Electrorheology of aniline oligomers

Miroslav Mrlik[a,b] · Michal Sedlacik M.[a,c*] · Vladimir Pavlinek[a,b] · Patrycja Bober[d] · Miroslava Trchová[d] · Jaroslav Stejskal[d] · Petr Saha[a,b]

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

[b] Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, T.G. Masaryk Sq. 275, 762 72 Zlin, Czech Republic

[c] Department of Production Engineering, Faculty of Technology, Tomas Bata University in Zlin, T. G. Masaryk Sq. 275, 762 72 Zlin, Czech Republic

[d] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

[*] Corresponding author. Tel. +420 57 603 8128; fax: +420 57 603 1444.
E-mail: msedlacik@ft.utb.cz

Abstract Aniline oligomers were prepared by the oxidation of aniline with *p*-benzoquinone in aqueous solutions of methanesulfonic acid (MSA) of various concentrations. Their molecular structures were assessed by FTIR spectroscopy. The electrorheological (ER) behaviour of their silicone oil suspensions under applied electric field has been investigated. Shear stress at a low shear rate, $\tau_{0.9}$, was used as a criterion of the rigidity of internal structures created by the application of an electric field. It was established from the fitting of the dielectric spectra of the suspensions with the Havriliak-Negami model that dielectric relaxation strength, as a degree of polarization induced by an external field contributing to the enhanced ER effect, increases and relaxation time, i.e. the response of the particle to the application of the field, decreases when a higher molar concentration of MSA is used. The best values were observed for suspensions of the sample prepared in the presence of 0.5 M of MSA. This suspension creates stiff internal structures under an applied electric field strength of 2 kV·mm^{-1} with $\tau_{0.9}$

of 50 Pa, which is even slightly higher value than that obtained for standard PANI base ER suspension measured at the same conditions. The concentration of the MSA used in the preparation of oligomers seems to be a crucial factor influencing the conductivity, dielectric properties and, consequently, rheological behaviour and finally ER activity of their suspensions.

Introduction

Electrorheological (ER) suspensions are commonly two-phase systems consisting of an insulating liquid, such as silicone oil, and a dispersed phase formed by solid particles including dipoles, which are able to be polarized under an electric field. Such systems were previously reviewed in detail [1-7]. As a dispersed phase, both inorganic [8-13] and organic particles have been used. The latter group is widely represented by conducting polymers such as polyaniline (PANI) and polypyrrole [14-19]. Especially, conducting polymers with tuneable conductivity have become promising materials for ER suspensions [20-22].

ER suspensions are smart fluids changing their state from liquid-like to solid-like within several milliseconds under the application of an external electric field. This change is reversible and is expressed as a rapid increase of rheological parameters such as shear stress, shear viscosity, and viscoelastic moduli. This increase is connected with the electrically-induced formation of structures created between electrodes [23]. The formation and stiffness of these structures depends mainly on the conductivity and consequently on dielectric relaxation strength of suspended particles [24-27].

The previous paper published by this group [22] was aimed at the preparation of PANI particles with the help of protonation by various organic acids. The molar concentration of the acid determined the conductivity of particles: the higher the molar concentration of acid used, the higher the conductivity obtained. On the other hand, not only PANI particles can be used as an ER material; other materials based on aniline could be applied due to their semi-conducting character [28].

New materials are represented e.g. by aniline oligomers. They are produced by the oxidation of aniline with ammonium peroxydisulfate at alkaline conditions [28, 29]. Alternatively, aniline oligomers can be prepared also under acidic conditions, when aniline is oxidized with p-benzoquinone. Such materials have not been tested in ER so far. They are

prepared by a single-step oxidation process. In contrast, PANI has to be deprotonated with ammonia to PANI base after such synthesis, i.e. the second preparation step is required.

In the present study, the organization of suspended aniline oligomers in an electric field is assessed by optical microscopy and discussed with respect to steady-shear rheological measurements under various external electric field strengths, as well as in relation to dielectric properties of suspensions. The reproducibility of the transition from liquid-like to solid-like states and back was evaluated during these periods.

Experimental section

Synthesis of aniline oligomers and standard PANI base

The single-step preparation of ER-active aniline oligomers was performed as follows: Aniline (0.2 M; Fluka, Switzerland) was oxidized with p-benzoquinone (0.5 M; Sigma-Aldrich, USA) in aqueous solutions of methanesulfonic acid (Fluka, Switzerland) of various concentrations. After mixing the aniline and oxidant solutions, the mixture was left at room temperature for 24 h. The solids were isolated by filtration, rinsed with acid solution, then with acetone, dried in air, and then over silica gel. Separate studies have shown that aniline oligomers of limited conductivity are produced by the oxidation of aniline with p-benzoquinone, in contrast to other oxidants, such as ammonium peroxydisulfate, which yield a conducting polymer, polyaniline, under such reaction conditions [28-33].

PANI base particles were prepared according to the standard procedure [30] using the oxidation of aniline hydrochloride (0.2 M; Fluka, Switzerland) with ammonium peroxydisulfate (0.25 M; Lach-Ner, Czech Republic). After the polymerization, PANI salt was suspended in the excess of 1 M ammonium hydroxide and converted to PANI base, in order to sufficiently reduce conductivity for ER measurements.

