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Influence of thermal treatment of nanometer-sized titanate and barium orthotitanate precursors on the electrorheological effect

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The results for the sol-gel synthesis of acylate gels are reported in the titanium tetra-n-butoxide – barium hydroxide – acetic acid system at a molar ratio of Ba:Ti components of 1:1 and 2:1. The thermal decomposition of these gels over temperatures ranging from 85 –1200 °C was investigated using thermal analysis methods, XRD, FTIR spectroscopy, electron microscopy, and dielectrometry at frequencies from 25 – 106 Hz. The electrorheological effect in suspensions of powders synthesized at different temperatures with a stoichiometric Ba:Ti ratio = 1:1 and 2:1, in polydimethylsiloxane was studied. The influence of thermal gel treatment was analyzed on their dielectric properties as fillers of electrorheological fluids and on the magnitude of the electrorheological effect.

Keywords: sol-gel synthesis, barium titanate, electrorheological fluids, dielectric liquids, nanometer-sized, thermal treatment.

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1. Introduction

Electrorheological (ER) fluids are suspensions of polarizable semiconductor particles in dielectric liquids. The viscoplastic properties of ER fluids depend on the strength of the applied electric field up to the total loss of fluidity [1, 2]. The loss of fluidity of the ER fluid in an electric field occurs due to polarization interactions, leading to structuring of the dispersed phase. The formation of chain or pillar structures from separate particles and closing of the interelectrode gap occurs within milliseconds. The presence of a limiting value of the electric field strength is typical for the electrorheological effect, after which the structure formation takes place and the fluid enhances its viscoplastic properties.

The magnitude of the ER effect is significantly affected by such factors as polarization, dielectric constant, conductivity, the applied electric field strength, the size, shape and structure of particles [3–9]. Another important factor affecting the properties of ER fluids is the water content in the dispersed phase [10]. Obviously, the aggregate functional properties of an ER fluid are determined by the composition and nature of the components.

The barium titanyl acylates complexes are considered promising among other fillers of ER fluids [11–14]. The yield strength of an ER fluid based on barium titanyl oxalate, with the surface of nanoparticles covered by adsorption layer of urea molecules, can exceed 100 kPa in a 4 kV/mm field [15–17]. At the same time, the yield strength of barium titanate suspension obtained by calcination of acylate complexes in an electric field of 4 kV/mm does not exceed 1 kPa [18]. Thus, the ER efficiency of the acylate complexes is significantly reduced during calcination. Apparently, this occurs as a result of polar organic group elimination from the material, leading to a decrease in the polarizability of the filler particles.

This work aims to reveal the influence of thermal treatment of acylate gels – the precursors of barium titanate and orthotitanate, used as ER fluid fillers, on the magnitude of the ER effect.

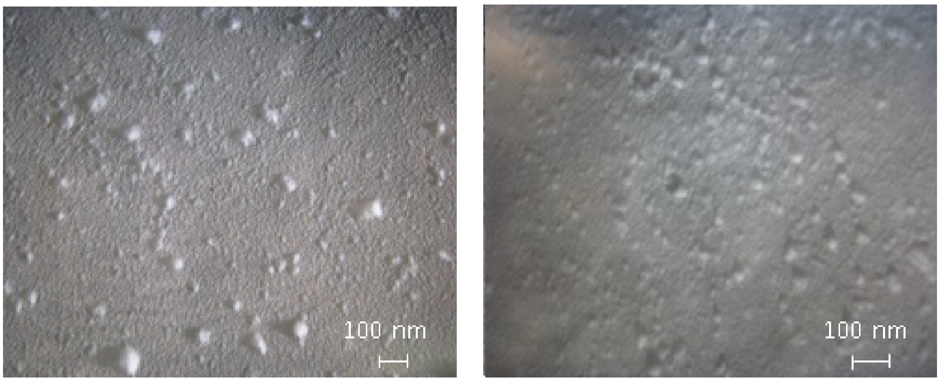
2. Experimental section

Barium hydroxide $Ba(OH)_2 \cdot 8H_2O$, glacial acetic acid CH_3COOH and 99 % pure titanium tetra-n-butoxide $Ti[O(CH_2)_3CH_3]_4$ were used as starting materials. All reagents were purchased from SIGMA-Aldrich.

