Electrorheological behaviour under oscillatory shear of TiO$_2$ rod-like particles prepared via microwave-assisted molten-salt synthesis

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Abstract. Titanium dioxide (TiO$_2$) rod-like particles were synthesized by a simple and rapid microwave-assisted molten-salt method. The X-ray diffraction analysis and electron microscopy provided information on particle composition and morphology, respectively. It was found that during the synthesis process the crystalline phase of TiO$_2$ transformed from anatase into rutile while the morphology changed from nanospheres into micrometer sized rod-like particles. The electrorheological (ER) properties were investigated via oscillatory shear tests. It was found that TiO$_2$ rod-like particles based silicone oil suspensions exhibited higher ER activity than those of original anatase TiO$_2$ nanoparticles probably due to side-by-side solid friction between particles as well as shorter time of their polarization. The changes in ER properties of rod-like particle based suspensions as a function of the applied electric field strength and particles weight fraction were also investigated.

1. Introduction
Electrorheological (ER) fluids are usually two-phase systems that undergo a tunable and reversible liquid to solid-like state transition upon external electric field application [1-3]. Typical ER fluids are composed of electrically polarizable particles dispersed in a non-conducting carrier liquid. In the absence of an electric field, ER fluids typically exhibit Newtonian behaviour. When the electric field is applied, the interfacial polarization of particles occurs resulting in the aggregation of particles into chain-like structures aligned in the direction of the field streamlines [4, 5]. Such a response usually takes place in a millisecond scale and is accompanied with the increase of rheological properties including viscosity, shear stress, and viscoelastic moduli. This phenomenon called ER effect is moreover completely reversible when the electric field is switched off. Hence, ER fluids could be used in various technical applications such as in automotive industry for clutches, brakes or damping systems [6].

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Basically, the particle geometry can play a significant role in their ER response, since one-dimensional particles, whose major axis is aligned according to the field direction and have the same relative permittivity and volume as spherical particles, will form stronger internal structures [7,8]. Great influence of particles anisotropy was examined for example in ER fluids based on conducting polymers in which the ER performance was enhanced in comparison with fluids based on microspheres [9,10]. It is also obvious that anisotropic particles exhibit better sedimentation stability due to the hindered settling, easier redispersion as well as lower concentration necessary for the formation of chain-like structures spanning the operating gap [7]. However, the ER performance of anisotropic particle based ER fluids has been scarcely studied probably due to the lack of suitable methods for preparation of such particles.

In this study, with a view to prepare a novel anisotropic material with a good ER performance, the rod-like particles of titanium dioxide (TiO_2) were synthesized via a simple and rapid microwave-assisted molten-salt method. This technique is based on the use of low-melting salts to accelerate diffusion and thus formation of required structures with high crystallinity [11]. Moreover, a novel principle of microwave heating was used instead of classical heating in an oven that shortened the reaction time significantly. Furthermore, a comparison with the viscoelastic behaviour of suspensions of spherical TiO_2 particles was performed.

2. Experimental

2.1. Materials
Starting material for the synthesis titanium (IV) dioxide powder consisted of anatase crystalline phase (99.8% trace metal basis) was purchased from Sigma-Aldrich (USA). Salts used as molten environment were sodium chloride (NaCl, Penta, Czech Republic) and sodium phosphate dibasic dodecahydrate ($Na_2HPO_4.12H_2O$, Penta, Czech Republic) and they form eutectic mixture at 735°C. All chemicals were used as received.

2.2. Synthesis of TiO_2 rod-like particles
Titanium dioxide rod-like particles were prepared by a solvent-free and rapid microwave-assisted molten-salt method in a ceramic kiln with microwave-absorbing layer which enables fusing at high temperatures while the kiln is exposed to microwaves in a microwave oven [12]. Briefly, original TiO_2 of anatase crystalline phase was homogenized with eutectic mixture of NaCl / $Na_2HPO_4.12H_2O$ in a ratio of 4:5. The as prepared powder mixture was placed into corundum crucible, covered by a lid and placed into the ceramic kiln. The kiln was subsequently placed into microwave oven (Hyundai, Korea) and exposed to microwaves at standard frequency 2.45 GHz for 30 minutes at 750 W. After the reaction, the whole kiln was allowed to cool down to room temperature prior opening the corundum crucible. The obtained product was washed several times with distilled water and vacuum dried at 80°C for 12 hours.

