MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Influence of Surface Modification of Potassium Polytitanates on the Mechanical Properties of Polymer Composites Thereof

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Abstract—A comparative analysis of the influence of various finishing agents on the properties of epoxy compounds filled with potassium polytitanates was carried out. The addition of such micro- and nanodisperse fillers is essential for preparation of composite materials with improved mechanical properties which are largely determined by the processes occurring at the binder–filler interface. The mechanisms of interaction of the finishing agents with the binder and filler were determined. The properties of the composite materials were examined in relation to the content of the finishing agent and the filler addition procedure.

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Potassium titanates of the general chemical formula $K_2O \cdot nTiO_2$ have recently been recognized as novel functional materials whose structure and properties depend substantially on the K_2O to TiO_2 molar ratio and on the synthesis temperature [1–3]. Potassium titanates synthesized at temperatures below 500°C possess a layered structure, exhibit high intercalation capacity and catalytic activity, and have a low interlayer shear energy, which properties makes them are suitable as catalysts, ion-exchange materials, and antifriction fillers [4–6]. Potassium titanates with $n \geq 4$, obtained at 900–1100°C, have a fiber-shaped structure and can be used as microreinforcing additives for different composite materials [7–9].

Studies aimed at development of potassium titanate-based composites are mostly concerned with fibrous potassium hexa- and tetratitanates [8–11] and thermoplastic polymeric binders (polyamides, polyolefins, acryl-butadiene-styrene plastics, polyether ketones, etc.). Of great scientific and practical interest are composite materials based on thermoreactive binders whose properties are strongly influenced by network formation during the cur-

ing process. The introduction of small additives of various structure-forming components has a very significant effect on this process and thereby allows controlling the structure of the polymeric matrix. The properties of materials modified by small additives of structure-forming fillers are largely determined by the processes occurring at the interface. Hence, surface finishing of fillers [12], in particular, of potassium polytitanates [13, 14], is an effective means to improve the strength properties of the composites.

Here, we evaluated the influence of surface modification of the potassium titanate particles on their properties, interaction with epoxy diane oligomers, and strength characteristics of epoxy compounds.

EXPERIMENTAL

We used potassium polytitanates (PPTs) prepared by the crystallization route from a molten mixture of potassium hydroxide and potassium nitrate with titanium
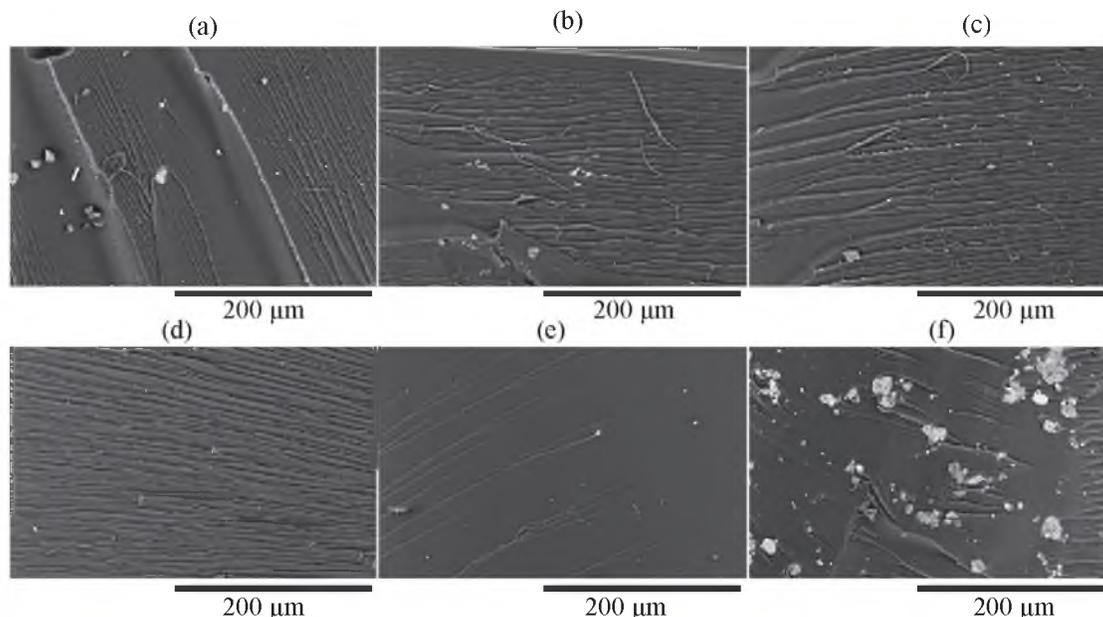
Fig. 1. Scanning electron micrographs of the cleaved surface of the cured epoxy compounds, modified by PPTs, finished with AGM-9. PPT content, %: (a–e) 0.1 and (f) 20. Grinding time, min: (a, f) 0, (b) 30, (c) 60, (d) 120, and (e) 180.

