Electrorheological Properties of Polypyrrole–Silver Composite Particles

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Abstract: Polypyrrole–silver (PPy–Ag) composite particles were synthesized by an oxidation of pyrrole with mixture of ammonium peroxydisulfate and silver nitrate. The molecular structure of PPy was assessed by Fourier transform infrared spectroscopy while the presence and amount of Ag was confirmed by X-ray diffraction analysis and thermogravimetric analysis, respectively. The scanning electron microscopy further revealed that the incorporation of Ag into PPy did not change the particles size and shape. Although the Ag presented in the composite particles increased their conductivity in one order of magnitude, the electrorheological (ER) performance did not change significantly above 63 wt.% of Ag, which was still below the percolation, compared to that of pure PPy. Moreover, it appeared that this amount of Ag improved the compatibility of dispersed particles with silicone oil used as a carrier liquid in ER suspensions. Furthermore, a faster interfacial polarization of PPy–Ag composite particles was observed from dielectric spectra.

Key-Words: Electrorheological suspensions, intelligent system, polypyrrole, silver, deprotonation, conductivity

1 Introduction
Electrorheological (ER) suspensions, typically composed of polarizable particles in non-conducting carrier liquid, attract the attention due to their ability to reversibly change their viscosity according to the external electric field applied [1,2]. In principle, the imposed electric field polarized dispersed particles which consequently join together and form chain-like structures just in the direction of field intensity. These internal structures restrict the motion of the suspension and the system changes its state from
liquid to solid-like. The controllable and reversible change of rheological properties (viscosity, yield stress) manifested macroscopically in the increased stiffness of ER suspensions offer potential applications in electric clutches or brakes, shock absorbers, valves and others [3,4].

2 Problem Formulation

However, there are still some significant limitations for their wider application including narrow operation temperature, device corrosion as well as the system instability due to the big difference in densities between the dispersed phase and the carrier liquid. To overcome some of drawbacks, conducting polymers were recently used. Polypyrrole (PPy) together with its derivatives either in particulate shape [1] or fiber [5] or shell material in core-shell structured [6] particles represents one of the most promising conducting polymers in this field due to its easy preparation, thermal stability and easy deprotonation. In the present work, a new strategy based on the incorporation of conducting Ag into the PPy was adopted as a possible method for the controlling of resulting particles conductivity. The incorporation of Ag was made by the oxidation of pyrrole with mixed oxidants, silver nitrate and ammonium peroxysulfate.

2.1 Synthesis of PPy–Ag composite

Pyrrole (Py, 98%), which was distilled twice under reduced pressure before the use, was oxidized either with ammonium peroxysulfate (APS; 98%, (NH₄)₂S₂O₈) or with mixture of APS and silver nitrate (≥ 99%, AgNO₃). The concentrations of oxidants are given in Tab. 1. The oxidant concentration was set on the 0.2 M APS in all polymerizations. APS is a two-electron oxidant while AgNO₃ is a one-electron oxidant. For example, the molar concentrations of the oxidants for Sample 3 were [APS] = 0.1 M and [AgNO₃] = 0.2 M, i.e. each oxidant was expected to oxidize a half of the Py. After mixing the solutions of Py with those of oxidants, the mixture was mixed at room temperature for 4 h. Formed particles were separated by filtration, rinsed with distilled water, then with acetone. Then, particles were dried, first in air, and then under vacuum at 60 °C for 6 h. To adjust the particles conductivity into the optimal range of 10⁻⁷–10⁻⁸ S·cm⁻¹, the prepared particles were deprotonated by immersion in a large excess of 1 M ammonium hydroxide, and dried again. All the chemicals used for the particles synthesis were purchased from Aldrich Chemicals Company, USA.

2.2 Characterization methods

A scanning electron microscope (SEM, VEGA II LMU, Tescan Ltd., Czech Republic), with an operating voltage of 10 kV, was adopted to observe the morphologies of PPy–Ag composites. Further, the presence of Ag in particles was confirmed via the X-ray diffraction (XRD) patterns collected on an X’Pert PRO (Philips, The Netherlands) diffractometer with Cu Kα₁ radiation (λ = 0.154 Å) and a scanning rate of 4° min⁻¹ for the recording data in the wide range of 2θ = 5–95°. In order to obtain the content of Ag in samples, thermogravimetric analysis (TGA, TA Instruments Q500, USA) under air atmosphere at a heating rate of 10 °C·min⁻¹ in the temperature range 25–700 °C was used. Fourier transform infrared spectroscope (FTIR, Thermo Scientific, USA) was used for recording infrared spectra in the range 680–4000 cm⁻¹ at 64 scans per spectrum at 2 cm⁻¹ resolution using attenuated total reflectance (ATR) technique with Germanium crystal. The conductivity of PPy–Ag composite particles after deprotonation was measured at room temperature by a four-point van der Pauw method on pellets (13 mm in diameter and 1.0–1.3 mm thick) compressed at 600 MPa with manual hydraulic press at 600 MPa using a Keithley 6517A and 7002 (Keithley Instruments Inc., USA). Density of the synthesized PPy–Ag composites was measured by a pycnometer at 25 °C.

