Core-shell Structured Polypyrrole-coated Magnetic Carbonyl Iron Microparticles and their Magnetorheology

Michal Sedlacik[a], Vladimir Pavlinek[a], Petr Saha[a], Petra Svrcinova[b] and Petr Filip[b]

[a]Centre of Polymer Systems, Polymer Centre, Tomas Bata University in Zlin, nam. T. G. Masaryka 5555, 760 01 Zlin, Czech Republic
[b]Institute of Hydrodynamics, Academy of Sciences of the Czech Republic, Pod Patankou 5, 166 12 Prague 6, Czech Republic

Abstract. The substantial sedimentation problem of magnetorheological (MR) suspensions, due to the large density mismatch between dispersed particles and carrier medium, is a significant obstacle for their broader applications. The present paper reports the MR properties and enhanced sedimentation stability of novel core-shell structured particles with carbonyl iron as a core and polypyrrole as a shell layer dispersed in silicone oil. The coating morphology was analyzed via scanning electron microscopy and magnetic properties via vibrating sample magnetometry. The steady shear flow and small-amplitude dynamic oscillatory shear measurements were carried out to show improved MR performance. The sedimentation test showed positive role of polymeric coating, as well.

Keywords: Carbonyl iron, Core-shell, Magnetorheological suspension, Polypyrrole, Sedimentation, Viscoelasticity.
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INTRODUCTION

Magnetorheological (MR) suspensions are smart systems known as suspensions consisting of nano- to micro-sized magnetizable particles dispersed in a non-magnetic medium. Generally, in the absence of external magnetic field, they exhibit Newtonian or slightly pseudoplastic behavior. Under an applied magnetic field in orders of hundreds of milliteslas, nevertheless, the dispersed particles start to magnetize, attract each other and form chain or columnar structures [1-4]. The chain-like structure enables MR suspension rapidly to increase its apparent viscosity, which is connected with the transition from liquid to solid-like state accompanied with a large yield stress of about several kPa. When the system is sheared in a flow field afterwards and the yield stress is overcome, the MR structure ruptures and chains break down due to the shear forces. As a result, the apparent viscosity shows shear-thinning behavior and at very high shear rates reaches the same value as observed in the absence of magnetic field. Interestingly, when the external magnetic field is switched off, the particles

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formerly aligned into columns can return to the original random distribution. This phenomenon is commonly known as the MR effect [5, 6].

Such behavior makes MR suspensions ideal for a wide range of potential applications in mechanical engineering for clutch, brake or damping systems [7-9]. Although there have been performed a large amount of various studies by now, the comprehensive qualities are still far from their wider commercialization because of large sedimentation of magnetic nanoparticles in the absence of frequent mixing due to predominant gravity forces; i.e. density mismatch between dispersed particles and carrier medium. Moreover, once sedimented, the residual magnetic attractions between particles make re-dispersion difficult, which result in much lower MR effect of the system. Following the purpose of overcoming these limitations the core-shell structured particles can be used as a dispersed phase. If the magnetic material is used in a shell layer, a good bonding of the shell to the non-magnetic core is required to prevent eventual fragmentation in shearing [10]. Thus, better variant is based on the use of magnetic material as a core, which enhances also the chemical and oxidation stability [11, 12]. The use of both types of core-shell particles results in an improved system stability (i.e. reduced density of dispersed particles and their better compatibility with carrier medium) and may also promote the MR performance defined as a difference between apparent viscosities in the absence and presence of the external magnetic field [11].

In this paper, core-shell structured particles with a carbonyl iron (CI) magnetic core and polypyrrole (PPy) shell were prepared and their suspensions in silicone oil investigated. The main idea is, therefore, to study the effect of polymer coating on the MR properties including steady shear and viscoelastic properties, and stability of the suspensions.

