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Effect of Polydimethylsiloxane Viscosity on the Electrorheological Activity of Dispersions Based on It

O. I. Davydova, A. S. Kraev, A. A. Redozubov, T. A. Trusova, and A. V. Agafonov

Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia

e-mail: olgaivdav@mail.ru

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Abstract—The effect the viscosity of a dispersion medium of a polymethylsiloxane fluid (PMS) with a kinematic viscosity over a wide range of values from 5 to 300 cSt has on the electrorheological properties of suspensions based on nanosized titanium dioxide obtained via the sol-gel method is investigated. The investigations are conducted in a wide range of concentrations of suspensions: from 30 to 60 wt % (from 15 to 38 vol %) of the dispersed phase. The role the dispersion medium in two-phase disperse systems plays in the formation of structures of dispersed phase in the presence of an electric field is determined from the dependence of yield points of TiO_2 in PMS with different viscosities on the applied electric field strength.

Keywords: viscosity, electric field, electrorheological effect, suspension, titanium dioxide, dispersion medium, electrorheological fluids, polydimethylsiloxane, shear stress.

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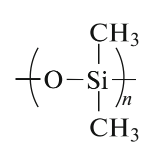
INTRODUCTION

The electrorheological effect (ERE), a rapid reversible change in the viscous–plastic properties of suspensions of polarizable materials in dielectric liquids upon the application of an external electric field, has been known for some time (since 1949); however, it has yet to receive wide practical application. One of the main obstacles to this is the dearth of high-performance electrorheological fluids (ERFs). ERFs should generally be considered microstructured liquid-phase systems that include liquid dielectric solvents and solid particles whose structure and chemical composition are arranged in such a manner as to, on the one hand, maximize the electrorheological effect, and, on the other hand, ensure the high stability of a disperse system. Electrorheological fluids with low conductivity that are non-toxic, capable of high aggregation and stable sedimentation, and have high resistance to chemical effects are needed for the practical use of ERFs. At the same time, high demands are made on ERFs with respect to their abrasion and corrosion effects and the constancy of properties over a wide temperature range. It is obvious that the set of required ERF properties is determined by the composition and nature of their constituents. The main problem in conducting experiments in electrorheology is therefore developing ERF compositions. For this we must not only choose the materials of the dispersed phase and the dispersion medium, but also provide a theoretical basis for the proposed choice.

Nonpolar or weakly polar, nonconductive (with resistance of about 10^{10} Ω cm) fluids, different oils (paraffinic, transformer, silicone, castor), diesters (dibutyl sebacate, dimethylhexyl adipate), naphthene hydrocarbons, aromatic hydrocarbons, olefins, paraffin hydrocarbons, and so on are usually used as dispersion media for ERFs. In our view, it is best to use mineral silicone oil as an ERF dispersion medium, since it has the required dielectric properties and wide ranges of operating temperatures and viscosities. Chemical and biological inertness are also typical of organosilicon fluids at low saturated vapor pressures. Polymethylsiloxanes are insoluble in water, they are effective waterproof compounds. This is particularly important for electrorheological systems where moisture is avoided due to possible electrical breakdown upon the application of external fields. Constituents of ERF should have dielectric parameters that are stable over time and a broad range of frequencies. Polymethylsiloxanes (PMSs) have good electrical insulation properties, high dielectric strength (dielectric constant, 2.7), and low loss factors (dielectric loss tangent, 0.0001–0.0002). The unique rheological properties of polymethylsiloxanes (a low dependence of viscosity on temperature) could be due to the lack of hydrogen bonds between the chains of molecules,



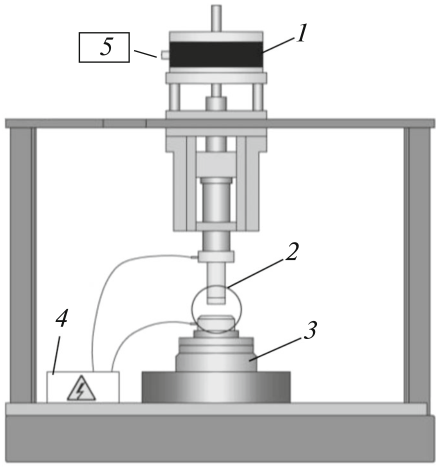


Fig. 1. Setup for measuring the tension/compression characteristics of electrorheological fluids under the conditions of applying an external electric field: (*1*) screw press with stepping motor, (*2*) measuring cell, (*3*) tensometer, (*4*) high-voltage direct current source GPI-825, and (*5*) control computer.

or to the free rotation of structural units around siloxane bonds [1]. These both hinder the close packing of molecules and result in low interaction between molecules, which is by no means unimportant in ensuring the dynamic state in suspensions based on PMSs.