The ER suspensions (5 vol.%) were prepared by dispersing PPy or PPy–Ag composite particles in silicone oil (Lukosiol M200, Chemical Works Kolin, Czech Republic; η = 194 mPa·s, ρ = 0.97 g·cm⁻³) using the sonicator for 1 min to obtain well-dispersed system. Measurements of rheological properties of the prepared ER suspensions were carried out using a rotational rheometer Bohlin Gemini (Malvern Instruments, UK) with parallel plates 40 mm in diameter and a gap of 0.5 mm, modified for ER experiments. A direct current (DC) voltage was generated by a TREK DC high-voltage source (TREK 668B, USA). A DC voltage was applied for 60 s to generate an equilibrium chain-like structure of particles in suspension prior to shearing. The steady-flow measurements in the controlled shear rate (CSR) mode were performed in the shear rate range 0.1–300 s⁻¹. The temperature in all experiments was kept at 25 °C.
Table 1 Composition and properties of particles used for the preparation of ER suspensions

<table>
<thead>
<tr>
<th>Sample</th>
<th>$c_{APS}$ [mol·l$^{-1}$]</th>
<th>$c_{AgNO_3}$ [mol·l$^{-1}$]</th>
<th>$w_{Ag}$ [mass %]</th>
<th>$\sigma_{DC}$ [$\times 10^{-6}$ S·cm$^{-1}$]</th>
<th>$\rho$ [$\times 10^{-6}$ S·cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.20</td>
<td>0.0</td>
<td>0.0</td>
<td>1.28</td>
<td>1153</td>
</tr>
<tr>
<td>S2</td>
<td>0.15</td>
<td>0.1</td>
<td>44.1</td>
<td>9.21</td>
<td>1628</td>
</tr>
<tr>
<td>S3</td>
<td>0.10</td>
<td>0.2</td>
<td>63.5</td>
<td>10.72</td>
<td>2632</td>
</tr>
</tbody>
</table>

Fig.1 SEM image of samples S1 (a), S2 (b), and S3.

The dielectric properties of the prepared ER suspensions were measured with an impedance analyzer (Agilent 4524, Japan) in a frequency range of $1\times 10^2$–$4\times 10^6$ Hz.

3 Problem Solution

SEM images of the PPy (a) and PPy–Ag composites (b, c) are depicted in Figure 1. As can be seen, the particles have globular shape and their size a little bit increase as the concentration of AgNO$_3$ in the reaction mixture has been increased. The light parts in Fig. 1b and 1c can be attributed to the Ag particles.

In order to prove the presence of pure Ag in PPy–Ag composites, the XRD analysis was performed. All the peaks in the XRD pattern in Fig.2 can be indexed to the cubic Ag structure with lattice constant $a = 4.0862$ Å for sample S3. Furthermore, a small amorphous halo due to PPy is also presented in the pattern.

FTIR analysis was carried out to identify whether any changes in chemical structure happened if different concentrations of oxidants were used (Fig.3). For all samples, the characteristic peaks are observed at 823 cm$^{-1}$ (=C–H out of ring plane vibrations), 914 cm$^{-1}$ (C–C out of phase), 1043 cm$^{-1}$ (=C–H in plane vibrations), 1196 cm$^{-1}$ (PPy-ring bending), 1290 cm$^{-1}$ (C–C bond), 1475 cm$^{-1}$ (PPy-ring vibrations), 1558 cm$^{-1}$ (C=C bond), 1684 cm$^{-1}$ (C=N bond), 3108 cm$^{-1}$ (N–H stretching vibrations), confirming the formation of PPy [7,8]. However, some small shift toward lower wave numbers as well as their broadening due to addition of Ag into the composite for certain peaks can be observed. Representative of such shifting and broadening is for example PPy-ring vibrations peak at 1475 cm$^{-1}$.

Fig.2 Powder XRD patterns of the sample S3.

Fig.3 FTIR spectra of prepared samples.
The data for Ag content in the composite, \( w_{Ag} \), the direct current conductivity, \( \sigma_{DC} \), as well as the particles density, \( \rho \), for all samples is listed in Table 1. It is evident that with increasing AgNO\(_3\) concentration used, the content of Ag in particles \( w_{Ag} \) increased which was reflected in higher \( \rho \). Surprisingly, the Ag in the samples does not enhance the overall conductivity of the PPy–Ag composites significantly. This is caused by insufficient concentration of Ag to form an infinite percolating cluster which would lead to an expected conductivity increase proportional to the high conductivity of this metal. Moreover, no indications of the presence of percolating Ag clusters are found in the samples’ microscopic images either (Fig.1). Since the conductivity of samples is given by that of PPy, the overall conductivity of PPy–Ag composites will be more thermally stable due to the presence of Ag compared to pure PPy [9]. Hence, the PPy–Ag samples can be used as a novel dispersed phase for ER suspensions, because they have conductivity inside desired range. It should be mention here, that the used synthesis procedure enables to tailor conductivity of particles in dependence on required application, since when Ag percolation is overcame, the high conductive particles could be used for preparation electromagnetic shielding composite material [10].

