

The role of particle conductivity in electrorheology of suspensions of variously protonated polyaniline

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Abstract. Electrorheological behaviour of silicone oil suspensions of particles of polyaniline protonated to various doping level with orthophosphoric and tetrafluoroboric acids has been studied. The dynamic yield stress obtained by extrapolation of shear stress to zero shear rate using Herschel-Bulkley equation was used as a criterion of the ER efficiency. At a same molar concentration of doping acids, various protonation effects appeared and the dependences of the yield stress on the acid concentration differed. The comparison of the yield stresses with dielectric characteristics calculated from the Havriliak-Negami equation revealed that the particle conductivity unlike particle permittivity especially at higher protonation degree is dominant in polarization process. Consequently, particle conductivity or dielectric relaxation time proved to be the parameters providing the common dependences of the yield stress regardless of the way of polarization.

1. Introduction

Intrinsically conducting polymers [1–3] rank among particulate materials in electrorheology (ER) due to relatively low density, good thermal stability, and controllable electric and dielectric properties. Among them polyaniline (PANI) has been the object of many ER studies [4–7]. Its conductivity can be advantageously easily arranged by protonation to various doping levels to obtain particle suspension with a high ER performance. In present study the comparison of the ER efficiency of PANI particles protonated by two doping agents, orthophosphoric (PA) and tetrafluoroboric (TA) acids, in silicone oil suspensions has been performed.

2. Experimental

2.1. Controlled protonation of PANI with PA and TA

PANI powder was prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M ammonium peroxydisulfate in water starting at 20 °C. The produced PANI salt was deprotonated into the PANI base by two-day immersion in an excess of 1 M ammonium hydroxide. Portions of the PANI base (0.5 g) were immersed in 100 mL of aqueous solutions of either PA or TA of various molar concentrations (C_A) for 24 h, separated, and dried. The conductivity of the samples pressed into pellets rises with the increasing C_A of the acid used (table 1). Both acids show the significant differences in

achieved values of conductivity at the same C_A , obviously due to different pH of equally concentrated solutions.

Table 1. The conductivity, σ , of PANI base protonated in the aqueous solution of PA and TA of various molar concentrations, C_A .

Sample	C_A (mol L ⁻¹)	σ (PA) (S cm ⁻¹)	σ (TA) (S cm ⁻¹)
B	0	3.6×10^{-9}	3.6×10^{-9}
PA1/TA1	0.0001	4.7×10^{-9}	4.9×10^{-9}
PA2/TA2	0.0005	6.8×10^{-9}	4.9×10^{-9}
PA3/TA3	0.001	2.7×10^{-8}	9.0×10^{-9}
PA4/TA4	0.005	5.8×10^{-7}	1.6×10^{-8}
PA5/TA5	0.01	4.7×10^{-5}	1.2×10^{-5}
PA6/TA6	0.05	3.1×10^{-3}	2.5×10^{-4}

2.2. Suspension preparation

Suspensions (10 wt%) were prepared by mixing PANI powders with corresponding amounts of silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic; $\eta_c = 200$ mPa s, $\sigma_c \approx 10^{-11}$ S cm⁻¹, $\epsilon'_c = 2.6$). At first, the samples were stirred mechanically and then in an ultrasonic bath for 30 s before each measurement.

2.3. Electrorheological and dielectric measurements

Shear stress in the range of shear rates 1–100 s⁻¹ and at the DC electric field strengths 0–3 kV mm⁻¹ using a rotational rheometer (Bohlin Gemini, Malvern Instruments, UK) with parallel plates 40 mm in diameter and a gap of 0.5 mm was carried out at the temperature of 25 °C.

The frequency dependences of dielectric properties (ϵ' , ϵ'') of 10 wt% suspensions were measured with a Hioki (3522 RCL HiTester, Japan) in the range 10¹–10⁵ Hz.

