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STRUCTURAL CHANGES IN A CLAY-CONTAINING NANOCOMPOSITE WITH A DIFFERENT MOISTURE CONTENT CAUSED BY ITS DEFORMATION

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This paper presents the results of an investigation of the properties of a clay-containing nanocomposite with an epoxy binder under moisture-temperature and mechanical action. It has been established that whatever the moisture content, the nanocomposite crystallizes under the thermomechanical action (upon reaching the glass-transition temperature). When the nanocomposite is heated to 70^{o}C, the restructuring process is reversible, and its heating to above 150^{o}C leads to its amorphization. The presence of clay nanoparticles (up to 6 mass percent) does not influence the temperature of structural transitions of the nanocomposite and does not cause a substantial strengthening effect. The sorbed moisture plasticizes the nanocomposite and decreases its glass-transition temperature by 10^{o}C. The specific features of the thermomechanical behavior of nanocomposites upon their tensile prestrain or creep are due to the formation of an oriented structure. Their crystallization begins at lower temperatures and with a higher degree of crystallinity than that of unloaded nanostructures.

Keywords: *adsorption-active medium, microheterogeneity, X-ray structural analysis, morphological changes, induced elasticity.*

Introduction. In modern thermal physics of polymer materials, along with the development of phenomenological notions, the thermophysical properties and the processes proceeding in them connected with structural changes are being studied extensively. Such an approach appears to be particularly important, since it is necessary to take into account the microheterogeneity of polymer bodies due to the presence in them of regions with different types of elasticity, as well as the morphological changes caused by strains with energy transformations. In this connection, the question of the interrelationship between the mechanical characteristics of composite materials (CM) and the structural changes accompanying the deformation process in adsorption-active media and of establishing general laws for them is of great importance. The mechanical phenomena taking place in the process of sorption and swelling in polymer CMs, while being of certain theoretical and practical interest, have been studied very little, especially in nanocomposites (NC) that are of interest in developing high-efficiency materials. For example, for clay-containing NCs exhibiting improved mechanical, thermal, and barrier properties compared to unfilled polymers, the majority of papers [1–5] presented results without conclusions about the processes proceeding in them.

Resistance to various kinds of action is a characteristic of the material in the unloaded state whereas the fracture strength under load under service conditions characterizes the material in the stressed state. In this case, the structure inhomogeneity of NCs is one of the necessary conditions providing their plastic deformation ability at temperatures below the glass transition temperature T_g [6, 7]. But even in the absence of stresses applied from the outside, internal stresses may arise in the material as a result of the swelling inhomogeneity. The swelling accompanying the sorption is inhomogeneous due to the presence in the material of parts not affected by this process, and it is only when the whole of the material is saturated with moisture that it becomes heterogeneous again. The concentration of internal stresses upon swelling and the degree of swelling of the NC depend strongly on the strength of the binder-filler interaction, as well as on the plasticizing action of the substance sorbed by the NC [6, 8, 9].

The aim of the present work is to establish the relation between the thermophysical and mechanical characteristics of the clay-containing nanocomposite that has sorbed the moisture and the structural changes attending the deformation process under different kinds of load and at different temperatures.

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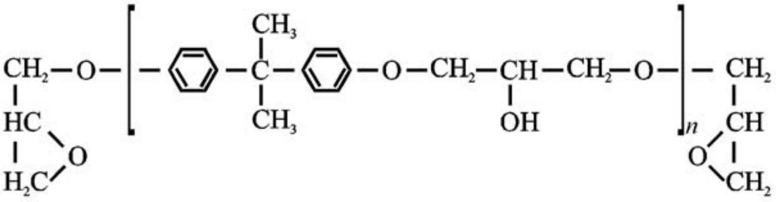
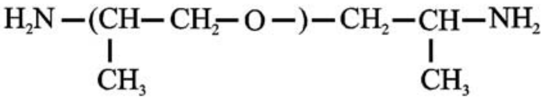
Objects and Methods of Investigation. We have investigated a nanocomposite whose composition included epoxy resin, a hardener — polyoxypropylene with end amine groups (Jeffamine® D-400), and a filler — clay nanoparticles (content $c = 2, 4, 6$ mass %).

