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INFLUENCE OF AN ELECTRIC FIELD ON THE HARDENING PROCESS AND THE PROPERTIES OF AN EPOXY COMPOSITE DISCRETELY REINFORCED WITH PHOSPHOCARBON FIBERS

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The influence of an electric field on the hardening process, the structure, and the properties of an epoxy composite in the presence of a phosphorus-containing carbon filler has been investigated. It has been shown that under the action of an electric field the process of formation of a three-dimensional epoxy polymer in the presence in the system of phosphocarbon fibers proceeds more intensively with the formation of a more rigidly bound structure of the polymer as compared to the same composition hardened in the absence of the field. It has been established that the fibrous filler–binder interface has a dominant role in the formation of a spatially cross-linked polymer and in the properties of the product hardened both under the action of the electric field and without it.

Introduction. The latest advances in science and technology point to wide possibilities of applying various physical actions in developing polymer composites with given physicotechnical and service properties. The use of, e.g., electric fields, especially in combination with other fields (magnetic, thermal ones), has become a promising direction in material science [1]. In particular, in [2] the efficiency of modifying polymer materials with the help of an electric field in obtaining electret composites for nontraditional fields of their application was shown. The methods of energy action at the stage of physicochemical transformations of the binder in the formation of composites are worthy of notice, because precisely this stage of structurization of a composite on the whole is determining in the properties of materials. Of great interest for investigations are composites including fillers that exhibit the property of conduction, e.g., carbofibrous materials.

At the Institute of General and Inorganic Chemistry, NAS of Belarus, a special kind of carbon fibers (CFs) has been developed. These are element-containing fibers distinguished by the fact that their structure contains various structure-active centers in the form of oxides and/or reduced metals or various functional groups. Due to their highly developed active surface, the element-carbon fibers, which in many cases are carriers of electric and magnetic fields, are among the most promising components for obtaining, on their basis, composites under the action of physical fields.

This papers presents the results of investigations of the influence of an electric field on the formation process and the properties of an epoxy composite discretely reinforced with phosphorus- containing carbon fibers (PCFs) obtained on the basis of phosphorus-modified mercerized cellulose. For comparison, we investigated the compositions of composites in the presence of nonmodified carbon fibers obtained under the same carbonization conditions as for phosphorus-containing ones . Earlier we showed the possibility of using effectively the phosphate-cellulose precursor of carbon fibers in electrorheological suspensions [3]. This effect, as well as the specificity of phosphocarbon materials having ionogenic groups on the fiber surface, gave us reason for considering electrical effects on the process of formation of epoxy composites reinforced with them as a very promising method of obtaining composites with improved or special properties.

Experimental. The structure and properties of reinforced polymers are largely determined by the physicochemical interaction at the filler–polymer interface, as well as by the influence of this interaction on the processes of transformations of the binder in the interphase zone and in the composite bulk. Earlier we elucidated the influence of an electric field on the processes of physicochemical transformations of the unfilled epoxy binder [4]. An important

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role of the component composition in the efficiency of action of the electric field on the structurization process of the system was established. Therefore, to obtain reliable and reproducible results with the aim of their subsequent comparison and estimation of the influence of the fiber surface on the process of formation of the three-dimensional structure of the epoxy polymer under the conditions of forming composites in an electric field, we used one and the same epoxy-amine binder.

Various methods of investigating the formation process of the epoxy polymer three-dimensional structure exist. Under the conditions of actions of physical fields, for monitoring the rate and duration of binder polymerization, nondestructive methods of investigation are required [5]. Of these, the most universal ones are the electrophysical methods, since practically all electrical indices (dielectric loss tangent tan δ, capacity C, and specific volume resistance ρ_v) are sensitive to internal changes in the molecular structure that take place in the process of formation of a spatially cross-linked polymer [6]. The electrophysical methods are also highly informative in investigating finished polymer products [7]. Therefore, to investigate the influence of the electric field on the hardening kinetics of the epoxy binder, as well as to investigate the molecular mobility of the spatial-net structure of the epoxy polymer formed, we chose the capacity method for checking the dielectrical characteristics [8].