2.3. Particle characterization
The crystallinity and phase composition of starting TiO_2 with anatase crystalline phase and prepared powder was carried out with X'Pert PRO (XRD, Philips, the Netherlands) X-ray diffractometer, fitted with copper target, Kα ray, scanning rate of 4° min^{-1} for the recording data in the range of $2\theta = 20° - 90°$ (360 kV, 20 mA). The morphology of starting TiO_2 and prepared powder was determined with TEM (Transmission Electron Microscopy JEOL 1200, JEOL Ltd., Japan) and SEM (Scanning Electron Microscope VEGA II LMU, Tescan, Czech Republic) operated at 10 kV, respectively.

2.4. Electrorheological measurements
The 5, 10, 15, and 20 wt.% ER fluids were prepared by dispersing the original anatase TiO_2 or prepared rod-like TiO_2 particles in a corresponding volume of silicone oil (Lukosiol M200, Chemical

Works Kolín, Czech Republic, viscosity $\eta_c = 200$ mPa·s). Before each measurement, the fluid was stirred first mechanically and then in an ultrasonic bath for 60 s.

Rheological measurements were performed using a rotational rheometer (Bohlin Gemini, Malvern Instruments, UK) modified for ER experiments, with a coaxial cylinder geometry. The fluids were placed into a Couette cell with a rotating inner cylinder of 14 mm diameter and stationary outer cylinder separated by 0.7 mm gap. DC high-voltage source TREK (TREK 668B, USA) was connected to the rheometer to generate the electric field strength 0–3 kV·mm^{-1}. Before each measurement at new electric field strength used, the formed internal structure within the suspension was destroyed by shearing of the sample at a shear rate 20 s^{-1} for 150 s. Further, dynamic viscoelastic tests were carried out by dynamic strain and frequency sweeps. The strain sweep was performed with applied strain in the range from 10^{-4} to 10^{-2} at the frequency of 6.28 rad·s^{-1} under an electric field to determine the linear viscoelastic region (LVR). The viscoelastic moduli were subsequently obtained from the frequency sweep tests (0.63 – 62.83 rad·s^{-1}) at a fixed strain amplitude in the LVR. The temperature in all experiments was kept at 25°C.

2.5. Dielectric properties
The frequency dependence of dielectric properties (relative permittivity, ε', and dielectric loss factor, ε'') were obtained with an impedance analyzer (Agilent 4524, Japan) in the frequency range $4 \times 10^1 - 5 \times 10^6$ Hz. The dielectric spectra were characterized with a Cole–Cole model [13,14] (Equation 1).

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\Delta\varepsilon'}{(1 + i\omega\lambda)^{1-\alpha}} \tag{1}$$

where polarizability, $\Delta\varepsilon'$, is the difference between static, ε'_0, and high frequency, ε'_∞, relative permittivities, ω, is angular frequency (=$2\pi f$), λ, is dielectric relaxation time (=$1/2\pi f_{max}$), in which f_{max}, is defined by a local maximum of the dielectric loss of ER fluid, and, α, is the scattering degree of relaxation times.

