

DIELECTRIC RELAXATION OF EPOXY POLYMER IN COMPOSITES CURED IN AN ELECTRIC FIELD

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Results of a study of the effect of various fillers (discrete aluminum-oxide fibers and powdered barium titanate) on the molecular mobility of the epoxy polymer in composites cured under the action of an electric field are given.

A fundamental characteristic of the set of properties of polymer composites is the molecular mobility of the polymer chains, which is sensitive not only to the material composition but also to any structure changes and heterogeneity of the polymer in the surface layers of a multiphase system [1]. The highly sensitive methods used for determination of molecular mobility in polymers include dielectric relaxation, which consists in determination of dielectric characteristics in a wide range of temperatures and frequencies [2]. Polymers are characterized by the presence of several forms of molecular relaxation caused by thermal motion of both the macromolecular chain itself and its individual structural units (monomeric links), individual atoms, and atomic groups in lateral branches [3]. In a filled polymer, the interface contributes a great deal to these processes [4]. Therefore, information about thermal motion that is inseparably linked with the polymer structure is important for characterization of the general properties of composites and relations of their formation and for development of prerequisites for optimization of composites and improvement of technologically important characteristics in the development of materials.

The goal of the present work is to investigate the effect of various fillers on the molecular mobility of an epoxy polymer in composites cured under the action of an external electric field.

Epoxy composites with an amine curative taken in a stoichiometric ratio to the resin were objects of the study. Powered barium titanate and discrete aluminum oxide fibers with a specific surface area of $200 \text{ m}^2/\text{g}$ and acidity of 0.5 mg-eq./g produced following [5] were used as fillers. The composites were cured under the action of a constant electric field with an intensity of 1.65 kV/cm . For this, the freshly prepared composites were placed in a specially designed cell of a constant-temperature measuring unit. The unit had a high temperature uniformity over the whole working volume due to the use of a double wall, and it was possible to replace the measuring electrode by a capacitive sensor and control of the pressure exerted on the test specimen by a spring. Temperature was controlled directly at the specimen by a mercury thermometer within $\pm 0.1^\circ\text{C}$. Polarizing voltage was supplied to the specimen from a UIP-2 power source. The composites were cured at 25°C , and in the second version, specimens kept at room temperature were subjected to heat treatment at 150°C for 1 h.

After curing, with the specimen remaining in the cell, the temperature dependence of the electrical properties of cured composites was studied. The temperature in the working zone of the cell was raised at a constant rate of $1^\circ\text{C}/\text{min}$ with continuous recording of electric parameters, for the simultaneous recording of which a set of measuring instruments was used: an E7-12 digital LCR meter (the measurement error was within $\pm 0.02\%$ for capacitance and resistance, $\pm 2 \cdot 10^{-4}$ for the loss tangent and slope tangent); a V7-23 universal digital voltmeter with a maximum admissible measuring error in d.c. resistance $\Delta R \leq \pm(3 \cdot 10^{-4}R_x + 3 \cdot 10^{-4}R_k)$ for ranges of 0.1, 1.0, 10, 100, and 1000 k Ω ; $\Delta R \leq \pm(10 \cdot 10^{-4}R_x + 5 \cdot 10^{-4}R_k)$ for a range of 10,000 k Ω , where ΔR is the main measuring error of resistance, k Ω ; R_x is the voltmeter readings, k Ω ; R_k is the measuring range, k Ω . Thermomechanical studies were carried out with a Hepler instrument under a continuous constant load of 0.6