To measure the dielectrical characteristics of the material (tan δ, C, and ρ_v) and the average thickness d of flat specimens, we developed a special measuring cell, in which the influence of the edge capacitances and the residual impedance of the electrode system was reduced to a negligibly small value due to the use of a guard ring. The measuring cell represented a cylindrical capacitor whose interelectrode space was filled with newly made compositions of the composite. The constructional arrangement of the measuring cell allowed for parallelism of the working surfaces of the electrodes and an invariable spacing between them during the experiment. The working surface of the electrodes, made of stainless steel, was given a high polish, which provided weak adhesion of the material to the electrode. The system's characteristics were easy to determine due to the application of the mechanism of fine control of the interelectrode gap. The accuracy of reading the gap reached ± 0.005 mm, which permitted determining the relative dielectric constant e (volume ratio between the specimen and the air gap for a given thickness) and the loss factors tan δ to an accuracy of $\pm 0.2\%$ and $\pm 2\%$ respectively. To determine the volume specific resistance ρ_v of the specimen from the measured capacity C and resistance R_v values, we found the dielectric relaxation time constant

$$\tau_r = CR_v = \varepsilon_0 \dot{\varepsilon}\, (S/d)\, \rho_v\, (d/S) = \varepsilon_0 \dot{\varepsilon} \rho_v\,, \quad \varepsilon_0 = 8.854 \cdot 10^{-12}\,.$$

The calculation of ρ_v from this equation makes it possible to exclude the geometry of the measuring electrodes and, therefore, decrease errors in determining the dielectrical characteristics. In such an event, the resolution in measurements is determined by the sensitivity and stability of the measuring equipment used, in our case, an E7-14 immitance meter. The operating frequencies of the instrument are 0.1, 1, and 10 kHz with an instrument error of no more than 0.01%, and the average duration of one measurement is no more than 200 msec. The instrument provides for the regime of averaging of the results in 10 or 100 measuring cycles, as well as for automatic compensation of the initial parameters (zero correction). Thus, the resolution in measuring tan δ, C, and ρ_v was largely determined by the resolution of the E7-14 immitance meter (by its last significant digit), and the error was $\pm 0.006\%$ for resistance and capacity, $\pm 1 \cdot 10^{-9}$ sec for the time constant, and $\pm 2 \cdot 10^{-4}$ for the dielectric loss tangent.

Since it is known that all electrophysical indices can vary over a wide range with a change in any state of the substance, to obtain reliable and reproducible results with the aim of their subsequent comparison, all investigations were conducted under exactly the same experimental conditions and using the same experimental technique with the preservation of equal conditions of preparation of individual components and compositions of the composite. Fibers of length ~1 mm were introduced into the preevacuated binder heated at a temperature of 60°C immediately upon their drying, without cooling, to avoid absorption by them of the environmental moisture. The compositions of the composite (at least three identical ones to control the reproducibility) were prepared just before the experiment by mixing the previously prepared components, then they were quickly charged into the cells so that the time needed to prepare the composite and charge into the measuring cells was constant and as short as possible (≈2 min) before the beginning of tests for all experiments. As a reference point, the initial instant of time of mixing the composite with the hardener was taken. The composites of fibers with the binder were hardened under the action of a constant electric field of strength 1.65 kV/cm. The polarizing voltage was fed to the specimen from a UIP-2 power source. Hardening was car-

