Electrorheological behavior under oscillatory shear of TiO_2 rod-like particles prepared via microwave-assisted molten-salt synthesis

M. Sedlacik[1, 2], M. Mrlik[1, 2], V. Pavlinek[1, 2], Z. Kozakova[1, 2], P. Saha[1, 2]

1 Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic

2 Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, namesti T. G. Masaryka 275, 762 72 Zlin, Czech Republic

Corresponding author: Tel.: +420576038128; fax: +420576031444;
e-mail: msedlacik@ft.utb.cz

Abstract

Titanium oxide (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 appeared that during the synthesis process the crystalline phase of TiO_2 transformed from anatase into rutile one while the morphology changed from nanospheres into micrometer 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 suspension exhibited higher ER activity than that of starting 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 suspension as a function of the electric field strength applied and particles weight fraction were also performed.

Keywords: Electrorheological suspension; Rod-like particles; Titanium oxide; Anatase; Rutile; Microwave-assisted molten-salt synthesis; Viscoelasticity; Dielectric properties

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 nonconducting 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 particles aggregation into chain-like structures aligned in the direction of the field [4,5]. Such a response usually takes place on a millisecond scale and is accompanied with the increase of rheological properties including viscosity, shear stress, and viscoelastic moduli. The intensity of rheological properties changes is quite remarkable, over several orders of magnitude. 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].

Basically, the particle geometry can play a significant role in their ER response, since one-dimensional particle, whose major axis is aligned with the electric field and has the same dielectric constant and volume as a spherical particle, will form stronger internal structures [7,8]. Great influence of particle anisotropy was examined for example in ER fluids based on conducting polymers in which the ER performance was enhanced in comparison with conventional fluids of microspheres [9,10]. It is also obvious that anisotropic particles possess better sedimentation stability due to the hindered settling, easier redispersion due to the formation of less compacted sediment 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 their preparation.

In this study, with a view to prepare a novel anisotropic material with a good ER performance, the rod-like particles of titanium oxide (TiO_2) were synthesized via a simple and rapid microwave-assisted molten-salt method. This technique is based on the use of lo-melting salts to accelerate diffusion and thus formation of required structure with high crystallinity [11]. Moreover, a novel principle of microwave heating was used instead of classical heating in an oven, which shortened the reaction time significantly. Furthermore, a comparison with the viscoelastic behaviour of suspension 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 ($Na_2HPO_4 \cdot 12\ H_2O$, Penta, Czech Republic) which form eutectic mixture at 735 °C. All chemicals were used as received.

2.2 Synthesis of TiO_2 rod-like particles

Titanium oxide 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 domestic microwave oven [12]. Briefly, starting TiO_2 of anatase crystalline phase was homogenized with eutectic mixture of NaCl / $Na_2HPO_4 \cdot 12\ H_2O$ in a ratio of 4:5. The as prepared powder mixture was placed into corundum crucible, cover by a lid and placed into the ceramic kiln. The kiln was subsequently placed into domestic 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 to room temperature prior opening the corundum crucible and then obtained product was washed several times with distilled water and dried at 80 °C in the vacuum 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 on an 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 was prepared by dispersing of starting 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 η_c = 200 mPa·s).Before each measurement, the fluids were stirred first mechanically and then in a 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). A 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 sweep and frequency sweep. The strain sweep was performed with applied strain of 10^{-4} to 10^{-2} at a frequency of 6.28 rad·s^{-1} under an electric field to determine the linear viscoelastic region (LVR). The rheological parameters 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 dependences of dielectric properties (relative permittivity, ε', and dielectric loss factor, ε'') were obtained with an impedance analyzer (Agilent 4524, Japan) in the frequency range 4×10^{1} – 5×10^{6} Hz. The dielectric spectra were characterized with a modified Cole–Cole model [13,14] (Eq. 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 permittivity, ω is angular frequency ($=2\pi f$), λ is the 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 (Fig. 1), the microwave-assisted molten-salt synthesis transformed the originally 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 peak of anatase phase in the XRD pattern of prepared TiO_2 particles, the narrow and most intensive peaks signify very good crystallinity and can be indexed to the tetragonal rutile phase.