dioxide [2]. After cooling, the product was thoroughly washed with distilled water, left to stand, and centrifuged. The resulting pasty residue was treated successively with 10% aqueous sulfuric acid until the desired pH was achieved (protonation) and with aqueous solutions of the finishing agents taken in amount of 1% of the PPT content on a dry basis. The content of the finishing agent was optimized by variation within the 0–1.6% range. Prior to examinations, the resulting powdered product was dried at 200±10°C to constant weight and ground in a 62 ML-A (Russia) planetary mill at the weight ratio of the grinding bodies to the product to be ground of 8 : 1 at the rpm speed of 50.

As finishing agents served OP-10 oxyethylated alkyl phenols with the general formula $RC_6H_4O(CH_2CH_2O)_nH$, where $R = C_8-C_{10}$, $n = 7-10$; γ-aminopropyltriethoxysilane AGM-9, $H_2N(CH_2)_3Si(OC_2H_5)_3$ [TU (Technical Specifications 6-02-724–77]; γ-glycidoxypropyltrimethoxysilane A-187, $H_2C(O)CH-CH_2-O-(CH_2)_3-Si(OCH_3)$; cetyltrimethylammonium bromide (CTAB), $CH_3-(CH_2)_{15}-N(CH_3)_3^+Br^-$; synthamide $R-CONHCH_2CH_2O(CH_2CH_2O)_nH$, where R is radical containing 10–16 carbon atoms, $n = 5-6$; and sodium lauryl sulfate $C_{12}H_{25}SO_4Na$.

The wettability of the PPTs was characterized by contact angle measurements on an EasyDrop DSA 20 (Kruss, FRG) instrument. To this end, the PPT powders

were pelletized by cold pressing at 125±5 MPa. Due to their layered structure, PPTs are readily pressable at the pressure indicated into sufficiently dense pellets which absorb negligible amounts of a viscous model liquid, a 70:30 mixture of ED-20 epoxy resin with trichloroethyl phosphate (TCEP) plasticizer. Subsequently, the components were taken in this specific ratio for preparation of the compounds to be examined.

Prior to mechanical tests, the epoxy compounds were modified with 0.1 wt% PPTs. Uniform distribution of PPTs in the epoxy compound was achieved by stirring in a laminar regime of a mechanical stirrer for 30 min or in a 62 ML-A (Russia) planetary mill at the rpm speed of 50. The PPTs were added to the ED-20–plasticizer mixture preformed on the mechanical stirrer. The compounds were cured with polyethylene polyamine (PEPA) taken in the amount of 15 wt% of ED-20; prior to curing the composition was subjected to vacuum (p≈10 Pa) for 5 min. The specific surface area was determined on a Quantachrome Nova 2200 specific surface and porosity analyzer by the low-temperature nitrogen adsorption technique.