The following sol-gel synthesis of nanometer-sized barium titanyl acylate powders at stoichiometric Ba:Ti ratios of 1:1 and 2:1 was applied: 10 g of barium hydroxide octahydrate was dissolved in 17.31 g of glacial acetic acid at constant stirring until a clear solution was obtained, followed by dropwise addition of 10.8 g (or 5.4 g) of titanium tetra-n-butoxide via a syringe. The contents of the reaction flask were stirred for an hour, then the temperature of the solution was raised to 85 °C. After a short period of time, the solution changed into a transparent, durable gel. Drying the gel in air at 85 °C to a constant weight afforded white powders. According to elemental analysis, the content of organic phase in samples of dry gel powders with stoichiometric Ba:Ti ratios = 1:1 and 2:1 amounted to some 35 and 17 % (with an accuracy of 1 %). The resulting powders were calcined for an hour in air at temperatures of 200, 400, 600, 800 and 1200 °C and used for subsequent analysis and for the preparation of ER fluids.

3. Thermal evolution characterization of the obtained materials

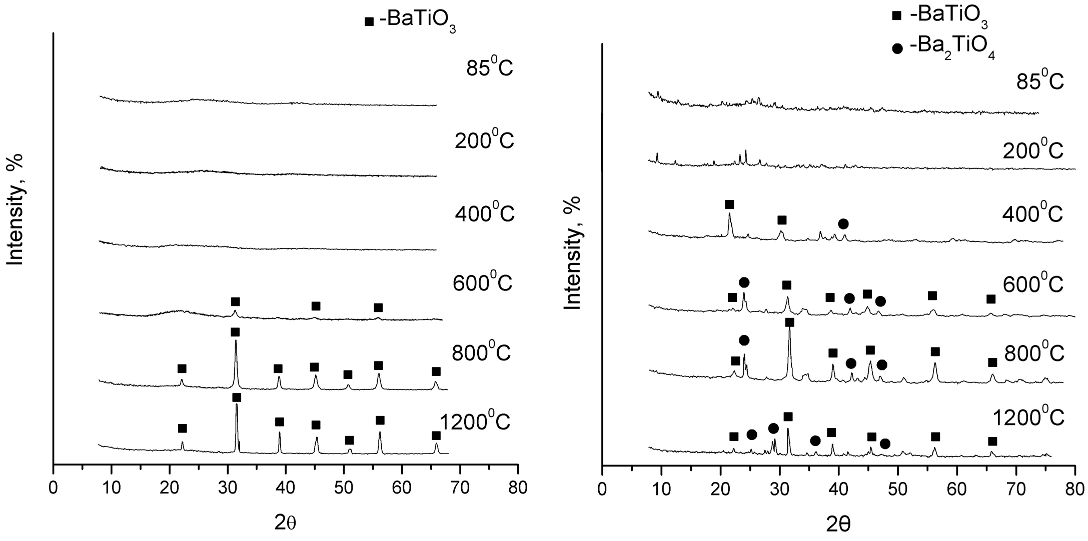
Transmission electron microscopy (electron microscope 2MB-100L) was used to study the shape and particle size of the powders obtained. According to electron microscopy, when the Ba:Ti molar ratio in the synthesis is 1:1, the 50 – 200 nm polydisperse particles are formed, while an initial 2:1 Ba:Ti ratio affords 50 – 80 nm polydisperse particles (Fig. 1). From the electron microscopic images it can be seen that the particles have a rounded shape.



(a) (b)

FIG. 1. TEM images of dried at 85 °C acylate gels obtained at Ba:Ti 1:1 (a) and 2:1 (b) molar ratios