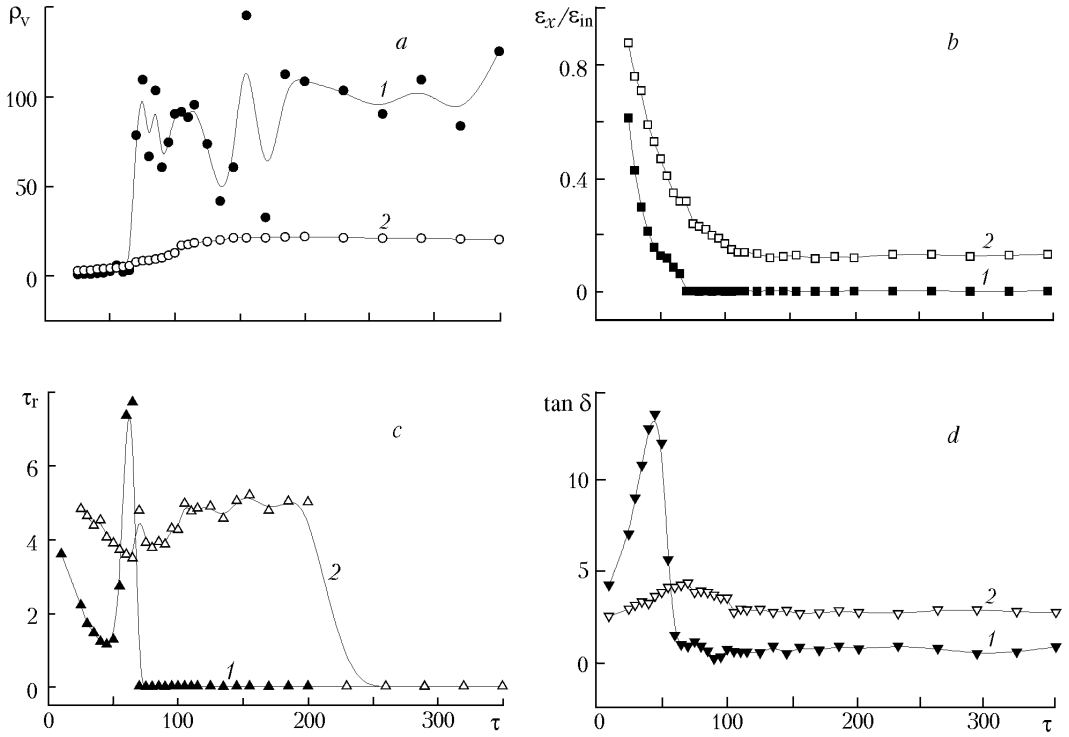

Fig. 1. Specific bulk electrical resistance (a), relative dielectric constant (b), relaxation time (c), and dielectric loss tangent (d) versus the hardening time in the electric field (1) and without it (2) of the epoxy composite discretely reinforced with phosphorus- containing carbon fibers. $\rho_v \cdot 10^3$, Ω·m; $\tau_r \cdot 10^{-1}$, sec; τ, min.

ried out at a temperature of 25°C. Concurrently, the same composition was hardened without the field. In the hardening process of composites, the electrophysical indices were registered at a frequency of 100 Hz. Measurements were made at established time intervals and realized about 5 sec upon tapping off voltage from the specimen. In this case, only steady current was registered.

Upon hardening, without removing the specimen from the cell, the temperature dependence of electrical properties of hardened compositions was investigated. To this end, the cell was placed in a thermostated unit. A distinguishing feature of the unit is the high temperature homogeneity throughout the working zone volume due to the use of a double wall. The temperature was checked near the specimen by a mercury thermometer with an error of ±0.1°C. The temperature in the working zone was increased at a constant heating rate of 1°C/min with continuous recording of electrical parameters. The transformation depth of the epoxy binder of the composite hardened both in the electric field and without it was estimated by the gel-fraction yield using the method of extraction of hardened specimens by boiling acetone in a Soxhlet apparatus for 24 h [9]. The thermomechanical studies of hardened compositions of composites were made on specimens of diameter and height 10 mm under the conditions of continuous action of a constant stress of 0.6 mPa and at a rate of temperature rise of 3°C/min. The changes in the deformation caused by the heating and uniaxial compression of specimens were recorded by means of a modernized Heppler consistometer (VEB MLW Prufgerate-Werk Medingen, Dresden, Germany). The physicochemical tests of hardened specimens were conducted by the standard methods [10].

Results and Discussion. Figure 1 presents the data on the change in the dielectric loss tangent tan δ, the specific electrical resistance ρ_v, the relaxation time of dipole polarization τ_r, and the relative value of the dielectric constant $\varepsilon_x/\varepsilon_{in}$ of the discretely PCF-reinforced epoxy binder in hardening the composite under the action of the electric field and without it. The fiber content in the composite is 60 mass %. It is seen that the shape of the curves is different. All electrophysical indices in the composite containing fibers with surface-active groups from the very beginning of the process change more intensively under the action of the electric field compared to the indices for the same