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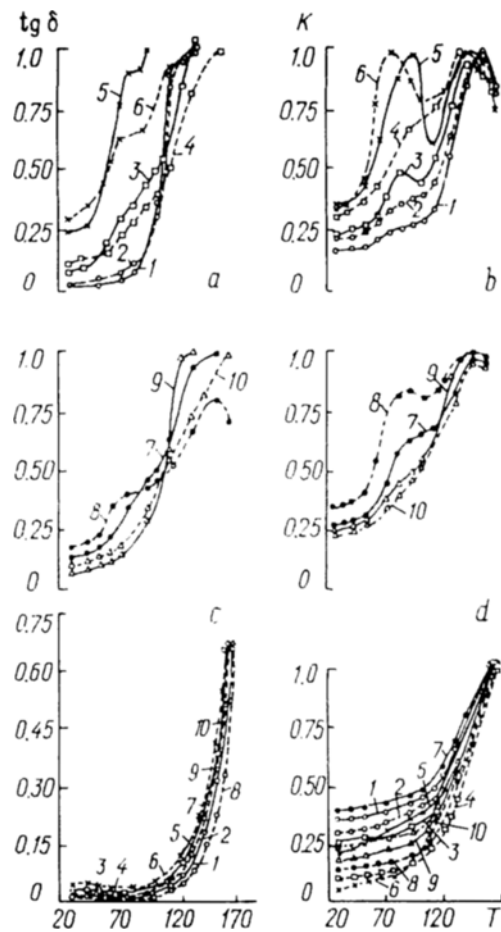


Fig. 1. Temperature curve of dielectric losses $\tan \delta$ (a, b) and relative capacitance K (b, d) of epoxy binder without filler (1, 2), filled with barium titanate (3, 4), aluminum oxide fibers (5, 6), mixture of fibers and barium titanate untreated (7, 8) and treated by passivator (9, 10). Cured without field (1, 3, 5, 7, 9) and with electric field (2, 4, 6, 8, 10) with additional heat treatment (c, d). T , $^{\circ}\text{C}$.

MPa. Simultaneously, experiments were carried out for compositions cured under the same conditions but without any physical actions.

Figures 1a, 1b, and 2c show temperature curves of the loss tangent, relative capacitance, and electrical conductivity of composites of the epoxy binder cured at 25°C without fillers and with ingredients introduced separately and in combinations. It can be seen that irrespective of the curing procedure, the introduction of fillers (both fibrous and powdered) increases the conductivity of the system and, accordingly, degrades the dielectric characteristics. Under heating all the parameters indicated increase gradually and this increase is sharp in the range of the glass transition temperature of the system. This is caused by an increase in the mobility of segments of the forming polymer chain, which satisfactorily agrees with the results of thermomechanical analysis. However, the behavior of relaxation processes for the binder without a filler and filled by a powder or fibers is different under normal conditions (free formation without application of voltage) and under the action of an electric field, which indicates formation of spatially cross-linked structures bound to various degrees.

Studies show that in the case of heated composites with disperse fillers the electrophysical characteristics start to grow intensely at lower temperatures in comparison with an unfilled binder (Figs. 1a and 2b, curves 1-4). This shift is even more pronounced for a composite discretely reinforced by aluminum oxide fibers (Figs. 1a, 1b, and 2c, curves 5 and 6). Moreover, for a composite with a fibrous binder cured both under free forming and under

