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Magnetorheology of core-shell carbonyl iron/ZnO rod-like particle silicone oil suspensions under oscillatory shear

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Abstract. The aim of this study is a preparation and application of inorganic coating on the surface of carbonyl iron particles. The two step solvothermal synthesis provides core-shell CI/ZnO rod-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 213 mT); however, there is a suitable magnetorheological performance investigated under oscillatory shear, suitable to be applied in real applications.

1. Introduction

Suspensions consisting of the solid magnetic particles dispersed in the liquid medium usually silicone oil, changing their basic rheological quantities (viscosity, viscoelastic moduli) upon external magnetic fields are called generally Magnetorheological (MR) [1-9]. Nowadays, material exhibiting this behaviour repeatedly can find various applications as shock absorbers [5] or also in the medical application in the local cancer hyperthermia treatment [9].

In order to obtain the highest MR efficiency of the suspensions usually ferromagnetic particles with low value of coercivity dispersed in medium with negligible magnetic properties are employed [11, 12]. Furthermore, sedimentation stability is another factor significantly influences the MR efficiency. MR suspensions exhibit poor stability, especially when the carbonyl iron is employed as a dispersed phase. Therefore, various techniques were utilized to obtained sufficient sedimentation properties such as bidispersed or dimorphic MR fluids [11, 13-15]. 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 [16, 17].

In the preceding study [18] another approach based on inorganic-inorganic CI/ZnO core-shell particle silicone oil suspension was developed. The sedimentation stability as well as thermo-oxidation one were significantly enhanced and also improved MR efficiency under steady state conditions were confirmed.

In this study, the viscoelastic behaviour of the CI/ZnO was discovered in detail. While the results from steady state conditions provide mostly information about the MR efficiency, the viscoelastic ones describing the behaviour close to the real-life applications.

2. Experimental

2.1 Materials

Carbonyl iron microparticles (SL grade, α -iron content >99.5 %, BASF, Germany), zinc acetate dihydrate Zn(CH3COO)2.2H2O (ZAD), zinc nitrate hexahydrate Zn(NO3)2.6H2O and hexamethylenetetramine (CH2)6N4 (HMTA) were all purchased from PENTA (Czech Republic) and used as received without further purification. Demineralized water with conductivity about 10-7 Scm-1 and ethanol were used throughout experiments.

2.2 Synthesis of core-shell particles

ZnO/CI particles were synthesized via two step reaction. In the first step the seeds of the ZnO particles were created on the surface of the CI. In this case the 0.005 M solution of ZAD and ethanol was prepared and sonicated with CI particles. Then the mixture was heated up to 80°C for 2 hours, filtered and dried at 60°C under vacuum. The second step is creation of the ZnO-rodlike structures on the surface of the CI. Here the mixture of aqueous solution of zinc nitrate hexahydrate (0.05 M) and HMTA (0.05 M) was carried out at 80 °C for 2 h. Finally, the synthesized CI/ZnO particles were dried under vacuum at 60°C.

2.3 Characterization of the prepared particles

Crystalline phase of particles was characterized by the powder X-ray diffractometer X´Pert PRO X-ray (PANalytical, The Netherlands) with a Cu-Kα X-ray source (λ = 1.5418 Å) in the diffraction angle range 5-85° 2θ.

The magnetic properties were studied using a vibrating sample magnetometer VSM 7400 (Lake Shore, United States).

2.4 Suspension preparation

ZnO/CI core-shell particles were suspended in silicone oil (Lukosiol M 200, viscosity η_c = 194 mPa s, density d_c = 0.970 g cm^{-3}, relative permittivity ε' = 2.89, loss factor tan δ = 0.0001, Chemical Works Kolín, Czech Republic) with 20, 40, and 60 wt. % particle concentrations. The suspensions were mechanically stirred before each measurement. The rheological properties under an external magnetic fields in the range 0–300 mT were investigated using a rotational rheometer Physica MCR502 (Anton Paar GmbH, Austria) equipped with a Physica MRD 170/1T magneto-cell. The true magnetic flux density was measured using a Hall probe.

3. Results and Discussion

3.1 Particles morphology and structure characterization

As can be seen from the SEM images bare CI particles (Fig. 1a) are mostly spherical including the two main fractions. First and smaller particles are about two microns in diameter. Second and bigger ones are nearly 5 microns in diameter. After the first step of the synthesis the CI particles were coated with ZnO small particles (Fig. 1b), which in the second step promote the radial crystal growth on the ZnO. After the second step, the CI/ZnO rod-like particles (Fig. 1c) can be seen as a result of the solvothermal synthesis.

From the XRD patterns of bare CI, CI with small ZnO particles, and CI/ZnO rod-like particles are can be seen various peaks at 2θ = 44.6°, 65°, and 82.3° correspond to (110), (200), and (211) reflections of iron with the cubic structure (ICDD PDF-2 entry 01-087-0722). The diffraction patterns of CI with small ZnO particles seem to remain unchanged comparing to diffractogram of bare CI, while no more peaks corresponding to ZnO crystal phase were detected. On the other hand the presence of the small ZnO particles on the CI surface was further confirmed by SEM. Diffraction patterns of CI/ZnO rod-like particles contain peaks related to iron cubic structure peaks at 2θ = 44.6°, 65°, and 82.3° and as expected also peaks located at 2θ = 31.7°, 34.3°, 36.1°, 47.4°, 56.5°, 62.8°, 67.8°

and 68.9° which correspond well to hexagonal wurtzite crystal structure of ZnO (ICDD PDF-2 entry 01-079-0207).