3. Results and discussion

3.1. Particles characterization
According to the XRD analysis (Figure 1), the microwave-assisted molten-salt synthesis transformed the original anatase crystalline phase of starting TiO$_2$ almost completely into the rutile crystalline phase in prepared particles, i.e. although there are presented some low diffraction peaks of anatase phase in the XRD pattern of prepared TiO$_2$ particles. The narrow and most intensive peaks show very good crystallinity and can be indexed to the tetragonal rutile phase.
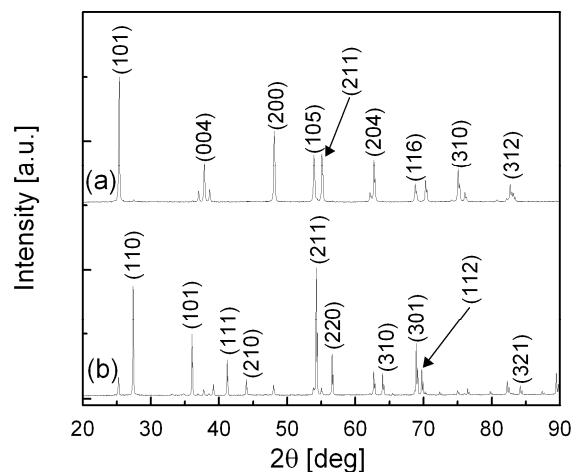
Figure 1. Powder XRD patterns of original anatase TiO$_2$ particles (a) and prepared TiO$_2$ rod-like particles via microwave-assisted molten-salt synthesis (b).

The changes in TiO_2 particle size and shape resulting from the use of microwave-assisted molten-salt synthesis were determined by TEM and SEM image analysis shown in Figure 2. Particles of original anatase TiO_2 are approximately spherical with mean particle size of about 200 nm. On the other hand, the successful transformation from spherical nanoparticles to rod-like microparticles is evident from Figure 2b. The length of rod-like particles is ranging from 5 to 10 μm while the diameter from 0.5 to 2 μm. The geometric aspect ratio, *L/D*, of prepared TiO_2 particles is correspondingly ranging from 5 to 10.
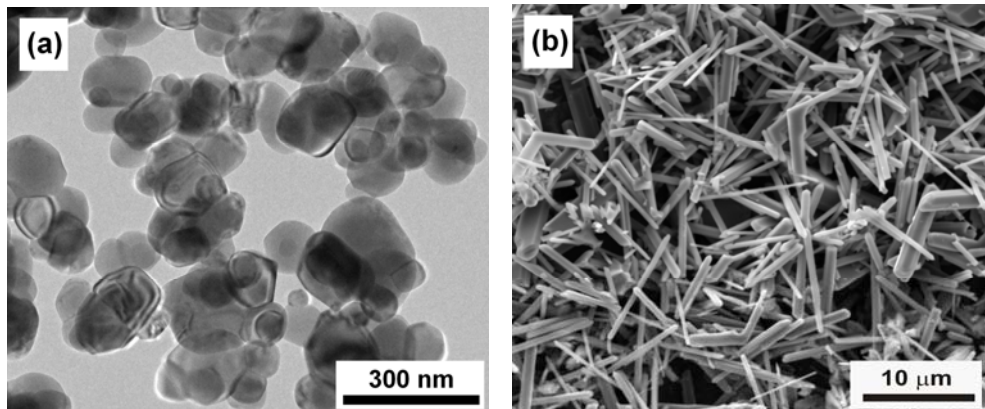
Figure 2. Electron micrographs of original anatase TiO_2 (a) and prepared rutile TiO_2 rod-like particles (b).

3.2. ER activity of prepared ER fluids

In order to check the structure formation within the ER fluid (Figure 3), dilute suspension of prepared rod-like TiO_2 particles was placed between microscope slides (the gap was fixed to 1 mm) connected to DC high-voltage source KEITHLEY (2400, USA). As can be seen in Figure 3a, in the absence of external electric field strength the particles are randomly dispersed. However, although the suspension was carefully mixed right before the observation, some particles are gathered together into aggregates. Such phenomenon could be caused by short-range attractive forces (Van der Waals or electrostatic) or mechanical cohesion between rod-like particle surfaces due to the solid friction between particles [13,14]. When the electric field is applied (Figure 3b), particles start to be polarized and the chain-like structure from connected particles is created between electrodes. Agglomerates formed in the absence of the field remain gathered resulting in incomplete alignment of individual particles with the field.
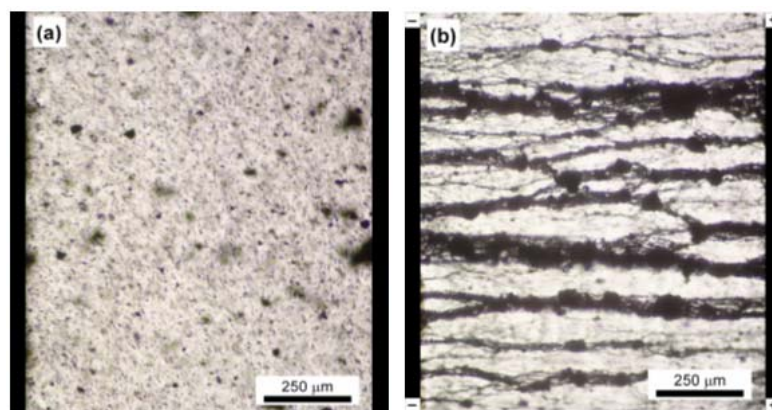

