

Solvothermal synthesis of different TiO₂ morphology and their electrorheological characteristics

S Almajdalawi¹, V Pavlinek^{1,2,4}, M Mrlik^{1,2}, Q Cheng¹, P Piyamanocha^{1,2},
M Pastorek^{2,3} and M Stenicka^{2,3}

¹Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, Namesti
T. G. Masaryka 275, 762 72, Zlin, Czech Republic

²Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad
Ovcirnou 3685, 760 01, Zlin, Czech Republic

³Department of Polymer Engineering, Faculty of Technology, Tomas Bata University
in Zlin, Namesti T. G. Masaryka 275, 762 72 Zlin, Czech Republic

E-mail: pavlinek@ft.utb.cz

Abstract. Titanium dioxide (TiO₂) with different morphologies was prepared using solvothermal synthesis. The morphology and crystalline structure were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Electrorheological (ER) effect and dielectric properties of 5 wt. % suspensions were evaluated.

1. Introduction

Electrorheological (ER) fluids are smart materials showing a dramatic change in the rheological properties upon the application of an external electric field [1]. A typical ER fluid consists of polarisable particles dispersed in an insulating liquid medium. After the application of the electric field, the polarized particles form columns in a very short time and thus change the consistence of ER fluid from a liquid-like to a gel-like. Once, the electric field disappears, particles can return to the original disordered state and ER fluid behaves as a liquid again. This is an attractive topic from research point of view [2–5] with an interesting possible application for brakes, engine mounts or shock absorbers.

Various materials have been employed for preparation of ER fluids [6–9]. However, ER performance can be significantly affected by the morphology of dispersed particles, too [10]. The solvothermal synthesis seems to be an easy method how to prepare particles with controlled morphology by changing of reaction temperature and time, concentration and type of the solvent, pH value of the solution, *etc.* [11].

In this work, TiO₂ particles with different morphologies were synthesized by controlling concentration of the reactant and duration of synthesis. The influence of these variables on the morphology and subsequently on ER behaviour and dielectric properties of prepared TiO₂ based suspensions was studied.

⁴ Corresponding author

2. Experimental

2.1. Chemicals

TiO₂ anatase powder, sodium hydroxide (NaOH) and absolute ethanol were used as received without any further purification.

2.2. Synthesis of TiO₂ particles with different morphology

TiO₂ anatase powder, 10M NaOH solution and absolute ethanol were mixed in predefined ratio. Subsequently, the solution was transferred to 100 mL Teflon autoclave and heated at 200°C for different times (Table 1). The obtained product was filtered, washed with distilled water until pH = 7. Finally, the synthesized TiO₂ particles were dried at 80°C for 24h.

Table 1. Experimental conditions of TiO₂ particles synthesis.

Sample code	Weight of TiO ₂ [g]	Time of heating [h]	Temperature [°C]
S1	0.3	24	200
S2	1.2	24	200
S3	1.2	48	200

2.3. Structure characterization

Morphology of synthesized TiO₂ particles was characterized by scanning electron microscopy (SEM) VEGA II LMU (Tescan, Czech Republic). The XRD spectra were obtained via X-ray diffractometer X'Pert PRO (PANalytical, The Netherlands).

2.4. Preparation of ER fluid and rheological measurements

ER suspensions (5 wt.%) were prepared by mixing of TiO₂ particles with corresponding amount of silicone oil Lukosiol M200 (Chemical Works Kolin, Czech Republic; viscosity $\eta = 200$ mPa s, density $\rho = 0.965$ g cm⁻³, conductivity $\sigma \approx 10^{-11}$ S cm⁻¹).

A rotational rheometer Bohlin Gemini (Malvern Instruments, UK) equipped with coaxial cylinders (inner and outer diameters 14 and 15.4 mm) was used for steady shear measurements. The cylinders were connected to the external DC source providing electric field strengths from 0 to 3 kV mm⁻¹. All measurements were carried out under constant temperature of 25°C in the shear rate range of 0.5 to 200 s⁻¹.

ER fluids were stirred first mechanically and then for 1 min in ultrasonic bath before each measurement. Structures developed in the presence of electric field were destroyed by shearing at 40 s⁻¹ for 60 s in the absence of electric field.

2.5. Dielectric measurements

Dielectric properties for 5 wt.% suspensions were measured using Impedance Material Analyzer Agilent 4294-A (Agilent, Japan) in the frequency range 50 Hz – 1 MHz.

