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Effect of Modification by Double Doping of Titanium Dioxide Particles on the Rheology of Dielectric Suspensions

Evguenia Korobko[1], Natalia Bedzik[2], Anna Murashkevich[3]

[1, 2] A. V. Luikov Heat and Mass Transfer Institute of NAS Belarus, 220072, 15 P . Brovka str., Minsk, Belarus
[3]The Belorussian State Technological University, 13a Sverdlova Street, Minsk 220006, Belarus

E-mail***:*** evkorobko@gmail.com

Abstract. The characteristic features of the rheological behavior of dielectric suspensions based on titanium dioxide modified by aluminum and phosphorus and the inter relation between the nature of modifiers and the modifiers-initiated polarization processes at the interface is shown. It has been established that ERFs based on titanium dioxide simultaneously modified by donor and acceptor impurities function stably in the temperature interval 20−80°C, which predetermines the possibility of using them in electrically controlled devices that heat up during operation. The participation of both modifying components in polarization processes proceeding on the titanium dioxide surface is confirmed by its dielectric spectrum. Thus, on the dependence of dielectric loss factor on frequency two maxima have been identified that correspond to the number of different-type inclusions in a sample.
Keywords: Suspensions, Electric field, Shear stress, Temperature range, Polarization

1. Introduction

The features of the rheological behavior of electrorheological suspensions (ERS) in electric field are mainly determined by the properties of the dispersed phase of different composition. The ordering of particles alters the hydromechanical characteristics of ERS by several orders of magnitude (from a liquid to a solid-like state). The possibility of controlling the viscoelastic state in a wide range, on the one hand, and the simplicity of implementing the electric effect, on the other, make it possible to devise vibro protecting constructions, micro engines, clutches, different hydraulic apparatuses, controlled viscoelastic elements, lubricating compounds, reversible glues for fixing mechanically treated workpieces, and other functional materials [1].So, titanium oxide, characterized by high dispersion and polymorphism, is widespread. Its use makes it possible to achieve an increase in the rheological parameters – the shear stress and the effective viscosity of the suspensions – by several orders of magnitude. However, the operability of most ERSs is limited to a rather narrow temperature range of use (< 60 ^{0}C), which excludes their use in heat exchangers and dynamic devices (dampers, couplings) heated during operation. Therefore, the creation of effective ERS in the extended temperature range is an important task. It is known that the polarization arising in such suspensions in an electric field, which determines the strength of the interaction of particles of the dispersed phase, should be predominantly “slow” (Maxwell - Wagner polarization).

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Heterogeneous and polyphase media with a given type of polarization consist either of several phases with different conductivities, or have structural defects. Those the deliberate distortion of the lattice parameters by introducing impurity atoms into its nodes or interstices can contribute to an increase in
the ER effect.

The aim of the present work was to study the characteristic features of the rheological behavior of dielectric suspensions based on modified titanium dioxide and to establish the interrelation between the nature of modifiers and the modifiers-initiated polarization processes at the interface, which determines the ability of fillers to exhibit the ER effect at elevated temperatures.

2. Materials and methods

2.1.Preparation of silica- encapsulated liposome particles

Titanium dioxide was chosen as the filler material for ERS , the particles of which, modified with aluminum, have high electrorheological activity, as shown in [2]. The TiO_2 was synthesized by the sol-gel method that includes the stages of deposition of nanodisperse titania, washing off undesirable hydrolysis products, peptization in the presence of a solution of nitric acid that yields a sol. Then, an aqueous solution of the modifiers was added to the prepared TiO_2 sol. The source of aluminium was aluminum nitrate nonahydrate, $Al(NO_3)_3{\cdot}9H_2O$ (10 mol. % in relation to titanium) and (or) an of phosphoric acid, H_3PO_4 provided the presence of phosphorum (2 mol. % in relation to titanium). Then to preserve the developed specific surface, an etanole solution of dodecyclamine was introduced which played the role of a structuring component. After the treatment of samples by an ultrasonic irradiation (with the conversion of the sol into a gel) the samples were dried at 150°C in an air static oven, and subsequently were calcined at 700°C for 3 h in the air. The synthesized samples of nanodisperse materials are further denoted as sample-1 (P-doped TiO_2), sample-2 (Al-doped TiO_2), sample-3 (P, Al-doped TiO_2) and sample-4 (pure TiO_2). The disperse medium for the ER fluids was mineral oil that has the proper characteristics: nonpolarity, nontoxicity, permittivity $\varepsilon = 2{,}3$, maximum of dielectric losses at a frequency of 10 Hz, and a breakdown voltage of 5 kV/mm.

