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ORIGINAL CONTRIBUTION

Conductivity of flowing polyaniline suspensions in electric field

Martin Stěnička · Vladimír Pavlínek · Petr Sáha · Natalia V. Blinova · Jaroslav Stejskal · Otakar Quadrat

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Abstract The formation of chain structures by polarized polyaniline (PANI) particles suspended in silicone oil in the electric field has been monitored by recording suspension conductivity in the course of time. For that purpose, three types of PANI particles differing in the conductivity (3.1×10^{-3}, 1.7×10^{-1}, and 2.0×10^{-1} S cm^{-1}) have been chosen out of a series of nine samples prepared by controlled protonation of PANI base in orthophosphoric acid solutions. Relaxation times reflecting this process and characterizing the rate of the response to the electric field decreased with particle conductivity, indicating a higher polarizability of particles. At the same time, the maximum conductivity of suspension increased as a consequence of the electric and shear forces acting on the particles. In the shear fields, shorter relaxation times appeared than at rest. The simultaneous measurement of the shear stress confirmed that the conductivity investigation can reliably characterize the development of electrorheological structures.

Keywords Electrorheology · Polyaniline · Conducting polymer · Protonation degree · Conductivity · Relaxation time

M. Stěnička · V. Pavlínek (✉) · P. Sáha
Faculty of Technology, Tomas Bata University in Zlín,
TGM Sq. 275,
762 72 Zlín, Czech Republic
e-mail: pavlinek@ft.utb.cz

N. V. Blinova · J. Stejskal · O. Quadrat
Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic,
Heyrovsky Sq. 2,
162 06 Prague 6, Czech Republic

Introduction

It is generally known that particle polarization occurs in suspensions of semiconducting particles in non-conducting liquid in external electric field. The induced particle dipoles oriented along the field direction interact and link the particles into chains spanning the gap between electrodes. Consequently, the rigidity of this structure increases, and when a shear force is applied, viscosity at low shear rates is much higher than that in the absence of electric field. In some cases, quasi-gel suspensions with a high-yield stress may arise. This electrorheological (ER) phenomenon, discovered more than 60 years ago [1], has been the object of a number of studies summarized in several reviews [2–7].

For practical exploitation in various hydraulic or robotic applications, a high efficiency of the effect associated with the shortest reversible response to the electric field is needed. The experiments showed that, at an electric field strength of several kilovolts per millimeter, the particle polarization and subsequent buildup of a stiff ER structure may appear in milliseconds.

It has been shown that conducting polymers, such as polyaniline (PANI) or its substituted derivatives, are promising suspension materials in electrorheology because of their high polarizability [8–12]. Their conductivity is determined by the chemical structure of polymer chains comprising alternating π- and σ-bonds, hence forming a conjugated system. In addition, the presence of charge carriers is an essential condition for conductivity. The increase in conductivity of many orders of magnitude is mostly achieved through protonation with various acids by the process known as doping [13–15]. Different dopants can remarkably affect its structure and degree of crystallinity [16]. A large change in conductivity allows obtaining materials ranging from insulators to semiconductors.

Table 1 The density ρ and conductivity σ of protonated polyaniline base in aqueous solutions of orthophosphoric acid of various molar concentrations C_A

Sample	C_A (mol L^{-1})	ρ (g cm^{-3})	σ (S cm^{-1})
S0	0	1.132	3.6×10^{-9}
S1	0.0001	1.144	4.7×10^{-9}
S2	0.0005	1.114	6.8×10^{-9}
S3	0.001	1.112	2.7×10^{-8}
S4	0.005	1.145	5.8×10^{-7}
S5	0.01	1.264	4.7×10^{-5}
S6	0.05	1.333	3.1×10^{-3}
S7	0.1	1.362	1.7×10^{-1}
S8	0.5	1.415	2.0×10^{-1}
S9	1	1.412	3.3×10^{-1}