Characterization of the prepared particles

Fourier-transform infrared (FTIR) spectra of samples dispersed in potassium bromide were recorded in the range 400–4000 cm^{-1} at 64 scans per spectrum at 2 cm^{-1} resolution using a fully-computerized FTIR Spectrometer (Thermo Nicolet NEXUS 870, USA) with a DTGS TEC detector. The spectra were corrected for the presence of moisture and carbon dioxide in the optical path. The morphology of the prepared samples was observed with a scanning

electron microscope (SEM, Vega II LMU, Tescan, Czech Republic). The powders of prepared aniline oligomers were pressed into pellets of 13 mm diameter and 0.8–1.2 mm thickness at 7 MPa. The conductivity was measured at room temperature on three pellets prepared from each sample using two-point method after deposition of gold electrodes on both sides of pellets. The density of PANI was determined by weighing of compressed pellets on Sartorius R160P balance on air and immersed in decane.

Rheological measurements

Suspensions (10 vol. %) were prepared by mixing aniline oligomers with corresponding amounts of silicone oil (Fluid 200, Dow Corning, UK; viscosity $\eta_c = 108$ mPa s, density $\rho_c = 0.965$ g cm^{-3}). Before each measurement, the suspensions were stirred at first mechanically and then sonicated for 30 s.

Rheological measurements were performed under controlled-shear-rate (CSR) mode using a rotational viscometer (Bohlin Gemini, Malvern Instruments, UK). The suspensions were placed into parallel-plate geometry 40 mm in diameter with a 0.5 mm gap. The instrument, modified for ER experiments, was connected to the DC high-voltage source TREK (TREK 668B, USA) to generate electric field strengths 0–2.0 kV mm^{-1}. Before each measurement step, the previously built-up particulate structures were destroyed by shearing the sample at the shear the rate 50 s^{-1} for 80 s.

Dielectric measurements

The dielectric properties of the prepared suspensions were measured with a Broadband Dielectric Impedance Analyser Concept 40 (Novocontrol, Germany) connected to the cylindrical sample cell BDS 1307 for liquid materials. Dielectric properties such as relative permittivity, ε', and dielectric loss factor, ε'', were investigated in a frequency range from 1 Hz to 5 MHz. The dielectric spectra were analyzed using the Havriliak-Negami model [34],

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

where $\Delta\varepsilon' = \varepsilon'_s - \varepsilon'_\infty$ is dielectric relaxation strength, ε'_s, and ε'_∞, are relative permittivities at zero and infinite frequency, f, respectively and, ω, is angular frequency $(= 2\pi f)$, t_{rel} is the relaxation time, and a and b are shape parameters which describe the asymmetry of the dielectric function.

Optical microscopy

Suspensions consisting of 1 vol. % particles in silicone oil were placed between two copper electrodes deposited on glass with a gap of 1 mm connected to a DC high-voltage source (Keithley 2400, USA). The formation of ER structures was observed with the help of an optical microscope (N 400M, China) linked to a digital camera.

Results and discussion

Particle characterization

As can be seen in (Fig. 1), the concentration of the MSA used in the synthesis had little effect on the flake-like particle morphology.
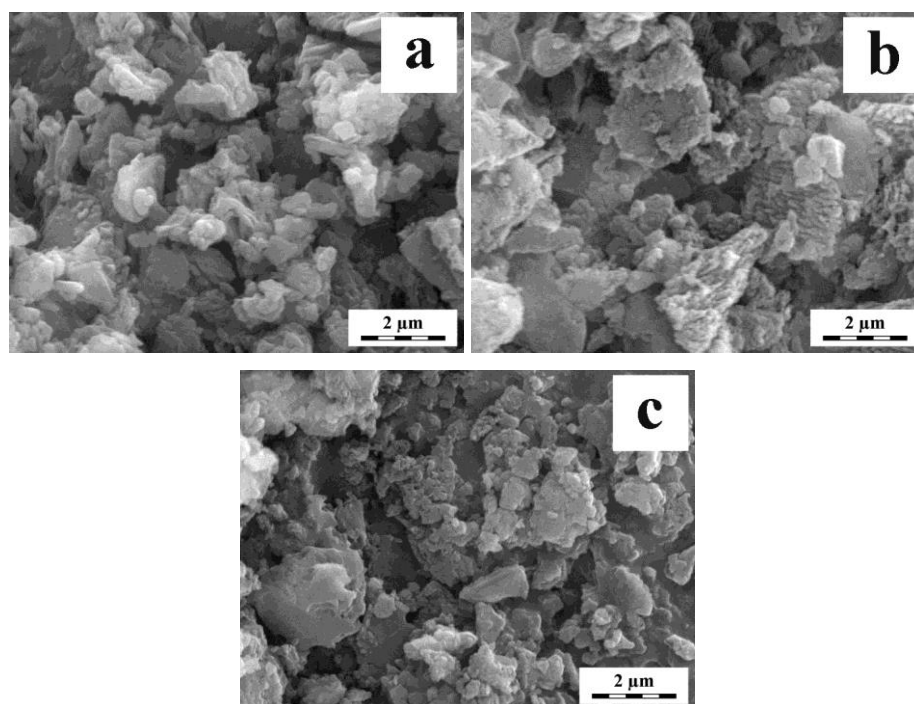

Fig. 1 Aniline oligomers prepared in (a) 0.1 M MSA, (b) 0.2 M MSA, and (c) 0.5 M MSA

Furthermore, the conductivity of the prepared samples strongly depends on the molar concentration of MSA since the concentration changes the conductivity in two orders of magnitude. On the other hand the density of prepared samples is changed only negligibly (Table 1).