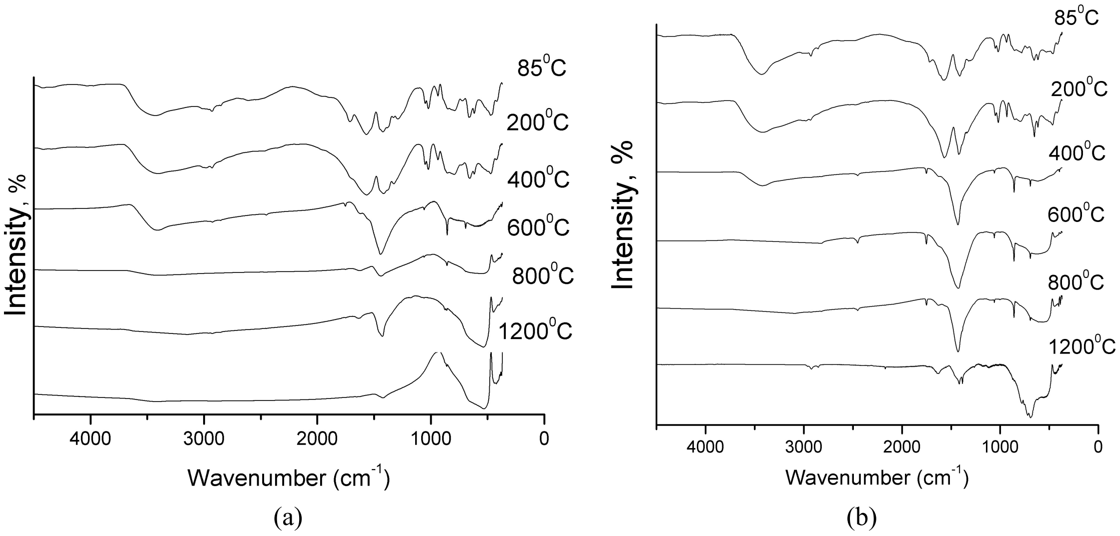
The analysis of phase composition was performed on a DRON-2 diffractometer using Cu-Kα radiation. According to the results of X-ray diffraction, when the initial stoichiometric Ba:Ti ratio is 1:1 (Fig. 2(a)), the formation of barium titanate starts at 600 °C and terminates at 800 °C. When the initial Ba:Ti molar ratio of components is 2:1 (Fig. 2(b)), the reflexes corresponding to barium titanate and barium orthotitanate are observed at 400 °C. With an increase of temperature to 1200 °C, the reflexes of $BaTiO_3$ and Ba_2TiO_4 are observed.



(a) (b)

FIG. 2. X-ray phase analysis of barium-titanium acylate complexes obtained at Ba:Ti 1:1 (a) and 2:1 (b) molar ratios and their calcination products at various temperatures

The IR spectra of the synthesized compounds were recorded in a potassium bromide matrix on a VERTEX 80v FT-IR spectrometer. IR spectra of synthesized ultradispersed materials (Fig. 3) contain absorption bands characteristic for barium acetate, titanium dioxide and its hydroxy-forms, butoxy groups, as well as titanium butoxide and water molecules: Ba–OH 1459, 1420 and 1379 cm^{-1}; titanium butoxide 1458, 1429, 1371 and 1362 cm^{-1}. The band at 1125 cm^{-1} can be attributed to the vibrations of the Ti–O–C bond, the band at 948 cm^{-1} – to Ti–OH vibrations, and the band at 3390 cm^{-1} may correspond to the stretching of OH groups. The CO_3^{2-} ion has a characteristic absorption maximum at 1540 cm^{-1}, and the band at 1461 cm^{-1} characterizes asymmetric oscillations in the stretching of the C–O bond. For the acetate ion, depending on the type of coordination, absorption maxima for symmetric (νS) and antisymmetric (νA) C–O vibrations are observed at different positions [19] for monodentate ($\nu S = 1295$ cm^{-1}, $\nu A = 1720$ cm^{-1}), bridged bidentate ($\nu S = 1430$ cm^{-1}, $\nu A = 1590$ cm^{-1}) and chelate bidentate complexes ($\nu S = 1470$ cm^{-1}, $\nu A = 1550$ cm^{-1}). An intense absorption band at 650 cm^{-1} characterizes the vibrations of the Ti–O–Ti bond. The Ba–O oscillations correspond to the band at 474 cm^{-1}. As the samples are thermally processed, the IR spectra begin to correspond to the spectra of the corresponding titanates.



(a) (b)

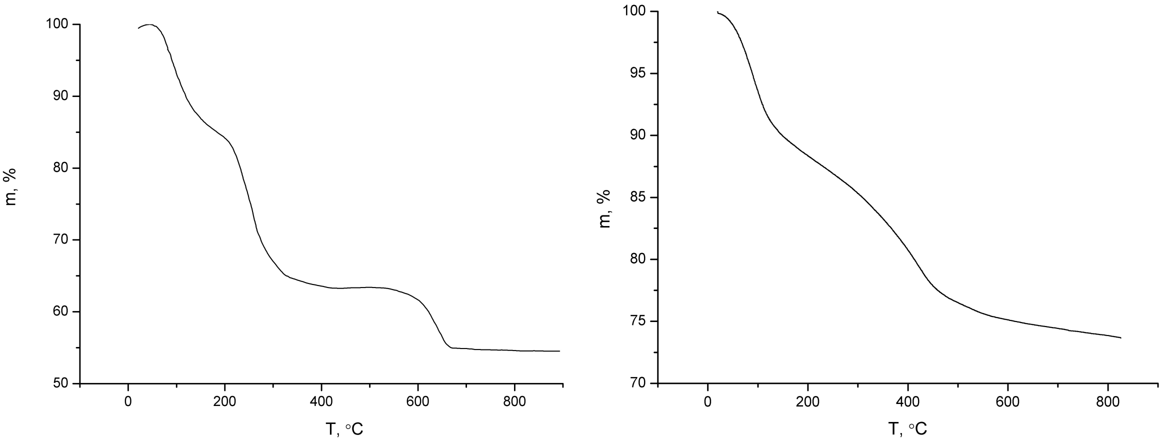
FIG. 3. IR spectra of acylate complexes powders with Ba:Ti 1:1 (a) and 2:1 (b) molar ratios and their calcination products at different temperature