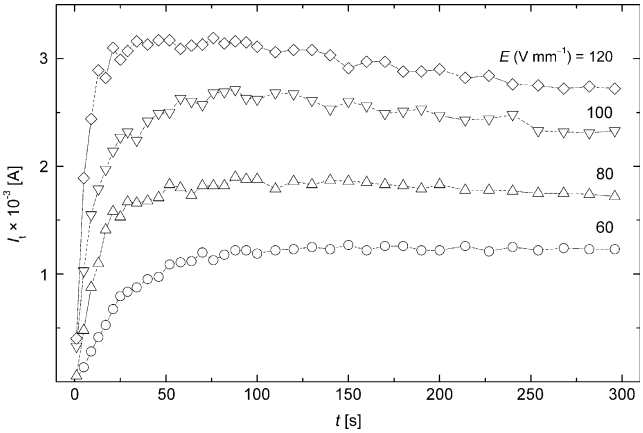
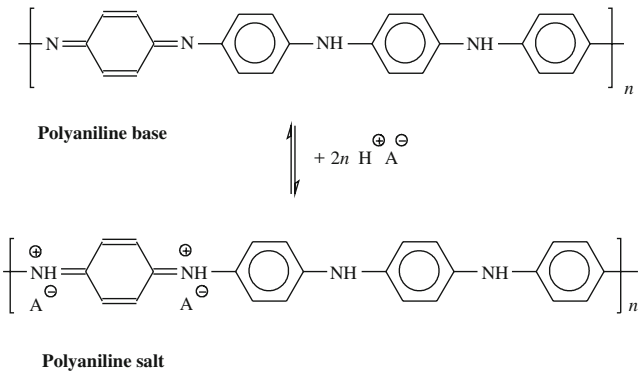


Fig. 1 Time dependences of the electric current I_t for suspensions of sample S8 at various electric field strengths E

Compared with similar polymers, PANI has several advantages, such as a simple preparation, easy conductivity control, good thermal and environmental stability, as well as favorable production costs. Consequently, investigation of its preparation and properties has attracted significant attention in the last three decades.

In our previous study [17], we have demonstrated that the ordering of PANI particles dispersed in a non-conducting liquid (1,2,4-trichlorobenzene) and slow formation of particle-chain structure sets in also in an electric field of low intensity. The results suggest that a systematic analysis of the relaxation times of the conductivity increase at various field strengths in relation to electric and dielectric properties of particles should be performed to understand the mechanism of the ER phenomenon. The aim of the present study is to investigate the time dependences of conductivity of protonated PANI suspensions in the course of the formation of chain structures in the direct electric field. The influence of the flow field on this process was examined in detail. Relaxation times of these changes and the maximum conductivity proved to be the basic parameters characterizing this process.



Scheme 1 PANI (emeraldine) base can be protonated with an acid (HA), like orthophosphoric acid, to various degrees of protonation. A^- is an anion. Taken from [19]

Experimental

Controlled protonation of polyaniline with orthophosphoric acid Polyaniline was prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in water [18] starting at 20 °C; its conductivity was 4.4 S cm^{-1}. The obtained PANI salt was transformed into the PANI base by 2-day immersion in a fivefold molar excess of 1 M NH_4OH (50 mL per gram of PANI salt), filtering of the precipitate, and drying in air. The conductivity of the PANI base was 3.6×10^{-9} S cm^{-1}. Portions of the PANI base (0.5 g) were added to 100 mL of aqueous solutions of orthophosphoric acid of various concentrations, separated after 24 h, and dried as above [19]. The conductivity of ten samples (S0–S9, Table 1), pressed at

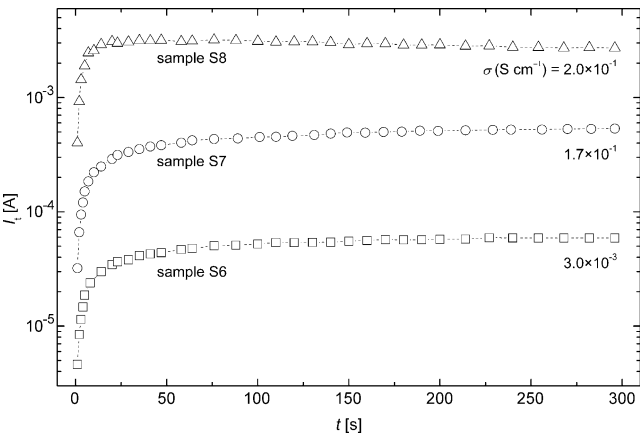


Fig. 2 Time dependence of the electric current I_t for suspensions of samples S6, S7, and S8 at various conductivities, σ, at the field strength E=120 V mm^{-1}