The aim of this work was to study the effect the viscosity of polydimethylsiloxane fluids (kinematic viscosity, 5 to 300 cSt) has on the electrorheological properties of suspensions based on them. Nanosized titanium dioxide powder was chosen as dispersed phase of ERFs for our studies.

EXPERIMENTAL

Standard (GOST 13032-77) polydimethylsiloxane fluids with viscosities of 5, 20, 50, and 300 cSt were used in this work. Nanosized titanium dioxide powder was synthesized in our laboratory via sol-gel technology; details of the procedure for synthesizing and investigating the properties of powder were presented in [2]. Electrorheological suspensions were prepared using the weight method. The required amounts of TiO_2 powder and polydimethylsiloxane were triturated in an agate mortar to obtain a uniform suspension. The content of the dispersed phase varied from 30 to 60 wt % or from 15 to 38 vol %. Since a rather wide range of dispersion compositions was chosen (from dilute to highly concentrated), we had to choose a reliable way of measuring the rheological characteristics of the obtained ERFs in order to compare their electrorheological activities.

The problem of damage to the structural homogeneity of suspensions under shearing strain has been actively discussed lately in articles dealing with the rheology of concentrated disperse systems [3–6]. It has been shown that flowing dispersion systems fall into several areas that slip in layers along an interface with tangential stresses (the so-called shear banding effect). It was shown in [3] that when measuring the rheology of concentrated suspensions of dioxides of metals in transformer oil on a viscometer with flat parallel plates, the dispersion flow between the plates is divided into three layers: a virtually stationary layer against a stationary plate, a high-speed layer near a rotating plate, and an intermediate layer in which there are virtually no dispersion particles. There is no velocity gradient in the two boundary layers, and the system flows in the middle layer, which is an essentially pure low-viscosity solvent. Suspension viscosity can in this case be erroneously estimated as the viscosity of pure solvent.

In a high-performance electrorheological system, the structuring of the dispersed phase under the influence of an applied external field proceeds rapidly, starting at relatively low concentrations (15 vol %). As a result, there is a sharp increase in the viscosity of the system until a solid-like nonflowing state is achieved. Under the influence of tangential deformation stresses, the ERF is layered into hard structures formed by polarized particles of the dispersed phase against the viscometer plates, and by the low-viscosity dispersion medium of the intermediate layer in which the suspension flows. Measurements of ERF viscosity on a plate–plate type rheotest therefore yield distorted results, so we decided to assess the electrorheological effects of our ERFs using the tension/compression deformation stresses of suspension in the presence of an external electric field.

Tensile tests of ERFs in electric field were performed on a specially constructed device (Fig. 1) consisting of a screw press controlled by a stepping motor that allowed vertical movement of a working electrode at a rate of 0.003 mm/s. A tensometer with data output on a computer at a rate of one measurement per second was used as a stress sensor. The design of the measuring cell (Fig. 2) allowed us to perform the tension/compression of ERFs in the mode of free flow from the electrode gap at electric field strengths of up to 8 kV/mm. When testing the strength of an electrorheological fluid, an initial distance of 1 mm was set between the electrodes of the cell during tension (when the upper electrode touched the surface of the suspension). Electric voltage of a certain value was then applied to the system, and the upper electrode was raised at a prescribed rate until the gap between the electrodes was 4 mm. After the motion of the upper electrode was stopped, the electric voltage turned off. The accuracy of measuring the stress on the system was no less than ±5 Pa at the maximum possible stress of 90 kPa.

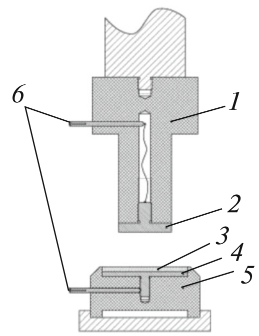


Fig. 2. Cell for tension/compression tests of ERF under the conditions of applying an external electric field: (*1*) insulator of the upper electrode, (*2*) upper movable electrode, (*3*) ERF, (*4*) lower electrode, (*5*) insulator of the lower electrode, and (*6*) connectors to the high voltage source.

RESULTS AND DISCUSSION

The setup shown in Fig. 1 allowed us to measure the electrorheological tensile and compression strengths of ERFs; in our study, only the strength characteristics of suspensions in tensile tests were measured in order to eliminate the influence of tangential stresses possible with a liquid flow under compression. Figure 3 shows typical stress–strain curves for a titanium dioxide suspension based on polydimethylsiloxane fluids of different viscosities in the presence of an electric field with an intensity of 5 kV/mm. The values of the yield points of disperse systems for the given field strengths were determined from the upper segments of the stress–strain curves, which depended relatively little on the relative elongation of the sample. The yield points of suspensions at different strengths of the applied field were determined in a similar manner. As we can see from the plots shown in Fig. 3, the viscosity of the dispersion medium has a considerable impact on the value of the ERE of titanium dioxide–based suspensions.