Table 1 The conductivity, σ, and density, ρ, of aniline oligomers prepared in MSA solution of molar concentration C_A

C_A [mol L^{-1}]	σ [S cm^{-1}]	ρ [g cm^{-3}]
0.1	2.3×10^{-10}	1.36
0.2	1.02×10^{-9}	1.33
0.5	1.49×10^{-8}	1.35

The molecular structure of aniline oligomers is still open to discussion and a detailed characterization is under progress. Infrared spectra of the prepared samples confirm the oligomeric nature of the oxidation products (Fig. 2) [28]. The sharp peak at 1638 cm^{-1} corresponds to the carbonyl stretching vibration. The bands at 1566 and 1504 cm^{-1} (various quinonoid and benzenoid ring-stretching vibrations), a shoulder observed at about 1630 cm^{-1} (most probably to N–H scissoring vibrations of aromatic amines with the contribution of benzoquinones), and a shoulder at about 1357 cm^{-1} (attributed to C–N bonding of variously substituted aromatic rings) are observed in the spectra. The sharp peak at 1441 cm^{-1} is attributed to the skeletal C=C stretching vibration of the substituted aromatic ring, typical of aniline oligomers, and the sharp peak at 1296 cm^{-1} indicates the presence of the C─N stretching vibration of a primary aromatic amine. A broad band of C–H bending in-plane vibrations reaches its maximum at 1182 cm^{-1}. A prominent band at 828 cm^{-1} is due to the C–H out-of-plane bending vibrations of two adjacent hydrogen atoms on a 1,4-disubstituted benzene ring. In addition to this band, those at 744 and 692 cm^{-1} correspond to the C–H out-of-plane bending and out-of-plane ring-deformations of a mono-substituted benzene ring, respectively. The spectrum of the oligomers displays a sharp peak at 3230 cm^{-1}, which is connected to the stretching vibrations of hydrogen bonded N–H groups with carbonyl groups.

We conclude that oxidation products include both aniline and *p*-benzoquinone constitutional units.
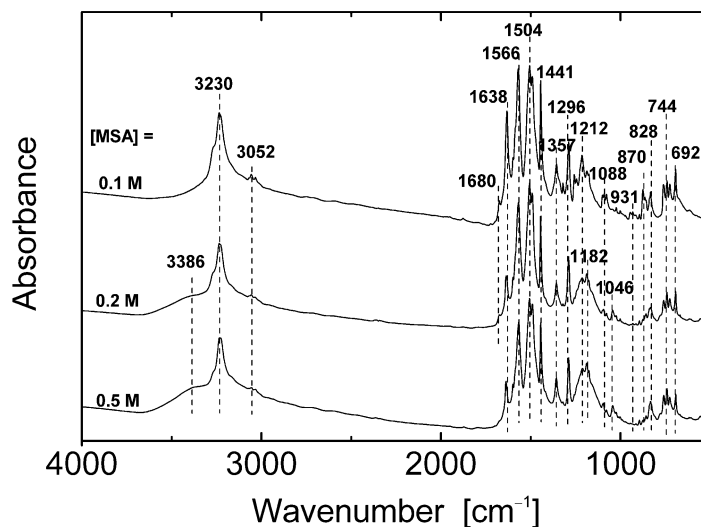

Fig. 2 FTIR spectra of aniline oligomers synthesized in 0.1, 0.2, and 0.5 M MSA

Steady-shear viscometry

Experimental results for the suspension containing 10 vol. % of particles in silicone oil (Figs. 3a–c) demonstrate that the suspensions of aniline oligomers prepared in 0.1 M MSA exhibit nearly Newtonian behaviour in the absence of the external electric field, while suspensions of samples prepared in 0.2 M and 0.5 M MSA show pseudoplastic flow character. The suspension containing the sample prepared in 0.1 M MSA exhibits typical yielding behaviour under application of an electric field (Fig. 3a). The values of the shear stress, $\tau_{0.9}$, at the given shear rate, $\dot{\gamma} = 0.9$, are considerably lower in comparison with other samples because the chain-like structures have not been properly developed, because the conductivity of this sample (Table 1) is out of the range (10^{-5} S/cm to 10^{-9} S/cm) which was estimated by Block *et. al.* [24] as suitable values for creation of internal structures.

The yielding behaviour in the presence of the electric field is observed on suspensions consisting of the oligomers prepared in 0.2 M and 0.5 M MSA (Fig. 3b–3c). Higher values of yield stress were obtained for the suspensions composed of oligomeric particles synthesized in 0.5 M MSA (Fig. 3c). These results imply that the suitable conductivity of sample prepared in 0.5 M MSA promotes the development of the proper chain-like structures between electrodes.