Fig.4 illustrates the ER activity of the PPy particles as well as PPy–Ag composites based ER suspensions. Almost linear log–log plot of the shear stress on the rate of shear for all ER suspensions in the absence of the electric field suggests nearly Newtonian rheological behaviour. The shear stress and simultaneously the viscosity of PPy–Ag composites based ER suspensions is lower compared to suspension of neat PPy particles due to their better compatibility with the oil medium which is probably given by their higher hydrophobic character [11]. On the other hand, when the electric field is applied, the low-shear apparent viscosity of all ER systems increased. The flow became pseudoplastic, and the ER responses of suspensions of samples S1 and S3 were similar while suspension of sample S2 was the lowest one. The weaker ER response of this system is attributed to the rearrangement of internal structures within the system from chain-like structures spanning the gap between electrodes to lamellar ones during the shearing, which is probably caused by the incorporation of Ag into the particles [12]. However, when the concentration of Ag is high enough (sample S3), the ER response of its suspension is comparable to that of neat PPy and, thus, such systems can be used as a novel dispersed phase for ER suspensions with comparable ER behaviour under given electric field strength with state-of-art systems based on conducting polymers.

![Graph showing shear stress vs. shear rate](image)

Moreover, the improved compatibility of these particles resulting in lower field-off viscosity consequently improves a little bit the ER efficiency (Fig.5) defined as \( e = (\eta_E – \eta_0)/\eta_0 \), where \( \eta_E \) is a viscosity of ER structure and \( \eta_0 \) is the field-off viscosity [13]. The dependence of ER efficiency on applied shear rate represents characteristic course ER phenomenon in Fig.5. Chain-like structures are broken during shearing but parts of chains can immediately join together again due to the dominance of electrostatic forces in the system at very low shear rate. Thus continuous rupture and recovery process takes place. On the other hand, the hydrodynamic forces start to dominate over electrostatic ones at moderate shear rates and rupturing process is not followed by recovering of chains resulting in the reduction of viscosity in the presence of electric field. Thus ER efficiency significantly decreases as shear rate increases.

Generally, dielectric properties of ER suspensions are closely connected to the ER effect since the chain-like structure is formed by induced electrostatic interactions between dispersed dielectric particles caused by interfacial polarisation. The dielectric spectra are presented in Fig.6. Evidently, samples S2 and S3 exhibit an extra relaxation in the low-frequency region stemming from the electrode polarisation given by the presence of Ag in the dispersed phase of studied ER suspensions. Suspensions of PPy–Ag composite
particles studied in this work exhibit sufficient ER performance under given electric field strength which is even comparable with that of neat PPy generally used as a dispersed phase in state-of-art ER suspensions. The relaxation time representing the rate of forming induced dipoles is an important parameter of ER suspensions and can be evaluated as a reciprocal value of the peak maximum of the dielectric loss factor, $\varepsilon''$, in the frequency range corresponding to the interfacial polarization, i.e., $10^4$–$10^7$ Hz (Fig.6). Evidently, PPy–Ag composite particles based ER suspensions exhibit faster relaxation time comparing to that consisted of neat PPy. Thus, PPy–Ag composite particles can be used in ER applications in which the fast response to the electric field and low electric field strengths are required.

4 Conclusion
The composite PPy–Ag particles were synthesized via oxidation of Py with a mixture of APS and AgNO$_3$ and their silicone oil suspensions were investigated. Such composite particles can be used in applications with wide range of conductivity since it can be tailored depending on the ratio of oxidation agents concentration used. In this study, such particles were prepared as a dispersed phase of a novel ER suspension. To obtain insight into the ER activity of prepared ER suspensions, rheological as well as dielectric properties were evaluated. The steady-shear measurements showed that the ER efficiency of suspensions of PPy–Ag particles was comparable with the state-of-art suspension of neat PPy particles under lower electric field strengths applied only above certain concentration of Ag below its percolation. The dielectric spectroscopy measurements further revealed that the relaxation time is shorter for PPy–Ag composite particles based ER suspensions. These findings can be reflected in ER applications of such a smart systems exploiting fast relaxation time under low electric field strengths applied. Finally, the incorporation of Ag into the composite can improve the stability of particles conductivity at elevated temperatures which can broaden the application area of ER suspensions as a whole.

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References:


