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ORIGINAL CONTRIBUTION

Structure changes of electrorheological fluids based on polyaniline particles with various hydrophilicities and time dependence of shear stress and conductivity during flow

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Abstract Particles of polyaniline protonated with perfluorooctanesulfonic acid provided a material with hydrophobic surface. This property enabled its perfect dispersion in silicone oil due to its good compatibility with the hydrophobic medium. In contrast, in a suspension of hydrophilic polyaniline particles doped with sulfamic acid, strong interactions of particles prevailed, which led to the formation of entangled chains of aggregated particles in suspension. The difference in structural properties of suspensions exists already in the absence of electric field and significantly influences their electrorheological behavior after application of electric field. The formation of electrorheological structure has been monitored by recording time dependences of the shear stress and the electric current passing through the flowing suspensions.

Keywords Hydrophilicity · Hydrophobicity · Electrorheology · Polyaniline suspension · Protonation · Conductivity · Time dependence

Introduction

The factors affecting the formation of oriented structures by polarized suspension particles in electrorheological (ER) liquids in the electric field have been analyzed in many studies and the results were summarized in several reviews [1–8]. Polarizability of particles, depending on dielectric and conductance properties of the suspended solid phase, has been recognized as the crucial parameter controlling the ER phenomenon [9–12]. In addition, the morphology, size, and shape of particles as well as their concentration [13], which determine the field-off rheological behavior of the suspensions, proved to be important.

Many powdered materials, both inorganic and organic, have been used as dispersed phases in ER suspensions. A very promising material, polyaniline (PANI), has been the object of many ER studies [8, 14] due to possibility to control conductivity and dielectric properties by adjusting its degree of protonation [15–17] or polymerization temperature [10, 18]. In our previous paper [19], by protonation of PANI particles with four acids, particles of different compatibility with the oil medium have been prepared and a significant role of the hydrophilicity of particle surface on the ER efficiency has been demonstrated. The surface properties of particles affected both the field-off viscosity of the suspensions and its increase in the electric field (electroviscosity). The results revealed that, in spite of high viscosity of suspensions of aggregated hydrophilic particles in the electric field, its ER performance may be low [20].

The current study elucidates the influence of particle hydrophilicity on suspension structure in the absence and in the presence of electric field. Using two model materials—suspensions of hydrophilic PANI particles protonated with sulfamic acid and suspensions of hydrophobic particles protonated with perfluorooctanesulfonic acid, monitoring of the changes of the shear stress and the electric current passing through the suspensions in time revealed the differences in mechanism of the build-up of the ER structures.

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Table 1 Conductivity (σ), density (ρ), and the water contact angle (θ) of PANI base protonated with aqueous solutions of acids

PANI sample	Aqueous acid	σ [S cm^{-1}]	ρ [g cm^{-3}]	θ [°]
S1	5% perfluorooctanesulfonic acid	7.5×10^{-3}	1.448	102
S2	1 M sulfamic acid	4.5×10^{-1}	1.333	36

Experimental

Preparation of PANI and its protonation PANI powder was prepared by the oxidation of 0.2 mol L^{-1} aniline hydrochloride with 0.25 mol L^{-1} ammonium peroxydisulfate [21]. A PANI salt obtained as a precipitate after polymerization was converted to a PANI base with excess of 1 mol L^{-1} aqueous ammonia. The conductivity of PANI base was 3×10^{-9} S cm^{-1}. PANI base (1.81 g, 5 mmol, based on the segment of four aniline units) was suspended in 40 mL of aqueous perfluorooctanesulfonic or sulfamic acid solution for 24 h (Table 1). The resulting protonated PANI was filtered off, washed with acetone, and dried at room temperature in air, and then in a desiccator. Conductivities of PANI powders were measured by a four-point van der Pauw method on pellets, 13 mm in diameter, compressed at 700 MPa with a manual hydraulic press, using a current source SMU Keithley 237 and a Multimeter Keithley 2010 voltmeter (Keithley, USA) with a 2,000 SCAN 10-channel scanner card. The water contact angles measured on the same pellets were assessed with a measuring system OCA20 (Dataphysic, Germany) [16]. The particles protonated with perfluorooctanesulfonic acid (S1) were hydrophobic as reflected by high water contact angles (Table 1). On the other hand, protonation with sulfamic acid yielded hydrophilic PANI particles (S2).

Preparation of PANI particle suspensions PANI powders were ground in an agate mortar, sieved to obtain particle sizes below 45 μm, and dried at 80 °C in vacuum. Suspensions (1 vol.% and 10 vol.%) were prepared by mixing PANI powders with corresponding amounts of silicone oil (Lukosiol M200, Chemical Works Kolin, Czech Republic, viscosity, η_c=200 mPa s, density, ρ_c=0.965 g cm^{-3}, conductivity, $\sigma_c\approx 10^{-11}$ S cm^{-1}). Before each measurement, the suspensions were stirred at first mechanically, then in an ultrasonic bath for 30 s.

Particle morphology The shape and size of protonated PANI particles were characterized by scanning electron microscopy (SEM, VEGA II LMU, Tescan, Czech Republic). The particle aggregates in order of microns (Fig. 1) showed high agglomeration for both types of protonation.

Formation of ER structures The formation of ER structures was observed with an optical microscope Olympus (CX31, Japan). The source of electric field, E=200 V mm^{-1} was a Keithley 6517B (Keithley, USA) apparatus. The micrographs were taken by a digital camera Olympus (C-4000 Camedia Zoom, Japan).

ER measurements The steady-flow measurements in the controlled shear rate mode were performed using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK), with parallel plates 40 mm in diameter and an 0.5 mm gap, modified for ER experiments. The plates were connected to a high-voltage DC source TREK 668B (TREK, USA) providing the electric field intensity, E=0–500 V mm^{-1}. Before each measurement at new

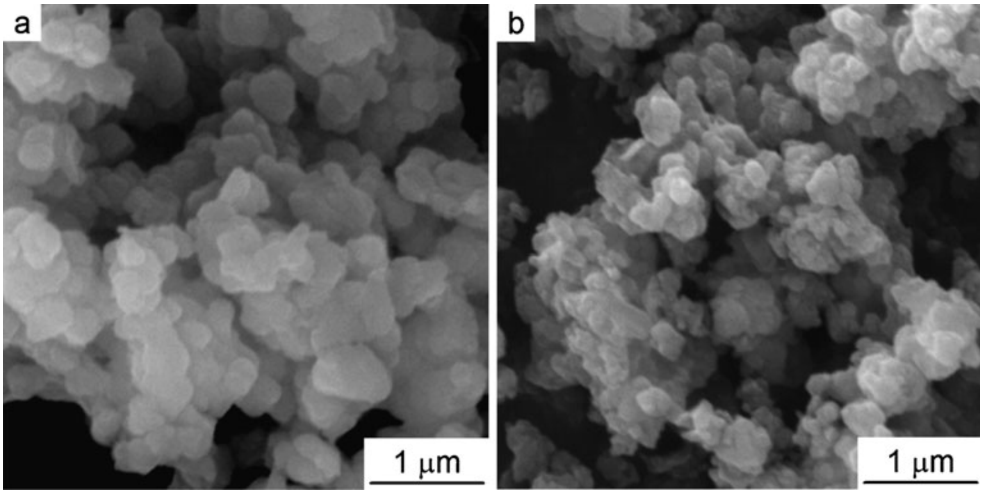

Fig. 1 SEM micrographs of PANI particles protonated with either perfluorooctanesulfonic (**a**) or sulfamic acid (**b**)

