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Electrorheology of Barium Titanates – The Role of the Particle Size

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ABSTRACT

This study deals with the effect of the particle dimensions on the electrorheological (ER) behavior of barium titanates silicone-oil suspensions. Barium titanates were prepared via a microwave-assisted molten-salt synthesis which offered a good control of particles dimensions. Huge impact of particle size on the ER behavior has been found.

INTRODUCTION

Materials whose applications attributes can be controlled via an external stimulus are of high interest due to their unique properties. One of them are electrorheological (ER) fluids that alter their rheological parameters by means of external electric field strength application. They are composed of electrically polarizable particles dispersed in a non-conducting liquid medium, and act as Newtonian or pseudoplastic fluids in the absence of an electric field; however, after an application of an electric field, they start to behave as Bingham fluids exhibiting a yield stress instead. This transition from liquid-like to a solid-like state is caused by a creation of chain-like structures from electrically polarizable particles spanning the electrodes[1]. Such behavior leading to a steep increase in viscosity is called ER effect.

It has been found that conductivity of the particles and mismatch between dielectric constants of particles and liquid medium is responsible for this formation[2-5] and, thus, determine the rate of ER effect. Other important factor influencing the intensity of ER effect is morphology of the dispersed particles. However, there is a lack of studies dealing with ER performance of an ER fluid based on particles possessing cube-like morphology.

Many materials have been used as a dispersed phase in ER fluids. Among organic materials, mainly conducting polymers and various carbon forms have been of the main interest. Inorganic particles are represented by clays, silica, and titanates. The last mentioned are materials with low conductivity and high dielectric constant. Therefore, their ER fluids have been intensively studied. The main drawbacks of titanium oxides regarding their potential application in ER fluids are their high density and a time-consuming synthesis. The titanates are commonly prepared via sol-gel, molten-salt, or hydrothermal methods taking up to few days to produce the titanates[6-9]. Recently, the preparation of lithium titanates via a microwave-assisted molten-salt synthesis has been reported[10]. The implementation of microwaves led to a considerable reduction of a synthesis time from tens of hours to tens of minutes.

This study deals with preparation of barium titanates particles via a microwave-assisted molten-salt synthesis, and their further use as a dispersed phase in a mixture with silicone oil as ER fluids.

EXPERIMENTAL

Preparation of the particles

A eutectic mixture consisting of $BaCO_3$ (Sigma Aldrich, USA) and $BaCl_2 \cdot 2H_2O$ (Sigma Aldrich, USA) in a molar ratio 0.47:0.53 was prepared. This was further mixed with TiO_2 anatase (99.8% Sigma Aldrich, USA; predominantly anatase) in a weight ratio 1:8. After homogenization of the mixture in a mortar it was put into a corundum crucible, which was then placed into a ceramic kiln with its inner side coated with a microwave absorbing layer. This setup enables rapid increase of temperature when placed into microwaves. As a source of microwaves, a domestic oven was used. Two batches of the particles were prepared regarding the synthesis time. The first synthesis time was 20 minutes (the product is further labelled as $BaTiO_3$ 20), the second was 35 minutes ($BaTiO_3$ 35). After the synthesis, the particles were left to cool down to room temperature, and then rinsed with distilled water, and dried in a vacuum oven.

<u>X-ray diffraction and scanning electron microscopy</u>

X-ray diffraction (XRD) analysis was used in order to confirm the transition of precursor materials into $BaTiO_3$ particles. XRD patterns were collected in angle range of 10–95° 2θ using an X´Pert PRO (PANalytical, Netherlands) diffractometer with Cu $K_{\alpha 1}$ radiation. A scanning electron microscope (SEM; VEGA II LMU, Tescan, Czech Republic) was used to determine the particles size and morphology.

<u>Preparation of ER fluid</u>

ER suspensions of 10 wt% concentration were prepared by mixing of prepared dried particles with dried silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 194$ mPa s, conductivity $\sigma_c \approx 10^{-11}$ S cm^{-1}). Before each measurement, the suspension was mixed with a glass stick for ca 5 min and subsequently sonicated for 60 s to get homogeneous distribution of particles within the suspension.

<u>Rheological measurements</u>

Rheological parameters of the prepared ER suspensions in the absence and in the presence of external electric field were measured using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) with the coaxial-cylinder geometry (length 27.4 mm, inner cylinder separated by a gap of 0.7 mm) at 25 °C. The external electric fields of electric field strengths within 0.5 – 1 kV mm^{-1} were produced by a DC high-voltage supplier TREK 668B (TREK, USA). The electric field was applied one minute before shearing in order to provide time enough for suspension particles to create internal structures. The experiments were performed in steady shear mode in the shear rates range 0.1 – 300 s^{-1}. After each measurement, the suspension was sheared at a shear rate of 40 s^{-1} for one minute in order to destroy residual structures within the suspension.