2.2. Instrumental analysis

The morphologies of the synthesized particles were investigated by scanning electron microscopy (REM5-4800 at an accelerating voltage of 5 kV). The material structure was analyzed using X-ray powder diffractometer (Bruker D8-advance with CuKα radiation (λ = 1.54178 A). The crystalline size of samples was estimated by broadening the characteristic peaks on the XRD-patterns using the Scherrer formula. The specific surface was determined from the adsorption of phenol from the solution in n-heptane. To examine ER properties of suspensions, the dependence of the shear stress on the shear rates at different electric field strength were obtained by the method of rotary viscosimetry in the range of shear rates 1–1000 s^{-1} using a Physica MCR 301 Anton Paar rheometer (a measuring cell is cylinder-cylinder with a gap of 1.16 mm) with a change in the electric field strength E within the range 0–4 kV/mm. in the temperature range 20–80°C. The electrophysical properties of the ER materials and ER suspensions were measured by an E7-20 immitance meter in the 0.1-100 kHz frequency range.

3. Results and discussion

Figure 1 presents the images of the surface of the samples of modified titanium dioxide obtained with the aid of a REM5-4800 Scanning Electron Microscope (SEM) at an accelerating voltage of 5kV. Sample 2 consists of titanium dioxide with specific surface 114m^2/g modified with aluminum (10 mol. %). Sample 3 consists of titanium dioxide with specific surface 116 m^2/g modified with aluminum and phosphorus (10 mol. %, 1% P_2O_5). Despite the difference in the composition of the modifying component, both samples (2 and 3) are characterized by the similar morphology: these are irregular aggregates of fine crystallites. Crystallite structure and some quantitative characteristic data are summarized in Table 1. It can be seen that the presence of doping components (both Al and P) decreases crystalline size and stabilizes anatase structure. This is in a good agreement with [3] and our previous paper [4].

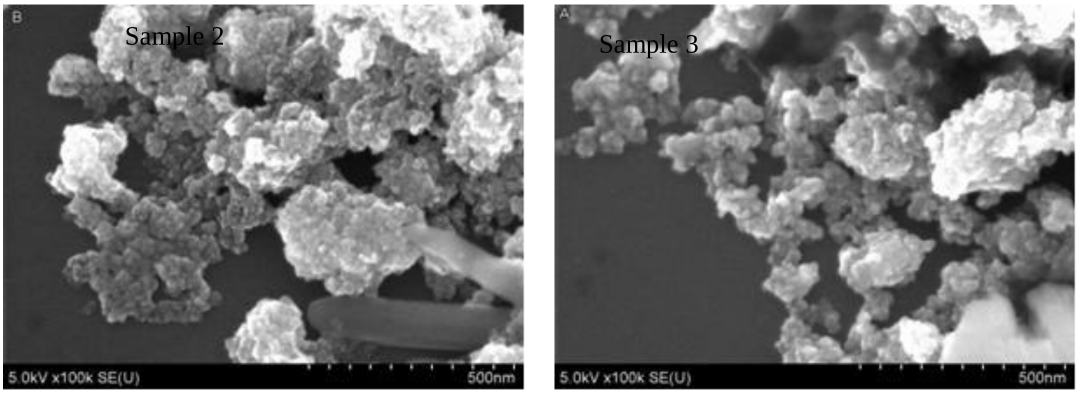
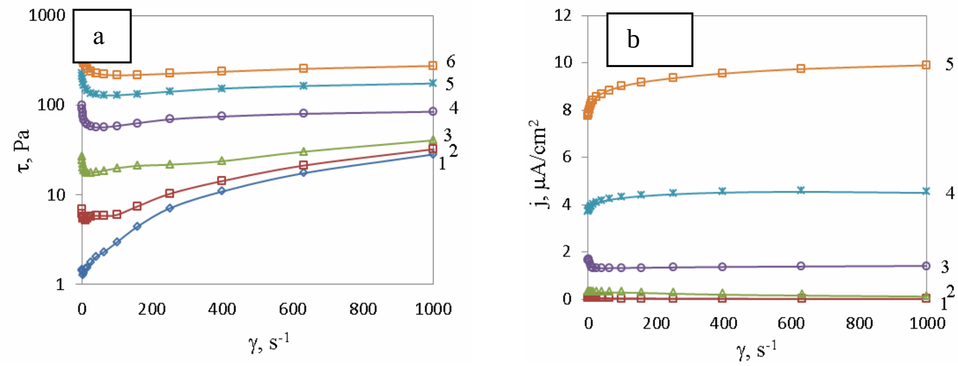