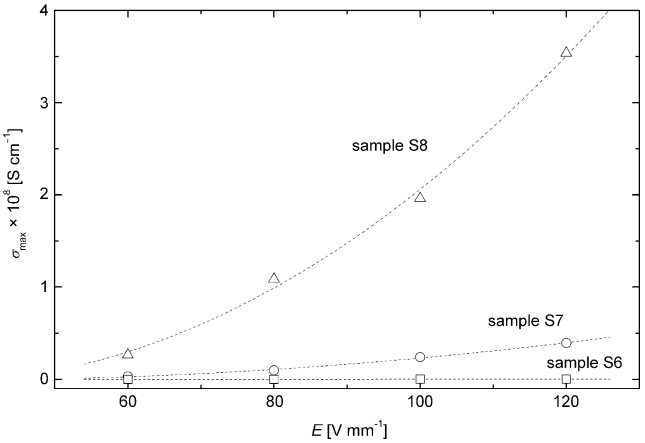


Fig. 3 The dependence of the maximum conductivity σ_{max} on the electric field strength E for the PANI particles of various conductivity

700 MPa into pellets 13 mm in diameter and 1-mm thick, was determined by a four-point method for the conducting samples and by a two-point method (after sputtering of gold electrodes) for the samples with a conductivity lower than 10^{-5} S cm^{-1}.

Suspension preparation In this study, three samples (S6, S7, and S8) with conductivities of 3.1×10^{-3}, 1.7×10^{-1}, and 2.0×10^{-1} S cm^{-1}, respectively, have been used. Conductivities of the samples with lower protonation degrees (S1–S5) were too low, and their time dependences could not be monitored. On the other hand, the conductivity of the most conducting sample (S9) was too high for this type of experiments. Electrorheological properties of suspensions with low protonation degrees (S1–S5) will be investigated in a forthcoming study.

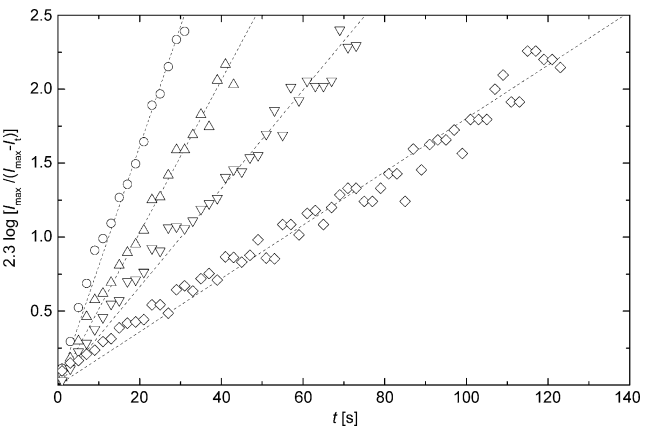


Fig. 4 Dependences for estimation of the relaxation times in suspension of sample S7 at various field strengths E (*diamond* 60, *inverted triangle* 80, *triangle* 100, *circle* 120 V mm^{-1})

Table 2 The dependence of the relaxation time t_s on the applied electric field strength E for the suspension of sample S7 in silicone oil

E (V mm^{-1})	60	80	100	120
t_s (s)	54.6	29.6	19.3	13.3

PANI powders were ground in an agate mortar, sieved to obtain particle sizes lower than 45 μm, and dried at 80 °C in a vacuum oven to constant weight. The 10-wt.% suspensions were prepared by mixing PANI powders with an appropriate amount of silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic; viscosity, η_c= 200 mPa s; density, ρ_c=0.965 g cm^{-3}; conductivity, $\sigma\approx10^{-11}$ S cm^{-1}; relative permittivity, ε_c=2.6; and loss factor, tan δ=0.002). The suspensions were stirred at first mechanically, then in ultrasonic bath for 30 s before each measurement.

Current-voltage measurements A Bohlin Gemini (Malvern Instruments, UK) rheometer of coaxial cylindric shape (length 27.4 mm, and diameters 15.4 and 14.0 mm) modified for ER experiments was used for measurement of the time dependence of the current passing through the suspension at rest and flowing in the time interval 0–300 s. The applied DC voltages, 42, 56, 70, and 84 V, corresponded to the electric field strength of 60, 80, 100, and 120 V mm^{-1}, respectively. A Keithley electrometer (6517A and 2100 Keithley, USA), and a high-voltage source TREK (668B TREK, USA), together with a Hexagon multimeter (Hexagon 720, Germany), were used. Before each measurement at a new electric field strength, the built-up particulate structure was always destroyed by shearing the sample at the shear rate of 20 s^{-1} for 80 s.

