Synthesis and electrorheology of rod-like titanium oxide particles prepared via microwave-assisted molten-salt method

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Abstract

The rod-like titanium dioxide (TiO_2) particles were synthesized by a simple and rapid microwave-assisted molten-salt method. The X-ray diffraction analysis revealed the phase composition transformation from the anatase phase of original TiO_2 nanomaterial to the rutile phase of high crystallinity. Scanning electron microscopy proved the conversion of originally globular particles of original anatase TiO_2 sized from 200 to 500 nm into rods with a length of 5 to 10 μm and a diameter between 0.5 and 2 μm. The electrorheological (ER) measurements performed under steady-state flow as a function of the applied electric field strength and particle concentration showed that suspended rutile rod-like TiO_2 particle-based fluid exhibits much higher ER activity than that of original anatase TiO_2 material powder. These observations were clearly demonstrated by viewing their dielectric spectra analyses.

Keywords: Electrorheology, Titanium oxide, Rod-like particles, Rutile, Anatase, Microwave-assisted molten-salt method, Dielectric properties

1 Introduction

Electrorheological (ER) fluids are two phase systems consisting of polarizable semiconducting particles homogenously dispersed within an insulating carrier liquid. These systems are worthy of research thanks to their phase-controllable behaviour under an external electric field. In principle, the imposed electric field polarizes originally randomly dispersed particles and forms a chain-like or columnar internal structure of particles spanning the gap between electrodes [1-4]. As a result, rheological properties such as shear stress, apparent viscosity or viscoelastic moduli of the fluids change by several orders of magnitude. When the electric field is switched off, the suspension properties return to their original state. The changes are very fast and reversible. Due to this behaviour the ER fluids could be exploited for various technical applications, such as hydraulic valves or clutches, torque transducers or various hydraulic damping systems [5].

Recently, developments in the fabrication of one-dimensional inorganic particle have greatly progressed. These materials offer promise as a dispersed phase of novel ER fluids since they exhibit enhanced polarizability and thus improved ER performance under an external electric field compared to classic globular particular systems [6-9]. Previous studies concentrating on the synthesis of one-dimensional particles suitable for ER fluids were based on hydrothermal methods under alkali conditions [10,11]. However, these methods are time-consuming, and the use of an alkali solution at high temperatures under high pressure can be rather dangerous.

This paper is focused on the study of the ER and dielectric properties of suspensions of rod-like titanium dioxide (TiO_2) particles prepared by a molten-salt microwave-assisted method [12]. Molten-salt synthesis based on the use of a low-melting solvent to accelerate diffusion and thus the formation of the required structure is one of the simple one-step methods to obtaining a product with high crystallinity [12]. Due to introducing microwaves into the synthesis process, uniform heating provides a faster reaction in comparison to the conventional method.

2 Experimental

2.1 Materials

Titanium(IV) dioxide powder in an anatase crystalline phase (99.8 % trace metal basis, Sigma-Aldrich, USA) was used as a precursor for the synthesis. Sodium chloride (NaCl, Penta, Czech Republic) and sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12\ H_2O$, Penta, Czech Republic) which has a eutectic at 735 °C when the molar ratio of disodium phosphate is 20 % [13], were used as a molten environment. All chemicals were used as received without further purification.

2.2 Synthesis of rutile TiO_2 rod-like particles

TiO_2 rod-like particles were obtained by applying a simple and rapid microwave-assisted molten-salt method in the presence of a molten sodium salt flux (Fig. 1). The first step in the synthesis was grinding the TiO_2 powder with an eutectic mixture of NaCl / $Na_2HPO_4 \cdot 12\ H_2O$ in a mortar in order to obtain homogenous reaction mixture. The ratio of raw material to the flux mixture was set at 4:5. This mixture was subsequently transferred into the corundum crucible and covered by a corundum lid. The crucible was placed into a special ceramic kiln suitable for heating in microwaves. The inside cover of this kiln is coated with a microwave absorbing layer that speeds up heating when exposed to microwaves and, thus, enables a rapid increase of temperature inside the kiln. The kiln was placed into the cavity of a common domestic microwave oven (Hyundai, Korea) and exposed to microwaves at the standard frequency of 2.45 GHz for 30 min at 750 W. After heating, the kiln was removed from the oven and allowed to cool to room temperature. The obtained powder was washed several times with demineralized water and filtered off. The product as-prepared was then dried at 60 °C in a vacuum to a constant weight.