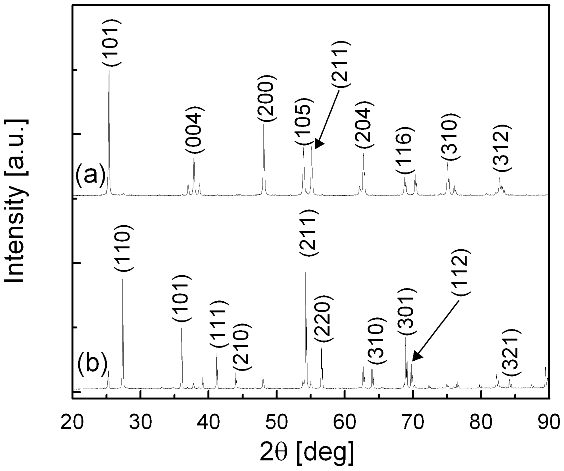

Fig. 1. Powder XRD patterns of starting anatase TiO_2 particles **(a)** and prepared TiO_2 particles via microwave-assisted molten-salt synthesis **(b)**

The changes in TiO_2 particles size and shape resulting from the use of microwave-assisted molten-salt synthesis were determined by means of TEM and SEM image analysis in Fig. 2. Particles of starting 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 Fig. 2b. The length of rod-like particles is then 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 2.5 to 20.

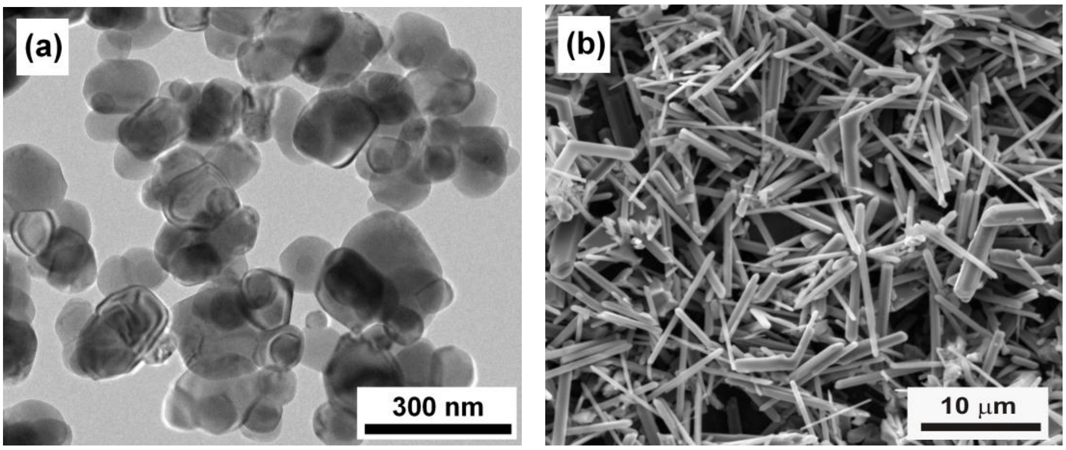

Fig. 2. Electron micrographs of starting anatase TiO_2 **(a)** and prepared rutile TiO_2 particles (b)

3.2 ER activity of prepared ER fluids

In order to check the structure formation within the ER fluid (Fig. 3), dilute suspension of prepared rod-like TiO_2 particles was placed between two parallel glass slides (the gap was fixed to 1 mm) connected to DC high-voltage source KEITHLEY (2400, USA). As can be seen in Fig. 3a, in the absence of external electric field strength the particles are approximately isotropic oriented. 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 of 0.5 kV mm^{-1} is applied (Fig. 3b), particles start to be polarized and the chain-like structure from connected particles is created between electrodes. It worth noting that agglomerates formed in the absence of the field remain gathered resulting in incomplete alignment of individual particles with the field.