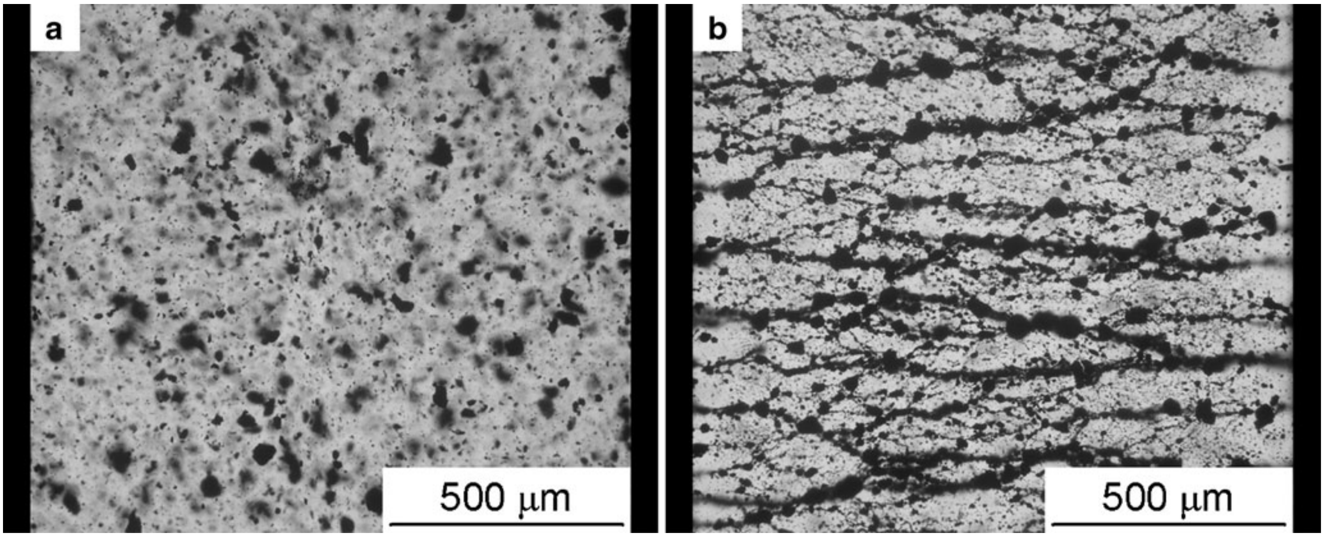

Fig. 2 Micrographs of 1 vol.% silicone oil suspension of PANI particles protonated with perfluorooctanesulfonic acid before (**a**) and after (**b**) application of the electric field, E=200 V mm^{-1}

electric field strength, the built-up particle structure was destroyed by shearing the sample at the shear rate 20 s^{-1} for 80 s. The temperature during all experiments was kept at 25 °C.

Current measurements The time dependence of the current passing through PANI suspensions in both static and dynamic flow fields was measured in the gap between the parallel plates of a rotational rheometer Bohlin Gemini (Malvern Instruments, UK). The applied DC voltage corresponded to the electric field strength, E=0–500 V mm^{-1}. Keithley electrometers 6517B and 2,100 (Keithley, USA) and a high-voltage source TREK 668B (TREK, USA) were used for this purpose.

Results and discussion

Structure of suspensions Micrographs in Figs. 2a and 3a demonstrate a crucial difference in the field-off structure of particles of hydrophobic and hydrophilic samples in silicone oil. A good oil compatibility of hydrophobic particles protonated with perfluorooctanesulfonic acid provided a homogeneous suspension of isolated dispersed particles, obviously with weak particle interactions (Fig. 2a). In the electric field, the particles were ordered in chains between the electrodes (Fig. 2b) due to polarization. In contrast, the incompatibility of hydrophilic particles, protonated by sulfamic acid, with hydrophobic oil caused strong particle interactions. In the absence of electric