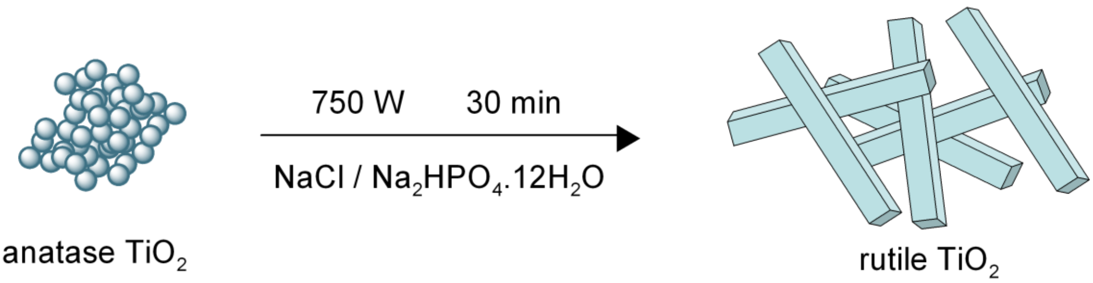

Fig. 1 Schematic illustration of the formation of rutile TiO_2 rod-like particles

2.3 Particle characterization

The crystalline and phase composition of original TiO_2 powder with anatase phase and prepared rod-like particles were examined via the X-ray diffraction (XRD) patterns collected on an X'Pert PRO (Philips, the Netherlands) diffractometer with Cu $K_{\alpha 1}$ radiation (λ = 1.54 Å) and a scanning rate of 4° min^{-1} for the recording data in the wide range of $2\theta = 10°–95°$.

Obtained patterns were evaluated by a semi-quantitative analysis performed through PANalytical X'Pert High Score on the basis of reference intensity ratio values.

The TiO_2 phases of original anatase material and prepared rod-like particles from powder XRD patterns are shown in Fig. 2. The narrow and most intensive peaks signify good crystallinity and can be indexed to the tetragonal rutile phase according to JCPDS card No. 21-1276 with lattice constants a = 4.593 Å and c = 2.959 Å. Hence, the use of molten-salt microwave-assisted synthesis with a reaction time of 30 min is sufficient for the TiO_2 phase transformation from anatase phase to rutile phase with high crystallinity. It is worth noting the presence of diffraction peaks of the residual anatase phase (JCPDS card No. 21-1272) in the XRD pattern of the prepared rod-like particles. However, the crystalline ratio is 92 % of rutile and 8 % of anatase in the sample according to the semi quantitative analysis of the XRD pattern.

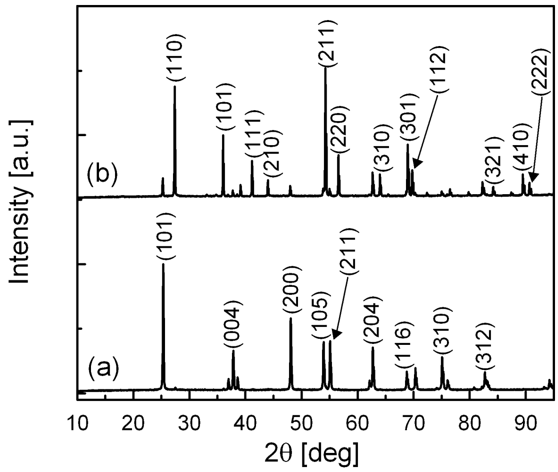

Fig. 2 Powder XRD patterns of the original anatase TiO_2 particles **(a)** and prepared rod-like TiO_2 particles **(b)**