EXPERIMENTAL

Materials

Carbonyl iron particles (HS grade, BASF, Germany) were selected as a magnetic core in core-shell particles and as a comparative system to structured particles. The main material characteristics of HS grade of mere CI are following: spherical shape of particles with the average size of about 2 μm, non–modified surface, and content of α–iron > 98%. The other chemicals for the PPy coating were pyrrole (Py, purity ≥ 98%) and ammonium persulfate (APS, purity 98%), which were purchased from Sigma–Aldrich Incorporation (St. Louis, USA). Polymerization surfactant cetyltrimethylammoniumbromide (CTAB, purity 98%) was obtained from Lach–Ner, Ltd. (Neratovice, Czech Republic). All chemical were used without further purification.

Preparation of CI/PPy Particles

To polymerize PPy on the CI surface, typically 3.69 g of CTAB surfactant was dissolved in 100 mL of distilled water and 4 g of CI particles were added.

The suspension was sonicated for 30 minutes and cooled to 0 – 5°C during vigorous stirring. Then 1 mL of precooled Py monomer and 3.32 g of precooled initiator APS were added to the reaction mixture dropwise. The polymerization reaction was carried out at 0 – 5°C for 9 hrs and another 12 hrs kept under room temperature. The obtained CI/PPy powder was collected on the filter, rinsed with distilled water and ethanol several times to remove residual surfactant, and dried at 60°C for 6 hrs.

Morphology

The morphology of the core-shell particles with a CI core and PPy shell was observed with scanning electron microscopy (SEM, VEGA II LMU, Tescan Ltd., Czech Republic) operated at 10 kV. All samples were coated with a thin layer of gold using a polaron sputtering apparatus.

Magnetic Properties

The effect of particles coating in terms of magnetization curve was ascertained using a vibration sample magnetometer (VSM, EG&G PARC 704, Lake Shore, USA). The external magnetic field was swept from +1 to –1 T and then back to +1 T. Measurements were carried out at room temperature.

Rheological Properties

The MR properties of suspensions containing 40 wt. % of mere CI and its PPy-coated analogue in silicone oil (Lukosiol M100, Chemical Works Kolín, Czech Republic; viscosity 100 mPa s) were measured using a rotational rheometer Physica MCR501 (Anton Paar GmbH, Austria) with a Physica MRD 180/1T magneto-cell. The true magnetic flux density in the range 0 – 300 mT was measured using a Hall probe and the temperature (25°C) was set using an Anton Paar Viscotherm VT2 circulator and checked with the help of an inserted thermocouple; for details of arrangement see [13]. The parallel-plate geometry with a diameter of 20 mm and gap of 1 mm was employed.

All steady flow measurements in the controlled shear rate (CSR) mode were performed in the shear rate range 0.1 – 300 s^{-1}. The oscillatory measurements were carried out through dynamic strain and frequency sweeps. Strain sweeps were performed in the strain range of 10^{-5} to 0.1 at a fixed angular frequency of 62.8 rad.s^{-1} in order to get the position of the linear viscoelastic region (LVR). Afterwards, the viscoelastic moduli were obtained from the frequency sweep tests (1 to 100 rad.s^{-1}) at fixed strain amplitude in the LVR. All the oscillatory measurements were performed in the CSR mode. During each run under a magnetic field, the MR suspension was firstly sheared ($\dot{\gamma}$ = 100 s^{-1}) at zero field for 60 s to destroy previously formed structures and after the measurement the system was completely demagnetized.

Suspension Stability Test

Stability of MR suspensions consisted of 40 wt. % mere CI or CI/PPy core-shell particles in silicone oil M100 was examined by a sedimentation ratio test. The settling of the macroscopic phase boundary between the concentrated suspension and the relatively clear oil-rich phase was measured as a function of time for 30 hrs. Afterwards, the sedimentation ratio is defined as the height of particle-rich phase relative to the total suspension height.

RESULTS AND DISCUSION

The size and surface morphology of mere CI particles (a) and their PPy coated variants are shown in SEM images (Figure 1). As can be clearly recognized, polymer forms a rough surface layer on particles not exceeding 0.5 μm. In addition, the core-shell particles keep their spherical shape, which proves the uniform and complete coating.