Figure 1. SEM images of the particles of the modified titanium dioxide used for ERS

Table 1. The characteristic data of the synthesized ER materials

Sample	Doping element	Content of dopant, mol% in relation to Ti	Crystallite phase	Crystallite size, nm	Specific surface, m^2/g	Specific resistance, MO hm·m
1	P	2	anatase	24	51	0.041
2	Al	10	anatase	10	103-106	0.004
3	Al, P	10, 2	anatase	16	101	0.056
4			rutile	30	24-26	0.031

Figure 2 presents the flow curves of ERS-3 with (Al, P)-doped TiO_2 at different electric field strengths.



E, kV/mm : 1 - 0; 2 - 0.5; 3 - 1.0; 4 - 2.0; 5 - 3.0; 6 - 4.0

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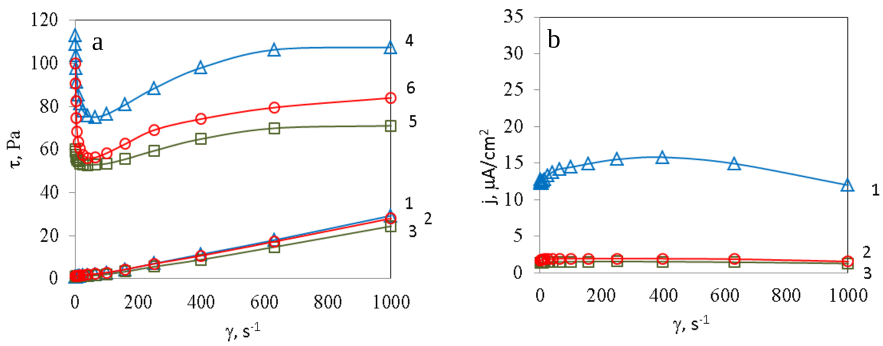
Fig. 2. Shear stress τ (a) and current density j (b) of ERS-3 with 20 wt.% of modified TiO_2 samples vs. shear rate in the range of electric field strength E = 0–4 kV/mm at T = 20°C

According to Fig.2, the values of the shear stresses of suspensions increase from 1–2 Pa to 200 –400 Pa within the range of shear rates 1–100 s^{-1}, i.e., by about 2 orders of magnitude. At a shear rate > 10

s^{-1} and an electric field strength of up to 2 kV/mm the destruction of the bridges is initiated, which results in a small decrease in the shear stress values τ.