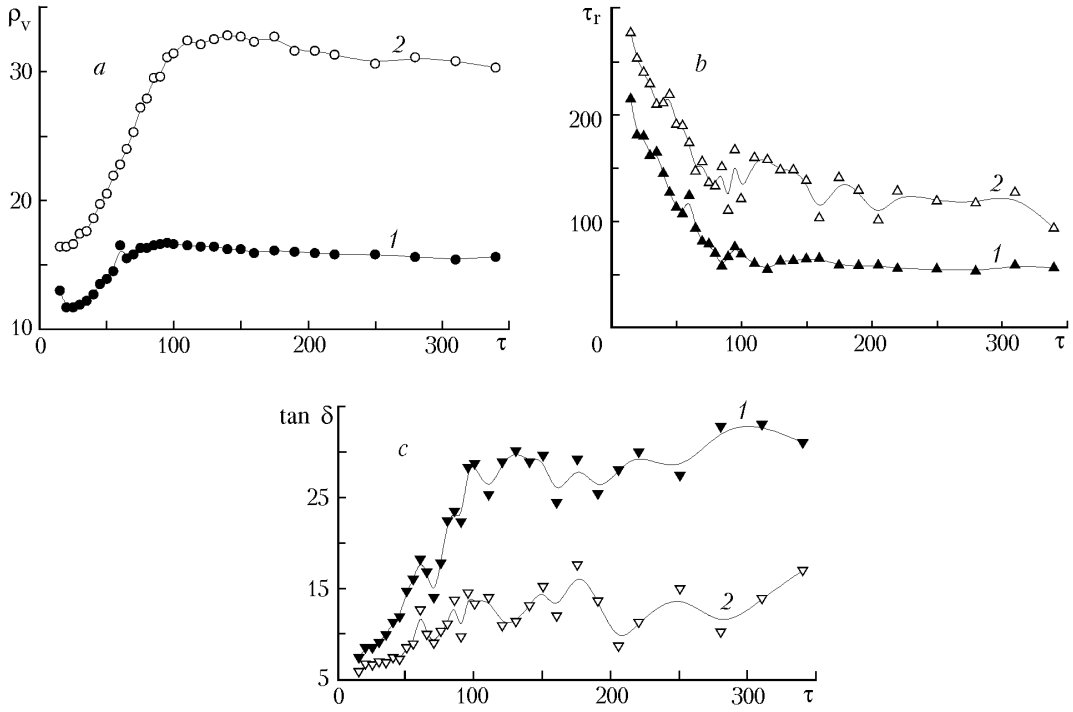

Fig. 2. Specific bulk electrical resistance (a), relative dielectric relaxation time (b), and dielectric loss tangent (c) versus the hardening time in the electric field (1) and without it (2) of the epoxy composite discretely reinforced with nonmodified carbon fibers; degree of filling 60 mass %; hardening temperature 25°C. $\rho_V \cdot 10^3$, Ω·m; $\tau_r \cdot 10^{-3}$, sec; τ, min.

composition of the composite hardened without it. From the very first minutes the mobility of the system markedly increases, which is evidenced by the considerable decrease in the relaxation time and the increase in the dielectric loss tangent (Fig. 1c and d). On the one hand, this is due to the cooperative motion of the polar components of the binder and the surface-active groups of the fibers under the action of the field and their orientations along the field. On the other hand, the variant of additional stimulation of the low-molecular component migration from the binder bulk to the fiber surface upon application of the field is not excluded. Earlier it wa established that upon the introduction of element-containing fibers into the epoxy binder preferable sorption of the low-molecular component by the fibrous filler can be observed [11]. This leads to a depletion of the binder bulk by the hardening component and, therefore, to an increase in the number of active groups that nave not reacted. The decrease (by about 2–4 mass %) in the degree of hardening for the composite reinforced with phosphorus-carbon fibers formed in the electric field, as compared to the same composition hardened without the field, is evidence in favor of the aforesaid.

A distinguishing feature of the kinetic τ_r curve at an early stage of hardening under the conditions of the physical action is a subsequent strong spike and a simultaneous sharp decrease in tan δ caused by the considerable restriction of the molecular mobility by the surface of the active carbon-fibrous component under the action of the field. The subsequently observed increase in the specific electrical resistance, as sharp as for tan δ, points to the changed topography of the conductive elements of the structure of the composite oriented in the field. The system becomes bound to a greater extent. As is seen from Fig. 1a, after 1 h the composite has much higher values of the volume electrical resistance and lower values of tan δ and ε compared to the same composition hardened without the field (Fig. 1b and d).