The thermal analysis of the synthesized powders was performed on a 1000D Paulik–Paulik–Erdei derivatograph at a heating rate of 5 °C/min. One can distinguish three ranges associated with a change in the mass of the sample on the thermograms of synthesized materials (Fig. 4). The first range (50 – 150 °C) might be associated with the removal of acetic acid and the adsorbed water. The second range (150 – 450 °C) corresponds to the decomposition of titanium butoxide complexes with acetate ions to titanium dioxide. At temperatures of 500 – 750 °C the thermal decomposition of barium carbonate, which is present as an impurity in the material, is likely to occur with the formation of barium titanate. The total weight loss for each of the samples does not exceed 45 %.

The analysis of materials calcined at 1200 °C with differential scanning calorimetry (DSC) was performed on a DSC 204 F1 Phoenix calorimeter with the μ-sensor. The maxima on the heat capacity-temperature curves, which indicate a phase transition, are observed at temperatures ranging from 0 – 200 °C for both materials with 1:1 and 2:1 Ba:Ti molar ratio. For the system with a stoichiometric 1:1 Ba:Ti molar ratio, the phase transition temperature is 119 °C and for the system with a 2:1 Ba:Ti ratio, the phase transition temperature is 122 °C (Fig. 5).

The dielectric spectra of 30 % suspensions of the resulting powders in silicone oil PMS-20 were measured in a cylindrical cell of the condenser type at $T = 293$ K using an E7-20 immittance meter in the frequency range from 25 to 1×106 Hz. Fig. 6 shows the dependences of ε and $\tan\delta$ on the frequency of the electric current.

The $\tan\delta$ frequency dependences of suspensions indicate the relaxation character of the dielectric spectra. As it follows from Fig. 6(a), a suspension of the initial powder is characterized by the presence of a relaxation maximum, which disappears after calcination. As is evident from the Fig. 6(b), the position of relaxation maximum for the suspension of the initial powder with the 2:1 Ba:Ti ratio is at lower frequency in comparison to the powder with the 1:1 Ba:Ti ratio. In that regard, the relaxation shape of the dielectric spectrum persists for suspensions with filler particles calcined at 200 and 400 °C. An increase in the temperature of heat treatment of fillers with



(a) (b)

FIG. 4. Thermal analysis of acylate complexes powders with Ba:Ti 1:1 (a) and 2:1 (b) molar ratios

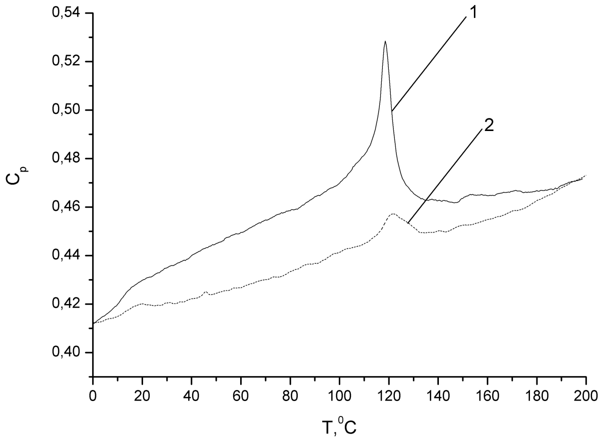


FIG. 5. DSC of materials obtained by calcination at 1200 °C with Ba:Ti 1:1 (1) and 2:1 (2) molar ratios

BaO:TiO$_2$ ratios of 1:1 and 2:1 results in a similar shape of ε and $\tan\delta$ frequency dependences for these systems and an absence of relaxation maxima in them.