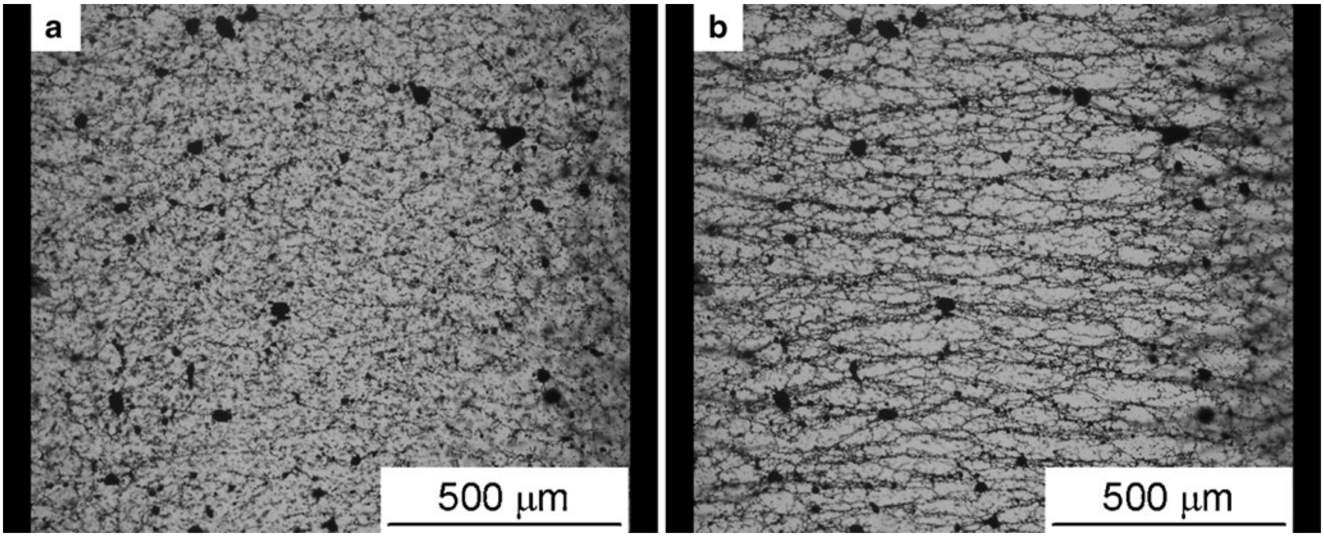

Fig. 3 Micrographs of 1 vol.% silicone oil suspension of PANI particles protonated with sulfamic acid before (**a**) and after (**b**) application of the electric field, E=200 V mm^{-1}

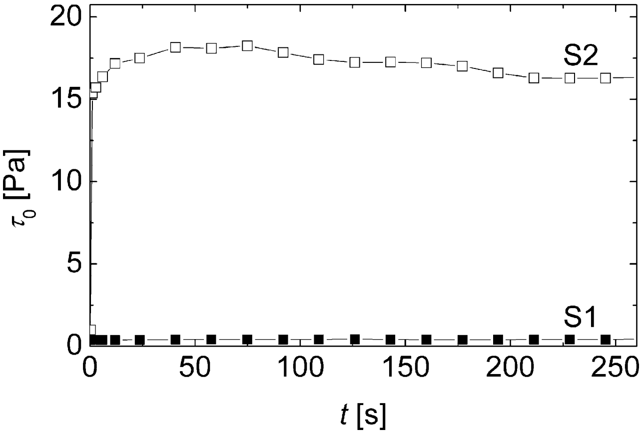

Fig. 4 The dependence of the field-off shear stress (τ_0) for suspensions (S1) and (S2) on time (t) at constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$

field, a fine network of entangled chains of particles linked by physical bonds arises (Fig. 3a). Polarization of this structure in the electric field caused its stretching along the streamlines of the field (Fig. 3b).

Time dependences of the shear stress In the absence of electric field, time dependences of the shear stress of hydrophobic (S1) and hydrophilic particle (S2) suspensions differed due to quite different suspension structures (Fig. 4). In the former case, the shear stress practically immediately attained a constant value. In the latter case, after a steep jump of more than one order of magnitude, the shear stress increased even further to a maximum and then slowly decreased, obviously owing to further reorganization of the particles in the flow (Fig. 4).

Also, the changes in the shear stress during the flow, reflecting the evolution of the ER structure in the course of time, were closely related to the field-off particle arrangement in suspensions. Due to the polarization of particles and formation of a chain structure (see the micrograph in Fig. 2b), the shear stress of sample (S1) rose the more, the higher was the electric field strength used. Reaching a stable shear stress took a longer time than in the absence of electric field (Fig. 5). The shear stresses obtained by switching on and off the electric field in short regular intervals showed similar values (Fig. 6).

