

Viscoelastic properties of electrorheological suspensions of core-shell (carbon/polyaniline) particles in silicone oil

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Abstract

Carbon/polyaniline particles with core-shell structure were synthesized as novel dispersed phase for electrorheological (ER) suspensions in this study. Core of these composite particles was obtained by carbonization of polyaniline base in an inert atmosphere of nitrogen at 650 °C and coated with polyaniline shell. The morphology and composition of prepared particles were examined with scanning electron microscopy and Fourier transform infrared spectroscopy, respectively. The analysis revealed the conversion of polyaniline to carbon via ring-opening happened during the carbonization process and successful coating of carbonized particles with shell layer. The products retained the original granular structure after carbonization as well as after the coatings. The dielectric spectra analysis suggests high particle polarizability of carbonized material. Thus, the measurements performed under oscillatory shear flow showed a remarkably high ER intensity at relatively low electric field strength. Coating of carbonized particles by polyaniline base changes compatibility of particle surface with silicone oil medium and, consequently, flow properties of suspensions in the absence of electric field, but does not influence the shear rate dependence of the complex viscosity in the electric field.

Keywords: Electrorheology, Polyaniline, Carbonization, Core-shell particles, Dielectric properties.

Introduction

Investigation of new materials with high efficiency still ranks among topical subjects in electrorheology (ER). Since Winslow's discovery [1] more than 50 years ago a number of studies have been performed. It appeared that not only high permittivity and low conductivity of materials provide high particles polarizability necessary for high ER performance. The results suggest that also particle structure and morphology may be very important. Various inorganic or organic powder materials have been used as a solid phase in ER suspensions. Among them, semi-conducting polymers such as polyaniline [2], polypyrrole [3], or paraphenylenediamine [4] proved to be very suitable. Their chemical structure with conjugated system of π -bonds enables charge transfer and thus good particle polarization. Polyaniline (PANI) as the most interesting polymer in this group showed good thermal stability and possibility to control the conductivity via deprotonation.

This study deals with ER viscoelastic behaviour of silicone oil suspensions of core-shell particles in oscillatory shear. The particle core of carbonized polyaniline coated with polyaniline base shell provided material with various compatibility with oil medium and thus different field-off flow properties.

2. Experimental

2.1. PANI base preparation

The PANI base was prepared according to the report [5]. In this way 0.2 M aniline hydrochloride (Fluka, Switzerland) was oxidized with 0.25 M ammonium peroxydisulfate (Lach-Ner, Czech Republic) in water for 24 h at room temperature. The obtained particles were collected on a filter and washed with 0.2 M hydrochloric acid (Sigma, USA) and acetone (Sigma, USA) several times. Synthesized particles of polyaniline hydrochlorid (emeraldine) were thereafter deprotonated with excess of 1 M aqueous ammonia (Sigma, USA) to obtain PANI base. After washing with acetone the product was dried at 60 °C in vacuum.

2.2. Carbonization of PANI base

PANI base particles were heated under a nitrogen atmosphere in an electric oven from the laboratory temperature at the rate of 15 °C/min to the temperature 650 °C which was maintained for 1 h. Then, the carbonization process was switched off and the sample was left to cool to laboratory temperature. Then, the prepared carbonized particles were sieved to obtain particle sizes lower than 45 µm (sample A). According to the previous work [6] most of structural changes have already occurred at 650 °C. Thus, this temperature was used in the present study.

2.3. Coating of carbonized particles with PANI layer

Two samples B and C of composite particles from the sample A as a core coated with a PANI base layer of different thickness were prepared. In case of the sample B the PANI content in the particle shall was the same as in the particle core before carbonization. The content of PANI base in the shell of the sample C was half.

2.4. Scanning electron microscopy and FTIR spectroscopy

A scanning electron microscopy (SEM, VEGA II LMU, Tescan Ltd., Czech Republic), with an operating voltage of 30 kV, was adopted to observe the morphologies of prepared samples. On the other hand, the chemical composition of particles was examined with Fourier transform infrared spectroscopy (FTIR, Thermo Scientific, USA). The FTIR spectra were recorded using attenuated total reflectance (ATR) technique with Germanium crystal in the range 500 – 4000 cm⁻¹ at 64 scans per spectrum at 2 cm⁻¹ resolution.

