Rheological properties of magnetorheological suspensions based on core-shell structured polyaniline-coated carbonyl iron particles

M Sedlacik[1], V Pavlinek[1], P Saha[1], P Svrcinova[2], P Filip[2] and J Stejskal?

Abstract

The sedimentation caused by the high density of suspended particles used in magnetorheological fluids is a significant obstacle for their wider application. In the present paper, core-shell structured carbonyl iron-polyaniline particles in silicone oil were used as a magnetorheological suspension with enhanced dispersion stability. Bare carbonyl iron particles were suspended in silicone oil to create model magnetorheological suspensions of different loading. For a magnetorheological suspension of polyaniline-coated particles the results show a decrease in the base viscosity. Moreover, the polyaniline coating has a negligible influence on the MR properties under an external magnetic field *B*. The change in the viscoelastic properties of magnetorheological suspensions in the small-strain oscillatory shear flow as a function of the strain amplitude, the frequency and the magnetic flux density was also investigated.

1. Introduction

Magnetorheological fluid (MRF) is a suspension consisting of solid micrometer-sized magnetically polarizable particles dispersed in a non-magnetic carrier liquid such as mineral oil, which reversibly transforms from a liquid to a solidlike structure under an applied magnetic field in milliseconds. The transformation between these two states is due to the formation of chain clusters in the direction of the exerted external field, which has a consequence in changes of the rheological properties, such as the increase of the apparent yield stress and the shear viscosity [1, 2]. The importance of MRFs has considerably increased in the last 15 years. This is caused by the continuous growth of concrete applications utilizing these smart materials in many areas like damping systems [3], clutches [4], drug targeting [5, 6], prosthetic knees [7], etc. Many recent studies have also focused on the heating of ferrofluid (nanometer-sized ferromagnetic particles suspended in a carrier fluid) to achieve hyperthermia (the heating of certain tissues to temperatures between 41 and 46 °C) in cancer therapy [8].

However, since the density of the magnetic particles used for the MRF is considerably higher than that of the liquid phase, sedimentation represents a significant problem in the development of MRFs suitable for practical applications. The driving force of the sedimentation is the gravity that dominates in comparison with the Brownian motion for particles larger than approximately 0.1 ¡im. Nevertheless, if smaller particles are used, the Brownian motion also hinders the formation of internal structures in the fluid in a magnetic field. Thus the optimum particle size is in the range of 0.1-10 ¡xm and further improvement of MRFs stability is necessary. Several studies have been done to alter the sedimentation, e.g., the addition of thixotropic additives [9], non-spherical particles [2] to the suspension, or the choice of water-in-oil emulsion as a continuous phase [10]. Nevertheless, the additions of stabilization particles may deteriorate the chain structure of MR particles in external fields. A very interesting possibility of how to suppress sedimentation consists in an application of core-shell structures, where a magnetic particle creates either the core [11-15] or the shell [16, 17]. The former case represents different types of coatings improving the chemical and oxidation stability [18]. To prevent eventual fragmentation in shearing, the latter case requires a good bonding of the shell to the non-magnetic core. Both variants result in a decrease of the density of the dispersed phase, which improves the sedimentation stability and may also promote the MR effect of this smart system. This effect is defined as a difference between apparent viscosities in the absence and presence of the applied magnetic field.

Suspensions of carbonyl iron coated with a conducting polymer and carbon nanotubes have been proposed as a new type of MRF [14]. In the present study, core-shell composite particles with a carbonyl iron (Cl) magnetic core and poly aniline (PANI) conducting shell were prepared by using a PANI colloidal dispersion in chloroform [18]. The effects of the PANI coating on the viscosity and MR properties, including the viscoelastic properties of the MR fluid containing core-shell particles stabilized further by fumed silica dispersed in silicone oil, have been evaluated.

2. Experimental details

2.7. *Materials*

For a model particle-suspended system, carbonyl iron (EA grade, BASF, Germany) and PANI were selected as a core and shell, respectively. The main material characteristics of bare Cl according to the product information (G-CAS/BS0106 CIP2) are: the spherical shape of the particles with an average size of about 3.5 *jju*m, the content of a-iron >97%, and the silicated surface. The other chemicals for the PANI coating were of reagent grade (purchased from Sigma-Aldrich, USA).