On the contrary, the flow behavior of the polarized primary network of aggregated particle chains (Fig. 3b) was different. The maxima on the time dependences of the shear stress for the (S2) suspension and its gradual decrease on applying the electric field became more pronounced than in the absence of the electric field due to quite different suspension structures (Fig. 7). After switching on and off

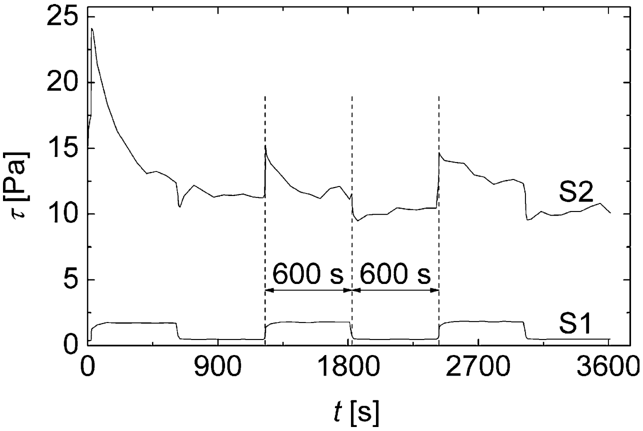

Fig. 6 Time dependence of the shear stress (τ) in the alternate regime of switching on (E=200 V mm^{-1})/off (E=0 V mm^{-1}) for hydrophobic (S1) and hydrophilic (S2) samples at constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$

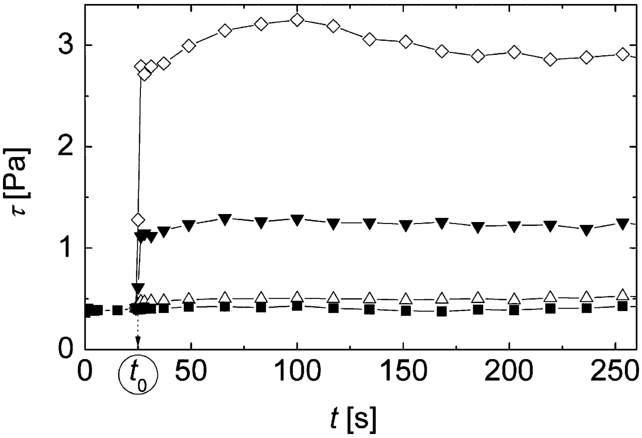

Fig. 5 The dependence of the shear stress (τ) for hydrophobic sample (S1) on time (t) at various electric field strengths, E [V mm^{-1}]: *black square* 0, *unfilled triangle* 100, *filled inverted triangle* 200, *diamond* 300. The electric field strength was switched on at time, t_0. Constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$ was used

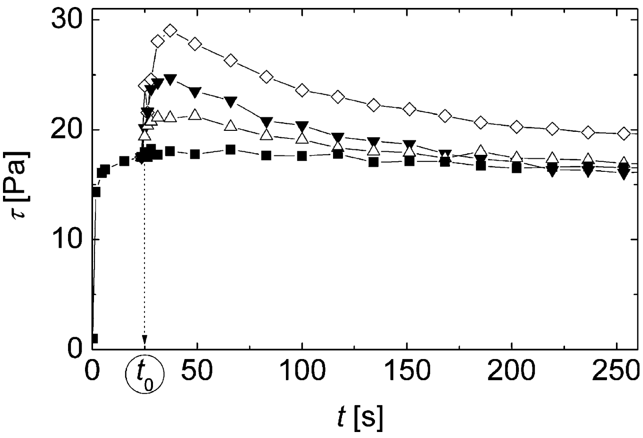

Fig. 7 The dependence of the shear stress (τ) for hydrophilic sample (S2) on time (t) at various electric field strengths, E [V mm^{-1}]. Points denoted as in Fig. 5. Constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$ was used

the electric field, further initial shear stress values were lower than in the first run (Fig. 6).

Time dependence of conductivity An increase in conductivity of the suspensions with time during the evolution of the ER structure of polarized particles depends on properties of the original suspension, which are closely associated with hydrophilicity of particles. The initial steep rise in the shear stress of suspensions of hydrophobic sample (S1) (Fig. 5) was accompanied by a moderate increase in conductivity (Fig. 8a). Alternate switching on and off the electric field always provided a similar current value (Fig. 9). On the other hand, in contrast to the shear stress time dependence for sample (S2) displaying a maximum (Fig. 7), the current, much lower than in the former case, increased slowly in the whole range of the times (Fig. 8b). When the flow was stopped and, after a short time, switched on again, an increase in the current continued (Fig. 9). This suggests the presence of a memory effect.