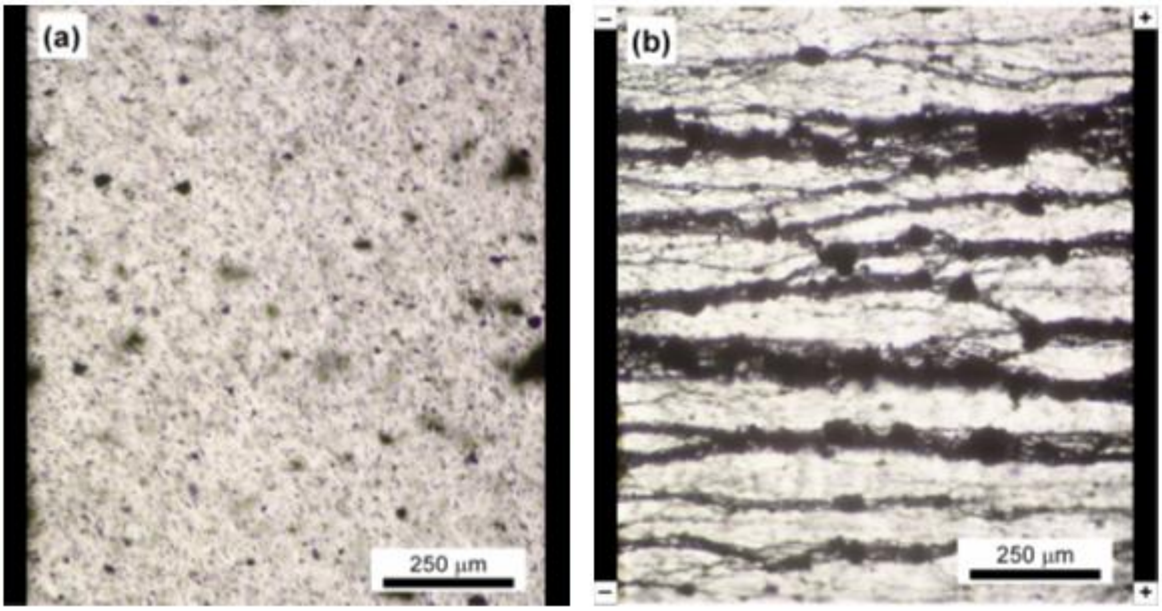

Fig. 3. Optical micrographs of dilute ER fluid of TiO_2 rod-like particles in the absence **(a)** and in the presence of external electric field strength of 0.5 kV·mm^{-1} **(b)**

It is generally accepted that interfacial polarization of particles connected with the formation of chain-like structures in the presence of electric field is closely related to dielectric phenomena (Fig. 4). Hence, parameters obtained from eq. 1 were used to help understand the ER activity of ER fluids based on TiO_2 spherical or rod-like particles (Tab. 1). Although the 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 a faster response to an electric field. It means that TiO_2 rod-like particles of rutile crystalline phase are polarized in the direction of the long axis 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 Eq. 1 for starting anatase TiO_2 particles and prepared rod-like TiO_2 particles based ER fluids of 5 wt.% 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}

