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INVESTIGATION OF THE PROCESS OF HARDENING OF DIGLYCIDYL ETHER BISPHENOL A BY PHOSPHATE BINDERS

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The interaction between diglycidyl ether bisphenol A and conventional and water-deficient phosphate binders has been investigated. The data of chemical analysis, IR spectroscopy, and differential-thermal analysis point to the formation of a spatially cross-linked epoxy polymer under the influence of the phosphate binders. It has been shown that conventional binders can be used as high-temperature hardeners of epoxy oligomers. When water-deficient binders are used, the formation of a three-dimensional polymer structure is observed at room temperature.

Epoxy resins occupy a highly important place in the series of commercial polymer materials owing to the combination of adhesion, mechanical, and electrical properties, and in many cases they are indispensable as the base of carbon-fiber-reinforced plastics, mastics, impregnation compounds, and paint coatings [1, 2]. However, a substantial drawback of the materials produced is their low fire-proofness. The range of hardeners and fire-retardants used for epoxy materials is very limited, since many components are toxic or release harmful products under the action of the flame. Furthermore, the epoxy oligomers themselves are toxicologically unsafe. For this reason, problems on development of new nontoxic hardeners and composite materials with a lower-than-average content of the epoxy binder are topical.

Recent trends are toward increased use of the epoxy resins of orthophosphoric acid (enabling one to totally eliminate toxic modifiers and hardeners of the amine type from the composition of the binders) as fire-retardants and hardening agents [3, 4]. Orthophosphoric acid is most frequently used for high-temperature hardening of compositions based on medium- and high-molecular-weight epoxy binders; the hardening occurs with the participation of secondary hydroxyl groups of the epoxide [1]. The acid is more rarely used in compositions based on low-molecular-weight epoxy oligomers not containing organic solvents, which is, probably, due to the negative influence of water contained in the acid on the process of hardening of low-molecular-weight epoxy oligomers [5].

However, orthophosphoric-acid-containing materials have a number of drawbacks. Thus, when concentrated solutions of the acid are used, they are characterized by a low vitality, and in the case of introduction of diluted solutions of the acid as the cross-linking agent the mechanical characteristics are deteriorated and the atmosphere- and water-resistance of the end products becomes lower. Furthermore, according to [5, 6], only 5 to 29 wt.% of the acid is needed to produce a hardened epoxy oligomer. Water contained in the acid improves the system's vitality, acting as a low-molecular-weight plasticizer, but it also exerts a negative influence on the material. The system becomes poorly compatible and the content of the gel fraction in the hardened material decreases. This is related ([7]) to the phenomenon of termination of the chain by a nucleophilic reagent — water — and to the processes of hydrolysis of tri- and dihydroxyether phosphate groups in catalysis by the acidic components of the system (when the content of water in the hardening acid is high, the mono- and dihydroxyether phosphate bunchings are the main products of hardening) [6].

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The aim of this work is to investigate the process of hardening of diglycidyl ether bisphenol by phosphorus-containing inorganic compounds. As the latter we have used both conventional phosphate binders — aqueous solutions of orthophosphoric acid partially neutralized by metal oxides and hydroxides — with a content of water of up to 45–55 wt.% and modified water-deficient phosphate binders with a content of water of 25–30%.

Phosphate binders were produced on addition of different oxides and hydroxides of metals to orthophosphoric acid. We carried out synthesis in a reaction vessel with a return refrigerator, introducing the calculated amounts of neutralizing components in small portions until totally dissolved and evaporating the solution to the prescribed density according to the procedure of [8]. We varied the acidity of the binder from 2.5 to 4.5, the pH from 1.5 to 2.2, and the density from 1550 to 1700 kg/m^3. Based on the experiments conducted preliminarily, it was established that the highest reactivity in relation to the epoxy oligomer and the smallest tendency toward rehydration in air are exhibited by alumozinc phosphate binders (AZPhBs), which were selected as the hardening components for the investigations. Alumozinc phosphate binders were produced in successive dissolution of zinc oxide and aluminum hydroxide in a hot orthophosphoric acid. The content of the free orthophosphoric acid in the phosphate binders and the compositions were determined by acid-base titration in the presence of a bromocresol-green indicator [8]. We also investigated the possibility of using water-deficient binders produced in partial dehydration of phosphate binders at higher-than-average temperatures for hardening of the epoxy oligomer.