Generally, after application of an electric field, suspensions change their state from liquid-like to solid-like, accompanied by the development of internal structures. In order to investigate the stiffness of these internal structures, the shear stress $\tau_{0.9}$ at minimum shear rate was used. The data in the double-logarithmic plot of $\tau_{0.9}$ and electric field strength, E, were applied to power-law model, where $\tau_{0.9} = q \cdot E^a$ (Fig. 4). Parameter q is related to the stiffness of the internal structures, and parameter a characterizes the response of the particles to the application of an electric field. These parameters rise with the increasing concentration of MSA, which denotes the enhanced ER activity of such systems (Table 2).
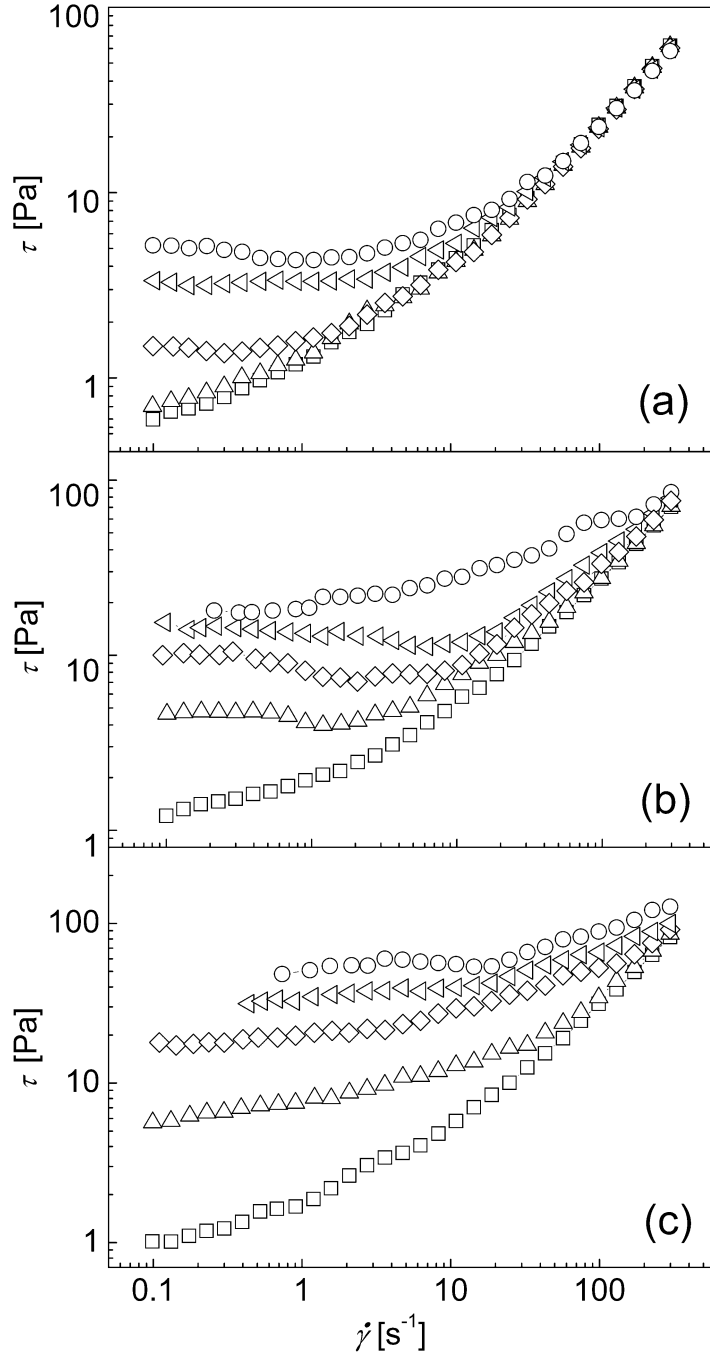
Fig. 3 Dependence of the shear stress, τ, on the shear rate, $\dot{\gamma}$, for 10 vol. % silicone suspensions of aniline oligomers particles prepared in (a) 0.1 M MSA, (b) 0.2 M MSA, and (c) 0.5 M MSA at various external electric field strengths, E, (kV mm^{-1}): 0 ($\square$), 0.5 ($\triangle$), 1 ($\diamond$), 1.5 ($\triangleleft$), 2 ($\bigcirc$)

Table 2. Parameters of the power-law model $\tau_{0.9} = q \cdot E^a$ (Fig. 4) for aniline oligomers prepared in a methanesulfonic acid solution of various molar concentrations C_A

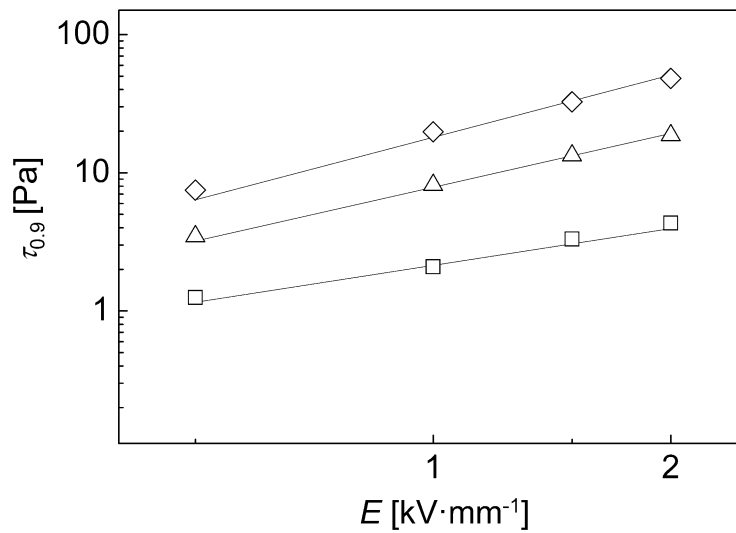| C_A [mol·L^{-1}]	q [Pa]	a
0.1	2.1	0.89
0.2	7.9	1.29
0.5	18.0	1.50

Fig. 4 Dependence of the shear stress, $\tau_{0.9}$, at minimum shear rate, $\dot{\gamma} = 0.9$ s^{-1}, on the electric field strength, E, for 10 vol. % suspensions in silicone oil of aniline oligomers particles prepared in 0.1 M MSA ($\square$), 0.2 M MSA ($\triangle$), and 0.5 M MSA ($\diamond$).