As for the composite discretely reinforced with nonmodified carbon fibers, the reverse situation is observed. The curve of the rate of rise of the specific electrical resistance lies higher for the case of composite hardening without the field (Fig. 2a), and the curve of change in tan δ in the process of composite hardening without the electric field lies lower than the tan δ curve for the composite exposed to it (Fig. 2c). Thus, the data obtained point to the

TABLE 1. Influence of the Electric Field on the Electrophysical Properties of Epoxy Composites Discretely Reinforced with Carbon Fibers

Properties	Hardening conditions	PCF			Nonmodified CF
		Degree of filling, mass %			
		10	50	60	60
ρ_v, Ω·m	+	$19.5 \cdot 10^4$	$80.8 \cdot 10^3$	$26.4 \cdot 10^3$	$18.1 \cdot 10^3$
	—	$15.3 \cdot 10^4$	$47.9 \cdot 10^3$	$15.3 \cdot 10^3$	$26.2 \cdot 10^3$
τ_r, sec	+	$11.8 \cdot 10^{-5}$	$36.3 \cdot 10^{-5}$	$0.59 \cdot 10^{-6}$	$48.0 \cdot 10^{-6}$
	—	$6.0 \cdot 10^{-5}$	$27.3 \cdot 10^{-5}$	$0.52 \cdot 10^{-6}$	$81.7 \cdot 10^{-6}$

Note. +, hardening in the electric field; −, hardening without the field.

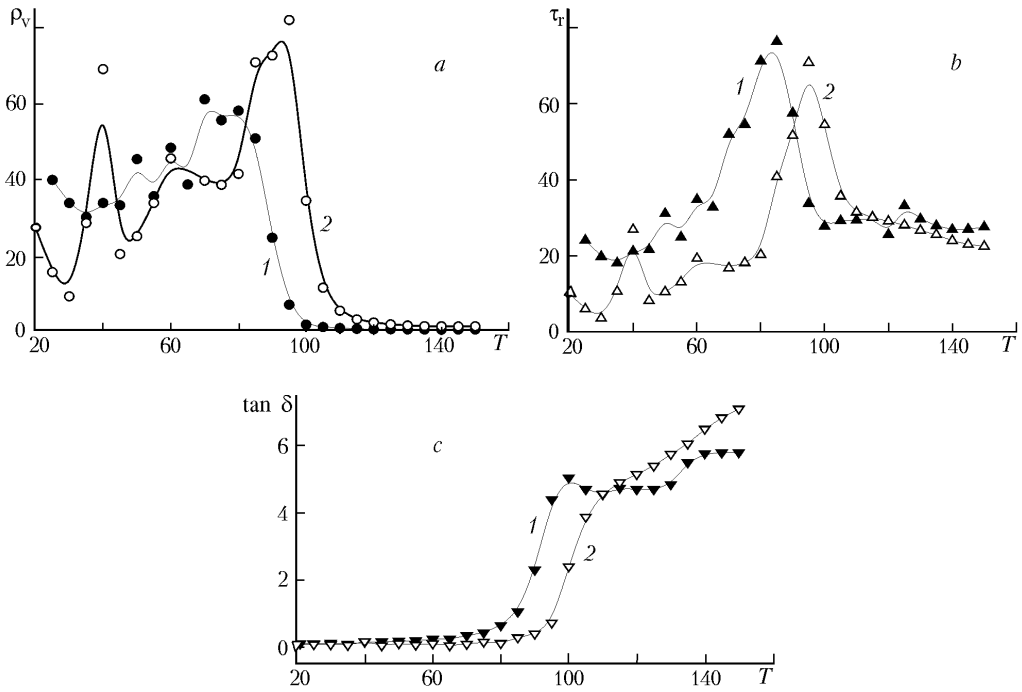

Fig. 3. Temperature dependence of the specific bulk electrical resistance (a), the relaxation time (b), and the dielectric loss tangent (c) for the epoxy composite discretely reinforced with phosphorus-containing carbon fibers and hardened in the electric field (1) and without it (2); degree of filling is 8 mass %. $\rho_v \cdot 10^4$, Ω·m; $\tau_r \cdot 10^{-6}$, sec; T, °C.

fact that in using a composite of nonmodified carbon fibers a more mobile system is observed for a composition hardened in an electric field. And the process thereby proceeds fairly uniformly, without sharp jumps both in the field and without it. Upon completion of the hardening stage the composite with nonmodified carbon fibers formed without the field has higher values of ρ_v and tan δ (see Table 1). But in the composites with phosphorus-containing carbon fibers, as mentioned above, this dependence is reverse: it has higher values of the specific electrical resistance and relaxation times in the case of composite formation under the conditions of the electric field action. The results of the investigations point to the nonidentical character of interaction of the phosphorus-containing and nonmodified carbon fibers with the epoxy binder. In so doing, differences are observed in hardening fiber-reinforced composites both under the action of the electric field and without it.