The relation of the oligomer and inorganic components in the composition was varied over wide limits. In so doing, we took into account the results of [6], according to which the vitality of a composite material is enhanced and the degree of hardening of epoxydian resins drops at room temperature, as the content of water in the inorganic component increases. According to one variant, the inorganic components were mixed with diglycidyl ether bisphenol A, following which the organomineral mixtures were transferred to Teflon molds and were left in air at room temperature (the relative humidity of the air was 50–70%). According to the second variant, the composite mixtures were heat-treated in a drying cabinet in the temperature interval 80–180^{o}C.

The vitality of a composition was determined according to the procedure of [2]. The intensity of transformation of the epoxy binder as part of the compositions was evaluated by the method of gel-sol analysis. The extraction was carried out for 24 h with boiling acetone in a Soxhlet apparatus. After the extraction the samples were dried to a constant mass and weighed. The size of the gel fraction was determined from the ratio of the mass of the sample after the extraction to its initial value [9].

To identify the products of hardening of the compositions we used different physicochemical methods of investigation, including infrared spectroscopy. The hardened compositions were investigated by the method of pressing of samples with KBr, finely ground on a vibrating mill. The IR spectra of freshly prepared formulas were recorded on silicon substrates. On them, we studied the kinetics of hardening of a binder at the early stages of hardening. The spectra were taken on a UR-20 spectrometer in the frequency range 650–4000 cm^{-1}. We used x-ray phase analysis to identify the initial phosphated salts of the metals.

For evaluation of the thermochemical transformations in the compositions we used the method of differential thermal analysis (DTA) in combination with thermogravimetry (DTA and TG) in the temperature interval 20–250^{o}C in air (rate 2.5–5.0 deg/min). The investigations were carried out on an OD-103 MOM derivatograph (Hungary). Chemically pure aluminum oxide precalcined at 1400^{o}C was used as the comparison standard.

We have also investigated the physicochemical and electrophysical characteristics of the hardened organomineral binders and the compositions based on them.

As has already been noted, of all the tested forms of phosphate binders, the best reactivity to the epoxy oligomer (content of the gel fraction higher than 90%) and compatibility with the organic component are exhibited by the AZPhBs; their acidity of 4.0–4.5 is optimum. Such binders also ensure the stability properties of the compositions produced based on them and their low tendency toward rehydration in air for a humidity of higher than 50% and a high content of the phosphate binder in the compositions (higher than 30%). Alumozincphosphate binders were used for production of water-deficient phosphate binders (WAZPhBs) and study of the process of hardening of an epoxy binder by them. The vitality of compositions containing aqueous solutions grows, according to [6], not only due to dilution but also due to the formation of solvate layers at the mineral–epoxy oligomer boundary.

The data of the IR spectroscopy and the chemical analysis point to the fact that one observes physicochemical interaction in heating of compositions based on diglycidyl ether bisphenol A and the conventional alumozinc phosphate

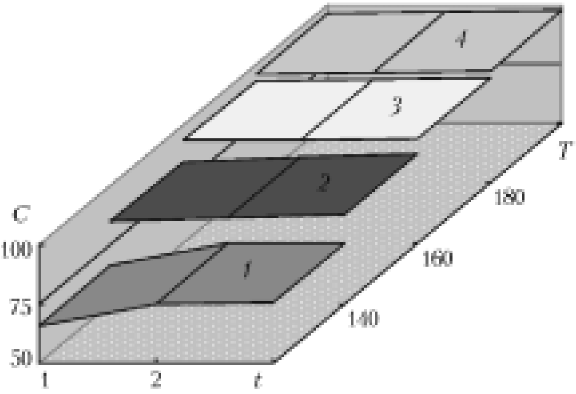

Fig. 1. Influence of the temperature and time of treatment on the yield of the gel fraction of the epoxy-phosphate binder produced with the use of an AZPhB: 1) T = 140, 2) 160, 3) 180, and 4) 200°C.

