Magnetorheology of carbonyl iron particles coated with polypyrrole ribbons: The steady shear study

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Abstract. The aim of this study is a preparation and application of polymer coating on the surface of carbonyl iron particles. Oxidative polymerization of the pyrrole provides ribbon-like morphology. Compact coating of particles has a slightly negative impact on their magnetic properties (measured for magnetic field strength in the range from 0 to 300 mT); however, there is a significant increase in sedimentation stability. The effect of the particle concentration and temperature on the toughness of the internal structures was also investigated.

1. Introduction

Magnetorheological (MR) suspensions belong to the class of smart materials whose characteristic properties are changed upon application of the external stimuli [1-3]. In the case of MR suspensions this stimulus is represented by a magnetic field [4-6].

Generally, MR suspensions are two-phase system consisting of ferromagnetic particles with low value of coercivity dispersed in medium with negligible magnetic properties [7, 8]. This composition enables to create internal structures after application of the magnetic field. This phenomenon is fully reversible and thus after the demagnetization, internal chain-like structures are destroyed and suspension reverts to its original liquid state. Such behaviour has great potential and is used in real applications as e.g. in active damping systems and torque transducers [5].

The sedimentation is a very important factor which influences the applicability of these materials in industry. Magnetic particles are mainly based on the metal (iron, zinc, cobalt) having relatively high density, thus very fast sedimentation appears when they are dispersed in the liquid medium. There are several approaches to improve the sedimentation stability such as adding various additives (surfactants, thixotropic agents, nanofillers), or usage of bidispersed or bimorphic MR fluids [7, 9, 10]. Promising approach consists of preparation of the core-shell based magnetic particles, where a magnetic core is coated with a suitable layer decreasing the overall density of the core-shell particles and enhancing interactions between particles and liquid medium [11,12].

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In this study, the carbonyl iron (CI) particles were coated with polypyrrole (PPy) ribbons synthesized via oxidative polymerization. The magnetic properties of the prepared particles were examined. Steady shear measurements in the absence and presence of magnetic field were performed and from the obtained flow curves a yield stress was evaluated for various strengths of magnetic field. The effect of the particle fraction and temperature was also analysed. Finally, the positive influence of the particle coating on the sedimentation stability was proved.

2. Experimental

2.1 Materials
Carbonyl iron (HS grade) consisting > 97% of iron particles, was produced by BASF (Germany), Pyrrole (Py, 98%, Aldrich Chemicals, USA) was distilled twice under reduced pressure before use. Both, oxidizing agent ammonium persulfate (APS, $(NH_4)_2S_2O_8$, 98%, Aldrich Chemicals, USA), and surfactant cetyltrimethyl ammonium bromide (CTAB, LACH-NER, Czech Republic), were used as received.

2.2 Synthesis of core-shell particles
First, CI particles were treated with 0.5M HCl following a procedure according to reference [13] and hydroxyl groups were created on the surface of the particles. Later, the particles modified in this way were sonicated with the surfactant CTAB water solution for 1 hour. Then the dispersion of CI particles was moved to the three-neck flask cooled down to 0-5°C and monomer Py was added under vigorous stirring. After 20 minutes, the oxidizing agent APS was added drop-wise. The reaction was carried out for additional 18 hours [14].

2.3 Characterization of the prepared particles
Morphology of the bare CI microparticles and the ones coated with PPy ribbon-like particles was studied using a scanning electron microscopy (SEM, VEGA II LMU, Tescan Ltd., Czech Republic), with an operating voltage of 5 kV. FT-IR spectra of the prepared samples were obtained using a Nicolet magna-550 spectrometer, USA, in the range of 4000-700 cm^{-1}. Further, magnetic properties of particles were examined using a vibration sample magnetometer (VSM, EG&G PARC 704, Lake Shore, USA) at room temperature.

2.4 Suspension preparation
Bare CI and CI/PPy ribbon-like particles were suspended in silicone oil (Dow Corning, Fluid 200, USA, η ~ 100 mPa s) with 20, 30 and 40 wt.% particle concentrations. Suspensions were stirred mechanically and than placed in an ultrasonic bath for 30 s before each measurement.