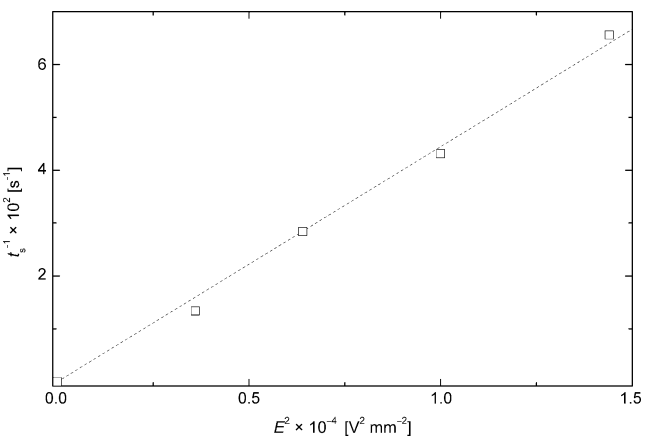


Fig. 5 The dependence of reciprocal relaxation time t_s on E^2 for the suspension of sample S7

Table 3 The relaxation time t_s, particle dipole coefficient, β, and permittivity of suspension particles, ε_p, at the electric field strength 120 V mm^{-1} from Eq. 2

Sample	t_s (s)	β	ε_p
S6	16.1	0.79	21
S7	13.3	0.87	37
S8	10.8	0.96	130

Results and discussion

Control of particle conductivity Non-conducting polyaniline base was used in many ER experiments [8, 11, 14] due to its good polarizability. Polyaniline base can be protonated (Scheme 1) to various degrees in acid solutions of various concentrations (Table 1). In particular, orthophosphoric acid is well suited for this purpose [19]. The protonation, i.e., the conversion of PANI base into PANI salt (Scheme 1), manifests itself in density increase and, more importantly, in a conductivity increase (Table 1). The particle conductivity can be adjusted to a required level. The influence of the conductivity on the electric and ER properties of PANI suspensions is analyzed in the present study.

Time dependence of electric current The formation of chains of conducting particles oriented along the power lines of the direct electric field at a constant field strength manifested itself in an increase in electric current I_t passing through the suspension. At higher electric field strengths (80, 100, and 120 V mm^{-1}) in case of sample S8, the current reached a maximum (I_{max}) in the time interval used and then slowly decreased. The decrease may be explained by migration of the particles to electrodes due to the electrophoretic effect. The density of particle structure is thus reduced. At the lower electric field strength (60 V mm^{-1}) and for the samples S6 and S7 at all electric field strength used, the current tended only to a limiting value (Figs. 1 and 2). The higher the applied voltage, the steeper the initial current increase and the higher the maximum current was reached. Both the initial increase and the maximum current were significantly influenced by the protonation degree, i.e., by the conductivity of particles (Fig. 2). The higher particle conductivity, the steeper the increase in the maximum conductivity of the organized particle structure at the applied electric field strength appeared (Fig. 3).

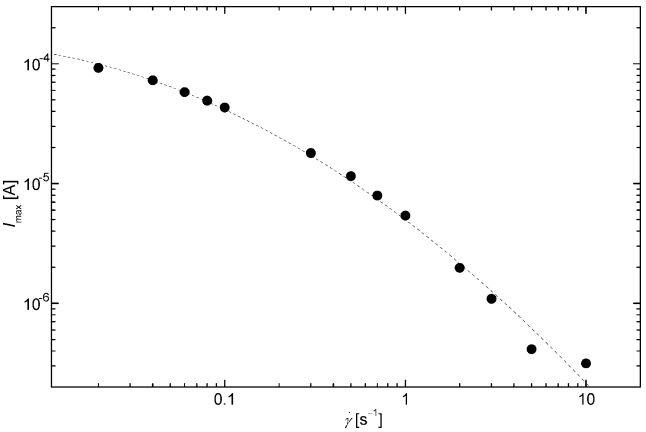


Fig. 7 The dependence of the maximum electric current I_{max} on the shear rate $\dot{\gamma}$ of sample S7 at the electric field strength 120 V mm^{-1}