Suspension with ERS-1 has the highest ER activity at 20°C (Fig. 3a, curve 4); however, at 80°C its ER activity decreases sharply and becomes the least one among the samples investigated (Fig. 4a, curve 4). The suspension containing ERS-2 reveals ER activity among the compared samples at 20 ° C (Fig. 3a, curve 5), but at 80 ° C its activity increases and becomes the highest among of other liquids (Fig. 3a, curve 5). In addition, the magnitude of the leakage currents is negligible (up to 25 $\mu A/cm^2$) (Fig. 2b, curve 2). ERF-3 containing Sample 3 exhibits a high ER activity at both 20°C (Fig. 2a, curve 6) and 80°C (Fig. 3a, curve 6). Figure 5 presents the dependences of the real and imaginary parts of the permittivity on the electric field frequency for 20 wt.% suspensions of TiO_2 modified with phosphorus (P) (ERS-1) or aluminum (Al) (ERS-2), as well as in the case of double modification of TiO_2 with these elements (Al +P)(ERS-3).



a)

1 - ERS-1, 2 - ERS-2, 3 -ERS-3, E = 0 kV/mm

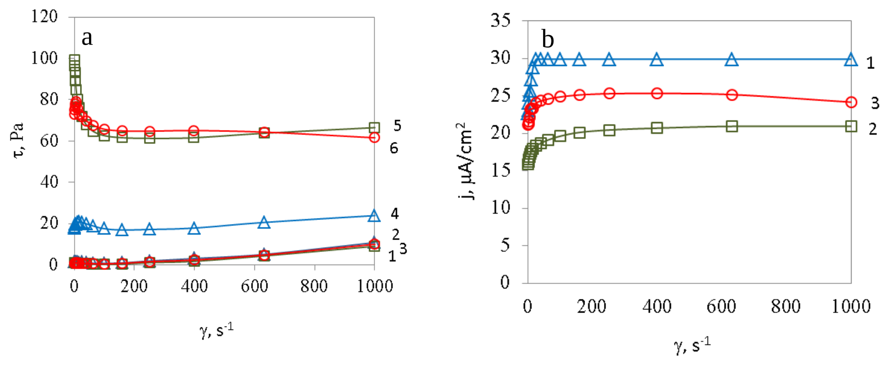
4 - ERS-1, 2 - ERS-2, 3 - ERS-3, E = 2kV/mm

b)

1 - ERS-1, 2 - ERF-2,

3 - ERS-3, E = 2kV/mm

Figure 3. Shear stress τ (a) and current density j (b) of ERS with 20 wt.% of modified TiO_2 samples modified vs. shear rate at electric field strength E = 2 kV/mm and T = 20°C



a)

1 - ERS-1, 2 - ERS-2, 3 - ERS-3, E = 0 kV/mm

4 - ERS-1, 5 - ERS-2, 6 - ERS-3, E = 2 kV/mm

b)

1 - ERS-1, 2 - ERS-2, 3 - ERS-3, E = 2kV/mm

Figure 4. Shear stress τ (a) and current density j (b) of ERF with 20 wt.% of modified TiO_2 samples vs. shear rate at electric field strength E = 2 kV/mm and T = 80°C

