Behaviour of the suspensions of polyaniline–poly-*p*-phenylenediamine copolymers with incorporated silver particles under electric field

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Abstract: Composite particles of poly(aniline-*co*-*p*-phenylenediamine) with silver were prepared by oxidation of aniline with silver nitrate in the presence of camphorsulfonic acid. Various amount of phenylenediamine provided materials with different conductivity and different particle morphology. In spite of high silver content, the conductivity of composite particles was relatively low, which enabled measurement of electrorheological (ER) activity of suspensions at high electric-field strengths. By using an optical microscope, a different chain-like structure of particle organization in the electric field depending on particle morphology has been found. The results demonstrated good reproducibility of the phenomenon.

Keywords: Polyaniline, *p*-Phenylenediamine, Silver, Copolymer, Suspensions, Electrorheology

1 Introduction

Electrorheological (ER) suspensions usually consist of polarizable particles suspended in insulating liquid medium. When the suspension is placed between two electrodes, after application of an external electric field, particles suspended randomly in the medium become polarized and create chain-like structures. Formation of such structures can be observed as an increase of the rheological properties such as shear stress and viscoelastic moduli more than several orders of magnitude. Development of the chain-like structures under applied electric field is followed by changing the state from originally liquid-like to solid-like. Generally, this change is very fast, usually in several milliseconds, and infinitely reversible. When the electric field is switched-off, developed structures can be broken and the suspension reverts to the previous liquid-like state.

Since ER phenomenon was recognized by Winslow in 1949 [1], many studies were focused on the basic mechanisms of these systems and results have been summarized in several papers [2-7]. ER suspensions containing water-based materials were mostly replaced by suspensions of conducting polymers such as polypyrrole [8-10] polyaniline (PANI) [11-14] poly-*p*-phenylenediamine (PPDA) [15,16] and polythiophene [17] due to their enhanced temperature and sedimentation stability and also corrosion resistivity.

2 Problem Formulation

Preliminary study was aimed at elucidation of the dependence of the ER effect on conductivity of PANI particles prepared with the help of protonation with various organic acids [18]. In the present paper the ER behaviour of suspensions of poly(aniline-*co*-*p*-phenylendiamine (PANI-PPDA) containing silver nanoparticles with various particle morphology were investigated. In addition to conductivity, silver nanoparticles are expected to affect the particle polarizability.

2.1 Preparation of PANI-PPDA copolymers with silver particles

Aniline (0.2 M) or mixtures with various concentrations of *p*-phenylenediamine (PDA) from 0.02 M up to 0.12 M (both from Fluka, Switzerland) were oxidized with 0.5 M silver nitrate (Lach-Ner, Czech Republic) in 1 M aqueous solution of camphorsulfonic acid at 20 °C. The oxidation of aniline alone was slow (several weeks), other reactions including PDA alone proceeded within hours or even tens of minutes. PANI-PPDA and metallic silver are the products. The solids were collected on a filter, rinsed with the corresponding acid solution, again with acetone, and dried at room temperature over silica gel. The molar concentration of the PDA was different as can be seen in the Table 1, where the number in sample codes represents PDA concentration.

2.2 Conductivity measurement

The powder of copolymer samples was pressed into the pellets of 13 mm diameter and 0.8–1.2 mm thickness at 7 MPa with manual hydraulic press. The conductivity of the pellets was measured by van der Pauw method at room temperature (Table 1).

Table 1: Conductivities and amount of silver in the samples

Sample codes	Conductivity [S.cm^{-1}]	Wt. % Ag
PANI-PPDA-0.02	2.3×10^{-4}	54.1
PANI-PPDA-0.04	1.4×10^{-5}	43.0
PANI-PPDA-0.1	1.9×10^{-5}	36.4
PANI-PPDA-0.12	7.1×10^{-5}	37.1

2.3 Suspension preparation

Suspensions (10 wt.%) were prepared by mixing PANI-PPDA/Ag composites with corresponding amount of silicone oil (Chemical Works Kolín, Czech Republic: Lukosiol M200, viscosity η_c = 200 mPa.s, density ρ_c = 0.970 g cm^{-3}, relative permittivity ε'_c = 2.89, loss factor tg δ = 10^{-4}). Before each measurement, the samples were stirred at first mechanically and then in ultrasonic bath for 30 s.

2.4 Rheological properties

Rheological measurements were performed under controlled-shear-rate (CSR) mode using coaxial cylinder viscometer (Bohlin Gemini, Malvern Instruments, UK). The suspensions were placed into the Couette cell with a rotating inner cylinder of 14 mm diameter and stationary outer cylinder separated by 0.7 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^{-1}. Before each measurement at new electric field strength, the built-up particulate structures were destroyed by shearing the sample at shear rate 50 s^{-1} for 80 s.

2.5 Optical microscopy

Suspensions consisting of 1 wt.% particles in silicone oil were placed between two gold electrodes deposited on glass with the gap of 1 mm connected to DC high-voltage source KEITHLEY (2400, USA). Formation of ER structures was observed with the help of optical microscope Olympus (CS31, Japan) linked to digital camera Olympus (C-4000, Camedia Zoom, Japan).

