	55	1	5

*The quantity of catalyst indicated in % of the total weight of isocyanates.

Master curves are shown in Figure 6.

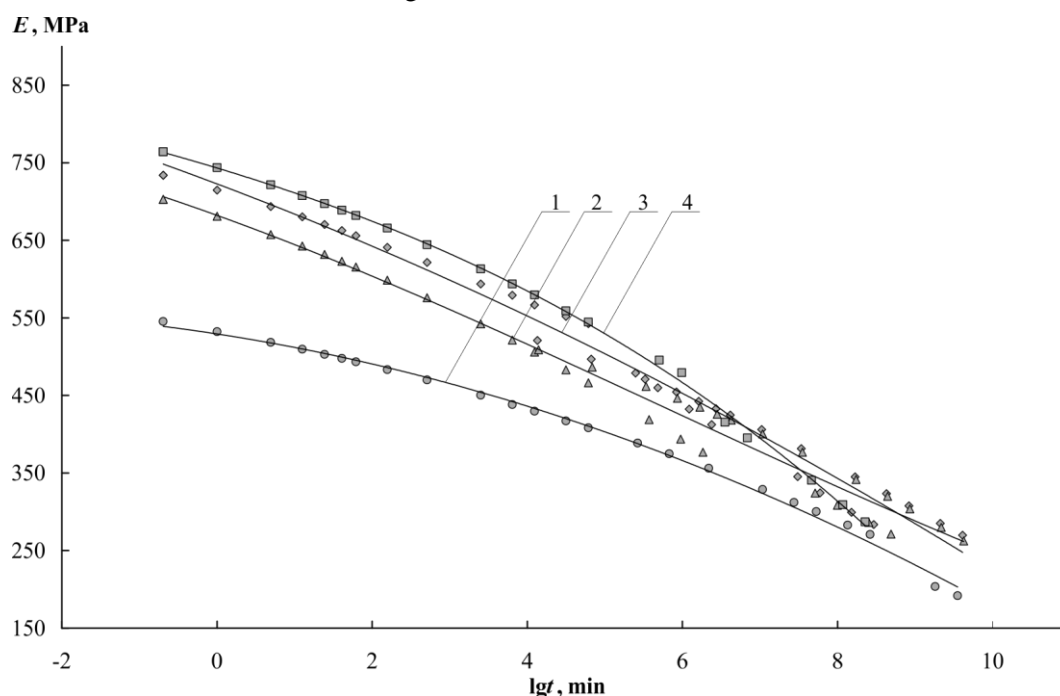


Figure 6. Master curves for samples **I-1**, **I-2**, **I-3**, and **I-4**.

In the interval of the duration of stress relaxation from $\lg t = -0.5$ to $\lg t = 6$ min most of the relaxation module has a sample **I-4** in which the smallest content of the liquid glass and the highest content of the PIC takes place. This is due to the fact that most structured network formed by the reaction of trimerization of the PIC.

4. Conclusion

Investigated the relaxation properties of hybrid organic-mineral composite materials based on sodium LG, 2.4-TDI and PIC, modified epoxy oligomer ED-20. Curing in the mild conditions at temperatures of 60-70°C leads to the formation of network structures. Monitoring meth-IR spectroscopy showed that the final product remains the only band of stretching vibrations of NH-groups. The IR spectrum corresponds to mainly the spectrum of the epoxide, and the differencing spectrum matches the

spectrum of the polyurethane. Chemical interaction is via the terminal groups of epoxy oligomer, i.e. for oxirane cycles.

The analysis of the glass transition temperature for the technologically compatible blends of the reaction products allowed the identification of the composition of the hybrid materials and to establish the complex nature of mesh structures. Spectral studies and related calculations using the computer program "Cascade" (INEOS RAS) indicate the complex nature of the chemical transformations during thermal exposure in preparing monolithic samples. Modification of the initial mixtures of ED-20 results in more uniform grain structure of the composites and improving their mechanical properties. The detailed study of the process of stress relaxation at different temperatures in the range 20-100°C has been provided. The physical parameters of the memory function were found. The initial relaxation modulus reached values of 1000 MPa at 20°C and 540 MPa at 100°C. For non-modified epoxide starting materials of the relaxation module was 730 MPa at 20°C and at 100°C to 520 MPa. The master curves allow prediction relaxation behavior for large durations of relaxation. The greatest relaxation module has material containing an maximal amount of PIC.

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