Epoxy resin based on epichlorohydrin and diphenylolpropane (bisphenol A) contains end epoxy groups:



Polyoxypropylene



$$H_2N-(\underset{CH_3}{CH}-CH_2-O-)-CH_2-\underset{CH_3}{CH}-NH_2$$

has a high degree of crystallinity (~95%), an amorphous phase T_g equal to ~75°C, and a glass transition temperature of the crystalline phase ~60–65°C. It has a fairly close molecular packing since the bond between carbon and oxygen atoms is shorter than between carbon atoms, is easy to orient in tension, and, when heated, is destroyed with the formation of low-molecular-weight products [10].

The clay is montmorillonite having the composition

$$[(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2]Na_{0.33}\,,$$

which crystallizes in a monoclinic system in the form of scales of thickness ~1 nm and diameter ~100 nm. The presence of hydroxyl groups on its surface determines the strengthening properties. Octadecylamine served as the surface modifier.

Specimens of the unfilled binder and the NC were held in atmospheres with humidity $\varphi = 24$, 77, and 98% until they reached the equilibrium state. The equilibrium moisture content in the specimens at 20°C was attained after 270 days and equaled $w = 0.2$, 1.7, and 3.0%, respectively.

Thermomechanical investigations were carried out with the use of an UIP-70M device with specimens heated to 150°C at a rate of 20°C/min with subsequent cooling.

The mass loss kinetics at physical and chemical transformations in the NC was investigated by the thermogravimetric (TG) method. Measurements were made on a "Mettler" TA3000 instrument in the temperature range 20–280°C; the heating rate was 10°C/min.

The structure was investigated by the X-ray diffraction method on a DRON-3M device with photography "in transmitted light" on CuK_α radiation. Scanning of angular intervals was carried out with a 0.1°C step and with a pulse collection time in each step of 90 sec.

Quasi-static tension tests were carried out with the aid of a Zwick 2.5 machine at 20°C with a deformation rate of 5 mm/min.

Creep studies were made at tensile stresses $\sigma = 0.5\sigma_{max}$ on wet specimens; the duration of the experiment was 7.5 h for forward and 17 h for backward creep.

Results and Discussion. The features of the phase and relaxation transitions in heating the NC specimens have been studied by the method of thermomechanical analysis (TMA) in the absence of external load. The typical TMA curves of the NC specimens held in an atmosphere with a relative humidity of 24 and 98% until they reached the equilibrium state are presented in Fig. 1.

The general rule for all NC modifications, including those held in an atmosphere with a humidity of 77%, is the presence on the thermal expansion curves of a narrow (5–10°C) temperature range of a sharp change in the character of deformability when in the course of heating the expansion at T_1 is replaced by a shrinkage, and then at T_2 a new growth of deformation begins just as quickly. Such dependences are characteristic of amorphized polymers [11] in which, after passing through T_g, crystallization occurs very quickly to cause hardening of the material. Then, also