The relaxation time and particle polarizability The increase in electric conductivity of the chain structures in the organization of suspension particles at the electric field

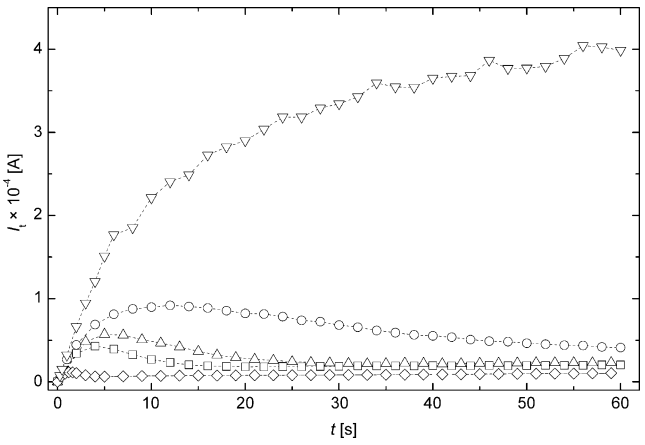


Fig. 6 Time dependences of the electric current I_t in the suspensions of sample S7 at the electric field strength 120 V mm^{-1} at various shear rates $\dot{\gamma}$(s^{-1}): *inverted triangle* 0, *circle* 0.02, *triangle* 0.06, *square* 0.1, *diamond* 0.5

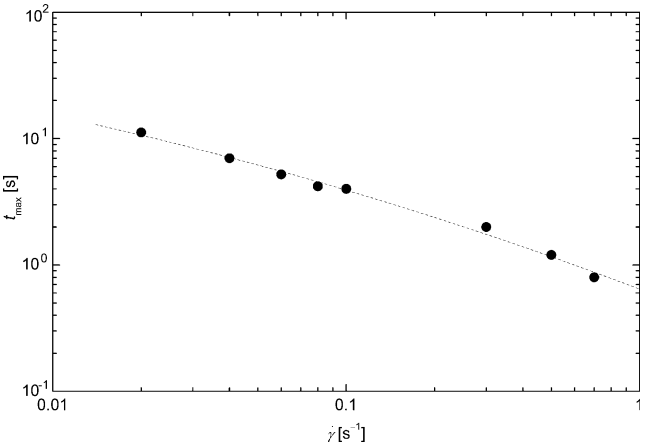


Fig. 8 The dependence of the time t_{max} of reaching the maximum current value on the shear rate $\dot{\gamma}$ of sample S7 at the electric field strength 120 V mm^{-1}

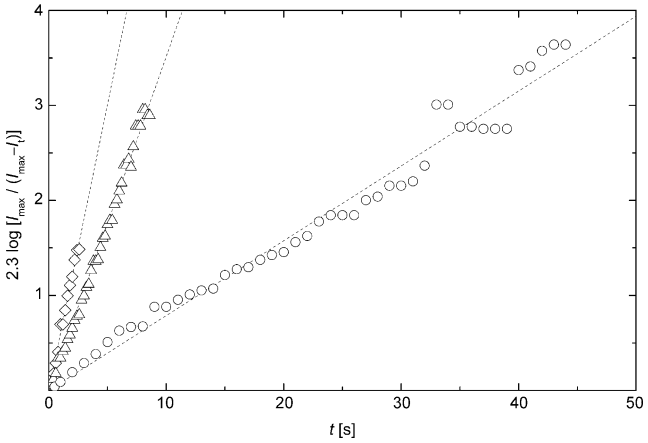


Fig. 9 Estimation of the relaxation times at rest and in flow in suspensions of sample S7 at the electric field strength 120 V mm^{-1} at rest (*circle*), and at the shear rates of 0.02 s^{-1} (*triangle*) and 0.04 s^{-1} (*diamond*)