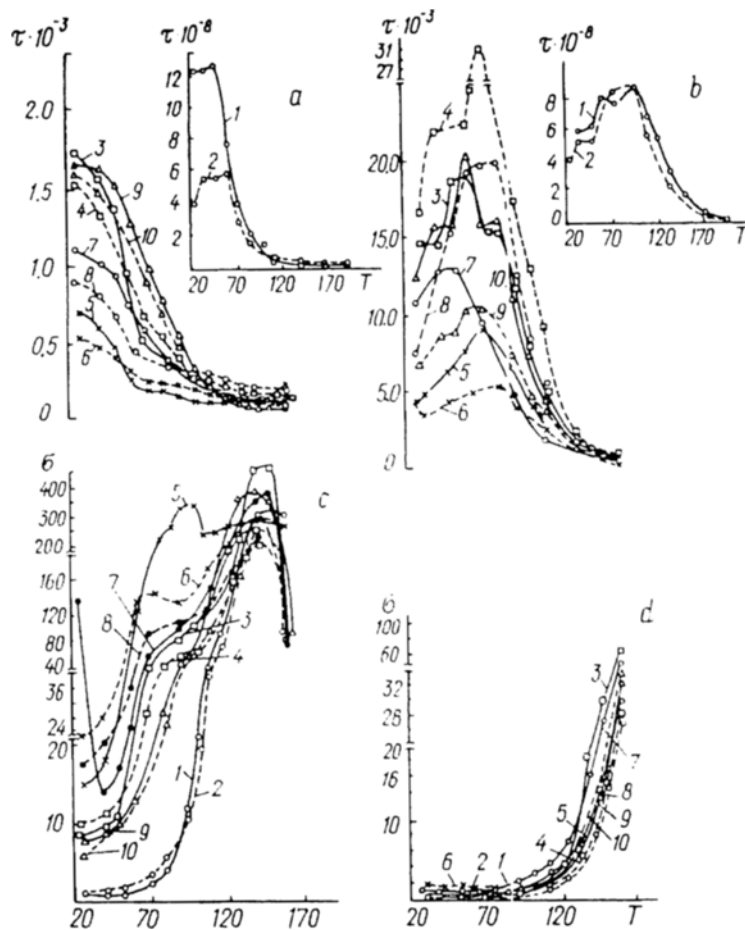


Fig. 2. Curves of relaxation times (a, b) and electric conductivity (c, d) of epoxy binder without filler (1, 2), filled with barium titanate (3, 4), aluminum oxide fibers (5, 6), and fiber-barium titanate mixture untreated (7, 8) and treated by passivator (9, 10). Cured without field (1, 3, 5, 7, 9) and with electric field (2, 4, 6, 8, 10) with additional heat treatment (b, d). τ , sec; σ , nS; T , $^{\circ}\text{C}$.

voltage, when the composite is heated to a temperature higher than the glass transition temperature ($>50^{\circ}\text{C}$, according to thermomechanical analysis), there are two maxima in the curve of the loss tangent caused by segmental dipole relaxation (α -process). In this case the values of the first maximum $\tan \delta_{\max}$ for the composite cured under the action of an electric field are lower than without a field, and the region of the second maximum of $\tan \delta$ of segmental dipole losses is shifted toward higher temperatures (see Fig. 1a, curves 5 and 6). Accordingly, there are also differences in the relaxation time spectra (Fig. 2a, curves 5 and 6).

It should be noted that in the curve of $\tan \delta$ versus temperature for the barium titanate-filled composite small steps are also observed in the region of the relaxation process caused by segmental thermal motion. However, unlike the composite filled with aluminum oxide fibers, these steps manifest themselves when the composite is cured without a field (Fig. 1a, curves 3 and 4). For these steps the values of $\tan \delta$ are much lower than these values for the composite with Al_2O_3 and the value of the relative capacitance corresponding to a given temperature is correspondingly lower (Fig. 1b, curves 3 and 4). For the barium titanate-filled epoxy composite cured under the action of an electric field, $\tan \delta$ gradually and uniformly increases; growth of $\tan \delta$ is slow and the maximum of $\tan \delta$ of segmental dipole losses is shifted towards higher temperatures in comparison with the temperatures for the composite cured without a field (Fig. 1a, curves 3 and 4).

The introduction of fillers into epoxy binders also brings about new maxima in the temperature curve of the relative capacitance in the temperature range of 50–105°C, and this is most pronounced for composites discretely reinforced by aluminum oxide fibers (see Fig. 1b, curves 5 and 6). When composites with Al₂O₃ are cured in an electric field, the first maximum is shifted by 20°C towards lower temperatures as compared with curing without a field.

For a barium-titanate-filled composition cured without a field, in the curve of the relative capacitance the first distinct maximum appears at 80°C. When the composition is cured under the action of an external electric field, a more intense increase in the absolute values of the capacitance is observed in the temperature range 60–110°C. However, unlike the first maximum for the composite with Al₂O₃, for the barium-titanate-filled composite the first maximum is shifted towards higher temperatures and, increasing sharply, immediately becomes the second maximum (Fig. 1b, curve 4).