2.5. Electrorheological measurements

Suspensions containing 10 wt.% of the sample A, B, or C in silicone oil (Lukosiol M200, Chemical Works Kolín, Czech Republic; $\eta \approx 200$ mPas·s) were prepared. Measurements of their electrorheological properties were carried out on a rheometer Bohlin Gemini (Malvern Instruments, UK) with parallel plates 40 mm in diameter and 0.5 mm gap. The plates were connected to a DC high-voltage source TREK (TREK 668B, USA) with the applied voltage (0.125 – 0.5 kV) corresponded to the electric field strength 0.25 – 1 kV·mm⁻¹. Dynamic viscoelastic tests were performed by dynamic strain and frequency sweeps. The rheological parameters were obtained from frequency sweep tests (0.1 – 10 Hz) at fixed strain amplitude in the viscoelastic region ($\gamma_A = 4 \times 10^{-4}$). The particle aggregated structures in the system

were destroyed by shearing of the suspension at a shear rate 20 s^{-1} for 150 s before each measurement at new electric field strength applied. The measurements were carried out at 25, 45, 65, and 85 °C.

2.6. Dielectric measurement

The frequency dependences of complex permittivity, ε^* , involving the relative permittivity, ε' , and dielectric loss factor, ε'' , of studied ER suspensions were measured with an impedance analyzer (Agilent 4524, Japan) in the range $f = 5 \times 10^3 - 5 \times 10^6 \text{ Hz}$.

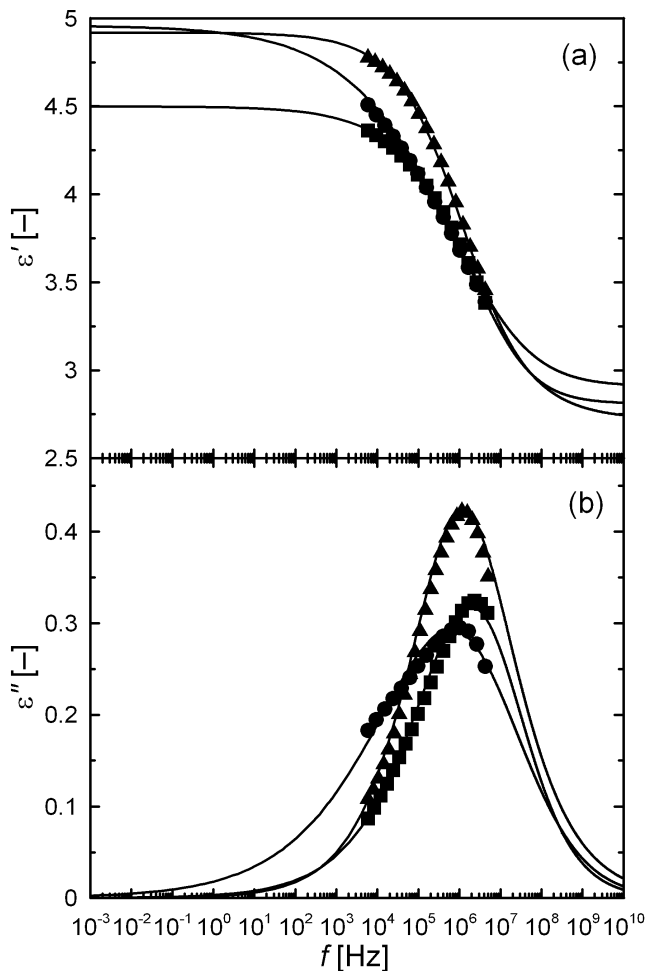


Figure 1. Relative permittivity, ε' , **(a)** and dielectric loss factor, ε'' , **(b)** as a function of the frequency, f , for 10 wt.% ER suspensions of the samples: A (triangles), B (squares) and C (circles) in silicone oil at 25 °C.