Figure 3. Optical micrographs of dilute ER fluid of TiO_2 rod-like particles in the absence (a) and in the presence of external electric field strength of 0.5 kV·mm^{-1} (b).

It is generally accepted that interfacial polarization of particles connected with the formation of chain-like structures in the presence of electric field is responsible for rheological changes of ER fluids (Figure 4). Hence, parameters obtained from equation 1 were used to help understand the ER activity of ER fluids based on TiO_2 spherical or rod-like particles (Table 1). Although, polarizability of particles, $\Delta\varepsilon'$, is relatively low, the time of their relaxation, λ, is much lower in the case of rod-like particles than those reported in ER fluids of various spherical particles [15,16], which indicates faster response to an electric field. It means that TiO_2 rod-like particles of rutile crystalline phase are polarized in shorter time, which may, consequently, contribute to their better ER activity in comparison with TiO_2 nanospheres of anatase crystalline phase.

Table 1. Dielectric parameters in equation 1 for original anatase TiO_2 particles and prepared rod-like TiO_2 particles based ER fluids (5wt.% concentration).

| Parameter	Anatase TiO_2	TiO_2 rod-like
ε'_0 [−]	3.09	3.30
ε'_∞ [−]	2.93	3.07
$\Delta\varepsilon'$ [−]	0.16	0.23
λ [s]	4.45×10^{-5}	9.06×10^{-6}
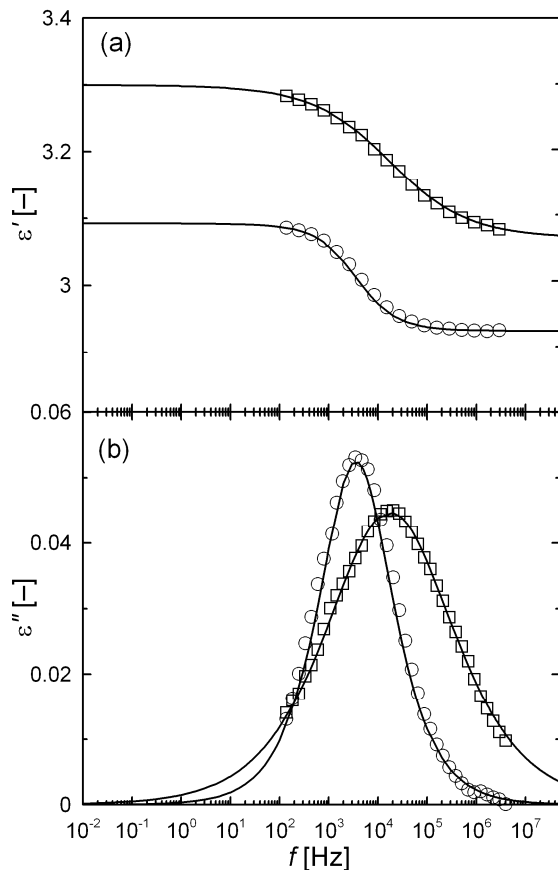
Figure 4. Relative permittivity, ε', (a) and dielectric loss factor, ε'', (b) as a function of frequency, f, for 5 wt.% suspension of original anatase TiO_2 particles (O) and prepared TiO_2 rod-like particles (□).

