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INVESTIGATION OF THE EFFECT OF A MICROWAVE FIELD ON THE CURING PROCESS AND PROPERTIES OF EPOXY COMPOSITIONS

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We present experimental data on the rate and degree of curing of epoxy compositions discretely reinforced with alumina fibers and filled with barium titanate powder on exposure to microwave radiation. We observed the enhancement of the process of epoxy polymer formation, revealed the dominating effect of the filler–polymer interface on the extent of the conversion of a binder and on the properties of heterogeneous compositions cured in a microwave field.

The achievements of modern science and technology have opened up wide avenues for the use of physical methods of action on polymer systems and compositions at different stages of the technological process of their synthesis and treatment [1]. Among the most promising trends in the search for the means of creating materials with prescribed and adjustable (while in use) properties is exposure to electromagnetic fields at the stage of the formation of composite materials [2]. It is known, for example, that high-frequency heating is used in the technology of treatment of thermosetting plastics for gluing different materials and increasing the quality of articles [3]. It is noted in [4] that the process of microwave irradiation of polymers has a multitude of potential advantages over traditional thermal treatment, among which are the rate of development of the full set of properties and elimination of residual stresses. In this case, the ingredient composition and relationship between the components exert a substantial effect on the interaction of electromagnetic radiation with polymer systems and compositions.

The aim of the present work is investigation of the effect of microwave electromagnetic energy on the rate, degree of conversion, and properties of epoxy compositions that contain fiber and powder fillers.

We investigated an epoxyamine composition discretely reinforced with alumina fibers obtained as described in [5]. As a powder filler we used barium titanate. Freshly prepared compositions of mass 0.5–1.5 g were placed into a microwave module with a rectangular resonator with a frequency of 2.45 GHz and an output power of 650 W. The local magnitude of incident microwave power was determined by static calorimetric measurement.

We evaluated the conversion of epoxy groups by IR spectroscopy. For an uncured binder and its compositions with fillers we applied a liquid-film method using a KBr plate. We made sure in advance concerning the indifference of the individual components of the compositions with respect to the plate itself. For cured compositions we used the immersion method, i.e., by pressing KBr-powder-containing specimens that were finely ground by a vibratory mill. The IR spectra in the region of 4000–400 cm^{-1} were recorded on an UR-20 spectrophotometer. The formation of an insoluble gel-fraction due to the origination of a three-dimensional network structure was controlled by extracting irradiated specimens of the compositions. Extraction by boiling acetone was carried out in a Sohxlet apparatus for 16–24 h. After extraction, the specimens were dried to a constant mass and weighed. The magnitude of the gel-fraction expressed in per cent was determined as the ratio of the mass of a specimen after extraction to its initial value. As a structurally sensitive method we used a thermomechanical analysis that makes it possible to determine the deformation of the three-dimensional network of a forming polymer under conditions of a specified nonisothermal relaxation process. We carried out investigations in a Höppler consistometer

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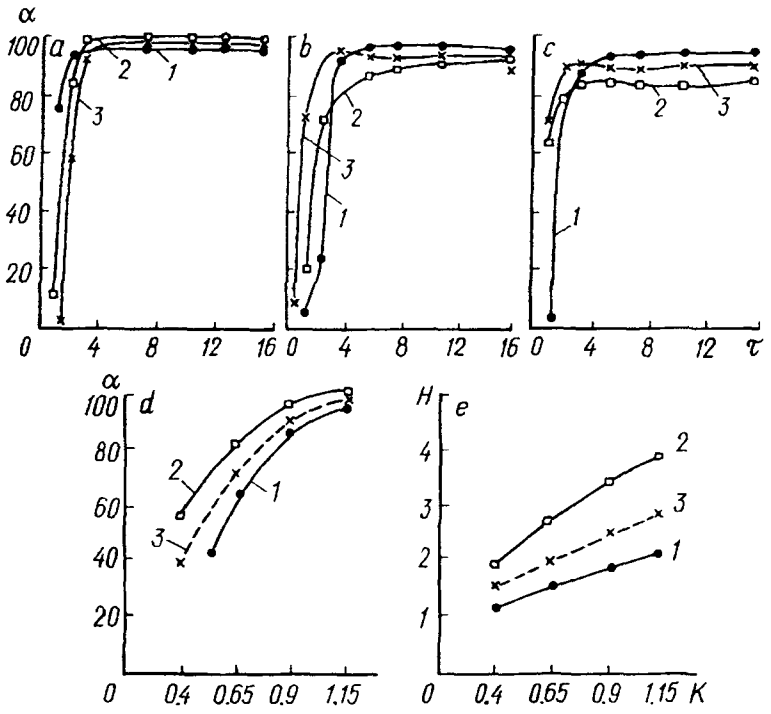