2.5 Rheological characterization
The rheological properties under external magnetic field in the range 0-300 mT were investigated using a rotational rheometer Physica MCR501 (Anton Paar GmbH, Austria) with the Physica MRD 180/1T magneto-cell. The true magnetic flux density was measured using a Hall probe and the temperature was checked with the help of an inserted thermocouple [15]. Rheological measurements at temperatures 25, 45 and 65°C were performed using a Viscotherm VT2 circulator with temperature stability ±0.02°C.

3. Results and discussion

3.1 Morphology of the particles and structure characterization
Morphology of the prepared particles is depicted in Figure 1. The bare CI particles (Figure 1a) exhibit nearly spherical shape with a diameter around 1 μm. The coating of CI particles with PPy ribbons (Figure 1b) changes their shape and size negligibly.

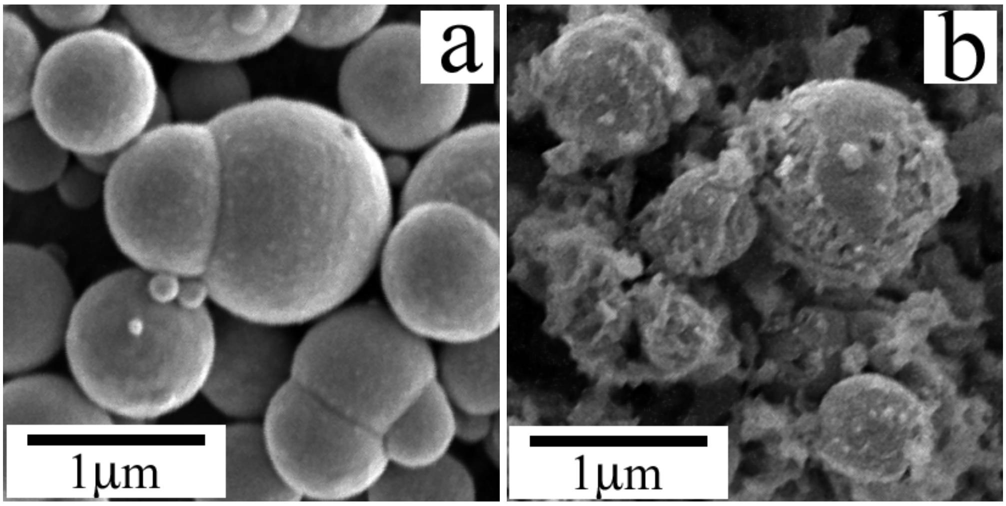

Figure 1. SEM images of CI particles: (a) bare, (b) coated with PPy ribbon-like particles.

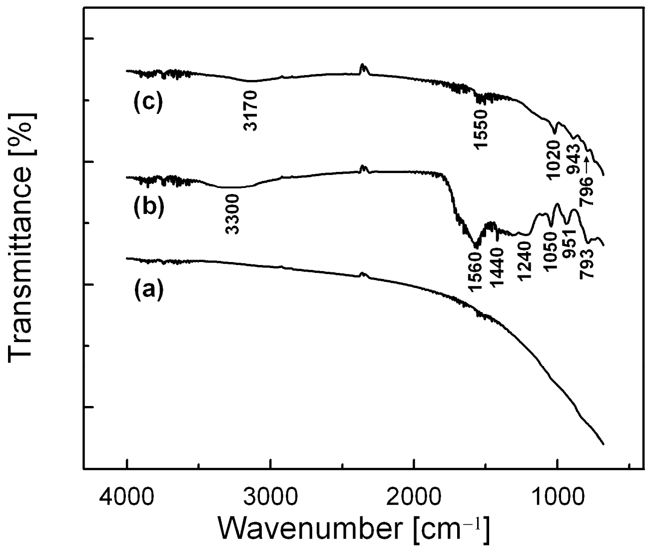

Figure 2. FT-IR spectra of (a) bare CI particles, (b) bare PPy ribbon-like particles, (c) coated CI with PPy ribbon-like particles.

