

## Electrorheology of aniline-oligomer suspensions under oscillatory shear

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**Abstract.** Preparation of the aniline oligomers by the oxidation of aniline with *p*-benzoquinone in the solutions of methanesulfonic acid (MSA) and the rheology of their suspensions in silicone oil are presented in this study. This synthesis provides particles of flake-like morphology and various conductivities depending on the molar concentration of MSA. Further, the electrorheological (ER) performance of the particles suspended in the silicone oil was measured as well as dielectric properties of suspensions. Finally, the effect of the temperature on the ER activity was investigated.

### 1. Introduction

Electrorheological (ER) suspensions are basically two-phase liquid systems usually consisting of solid particles (dispersed phase) and liquid medium (continuous phase) [1–3]. Solid particles have to be polarizable under application of the electric field while the liquid medium should be in this case an electric insulator (usually silicone oil). Suspensions having these parameters provide a unique property to change the state from liquid-like to solid-like after application of the external electric field [4–6]. This transition is connected to the development of the internal structures within the application of electric field and also leads to rapid increase in the basic rheological properties, such as viscosity and viscoelastic moduli [7–10].

Solid particles are mostly represented by conducting polymers such as polyaniline [11–13], polypyrrole [14–16], polyphenylenediamine [17], and also polythiophene [18]. The advantages of conducting polymers over other ER materials (based on inorganic particles mostly titanates and titanium dioxides) represent fast preparation, suitable density (enhanced sedimentation stability), no abrasivity and, finally, tunable conductivity, which enables to control the ER performance.

However, aniline oligomers which are represented by several aniline constitutional units linked together seem to be promising material for ER suspensions due to their suitable conductivity [19]. Faster preparation in comparison to polymers and also tunable conductivity predict promising applicability of this material in ER suspensions.

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In this study aniline oligomers were prepared by oxidation of aniline with an organic oxidant, *p*-benzoquinone. The synthesis was carried out in the presence of different molar concentration of methanesulfonic acid, thus providing samples of different conductivity. Dielectric properties of the sample silicone oil suspensions were measured and results were fitted with Havriliak-Negami model in order to obtain information about the polarizability of samples as well as their relaxation time. Finally, the effect of temperature on viscoelastic properties of suspensions was investigated.

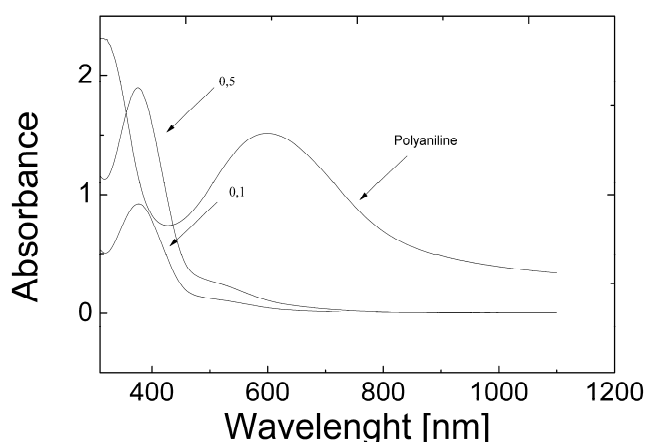
## 2. Experimental

### 2.1 Synthesis of aniline oligomers

Aniline (0.2 M; Fluka, Switzerland) was oxidized with *p*-benzoquinone (0.5 M; Sigma-Aldrich, USA) in aqueous solutions of 0.1–0.5 M methanesulfonic acid (MSA). After mixing the solutions of aniline and oxidant, the mixture was left at room temperature for a few hours. The solids were isolated by filtration, rinsed with acid solution, then with acetone, dried in air, and then over silica gel. A part of each sample was converted to a base form by immersion in a large excess of 1 M ammonium hydroxide, and dried as above.

### 2.2 UV–visible spectra

Polyaniline base displays the typical absorption spectrum of emeraldine base with absorption maxima at 330 and 620 nm [19]. In the case of aniline oxidation by *p*-benzoquinone, the latter absorption maximum is practically missing. This is due to the presence of dominating aniline oligomer fraction, which absorbs strongly below 400 nm and has only a long absorption tail extending to longer wavelengths (Figure 1).