2.2. *Coating of Cl powder by PANI*

A schematic diagram of the Cl particles coated with PANI is provided in figure 1. Briefly, the polymerization of aniline with ammonium peroxydisulfate was performed at room temperature in a chloroform/water emulsion in the presence of a sodium bis-(2-ethylhexyl) sulfosuccinate surfactant. These reaction conditions led to the separation of the colloidal dispersion of the PANI into the chloroform phase [18, 19]. Cl was subsequently suspended in the PANI colloid in chloroform, separated on a filter, and dried.

2.3. *Characterization of particles and magnetorheological fluids*

The surface characteristics of the core-shell particles with a Cl core and PANI shell were observed with SEM (scanning

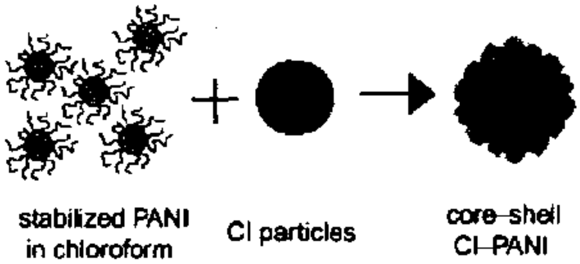

Figure 1. Schematic diagram of the synthesis of CI-PANI core-shell particles.
(This figure is in colour only in the electronic version)

electron microscope VEGA II LMU, Tescan, Czech Republic) operated at 10 kV. The magnetic properties of the microspheres were examined using a VSM (vibration sample magnetometer, EG&G PARC 704, Lake Shore, USA) at room temperature.

MR fluid containing 60 and 80 wt% of bare Cl and its PANI-coated analogue in silicone oil (Lukosiol Ml5, Chemical Works Kolin, Czech Republic; viscosity 14.5 mPa s, density 0.965 g cm^{-3}) were prepared. In both cases 0.5 wt% of nano-silica (average particle size ~10 nm, Aerosil A 200, Degusa, Germany) was added. The suspensions were mechanically stirred before each measurement. The MR characteristics in steady shear and oscillatory regimes of the suspensions were examined using a Physica MCR501 rotational rheometer (Anton Paar GmbH, Austria) with a Physica MRD 180/IT magneto-cell at 25 and 40 °C. The true magnetic flux density was measured using a Hall probe and the temperature was checked with the help of an inserted thermocouple. Both the Hall probe and the thermocouple were rectangular, located in the bottom plate; for details see [20]. The temperature was set using an Anton Paar Viscotherm VT2 circulator with a temperature stability ±0.02 °C. The maximum magnetic flux density used in all the measurements did not exceed 0.3 T, to ensure the sufficient homogeneity of the magnetic field perpendicular to the shear flow direction. A parallel-plate measuring system with a diameter of 20 mm and gap of 1 mm was used.

3. Results and discussion

3.1. *Micro structure of particles*

Figure 2 shows the size and surface morphology of both bare Cl (a) and carbonyl iron-polyaniline (CI-PANI) core- shell particles (b) observed by SEM. The average size of the particles was slightly larger than that of the bare Cl particles as a result of the coating layer not exceeding 0.5 *¡im.* Moreover, the encapsulated particles with a smoother surface kept their spherical shape, which confirms the uniform and complete coating.

3.2. *Magnetic properties of particles*

The magnetization curve measurements of the bare Cl powder and its PANI-coated analogue are depicted in figure 3. The