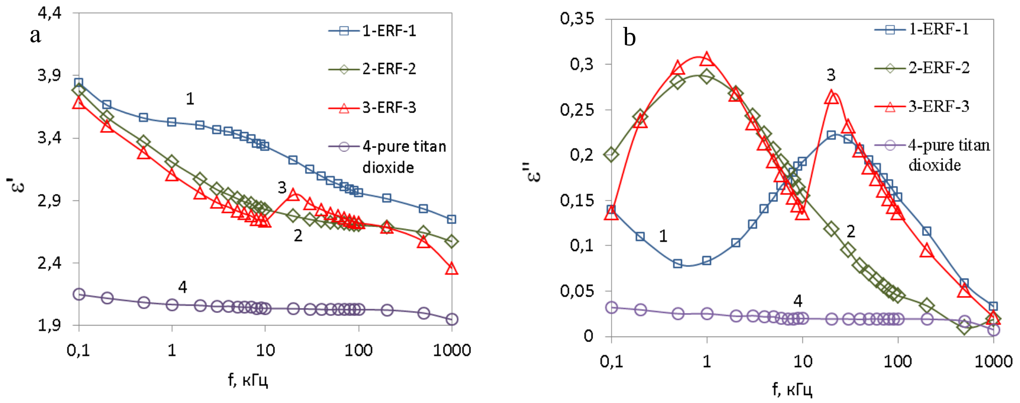


Figure 5. Frequency dependence of the real (a) and imaginary (b) parts of the impedance for 20 wt. % ERSs containing pure and modified TiO_2

Analysis of the Fig.5 shows that the relaxation frequency f_r for ERS-1 is displaced to a higher frequency region (22 kHz) as compared with ERF-2. Suspension ERS-1 with a higher value of f_r has also the highest conductivity among the samples being compared (curves 1, Fig. 3b and 4b). This means that on modification of titanium oxide with phosphorus (ERS-1) the charges are accumulated more rapidly on the surface, precisely which determines the higher rate of the interphase polarization in the ERS-1 sample. The doping of titanium oxide with aluminum leads to the slowing down of the interphase polarization and, correspondingly, to the shift in the relaxation frequency of ERS-2 to the side of lower frequencies (0.8 kHz), with the conductivity of ERS-2 also decreasing (curves 2 in Fig. 3b and 4b).

Analysis of the frequency dependences $\varepsilon''(f)$ of ERF-3 points to the development of several polarization processes in a sample that proceed at different frequencies and with different relaxation times [5]. One can distinctly see two maxima at 0.8 and 22 kHz. The polarization processes corresponding to the indicated maxima, can be easily identified, since the positions of the maxima coincide exactly with the corresponding maxima for the samples modified with individual admixtures of Al and P. It is seen that the first maximum in $\varepsilon''(f)$ at 0.8 kHz is much sloper and wider than the second one at 22 kHz, corresponding to which is the maximum on the dependence $\varepsilon'(f)$ at the same frequency. This means that the first maximum reflects the combined effect of several processes proceeding with different relaxation times [5], whereas the position of the second maximum corresponds to the progress of one definite polarization process. It may quite be that such process is the ionization of the phosphorus atom with the flopover of one of its electrons to the conductivity zone and conversion of the atom into positively charged ion P^+ or into a «hole». Thus, the assumption that the wide temperature interval of the activity of ER fluids can be provided on the condition of creating fillers possessing a wide maximum of $\varepsilon''(f)$ in the frequency range 100–100000 Hz is confirmed by the experimental data obtained. However, in the case of double modification of TiO_2, not one wide smeared maximum exists on the dependence $\varepsilon''(f)$, but rather there are two maxima corresponding to the number of different-type inclusions in a sample. The zone of the overlapping of the indicated maxima covers the entire interval 100–100000 Hz favorable for the electrorheology.

4. Conclusions

The data obtained indicate that the double modification of titanium oxide with aluminum and phosphorus made it possible to achieve high rates of suspension ER activity (20% wt.%) - the shear stress increased by 170 times at E = 4 kV/mm. In addition, stable rheological parameters were obtained in the temperature range up to 80 ° C. The participation of both alloying components in the polarization processes occurring on the surface of the modified titanium oxide is confirmed by its dielectric spectrum. Thus, it became possible to create effective electrorheological suspensions for practical use in modern devices and technologies. So, when using controlled ER-glues in the technology of fixing the part on the substrate, the use of ERS-1 with dispersed filler modified with phosphorus is promising. In the case of using ERS-2 in controlled devices that heat up during operation (dampers, couplings with dissipative heating, shock absorbers, mechanical friction mates), it is preferable to use aluminum alloyed TiO_2 particles as a dispersion filler. When developing ERS compositions that are effective over an extended temperature range, it is promising to use titanium oxide combined with aluminum and phosphorus as the dispersed phase.

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