4. Results and discussion

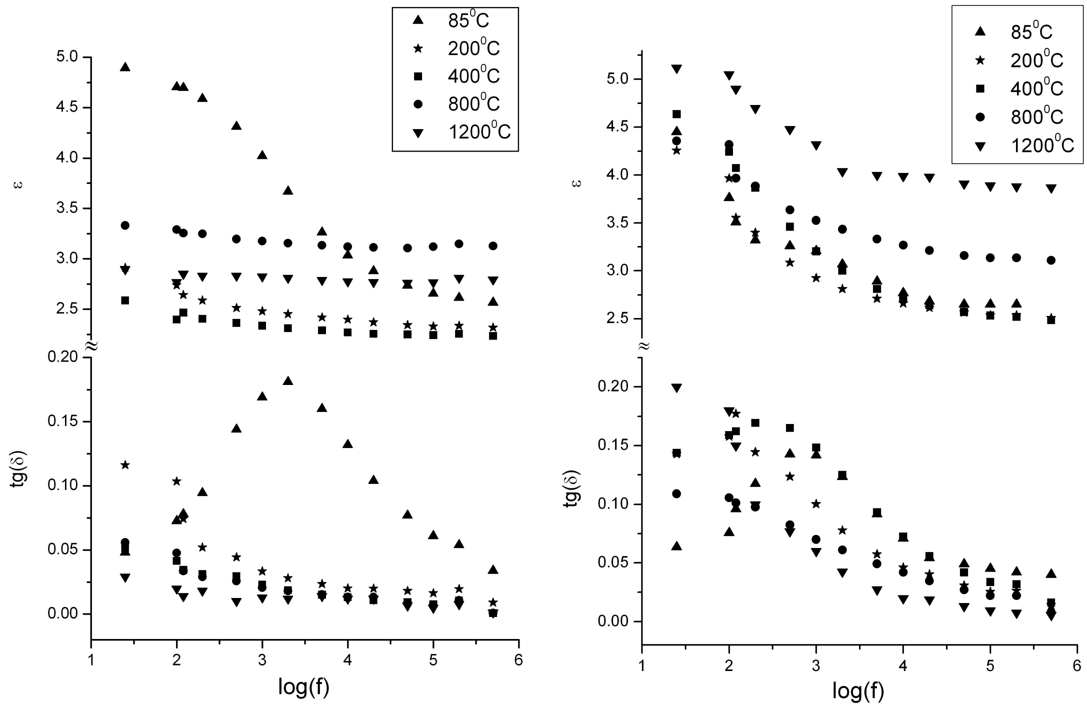
The obtained complex of data characterizing the phase composition of the obtained materials at different temperatures allows us to make assumptions about the patterns of structure formation during its thermal treatment.

The interaction of titanium tetra-n-butoxide with glacial acetic acid results in the gelation due to the formation of polynuclear complexes in which bidentate acetate ions act as ligands (Fig.7) [20]. When barium hydroxide is dissolved in glacial acetic acid, barium acetate forms, which, apparently, can be incorporated into the structure of the titanium acylate complex [21] or form clathrate complexes [22].

The thermal treatment of the obtained powders with a different ratio of reagents in the mixture leads to their decomposition. Thermal decomposition of the acylate polynuclear complex of titanium tetra-n-butoxide in an oxidizing atmosphere is accompanied by the removal of volatile organic components, oxidation of acetate and butoxide groups. In parallel, the decomposition of barium acetate occurs, which is accompanied by successive transformations [21]:

$$\mathrm{Ba(OOCCH_3)_2} \rightarrow \mathrm{BaCO_3} + \mathrm{CO} \rightarrow \mathrm{BaO} + \mathrm{CO_2}.$$

In general, thermal transformations of materials obtained from precursors with the 1:1 and 2:1 Ba:Ti ratios involve the same processes, however, product formation proceeds according to different schemes. To a considerable degree, this is determined by both the reactivity of barium orthotitanate and by the various molar ratios of water and titanium butoxide in the synthesis of Ba$_2$TiO$_4$ and BaTiO$_3$. As follows from Figs. 2(a), 3(a) and 4(1), in a



(a) (b)

FIG. 6. Dielectric parameters of 30 % suspensions of samples with Ba:Ti 1:1 (a) and 2:1 (b) stoichiometric ratio in silicone oil at 25 °C

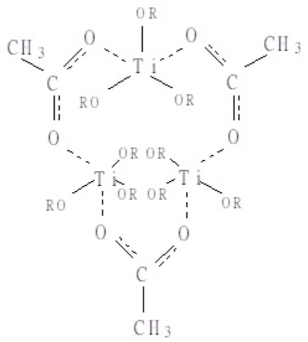


FIG. 7. Polynuclear acylate complex of titanium tetrabutoxide ([20])

system containing Ba and Ti in a ratio of 1:1 at 200 and 400 °C, the formation of X-ray amorphous products containing organic residues occurs as well as hydroxy compounds of these metals. At that the formation of $BaTiO_3$ phase begins at 600 °C. This process is accompanied by the decomposition of barium carbonate: $BaCO_3 \to BaO + CO_2$ and the reaction $BaO + TiO_2 \to BaTiO_3$. At 1200 °C, $BaTiO_3$ is present in the system as well as traces of BaO.