When the viscosity of a PMS is increased, the tensile stress in the presence of a field is reduced. Figure 4 shows the dependences of the yield points of TiO_2–PMS20 disperse systems with different concentrations of the dispersed phase, determined from the stress–strain curves at different values of the applied voltage, using the field intensity. As follows from Fig. 4, the electrorheological activity of TiO_2–PMS20 suspensions depends strongly on the concentration of the dispersed phase. At high concentrations, the character of the dependence changes: starting at a certain value of the strength of the external field, the growth of yield points slows and even falls, probably because the systems are closely packed at high concentrations of the dispersed phase, the number of contacts between the particles increases, and hard solid-like structures of polarized particles of the dispersed phase formed along the lines of the electric field even at low values of the applied field voltage. The partial or complete displacement of the dispersion medium from the gap between them is possible in such hard contacts, and the system becomes less elastic and more susceptible to mechanical effects.

With a further increase in tension under the action of dynamic tension stresses, the structural aggregates of particles of the ERF dispersed phase begin to break down until they decay into individual particles. The system loses its ability to relax, restoring the initial

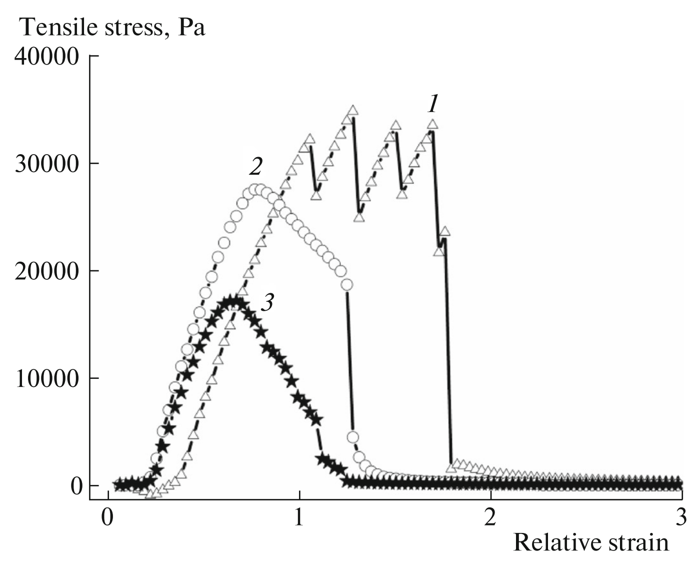


Fig. 3. Stress–strain curves of TiO_2 suspensions with dispersed phase concentrations of 45 wt % in polydimethylsiloxane with different viscosities: (*1*) TiO_2–PMS5, (*2*) TiO_2–PMS20, and (*3*) TiO_2–PMS300 upon the application of electric field with an intensity of 5 kV/mm.

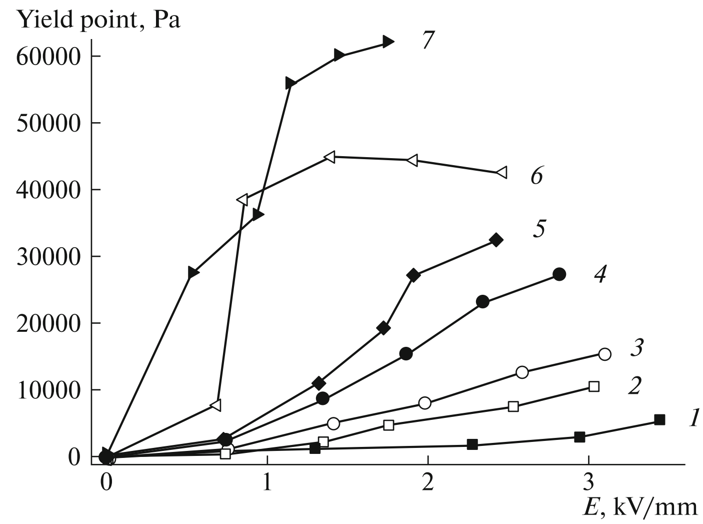


Fig. 4. Dependences of yield points of ERFs: TiO_2-PMS20 at different concentrations of the dispersed phase ((*1*) 30, (*2*) 35, (*3*) 40, (*4*) 45, (*5*) 50, (*6*) 55, and (*7*) 60 wt %) on external electric field intensity.