Conclusion

Unlike the usual chain or column formation in suspensions of polarized hydrophobic perfluorooctanesulfonic-acid-treated PANI particles compatible with the oil medium, the polarization of physical network of aggregated hydrophilic sulfamic-acid-treated PANI particles in electric field was more complex. In spite of a much higher conductivity of hydrophilic particles (Table 1), the current passing through their polarized structure proved to be more than one order of magnitude lower than that passing through the chains of less conducting polarized particles of a hydrophobic sample. This indicates a crucial influence of the particle hydrophilicity and, consequently, of the primary suspension structure on its conductivity.

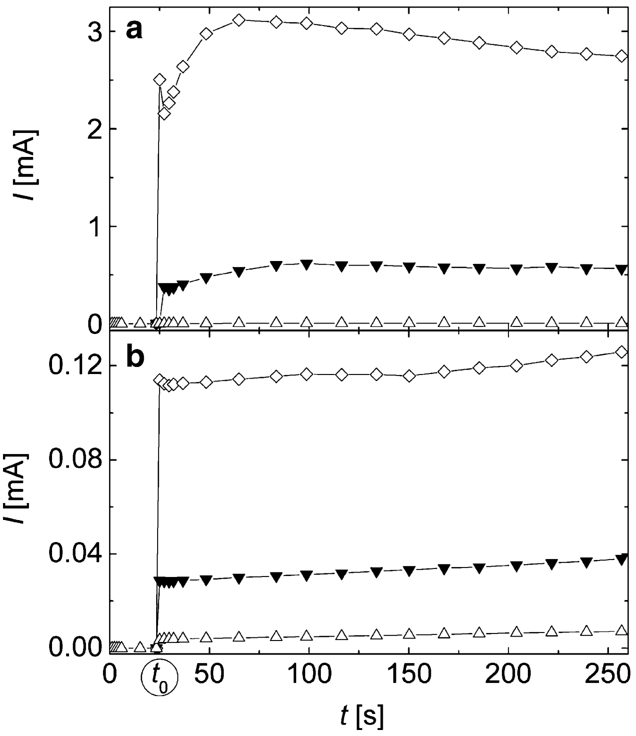

Fig. 8 The dependence of the current (I) passing through a suspension of hydrophobic sample (S1; **a**) and hydrophilic sample (S2; **b**) on time (t) at various electric field strengths, E [V mm^{-1}]. Points denoted as in Fig. 5. Constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$ was used

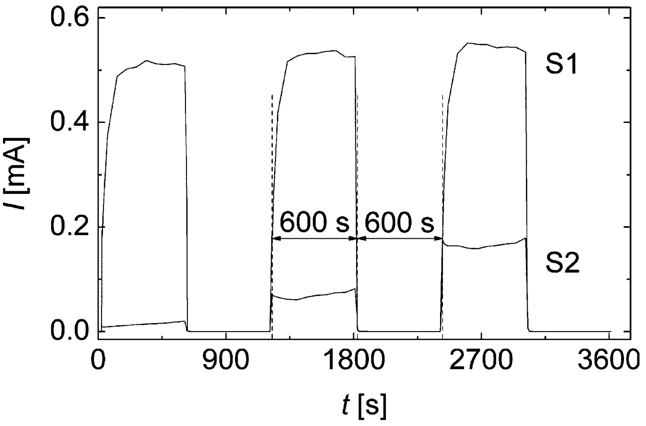

Fig. 9 Time dependence of the current (I) in the alternate regime of switching on (E=200 V mm^{-1})/off (E=0 V mm^{-1}) for hydrophobic (S1) and hydrophilic (S2) samples at constant shear rate, $\dot{\gamma} = 1\text{s}^{-1}$

Because of a high field-off viscoelasticity of suspensions of hydrophilic particles, its increase, characterizing the ER efficiency, was low even though a high value of shear stress was found in electric field. Thus, it turns out that hydrophilicity of suspension particles ranks among important factors influencing their ER performance.

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