**Figure 1.** The UV–visible spectra of the oxidation products dissolved in *N*-methylpyrrolidone prepared by the oxidation of 0.2 M aniline with 0.5 M *p*-benzoquinone in the aqueous solutions containing various molar concentrations of MSA and standard polyaniline base.

### 2.3 Conductivity measurements

Powders of prepared aniline oligomers were pressed into the pellets of 13 mm diameter and 1 mm thickness at 7 MPa. The conductivity was measured via van der Pauw method at room temperature (Table 1).

**Table 1.** Conductivity,  $\sigma$ , and density,  $\rho$ , of aniline oligomers prepared in the solutions of 0.1 and 0.5 M methanesulfonic acid.

Medium	$\sigma$ [S cm <sup>-1</sup> ]	$\rho$ [g cm <sup>-3</sup> ]
0.1 M MSA	$2.3 \times 10^{-10}$	1.36
0.5 M MSA	$1.9 \times 10^{-6}$	1.35

### 2.4 Suspension preparation

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

### 2.5 Rheological and dielectric characterization

Rheological measurements were performed under controlled-shear-rate mode using rotational viscometer (Bohlin Gemini, Malvern Instruments, UK). The suspensions were placed into the parallel plate geometry with 40 mm in diameter and 0.5 mm gap. The instrument modified for ER experiments was connected to DC high-voltage source TREK (TREK 668B, USA) to generate electric field strengths 0–3.0 kV mm<sup>-1</sup>. Before each measurement at new electric field strength, the built-up particulate structures were destroyed by shearing the sample suspension at the shear rate 50 s<sup>-1</sup> for 80 s.

Dielectric properties of prepared suspensions were measured with Impedance Analyzer 4294A (Agilent Technologies, Japan) connected to 16482A cell for liquid materials. To investigate appropriate dielectric properties such as relative permittivity,  $\epsilon'$ , and dielectric loss factor,  $\epsilon''$ , frequency range from 40 Hz to 5 MHz was selected. Measured dielectric spectra were fit with Havriliak–Negami (H–N) model (Eq. 1) [20].

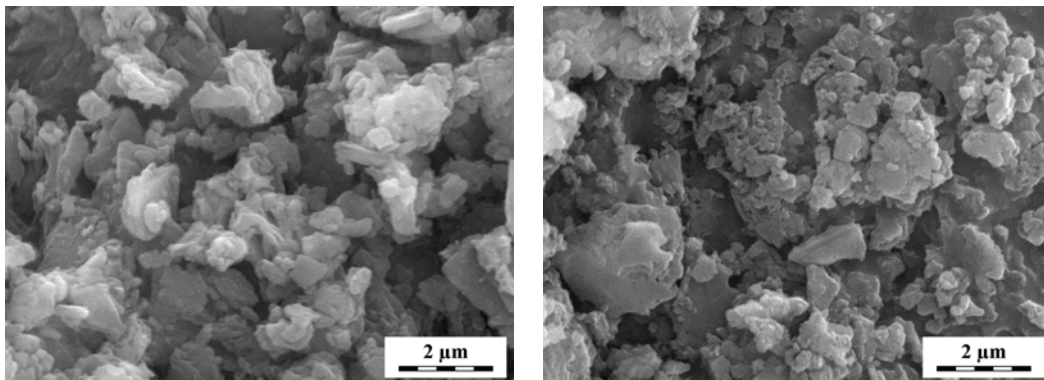
$$\epsilon_{HN}^*(\omega) = \epsilon'_\infty + \frac{\Delta\epsilon'}{(1 + (i\omega \cdot t_{rel})^a)^b} \quad (1)$$

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

## 3. Results and discussion

### 3.1 Morphology of particles

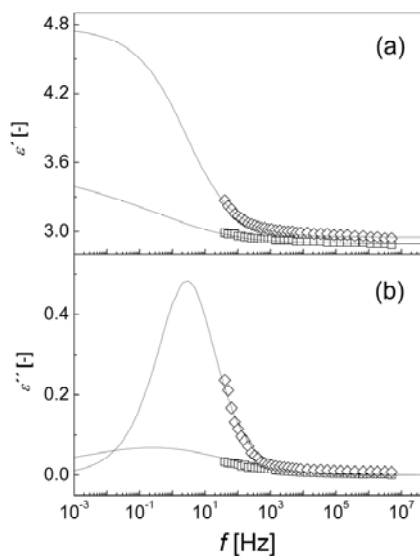
The oxidation of the aniline with *p*-benzoquinone in the aqueous solutions of MSA provided samples with particle size around two micrometers (Figure 2). Morphology of the samples depends on the molar concentration of MSA. In 0.1 M MSA, the product of the synthesis was nearly globular particles. On the other hand, when the 0.5 M MSA was used, particles with mostly flake-like morphology were prepared.