It should also be noted that the introduction of fillers (discrete fibers and powders) results in an increase in the electrical conductivity of the system, and this increase is most pronounced for composites with aluminum oxide fibers. An electric field during curing increases the electrical conductivity of the composite with Al₂O₃ even more. Subsequent heating of filled composites leads to a sharp increase in the conductivity of the system and brings about a maximum in the temperature curve in the range of 50–70°C (Fig. 2c, curves 3–10). For the unfilled cured binder no increase in the electrical conductivity is observed in this temperature range (Fig. 2c, curves 1 and 2). When the composites are heated above 90°C, in all the filled composites an intense increase in electrical conductivity, which leads to a substantial increase in the loss tangent, is also observed for the unfilled binder at these temperatures.

Thus, the present experimental results indicate that the effect of an electric field is more pronounced for filled epoxy composites. For unfilled binders it is less pronounced: for curing in a field and without a field, the curves of $\tan \delta$ and electrical conductivity practically coincide (Figs. 1a and 2b, curves 1 and 2), and the temperature curves are similar in shape and differ only in absolute value (Fig. 1b, curves 1 and 2). When the binder is cured in an electric field, the orientation of the polar groups of reacting components and forming macromolecules is manifested as a slight decrease (within the same degree) in the relaxation time of the dipole group β -process (the temperature range of 20–50°C, i.e., before the glass transition temperature of the system). As the temperature increases further, the relaxation times are equal for both composites (cured with and without a field) and decrease exponentially (Fig. 2a, curves 1 and 2). According to [6], the values of the relaxation times are characteristic of thermal dipole polarization. However, it should be noted that additional heat treatment results in a decrease in the relaxation time of the β -process for binders cured without a field, while for a composite cured under voltage the state of the relaxing particles of the group dipole process does not change (Fig. 2b, curves 1 and 2).

The results also indicate that there are differences in the relaxation processes when fibrous or powdered ingredients are used in the composites. These differences can be explained in terms of the active effect of the surface of the heterophase component on the structure of the product.

It is known that the surface of the solid phase even purely geometrically restricts the number of possible conformations that can be assumed by macromolecules at the phase interface [4]. It is also known that in complicated heterogeneous systems selective sorption of individual components in the composite by the surface of the binder is exhibited [7]. All these are reflected in the character of transformations of the oligomer matrix and affect the mobility of segments of the forming chain in the surface layer and in the bulk of the composite.

Earlier we established the possibility of sorption of the amine component in the epoxy binder by the surface of element-containing fibers (carbon and oxide) [5, 8]. It was also found that aluminum oxide fiber affected the viscoelastic properties of liquid-phase systems. It was shown that they were promising for use in suspensions with a high electrorheological sensitivity [9]. This suggests that in the epoxy composite studied, fibrous aluminum oxide, which has a developed surface, is not an indifferent ingredient of the composite. Changes in dielectric relaxation of the epoxy composite reinforced discretely by Al₂O₃ fibers described above testify to this.

As is known [6], a substantial increase in the electrical capacitance of inhomogeneous (laminated, foreign inclusion- and pore-containing) or multicomponent dielectrics is caused by the bulk charge polarization that results from migration and accumulation of electric charges at the boundaries of the inhomogeneities or the solid phase.

Reorientation or transfer of the bulk charge (macro-dipoles) produced due to the reorientation at the boundary is slower and the relaxation times are maximal.

The present experimental data (the appearance of a strong maximum in the relative capacitance curve at 70–90°, where this maximum is not observed for unfilled binders (Fig. 1b, curves 1, 2, 5, and 6) and a sharp increase in the relaxation time to values that, according to [6], occur in the region of migration polarization (Fig. 2a, curves 1, 2, 5, and 6)) suggest an intense effect of the fibrous filler on physicochemical transformations of the binder in the surface layer in the case of curing with and without an electric field. There occurs migration of the low-molecular (amine) component to the surface of the fiber, which results in redistribution of the reacting ingredients in the boundary layer and in the bulk of the composition. The amine adsorbed by the surface of the fiber does not take part in curing of the binder at 25°C. Because of this, the surface layer is depleted of the curative component, the cross-linking density is decreased, and the mobility of the structural components increases. This is confirmed by thermomechanical analysis: the glass transition temperature of the system is shifted towards lower temperatures (up to 47–52°C). The appearance of additional maxima in the temperature curve of $\tan \delta$ at 70°C and subsequent steps for composites reinforced discretely by Al₂O₃ fibers, which are not typical of unfilled binders, are caused by devitrification of the structural groups in the surface layer, whose mobility is different from the mobility of the molecular chain in the bulk of the composite.