The effect of MSA concentration used during the synthesis of aniline oligomers on the ER activity of their silicone oil suspensions can be clearly seen in Fig. 5. As noted in previous studies [22, 23], the character of acid used in the preparation of samples considerably influences the ER effect. Here, with an increasing concentration of MSA, the ER effect of suspensions increases. At the lowest concentration, the value of the $\tau_{0.9}$ is around 5 Pa. On the other hand, when the concentration of MSA is changed from 0.1 M to 0.5 M, the stress significantly increases by one order of magnitude and reaches nearly 50 Pa at 2 kV mm^{-1}.
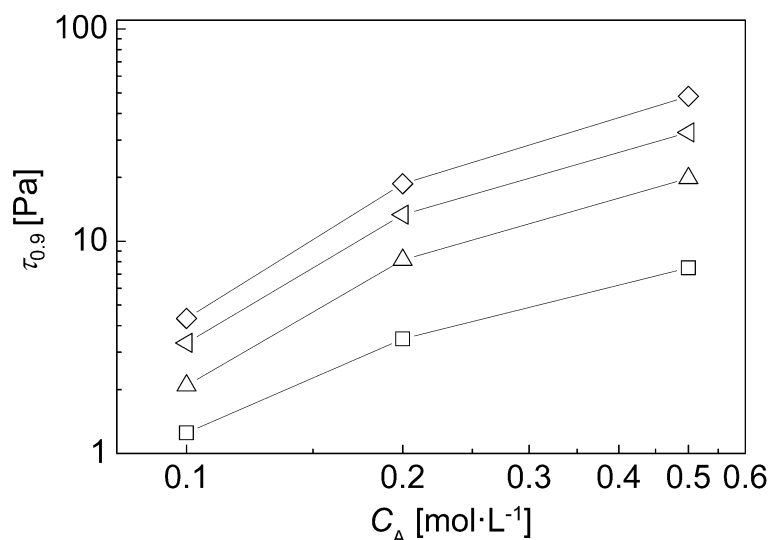
Fig. 5 Dependence of the shear stress, $\tau_{0.9}$, at minimum shear rate, $\dot{\gamma} = 0.9\,\mathrm{s}^{-1}$, on the molar concentration, C_A, (mol L^{-1}) of MSA for 10 vol. % suspensions of aniline oligomers particles in silicone oil at various external electric field strengths, E, (kV·mm^{-1}): 0.5 (□), 1 (△), 1.5 (◁), 2 (◇)

Finally, the ER behaviour of the aniline oligomers was compared to that of the standard PANI base suspension at the same volume concentration in the suspension (Fig. 6). The suspension of aniline oligomer particles prepared in 0.5 M MSA by single-step oxidation reaction exhibits slightly higher values of the shear stress in the absence of the external field. However, ER performance in the presence of the external electric field is visibly higher than that of PANI base suspension. In addition, PANI needs an additional step of deprotonation, after which it was established in previous studies as good ER material [35, 36]. Here it should be mentioned that, in the studies provided by other authors [37-39], ER systems exhibit considerably higher yield stress in comparison to these aniline oligomers. However, they usually do not properly study the off-state values of their ER systems with more than 30 vol. % particles in the suspension.
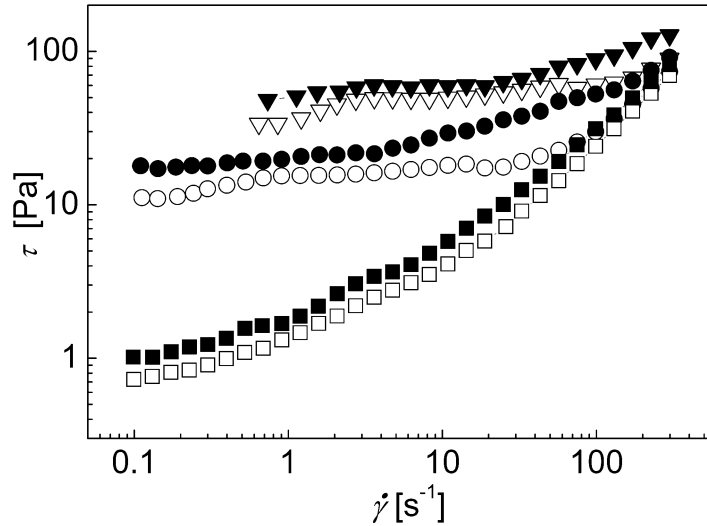
Fig. 6 Dependence of the shear stress, τ, on the shear rate, $\dot{\gamma}$, for 10 vol. % silicone oil suspension of aniline oligomers particles prepared in 0.5 M MSA (solid symbols) and PANI base (open symbols) at various external electric field strengths, E, (kV·mm^{-1}): 0 ($\square$, $\blacksquare$), 1 ($\bigcirc$, $\bullet$) and 2 ($\triangledown$, $\blacktriangledown$).

Behaviour during the periodic switching-on and off of the electric field

In the case of potential applications of ER suspensions, the reproducibility of the ER phenomenon is an important factor. For the purpose of investigating reproducibility, the dependence of the shear stress against time was plotted (Fig. 7). The response of the oligomeric particles, dispersed in the ER suspension, on the application of the electric field is clearly visible when the shear stress rapidly increases (Fig. 7a–c). This rapid increase is more evident for the suspension consisting of aniline oligomer particles prepared in 0.5 M MSA. This suspension had a faster response to the electric field as was observed from the parameters of power-law model (Table 2) and also from the investigation of dielectric properties, which are discussed below. When the electric field is switched-off, oriented structures created within the suspension are slowly destroyed by continuous shearing. The suspension of the oligomer prepared in 0.5 M MSA provides a stiffer solid-like state than other samples with simultaneously the same reproducibility of the phenomenon.
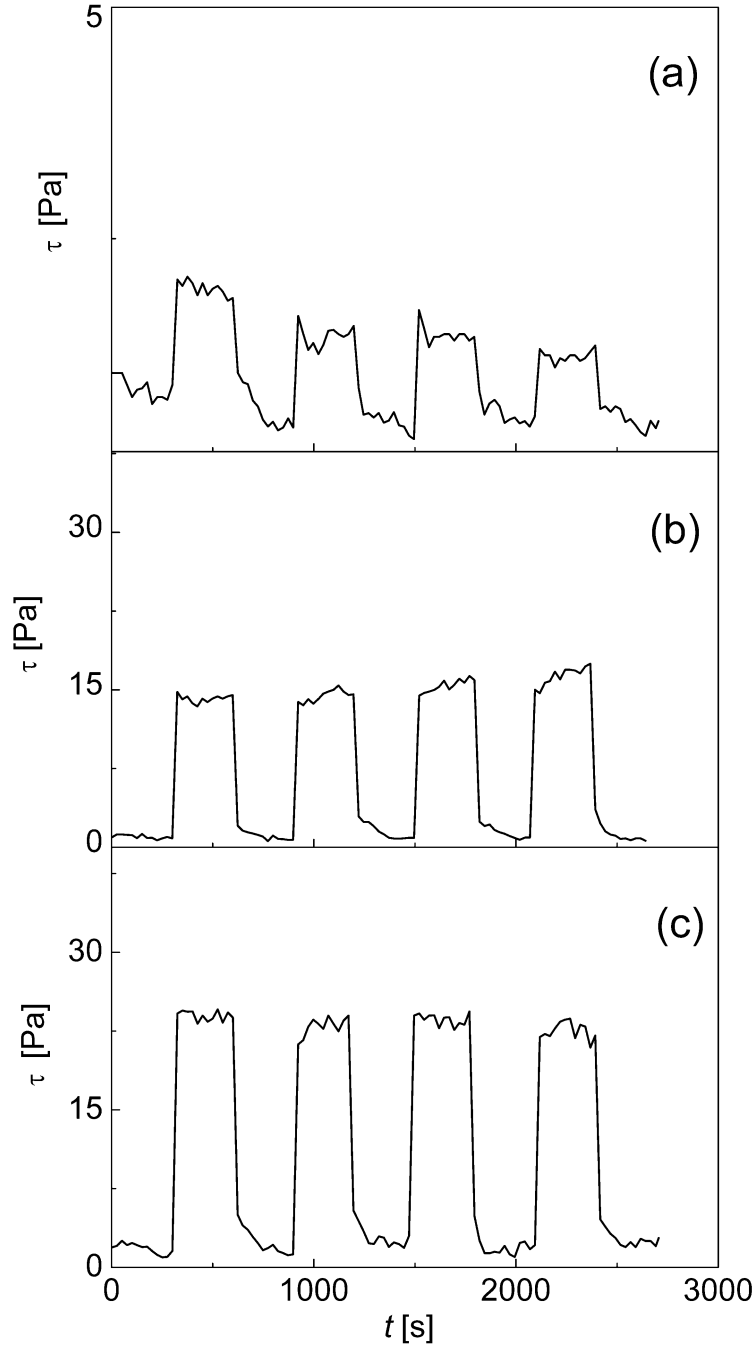
Fig. 7 Time dependence of the shear stress, τ, at 0 and 1.5 kV·mm^{-1} at shear rate 1 s^{-1} for 10 vol. % silicone oil suspensions of oligomers prepared in (a) 0.1 M MSA, (b) 0.2 M MSA, and (c) 0.5 M MSA

Dielectric characteristics

As mentioned in several papers [25-27], dielectric properties of ER suspension are closely connected to the ER effect. Especially, the dielectric relaxation strength and the relaxation time of ER suspensions are crucial factors influencing values of the yield stress of

suspensions in the presence of an electric field. In order to obtain the appropriate values of these quantities the dielectric spectra of suspensions (Fig. 8) were applied to the Havriliak-Negami model (eq. 1) (Table 3). The calculation showed that the dielectric relaxation strength of particles increases with the molar concentration of MSA used for synthesis. On the other hand, relaxation time as a response of the particles to the application of the electric field decreased with the increasing concentration of MSA. These findings suggest that materials with higher dielectric relaxation strength and shorter relaxation time provide a stronger ER effect, as confirmed by rheological measurements.

Table 3 Parameters of the Havriliak-Negami model applied to the suspensions of aniline oligomers prepared in the solutions of MSA of molar concentration C_A