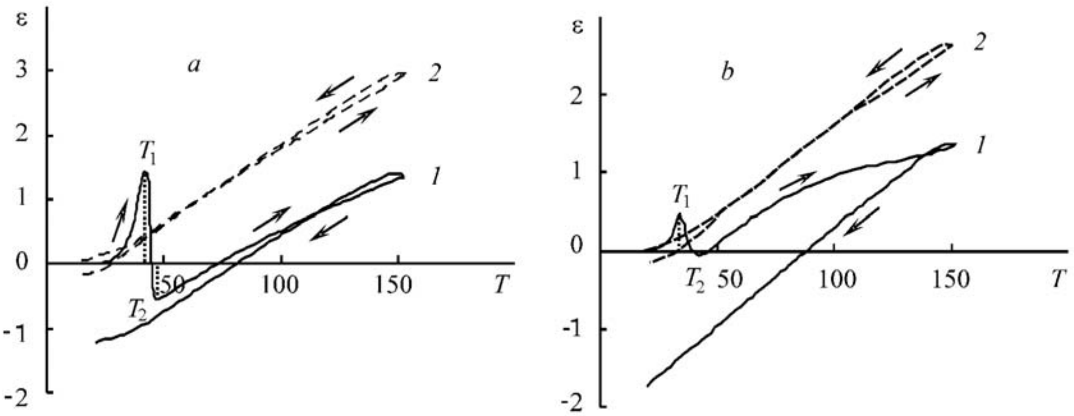
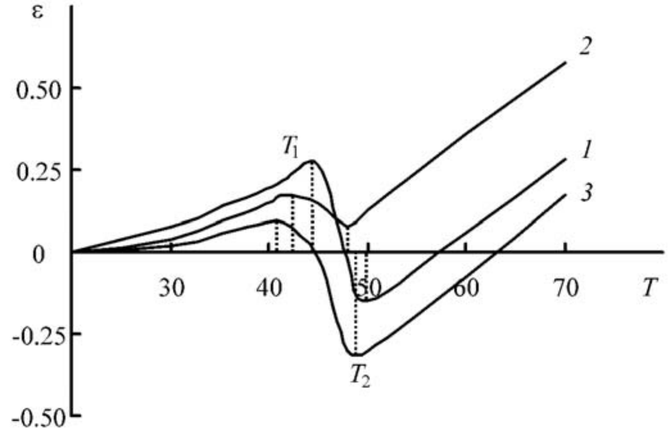


Fig. 1. TMA curves of NC specimens with c = 4%, φ = 24% (a) and 98% (b): 1, 2) heating–cooling cycles.



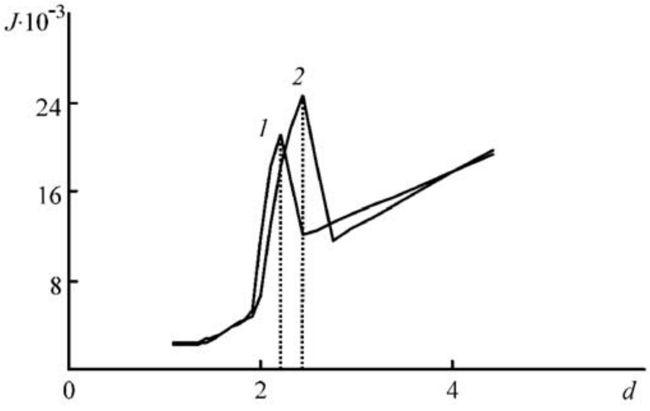


Fig. 2. TMA curves of the binder at φ = 24%: 1–3) heating–cooling cycles.

Fig. 3. Diffractograms of NC specimens with c = 0% (1) and 6% (2).

spontaneously, melting of the crystallites formed in them begins, which just causes a rise on the TMA curve. The fact that the process of shrinkage of the binder in the NC is caused by crystallization is confirmed by experiments with multiple heating of specimens to 70°C and their cooling to 20°C. Figure 2 gives the thermomechanical curves for three heating-cooling cycles and shows that the crystallization process was accompanied each time by shrinkage and the melting process — by spontaneous extension. Consequently, in the 20–70°C temperature range the restructuring process in the binder appears to be reversible; crystallization began at T_1 = 41–45°C, and melting at T_2 = 46–50°C.

X-ray structural analysis also confirms that upon preliminary annealing of specimens at 80°C and subsequent drying in a medium of humidity 24% in the binder the crystalline phase is preserved (Fig. 3, diffractograms 1).

The introduction into the NC composition of clay nanoparticles (diffractogram 2) leads to a change in the parameters of the crystalline reflex of the binder, for example, an increase in the interplanar spacing d and, accordingly, a change in the internal stress in the NC.

It was somewhat difficult to determine T_g from the TMA curves since the attaining by it of the glass transition temperature served as a prerequisite to the binder crystallization in the NC. We assumed that both processes (devitrification and onset of crystallization) proceeded practically simultaneously. Therefore, the deformation maximum temperature T_1 on the TMA curves (Fig. 1) was assumed to correspond to the crystallization temperature, and the T_g value was assumed to be slightly different from it. Comparison of the values of T_1 (T_g) (Fig. 4) of the investigated modifications has made it possible to establish that as a result of moisture sorption, the glass transition temperature of the specimens in a medium with a humidity of 98% decreases by about 10°C compared to the dried specimens. This fact proves that the moisture in the NC acts as a plasticizer.