On the other hand, migration of the low-molecular component to the surface of the fibers increases the number of weakly bound polar groups in the interphase layer, including the adsorption layer, which is exhibited by increase in the conductivity of the composite and its sharp increase from the first minutes of heating at temperatures far from the temperature of the segmental dipole α -process (see Fig. 2c, curves 5 and 6). The presence of several maxima in the conductivity curve suggests that various structural groups participate in charge transfer. For the filled composites considered, they are caused by the total contribution of the surface (boundary) layer and mobility of macromolecular segments in the subsequent layers, which satisfactorily agrees with the literature data [10].

The application of an electric field in the stage of forming the spatially cross-linked structure of the epoxy polymer intensifies the migration and sorption of the amine by the fibrous ingredient. Changing the height of the energy barriers between possible local positions of dipoles, the electric field leads to accumulation of a large number of charged weakly bound particles in energetically more favorable positions at the phase interface. This is indicated by a higher conductivity and a wider step of the first high-temperature α -relaxation process at 25°C for the composite with Al₂O₃ fibers cured under physical action (see Figs. 1a and 2a, 2b, curve 6). Meanwhile, as was mentioned above, for a composite oriented in an electric field and reinforced discretely by aluminum oxide fibers, it is found that the values of the first maximum of relaxation dielectric losses, which testifies to improvement of the conditions of interaction of heterogeneous components on the interface, the second maximum of $\tan \delta$ of segmental dipole losses is shifted towards higher temperatures and the relaxation times of segmental motion increase after reaching the glass transition temperature of the system. All of this indicates a higher structural organization of the polymer formed under the action of an electric field and the determining contribution of Maxwell-Wagner polarization (on the interface) to polarization of macromolecules of the epoxy polymer reinforced by fibers, which is consistent with the literature data [11].

Powdered barium titanate does not have such an extensive surface, and sorption of the curative is weaker: the relaxation processes of segments in the surface layer are hardly noticeable and only observed in composites cured without a field (Fig. 1a, curves 3 and 4). This is caused by the fact that the effects of loosening of the structure because of decreased packing density of macromolecules in the boundary layers inherent in composites with inert powdered fillers are compensated for by the formation of a physical network by the powders themselves with sufficiently high filling. It is most likely that the electric field perfects this network, which results in the formation of a more rigidly packed structure, which is indicated by the shift of $\tan \delta$ of the α -process towards higher temperatures (see Fig. 1a, curve 4).

The increase in the electrical conductivity and, accordingly, electrical capacitance of composites with disperse fillers before the phase transition temperature of the ferroelectric used is reached is caused, on the one hand, by inhomogeneity of the micro- and macrostructure of the three-dimensional composite formed and, on the

other, by the effect of the surface of the filler itself. It is known that compounds in a polycrystalline state (barium titanate is such a compound) are characterized by a high concentration of crystal-structure defects. Weakly bound electrons located near these defects have a rather high polarizability [6]. Thus, the longer relaxation times observed in a particular case for composites with a disperse filler (Fig. 2b, curves 3 and 4) can be explained by the total contribution of electron polarization caused by thermal motion and polarization of macrodipoles (domains in ferroelectrics). Partial migration of the low-molecular component under the action of the surface of the filler cannot be excluded either.