3 Problem Solution

3.1 Morphology of the particles

Figure 1 demonstrates that morphology of the particles of PANI-PPDA/Ag composites changed when the molar concentration of the PDA in the reaction mixture increased (Table 1). Sample PANI-PPDA-0.02 (Fig. 1a) has virtually globular shape of the particles which form clusters. On the other hand, with increasing amount of PDA the rod-like particle structures appeared (Fig. 1b–d).

3.2 Electrorheological properties

In the absence of external electric field, all suspensions exhibit nearly Newtonian behaviour (Fig. 2). Deviation from Newtonian behaviour is caused by increasing amount of rod-like particles in the samples. On the other hand, in the presence of the external electric field (Fig. 3), suspensions exhibit pseudoplastic behaviour with a value of the yield stress. Yield stress increased with increasing amount of rod-like particles in the sample.

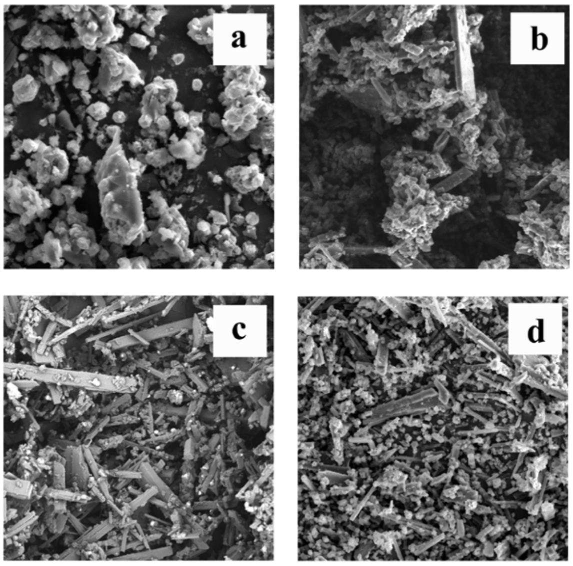

Fig. 1: SEM micrographs of the PANI-PPDA-0.02 (a), PANI-PPDA-0.04 (b), PANI-PPDA-0.1 (c), PANI-PDA-0.12 (d).

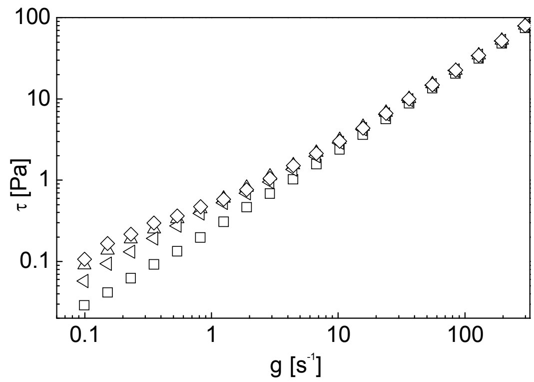

Fig. 2: The dependence of the shear stress, τ, on the shear rate, g, for 10 wt. % suspensions of PANI-PPDA-0.02 (□), PANI-PPDA-0.04 (△), PANI-PPDA-0.1 (◁), PANI-PPDA-0.12 (◇) in silicone oil in the absence of electric field.

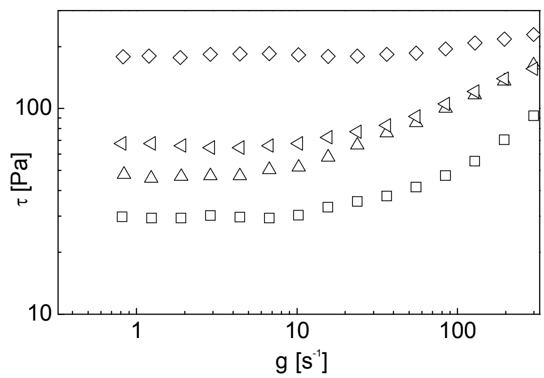

Fig. 3: The dependence of the shear stress, τ, on the shear rate, g, for 10 wt. % suspensions of PANI-PPDA-0.02 (□), PANI-PPDA 0.04 (△), PANI-PPDA-0.1 (◁), PANI-PPDA-0.12 (◇) in silicone oil at electric field strength E = 2.5 kVmm^{-1}.

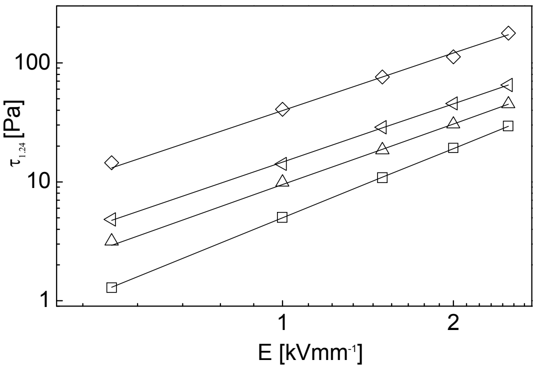

Fig. 4: The dependence of the shear stress, τ, at a minimum shear rate g = 1.24 s^{-1}, $\tau_{1.24}$, on the electric field strength E, for suspensions of the PANI-PPDA-0.02 (□), PANI-PPDA-0.04 (△), PANI-PPDA-0.1 (◁), PANI-PPDA-0.12 (◇) in silicone oil.