The size and morphology of studied particles were observed with a SEM (Scanning Electron Microscope VEGA II LMU, Tescan, Czech Republic) operated at 30 kV for the starting anatase TiO_2 and 10 kV for the prepared rutile TiO_2 (Fig. 3). As demonstrated, the starting TiO_2 particles of anatase phase have a rather globular shape with a size ranging from 200 to 500 nm. On the other hand, TiO_2 particles of rutile phase prepared via molten-salt microwave-assisted synthesis have a rod-like shape with a length from 5 to 10 μm and a diameter from 0.5 to 2 μm. Thus, the geometric aspect ratio, *L/D*, of prepared TiO_2 particles ranges from 2.5 to 20.

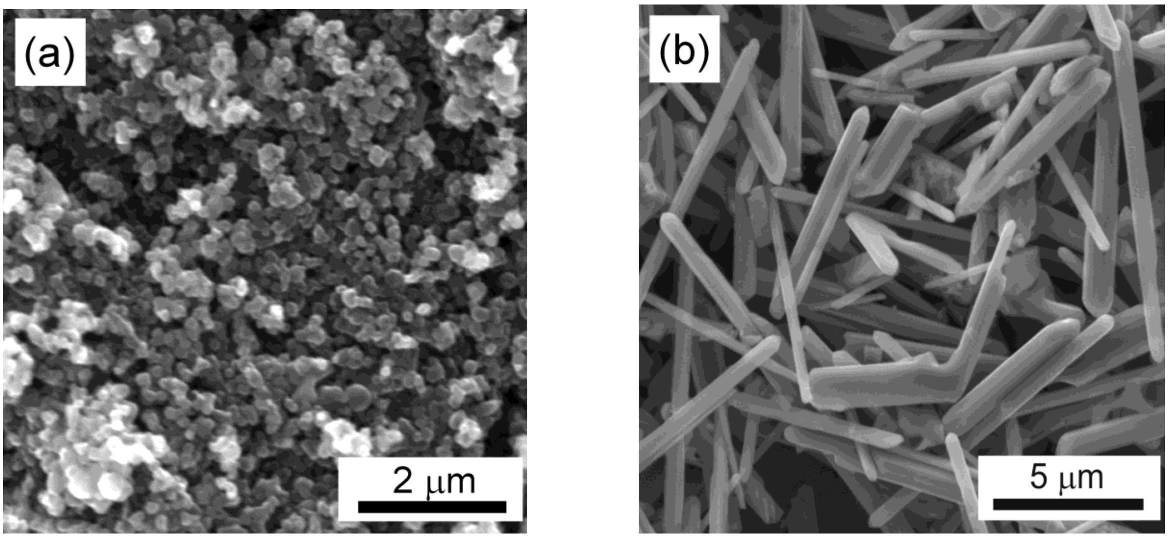

Fig. 3 SEM images of original anatase TiO_2 **(a)** and prepared rutile TiO_2 **(b)** particles prepared via molten-salt microwave-assisted synthesis

2.4 Preparation of ER fluids

The ER fluids (5, 10, 15 vol.%) were prepared by mixing anatase powder or rutile TiO_2 rod-like particles with a corresponding volume of silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic, viscosity $\eta_c = 200$ mPa·s, density $\rho_c = 0.965$ g·cm^{-3}, conductivity $\sigma_c \approx 10^{-11}$ S·cm^{-1}, relative permittivity $\varepsilon'_c = 2.6$, loss factor tan $\delta = 0.002$). To avoid the influence of moisture the silicone oil was dried at 80 °C for 24 h. The ER fluids were stirred mechanically and then placed in an ultrasonic bath for 60 s before each measurement.