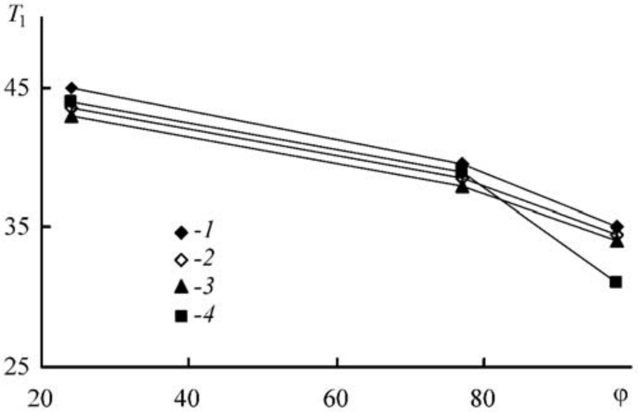


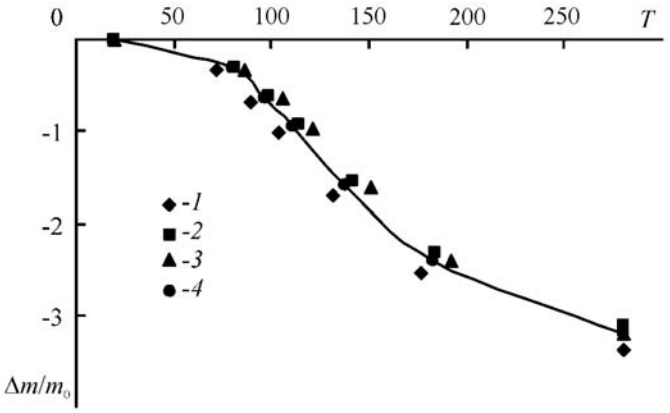
Fig. 4. Glass transition temperature as a function of the atmospheric humidity for NCs with different filling: 1) 0%; 2) 2; 3) 4; 4) 6.

TABLE 1. Values of the Thermal Expansion Coefficients of NCs with Different φ and *c*

φ, %	*c*, %	$\alpha_1 \cdot 10^{-5}$, °C^{-1} $T \in$ (20–35) °C	$\alpha_2 \cdot 10^{-5}$, °C^{-1} $T \in$ (35–50) °C	$\alpha_3 \cdot 10^{-5}$, °C^{-1} $T \in$ (50–70) °C	$\alpha_4 \cdot 10^{-5}$, °C^{-1} $T \in$ (100–150) °C
24	0	11.9	–123.0	21.4	21.6
	2	7.6	–200.0	25.6	20.1
	4	8.0	–130.0	19.4	19.0
	6	5.3	–65.0	23.9	18.3
77	0	6.5	–68.8	20.0	15.2
	2	7.9	–50.0	20.1	13.3
	4	7.3	–38.0	21.7	12.6
	6	10.7	–16.0	18.4	13.0
98	0	11.8	–128.0	23.9	6.7
	2	9.7	–159.0	21.3	9.7
	4	8.0	–79.0	20.6	7.2
	6	5.2	–91.0	27.1	3.6

An increase in the filler content from 2 to 6 mass % practically does not affect the temperature values of the structural transitions in the NC within the atmosphere with equal humidity (Fig. 4). Apparently, shielding the clay surface by an ODA modifier decreases access to the surface hydroxyl groups. Therefore, the conditions for the formation of hydrogen bonds with an epoxy binder worsen. The weak strengthening effect from the filling is possibly associated with both the low mechanical strength of clay nanoparticles and their possible agglomeration [12, 13].