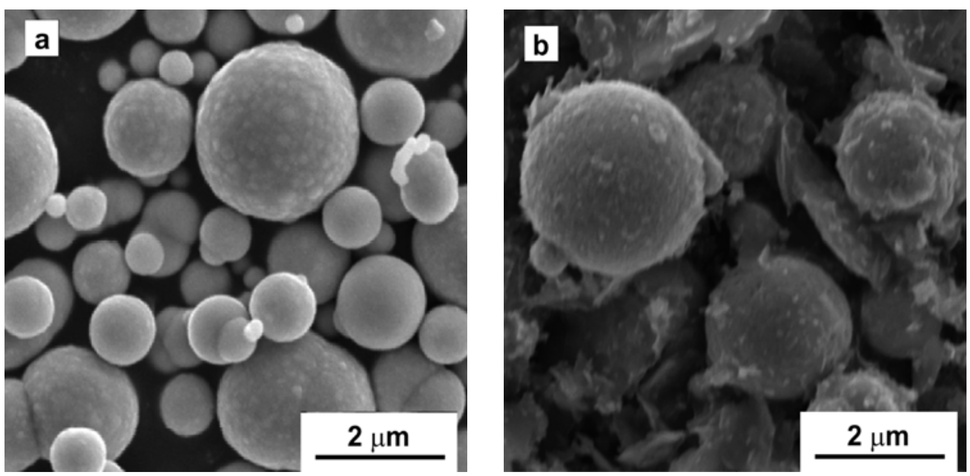

FIGURE 1. SEM images of (a) mere CI and (b) CI/PPy particles.

The magnetization curve measurements of the mere CI and CI/PPy structured particles are depicted in Figure 2. The saturation magnetization of core-shell particles is lower in comparison with uncoated CI variant, which predicates about magnetic properties reduction of particles by PPy coating. Although it is necessary to use particles with as high saturation magnetization as possible for the remarkable MR effect, the values obtained for CI/PPy particles are still sufficient [14].

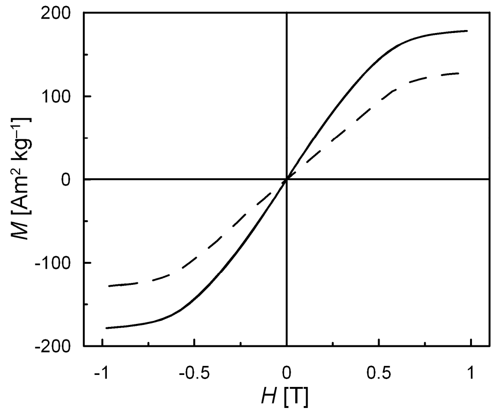

FIGURE 2. Magnetization curves of mere CI (solid line) and CI/PPy (dashed line) particles.

Moreover, for the practical use of MR suspensions it is also important to ensure their sedimentation stability. Figure 3 illustrates the stability test for model MR suspensions containing 40 wt. % of the mere CI particles and their PPy-coated analogues is silicone oil. The CI/PPy particles based MR suspension apparently exhibits better suspension stability than that of the mere CI suspension, which is probably due to the reduced particle density and rougher surface morphology. It is worth noting here, that the sedimentation stability can be further improved using some thixotropic additives [15]. However, such addition increases also the suspension viscosity in the absence of magnetic field, η_0, which consequently negatively influences the MR performance expressed as $e = (\eta_M - \eta_0)/\eta_0$, where η_M is a viscosity of the suspension in external magnetic field.