2.5 Electrorheological measurements

Measurements of the rheological properties of prepared ER fluids were carried out at 25 °C using a rotational rheometer (Bohlin Gemini, Malvern Instruments, UK), with coaxial cylinder geometry (length 27.4 mm, inner cylinder of 14 mm in diameter and the outer cylinder separated by a 0.7–mm gap), modified for ER experiments. A DC voltage (0.35 kV until 2.1 kV) corresponded to the electric field strength range 0.5 – 3 kV·mm^{-1} was generated by a DC high-voltage source TREK (TREK 668B, USA). A DC voltage was applied for 60 s to generate the equilibrium chain-like structure of particles before shearing. All steady-shear tests were performed in the shear rate range 0.1 – 300 s^{-1} (controlled shear rate mode). After the measurement at the given electric field strength, the formed internal structure within the fluid was destroyed by shearing the sample at a shear rate 20 s^{-1} for 120 s prior to characterization at a different electric field values.

2.6 Dielectric properties

Dielectric properties involving the frequency spectra of relative permittivity, ε', and dielectric loss factor, ε'', in the frequency range $4\times10^{1} - 5\times10^{6}$ Hz have been measured with an impedance analyzer (Agilent 4524, Japan). Although the Cole-Cole equation has been frequently used for investigation of dielectric properties of many ER fluids [14], the dielectric spectra (Fig. 4) expressed by complex permittivity ε^* were analyzed in this study using Havriliak–Negami model [15] fitted by the least square method (Eq. 1) by which the asymmetry of relaxation peak can be more properly fitted:

$$\varepsilon^* = \varepsilon'_\infty + \frac{\Delta\varepsilon'}{\left(1+\left(i\omega\cdot t_{\mathrm{rel}}\right)^a\right)^b} \qquad (1)$$

where ε^* is complex fluid permittivity, the dielectric relaxation strength, $\Delta\varepsilon'$, is defined as the difference between ε'_0 and ε'_∞, which are the limit values of the relative permittivity at the frequencies below and above the relaxation frequency, ω is angular frequency ($= 2\pi f$), t_{rel} is relaxation time, a is the scattering degree of relaxation times, and b is related to the asymmetry of the relaxation time spectrum. The relaxation frequency, at which the dielectric loss factor ε'' has is at its maximum, is proportional to the rate of polarization of suspension particles.

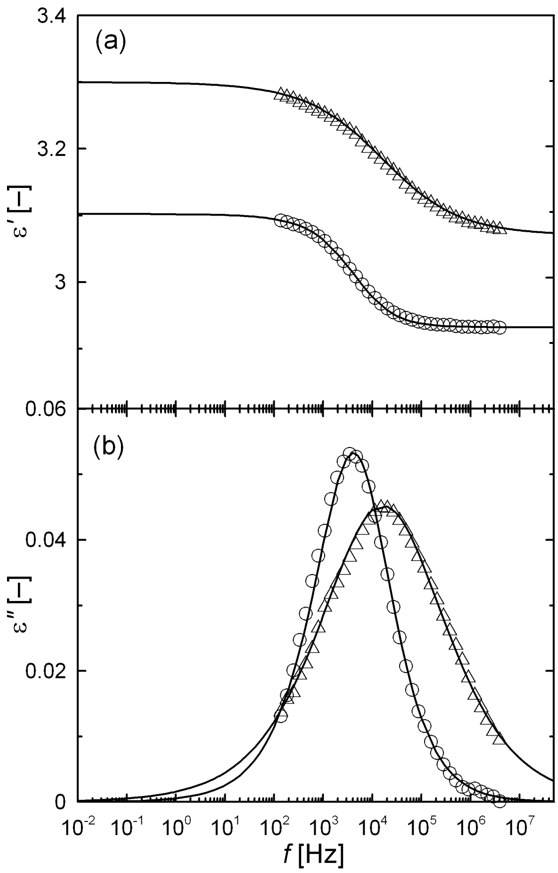

Fig. 4 Relative permittivity, ε', **(a)** and dielectric loss factor, ε'', **(b)** as a function of the frequency, *f*, for 5 wt.% suspension of original anatase TiO_2 powder (○) and TiO_2 rod-like particles (△) in silicone oil.