Fig. 1. Dependence of the extent of conversion α of an epoxy oligomer and hardness H of cured compositions on time of exposure of compositions to a microwave field τ and content of a hardener in an unfilled epoxy binder (1), in a binder discretely reinforced with alumina fibers (2), and in a binder filled with barium titanate powder (3) using a nonaqueous amine hardener (a, d, e), its 70% – (b) and 50% – (c) aqueous solution. K is a correction factor in the formula [7]. $K = 1$ (a, b, c); $\tau = 3$ min (d, e).

on specimens 4–5 mm in diameter and 3 mm in height exposed to a continuous constant force of 0.3 MPa. We also used the Höppler consistometer for determining the hardness of cured compositions over the depth of penetration of a hardened steel cone of special shape with an apex angle of 53° + 10′ under a load of 0.3 MPa.

We investigated the extent of conversion of an epoxy binder exposed to microwave radiation depending on the physical state of the amine used in the system (concentrated and in aqueous solutions), the mass relationships of the reacting ingredients, and the type of filler and its concentration. The results of the IR-spectroscopic analysis showed that almost immediately after the introduction of specimens into the microwave apparatus one observes intense depletion of the epoxy groups and an increase in the quantity of the hydroxyl groups, i.e., the overall intensity of the absorption at 920 cm^{-1}, which is responsible for vibrations of the epoxy cycle with a simultaneous increase in vibrations in the region of 3400–3600 cm^{-1}, decreases considerably. In this case, the intensity maximum of the absorption band at 3480 cm^{-1} shifts to the region of 3410–3420 cm^{-1}, which is typical of bound hydroxyl groups. The data obtained, which are indicative of the opening of epoxy groups with the formation of hydroxy ones, correlate with the literature data for systems cured by primary and secondary di- and polyamines. Therefore, we may assume that the scheme of the reactions of interaction of a hardener with an epoxy oligomer in specific case does not differ from the known one, and the process of curing of a binder proceeds with the formation of a heteropolymer by condensing the molecules of the epoxy oligomer with the molecules of a sewing agent [6].

An increase in the rate of conversion of epoxy groups exposed to microwave radiation is accompanied by an intense process of gel formation. Figures 1a, 1b, and 1c present kinetic curves of the curing of an unfilled epoxy binder, of a binder with introduced barium titanate, and of a binder discretely reinforced with alumina fibers. Precisely in a minute, one discovers a three-dimensional product and in three minutes the quantity of the unsolved gel-fraction attains its maximum value virtually in all of the compositions. Taking into account the fact that on curing of the investigated binder at 150 and 25°C the maximum degree of curing is attained in 30 min and 10 h,

respectively, we may state that there is a high efficiency of the effect of a microwave field on the process of the formation of a three-dimensional structure of a polymer. Here, we must note that while for an unfilled binder the degree of curing of an epoxide is independent of the physical state of the hardener used and the yield of the gel-product in a system with an aqueous or nonaqueous amine is the same and amounts to 94–96 wt.%, then in the presence of fillers the extent of conversion of the oligomer matrix is different. We also observe the manifestation of an ambiguous effect of fillers on the dynamics of the formation of the three-dimensional structure of a polymer when a concentrated amine component and its aqueous solutions are used. For compositions with an aqueous curing agent an earlier start of gel formation in filled systems is typical. At the same time the yield of the gel-fraction for them is lower than in an unfilled binder, and the decrease progresses with dilution of the amine. This manifests itself to the largest extent in compositions with alumina fibers (Figs. 1b and 1c, curves 2). On introduction of a nonaqueous amine into a binder the picture is reversed: the extent of conversion of an epoxy oligomer is higher in compositions with fillers, and in the presence of alumina fibers one observes the maximum yield of gel-product (Fig. 1a, curve 2).

A consequence of vigorously progressing exothermal reactions of the formation of a three-dimensional polymer initiated by the interaction of epoxy oligomer systems with a microwave field is intense heating of specimens that leads to the formation of inhomogeneously porous structures (in block polymerization). Investigations showed that a decrease in the quantitative relationship between reacting ingredients does not lead to suppression of the formation of pores; in this case one observes a decrease in the extent of conversion of an epoxide and the hardness of cured compositions (Figs. 1d, and 1e). The range $0.9 < K \leq 1.1$ can be considered optimal for the content of amine in a binder exposed to a microwave field. To improve heat removal it is advisable to carry out curing of compositions in thin layers.

The introduction of fillers also increases the thermal conductivity of the system. If the thermal conductivity and thermal diffusivity of an unfilled epoxy binder at 50°C are 0.34 W/(m·K) and $0.125 \cdot 10^{-6}$ m^2/sec, then on the introduction of 50 mass parts of fibrous alumina these values are 0.38 W/(m·K) and $0.25 \cdot 10^{-6}$ m^2/sec (the thermal conductivity of the materials was determined in accordance with the State Standards GOST 23630.2-79 using an IT-λ-400 device in the temperature range of 50–300°C).