The structure and size of the PPT particles were examined with a JEOL JEM 1400 transmission electron microscope, and the particle size distribution was determined by laser diffraction analysis on a Fritsch Analysette-22 Nanotech analyzer. The structure of the composites and the distribution of the filler were examined using a Hitachi
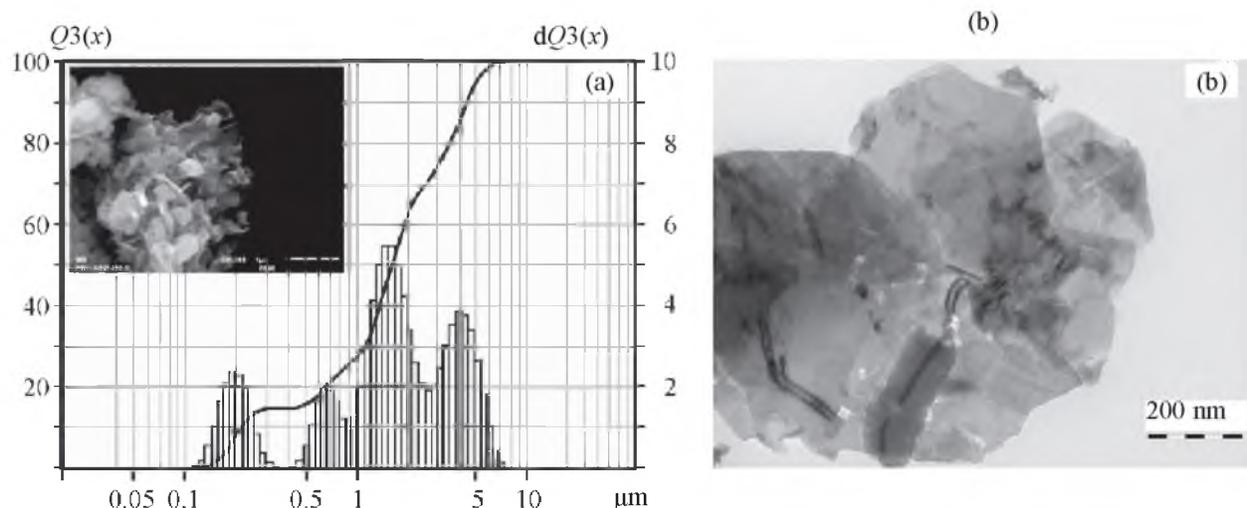
Fig. 2. (a) Particle size distribution and (b) particle structure of the basic unfinished and unprotonated PPT.

TM-1000 scanning electron microscope. The specimens were prepared by the cleavage technique from liquid nitrogen-cooled composites.

The transmission and reflection IR spectra were recorded on Specord M80 and Nicolet 380 FTIR spectrometers.

The mechanical tests were conducted in accordance with ISO 178 (flexural strength) and ISO 179 (Charpy impact strength).

The PPTs used as fillers possess a layered structure and have a multimodal particle size distribution (Fig. 1) due to the formation of agglomerates by elementary particles with the size of 0.1–0.5 μm [7]. The effect of finishing and protonation on the specific surface area and particle

size distribution of the PPTs was examined in [7]. The scanning electron microscopic (SEM) examination of the structure of the composites (Fig. 2) prepared without homogenization on the planetary mill demonstrated that the PPTs occur in the composite as relatively large agglomerates. Figure 1 shows data only for the composites modified by PPTs finished with AGM-9, because the SEM technique does not allow detecting differences among the samples modified by PPTs finished with different agents and having different degrees of protonation. Table 1 shows the interrelation between the mechanical characteristics of the epoxy compounds, indicator of the protonation state of PPTs (pH of an aqueous dispersion), specific surface area, and nature of the finishing agent. It is seen from Table 1 that the decisive influence on the

Table 1. Interrelation of the properties of the PPTs and mechanical characteristics of the composites

pH[a]	Finishing agent	S_{sp}, $m^2\,g^{-1}$	Contact angle θ, deg	Adhesion energy, $mJ\,m^{-2}$	Impact strength, $kJ\,m^{-2}$	Flexural stress at break, MPa
8–9	–	8.3	26.4 ± 0.7	83.4	8 ± 1	42 ± 2
8–9	OP	16.9	23.1 ± 0.7	84.5	7 ± 1	44 ± 2
8–9	A	18.6	23.0 ± 0.7	84.5	8 ± 1	49 ± 2
8–9	AGM	22.8	22.9 ± 0.7	84.5	10 ± 1	66 ± 2
6–7	CTAB	171.2	22.5 ± 0.7	84.7	7 ± 1	49 ± 2
6–7	Synthamide	191.3	19.5 ± 0.7	85.5	9 ± 1	48 ± 2
6–7	Lauryl sulfate	199.2	17.5 ± 0.7	86.0	7 ± 1	44 ± 2

[a] pH of an aqueous dispersion.

order of magnitude of the specific surface area of the PPTs is exerted by their protonation, which allows adjusting the pH of the aqueous extract within the 6–12 range. The largest specific surface area and the highest wetting ability (smallest contact angle) are characteristic for the PPTs protonated to pH 6–7. Addition of the finishing agents causes the surface area of the PPTs to increase 2–3 times, possibly due to exfoliation of the layered PPT structures, as described in [14, 15].