The thermal evolution of the product obtained from starting material with 2:1 Ba:Ti ratio proceeds according to a different scheme. As follows from Figs. 2(b), 3(b) and 4(2), calcination at 200 °C does not lead to significant changes in the physicochemical characteristics of the material.

The phases of $BaTiO_3$ and Ba_2TiO_4 start to form at 400 °C. This is 200 °C below the temperature of the $BaTiO_3$ phase formation in the synthesis with the 1:1 Ba:Ti ratio. We explain such differences by different ratios of Ba:Ti and H_2O:Ti in the reaction mixtures. Calcination at 600, 800 and 1200 °C favors an increase in the phase content of $BaTiO_3$ and Ba_2TiO_4. The product calcined at 1200 °C is a mixture of Ba_2TiO_4 and $BaTiO_3$ phases in a ratio of 30 % and 70 %.

The Ba_2TiO_4 and $BaTiO_3$ phases have different Ba:Ti stoichiometric ratios. This affects the packing density of ions in the Ba_2TiO_4 and $BaTiO_3$ lattices and determines the polarization parameters of the materials. Barium titanate with a tetragonal structure at room temperature ($\sim$ 25 °C) has a dielectric constant of about 1500, and barium orthotitanate with an orthorhombic structure of about 20 °C has a dielectric constant of about 1500 [19].

The described transformations of the acylate complexes obtained at different Ba:Ti ratios are reflected in the corresponding dielectric spectra of the powder suspensions in silicone oil PMS-20.

The influecne of thermal treatment of powders on the ER effect was determined from the change in shear stress, as a function of the applied DC electric field in the range 0 – 7 kV/mm. For the investigation, 30 % suspensions of the obtained materials in polydimethylsiloxane (PMS-20 Penta Silicones) were prepared. The required amount of powder was triturated in polydimethylsiloxane until a homogeneous suspension was formed. The measurements were carried out on a modified Brookfield DV-II viscosimeter at various shear rates and DC electric field strengths applied to a 1 mm parallel plane gap between the electrodes.

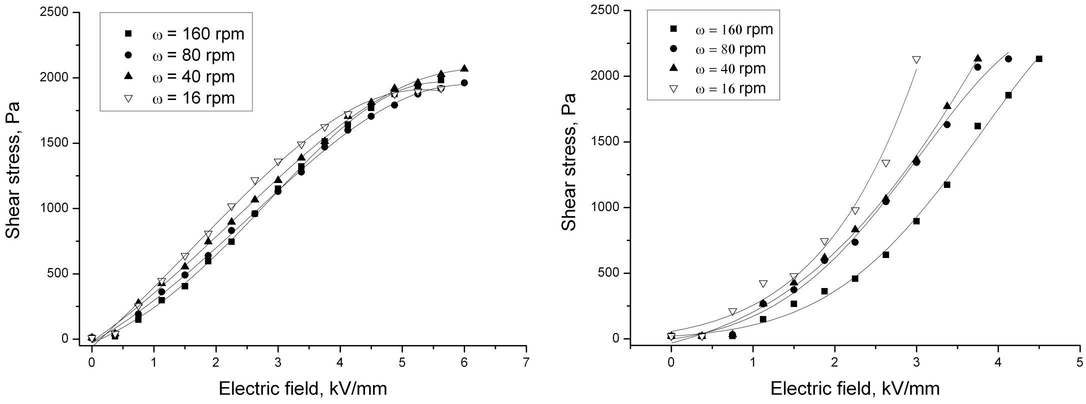
The ER effect theoretical models, based on the electrostatic theory of dipole-dipole interactions, describe the attractive force between the particles in an electric field according to the following equation [23]:

$$F = \frac{24a^6\varepsilon_0 E^2}{R^4}\frac{K_f(K_p-K_f)^2}{(K_p+2K_f)^2}, \tag{1}$$

where a – is radius of the filler particle, R – interparticle distance, ε_0 – dielectric constant of vacuum, E – the electric field strength, K_f – dielectric permittivity of a liquid dielectric (dispersion medium), K_p – dielectric constant of the filler particle material.