In our investigations we also discovered spatial inhomogeneity in the formation of a three-dimensional product in the first minutes of irradiation of filled compositions when the content of the solid phase is lower than the critical one; for fibers and powder it was different and amounted to 50 mass parts and 100 mass parts, respectively. In the first 30 sec of heating of compositions by microwave energy, a gel-fraction, insoluble by associates, was distributed in a viscous-liquid medium. This is most pronounced with a discrete fiber filler. Already in one minute the process of the formation of a three-dimensional product was equalized and as a result the mass was converted into a monolith with a hardness exceeding that of a cured unfilled binder. This testifies to the fact that in the case of the microwave effect an important factor is the character of the distribution of components in a composition determining the dielectric indices of the mixture that influence the absorption of the emitted energy. While in the case of a small amount of filling the composition can be considered as a matrix mixture, with an increase in the content of the solid-phase component it passes into a statistical one with a disordered distribution of the polymer and filler and possible formation of a physical network by the filler itself, which is very typical for highly filled systems [7]. In such multiphase composite systems, along with relaxation dielectric losses, which are typical of an oligomer binder and polar surface groups of a solid-phase component and attributable to the polarization effect on the microwave radiation, there will also be, as noted in [8], relaxation dielectric losses caused by the polarization of an inhomogeneous dielectric (the Maxwell–Wagner polarization). Since the microwave treatment was carried out at the stage of the formation of compositions, the interphase polarization must make a substantial contribution to the processes of physicochemical conversions of the binder on the filler–polymer interface. This is confirmed by the data obtained.

Earlier we considered the problem of physicochemical interaction of fiber and powder fillers with the investigated binder expressed in the sorption of the amine component by the solid-phase filler with the subsequent formation on a fiber of a complex compound with its surface reactive groups [9]. The absorption of microwave energy by the components of the binder and its scattering in the form of heat increase the mobility of molecules

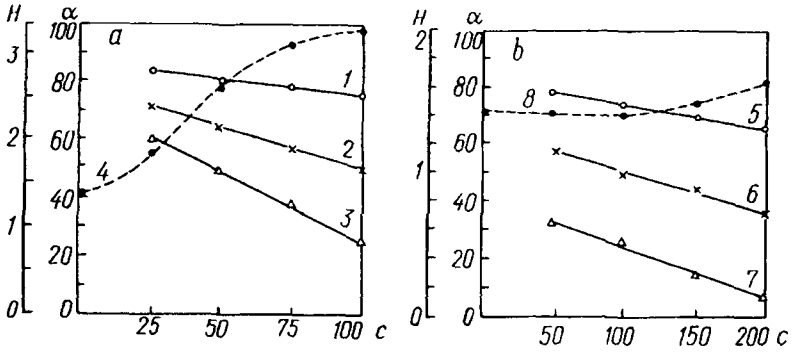

Fig. 2. Dependence of the extent of conversion α of an epoxy oligomer (1-3, 5-7) and of the hardness H (4, 8) of compositions cured in a microwave field on the content c of alumina fibers (a) and barium titanate powder (b) for a nonaqueous amine (1, 4, 5, 8), its 70% – (2, 6) and 50% – aqueous solutions (3, 7). $K = 0.75$.

and, as a result, enhance the process of migration of the low-molecular amine ingredient to the filler surface, thus favoring an increase in its sorption by its solid-phase component. This could explain the previously observed inhibition of the process of the formation of a three-dimensional product in the first minute of microwave heating of the specimens of filled compositions. Subsequently the orientational effect of the solid phase, enhanced by the effect of microwave irradiation, leads to ordering of the forming polymer structure near the interface. The amine sorbed by the surface of the fiber filler also enters into a reaction of interaction with the epoxy oligomer, ensuring a strong bond of the fiber with the polymer matrix. This is corroborated by the cured binder fraction, not extracted from the fiber surface, that reveals itself in IR spectra, with its absence on the powder filler after exposure of model systems of compositions to microwave energy under the same conditions. As a result, epoxy polymers structurized in the presence of a solid phase have a higher extent of curing compared to an unfilled binder and higher values of hardness that increase with an increase in the degree of filling of the composition and use of a nonaqueous amine as a hardener (Fig. 1a, curve 2; Fig. 2a, curve 4). The deeper structural conversions of an epoxy binder in the presence of a fiber filler is also evidenced by the IR spectra of cured compositions, which completely lack the absorption band at 920 cm^{-1}, in contrast to an unfilled binder and a binder filled with barium titanate powder, which display residual quantities of unreacted epoxy groups.

The introduction into the binder of an amine in the form of an aqueous solution with an increased ability to absorb microwave energy, enhances still more the processes of mass transfer of the low-molecular amine to the interface. Simultaneously, due to more rapid heating of the compositions the initial processes of gel formation are enhanced, and they proceed most intensely in the interphase zone, because of the formed increased concentration of the amine component in it. Therefore, already from the first minutes of heating one observes the formation of a considerable quantity of gel-product in filled compositions with an aqueous amine hardener (see Figs. 1b and 1c). However, the enhanced processes of migration of the cured component to the filler surface lead to a situation in which a portion of the filler is blocked by the solid phase, the volume of the binder is in turn depleted of the reacting component, and ultimately the degree of cure of compositions filled with fibers and powder is lower than for the initial nonfilled binder.

It is evident that while for the starting binder the determining factor in the depth of conversion of an oligomer binder exposed to microwaves is only the quantitative relationship between reacting components, irrespective of the physical state of the amine (concentrated or in an aqueous solution), then on introduction of fillers the dominating effect is exerted by the phase interface. This is evidenced by the results of studying the degree of cure of an epoxy binder depending on the concentration of discrete fibers and powder filler introduced into its composition. Figure 2 presents data on the yield of gel-fraction and on the hardness of the cured epoxide with an increasing content of solid-phase ingredients, testifying to a progressive decrease in the extent of conversion of the epoxide matrix with an increase in the quantity of the filler introduced. This reveals itself most distinctly with the use of an aqueous amine component (Figs. 2a and 2b, curves 2, 3, 6, 7). In compositions with a nonaqueous

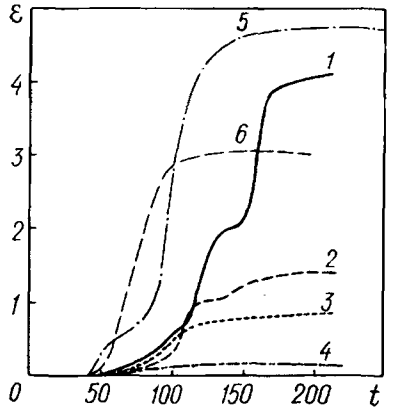

Fig. 3. Thermomechanical curves of unfilled epoxy binder $\varepsilon(t)$ (1), of a binder discretely reinforced with 50 mass parts (2), 75 mass parts (3), and 100 mass parts of alumina fibers, filled with 50 mass parts (5), and 200 mass parts (6) of barium titanate powder after treatment in a microwave field for 3 min.

TABLE 1. Adhesive Strength of Compositions Cured in a Microwave Field (in 3 h after exposure)

Composition	Ultimate strength on shear of adhesive joints, MPa	
	cardboard/cardboard	plywood/plywood
Unfilled binder	Fracture in cardboard	15.1
Discretely rainforced with Al_2O_3 fibers	Ditto	23.8
Filled with barium titanate	Ditto	14.9
Unfilled binder cured beyond the field	7.5	6.9

amine a decrease in the yield of insoluble product is expressed only by several per cents (Figs. 2a and 2b, curves 1, 5); at the same time the hardness number (Fig. 2a and 2b, cirves 4, 8) increases; this is expressed most distincty in compositions discretely reinforced with alumina fibers. The results of a thermomechanical analysis testify to the formation of more-structured systems in the presence of a solid-phase fiber filler when epoxy compositions are exposed to the effect of a microwave field. From Fig. 3 it is seen that the introduction of alumina fibers into an epoxy binder leads to a sharp decrease in the relative deformation of the compositions (curves 2-4). Consequently [10], the molecular mass of the segments between the nodes of the forming space network of the polymer is also decreased, which is responsible, as noted above, for the increase in hardness. In compositions with barium titanate that were cured in a microwave field, a decrease in the temperature of vitrification and increase in the relative deformation are observed because of a decrease in the density of packing of the polymer in the boundary layers. And only for large degrees of filling, when the filler itself forms a physical network in a polymer [11], does one observe improvement in the deformation properties of the cured composition (Fig. 3, curves 5, 6).

Structurization of a polymer in the interphase zone under the influence of heterophase components increases the limit of the strength of the compositions on 1.3–1.5-fold compression, as well as increases the adhesion of the composition to various materials (see Table 1).

Thus, the results showed that microwave radiation greatly accelerates the process of curing of epoxy oligomeric systems, and, with optimally selected compositions and regimes of treatment, it leads to an increase in the physicomechanical indices of the compositions, as well as favors the adhesion properties of glue compositions. This is expressed to the greatest extent in compositions discretely reinforced with alumina fibers.

NOTATION

α, degree of curing, %; τ, time, min; H, hardness, N/m^2; c, mass content, mass parts; t, temperature, °C; ε, compressive strain, mm.

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