Table 1. Dielectric parameters in Eq. 1 for original anatase TiO_2 particles and prepared rod-like TiO_2 particle-based ER fluids of 5 wt.% concentration

Parameter	Anatase TiO_2	TiO_2 rod-like
ε'_0	3.10	3.30
ε'_∞	2.93	3.07
$\Delta\varepsilon'$	0.17	0.23
t_{rel} [s]	3.00×10^{-5}	9.06×10^{-6}

3 Results and discussion

3.1 ER activity and dielectric properties

The flow curves of the shear stress and viscosity vs. shear rate for suspensions of the original anatase TiO_2 powder and prepared rutile TiO_2 rod-like particles are plotted in Fig. 5. The electric field-off shear stress depends almost linearly on the shear rate, indicating a Newtonian flow of non-polarized particles (Fig. 5a). Suspension viscosity of the anatase powder predominates (Fig. 5b), probably due to the nano-sized nature of particles having a much larger surface area. Under electric field application, both ER fluids exhibit a typical Bingham plastic behaviour in the low-shear rate region, showing the prevalent feature of the ER activity. The flow became pseudoplastic, and the ER response of rutile TiO_2 rod-like particles was higher as the stronger chain-like structure developed due to better particle dielectric relaxation strength [16]. Both systems also show typical shear thinning behaviour as the deformation rate of the chain-like structure produced by hydrodynamic forces becomes faster than its reformation rate given by the dielectric relaxation strength of the particles with an increase in the shear rate. Generally, the chain-like structure is formed by induced electrostatic interactions between dispersed dielectric particles caused by interfacial polarization. The dielectric spectra (Fig. 4) and their characteristics in Table 1 indicate that rod-like TiO_2 particles exhibit an enhanced magnitude of $\Delta\varepsilon'$ related to the electrostatic interactions between particles and decreased relaxation time, t_{rel}, reflecting the rate of interfacial polarization compared to original TiO_2 particles due to higher induced charges on the interface between the particles [17,18]. Similar rheological behaviour with the meaning of the stronger internal structures formation in one-dimensional particles based ER fluid compared to globular ones due to the difference in aspect ratio of the particles leading to different effective electrostatic forces between particles was observed using alternating electric field [19].

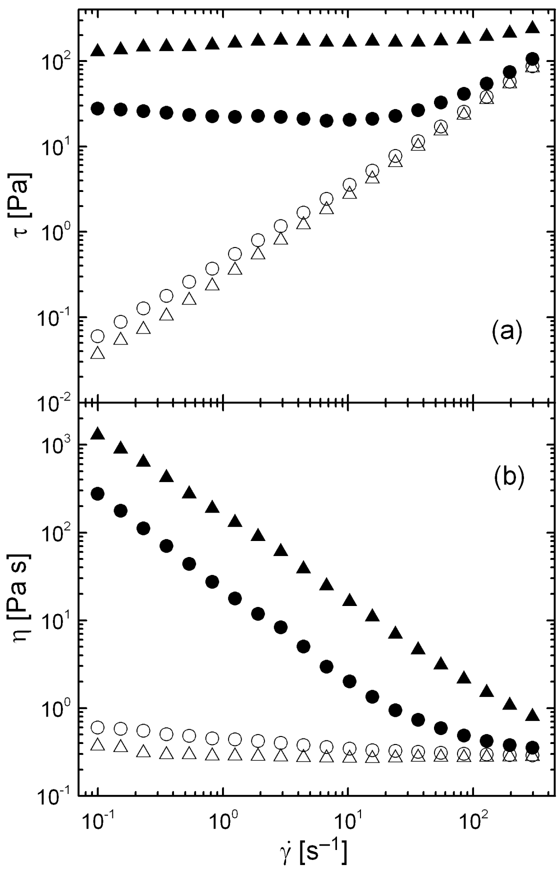

Fig. 5 Double-logarithmic plot of the shear stress, τ, **(a)** and the apparent viscosity, η, **(b)** vs. shear rate, $\dot{\gamma}$, for 15 wt.% suspension of original anatase TiO_2 (●,○) and prepared rutile TiO_2 rod-like (▲,△) particles in silicone oil. The electric field strengths, E (kV·mm^{-1}): 0 (○,△), 3 (●,▲)