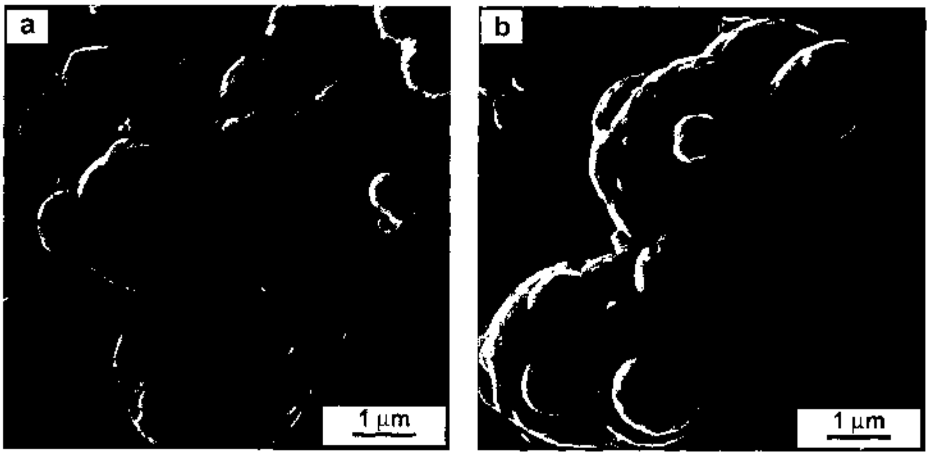

Figure 2. SEM images of (a) bare Cl and (b) CI-PANI particles.

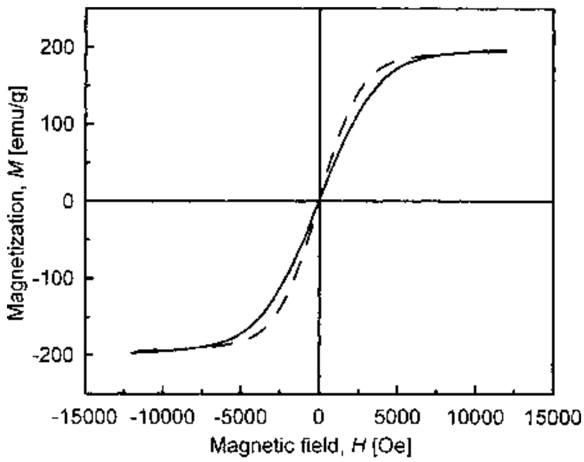

Figure 3. VSM image of bare Cl (dashed line) and CI-PANI (solid line) particles.

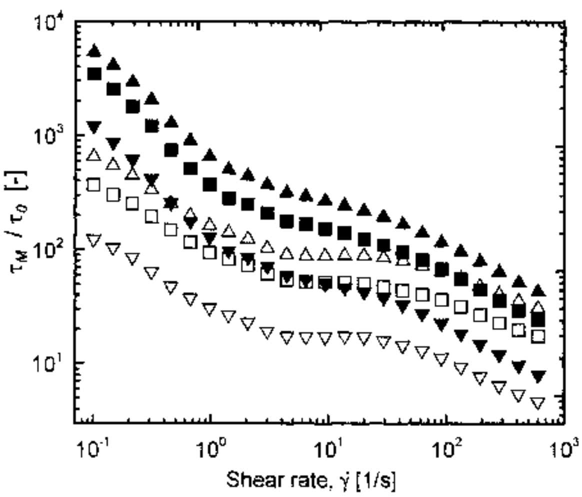

Figure 4. Ratio of shear stresses with/without a magnetic field (tm/to) versus shear rate,]>, for CI-PANI particles' (solid) and CI particles' (open) MR suspensions (80 wt%) in silicone oil in various magnetic fields applied at 25 °C. The symbols for the magnetic flux densities (mT): v 99; □ 205; and A 308.

saturation magnetization for the PANI-coated Cl particles is comparable with uncoated CL Hence, there is no significant influence of the polymeric coating on the magnetic properties, and an MR suspension based on CI-PANI core-shell particles exhibits similar MR performance as in the case of bare CI. Moreover, CI-PANI particles possess almost zero coercive force, which is the requested factor in cyclic applications for the maintenance of isothermal conditions in the system.