Figure 2 shows FT-IR spectra of the bare CI particles, bare PPy ribbon-like particles and coated CI with PPy ribbon-like particles. As expected there are no visible characteristic bands for the bare CI particles due to their composition >97% of iron. Further, typical absorption of PPy is illustrated in Figure 2b where the characteristic bands are: for N-H at 3300 cm^{-1}, for C-N at 1560 and 1440 cm^{-1}, and the vibrations related to C-H at 1240 and 1050 cm^{-1}. Strong bands near 943 cm^{-1} indicate the doping state of PPy [16]. Finally, Figure 2c documents successful coating of the bare CI particles with PPy ribbons. The broad band at 3170 cm^{-1} is related to the N-H stretching mode from PPy. However, the bands become weaker due to presence of bare CI in the CI/PPy ribbon-like system. Analogously to the reference [17], probably due to polymerization of PPy in the presence of the CI particles some of the vibrations are shifted to lower wavenumbers.

3.2 Magnetic properties

Magnetic properties of bare CI particles and CI coated with PPy ribbon-like particles are shown in Figure 3. Both types of particles exhibit minimal remanence. Coating of CI particles with a polymer layer implies lower magnetization saturation in comparison with the bare CI particles. However, a reduction of magnetic properties is more than balanced by their improved sedimentation stability.

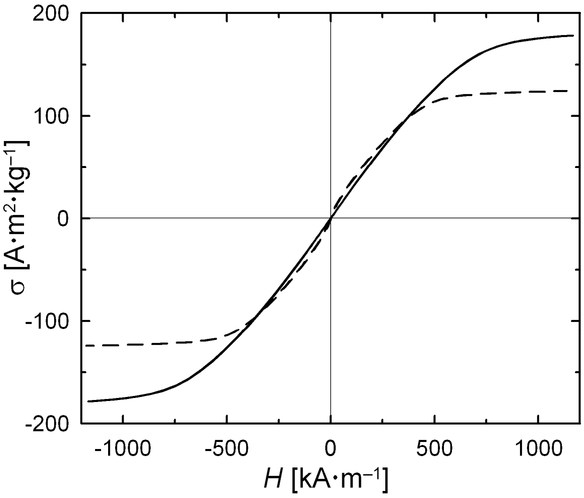

Figure 3. Magnetization curve of bare CI (solid line) and CI/PPy ribbon-like particles (dashed line).

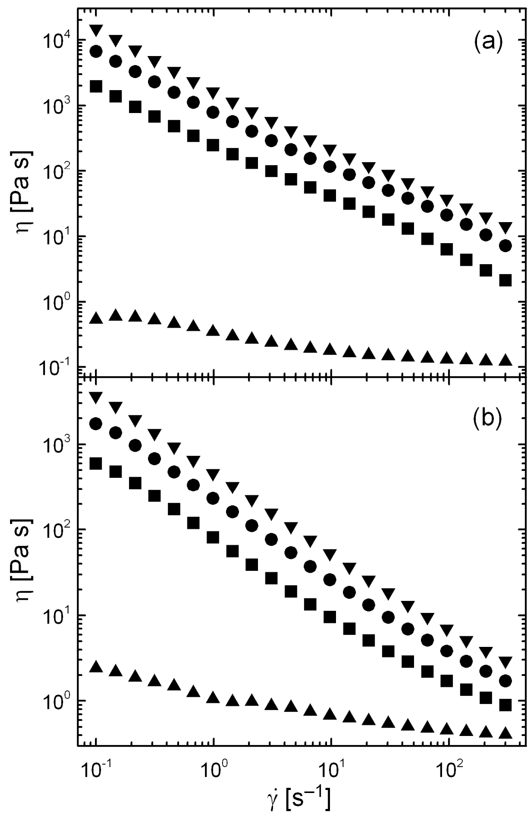

Figure 4. Dependence of shear viscosity, η, on shear rate, $\dot{\gamma}$, for 40 wt.% suspensions of (a) bare CI and (b) coated CI with PPy ribbon-like particles at various magnetic field strengths B (mT): (▲) 0, (■) 84, (●) 174, (▼) 263.