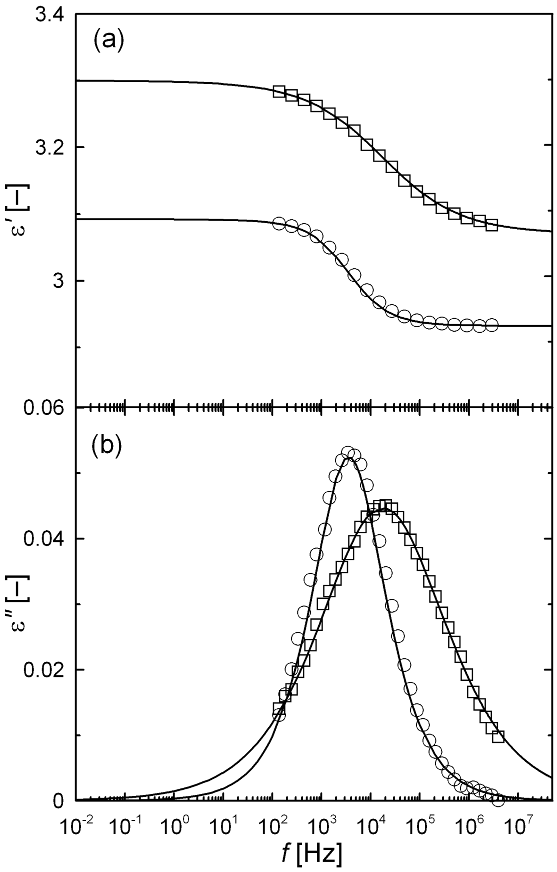

Fig. 4. Relative permittivity, ε', **(a)** and dielectric loss factor, ε'', **(b)** as a function of frequency, f, for 5 wt.% suspension of starting anatase TiO_2 particles (○) and prepared TiO_2 rod-like particles (☐)

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 starting TiO_2 nanoparticles at the same fluid concentration. In the absence of electric field, rod-like particle ER fluid exhibits almost Newtonian behavior while the system of starting anatase nanoparticles shows slight pseudoplastic behavior probably due to the formation of particles aggregates. On the other hand, strong electrostatic interactions in the presence of external electric field cause chain-like structure formation within the system which leads to a considerable increase in system stiffness. A further increase in pseudoplasticity appears with increasing electric field strength applied in the lower frequency region. Moreover, the thinning behavior is also clearly observed with increasing frequency. Evidently, much stronger structures are formed in the rod-like particle ER fluid in all electric field strengths applied probably due to higher solid friction between particles as well as shorter relaxation time. The lower field-off η* and higher stiffness in the electric field consequently indicate higher ER activity of TiO_2 rod-like particles.

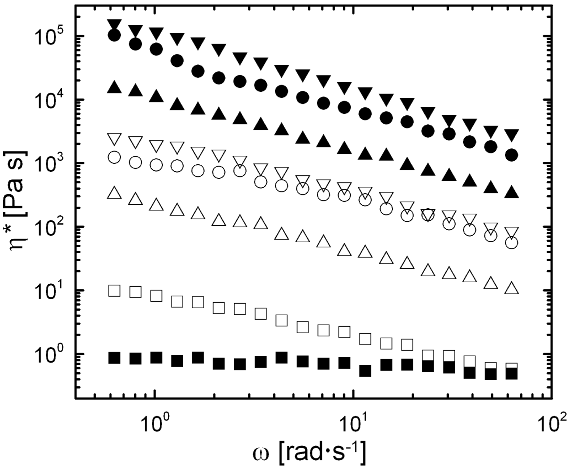

Fig. 5. Dependence of complex viscosity, η*, on angular frequency, *ω*, for 20 wt.% suspensions of TiO_2 rod-like (solid symbols) and anatase (open symbols) particles in silicone oil at 25 °C under various electric field strengths (kV mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

The formation of the internal chain-like structure of polarized particles in the presence of electric field is also accompanied by a change of viscoelastic moduli. Thus, Fig. 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, however, *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. Furthermore, as the strain amplitude is increased, the chain-like structure experience continuous deformation with its final destruction above some critical value of strain called linear viscoelastic region [17].