3. Results and discussion

Various morphologies of TiO₂ particles were obtained when treated under different conditions like time of heating or concentration of the starting material (Figure 1). At low initial concentration of TiO₂, the synthesized particles tend to form rod-like structures (S1, Figure 1a), whereas higher content of TiO₂ in mixture is reflected in more flat morphology of particles (S2, Figure 1b). This structure has higher diameter, but nearly the same length as S1. However, when time of heating increases, the TiO₂ particles (S3, figure 1c) become longer and thinner in contrast to S1 and S2, respectively.

Figure 2 shows the XRD patterns of TiO₂ particles. The crystalline structure was nearly the same for all prepared samples. After solvothermal treatment and washing with water, the TiO₂ precursor is transformed into a mixture of crystals; (Na₂Ti₃O₇) and (Na₂Ti₉O₁₉). However, the main part is Na₂Ti₃O₇ crystal according to the database. The anatase crystalline phase, having diffraction lines of planes at 2θ values of 25.1°, 29.7°, 43.5°, and 47.7°.

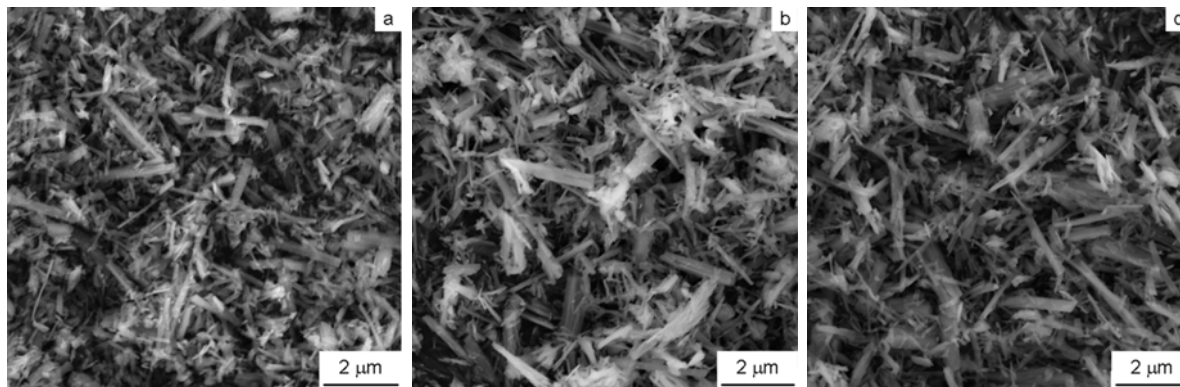


Figure 1. SEM images for S1 (a), S2 (b) and S3 (c).

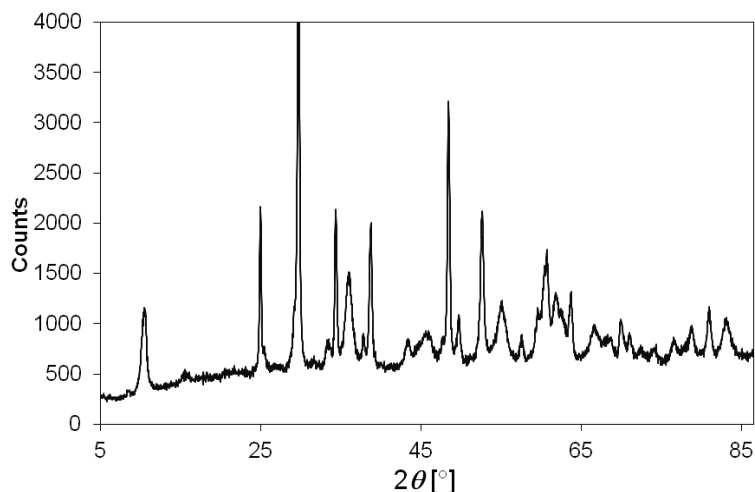


Figure 2. XRD-spectra of particles.

The rheological behaviour of 5 wt.% TiO₂ based suspensions under 0 and 3 kV mm⁻¹ is presented in figure 3. In the absence of the electric field, suspensions behave nearly as Newtonian fluids – the shear stress linearly increases with shear rate. By application of the electric field, the shear stress dramatically increases and suspensions show a significant yield stress. The yield stress appears as a result of interaction between the particles induced by the external electric field (Figure 3a).