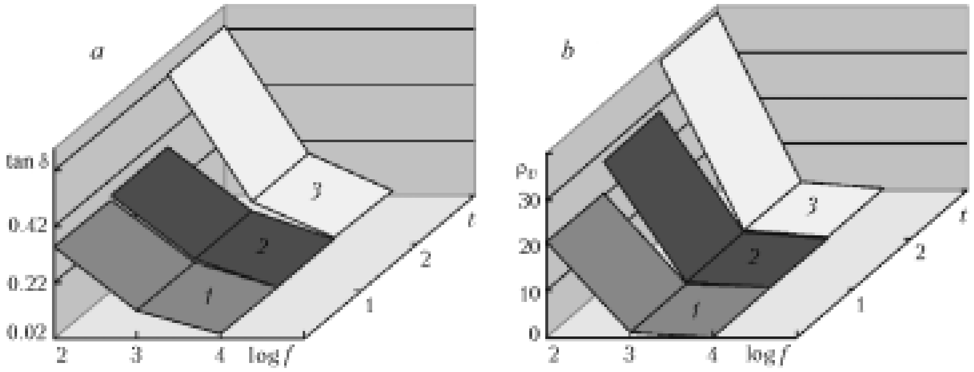

Fig. 2. Dielectric loss tangent (a) and specific bulk electrical resistance (b) vs. hardening time of the AZPhB-based epoxy-phosphate binder at a temperature of 200°C: 1) f = 100 Hz; 2) 1 kHz; 3) 10 kHz.

binder. Substantial changes occur in the composition in heat treatment — the intensity of the integral absorption bands responsible for the vibrations of the end epoxy and P–OH groups decreases. The conversion of the epoxy groups, which increases in heating, is accompanied by the intense process of gelation of the compositions. The yield of the insoluble gel fraction increases with temperature and with the duration of heat treatment of the compositions (Fig. 1). The results obtained correlate with the investigations of the kinetics of change of electrophysical characteristics in hardening of a composition and confirm the process of structurization of the system that occurs under heating (Fig. 2).

The mechanism of hardening of an epoxy oligomer by an AZPhB is fairly complicated; it represents a great number of chemical and phase transformations occurring in both the entire composition and its inorganic part, as demonstrated by the kinetic curves in Fig. 3. Interpretation of the results of the differential-thermal analysis of the compositions containing more than 30% AZPhB is also ambiguous, since the substantial endoeffects caused by its dehydration are superimposed on the exoeffect caused by the reactions of transformation of diglycidyl ether bisphenol A. We are able to record the exoeffect in the temperature interval 120–140°C only under the conditions of a low heating rate in derivatographic investigations (2.5 deg/min) upon the introduction of less than 20 wt.% of the phosphate binder into the formula of the composition (Fig. 4). The dehydration processes in heat treatment of the organomineral composition containing a conventional phosphate binder accelerate the process of hardening and contribute to the formation of a developed porous structure, which makes it possible to produce high-porosity materials on its basis.

Binders produced with partial dehydration of an AZPhB are of great interest from the viewpoint of the service properties of organomineral compositions. We have investigated the process of hardening of epoxydian oligomer upon the introduction of a WAZPhB into it. It has been established that the epoxy oligomer–dehydrated phosphate binder system is more compatible. The vitality of the composition decreases in the case of using it, whereas hardening occurs

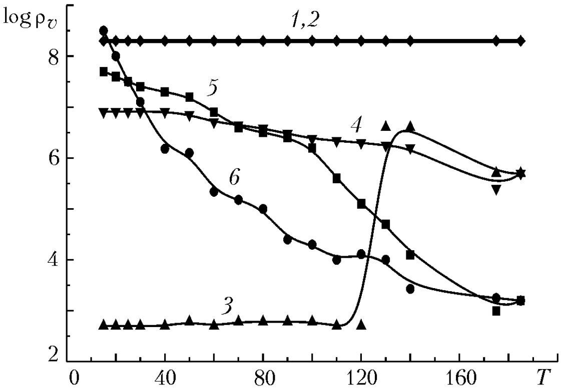

Fig. 3. Change in the logarithm of specific bulk electrical resistance in heating (1, 3, 5) and cooling (2, 4, 6) of the epoxy (1, 2) and phosphate (AZPhB) (3, 4) binders and their compositions (5, 6).