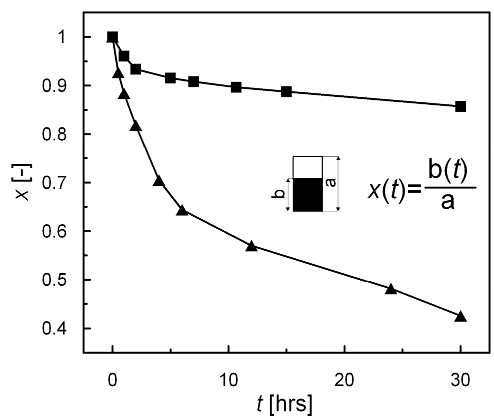

FIGURE 3. Sedimentation ratio of MR fluids (40 wt. %) based on mere CI (▲) or CI/PPy (■) particles dispersed in silicone oil M100.

The steady shear flow of mere and PPy coated CI particles based MR suspensions (40 wt. %) were investigated to evaluate the influence of the particles coating on the MR performance (Figure 4).

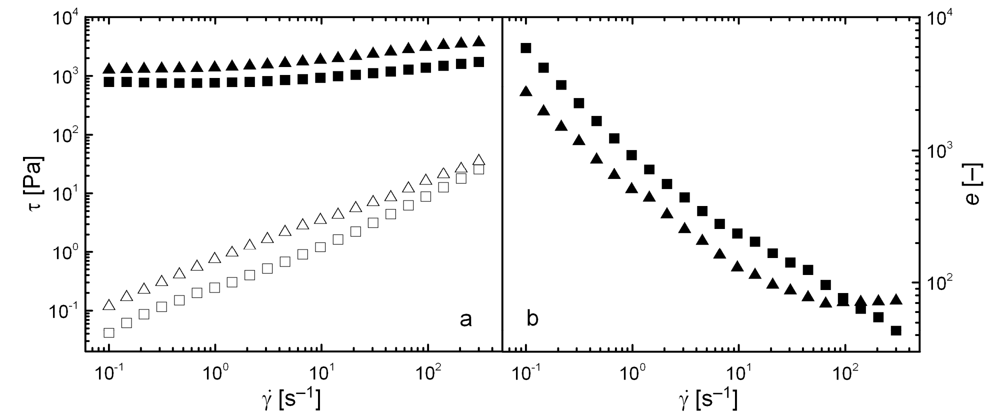

FIGURE 4. The shear stress, τ, (a) and performance, e, (b) vs. shear rate, $\dot{\gamma}$, dependence for 40 wt. % suspension of mere CI (▲,△) and CI/PPy (■,□) particles in M100. Magnetic flux density (mT): 0 (open) and 274 (solid).

The maximum reached yield stress in magnetic field applied was achieved in mere CI particles based suspension. However, the higher MR performance is observed in core-shell particles system due to its lower magnetic field-off viscosity. This is probably due to more hydrophilic surface of mere CI than PPy-coated one and, consequently, worse particle compatibility with the hydrophobic oil medium [16].

Results from a typical MR steady shear flow experiments of 40 wt. % CI/PPy particles suspension at magnetic field strengths ranging from 0 to 274 mT are shown in Figure 5. In the absence of a magnetic field, the CI/PPy suspension shows nearly Newtonian character. Evidently, when an external magnetic field and shearing is applied, the MR suspension starts to behave as a plastic material presenting a yield stress (Figure 5a). The generated yield stress is a manifestation of the formation of internal organized structures from magnetized particles. It is also obvious, that the larger the magnetic field is, the larger yield stress occurs. Furthermore, regardless of the magnetic flux density applied, a clear shear thinning is observed (Figure 5b) as a consequence of internal structures buckling due to shearing forces.