RESULTS AND DISCUSSION

<u>X-ray diffraction</u>

The X-ray diffraction patterns of $BaTiO_3$ (Fig. 1) particles have all specific peaks

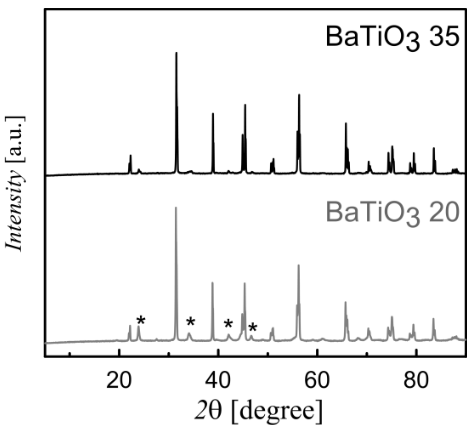

Fig. 1. X ray diffraction patterns of $BaTiO_3$ 20 and $BaTiO_3$ 35. The symbols (*) represent characteristic peaks of $BaCO_3$.

confirming the presence of $BaTiO_3$ crystals[11]; however, they also contain peaks representing the neat $BaCO_3$, which was one of the precursors of the synthesis, as impurity, mainly in the case of $BaTiO_3$ 20. The obtained results were also compared with the ICDD PDF-2 database confirming the formation of $BaTiO_3$ crystallographic phase in the particles.

Scanning electron microscopy

The prepared particles in both cases possess cube-like morphology (Fig. 2a and b). The $BaTiO_3$ 35 particles are bigger than the particles $BaTiO_3$ 20. This is a consequence of the longer synthesis time, which enables a growth of bigger crystals.

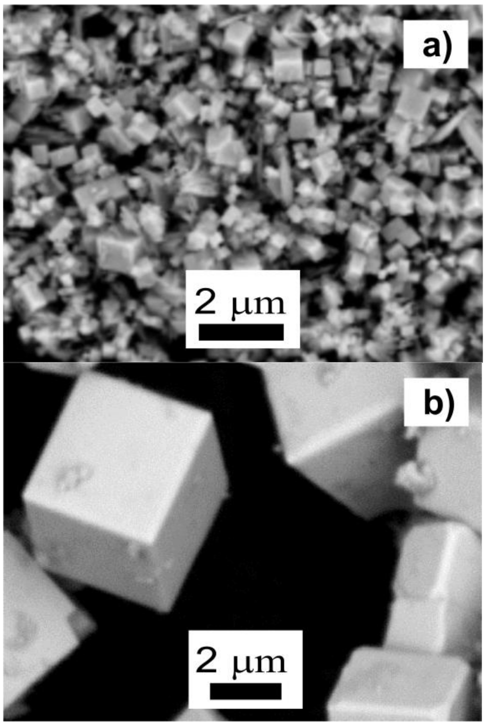

Fig. 2. SEM images of (a) $BaTiO_3$ 20 and (b) $BaTiO_3$ 35.

Rheological properties

Both prepared ER fluids behave as pseudoplastic fluids in the absence of an external electric field (Fig. 3), where the $BaTiO_3$ 20-based ER fluid exhibits higher pseudoplastic behaviour. This can be consequence of smaller particles size leading to higher interactions between particles and a liquid medium. Upon an application of an external electric field, the viscosity of both ER fluids increases due to a creation of organized chain-like structures within the ER fluids. It is also observed that with increasing electric field strength the viscosity further increases.

The change from pseudoplastic to Bingham fluids upon an application of an external electric field can be clearly observed in the Fig. 4. The slight increase of shear stress at low shear rates can be ascribed to structures reorganization (Fig. 4b), which is typically observed for dilute or weak ER fluids[12] and the decrease at higher

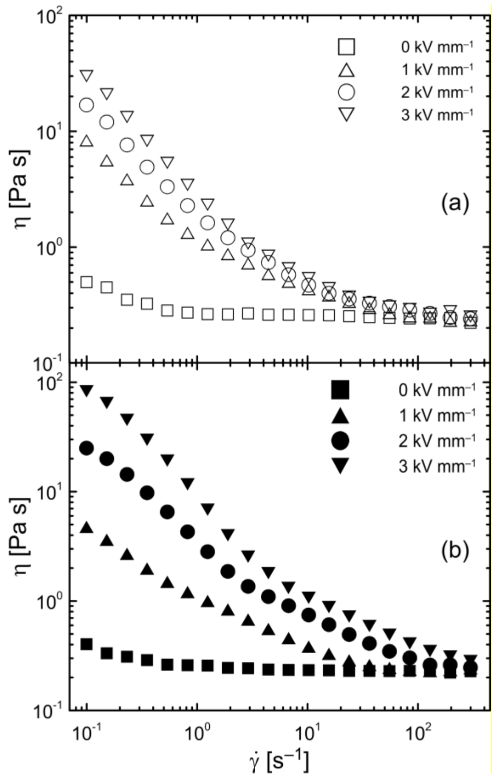

Fig. 3. The log-log dependence of the viscosity, η, on the shear rate, $\dot{\gamma}$, for ER fluids based on (a) $BaTiO_3$ 20 particles and (b) $BaTiO_3$ 35 particles in the presence of various electric field strengths of at 25 °C.

shear rates is ascribed to destroying of weak particles chains[13]. At electric field strength of 1 kV mm^{-1}, the ER effect is higher for the $BaTiO_3$ 20-based ER fluid. However, with upping the electric field strength, the ER effect of $BaTiO_3$ 35-based ER fluid starts to exceed the ER effect of the $BaTiO_3$ 20-based ER fluid. This can be connected with energy barrier which hinders the particles from movement in a viscous liquid medium. While movement of smaller particles is high enough even at low electric field strength, to induce the movement of bigger particles the higher electric field strength is needed. This elucidates the low ER effect of the $BaTiO_3$ 35-based ER fluids in comparison with the second one. At electric field strength 3 kV mm^{-1}, the bigger particles were then able to successfully join into chain-like structures which led to higher ER effect in comparison with the smaller particles-based ER fluids.