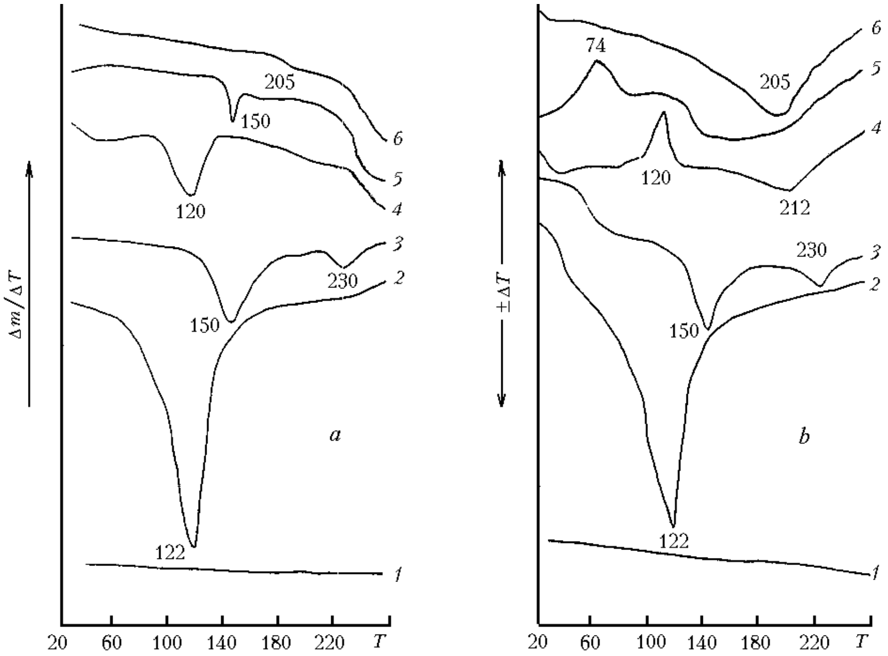

Fig. 4. Curves of DTG (a) and DTA (b) of diglycidyl ether bisphenol A (1), alumozinc phosphate binders (AZPhB) (2) and WAZPhB (3), and compositions containing 30 wt.% of these binders (4, 5) and 45 wt.% of the WAZPhB (6).

over the course of 60–90 min at room temperature, which makes it possible to perform necessary manipulations with the material before the beginning of gelation and ensures a uniform structurization of the system in hardening. The degree of hardening at room temperature attains 80–87%. In subsequent afterhardening at a temperature of 80–90^{o}C over 60 min, the content of the three-dimensional polymer in the composition increases to 95–97%. A decrease in the content of water in water-deficient inorganic binders enabled us to record the exoeffect with its maximum at a temperature of 74^{o}C (the maximum is caused by the hardening of diglycidyl ether bisphenol A) (Fig. 4).

Noteworthy are significant differences in the form of the DTA curves of the initial phosphate binder and its water-deficient analog. Thus, we observe one endoeffect on the DTA curves at 122^{o}C in the first case and two dehydration effects at 150 and 230^{o}C in the second case, which is in agreement with the data of [8] and points to a higher-than-average rehydration capacity of the dried phosphate binder. The acceleration of the process of formation of the three-dimensional network structure in the case of using a partially dehydrated binder is also demonstrated by the data of IR-spectroscopic investigations of the compositions (Fig. 5). At the same time, we cannot unambiguously interpret results of the chemical analysis of the sol part of the composition, since disproportionation processes with the