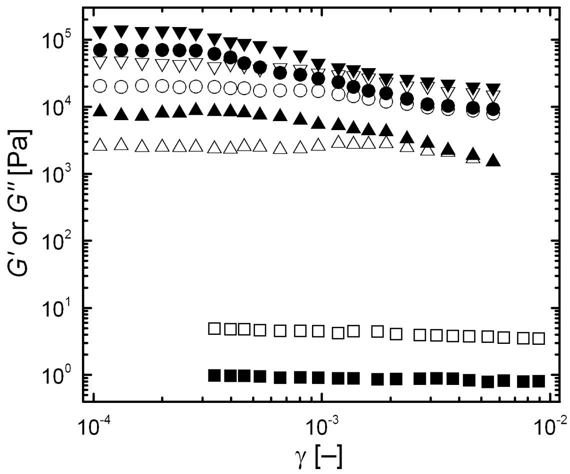

Fig. 6 Storage, G', (solid) shear and loss, G'', (open) viscoelastic moduli as a function of strain amplitude, γ, for 20 wt.% TiO_2 rod-like particles suspension in silicone oil at 25 °C under various electric field strengths (kV·mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

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 bee seen in Fig. 7, the rod-like TiO_2 particles based ER fluid exhibits liquid 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 due to dipole-dipole interactions leading into 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 applied. Moreover, G' become nearly independent on applied angular frequency or even slightly increase which is characteristic for stiff three-dimensional network formed within the system which is sufficiently strong to transmit the elastic force in such system [18].

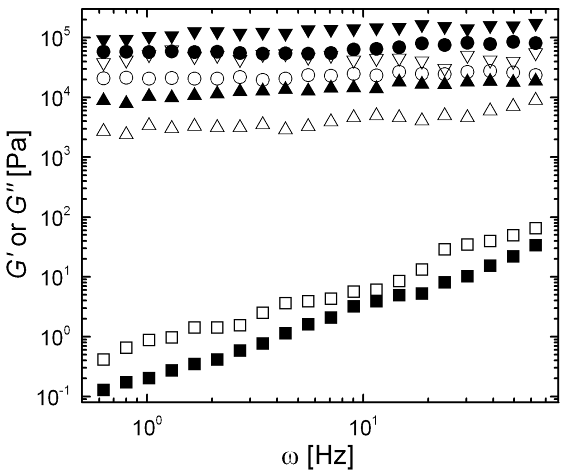

Fig. 7 Storage, *G'*, (solid) shear and loss, *G''*, (open) viscoelastic moduli as a function of angular frequency, ω, for 20 wt.% TiO_2 rod-like particles suspension in silicone oil at 25 °C under various electric field strengths (kV·mm^{-1}): 0 (■ □), 1 (▲ △), 2 (● ○), 3 (▼ ▽).

The ER activity of rod-like TiO_2 particles based fluids with different particle weight fraction is depicted in Fig. 7. It is clear that the stiffness of the system significantly increases as the electric field strength is increasing. The ER effect improves also with particle weight fraction since the formed chain-like structures are more robust and hence there exist stronger electrostatic interactions as well as higher solid friction between particles.

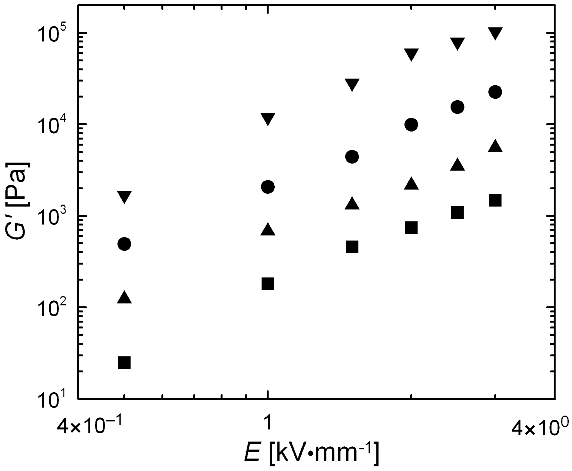

Fig. 7 : The dependence of storage, *G'*, viscoelastic modulus on the electric field strength, *E*, at $\omega = 1$ rad·s^{-1} for 5 (■), 10 (▲), 15 (●), and 20 (▼) wt.% suspension of TiO_2 rod-like particles in silicone oil at 25 °C.