However, a slight decrease of the shear stress observed in the range of small shear rates (1 – 35 s⁻¹) can arise from a negative synergistic interaction between hydrodynamic and polarization forces. At high shear rates, where the hydrodynamic forces dominate, both the shear stress and the shear viscosity approach the values as in the absence of the electric field due to structural changes in the suspensions: the destruction rate of the structures become faster than the reformation rate.

Figure 4 shows the dependence of the yield stress on the external electric field strength. The yield stresses for suspensions of all the samples (S1–S3) show an increase with electric field strength. While S1 and S2 present comparable yield stresses, the yield stress of S3 is slightly lower.

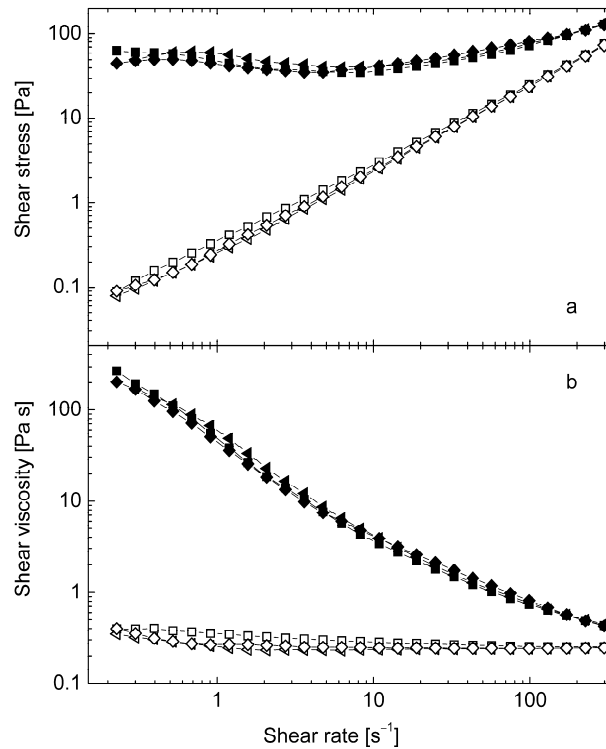


Figure 3. The shear stress (a) and the shear viscosity (b) vs. the shear rate dependence for 5 wt. % TiO_2 based suspensions in the absence of electric field strength (open symbols) and at $E = 3 \text{ kV mm}^{-1}$ (solid symbols). Sample codes: (\square \blacksquare) S1, (\triangleleft \blacktriangleleft) S2, and (\diamond \blacklozenge) S3.

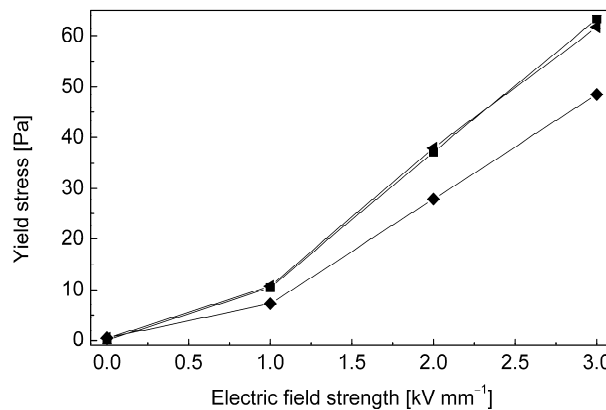


Figure 4. The yield stress vs. the electric field strength. Symbols as denoted in figure3.

As proposed in the literature [12], the ER response is significantly influenced by interfacial polarization. Therefore, the dielectric properties (relative permittivity and dielectric loss factor) of ER suspensions are very important for probing the mechanism that controls the electric properties of the materials [13]. Both parameters are plotted in figure 5 as a function of electric field frequency. The dielectric characteristics of suspensions were obtained from Havriliak-Negami equation [14]:

$$\varepsilon_s^*(f) = \varepsilon'_{s,\infty} + \frac{(\varepsilon'_{s,0} - \varepsilon'_{s,\infty})}{(1 + (i 2\pi f t_{rel})^a)^b} \quad (1)$$

where $\varepsilon_s^*(f)$ is a complex suspension permittivity and $\varepsilon'_{s,0}(f)$ and $\varepsilon'_{s,\infty}(f)$ are the limiting values of relative permittivity at below and above the relaxation frequency, f is frequency, t_{rel} is a relaxation time, a is the scattering degree of relaxation times, and b is related to the asymmetry of the relaxation time spectrum (table 2).