The dielectric characteristics of particle suspensions (Table 1) were obtained from the Havriliak–Negami empirical model [7] fitting by least square method:

$$\varepsilon^* = \varepsilon'_{\infty} + \frac{(\varepsilon'_0 - \varepsilon'_{\infty})}{\left(1 + (i\omega \cdot t_{\text{rel}})^a\right)^b} \quad (1)$$

Here, ε^* is a complex fluid permittivity, the particle polarizability, $\Delta\varepsilon'$, is defined as the difference between ε'_0 and ε'_{∞} , which are the limit values of the relative permittivity at the frequencies below and above the relaxation frequency, ω is angular frequency ($= 2\pi f$), t_{rel} is the relaxation time, a is the scattering degree of relaxation times, and b is related to the asymmetry of the relaxation time spectrum. The relaxation frequency, at which the dielectric loss factor ε'' has a maximum, is proportional to the rate of polarization of suspension particles.

Table 1. Dielectric parameters in Eq. 1 for 10 wt.% ER suspensions of samples A, B, and C

Parameter	Sample A	Sample B	Sample C
ε'_0	4.92	4.50	4.96
ε'_{∞}	2.72	2.81	2.91
$\Delta\varepsilon'$	2.2	1.69	2.05
t_{rel}	1.4×10^{-7}	2.1×10^{-8}	1.8×10^{-8}

3. Results and discussion

3.1. Characterization of prepared particles

The size and morphology of PANI base particles and samples A, B, and C are shown in Figure 2. As can be seen in Figure 2b, after carbonization of PANI base particles the granular morphology was retained and only some shrinkage may be observed, which is in good accordance with literature [8]. After coating of carbonized particles the size of samples B and C slightly increased while their morphology became preserved.

The infrared spectra showed the absorption around 1563 cm^{-1} in case of PANI base (Figure 3a), which is characteristic for the vibration of quinonoid rings, while the peak at 1485 cm^{-1} is attributed to the vibrations of C–C aromatic ring stretching [9]. The absorptions of these peaks were suppressed after carbonization (Figure 3b) indicating the ring-opening and possible crosslinking. The process of carbonization also reduced the absorption peak at 1298 cm^{-1} which is attributed to the C–N stretch of a secondary aromatic amine. On the other

hand, the quinonoid peak was moved to higher wavenumbers and C–C aromatic ring stretching to lower wavenumbers after coating of carbonized particles (Figure 2c, d). The characteristic absorption band in the range of 1010 – 1170 cm^{-1} was assigned to the aromatic C–H in-plane bending modes. The relatively intensive peak at 1128 cm^{-1} indicates a certain amount of protonated polymer in PANI base probably due to the presence of highly organized chains which are resistant towards the deprotonation [10]. Deformations of out-of-plane C–H bonds, i.e. in 1,4-disubstituted rings, are located in range of 800 – 880 cm^{-1} with the maximum at 798 cm^{-1} . The absorption of this band was lowered after carbonization due to the ring-opening and moved to higher wavenumbers after a coating with PANI layer.