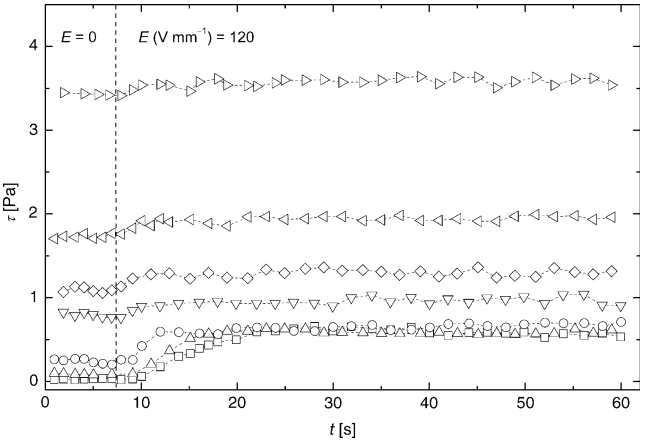


Fig. 11 The time dependence of shear stress τ of sample S7 at various shear rates $\dot{\gamma}$(s^{-1}) (s^{-1}): *square* 0.06, *triangle* 0.1, *circle* 0.5, *inverted triangle* 2, *diamond* 3, *left arrowhead* 5, *right arrowhead* 10

strength E can be characterized by a growth of the electric current I_t with time t expressed by Eqs. 1 and 2 [20]:

$$I_t = I_{\max}\left\{1 - [\exp(t/t_s)]^{-1}\right\} \quad (1)$$

where t_s is the relaxation time

$$t_s = 16\eta_c/\left(\varepsilon_0\varepsilon_c\beta^2E^2\right) \quad (2)$$

and the particle dipole coefficient $\beta = \left(\varepsilon_p - \varepsilon_c\right)/\left(\varepsilon_p + 2\varepsilon_c\right)$. Here, η_c and ε_c are, respectively, the viscosity and relative permittivity of the continuous phase, ε_0 is the absolute permittivity of the free space (8.854×10^{-12} F m^{-1}), and ε_p is the relative permittivity of suspension particles.

The relaxation time is closely related to dielectric and conducting properties of suspension particles [4, 21–24]. The dielectric relaxation of particles corresponds to the frequency at which a maximum dielectric loss sets in and the steepest decrease in permittivity with frequency arises. According to polarization theory, the particle dipole coefficient is a measure of particle polarizability and, consequently, of the strength of polarization forces. The higher the polarization of suspension particles, the shorter relaxation time appears and faster particle rearrangement is possible.

After rearranging Eq. 1, we obtain

$$\log[I_{\max}/(I_{\max} - I_t)] = t/(2.3t_s) \quad (3)$$

which suggests a linear dependence of the plot 2.3 log $[I_{max}/(I_{max}-I_t)]$ vs. t with the reciprocal relaxation time as a slope.

For a dispersion of sample S7 (Table 1), the relaxation time decreases with increasing electric field strength (Fig. 4, Table 2). Thus, a higher speed of building of the organized chain structure results in the reduced response to the electric field. According to Eq. 2, the relaxation time is

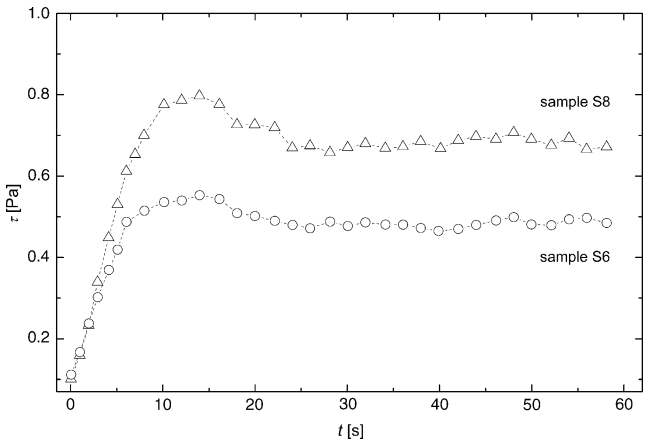


Fig. 10 The time dependence of the shear stress τ at electric field strength 120 V mm^{-1} for samples S6 (*circle*) and S8 (*triangle*) at shear rate 0.1 s^{-1}