3.2 Steady-state flow properties

As a representation of rutile TiO_2 rod-like particles, Fig. 6 shows typical flow and viscosity curves for 15 wt.% ER suspension under different electric field strengths. It is worth noting that a small peak in the shear stress develops during the shearing of the suspension at moderate shear rates in higher electric field strengths. This phenomenon is attributed to the rearrangement in the ER structures from chain-like structures to lamellar ones due to the lowering of the free energy in the system [20,21].

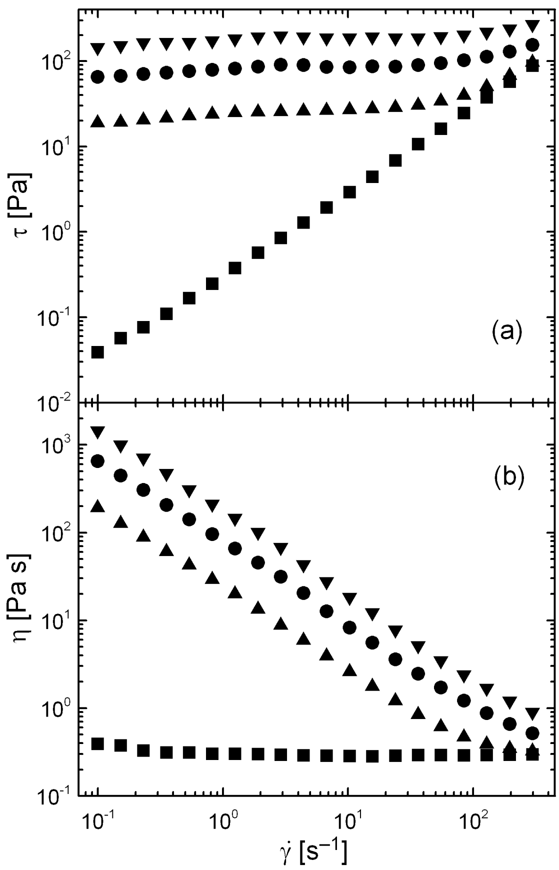

Fig. 6 Double-logarithmic plot of the shear stress, τ, **(a)** and viscosity, η, **(b)** vs. shear rate, $\dot{\gamma}$, for 15 wt.% ER fluid of rutile TiO_2 rod-like particles in silicone oil at various electric field strengths, E (kV·mm^{-1}): 0 ■, 1 ▲, 2 ●, 3 ▼

Furthermore, the value of electric field-off viscosity is another important factor in the evaluation of the efficiency of ER phenomenon for practical use. The efficiency of the ER effect corresponding to a relative increase in electroviscosity, $\Delta\eta_E = \eta_E - \eta_0$, can be characterized by a quantity $e = (\eta_E - \eta_0)/\eta_0$, where η_E is a viscosity of the ER structure [22]. The ER efficiencies for ER fluids based on original anatase and rutile TiO_2 rod-like particles of different weight concentrations are shown in Fig. 7. Obviously, the efficiency of ER fluid increases with the particle concentration, indicating that the maximum concentration for maximum ER efficiency, $e_{max.}$, was still not reached in this study. Comparing these results with those obtained for ER fluids consisting of globular rutile [23] or original anatase TiO_2 particles (open symbols), it is evident that rod-like particles posses higher ER efficiency, probably due to lower field-off viscosity and higher particle dielectric relaxation strength both given by the prevailing one dimensional morphology of the particles.