3.3 Steady shear behaviour

Figure 4 illustrates steady shear behaviour of the prepared suspensions. In the absence of magnetic field, both MR suspensions exhibit nearly Newtonian behaviour. This situation is dramatically changed when a magnetic field is applied. Its presence evokes chain-like structures in both suspensions resulting in an increase of shear viscosity by several orders of magnitude. Furthermore, the toughness of the internal structures increases with increasing magnetic field strength. As expected, PPy ribbon-like coating reflects in lower values of viscosity due to the suppressed magnetic properties in comparison to bare CI particles.

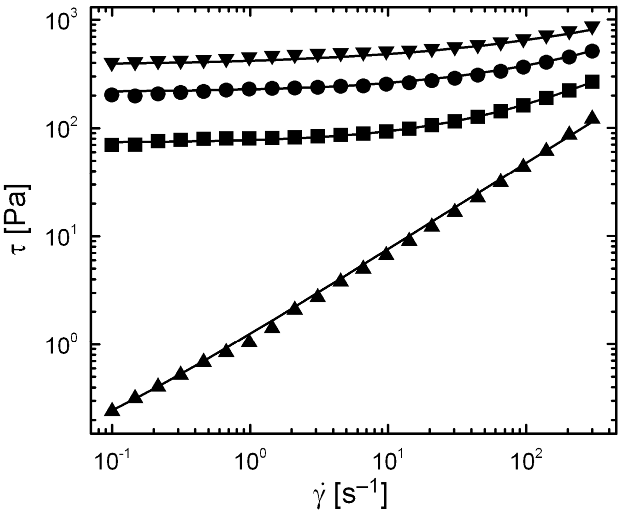

Figure 5. Dependence of shear stress, τ, on the shear rate, $\dot{\gamma}$, for 40 wt. % of coated CI with PPy ribbon-like particles in silicone oil at various magnetic field strengths, *B* (mT): (▲) 0, (■) 84, (●) 174, (▼) 263, where the solid lines represent the Herschel-Bulkley model.

In order to obtain an information about the internal structures, the dependence of shear stress, τ, on the shear rate, $\dot{\gamma}$, was evaluated using the Herschel-Bulkley model (as in [18])

$$\tau = \tau_y + k \cdot \dot{\gamma}^n \quad (1)$$

where, τ_y, is the yield stress, *k*, is the consistency parameter and ,*n*, is the flow behaviour index. The parameters in the Herschel-Bulkley model corresponding to the individual curves in Figure 5 are summarised in Table 1.

Table 1. Parameters of the Herschel-Bulkley model.

B [mT]	τ_y [Pa]	*k* [Pa·s^n]	*n* [-]
0	0.06	1.19	0.8
84	73.3	4.48	0.7
174	215.4	12.96	0.6
263	379.3	39.54	0.4

2.4 Effect of the particle concentration and temperature on the internal structure toughness

The yield stress obtained by fitting of the flow curves using the Herschel-Bulkley model was chosen as a measure of toughness of internal structures created under the application of magnetic field. As can be seen in Figure 6 the particle concentration represents a crucial parameter influencing the structure toughness. Toughness of the internal structures increases with increasing particle concentration. The increase from 20 to 40wt.% enhances a yield stress nearly by one order of magnitude.

The effect of temperature on toughness of the structures is depicted in Figure 7. Toughness of the structures increases with increasing temperature applied to the suspension under presence of magnetic field. Application of higher temperature results in an increase of the yield stress. Similar results were already reported by Kim *et al*. [19].

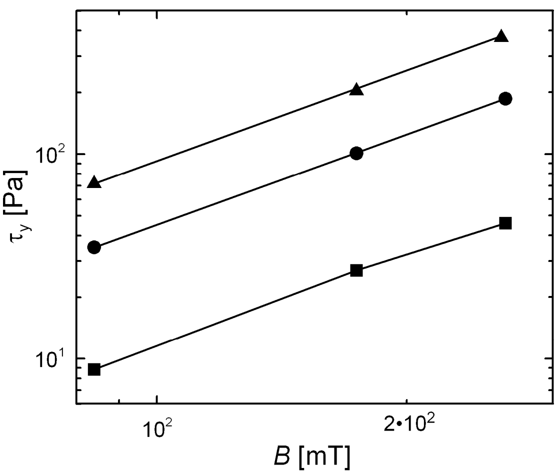

Figure 6. Dependence of the yield stress, τ_y, on the magnetic field strength, B, for suspensions in silicone oil of various concentrations (wt. %): (■) 20, (●) 30, (▲) 40 at temperature 25°C.