C_A [mol L^{-1}]	ε'_s	ε''_∞	$\Delta\varepsilon'$	t_{rel} [s]	a	b
0.1	3.65	2.90	0.75	0.30	0.24	1.67
0.2	4.32	2.89	1.43	0.08	0.33	1.44
0.5	4.63	2.98	1.65	0.03	0.58	1.40
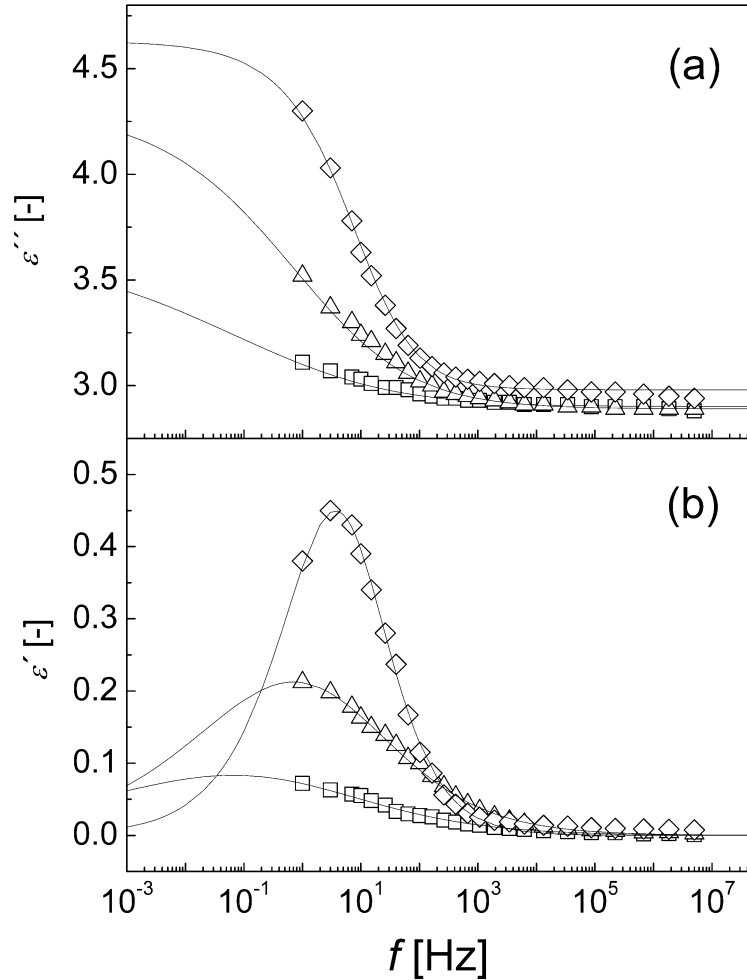
Fig. 8 The frequency dependence of relative permittivity, ε', (a) and dielectric loss factor, ε'', (b), for 10 vol. % suspensions of aniline oligomers in silicone oil. Aniline oligomers were prepared in 0.1 M MSA (□), 0.2 M MSA (△), and 0.5 M MSA (◇). Solid lines represent the Havriliak-Negami model application.

Development of ER structures

The transition from liquid-like to solid-like state after the application of an external electric field is connected with the creation of internal structures. In the absence of an electric field, particles of the sample prepared in 0.1 M MSA are randomly dispersed in the silicone oil (Fig. 9a). After application of an electric field of 1.5 kV mm^{-1}, the particles create only partial chain-like structures which were disable to connect the electrodes (Fig. 9b). This fact confirms previous investigation of the rheological and dielectric properties. On the other hand, randomly dispersed particles of sample prepared in 0.5 M MSA (Fig. 10a) create rather

compact internal structures in the presence of an electric field of 1.5 kV·mm^{-1} (Fig. 10b). Such developed structures are comparable to those observed for the PANI particles [23].
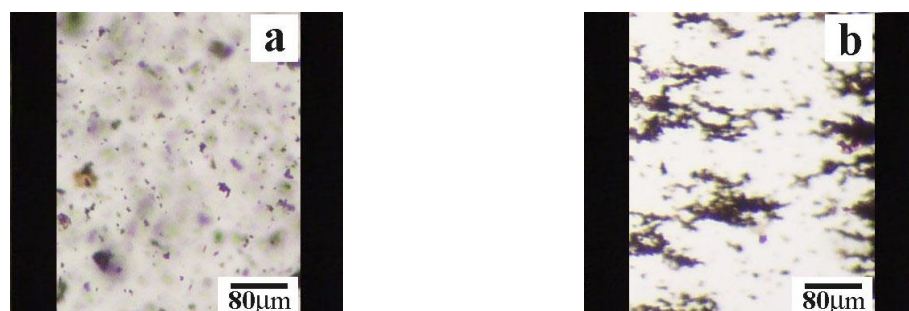

Fig 9 Optical microscopy of 1 vol. % silicone oil suspension of aniline oligomer prepared in 0.1 M MSA under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5

Fig. 10 Optical microscopy of 1 vol. % particle silicone oil suspension of aniline oligomer prepared in 0.5 M MSA under various electric field strengths, E, (kV·mm^{-1}): (a) 0, (b) 1.5

Conclusions

Aniline oligomers as promising ER particles were synthesized in the presence of methanesulfonic acid (MSA) via the oxidation of aniline with *p*-benzoquinone. Their conductivity was low and was influenced by the molar concentration of MSA in the reaction medium. A sample prepared in 0.1 M MSA had insufficient conductivity and was unable to produce compact internal structures under an applied electric field. On the other hand, the sample prepared in 0.5 M MSA provides a material of suitable conductivity, dielectric properties and the ability to develop compact internal structures confirmed by electrorheological measurements and optical microscopy. Finally, suspensions consisting of particles prepared via single-step oxidation reaction exhibit slightly higher ER activity in comparison to standard PANI base, which requires an additional reaction step involving deprotonation.

References

1. Block H, Kelly JP (1988) Electro-rheology. J Phys D: Appl Phys 21:1661–1677.
2. Fang FF, Choi HJ, Joo J (2008) Conducting polymer/clay nanocomposites and their applications. J Nanosci Nanotechnol 8:1559–1581.
3. Hao T, Xu ZM, Xu YZ (1997) Correlation of the dielectric properties of dispersed particles with the electrorheological effect. J Colloid Interface Sci 190:334–340.
4. Choi HJ, Jhon MS (2009) Electrorheology of polymers and nanocomposites. Soft Matter 5:1562–1567.
5. Jordan TC, Shaw MT (1989) Electrorheology. IEEE Trans Electrical Insul 24:849–878.
6. Parthasarathy M, Klingenberg DJ (1996) Electrorheology: Mechanisms and models. Mater Sci Eng R-Rep 17:57–103.
7. Sung JH, Cho MS, Choi HJ, Jhon MS (2004) Electrorheology of semiconducting polymers. J Ind Eng Chem 10:1217–1229.
8. 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.
9. Mrlik M, Pavlinek V, Saha P, Quadrat O (2011) Electrorheological Properties of suspensions of polypyrrole-coated titanate nanorods. Appl Rheol 21:52365.
10. Ramos-Tejada MM, Espin MJ, Perea R, Delgado AV (2009) Electrorheology of suspensions of elongated goethite particles. J Non-Newton Fluid Mech 159:34–40.
11. Rankin PJ, Ginder JM, Klingenberg DJ (1998) Electro- and magneto-rheology. Curr Opin Colloid Interface Sci 3:373–381.
12. Sedlacik M, Mrlik M, Pavlinek V, Saha P, Quadrat O (2012) Electrorheological properties of suspensions of hollow globular titanium oxide/polypyrrole particles. Colloid Polym Sci 290:41–48.