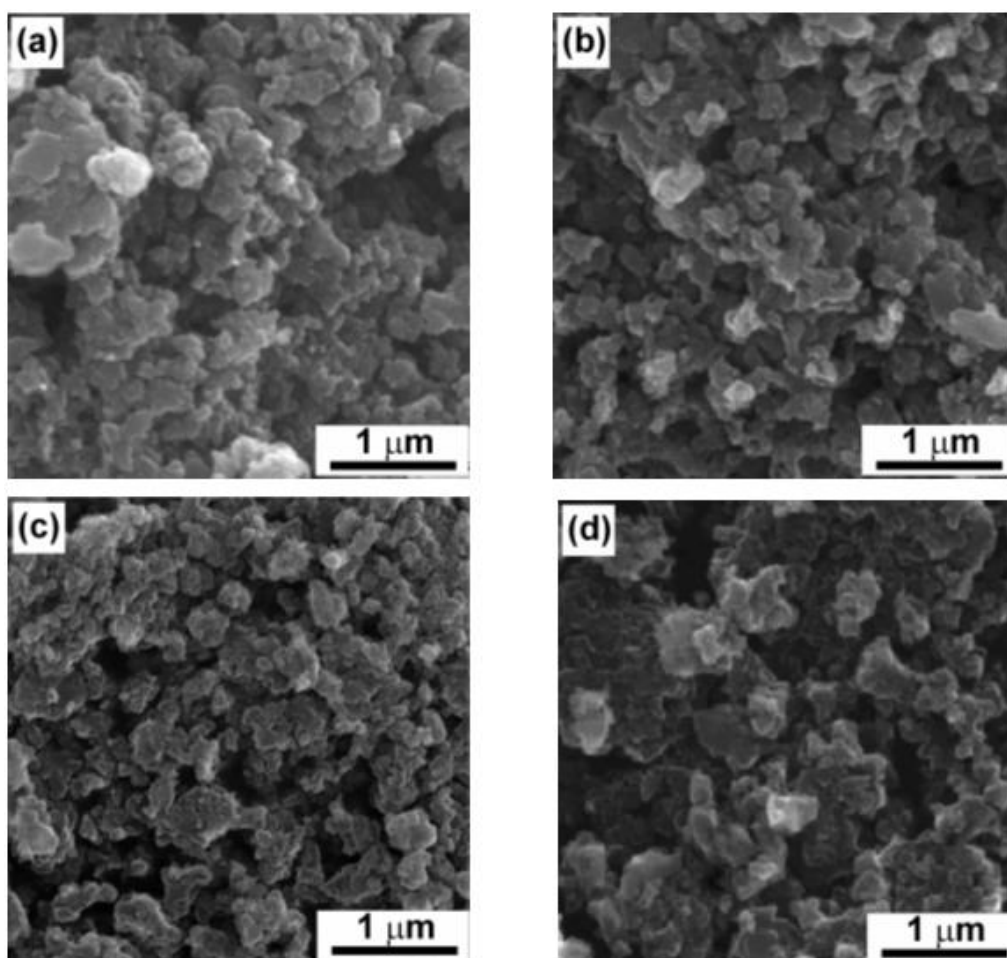


Figure 2. SEM images of PANI base (a), carbonized particles of sample A (b), and coated particles of sample B (c) and C (d).

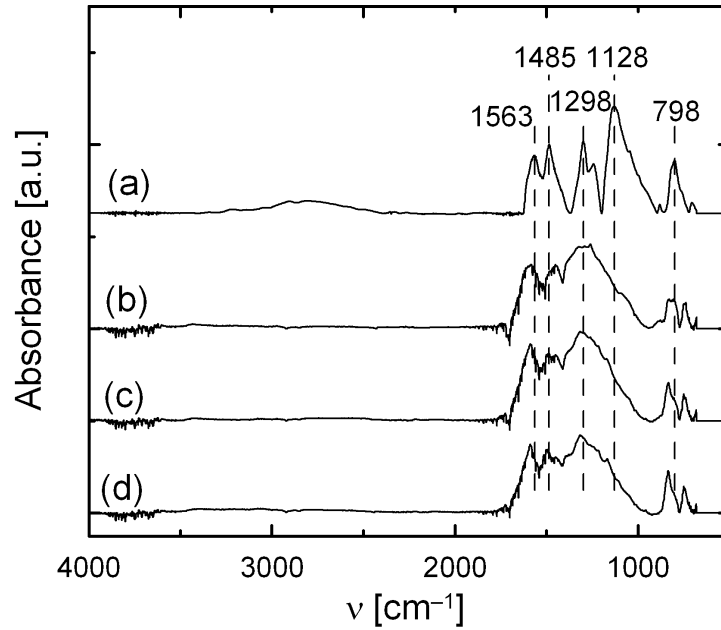


Figure 3. FTIR spectra of PANI base (a), carbonized particles of sample A (b), and coated particles of sample B (c) and C (d).

3.2. ER effect and dielectric properties

Figure 4 illustrates the ER properties of the prepared suspensions under oscillatory shear. Only the suspension of the sample B, i.e. carbonized particles coated with higher PANI base amount shows almost Newtonian behaviour in the absence of electric field. On the other hand, suspension of the sample C coated with thinner PANI layer or suspension of uncoated sample A exhibit slightly pseudoplastic behaviour probably due to particle aggregation caused by bad compatibility with silicone oil. The aggregates of the sample C are less stable than that of the sample A probably because of incomplete particle surface coating. Consequently the aggregates disintegrate with increasing frequency more easily.

When the external electric field was applied (Figure 4b) the internal chain-like structure of particles raised, the complex viscosity increased at relatively low electric field strength 0.5 kV mm^{-1} in several orders of magnitude and all suspensions under study reached very similar values regardless of electric field-off behaviour.