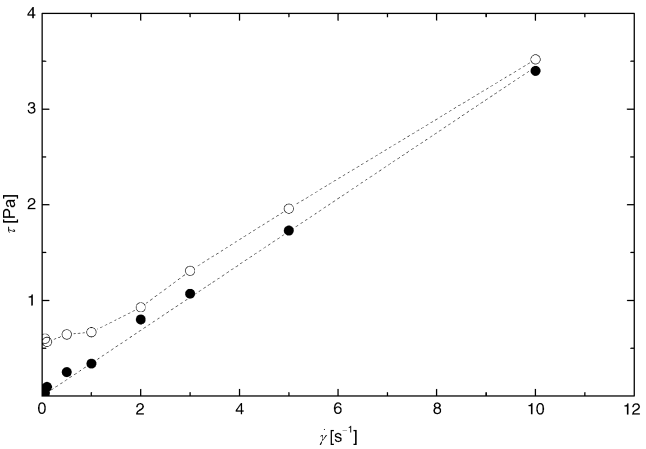


Fig. 12 The dependence of the field-off shear stress (*filled circle*) and maximum shear stress (*open circle*) on the shear rate $\dot{\gamma}$ for sample S7

inversely proportional to the square of the electrical field strength, and the plot of t_s^{-1} vs. E^2 should be a line passing through the origin with the slope β^2. Figure 5 confirms this assumption.

When conductivity of PANI particles increases by protonation, the permittivity may also increase by several orders of magnitude due to formation of additional free-charge carriers in the material. We found that the value of β calculated from the relaxation times at the applied field strength 120 V mm^{-1} increased with the protonation degree of particles; hence, considering the permittivity of the continuous phase ε_c=2.6, the particle permittivity steeply rises with the protonation degree (Table 3). This explains a steep increase in maximum conductivity with particle polarizability and with applied electric field strength (Figs. 1 and 2).

Flow influence When shearing was applied to the suspension and the flow started, the time dependences of electric current considerably changed (Fig. 6). At rest, the current gradually increased in the course of 300 s to a limiting value (see Fig. 2), whereas the current attained a much lower maximum value in approximately 10 s even at a small shear rate of 0.02 s^{-1}. With increasing shear rate, the current maximum steeply decreased (Fig. 7) and was reached after a shorter time (Fig. 8). The shear deformation results in a shorter relaxation time, probably as a consequence of easier reorganization of particles in the electric field (Fig. 9).

The time dependences of shear stress at a constant shear rate are similar to time profiles of electric current. This reflects the growing stiffness of the structure of organized particle due to the applied electric field. The higher protonation degree and conductivity of suspension particles, the higher maximum shear stress was obtained (Fig. 10). However, in contrast to the conductivity increase, the initial slopes for samples with various degrees of protonation differ only little at the same electric field strength.

When the shear rate increases, the relative growth of the shear stress to a maximum value diminishes (Fig. 11). The plot of the minimum and maximum shear stress vs. the shear rate (Fig. 12) is a characteristic linear field-off dependence of the electric field, and its course curved to a minimum limit plateau.

Concluding remark

PANI base is relatively hydrophobic (water contact angle, 78°); its salt with orthophosphoric acid is hydrophilic (water contact angle, 44°) [19]. This means that, in the course of protonation, the hydrophilicity of particles increases along with their conductivity. This parameter is likely to affect the interaction of particles in suspensions. It is expected that hydrophobic particles will be more easily dispersed in hydrophobic media, such as silicone oil. The more conducting and, consequently, more hydrophilic particles will be prone to aggregation. The effect can, in fact, promote the formation of conducting chains and clusters. By using different acids for protonation of PANI, samples of varying hydrophobicity and comparable conductivity and morphology can be prepared. The effect of surface properties of particles on electrorheology of suspension will be investigated in the forthcoming study.

Conclusion

This study demonstrates that the time dependence of the current passing through an ER suspension in electric field may be a useful tool elucidating the structure formed by polarized particles. A tight connection between the relaxation time of the process and the particle conductivity is in accord with previous measurement of dielectric properties of the materials. At that time, we found that the relaxation frequency of PANI particles with high protonation degrees and high conductivities corresponds to a shift of the maximum of dielectric loss spectrum to higher values, indicating a faster particle movement in the electric field.

It is clear and beyond a doubt that the applied shear stress destroyed the organization of the chain structure of polarized particles. It was confirmed that shorter relaxation times appeared under these circumstances. The organization proceeds faster, and conductivity increases more quickly than at rest, probably due to easier formation of contacts between particles moving in the flow field. On the other hand, the created chains oriented along the streamlines of the electric field are simultaneously disturbed by shear forces. The result in a lower maximum conductivity of suspension compares with a value reached at rest.

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