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 in ER fluid. 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.

Acknowledgments

The authors wish to thank to the Grant Agency of the Czech Republic and the Ministry of Education, Youth and Sports of the Czech Republic for the financial support of Grant No. 202/09/1626. This article was written with support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic, within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111).

References

[1] Hao T (2002) Electrorheological fluids. Adv Colloid Interface Sci 97:1–35.

[2] Fang FF, Choi HJ, Joo J (2008) Conducting polymer/clay nanocomposites and their applications. J Nanosci Nanotechnol 8:1559–1581.

[3] Yin JB, Zhao XP (2011) Electrorheology of nanofiber suspensions. Nanoscale Res Lett 6:256.

[4] Wen WJ, Huang XX, Sheng P (2008) Electrorheological fluids: structures and mechanisms. Soft Matter 4:200–210.

[5] Parthasarathy M, Klingenberg DJ (1996) Electrorheology: Mechanisms and models. Mater Sci Eng R-Rep 17:57–103.

[6] Stanway R, Sproston JL, ElWahed AK (1996) Applications of electro-rheological fluids in vibration control: A survey. Smart Mater Struct 5:464–482.

[7] de Vicente J, Segovia-Gutierrez JP, Andablo-Reyes E, Vereda F, Hidalgo-Alvarez R (2009) Dynamic rheology of sphere- and rod-based magnetorheological fluids. J Chem Phys 131:194902.

[8] Mrlik M, Pavlinek V, Saha P, Quadrat O (2011) Electrorheological properties of suspensions of polypyrrole-coated titanate nanorods. Appl Rheol 21:52365.

[9] Yin JB, Xia X, Xiang LQ, Qiao YP, Zhao XP (2009) The electrorheological effect of polyaniline nanofiber, nanoparticle and microparticle suspensions. Smart Mater Struct 18:095007.

[10] Mrlik M, Pavlinek V, Cheng QL, Saha P (2012) Synthesis of titanate/polypyrrole composite rod-like particles and the role of conducting polymer on electrorheological efficiency. Int J Mod Phys B 26:125007.

[11] Li HL, Du ZN, Wang GL, Zhang YC (2010) Low temperature molten salt synthesis of SrTiO(3) submicron crystallites and nanocrystals in the eutectic NaCl-KCl. Mater Lett 64:431–434.

[12] Kozakova Z, Mrlik M, Sedlacik M, Pavlinek V and Kuritka I 2011 Preparation of TiO2 powder by microwave-assisted molten-salt synthesis *3rd International Conference NanoCon: Proc. NanoCon 2011 (Brno, Czech Republic, 21–23 September 2011)* (Ostrava: Tanger) p 71.

[13] Lopez-Lopez MT, Kuzhir P, Bossis G (2009) Magnetorheology of fiber suspensions. I. Experimental. J Rheol 53:115–126.

[14] Mason SG (1950) The flocculation of pulp suspensions and the formation of paper. Tappi J 33:440–444.

[15] Fang FF, Sung JH, Choi HJ (2006) Shear stress and dielectric characteristics of polyaniline/TiO2 composite-based electrorheological fluid. J Macromol Sci Part B-Phys 45:923–932.

[16] Fang FF, Kim JH, Choio HJ, Seo Y (2007) Organic/inorganic hybrid of polyaniline/BaTiO3 composites and their electrorheological and dielectric characteristics. J Appl Polym Sci 105:1853–1860.

[17] He Y, Cheng QL, Pavlinek V, Li CZ, Saha P (2009) Synthesis and electrorheological characteristics of titanate nanotube suspensions under oscillatory shear. J Ind Eng Chem 15:550–554.

[18] Sedlacik M, Pavlinek V, Saha P, Svrcinova P, Filip P (2011) Core-shell Structured Polypyrrole-coated Magnetic Carbonyl Iron Microparticles and their Magnetorheology. AIP Conf Proc 1375:284–291.