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

14. Fang FF, Choi HJ, Seo Y (2010) Novel fabrication of polyaniline particles wrapped by exfoliated clay sheets and their electrorheology. J Nanosci Nanotechnol 10:285–289.

15. Cheng QL, He Y, Pavlinek V, Li CZ, Saha P (2008) Surfactant-assisted polypyrrole/titanate composite nanofibers: Morphology, structure and electrical properties. Synth Met 158:953–957.

16. Cheng QL, Pavlinek V, He Y, Li CZ, Saha P (2009) Electrorheological characteristics of polyaniline/titanate composite nanotube suspensions. Colloid Polym Sci 287:435–441.

17. Kim SG, Lim JY, Sung JH, Choi HJ, Seo Y (2007) Emulsion polymerized polyaniline synthesized with dodecylbenzenesulfonic acid and its electrorheological characteristics: Temperature effect. Polymer 48:6622–6631.

18. Liu YD, Park BJ, Kim YH, Choi HJ (2011) Smart monodisperse polystyrene/polyaniline core–shell structured hybrid microspheres fabricated by a controlled releasing technique and their electro-responsive characteristics. J Mater Chem 21:17396–17402.

19. Stenicka M, Pavlinek V, Saha P, Blinova NV, Stejskal J, Quadrat O (2010) Electrorheology of suspensions of variously protonated polyaniline particles under steady and oscillatory shear. Appl Rheol 20:1–11.

20. Lin C, Shan JW (2007) Electrically tunable viscosity of dilute suspensions of carbon nanotubes. Phys Fluids 19:121702.

21. Quadrat O, Stejskal J (2006) Polyaniline in electrorheology. J Ind Eng Chem 12:352–361.

22. Stenicka M, Pavlinek V, Saha P, Blinova NV, Stejskal J, Quadrat O (2009) The electrorheological efficiency of polyaniline particles with various conductivities suspended in silicone oil. Colloid Polym Sci 287:403–412.

23. Stenicka M, Pavlinek V, Saha P, Blinova NV, Stejskal J, Quadrat O (2011) Structure changes of electrorheological fluids based on polyaniline particles with various hydrophilicities and time dependence of shear stress and conductivity during flow. Colloid Polym Sci 289:409–414.

24. Block H, Kelly JP, Qin A, Watson T (1990) Materials and mechanisms in electrorheology. Langmuir 6:6–14.

25. Choi HJ, Hong CH, Jhon MS (2007) Cole-Cole analysis on dielectric spectra of electrorheological suspensions. Int J Mod Phys B 21:4974–4980.

26. Lengalova A, Pavlinek V, Saha P, Stejskal J, Kitano T, Quadrat O (2003) The effect of dielectric properties on the electrorheology of suspensions of silica particles coated with polyaniline. Physica A 321:411–424.

27. 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 26:1250007.

28. Stejskal J, Trchová M (2012) Aniline oligomers versus polyaniline. Polym Int 61:240–251.

29. Stejskal J, Sapurina I, Trchová M, Konyushenko EN (2008) Oxidation of aniline: Polyaniline granules, nanotubes, and oligoaniline microspheres. Macromolecules 41:3530–3536.

30. Stejskal J, Gilbert RG (2002) Polyaniline. Preparation of a conducting polymer (IUPAC technical report). Pure Appl Chem 74: 857–867

31. Ferreira DC, Pires JR, Temperini MLA (2011) Spectroscopic characterization of oligoaniline microspheres obtained by an Aniline-persulfate approach. J Phys Chem B 115:1368–1375

32. Surwade SP, Dua V, Manohar N, Manohar SK, Beck E, Ferraris JP (2009) Oligoaniline intermediates in the aniline–peroxydisulfate system. Synth Met 159:445–455.

33. Silva CHB, Ferreira DC, Ando RA, Temperini MLA (2012) Aniline-1,4–benzoquinone as a model system for characterization of products from aniline oligomerization in low acidic media. Chem Phys Let. 551:130–133

34. Havriliak S, Negami S (1967) A complex plane representation of dielectric and mechanical relaxation processes in some polymers. Polymer 8:161–172.

35. Cho MS, Choi HJ, Ahn WS (2004) Enhanced electrorheology of conducting polyaniline confined in MCM-41 channels. Langmuir 20:202–207.

36. Pavlinek V, Saha P, Kitano T, Stejskal J, Quadrat O (2005) The effect of polyaniline layer deposited on silica particles on electrorheological and dielectric properties of their silicone-oil suspensions. Physica A 353:21–28.

37. Yang SH, Gao X, Li CX, Wang Q, Shen R, Sun G, Lu KQ (2012) Composition of the giant electrorheological fluids. Modern Phys Lett B 26:1150023.

38. Orellana CS, He JB, Laeger HM (2011) Electrorheological response of dense strontium titanyl oxalate suspensions. Soft Matter 7:8023–8029.

39. Tang HZ, He JH, Persello J (2010) Giant electrorheological effects of aluminium-doped TiO_2 nanoparticles. Particuology 8:442-446.