As to the wetting properties of the composites, Table 1 shows that they are very weakly influenced by the addition of the finishing agents and protonation. The mechanical characteristics of the cured compounds also vary within a relatively narrow range, even when the specific surface area changes substantially. The most significant improvement of the properties was observed for the composites modified by PPTs finished with AGM-9.

The fact that the specific surface area of the PPTs does not noticeably affect the properties of the composites may be explained by agglomeration of the PPT particles (Fig. 1). The mechanical properties do not show any clear trends with increasing/decreasing wettability of PPTs by the epoxy binder, possibly because the decisive contribution to these properties comes from the chemical

interaction in the binder–finishing agent–filler system.

Let us analyze the possible interaction between the finishing agents and the binder, taking A-187 and AGM-9 as examples. When these agents are introduced into the composite, an epoxy ring contained in A-187 can react with the amine groups of PEPA, and the amine group of AGM-9, with the epoxy ring of the resin. In the experiments performed for determination of wettability, the model liquid droplet spreads over the pellet surface within several seconds which time period may be insufficient for appreciable degrees of conversion to be achieved in the chemical interaction of the binding agent with the finishing agent. Hence, these finishing agents do not significantly affect the wetting as assessed by the sitting drop method. At the same time, they cause significant improvement of the mechanical characteristics of the composite as determined after relatively prolonged curing and stress relieving heat treatment. The chemical aspects of the processes caused by modification could not be directly tracked using IR spectroscopy because of low concentrations of the titanates and, correspondingly, even lower concentrations of the finishing agents (Fig. 3): The absorption peaks characteristic for polytitanate and finishing agents are
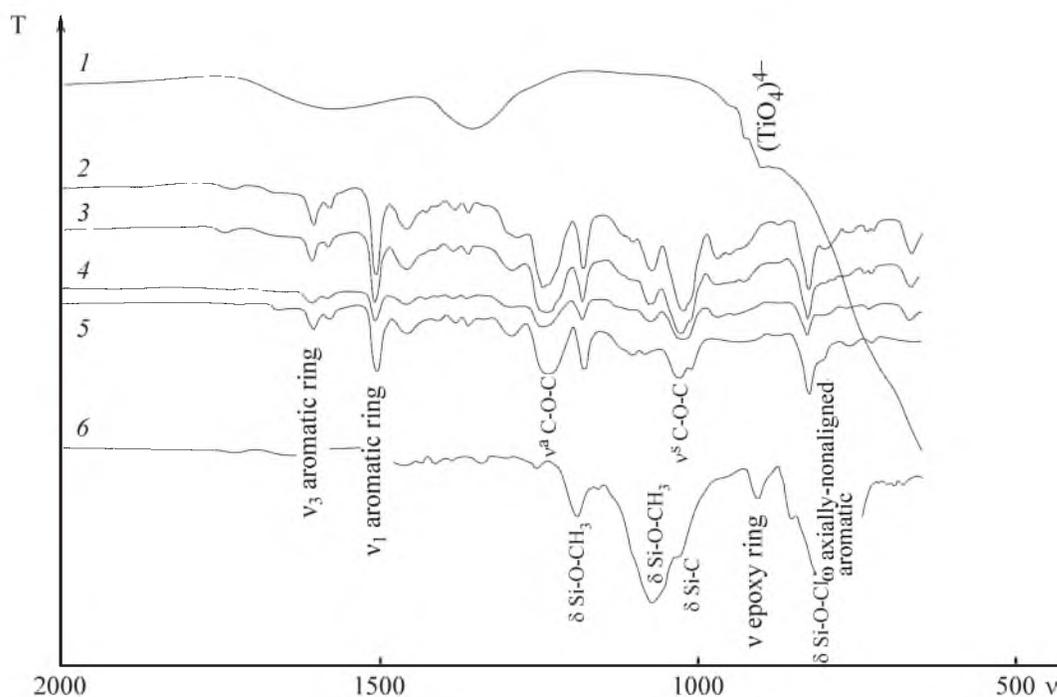
Fig. 3. IR spectra of the epoxy compounds modified by PPTs. (T) Transmission and (v) wavenumber, cm⁻¹; the same for Fig. 4. (*1*) Basic PPT, (*2–4*) epoxy compound, modified by 0.1% PPT, finished with (*2*) A-187, (*3*) OP-10, (*4*) AGM-9, (*5*) epoxy compound + 10% A-187, and (*6*) A-187.