pseudo-plastic structure after the removal of the external field. Based on the dependence obtained for subsequent investigations, we chose a working suspension concentration of 45 wt % (26 vol %). The electrorheological effects of an ERF with the prescribed concentration of the dispersed phase are quite strong, and the reversibility of the phase transition from a liquid viscous-fluid homogeneous state to a solid remains. Titanium dioxide dispersions with concentrations of 45 wt % were prepared on the basis of polydimethylsiloxanes PMS5, PMS20, and PMS300, and their stress–strain curves were recorded under an applied electric field. Figure 5 shows the dependences of the yield points of ERFs based on polydimethylsiloxanes with different viscosities on the strength of the external field. A clear ERE dependence in the values of the yield points of electrorheological liquids on the viscosity of a dispersion medium is observed (Fig. 5). The lower the viscosity, the higher the values of the electrorheological effects under the tension of suspensions in the presence of the field.

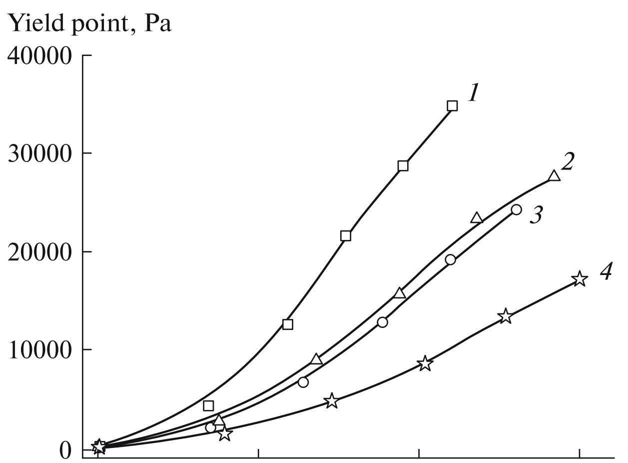


Fig. 5. Dependences of yield points of TiO_2 suspensions (with concentrations of 45 wt %) based on PMS with different viscosities: (*1*) PMS5, (*2*) PMS20, (*3*) PMS50, and (*4*) PMS300 on the applied electric field intensity.

The effect oil viscosity has on the value of the electrorheological effect of an ERF can be explained by the role of the dispersion medium in two-phase disperse systems of the solid phase–liquid medium type in the formation of the coagulation structure of the dispersed phase as a result of particle contacts [4]. The contacts observed during the structuring of suspensions occur through the thin layer of liquid in the composition of microgranules of solid phase particles formed during the formation of a two-phase system under dynamic conditions (mixing at trituration). The direct (molecular) contacts without the liquid layer that occur in highly dispersed powders have the strongest energy. The lower the viscosity of the dispersion medium of a suspension, the easier it is released from the microgranules of the dispersion particles upon the formation of ERF structures in the presence of an external field, and the conditions are created for more energetically stable direct contacts of the dispersed phase particles.

The resistance of a suspension structure formed from molecular contacts to external dynamic tension stresses grows considerably. In addition, the lower the viscosity of the ERF dispersion medium, the lower the resistance experienced by particles of the dispersion medium during their translational motion upon the formation of columnar structures along the lines of force of the external electric field. The TiO_2–PMS5 suspension displayed the greatest electrorheological activity, compared to ERFs based on PMS20, PMS50, and PMS300 (Fig. 5). However, the system rapidly lost homogeneity upon the application of the external field, due to the high fluidity of PMS5. Oil in the form of layers between the particles of the dispersed phase in the initial state easily follows from the contacts that form upon application of the field. The system of chain structures formed from polarized TiO_2 particles directed along the lines of force of the electric field becomes fragile and brittle, loses its elasticity, and behaves as a solid. This is clearly seen from stress–strain curve of TiO_2–PMS5 suspension (Fig. 4).

Sharp bends of the dependence of stress strain on relative tension are observed in the range of flows (at the top of stress–strain curve). These could be due to a break in the continuity of the ERF bulk structure. In addition, TiO_2–PMS5 suspension settling is irreversible, and the homogeneity of the system is not restored after removing the external electric field voltage. The TiO_2–PMS300 suspension has considerably lower values of the electrorheological effect at the yield points, compared to other oils. High oil viscosity complicates both the formation of structures of the dispersed phase in the field, and the relaxation of the initial state of suspension after the removal of external stresses. Suspensions based on PMS20 and PMS50 oils are the best for use as dispersion media of electrorheological suspensions: on the one hand, they ensure high rates of formation of the structures of polarized particles of ERFs; on the other hand, there is instant reversibility of structural formations upon the application and removal of external field voltage.

CONCLUSIONS

The rheological properties of a dispersion medium play an important role in the formation of the ERE value of a electrorheological fluid. It is proposed that PMS20 be used as the most promising and effective dispersion medium for titanium dioxide-based ERF.

ACKNOWLEDGMENTS

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