The results of investigations of the temperature dependences of the electrophysical characteristics of hardened compositions of composites are also evidence in favor of the effective influence of the surface of phosphocarbon-carb-

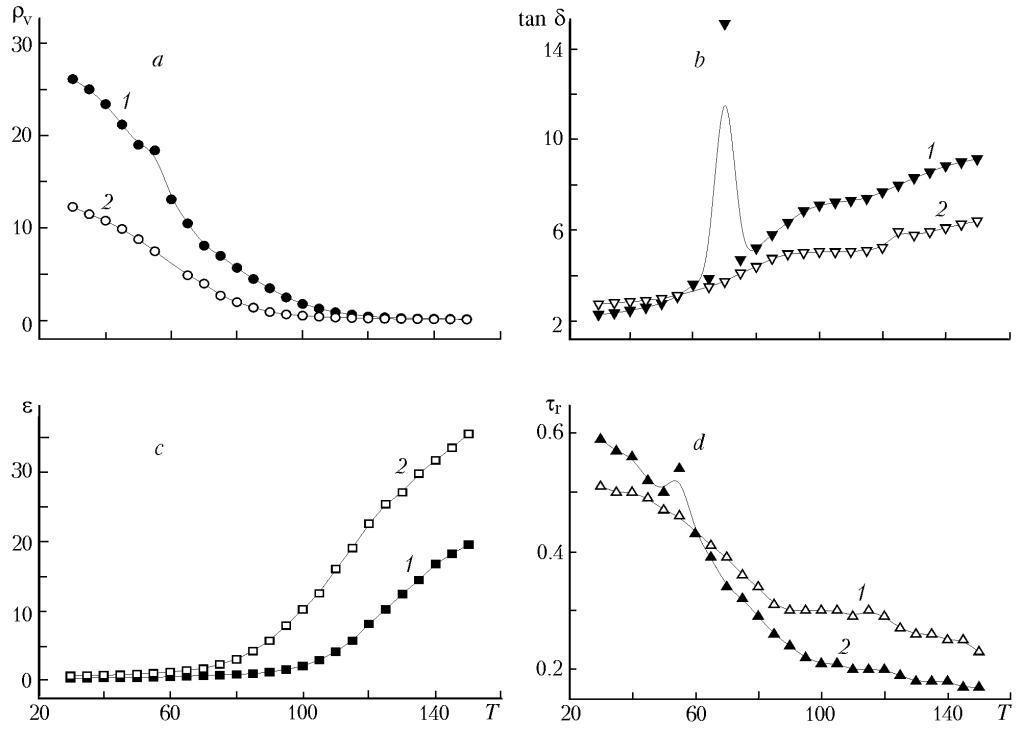

Fig. 4. Temperature dependence of the specific bulk electrical resistance (a), the dielectric loss tangent (b), the dielectric constant (c), and the relaxation time (d) for the epoxy composite discretely reinforced with phosphorus-containing carbon fibers and hardened in the electric field (1) and without it (2); the degree of filling is 60 mass %. $\rho_v \cdot 10^3$, Ω·m; $\tau_r \cdot 10^{-6}$, sec; T, °C.