3. Results and discussion

3.1. Electrorheological characterization

The typical ER behaviour of PANI suspensions at various electric field strengths is shown in figure 1. The field-off shear stress depends linearly on the shear rate and indicates a Newtonian flow. After electric field application, especially at low shear rates, the values of shear stress significantly rise by several orders of magnitude with increasing intensity of the electric field. The dynamic yield stresses (τ_0) indicate formation of the reinforced chain-like structures of organized polarized particles. A plateau region of the shear stresses appears at low shear rates due to the balance between electric and shear forces. At higher shear rates, when the hydrodynamic forces begin to dominate over the electrostatic ones, these organized particle structures are gradually destroyed and the suspension tends to return to field-off Newtonian behaviour.

3.2. Effect of PANI particle protonation

The findings suggest that the doping level of the same C_A of various acids on particle polarization may be different. Thus, at constant electric field strength τ_0 significantly depends not only on the protonation degree of PANI particles but also on the character of the acid used. At low protonation, τ_0 values achieve approximately similar constant values. At a higher protonation τ_0 of both suspensions of doped particles grew and became different. In case of PA at $C_A = 0.01$ mol L⁻¹ at the highest electric field strength used, τ_0 nearly doubled in value. For TA acid, τ_0 was a little lower (figure 2). In samples doped to higher protonation at $E > 1.5$ kV mm⁻¹ the current passing through the suspensions was too high, short-circuit between electrodes sets in and the measurement failed.

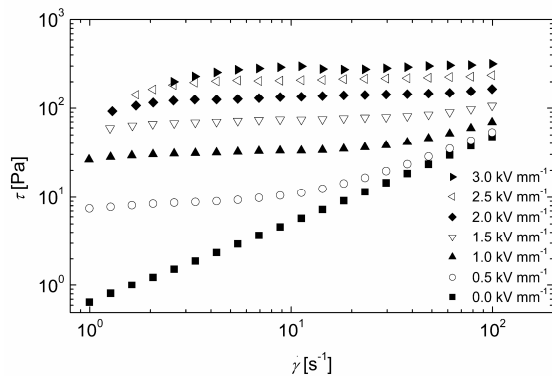


Figure 1. Double-logarithmic plot of the shear stress τ vs. shear rate γ for the suspension of the sample PA5 at various electric field strengths E .

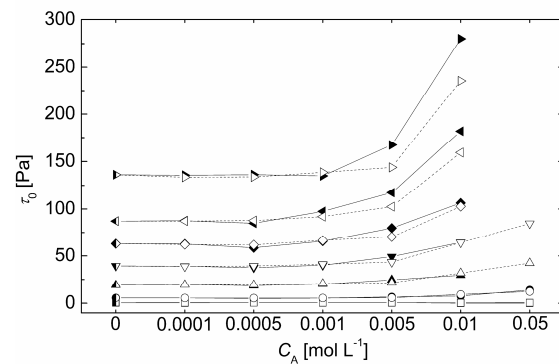


Figure 2. The dependence of τ_0 on C_A of used acids at various electric field strengths. PA (solid), TA (open), original PANI base (semi solid symbols). Electric-field strength E (kV mm^{-1}): (■□) 0, (●○) 0.5, (▲△) 1.0, (▼▽) 1.5, (◆◇) 2.0, (◀▶) 2.5, (▶▷) 3.0.

3.3. Particle polarizability and relaxation time

Dielectric characteristics of particle suspensions under this study (table 2) were calculated from the Havriliak-Negami empirical equation (1) [8]:

$$\epsilon^* = \epsilon'_\infty + \frac{(\epsilon'_0 - \epsilon'_\infty)}{(1 + (i 2\pi f t_{rel})^a)^b} \quad (1)$$

Here ϵ'_0 and ϵ'_∞ are the limit values of the relative permittivity at the frequencies below and above the relaxation frequencies, t_{rel} is a relaxation time, a is the scattering degree of t_{rel} and b is related to the asymmetry of the t_{rel} spectrum. Large values of a mean a great scattering of t_{rel} . When a differs much from zero and b significantly from unity, the t_{rel} spectrum becomes more asymmetrical. The dielectric spectra demonstrated an increase in limit permittivity ϵ'_0 and a steep decrease in t_{rel} with particle protonation.