3.3. Steady shear and yield stress

The rheological behavior of MR fluids based on CI and CI- PANI particles was investigated in the controlled shear-rate mode. In all measurements the range of the shear rate tested was from 0.1 to 600 s^{-1} in a log scale with 6 pts/decade. The resulting flow responses were examined as a function of the magnetic flux density ranging from 0 to 0.3 T. During each run under a magnetic field, the MR fluid was first sheared (y = 100 s^{-1}) at a zero field for 60 s to distribute the particles uniformly and after the measurement the system was completely demagnetized. Figure 4 shows the proportional changes of the MR effect expressed as a ratio of the shear stresses with/without a magnetic field for MR suspensions based on CI-PANI particles (solid symbols) and CI particles (open symbols). A noticeable increase in the shear stress with magnetic flux density is a typical feature of MR fluids and is caused by the formation of a robust chain structure [1]. Such a strong dependence on the external field is similar to the phenomenon observed for ER fluids [21], The systems in figure 4 can be characterized by a Bingham plastic model with a yield stress, meaning that the suspension acts as a solidlike material when exposed to an external shear stress below this yield stress. In other words, the structure formed in the MR fluid by the magnetic field is sufficiently rigid to withstand certain deforming stresses without any external manifestation of flowing. In comparison with the literature [14], the smoother

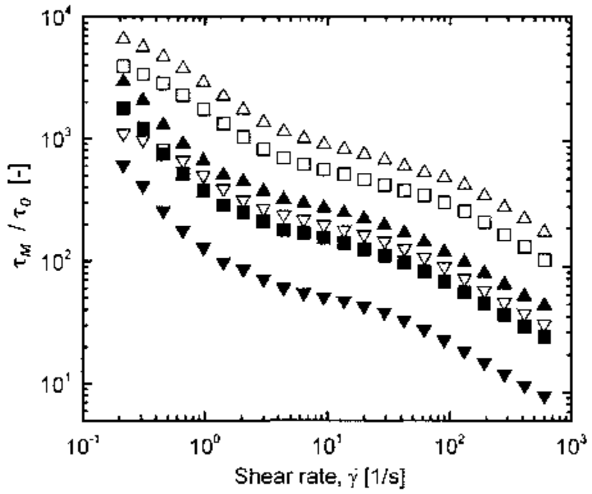

Figure 5. Ratio of the shear stresses with/without a magnetic field (m/m) versus shear rate, y, for core-shell particles based the MR suspensions in the various magnetic fields applied at 25 °C (solid) and 40 °C (open). The symbols for the magnetic flux densities (mT): ▼ 97; ■ 196; A 297.

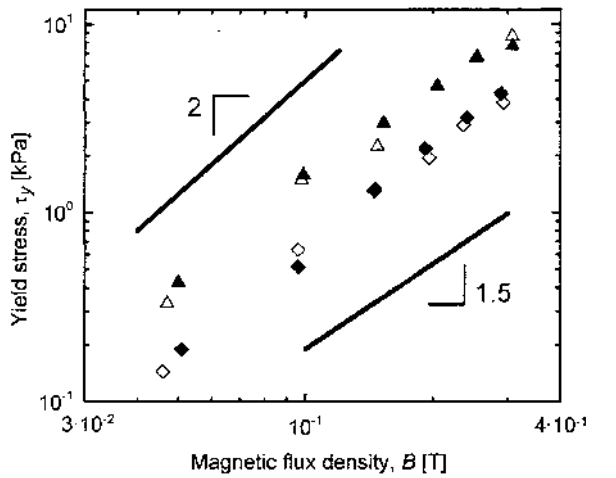

Figure 6. Dependence of the dynamic yield stress, r_y, on the applied magnetic flux density, B, for 60 wt% (diamonds) and 80 wt% (triangles) concentrations of CI-PANI particles (solid symbols) or Cl particles (open symbols) in silicone oil.

particles (CI-PANI) with nano-silica added used in this work seem to provide a reduction of the off-state viscosity and improve the sedimentation stability.

As can be seen in figure 4, the proportional change of the MR effect is higher in the case of the core-shell particles, which is due to lower zero field shear stress and viscosity of the MR suspension and confirms the fact that PANI coating reduces the density of suspended particles.