The stiffness of internal structures formed within the ER fluid in the presence of external electric field can be determined via the dependence of complex viscosity, η^*, on the angular frequency, ω. Figure 5 compares ER activity of TiO_2 rod-like particles with original TiO_2 nanoparticles at the same concentration. In the absence of electric field, rod-like particles based ER fluid exhibits almost Newtonian behavior while the suspension of original anatase nanoparticles is slightly pseudoplastic. On the other hand, strong electrostatic interactions in the presence of external electric field cause chain-like structure formation within the suspension which leads to a considerable enhancement of system stiffness. A further increase in pseudoplasticity occurs with increasing electric field strength applied. Moreover, the shear thinning behavior is also clearly observed with increasing frequency. Evidently, much stronger structures (higher viscosity) are formed in the rod-like particle based ER fluid at all electric field strengths applied due larger polarizability (Figure 4) and higher solid friction between particles [13]. The lower field-off viscosity and higher stiffness in the electric field consequently indicate higher ER efficiency of TiO_2 rod-like particle suspensions.
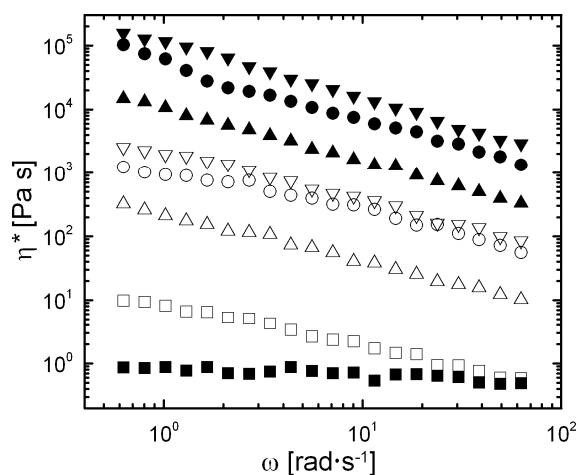

Figure 5. Dependence of complex viscosity, η^*, on angular frequency, ω, for 20wt.% suspensions of TiO_2 rod-like (solid symbols) and anatase TiO_2 (open symbols) particles in silicone oil at 25°C under various electric field strengths (kV mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

The formation of the internal chain-like structures of polarized particles in the presence of electric field is also accompanied by a change of viscoelastic moduli. Thus, Figure 6 shows the dependence of storage, G', and loss, G'', moduli on the strain amplitude, γ, in oscillatory flow for 20 wt.% ER fluid of TiO_2 rod-like particles. In the absence of electric field, the system exhibits liquid behavior when viscous portion is dominant over elastic one, i.e. G'' is larger than G'. When the electric field is applied G' becomes higher than G'' in the viscoelastic region and both moduli increase rapidly in several orders of magnitude from their field-off values. Especially in the case of electric field strength $E = 3$ kV·mm^{-1}, G' is higher than that at zero electric field by five orders of magnitude.
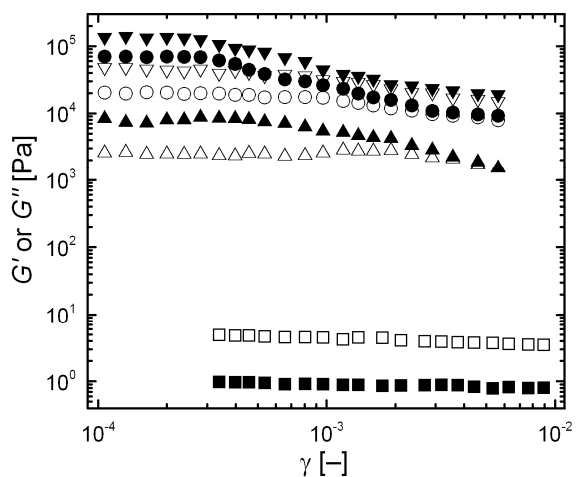

Figure 6. Storage, G', (solid) and loss, G'', (open) viscoelastic moduli as a function of strain amplitude, γ, for 20 wt.% TiO_2 rod-like particles suspension in silicone oil at 25 °C under various electric field strengths (kV·mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