Table 2. Parameters of Havriliak-Negami equation for TiO₂ based suspensions.

Sample code	$\varepsilon'_{s,0}(f)$	$\varepsilon'_{s,\infty}(f)$	t_{rel} [s]	a	b
S1	3.85	2.91	4.74×10^{-4}	0.34	1.65
S2	3.36	2.91	1.21×10^{-4}	0.32	1.75
S3	3.45	2.93	3.79×10^{-5}	0.39	1.75

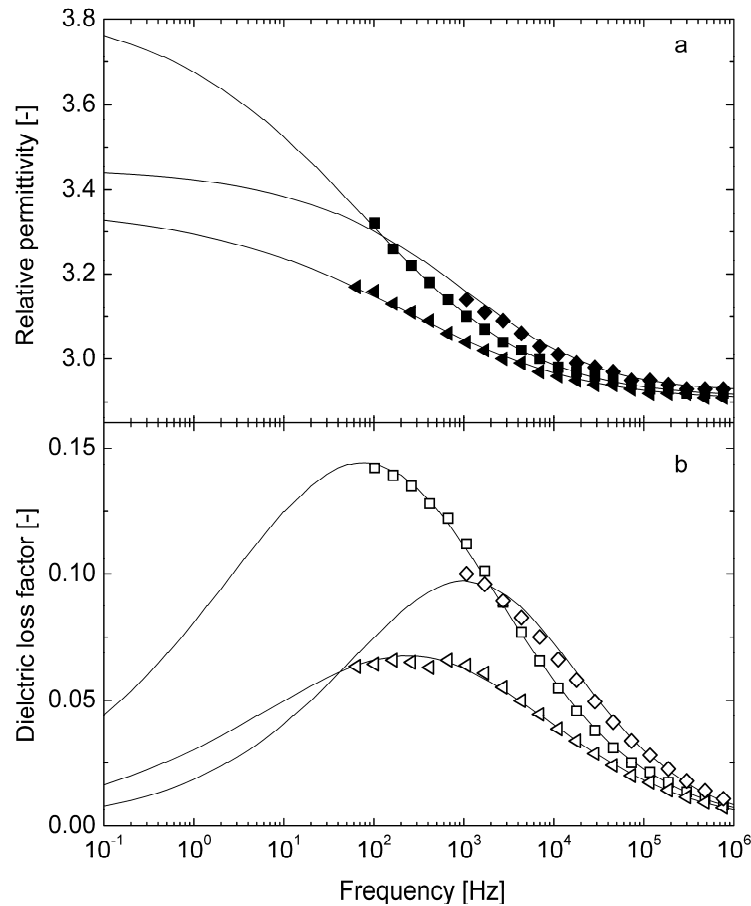


Figure 5. The relative permittivity (a) and the dielectric loss factor (b) vs. the frequency for 5 wt.% TiO₂ based suspensions. Symbols as denoted in figure 3.

Suspension S1 shows the highest polarizability of the particles given by difference between $\varepsilon'_{s,0}(f)$ and $\varepsilon'_{s,\infty}(f)$ compared to other two suspensions. The difference in relative permittivity for S1, S2 and S3 was 0.94, 0.45 and 0.52, respectively as comes from table 2. In contrast to e.g. other ER

systems [15], the polarizability of these ER fluids is rather low, but corresponds to the ER performance.

In addition to the polarizability of the particles, a proper relaxation time evaluated from the maximum of dielectric loss between $10^2 - 10^5$ Hz is necessary for a large ER effect [12].

Evidently, various morphology of prepared TiO₂ particles plays a role in particle organizations (Figure 5b and Table 2). ER fluid having higher relaxation time exhibited weaker ER effect because of slower chaining of particles.

4. Conclusions

TiO₂ particles with different morphology were synthesized using solvothermal synthesis method. These particles were mixed with silicone oil and ER performance was investigated. As pointed out, only 5 wt.% suspensions exhibited a moderate ER effect. In case of ER suspensions having similar polarizability, suspension with longer relaxation time exhibited weaker ER effect.

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