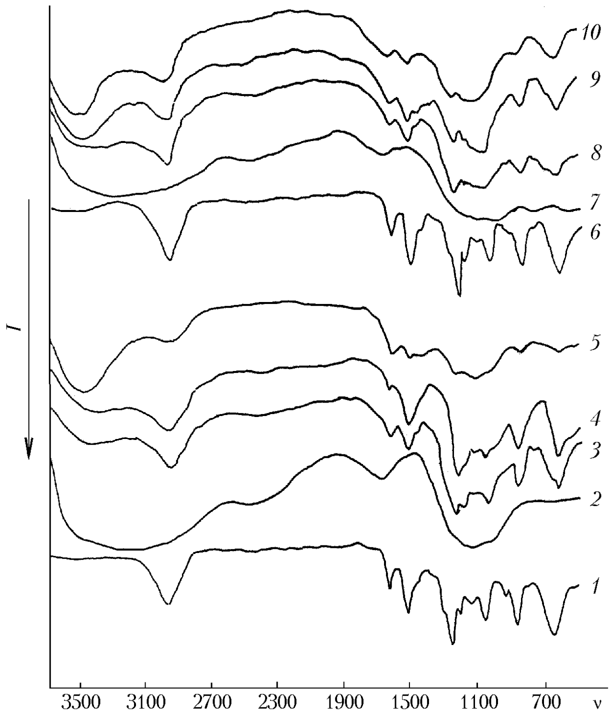

Fig. 5. IR absorption spectra of diglycidyl ether bisphenol A (1, 6), AZPhB (2), WAZPhB (7), and compositions of diglycidyl ether bisphenol A with an AZPhB (3–5) and a WAZPhB (8–10) just after the mixing (3, 8) and after being held at a temperature of 140°C for 1 h (5) and at a temperature of 20°C for 15 h (4), 24 h (9), and 336 h (10).

release of the free acid, which violate the general tendency toward change in its content in the system, are intense in the inorganic part of the binder in heat treatment of the composition.

Low-temperature hardening of diglycidyl ether bisphenol A enables one to produce composites with high indices of water resistance (97–98%) and compression strength (110–140 MPa). One can introduce up to 60% of the phosphate binder into the composition without deteriorating its service properties, which makes it possible to ensure a low combustibility of the materials produced.

As the hardening agent of epoxydian resins we have also tested acid aluminum phosphate. With allowance for the high hygroscopicity of this salt and with the aim of improving compatibility with the organic component of the binder we predried the salt at temperatures of the order of 100 and 200°C. According to the results of the x-ray phase analysis, it has been established that the salt dried at 100°C represents a well-crystallized A-modification of acid aluminum phosphate; at a higher temperature, it represents an x-ray amorphous salt intensely rehydrating in air with a humidity higher than 50%. This salt disproportionates with the formation of orthophosphoric acid and neutral aluminum phosphate in the form of berlinite and crystobalite. Condensed phosphate forms can also be formed in heat treatment.

The hardening capacity of the initial acid aluminum phosphate and of the product of its heat treatment are dissimilar. It has been revealed that the initial acid aluminum phosphate is characterized by a low hardening capacity, which is probably due to the high hygroscopicity of the salt. When a predried salt is introduced into the epoxy oligomer and the mixture is held at 20°C for 24 h, 65 wt.% of the insoluble product is formed. Further heat treatment of the compositions leads to their intense afterhardening. The yield of the gel fraction sharply increases and attains 96% even after the heat treatment of the compositions for 1 h at a temperature of 160°C. In high-temperature pretreatment of the acid aluminum phosphate, the hardening capacity of the salt somewhat decreases. The reason is probably the formation of condensed aluminum phosphates, which cannot be an efficient hardener of epoxy oligomers because of the absence of acid phosphoric-acid groups in them. In attempting to use poly- and pyrophosphates of metals as the hardening agents of epoxy-phosphate compositions and in variation of their content over wide limits, the yield of the gel fraction does not exceed 30–50% even after a long (4 to 5 hours) heat treatment at temperatures of the order of 180^{o}C.

Thus, the results of the investigations have shown the following. Whereas conventional phosphate boilers can be used as high-temperature hardeners of diglycidyl ether bisphenol A (hardening temperature $140–180^{o}$C), in the case of using water-deficient binders the compatibility of the organic and mineral components which results in the formation of a three-dimensional epoxy polymer even at room temperature ($20–25^{o}$C) is improved.

NOTATION

C, gel-fraction yield, %; T, treatment temperature, ^{o}C; t, time, h; tan δ, dielectric loss tangent; ρ_v, specific bulk electrical resistance, $\Omega \cdot m \cdot 10^6$; f, frequency, Hz; ν, wave number, cm^{-1}; I, absorption intensity; Δm, mass loss.

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