In the case of PANI-PPDA copolymer with silver, with increasing applied external electric field, shear stress of the samples increases and exhibits considerable change, especially at low shear rates due to strong electrostatic forces. Shear stress at minimum shear rate, $\tau_{1.24}$, expressed as the measure of the rigidity of the ER structures was obtained from the steady-shear measurements. The double logarithmic plot of the $\tau_{1.24}$ on the electric field strength E, exhibits linear fit corresponding to the power-law relation $\tau_{1.24} = q\ E^{a}$ (Fig. 4), where exponent, a, characterizes the particle response on the electric field and, q, is related to the rigidity of ER structures. Parameters for all suspensions are summarized in the Table 2.

Table 2: Parameters of the power-law model fit

Sample	q	a
PANI-PPDA-0.02	4.98	1.94
PANI-PPDA-0.04	9.47	1.70
PANI-PPDA-0.1	14.67	1.63
PANI-PPDA-0.12	39.76	1.60

3.3 Response of the ER suspensions on the switching on/off of the electric field

Response of repeated switching on/off of the electric field for suspensions of PANI-PPDA-0.12 containing rod-like particles and PANI-PPDA-0.02 including globular clusters, is nearly the same regardless of very different particle shape (Fig. 5).

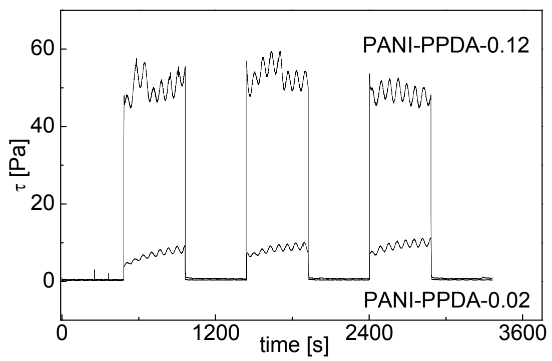

Fig. 5: Time dependence of the shear stress, τ, in the alternate regime switching on (E = 1 kV mm^{-1}) and off (E = 0 kVmm^{-1}) at constant shear rate 1 s^{-1} for 10 wt.% suspensions in silicone oil.

3.4 Development of the ER stuctures

The particles of the sample PANI-PPDA-0.02 are randomly dispersed in the absence of an electric field (Fig. 6a). After application of the electric field of 1 kV mm^{-1} particles start to move and create chains between electrodes (Fig. 6b). These particles, in spite of the high conductivity, develop relatively thick chains, but the amount of such structures is very low and this is the reason for a weak ER effect.

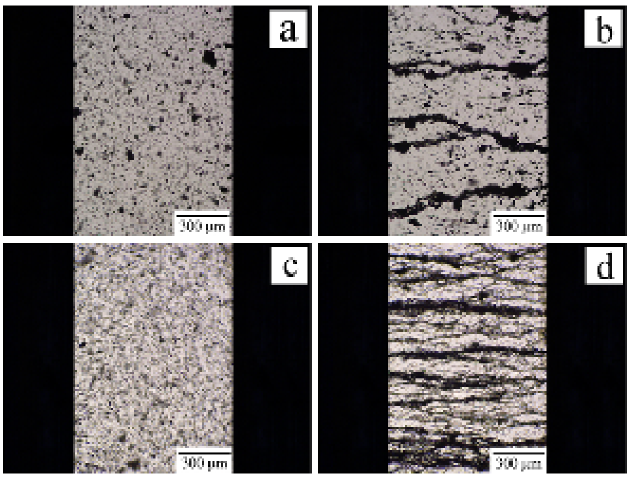

Fig. 6: Optical microscopy of 1 wt.% suspension of PANI-PPDA-0.02, (a) in the absence and (b) in the presence of the external electric field strength of 1 kVmm^{-1}, and of PANI-PPDA-0.12, (c,d) under the same conditions.

On the other hand, particles of the sample PANI-PPDA-0.12 (Fig. 6d) created large amount of thin columns. Thus, the different character of generated structures is reflected in development of yield stresses in the presence of electric field (Fig. 3). It is obvious that conductivity and shape of particles play dominant role in ER effect.

4 Conclusion

The results demonstrated that suspensions of PANI-PPDA/Ag composites exhibit good ER behaviour. Rigidity of developed structures in the electric field depended on particle conductivity and increased with higher fraction of rod-like particles in the samples. The different morphology of the particles in suspensions did not influence reproducibility of the change from the liquid-like to solid-like state and back during the alternating on/off switching of the electric field. The findings confirmed that both conductivity and particle shape may be crucial factors in design of ER suspensions.

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