Scheme 1.

$$R—NH_2 + CH_2 \overset{\diagdown}{\underset{O}{}} CH—CH_2—\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{Si}}—OCH_3 \longrightarrow R—NH—CH_2—\overset{}{CH}—CH_2—\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{Si}}—OCH_3$$

PEPA

OH

Scheme 2.

$$R—\overset{\diagup O \diagdown}{CH—CH_2} + H_2N—(CH_2)_3—\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}—OC_2H_5 \longrightarrow R—\overset{\overset{OH}{|}}{CH}—CH_2—HN—(CH_2)_3—\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}—OC_2H_5$$

Epoxy

not observed in the IR spectra of the composites (Fig. 3, spectra 2–4). In this situation, the potential possibility of these processes was confirmed via IR-spectroscopic examination of individual mixtures of the finishing agents and components of the epoxy compounds (Fig. 3).

The spectrum of A-187 contains an absorption band at 902 cm^{-1}, characteristic for the stretching vibrations of the epoxy ring; this band is lacking in the spectra of the cured compound finished with 10% A-187 (Fig. 3, spectrum 5). Hence, the main reaction of curing of the epoxy oligomer in the system is presumably paralleled

by the following reaction in Scheme 1.

In an AGM-9–ED-20 mixture, a slow reaction between the amine group of AGM-9 and the epoxy ring of the resin may proceed by the reaction on Scheme 2.

To achieve better resolution, the IR transmission spectroscopy technique was applied for examination of the interaction between of AGM-9 and ED-20 (Fig. 4). One day after mixing of AGM-9 with ED-20 at room temperature, no changes were observed in the absorption band intensity of the epoxy ring. After 7 days, the intensity of the absorption peak corresponding to the

Fig. 4. IR spectra of the epoxy compounds modified by AGM-9. (*1*) Neat AGM-9, (*2*) uncured ED-20, and (*3*) an AGM-9–ED-20 mixture kept for prolonged period.

epoxy ring decreased by 33% on the average (based on the data calculated for the intensity ratio of the peak associated with the stretching vibrations of the epoxy ring at 920 cm^{-1} to the most characteristic peaks of the epoxy resin: stretching vibrations of the aromatic ring at 1508 cm^{-1}, C–O–C symmetric stretching vibrations at 1032 cm^{-1}, and wagging axially-nonaligned vibrations of the aromatic ring at 840 cm^{-1}. Also, the spectrum contains a characteristic peak of the stretching vibrations of the hydroxy groups at 3470 cm^{-1}. These changes confirm the interaction of the amine groups of AGM-9 with the epoxy groups of ED-20.

The interaction of the siloxane-containing finishing agents with potassium titanates proceeds through the

$$H_2N-(CH_2)_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}-OC_2H_5 \ + \ H_2O \ \longrightarrow \ H_2N-(CH_2)_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}-OH \ + \ C_2H_5OH$$

$$H_2N-(CH_2)_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}-OH \ + \ HO-PPT \ \longrightarrow \ H_2N-(CH_2)_3-\underset{\underset{OC_2H_5}{|}}{\overset{\overset{OC_2H_5}{|}}{Si}}-O-PPT \ + \ H_2O$$
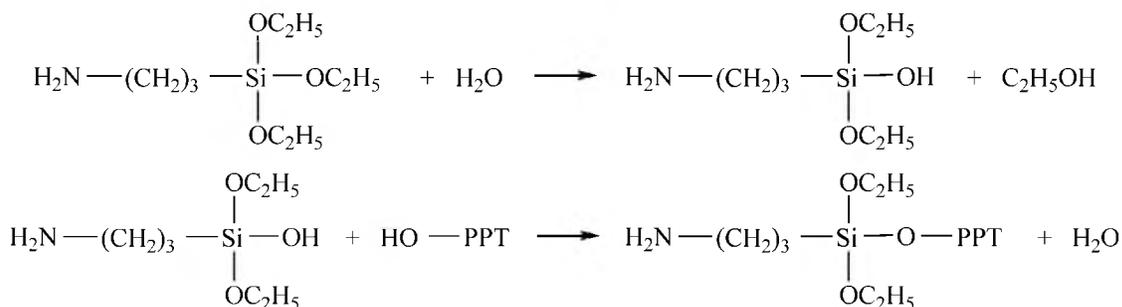
following mechanism [16]:

The finishing agent OP-10 does not contain groups able of actively reacting with the epoxy compound, which results in its worse properties compared to A-187 and AGM-9.