This equation emphasizes the role of the differences in the dielectric parameters of the dispersion medium and the dispersed phase in the formation of the ER effect and justifies the quadratic dependence of the electrorheological effect on the electric field strength.

The dependence of the shear stress on the electric field strength at various shear rates for suspensions of acylate complexes with the 1:1 and 2:1 Ba:Ti ratio of components dried at 85 °C are presented in Fig. 8. The results demonstrated in Fig. 8(b) obey the equation 1, while the results in Fig. 8(a) do not obey. A direct proportion of the shear stress on the field strength is characteristic for acylate complexes with a Ba:Ti ratio of 1:1 after saturation is achieved after $E = 4.5$ kV/mm starting from a field strength of 0.5 kV/mm. This may be due to presence of the adsorbed acetic acid on the surface of particles, which leads to the effects reported in [24].

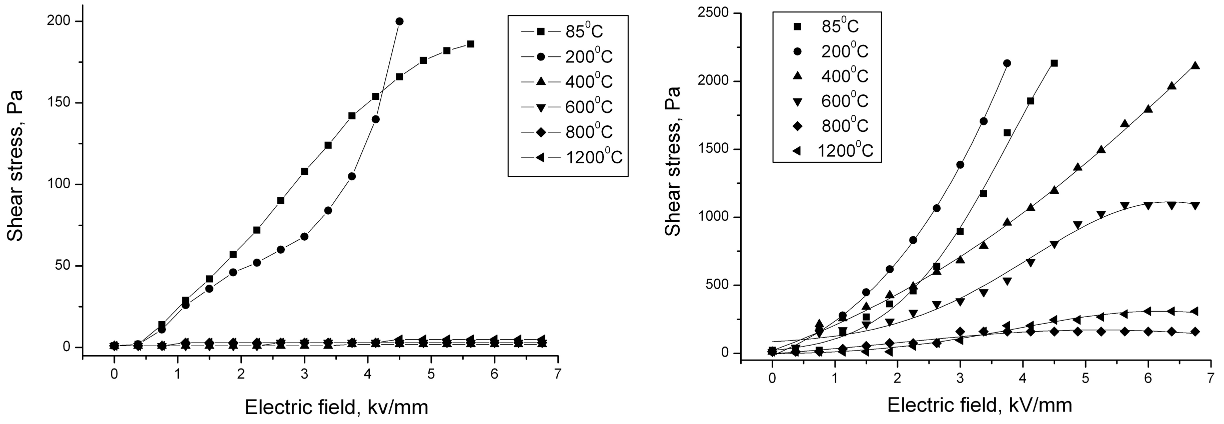


(a) (b)

FIG. 8. The dependence of shear stress on the electric field strength at different shear rates for 30 % suspensions of acylate complexes powders dried at 85 °C. 1:1 (a) and 2:1 (b) Ba:Ti ratios

The influence of the filler calcination temperature on the magnitude of the ER effect at a shear rate of 160 rpm is shown in Fig. 9. One can note that the ER effect regularities associated with the use of filler materials subjected to different thermal treatments can be explained from the standpoint of the classic electrostatic theory of the dipole-dipole interactions. As follows from Fig. 6, the permittivity of the suspensions is successively decreased with the increasing calcination temperature. In accordance with equation 1, this leads to a decrease in the attractive force between the filler particles and to a decrease in the ER effect, which is observed (Fig. 9).