Figure 4c demonstrates that the highest efficiency as a relative increase in electroviscosity, $e = (\eta^*_E - \eta_0)/\eta^*_0$ [11] corresponds to the composite particles of sample B due to lowest complex viscosity in the absence of electric field which suggests that the coating process of carbonized particles with PANI may significantly influence this quantity.

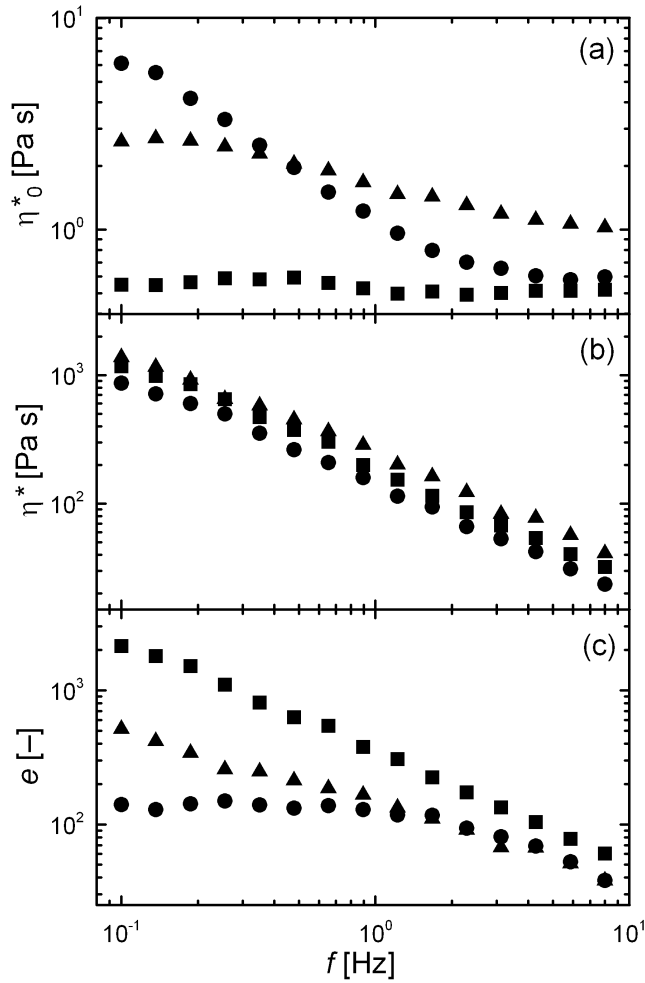


Figure 4. The complex viscosity in the absence of electric field, η^*_0 , **(a)**; in the presence of electric field strength of $0.5 \text{ kV}\cdot\text{mm}^{-1}$, η^*_{E} **(b)**; and the electro-rheological efficiency, e , **(c)** vs. frequency, f , for 10 wt.% suspensions of the sample A (triangles), the sample B (squares) and the sample C (circles) in silicone oil at $25 \text{ }^\circ\text{C}$.

It is generally accepted that dielectric properties of ER suspension play important roles in the interfacial polarization of dispersed particles and formation of chain-like internal structures within the system. The dielectric spectra (Figure 1) and their characteristics in the Table 1 indicate that dielectric properties of all three studied suspension are very similar. This fact correlates well with ER behaviour (Figure 4) in the presence of electric field and suggests, that not polarization of only PANI base coating but dielectric properties of carbonized core controls the ER behaviour.

3. 3. Viscoelastic characteristics

To illustrate the behaviour of viscoelastic moduli of ER materials in the electric field suspension of the sample B has been used. In the absence of electric field the system exhibits liquid character and the loss modulus dominates (Figure 5). When the electric field was applied the elastic modulus became remarkably higher due to an increase in the system rigidity caused by the formation of internal chain-like structures of polarized particles.