To destroy the PPT agglomerates and enhance the uniformity of PPT distribution in the epoxy binder, we prepared and examined compositions modified by PPTs, which were finished with AGM-9 by mixed grinding with the epoxy oligomer in the planetary mill (Table 2). An electron-microscopic examination of the cured compositions homogenized in the planetary mill showed that the particle size strongly decreased and that there was a negligible amount of large agglomerates (Fig. 1). It should be noted that the size and uniformity of distri-

bution of the particles vary appreciably with increasing time of grinding in the planetary mill. As to particle distribution and agglomerate destruction, the best characteristics were exhibited by the compositions ground for >120 min. Increase in the grinding time to 180 min causes an increase in brittleness of the composite (decrease in impact strength to 21 kJ m^{-2}), while the increase in flexural strength is within the experimental inaccuracy. Our experiments showed that the properties of the composite are substantially affected by the amount of the finishing agent deposited. Taking OP-10 and AGM-9 as examples, we examined how the mechanical properties of the compounds vary with increasing content of finishing agents (Fig. 5). It is seen that the dependences of the properties of the composites on the content of the finishing

Table 2. Mechanical characteristics of the composites prepared by mixed grinding of the PPT, finished by AGM-9, with an epoxy binder

Mixed grinding time, min	Impact strength, kJ m^{-2}	Flexural stress at break,[a] MPa
30	17 ± 1	73 ± 2
60	19 ± 1	47 ± 2
90	20 ± 1	50 ± 2
120	25 ± 1	55 ± 2
180	21 ± 1	57 ± 2

[a] The samples were not destroyed; deflection of 1.5 times the initial thickness of the sample.
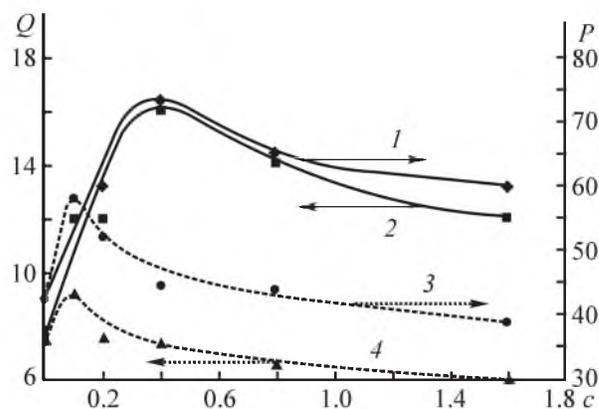
Fig. 5. Mechanical characteristics of the epoxy compounds vs. (1, 2) OP-10 and (3, 4) AGM-9 content c, %. (1, 3) Impact strength Q, kJ m^{-2}, and (2, 4) flexural stress at break P, MPa.

agents of different nature are described by similar curves with maxima. However, these maxima are observed at different concentrations, evidently due to the differences in the areas occupied by these finishing agents on the PPT particle surface, in the effects they exert on the processes of exfoliation of PPTs, and in the mechanisms of their interaction with the binder.

CONCLUSIONS

(1) The specific surface area and wettability of potassium polytitanates by epoxy model liquid were examined in relation to the nature of the finishing agents and the degree of protonation.

(2) The influence of the nature of the potassium polytitanate surface and the type of finishing agent on the properties of epoxy compounds was evaluated. It was shown that the effectiveness of the finishing additive depends essentially on the nature of its interaction with the polymeric binder. The finishing agents A-187 and AGM-9 enter into chemical interaction with the components of the epoxy compounds, leading to substantially improved strength properties of the compounds.

(3) With AGM-9 and OP-10 as examples, the properties of the composite material were examined in relation to the amount of the finishing agent, whose concentration range was accordingly optimized. Small additives of potassium polytitanates finished with AGM-9 and A-187 provide significant improvement to the mechanical properties of the epoxy compounds.

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