Table 2. Parameters of Havriliak-Negami equation (1) for PA and TA doped PANI particles.

Sample	$\epsilon'_{0,s}$ (PA / TA)	$\epsilon'_{\infty,s}$ (PA / TA)	t_{rel} (s) (PA / TA)	a (PA / TA)	b (PA / TA)
B	4.62	2.66	1.48×10^{-2}	0.80	0.69
PA1/TA1	4.62 / 4.64	2.66 / 2.62	$1.16 \times 10^{-2} / 1.46 \times 10^{-2}$	0.86 / 0.84	0.60 / 0.65
PA2/TA2	4.82 / 4.58	2.67 / 2.64	$9.88 \times 10^{-3} / 1.27 \times 10^{-2}$	0.76 / 0.81	0.70 / 0.67
PA3/TA3	5.03 / 4.81	2.70 / 2.69	$5.23 \times 10^{-3} / 7.39 \times 10^{-3}$	0.70 / 0.73	0.70 / 0.74
PA4/TA4	5.10 / 4.80	2.65 / 2.61	$1.27 \times 10^{-3} / 4.47 \times 10^{-3}$	0.61 / 0.63	0.69 / 0.90
PA5/TA5	5.19 / 5.13	2.60 / 2.66	$8.27 \times 10^{-6} / 1.86 \times 10^{-4}$	0.37 / 0.54	0.97 / 0.78
PA6/TA6	5.47 / 5.32	2.64 / 2.72	$3.33 \times 10^{-7} / 3.53 \times 10^{-6}$	0.59 / 0.50	0.73 / 1.00

Because of the high conductivity of particles this quantity appeared to be more important than permittivity in the process of particle polarization and the ER efficiency could be rather controlled by

the mismatch of conductivity of particles in the continuum [9]. The common dependence of τ_0 on the relative particle conductivity Γ as a ratio of conductivity of particles σ_p and that of continuum σ_c for both acids used confirmed this assumption (figure 3).

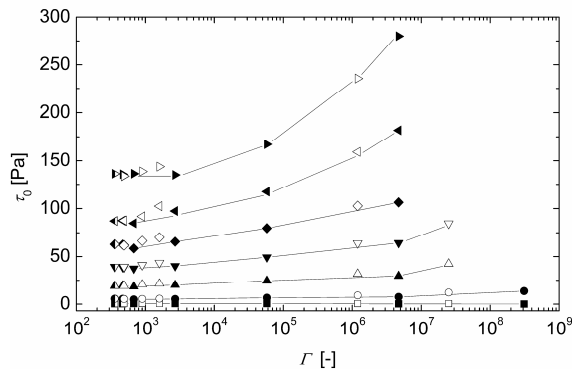


Figure 3. The dependence of τ_0 on $\Gamma (= \sigma_p / \sigma_c)$ at various electric field strengths. Points denoted as in figure 2.

For both studied suspensions, t_{rel} steeply decreased with the protonation degree of particles which indicates increasing particle mobility during restoration of the organized particle structure in the electric field. The common course of the correlations of t_{rel} with Γ regardless of the way of protonation indicated a close connection between conductivity and particle mobility in the electric field (tables 1 and 2).

Conclusions

The results of the study revealed that conductivity of PANI particles is a significant factor controlling their polarizability and thus the formation of ER structures in the electric field. The yield stress increases with conductivity of particles up to some critical value ($\approx 4.7 \times 10^{-5}$) where short-cut of the circuit prevents measurement of ER effect. The type of the acid used for PANI protonation seems to play minor role.

Acknowledgements

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