For a composite with a binary filler (with the joint use of discrete fibers and a disperse filler), the maximum of $\tan \delta$ of the α -process is shifted towards higher temperatures and the values of $\tan \delta$ decrease (Fig. 1a, curve 8). This suggests the formation of a more rigid polymer structure, which is confirmed by thermomechanical analysis: the glass transition temperature of the composite increases and deformability decreases. The effect of orientation of macromolecules that are formed under the action of an electric field in a composite reinforced discretely by Al_2O_3 is also exhibited in a decrease in the relaxation time of the group dipole process and in an increase in the relaxation time of segmental motion (Fig. 2a, curves 6 and 8), which agrees satisfactorily with the literature data [9]. It should be noted that in composites with binary fillers a dominant factor is processes occurring in the interphase zone, which is indicated by a broad region of segmental dipole polarization that is exhibited at 50–100°C. This is supported by the fact that in the case of a passivation of the surface of the filler by compounds with molecules with a length sufficient for manifestation of their natural molecular mobility, relaxation processes in the composite are identical with the processes in the initial unfilled binder (Fig. 1a, curves 9 and 10). On the other hand, the decreased effect of the interface on relaxation processes in the boundary layers due to the indicated modification of the filler observed in this case can be considered as a basis for a method of control of polymer surface properties in highly filled systems.

All the dielectric relaxation phenomena considered above occurred in composites cured at 25°C. In the case of additional heat treatment of the composite, segmental dipole polarization is not exhibited (Fig. 1c). The rapid growth of the loss tangent observed at temperatures higher than the glass transition temperature (>100–110°C) is caused by an increase in the electrical conductivity of the system (Figs. 1c and 2d). The decrease in the relative capacitance and relaxation times for composites with Al_2O_3 fibers in the temperature range of 20–120°C, which is more pronounced for composites cured under the action of an electric field (Figs. 1d and 2b, curves 5 and 6), suggests the formation of more ordered structures because of structuring of the polymer in the surface region of the polymer due to reactive ingredients of the binder adsorbed by the active surface of the fibers.

Thus, the studies have shown that the effect of an external electric field on the polymer structure that is formed is caused to a greater extent by heterophase ingredients introduced into the composite and the main contribution to polarization of macromolecules in systems with an active component is made by migration and interphase polarization, which is consistent with the literature data [6, 11]. Under the action of an electric field, orientation of macromolecules on the active fibrous filler-polymer interface improves the physicochemical characteristics of compositions highly filled with powdered ingredients, especially in the case of additional heat treatment of the composite, because of which electrosensitive aluminum oxide fibers can be recommended as a structuring component in development of complicated multicomponent systems that are formed under the action of physical fields.

NOTATION

T , absolute temperature; σ , electrical conductivity; C , electrical capacitance; R , electrical resistance; $\tan \delta$, loss tangent; τ , relaxation time, $K = C_x/C_{\max}$.

REFERENCES

1. Yu. S. Lipatov, Physical Chemistry of Filled Polymers [in Russian], Moscow (1977).

2. G. A. Lushcheikin, *Methods for Investigation of the Electrical Properties of Polymers* [in Russian], Moscow (1988).
3. *Encyclopedia of Polymers* [in Russian], Moscow (1977), Vol. 3, p. 330.
4. F. G. Fabulyak, *Molecular Mobility of Polymers in Surface Layers* [in Russian], Kiev (1983).
5. I. N. Ermolenko, V. I. Dubkova, R. N. Sviridova, and I. I. Kolpakova, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, No. 3, 30-34 (1978).
6. I. S. Rez and Yu. M. Poplavko, *Dielectrics. Main Properties and Use in Electronics* [in Russian], Moscow (1989).
7. L. M. Sergeeva, T. G. Todosiichuk, and F. G. Fabulyak, *Physical Chemistry of Polymer Composites* [in Russian], Kiev (1974).
8. V. I. Dubkova, I. N. Ermolenko, I. P. Lyubliner, and A. I. Rat'ko, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, No. 2, 97-103 (1983).
9. E. V. Korobko, V. I. Dubkova, and M. M. Ragotner, in: *Proc. VI Nat. Conf. Mechanics and Techn. Composites*, Sofia (1991), pp. 9-12.
10. B. I. Sazhin, *Electrical Properties of Polymers* [in Russian], Leningrad (1977).
11. V. A. Gol'dade and L. S. Pinchuk, *Electret Plastics: Physics and Material Science* [in Russian], Minsk (1987).