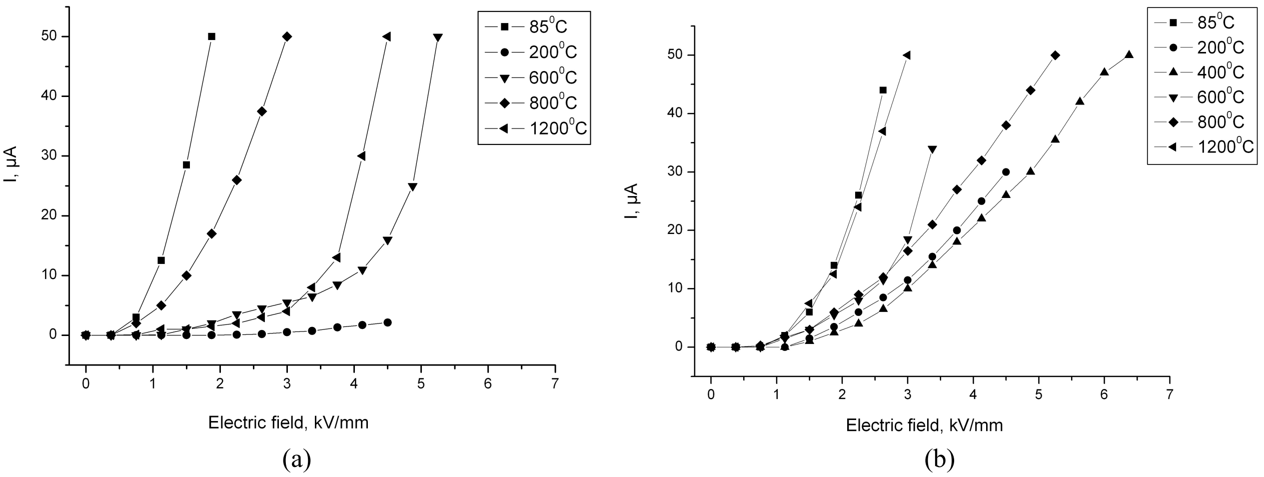
In the process of ER fluids structuring in electric fields with increasing field strength the distance between particles decreases (a decrease in the thickness of the dielectric liquid interlayer between the particles, the appearance of tight contacts), leading to an increase in conductivity. In this case, the conductivity increases proportionally to the number of formed contacts between the filler particles. The voltammetric parameters for 30 % suspensions of materials with 1:1 and 2:1 Ba:Ti ratios calcined at different temperatures at a shear rate of 160 rpm are significantly



(a) (b)

FIG. 9. Dependence of the shear stress of 30 % suspensions of acylate complexes with the 1:1 (a) and 2:1 (b) Ba:Ti ratios calcined at different temperatures on the electric field strength at a shear rate of 160 rpm

different (Fig. 10). For 30 % suspensions of materials with 1:1 Ba:Ti ratio, an increase in the calcination temperature leads to a consistent decrease in the current flowing through the suspension at an equal applied voltage. This may be due to the fact that molecules of acetic acid and polar acetate groups are present on the surface of filler particles that determine the value of the conductivity. As the organic components are removed, the conductivity of the suspensions decreases. For 30 % suspensions of materials with 2:1 Ba:Ti ratio (Fig. 1(b)), an increase in the calcination temperature of the filler material leads to an increase in the electrical conductivity of the suspensions. From Fig. 6, one can see that the value of the dielectric loss tangent for such suspensions is higher than for the systems with the 1:1 Ba:Ti ratio.



(a) (b)

FIG. 10. Voltammetric parameters for 30 % suspensions of acylate complexes with the 1:1 (a) and 2:1 (b) Ba:Ti ratios calcined at different temperatures at a shear rate of 160 rpm

5. Conclusions

The acylate gels were obtained via a sol-gel method in the titanium tetra-n-butoxide-barium hydroxide-acetic acid system in excess of acetic acid with a molar ratio of Ba:Ti components of 1:1 and 2:1. The regularities for the formation of Ba_2TiO_4 and $BaTiO_3$ phases during calcination of the obtained gels at 200, 400, 600, 800 and 1200 °C were investigated. A detailed study of phase transformations for the obtained materials was performed using thermogravimetric analysis, differential scanning calorimetry, X-ray phase analysis, FTIR spectroscopy, and electron microscopy. It was established that the thermolysis of acylate complexes with 1:1 Ba:Ti ratio at 200 and 400 °C affords X-ray amorphous products with a low organic phase content and significant metal hydroxy compounds content. The formation of the $BaTiO_3$ phase begins at 600 °C, and at 1200 °C, $BaTiO_3$ is present in the system with traces of BaO. The decomposition of the acylate complexes with the 2:1 Ba:Ti ratio leads to the formation of $BaTiO_3$ and Ba_2TiO_4 phases as low as at 400 °C. This is 200 °C lower than the temperature of $BaTiO_3$ phase formation in the synthesis with 1:1 Ba:Ti ratio. Calcination at 600, 800 and 1200 °C leads to a gradual increase of the Ba_2TiO_4 and $BaTiO_3$ phase content in the product. The product calcined at 1200 °C is a mixture of the Ba_2TiO_4 and $BaTiO_3$ phases in a ratio of 30 % and 70 %, respectively. For the first time, data was obtained on the influence of thermal treatment temperature on the magnitude of the ER effect in suspensions based on these materials. It was established that the regularities of the ER effect magnitude variation can be explained from the standpoint of the classical electrostatic theory of the dipole-dipole interactions in electric fields.

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