Furthermore, the MR effect defined as a difference between the flow curves in zero and applied magnetic fields can be increased by elevating the temperature. Figure 5 shows the proportional changes of the MR effect expressed as the ratio of shear stresses with/without a magnetic field for MR fluids with CI-PANI particles measured at 25 and 40 °C. It is worth noting that, in the absence of a magnetic field the system exhibits more Newtonian behavior at elevated temperatures due to stronger thermodynamic forces. However, the magnetic forces start to dominate over the thermodynamic ones in an applied magnetic field and the flow curves are very similar at both temperatures. Thus, the MR effect is higher at higher temperature.

In figure 6, the dynamic yield stresses of two different concentrations of MR suspensions based on Cl and CI-PANI particles are shown as a function of the applied magnetic flux density B. The yield stresses in all cases increase with the external magnetic field following the dependence of the magnetic flux density in the range $B^{l\,5-2}$. This value slightly deviates from the numerical and analytical models, according to which the dependence of the magnetic flux density is a consequence of the local saturation of the magnetization in the polar or contact zones of each particle [22, 23]. However, none of the curves in figure 6 show saturation of the system and all curves have the linear trend without any apparent yield stress plateau in the whole range of the applied magnetic flux densities. This is probably due to the presence of nano-silica in all MR suspensions. These sub-sized particles can fill the free space in the tetragonal column structure of magnetic particles, which might help the formation of more robust chain agglomerates resistant to the higher external stresses, which leads to higher yield stresses even above the saturation of magnetic particles [24].

3.4. Viscoelastic properties

As shown above, MR fluids exhibit Bingham plastic behavior with a yield stress and a system with such properties can be described as a viscoelastic material in the range of a small strain of oscillatory flow. In other words, oscillation experiments give information about the elastic (storage modulus, G^{f}) and viscous (loss modulus, G'') behavior of MR fluids. Figure 7(a) depicts the dependence of G' and G'' on the strain amplitude (y) in oscillatory flow for 80 wt% CI-PANI suspension at 25 °C. The chain structure development with increasing magnetic flux density can be observed from the storage modulus increase and the loss modulus decrease. This trend indicates the solid-like character of MR fluids under these conditions. In a very small-strain amplitude, the viscoelastic modulus, especially its elastic part, is independent of the applied strain; this range is called the linear viscoelastic region (LVR). In the LVR, the structure of the MR fluid is basically undisturbed. However, with increasing strain amplitude, the chain structure starts to break and the system shows nonlinearity and deviations from the viscoelastic behavior. At higher values of strain (which were not measured in our experiment) the elastic and viscous moduli intersect each other ($G' = G''$), the chain structure of the MR fluid breaks rapidly and the system starts to flow.

For practical applications it is important to know the values of G' and G'' in LVR and their strain frequency dependence. Figure 7(b) shows G' and G'' as functions of the strain frequency for an 80 wt% CI-PANI suspension at 25 °C in LVR under a very small strain (y = 0.002%). The storage modulus of such an MR fluid slightly increases with increasing

