MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Filled Latex Composites with High Dielectric Constant,
Based on Dispersed Ferroelectrics

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Abstract—The possibility of controlling the physicochemical properties of suspensions and the electrical properties of filled latex composites containing dispersed ferroelectrics was examined. The use of ferroelectrics as fillers allows preparation of polymeric composites with high dielectric constant \( \varepsilon \) and low dielectric loss, used, e.g., for the development of dielectric functional layers of electroluminescence light sources.

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Polymer electronics undergoes vigorous development today. The functional materials used in this field are organic compounds and composites based on them. This allows preparation of flexible items, use of cheap processes for printing active and passive components, and reduction of the production cost. A topical problem in this connection is the development of functional composites based on latexes, aqueous polymer dispersions, with the aim to abandon the use of expensive and environmentally harmful solvents. However, despite apparent advantages of latex technology, its wider use is restricted by problems with obtaining stable latex–dispersed filler suspensions with the required rheological properties and satisfactory aggregative and sedimentation stability.

In this study we examined the possibility of controlling the physicochemical and electrical properties of filled latex composites (FLCs) containing dispersed ferroelectrics. The use of ferroelectrics as fillers allows preparation of polymeric composite materials with high dielectric permittivity \( \varepsilon \) and low dielectric loss. Such materials are used, in particular, for preparing dielectric functional layers of electroluminescence light sources (ELLSs) [1].

EXPERIMENTAL

As investigation objects we chose latexes with high dielectric constant \( \varepsilon \): BMNK \( \varepsilon = 13 \), TU (Technical Specification) 38.103670–88 and DMMA \( \varepsilon = 11 \), GOST (State Standard) 13522–78] acrylate latexes and BN butadiene–nitrite latex \( \varepsilon = 17 \), TU 38.103562–84). As fillers we used BaTiO\textsubscript{3} (TU 6-09-3963–75, \( \varepsilon = 1500 \)) and VS-1 ceramic based on doped barium titanate (GOST 20419–83, \( \varepsilon = 1500 \)). The dispersity of the fillers was determined by turbidimetry [2, 3]. Rheological studies of suspensions were performed with a Rheotest 2 rotary viscometer. The filled latex composites were prepared by casting of films onto preliminarily degreased aluminum supports. After drying, the second aluminum electrode was rubbed in. The dielectric characteristics of the FLCs were studied in accordance with GOST 6433.4–71 using an E 8-4 digital bridge (measurement frequency 1 kHz).

To prevent destabilization and coagulation of latexes, the dispersed substances prior to introduction into the latex were converted to a pasty form by dispersing them in an aqueous solution of a surfactant (OADF-3А, oxyethylidenediphosphonic acid salt, sample from SintezPAV Research and Production Association) in a ball mill.
The surface properties of BaTiO₃ and VS ceramic based on it were studied using the procedure described in [4].

As seen from Fig. 1, the following main sites are present on the surface of dispersed BaTiO₃: Lewis base sites (pKₐ = -4.4) formed by two-electron orbitals of oxygen atoms on the surface (probably Ba–O: groups capable to interact with free orbitals of the adsorbed molecule by the coordination mechanism); Brønsted acid sites (pKₐ = 2.0, 2.5), ≡Ti–OH groups; Brønsted base sites (pKₐ = 10.5), surface –Ba–OH groups. The initial surface of VS-1 ferroelectric ceramic (Fig. 1) contains smaller amount of active sites (especially of acid sites) compared to BaTiO₃, which is due to the effect exerted by doping additives (Zr, Nb, Ca) incorporated in VS-1 ferroelectric ceramic on the composition of functional groups on its surface. The absence of the center with pKₐ = -4.4 on the VS-1 surface can be accounted for by its blocking as a result of interaction of the lone electron pair of the O atom with the free 4d orbitals of the Zr or Nb atom:

≡Ti–O: → Zr⁴⁺(Nb⁵⁺).

The egress of a part of doping admixtures to the surface of VS-1 ferroelectric ceramic decreases the content of titanol groups, which leads to a decrease in the concentration of Brønsted acid sites (pKₐ = 2.0, 2.5). The appearance of neutral Brønsted sites (pKₐ = 7.3) on the surface of VS-1 ferroelectric ceramic can be attributed to the formation of Zr–OH or Nb–OH groups.

As follows from Fig. 1, the most active sites of the BaTiO₃ surface are electron-donor sites with pKₐ = -4.4, 2.5, and in the case of VS-1 ferroelectric ceramic, the sites with pKₐ 2.5. Hence, for the adsorption modification it is necessary to use dispersing agents containing electron-acceptor functional groups (e.g., –OH) capable to interact with electron-donor surface groups of the fillers and thus to decrease the activity of the surface. Therefore, we chose OADF-3A agent [5]. Its optimal concentration was chosen using as criterion the dispersing performance, i.e., preparation of highly concentrated suspensions at minimal content of the dispersing agent. The quantitative measure of the performance was the moisture capacity of the filler in the presence of the dispersing agent.

The subsequent dispersion in a ball mill ensured efficient decrease in the ceramic particle size (Fig. 2). At the same time, rheological studies showed that the dependence of the effective viscosity on the dispersion time was different for the suspensions based on BaTiO₃ and VS-1 (Fig. 3). As seen from Fig. 3, in the first case we observed a monotonic decrease in the effective viscosity, and in the second case, its increase.

As shown in [6], the adsorption site distribution data reflecting the composition of functional groups on the surface of the dispersed material can be used for analysis of phase interactions. Comparison of Figs. 3 and 4 shows that there is a qualitative correlation between variations of the viscosity and of the acidity function of the ceramic surface Hₒ. Because the acidity function expresses a certain weighted-average value of pKₐ for the given surface, its increase (or decrease) for the materials in hand, with the acid sites prevalent on their surface, reflects a relative increase (or decrease) in the amount of Brønsted base sites. Presumably, an increase in the amount of Brønsted base sites on the particle surface, in turn, will enhance interaction with acid sites on the surface of adjacent