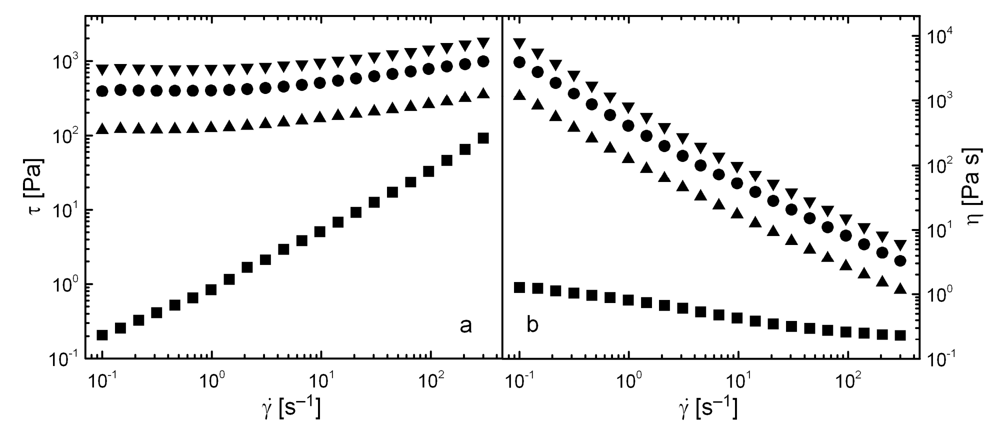

FIGURE 5. Shear stress, τ, (a) and shear viscosity, η, (b) vs. shear rate, $\dot{\gamma}$, dependence for 40 wt. % CI/PPy MR suspension in silicone oil M100 in various magnetic fields applied. The symbols for magnetic flux densities (mT): ■ 0; ▲ 88; ● 180; and ▼ 274.

The formation of internal organized structures under external magnetic field application is aligned with the change of viscoelastic characteristics. The storage, G', and loss, G'', moduli provide quantitative information about the magnetically induced structures in a wide range of time and frequency [17]. The dependence of G' and G'' on the angular frequency, ω, within the LVR ($\gamma = 5 \times 10^{-4}$ in our experiments) for 40 wt. % CI/PPy particles suspension under magnetic flux densities of 0 and 274 mT are included in Figure 6. Without a magnetic field, both moduli grow in the whole frequency range and G' slightly dominates over G'' probably due to a quite high particle loading in the suspension. When a magnetic field is applied, however, G' becomes significantly higher due to the internal structures formation than G'' and both moduli increase rapidly in several orders of magnitude from their magnetic field-off value especially at lower angular frequencies. Moreover, G' is constant or increase slightly over wide range of driving frequencies. This illustrates a typical behavior of stiff three-dimensional network formed by magnetized particles within MR suspension which is sufficiently strong to transmit the elastic forces in such systems [18].

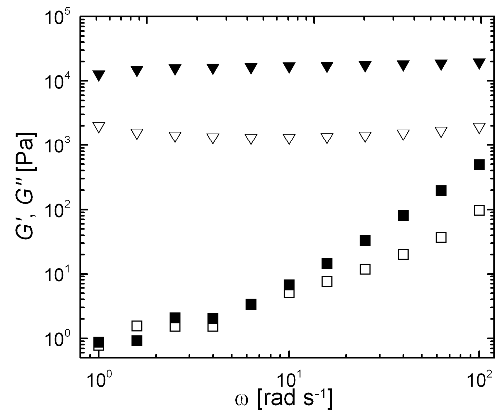

FIGURE 6. Storage, G', (solid) and loss, G'', (open) moduli as a function of the angular frequency, ω, in the various magnetic fields applied for 40 wt. % CI/PPy MR suspension in silicone oil M100. The symbols for magnetic flux densities (mT): (■,□) 0; and (▼,▽) 274.

CONCLUSION

PPy-coated CI particles were prepared as a dispersed phase of a novel MR suspensions. Core-shell structured particles exhibit slightly worse magnetic properties and lower yield stresses in magnetic field applied to MR suspensions in comparison with mere CI as a result of the weaker saturation magnetization. Nevertheless, the PPy coating contributes to lowered interactions between the particles and silicone oil as a carrier medium resulting in an increase of the system fluidity in the absence of a magnetic field and, thus, improved MR performance. In addition, the viscoelastic characteristics of CI/PPy particles MR suspension confirmed the strong elastic behavior within the LVR due to the compact chain-like structure formed under an applied external magnetic field. Finally, the sedimentation stability of the dispersed particles was improved significantly by the reduced density.

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