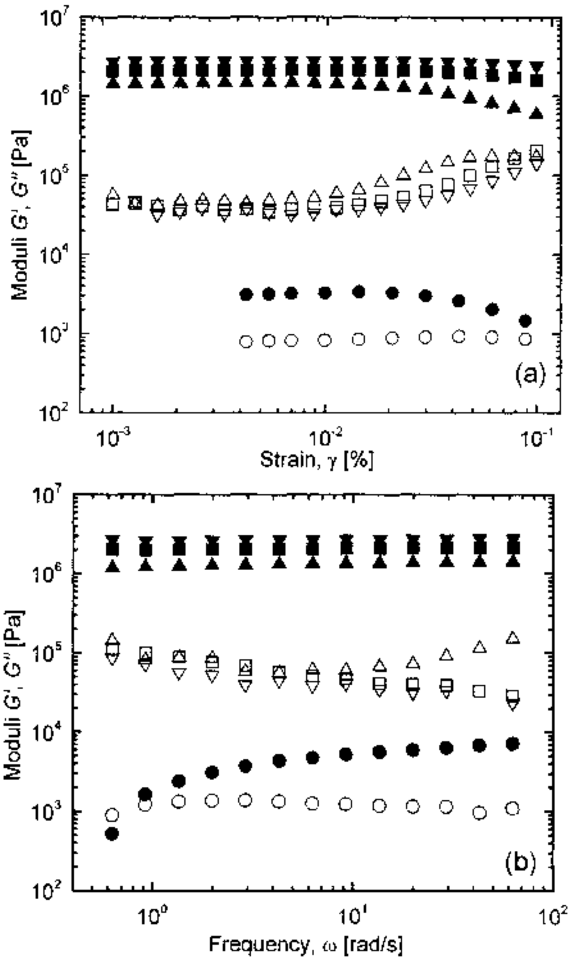

Figure 7. (a) Storage, *G*\ (solid) and loss, *G*\ (open) moduli as a function of the strain amplitude and (b) storage, *G'*, (solid) and loss, *G"*, (open) moduli as a function of the strain frequency in the various magnetic fields applied for an 80 wt% CT-PANT suspension in silicone oil at 25 °C. The symbols for magnetic flux densities (mT):
• 0; A 96; ■ 200; and V 307.

magnetic flux density. This is again evidence of the formation of higher magnetized structures. Moreover, the storage elastic modulus is constant over the wide range of driving frequencies. This trend confirms the fact that the thickness of the PANI coating layer used does not influence the magnetic properties of CI.

3.5. Sedimentation test

Finally, the effect of PANI coating on the sedimentation stability was investigated. MR fluids with the same weight fraction (60 wt%) but different dispersed particles were set in static conditions and the sedimentation ratios were measured until they approached asymptotic values. Figure 8 shows the sedimentation ratio as a function of time for bare CI and PANI- coated CI in suspensions with or without further stabilization by fumed silica. It is obvious that the CI-PANI suspension exhibits a higher sedimentation stability than that of bare the CI based one, in the same time period in a silica stabilized and

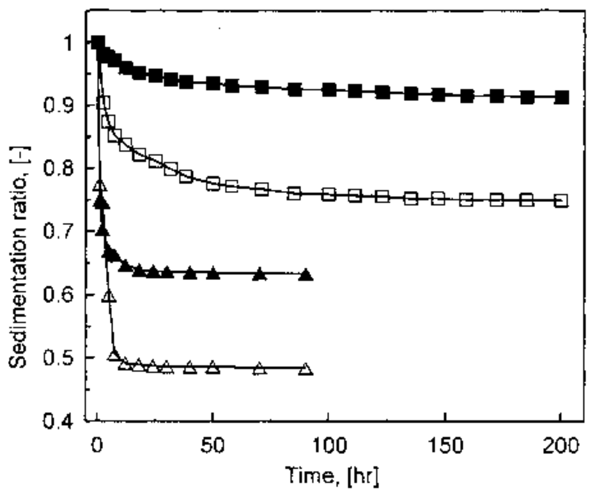

Figure 8. Sedimentation ratio of MR fluids (60 wt%) based on bare Cl (□) or CI-PANI (■) particles with 0.5 wt% and bare Cl (A) or CI-PANI (**A**) particles without silica added.

also a non-stabilized MR suspension. Within the initial 10 hrs the uncoated particles settled much faster than the coated CL Therefore, the coating of magnetic particles with polymers, such as PANI, can improve the sedimentation stability due to the reduction in the overall density. It is worth noting that the sedimentation stability can be further improved using higher concentrations of thixotropic additives such as nanosilica (0.5 wt% in our case). However, in both cases the positive role of PANI coating is apparent.

4. Conclusions

Core-shell CI-PANI particles can be used as a dispersed phase in a novel MR fluid. Particles with the coating exhibit magnetic properties comparable to bare CL Based on visual observation, the PANI coating contributes to reduced sedimentation, and thus to improved suspension stability. In addition, it lowers the interaction between the carrier fluid and the particles resulting in a decrease of the fluidity of the system in the absence of a magnetic field. Therefore the relative change in the magnetorheological effect is significantly higher. The temperature plays also a very important role in MRF activity, and the efficiency increases at elevated temperatures. The viscoelastic properties of the fluids suggest that the CI-PANI suspension exhibits strong elastic behavior within the linear viscoelastic region due to the robust chain structure under an applied magnetic field.

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