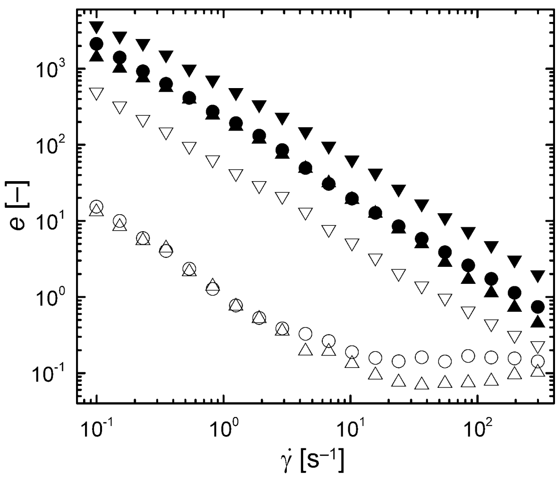

Fig. 7 The dependence of ER performance, *e*, on the shear rate, *g*, for the suspensions of original anatase TiO_2 (open) and prepared rutile TiO_2 rod-like (solid) particles in silicone oil. Particle concentrations (wt.%): 5 (△,▲), 10 (○,●), 15 (▽,▼)

3.3 The response to an electric field and shear rate

The increase in the rigidity of formed internal structures within the ER fluids with electric field applied is shown in Fig. 8. The shear stresses, τ_c, at low shear rates $\dot{\gamma} = 0.23$ s^{-1} have been used as a criterion of the rigidity of static particle chain-like structures due to the problematic determination of dynamic yield stress by the extrapolation of the shear stress to zero shear rate. Evidently, the log τ_c vs. log *E* obeys the power law $\tau_c = q \cdot E^{\alpha}$. The response of particles to the electric field strength is $\alpha = 2$ as expected from the polarization model [24]. The almost one order of magnitude higher *q* value for the suspension of rod-like TiO_2 particle confirms a strong increase in ER activity in comparison with the suspension of globular TiO_2 nanoparticles.

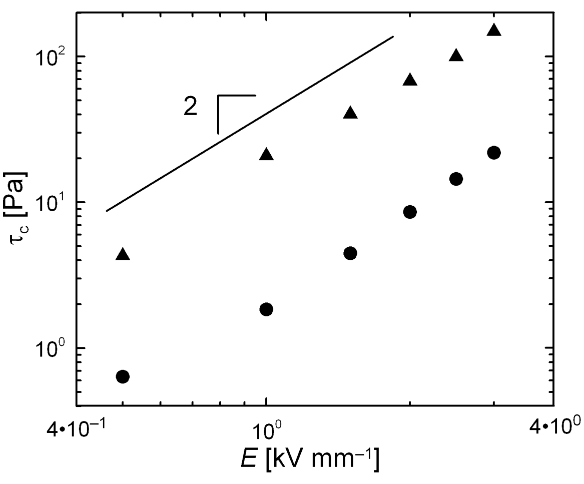

Fig. 8 Double-logarithmic plot of the shear stress, τ_c, vs. electric field strength, *E*, for 15 wt.% suspension of original anatase TiO_2 (●) and rutile TiO_2 rod-like (▲) particles in silicone oil.

Furthermore, a plot of normalized viscosity, η/η_c, versus the ratio of hydrodynamic to electrostatic forces, $\dot{\gamma}/E^2$, for ER fluids of globular and rod-like TiO_2 particles at 3 kV·mm^{-1} is shown in Fig. 9 to illustrate the competition between hydrodynamic and electrostatic forces. At low ratio of acting forces ($\dot{\gamma}/E^2 < 1$) the electrostatic forces are dominant over hydrodynamic ones and yielding values of normalized viscosity for rod-like particles based suspension is almost order of magnitude higher than that for globular ones. Moreover, both types of ER fluids have linear dependence with slope of - 1 in this region as can be expected from the literature [25]. For $\dot{\gamma}/E^2 > 1$, the hydrodynamic forces start to dominate over electrostatic ones as indicated by flat region for the curve of globular TiO_2 particles. On the other hand, rod-like TiO_2 particles have this region moved to higher values of $\dot{\gamma}/E^2$, which was not reached in this study, probably due to much stronger electrostatic forces given by one-dimensional character of particles in suspension.