on fibers on the process of spatially cross-linked epoxy polymer formation. The data obtained for the epoxy composite discretely reinforced with PCFs confirm the different degree of binding of the polymer structure formed in the process of composite formation in the electric field and without it. This is evident in studying the composition of composites with PCFs both with a small degree of filling, when the main contribution to the properties of the material is made by the polymer matrix, and with a filling close to maximum, when practically the whole of the binder is in the near-surface layer. For example, from Fig. 3 it is seen that in the composite hardened in the presence of a small number of phosphorus-containing fibers, practically from the very beginning of heating, long before the vitrification temperature, the mobility of individual unbonded groups under any hardening conditions manifests itself: in the field and without it. This is due to the redistribution of the reactive binder components in the composite bulk as a consequence of the possible sorption of the amine ingredient of the binder by the PCF surface. The increase in the specific volume electrical resistance observed thereby and its adequate increase in the values of the relaxation times point to the subsequent process of structurization of the system upon heating (Fig. 3a and b). At the same time, at the same character of changes in the electrophysical characteristics differences in the shapes of the curves upon hardening in the electric field and without it also show up clearly. All curves are displaced relative to one another. In the composite exposed, when being hardened, to the electric field, the processes of additional structurization upon subsequent heating proceed more intensively and terminate sooner: the maxima on the ρ_v and τ_r curves are shifted by about 10°C on the temperature scale towards decreasing temperatures. Devitrification of the system also begins sooner. On the tan δ curve, two maxima of dipole-segmental losses are more clearly defined, with the first maximum characterizing the mobility of the structural units on the interface being shifted towards lower temperature values, and the second one — towards higher values (Fig. 3c).

Figure 4 presents the results of investigations of the epoxy polymer molecular mobility in a highly filled composite when the hardened epoxy is mainly in the state of the surface layer in the phosphor-carbon fiber. Here, as at small degrees of filling, upon composite hardening in the electric field the characteristic maxima on the dielectric loss

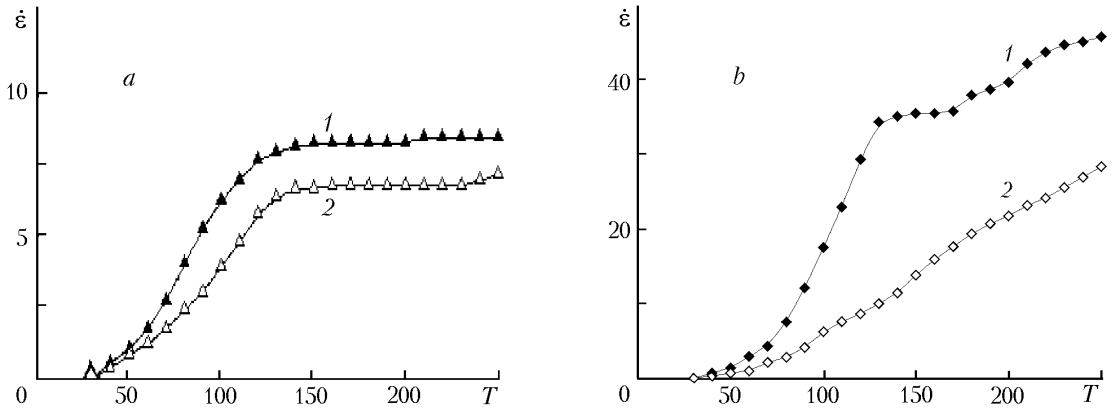

Fig. 5. Thermomechanical curves of the epoxy composite discretely reinforced with nonmodified (a) and phosphorus-containing (b) carbon fibers and hardened in the electric field (1) and without it (2); the degree of filling is 60 mass %. *T*, °C.