**Figure 2.** SEM images of synthesizes particles (right) in 0.1 M MSA and (left) in 0.5 M MSA.

### 3.2 Dielectric characterization

In order to obtain information about polarizability (ability to react on the application of the electric field) and relaxation time (how fast particles respond to the electric field), data from the dielectric measurements were fit with H–N model (Table 2, Figure 3). The polarizability is higher and the relaxation time is lower for suspension of the sample prepared in 0.5 M MSA in comparison to suspension of sample prepared in 0.1 M MSA having lower conductivity. Thus, the enhanced ER activity of the suspension containing particles obtained from 0.5 M MSA due to higher conductivity connected to improved charge motion should influence viscoelastic properties under applied electric field.



**Figure 3.** Frequency dependence of relative permittivity,  $\epsilon'$ , (a) and dielectric loss factor,  $\epsilon''$ , (b) for 10 vol.% suspensions of aniline oligomers in silicone oil. Samples were prepared in 0.1 M MSA ( $\square$ ) or 0.5 M MSA ( $\diamond$ ). Solid lines represent the H–N model fit.

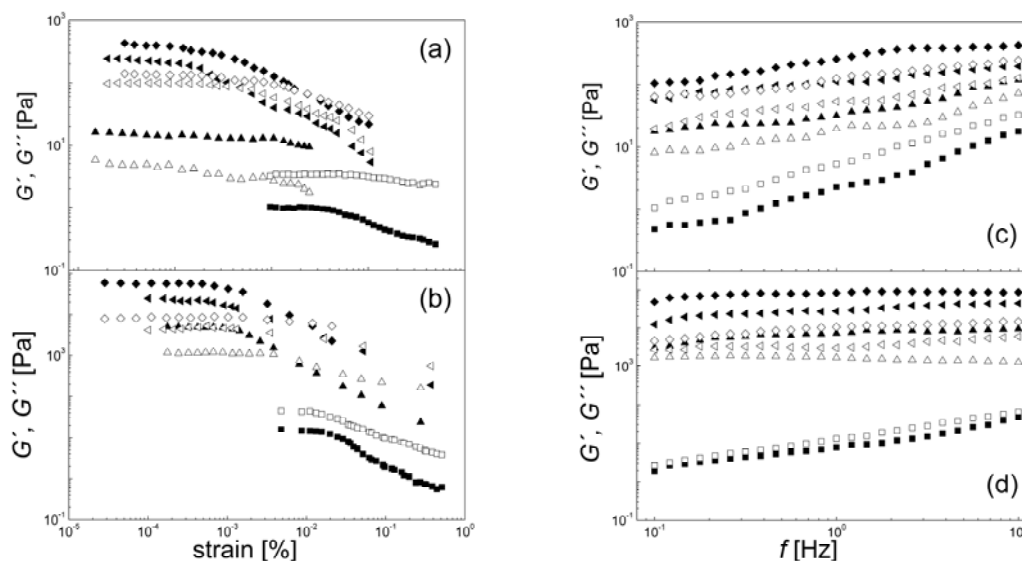
**Table 2.** Parameters of the Havriliak–Negami model.

Medium	$\epsilon'_s$	$\epsilon''_\infty$	$\Delta\epsilon'$	$t_{rel}$ [s]	$a$	$b$
0.1 M MSA	3.54	2.89	0.65	0.150	0.22	1.67
0.5 M MSA	4.74	2.95	1.79	0.048	0.62	1.12

### 3.3 Viscoelastic properties

Viscoelastic measurements provide information about dynamic characteristics of the prepared suspensions. Firstly, the linear viscoelastic regions from the dependence of the both viscoelastic moduli on the strain for the suspensions at various electric field strengths have to be established (Figure 4, left). Values of the strain will be further used for the frequency dependence of the moduli which is discussed below in the text.