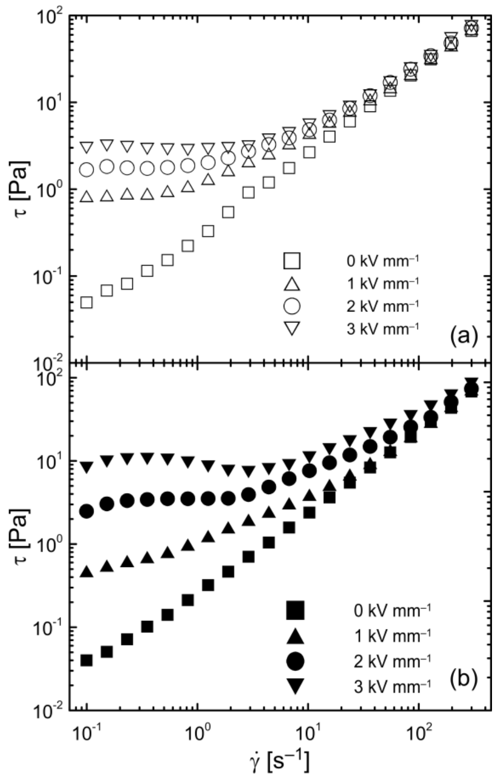

Fig. 4. The log-log dependence of shear stress, τ, on the shear rate, $\dot{\gamma}$, for ER fluids based on (a) $BaTiO_3$ 35 particles and (b) $BaTiO_3$ 20 particles in the presence of various electric field strengths of at 25 °C.

Not only that ER fluids should exhibit high ER effects, but a high difference between their viscosity in the presence of an external electric field, η_E, and field-off viscosity, η_0, is of high interest. This feature is well embodied in an equation of ER efficiency $e=(\eta_E-\eta_0)/\eta_0$. It can be seen that at electric field strength 1 kV mm^{-1} the ER efficiency is nearly the same for both prepared ER fluids. However, in the case of electric field strength 3 kV mm^{-1}, the ER efficiency is higher for the $BaTiO_3$ 35-based ER fluid in the whole shear rate region due to its significantly higher ER effect at 3 kV mm^{-1} which is a consequence of its significantly higher ER effect at stronger electric fields.

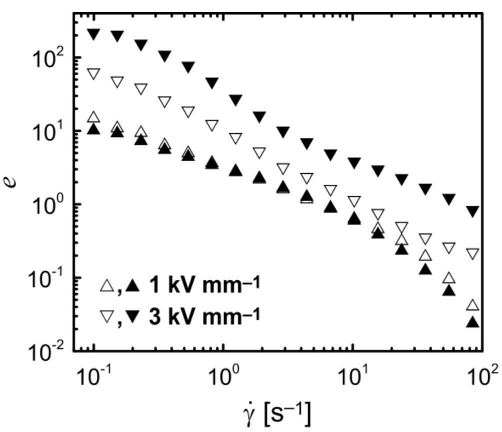

Fig. 5. The dependence of ER efficiency, e, on the shear rate, $\dot{\gamma}$, for prepared ER fluids based on $BaTiO_3$ 20 (open symbols) and $BaTiO_3$ 35 (full symbols) particles in the presence of electric field of strength 1 kV mm^{-1} and 3 kV mm^{-1}.

CONCLUSION

Barium titanates were prepared via a facile and fast molten-salt microwave-assisted synthesis. The particles size was controlled by a synthesis time, where the longer synthesis time leads to bigger particles. The barium titanates particles possessing cube-like morphology were mixed with silicone oil in order to obtain ER fluids, and the effect of the particles size on the electrorheological effect was investigated. It was found that at lower electric field strength, the ER fluid based on smaller particles exhibits higher ER effect that the ER fluid based on the bigger particles. However, at certain electric field strength, the ER effect of the ER fluids based on bigger particles starts to surpass the ER effect of the second one. It can be summarized, that the full-field-on-state performance of ER systems depends on stiffness of formed columnar particle structures which is higher for bigger particles while the threshold for turning on the ER effect lays lower for smaller particles, which gives more sensitivity to the system due to their enhanced mobility under external field. Nevertheless, the complex study on the influence of particles size on the ER effect is still missing. In our case and in literature[14], it was found that bigger particles lead to higher or effect. On the other hand, a study demonstrating contrary results has been introduced[15]. The detailed mechanism will be an object of further investigation.

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