For practical applications it is important to know the dependence of viscoelastic moduli on angular frequency, ω, in the linear viscoelastic region ($\gamma = 3 \times 10^{-4}$). As can be seen in Figure 7, the rod-like TiO_2 particles based ER fluid exhibits liquid-like behavior in the absence of external electric field since G'' dominates over G' in the whole frequency range. When the electric field is applied, polarized particles attract each other resulting in the increase of both moduli in several orders of magnitude. The G' starts to be higher than G'' indicating liquid to solid-like state transition and the stiffness of the system increases with increasing electric field strength. Moreover, G' becomes nearly independent of applied angular frequency which is characteristic for stiff three-dimensional network formed within the system which is sufficiently strong to transmit the elastic forces in such system [17].
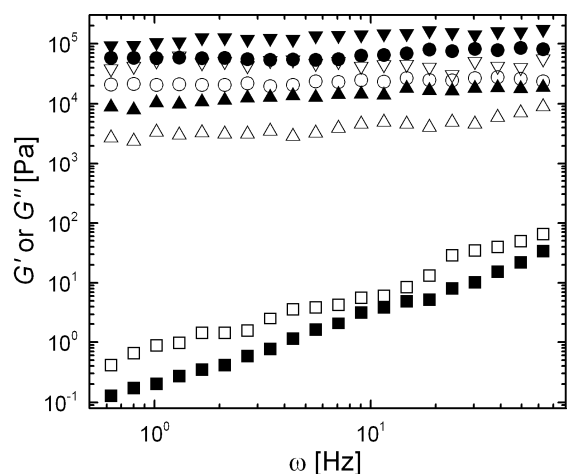
Figure 7. Storage, G', (solid) shear and loss, G'', (open) viscoelastic moduli as a function of angular frequency, ω, for 20 wt.% TiO_2 rod-like particles suspension in silicone oil at 25 °C under various electric field strengths (kV·mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

The ER activity of rod-like TiO_2 particles based fluids with different particle weight fraction is shown in Figure 8. Stiffness of the system significantly increases with the electric field strength applied. The ER effect rises also with particle weight fraction since the formed chain-like structures are more robust with stronger electrostatic interactions as well as with higher solid friction between particles.
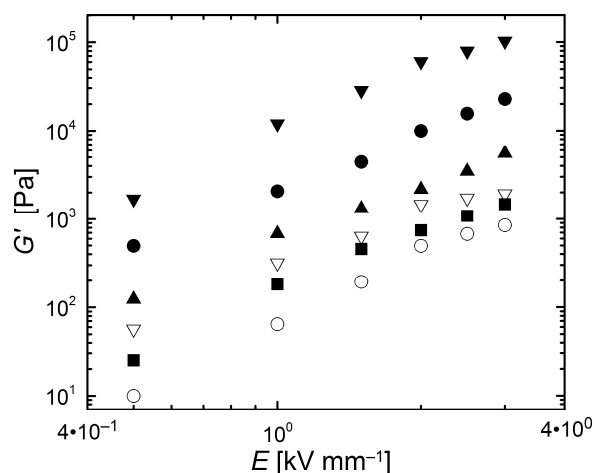
Figure 8. The dependence of storage, G', modulus on the electric field strength, E, at $\omega = 1$ rad·s^{-1} for 5 (■), 10 (▲), 15 (● ○), and 20 (▼ ▽) wt.% suspensions of rod-like (solid symbols) and spherical (open symbols) TiO_2 particles in silicone oil at 25°C.

4. Conclusions

Rod-like TiO_2 particles of rutile crystalline phase with high crystallinity were prepared via microwave-assisted molten-salt method as a novel one-dimensional dispersed phase of ER fluids. The oscillatory shear measurements revealed that silicone oil suspensions of prepared rod-like particles exhibit much higher ER activity than those based on TiO_2 nanoparticles of anatase crystalline phase due to side-by-side solid friction between particles. Moreover, the higher ER activity correlated well with dielectric

spectroscopy measurement since the polarization of rod-like particles in the direction of the long axis was reflected in shorter relaxation times.

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