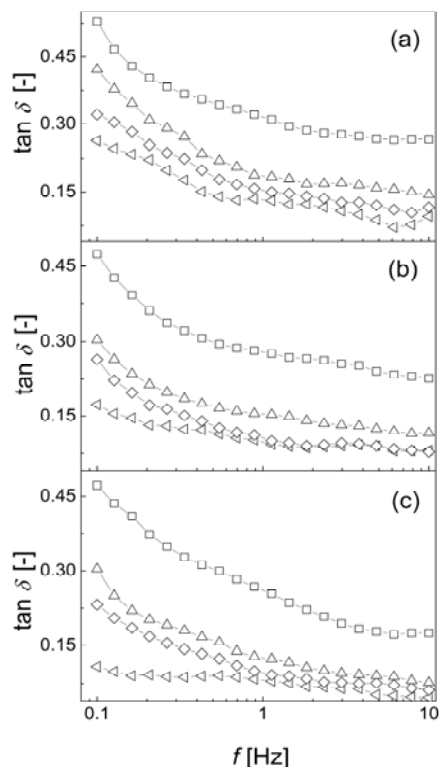
In the absence of external field the viscous modulus dominates over elastic one confirming the liquid-like state of the suspensions (Figure 4, right). On the other hand, in the presence of the electric field the elastic modulus overcome viscous one for both cases, confirming creation of the internal structures. Toughness of these chain-like columns increases with increasing electric field strength. Further, larger ER effect was observed for the suspension that contains particles prepared in 0.5 M MSA, due to suitable conductivity and also dielectric properties of their suspension.



**Figure 4.** Strain dependence (left) and frequency dependence (right) of elastic modulus,  $G'$  (solid symbols) and viscous modulus,  $G''$  (open symbols) for 10 vol.% suspensions of samples prepared in 0.1 M MSA (a, c) and 0.5 M MSA (b, d) under various electric field strengths,  $E$  ( $\text{kV}\cdot\text{mm}^{-1}$ ): ( $\square, \blacksquare$ ) 0, ( $\triangle, \blacktriangle$ ) 1, ( $\triangleleft, \blacktriangleleft$ ) 2, ( $\diamond, \blacklozenge$ ) 3, at 25°C.

### 3.4 Effect of the temperature on ER activity

In order to elucidate the influence of temperature on ER performance, the frequency dependence of the  $\tan \delta$  was plotted. When  $\tan \delta$  ( $\tan \delta = G''/G'$ ) decreases, elastic behaviour of the suspension increases. In this case,  $\tan \delta$  decreases with the increasing temperature (Figure 5). This trend is more pronounced at higher electric field strengths. Brownian motion stimulated at elevated temperatures inhibits the creation of the chain-like structures and decrease the ER activity.



**Figure 5.** Frequency dependence of  $\tan \delta$  for 10 vol.% suspension of aniline oligomers prepared in 0.5 M MSA at (a)  $1 \text{ kV}\cdot\text{mm}^{-1}$ , (b)  $2 \text{ kV}\cdot\text{mm}^{-1}$  and (c)  $3 \text{ kV}\cdot\text{mm}^{-1}$ , at various temperatures ( $^{\circ}\text{C}$ ): ( $\square$ ) 85, ( $\triangle$ ) 65, ( $\diamond$ ) 45, ( $\triangleleft$ ) 25.

#### 4. Conclusion

Aniline oligomers were prepared by the oxidation of aniline with *p*-benzoquinone in the solutions of methanesulfonic acid (MSA). Various molar concentrations of MSA provided samples with different conductivities. Using the concentration of 0.5 M MSA enables to synthesize rather flake-like than globular morphology. The suspension of sample particles prepared in 0.5 M MSA provided the highest ER efficiency due to suitable conductivity. Dielectric properties such as polarizability of the particles and relaxation time obtained from the fitting of the dielectric spectra with H–N model also supported the enhanced ER effect of oligomers prepared in 0.5 M MSA. Finally, rheological investigation under various temperatures shows decreased ER activity of the suspensions at elevated temperatures.

#### Acknowledgement

The authors wish to thank the Czech Grant Agency for the financial support (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 (CZ.1.05/2.1.00/03.0111).

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