We have also determined by the TMA curves the temperature ranges of a sharp change in the NC deformation rate. For the quantitative characteristic, we took the thermal expansion coefficient (TEC). The table gives the TEC values for four temperature ranges corresponding to the vitreous state of the NC α_1, as well as to its states of crystallization α_2, recrystallization α_3, and additional structuring α_4. From the analysis of the table it is seen that the NC specimens, both dried and wet, with a temperature below T_g are characterized by practically equal values of α_1 which, however, decrease with increasing degree of filling with clay. In the T_1–T_2 temperature range, the process is characterized by negative values of α_2, which also change with increasing degree of filling with clay. Characteristically, α_3 in all NC modifications and degrees of their moistening is practically the same. Upon reaching a temperature of 80°C in moist specimens the physicochemical processes lead to a significant rigidification of the structure and to a decrease in α_4 to values corresponding to the vitreous state. The decrease in the TEC of moist specimens can be due to at least two processes — loss of moisture and structurization. In so doing, a significant increase in the hysteresis effects is observed (Fig. 1b).



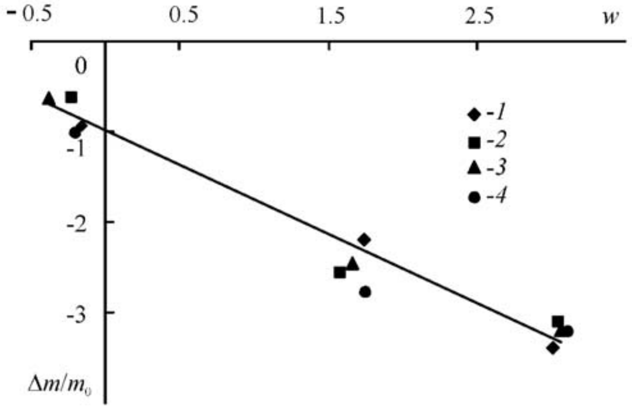


Fig. 5. Mass loss curves of NC specimens at φ = 98% with different filling: 1) 0%; 2) 2; 3) 4; 4) 6.

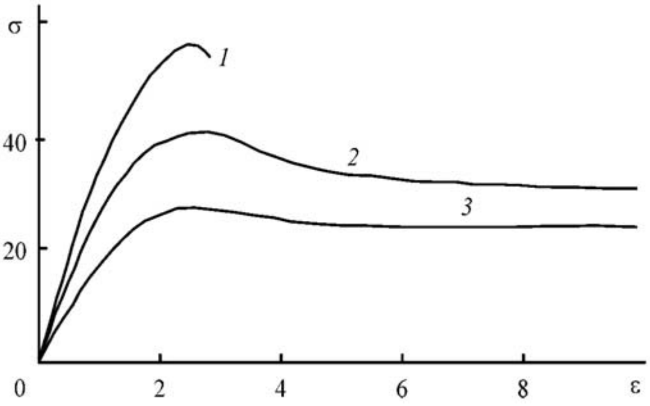
Fig. 6. Interrelation between the moisture content and the mass loss in heating NC specimens with different filling. Designations 1–4 are same as in Fig. 5.

From the mass loss curves of the thermogravimetric analysis (Fig. 5) it is seen that in the 80–170°C temperature range the mass loss process is the fastest, which agrees with the decrease in the TEC. The maximum mass loss is observed in specimens held in an atmosphere with a humidity of 98%. For instance, at a clay content of 6% the NC mass loss at 150°C is 1.5%, and in the binder it is 2% under the same conditions; however, no strict dependence on the degree of filling is observed. A further increase in the temperature leads to a decrease in the mass loss rate. Proceeding from the practically linear interrelation between the moisture content and the mass loss (Fig. 6), it may be stated that upon heating the NC up to 280°C the moisture desorption process prevails.

Thus, the thermal history of the first cycle of heating to 150°C and cooling to 20°C led to irreversible structural changes in the NC in the course of the TMA. Repeated studies enabled us to make certain of irreversible thermal processes in the NC. The TMA curves of the second cycle upon heating consists now of two portions connected at the point corresponding to T_g (curves 2 in Fig. 1). Hysteresis effects are practically absent, i.e., the TMA curves reflect a state of the composite close to equilibrium. Thus, combining the conditions of heating and cooling NC specimens, we can realize in them various structural transitions leading to complete amorphization. Accordingly, the crystalline phase too can not only be present in them in different quantities but be also represented by formations differing in the degree of perfection and sizes [7, 11].