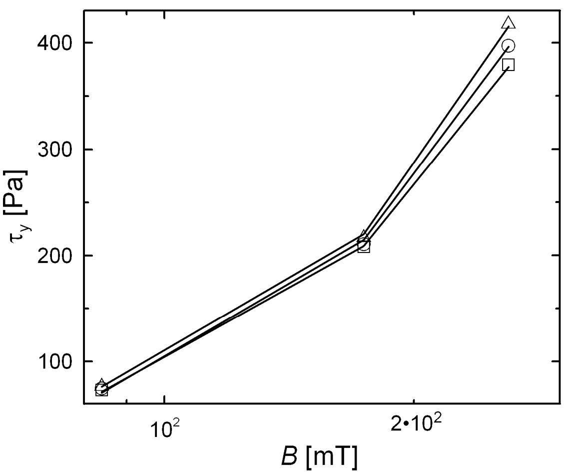

Figure 7. Dependence of the yield stress on the magnetic field strength for 40 wt.% particle suspensions in silicone oil at various temperatures (°C): (□) 25, (○) 45, (△) 65.

2.5 Sedimentation stability

Sedimentation strongly influences the use of MR suspensions in industry. The sedimentation test measured by a naked-eye method reveals that stability of bare CI particle suspension is poor (Figure 8). On the other hand, when the PPy ribbon-like structures were synthesized on the surface of CI particles, the sedimentation stability increased and the particles exhibited stable behaviour during 30 hours of test duration. Polymer coating on the CI particles with PPy ribbons partially decreases the particle density and probably increases the particle-silicone oil interactions [20] that contribute to enhancement of the sedimentation stability.

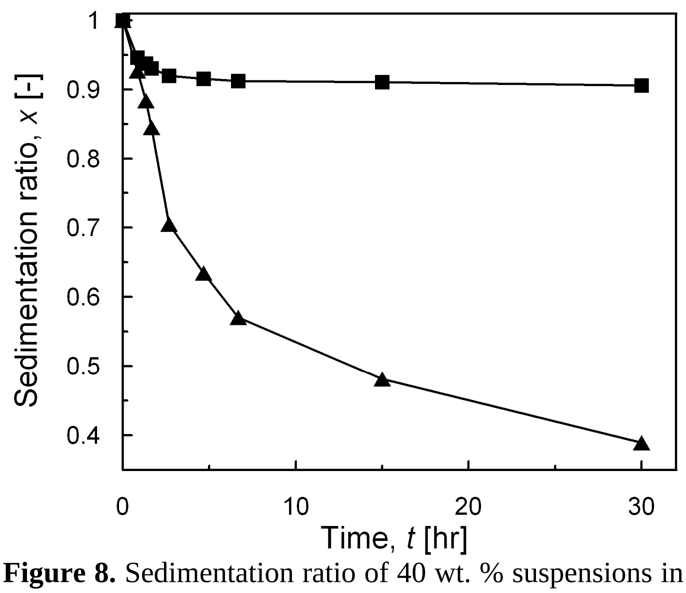

Figure 8. Sedimentation ratio of 40 wt. % suspensions in silicone oil for bare CI (▲) and CI/PPy ribbon-like particles (■) at temperature 25°C.

4. Conclusion

In the present study, the easy preparation of the CI/PPy ribbon-like particles was introduced. The coating of CI particles was realized via in situ oxidative polymerization of PPy. Magnetic properties of prepared particles are lower in comparison with the bare ones due to coating of CI particles with a polymer layer. When the magnetic field strength of 263 mT is applied, the magnitude of viscosity of the suspension of CI/PPy ribbon-like particles increases by three orders in comparison when no magnetic field is applied. Further, both particle concentration and temperature positively influence the toughness of the suspension structure (an increase in the yield stress). Finally, the sedimentation stability of the suspension consisting of coated CI with PPy ribbon-like particles was significantly improved, due to reduced particles density and enhanced particle-silicone oil interactions.

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