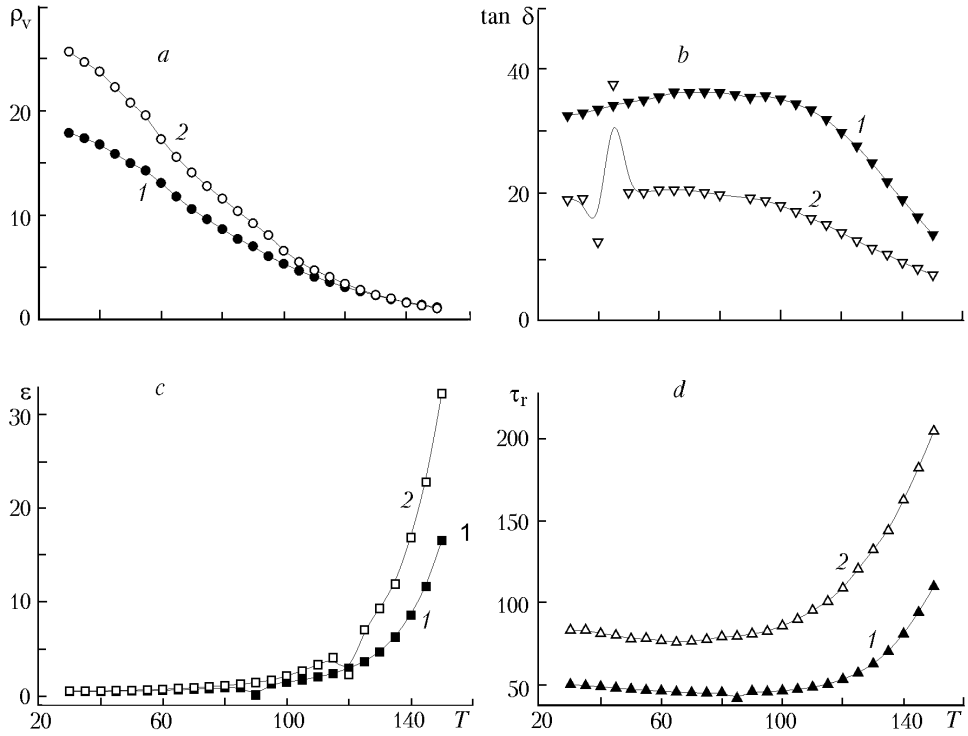

Fig. 6. Temperature dependence of the specific bulk electrical resistance (a), the dielectric loss tangent (b), the dielectric constant (c), and the relaxation time (d) for the epoxy composite discretely reinforced with nonmodified carbon fibers and hardened in the electric field (1) and without it (2); the degree of filling is 60 mass %. $\rho_V \cdot 10^3$, Ω·m; $\tau_r \cdot 10^{-3}$, sec; *T*, °C.

tangent show up more vividly (Fig. 4b). In the low-temperature region, a kink on the curves of the specific electrical resistance and relaxation times is noticeable (Fig. 4a, d). The data obtained correlate with the results of the thermochemical analysis (Fig. 5b). The molecular mobility of the polymer chains formed in the compositions highly filled with PCFs, which is associated with the segmental motion of molecules, is different for composites formed in the electric field and without it. For the composite hardened under the action of the field, upon heating to above 50°C the

mobility of the structural elements is much higher compared to the composition that was not subjected to the physical action. The deformation curve steeply slopes up (Fig. 5b), which is in fair agreement with the above-mentioned decrease in the relaxation time values in this region. In so doing, several inflection points on the relative deformation curve show up vividly, which is indicative of the formation in the surface layer of structures with a different degree of binding. For the composite with nonmodified carbon fibers, in the composite formation in the electric field and without it, multiplicity of manifestations of relaxation processes is not observed (Fig. 5a). The temperature dependences of all electrical indices (ρ_v, τ_r, tan δ, and ε) also differ for composites with nonmodified carbon fibers compared to composites with PCFs with the same degree of filling (Fig. 6).

Conclusions. Thus, the data obtained point to the fact that hardening of epoxy composites in the presence of phosphorus-containing carbon fibers leads to changes in the process of system structurization as a consequence of the orientational action due to the application of the electric field, on the one hand, and the intensification of the physicochemical action at the phosphor carbon fibrous filler–polymer interface, on the other. The interaction of phosphorus-acidic groups of the filler with the amine hardener leads to the formation of additional chemical mesh nodes with the filer surface, which in turn leads to growth in the microheterogeneity of the filled system and a change in the properties of the composite.

Analysis of the data obtained for various component ratios of the composites and account of the specific interactions of the binder components with the surface-active groups of fibers that progress upon application of the electric field have made it possible to obtain composites with improved properties compared to materials formed without the field. For instance, under optimally chosen conditions the composite discretely reinforced with PCF formed in the electric field has a higher elastic modulus (by 12.7%) and exceeds in hardness by 1.5–2.4 times (depending on the degree of filling) composite material of the same composition not exposed to the electric field. The optimally chosen compositions of composites with phosphorus- containing carbon fibers hardened in the electric field feature also a higher inflammation resistance.

NOTATION

C, capacity; *d*, thickness, mm; R_v, volume electrical resistance, Ω; *S*, area, m^2; *T*, temperature, ^oC; tan δ, dielectric loss tangent; ε, dielectric constant ($\times 10^2$); $\dot{\varepsilon}$, deformation, %; ρ_v, specific volume electrical resistance, Ω·m; τ, time, min; τ_r, dielectric relaxation time, sec. Subscripts: in, initial; *x*, current value of a parameter; v, volume; r, relaxation.

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