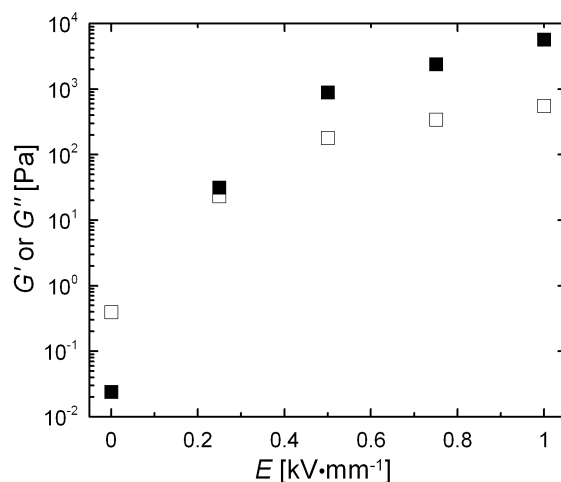


Figure 5. Storage, G' , (solid symbols) and loss, G'' , (open symbols) viscoelastic moduli vs. electric field strength, E , at $f = 0.14$ Hz for 10 wt.% ER suspension of sample B particles in silicone oil at 25 °C.

3. 4. The temperature dependence

The wide temperature range for application is another important factor for the utilization of ER suspension in real device. Thus, PANI having the temperature stability approximately till 200 °C [12] is a suitable candidate from the group of conducting polymers for the use as a dispersed phase in ER suspensions. The effect of temperature on the ER performance illustrates Figure 6. It is obvious that the elevated temperature increases the Brownian motion within the suspension reflected in a decreased viscoelastic moduli in the absence of electric field. In the presence of external electric field, the ER performance is lower at elevated temperatures since the internal chain-like structures of polarized particles are destroyed easily due to more intensive Brownian motion as well as lower silicone oil viscosity. However, the difference between viscoelastic moduli in the absence and in the presence of electric field is still higher than three orders of magnitude reflecting quite stiff internal structures formation even at high temperatures.

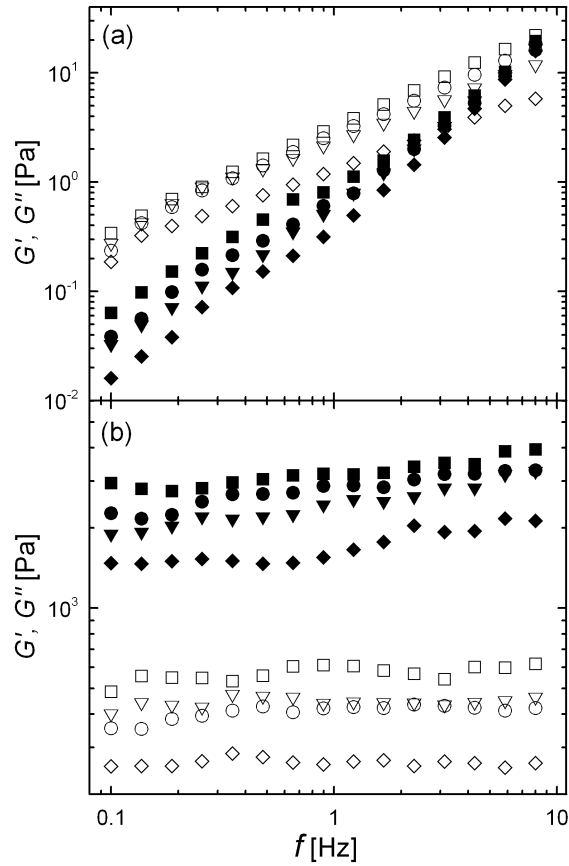


Figure 6. Storage, G' , (solid symbols) and loss, G'' , (open symbols) viscoelastic moduli vs. frequency, f , in the absence of electric field **(a)** and in the presence of electric field strength of $0.75 \text{ kV}\cdot\text{mm}^{-1}$ **(b)** for 10 wt.% ER suspension of the sample B in silicone oil at 25 °C (squares), 45 °C (circles), 65 °C (inverted triangles), and 85 °C (diamonds).

Conclusions

The results of the study suggest that the particles based on carbonized PANI can be interesting material with high polarizability suitable for suspensions providing high ER performance even at low electric field strengths. Coating of particles with PANI base layer changes compatibility of carbon surface with silicone oil medium. This affects electric field–off mutual particle interactions and changes flow behaviour in the absence of electric field. It appeared, however, that it did not influence markedly the suspension properties when the electric field was applied and thus very similar high values of shear dependence of complex viscosity of the chain structure of polarized particles of all studied suspensions were obtained.

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