The experiments described above were performed on unloaded NC specimens. To establish the relationship between the thermal characteristics and the structural changes attending the NC deformation process, we investigated their mechanical behavior under quasi-static tension. Figure 7 shows the deformation curves of an NC (c = 6%) whose specimens were held in atmospheres with a humidity of 24, 77, and 98% until they attained the equilibrium state. The deformation curves of the binder and an NC with a clay content of 2 and 4% have a similar character.

It has been established that as the degree of filling increases, there is an increase in the elastic modulus of the NC by about 30%, whereas with increasing moisture content its decrease is noted (Fig. 8). In turn, as is seen from Fig. 7, dried specimens fail in the air brittely, and their maximum strength is twice that of specimens held at a humidity of 98%. Intermediate strength values are observed in specimens held at a humidity of 77%. Characteristically, whatever the moisture content, maximum strength values are attained at a 2.5–3% deformation of the NC. These values should obviously be considered as corresponding to the limit of induced elasticity of the NC in a given atmosphere. Exceeding this limit in the process of extension of moist specimens leads to the initiation of transverse growth of microcracks. This conclusion is based on the fact that on the working part of the specimens whitening of the material and a loss of their transparency were observed. Such changes appear when the refractive indices of the microcrack material and of the block material of the NC differ [7, 15]. In [7, 11, 14, 15]; it has been shown that the microcracking effect manifests itself only when glassy- or crystal-state materials are loaded. Microcracks differ fundamentally from breaking macrocracks in that that they contain a material able to transfer stresses. In [7, 15], it has been



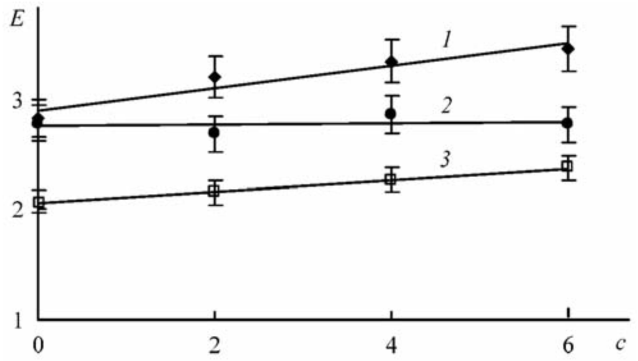


Fig. 7. Deformation curves of NC specimens at *c* = 6% and various values of φ: 1) 24%; 2) 77; 3) 98.

Fig. 8. Elastic modulus of the NC depending on the nanofiller concentration for various φ values. Designations 1–3 are same as in Fig. 7.

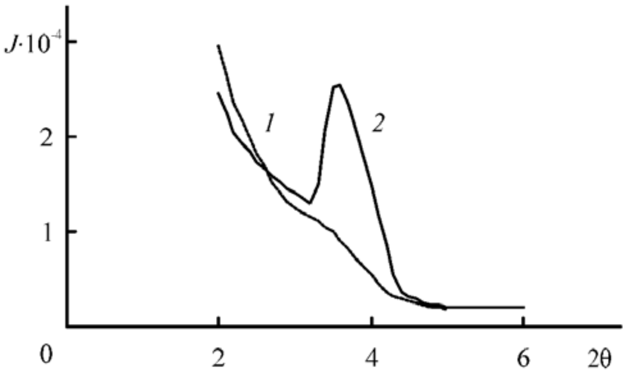


Fig. 9. Diffractograms of a tension predeformed NC specimen cut from the "neck" region: 1) meridian; 2) equator.

shown that the edges of microcracks are connected by thin fibrillas (~10 nm) whose length increases in tension and, therefore, the interface area increases. Consequently, in moist NC specimens at deformations exceeding the induced elasticity limit, specific zones of plastic deformation and microcracking are formed. With increasing deformation the curve goes to a plateau and a "neck" is formed. In so doing, the breaking deformation reaches ~60%, whereas in dry specimens it reaches no more than 3–4%. Apparently, the "neck" is formed when certain critical conditions are attained. The influence of such factors as plastification and orientation of the polymer in the NC should be considered simultaneously. Their role reduces to changing the position of the working test temperature with respect to the temperatures of transitions, which leads to changes in the strength — its increase due to the orientation and decrease due to the plasticization. Meanwhile, in [11] it was noted that the "necking" is not connected with plastic deformations, and the role of moistening is to facilitate significantly the development of induced-elastic deformation of the material. Then the tension-induced "necking" should be considered as a relaxation process of the localized nonoriented-oriented transition of the polymer inside the microcracks.