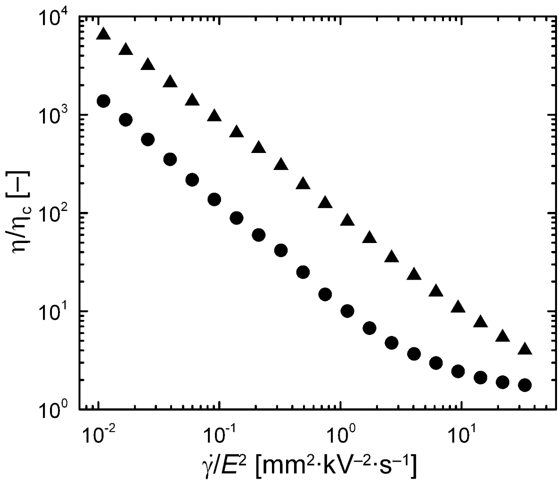

Fig. 9 Normalized viscosity, η/η_c, of 15 wt.% suspension of original anatase TiO_2 (●) and rutile TiO_2 rod-like (▲) particles in silicone oil as a function of ratio of hydrodynamic to electrostatic forces, $\dot{\gamma}/E^2$.

3.4 Reproducibility of ER structure

The reproducibility of the ER phenomenon is also an important factor for the practical application of ER fluids. The alternate switching on/off of the electric field should provide the same ER efficiency, i.e. the same ER structure should be formed rapidly. Fig. 10 depicts that the reproducibility after switching on/off cycles for rutile TiO_2 rod-like particle-based ER fluid sheared at 1 s^{-1} and 1.5 kV·mm^{-1} is fulfilled.

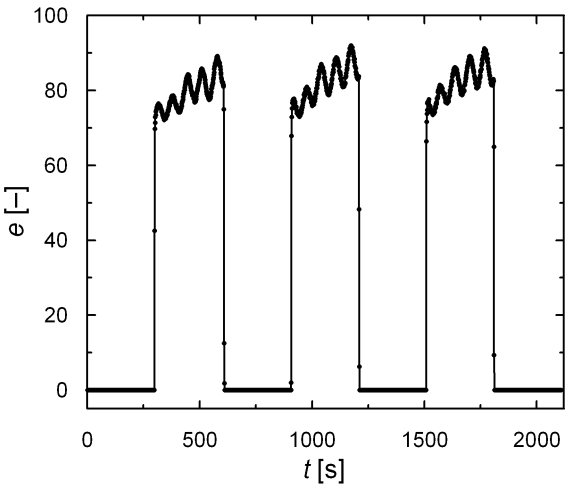

Fig. 10 Time dependence of ER performance, *e*, in the alternate switching on (E = 1.5 kV·mm^{-1})/off regime for 15 wt.% suspension of rutile TiO_2 rod-like particles in silicone oil M200 at the constant shear rate $\dot{\gamma}$ = 1 s^{-1}.

4 Conclusions

Rutile TiO_2 rod-like particles were prepared via microwave-assisted molten-salt synthesis as a dispersed phase of a novel ER fluid. To gain insight into the ER activity of prepared ER suspensions, rheological properties were evaluated under various experimental conditions, such as shear rate, electric field strength, and particle weight concentration. The steady-shear measurements showed that the ER efficiency of rod-like TiO_2 particles was significantly higher compared to original anatase TiO_2 particles. Moreover, the higher ER activity was in good correlation with dielectric spectroscopy measurements as the dielectric relaxation strength was improved and relaxation time lowered for rod-like particles. The maximal ER efficiency was moved to higher weight concentrations for rod-like particles used as a dispersed phase probably due to lower field-off viscosity and higher particle dielectric relaxation strength.

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