The data of X-ray structural analysis correlate well with the assumptions about structural changes in the NC at its deformations to high values. Figure 9 presents meridional and equatorial diffractograms of NC specimens prestretched to failure. It is seen that in the region of small angles on the equatorial diffractogram a peak caused by the crystalline phases is present, while it is absent from the meridional diffractogram. This effect can be explained by the fact that at large stretches the material acquires an almost completely fibrillized oriented structure, which leads to the disappearance of interfaces characteristic of microcrack walls. Apparently, joining of microcrack walls occurs and, therefore, no diffuse scattering is observed on the diffractogram meridian.

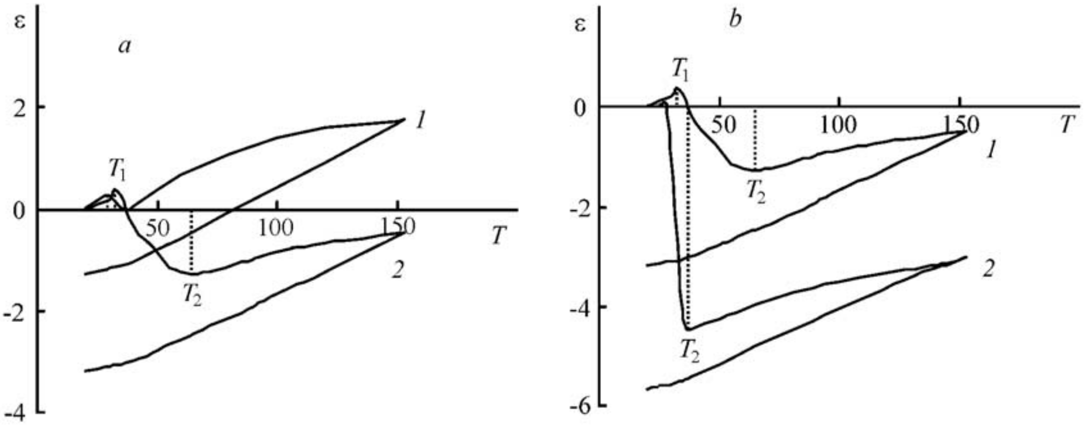


Fig. 10. TMA curves of NC specimens cut across (1) and along (2) the stretching directions under quasi-static tension (a) and specimens cut along the stretching direction under quasi-static tension (1) and creep (2) (b).

It is interesting to compare the deformation and "necking" mechanisms depending on the NC loading conditions and the plasticizing effect of moisture. Moist specimens ($\varphi = 98\%$) were predeformed in the air in the regime of quasi-static tension ($\dot{\varepsilon}$ = const) and creep (σ = const) until the whole of the working part material went into the "neck." Then we cut from them specimens along and across the direction of stretching. From the analysis of the TMA curves (Fig. 10a) it is seen that the thermal expansion of the NC specimens cut in mutually perpendicular directions differs markedly and there are anisotropic changes in the thermomechanical characteristic. Analogous laws have also been obtained for specimens upon creep tests. For heated NC specimens cut along the stretching direction, in both quasi-static tension and creep experiments, their clear similarity to the TMA curves is observed (Fig. 10b). For instance, in the glass transition temperature range their linear sizes sharply decrease. However, specimens oriented in the creep regime (curve 2) shrink to a greater extent and the process proceeds in a narrower temperature range than for specimens oriented under quasi-static tension (curve 1). Next, when temperatures of 37°C (under creep) and 64°C (under quasi-static tension) are attained, the process of their spontaneous stretching begins as sharply as shrinkage. From a comparison with the TMA curves of unloaded NC specimens (Fig. 1b), it is seen that crystallization of oriented specimens begins at lower temperatures, and the shrinkage value (assumed to be proportional to the degree of crystallinity) is much larger than that for loaded specimens. This is explained by the fact that at orientation a considerable ordering of the NC structure occurs, which is a kind of a crystalline "blank," and therefore its transition to the crystalline structure is considerably facilitated. As a consequence of the crystallization of fibrillar aggregates the NC specimens do not completely regain their sizes either. At the same time, the TMA curves of the specimens cut across the orientation, as the results of quasi-static tension and creep experiments show, practically coincide in terms of the character of the change in the deformability and in its value. The TMA curves of the second heating cycle of specimens reflect, as for unloaded specimens, only one transition connected with the NC devitrification. Thus, from the above data it follows that the specific features of the thermomechanical behavior of the nonequilibrium structure of the NC upon stretching is largely determined by the quantity of the initial binder, which has gone to the oriented state, from which fibrillar aggregates of microcracks have been constructed. Their strength determines the macroscopic strength of the material at "cold" stretching. With heating, the fibrillas acquire a greater mobility; they become able to coalesce, and the coagulation process occurs. This leads to a disorientation of fibrils with respect to one another, which shows up macroscopically as a shrinkage of the NC. The process proceeds in the region of the glassy state and, consequently, it is supermolecular in nature, i.e., it is not accompanied by a disorientation of molecules inside a fibril. Above T_{g} complete disorientation of the NC structure occurs and, as a consequence, "healing" of microcracks occur [7, 9]. It is possible that additional stitching of the NC also leads to a suppression of microcracks already in the first cycle upon heating to higher temperatures.

Conclusions. Investigation of clay-containing NC points to a complex influence of adsorption effects on its properties, which hampers obtaining a material exhibiting a wide variety of thermomechanical properties. The general rule for all NC modifications is crystallization that takes place in the course of the TMA. Restructuring begins in the region of reaching T_g. In repetitive heating to 70°C, crystallization and melting of crystallites in the NC binder are reversible. However, upon heating to 150°C the structure becomes completely amorphized and the TMA curves of the second heating cycle reflect an NC state close to equilibrium.

An increase in the content of clay nanoparticles to 6 mass % practically does not change the temperature values of the structural transitions in the NC and does not lead to a strengthening effect. Sorbed moisture plays the role of a plasticizer in the NC. A content of 3% of moisture in it leads to a decrease in T_g by about 10°C. The practically linear interrelation between the moisture content in the NC and the mass loss upon its heating to 280°C points to the prevalence of the moisture desorption processes.

The thermomechanical behavior of the NC depends not only on the moistening and thermal history, but also on the regime of their preloading. For instance, dried specimens fail brittely under tension. In moist specimens above the limit of induced elasticity, a plastic deformation (microcrak zone) is formed, "necking" occurs, and deformations reach ~60%. The data of X-ray structural analysis confirm that in the course of the stretching process almost the whole of the NC acquires a fibrillized oriented structure. Crystallization of oriented specimens begins in the course of the TMA at higher temperatures and their degree of crystallinity is much higher than in unloaded specimens. The features of the thermomechanical behavior of the NC upon quasi-static pretension or creep are largely determined by the quantity of the binder, which has gone to the oriented state, from which fibrillar aggregates of microcracks have been constructed. Changes take place in the region of T_g and, consequently, they have a supermolecular character. In heating, the fibrils acquire a greater mobility, and the coagulation process proceeds. This leads to a disorientation of fibrils with respect to one another and a decrease in the interface area, which shows up macroscopically as a shrinkage of the NC.

NOTATION

c, mass content of the filler, %; d, interplanar spacing, nm; E, elastic modulus, GPa; J, intensity of X-rays, pulse/sec; m, mass, g; T, temperature, °C; T_g, glass transition temperature, °C; w, relative moisture content, %; α, thermal expansion coefficient, $^{\circ}\mathrm{C}^{-1}$; ε, deformation, %; $\dot{\varepsilon}$, deformation rate, mm/sec; θ, stress, MPa; θ, scattering angle, deg; φ, relative humidity of the air, %. Subscripts: 0, initial; 1, 2, 3, 4, subsequent values; max, maximum; g, glass transition.

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