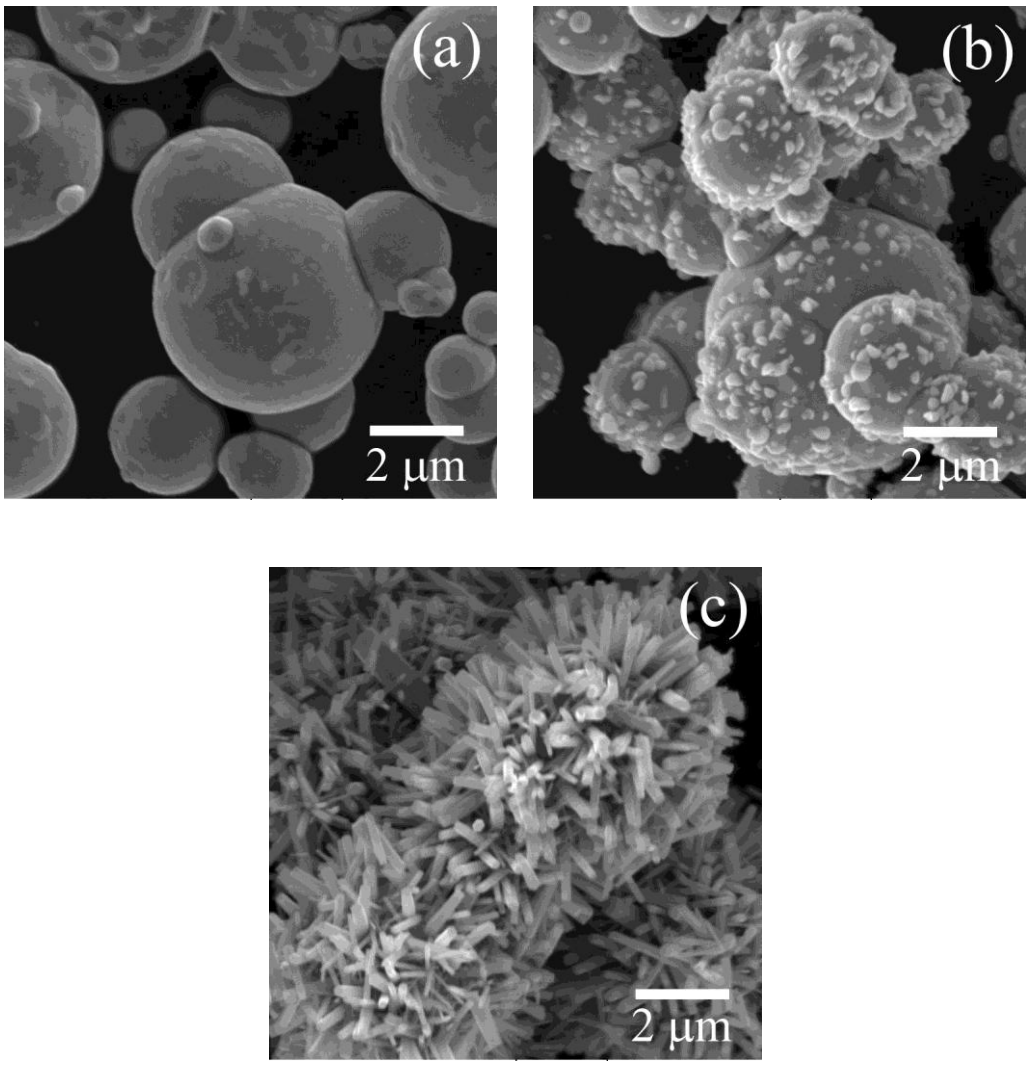

Figure 1. SEM images of (a) bare CI particles, (b) CI/ZnO seeded particles, (c) CI/ZnO rod-like particles.

3.2 Magnetic properties

The magnetic properties of the synthesized particles were measured due to predict the ability of them to respond on the magnetic field application. All samples exhibit soft magnetic behaviour with negligible remanence and coercivity. The highest magnetization saturation was observed for bare CI particles around 183 emu g^{-1}. After the coating of the CI particles with small ZnO ones, magnetization saturation decrease to the 160 emu g^{-1}. In the second step after the ZnO rod-like structures were synthesized on the surface of CI the magnetization saturation decrease to 127 emu g^{-1}, firstly due to the environmental presence during the synthesis and also due to substantial coating of CI with ZnO rod-like structures.

3.3 Magnetorheology of particle silicone oil suspensions.

As can be clearly visible from the viscoelastic investigation of the prepared suspensions, in the absence of the external magnetic field (Fig. 2a), particles are randomly dispersed in the system,

because viscous modulus exhibit higher values than that of elastic one. However, after the application of the external magnetic field particle are magnetized and oriented in the streamlines of the external field and form internal structures. Nevertheless, such structures are not strong enough, because with increasing oscillation material start to be more liquid-like (Fig. 2b). With further increasing the magnetic field strength (Fig. 2c and Fig. 2d) magnetostatic forces dominates over hydrodynamic ones and elastic modulus overcame the viscous one in the whole measured frequency range confirming appropriate stiffness of created internal structures.

Furthermore, in order to elucidate the influence of the particle wt. % fraction on the viscoelastic properties of prepared system, the elastic modulus obtained at angular frequency 1 rad s^{-1}, was plotted against magnetic flux density. Here can be clearly seen that with increasing particle fraction also increases the stiffness of the created internal structures and is highest for 60 wt. % of CI/ZnO rod-like particles in the suspension. Moreover, such values of the dynamic behaviour of this system can be very promising for their potential applications.

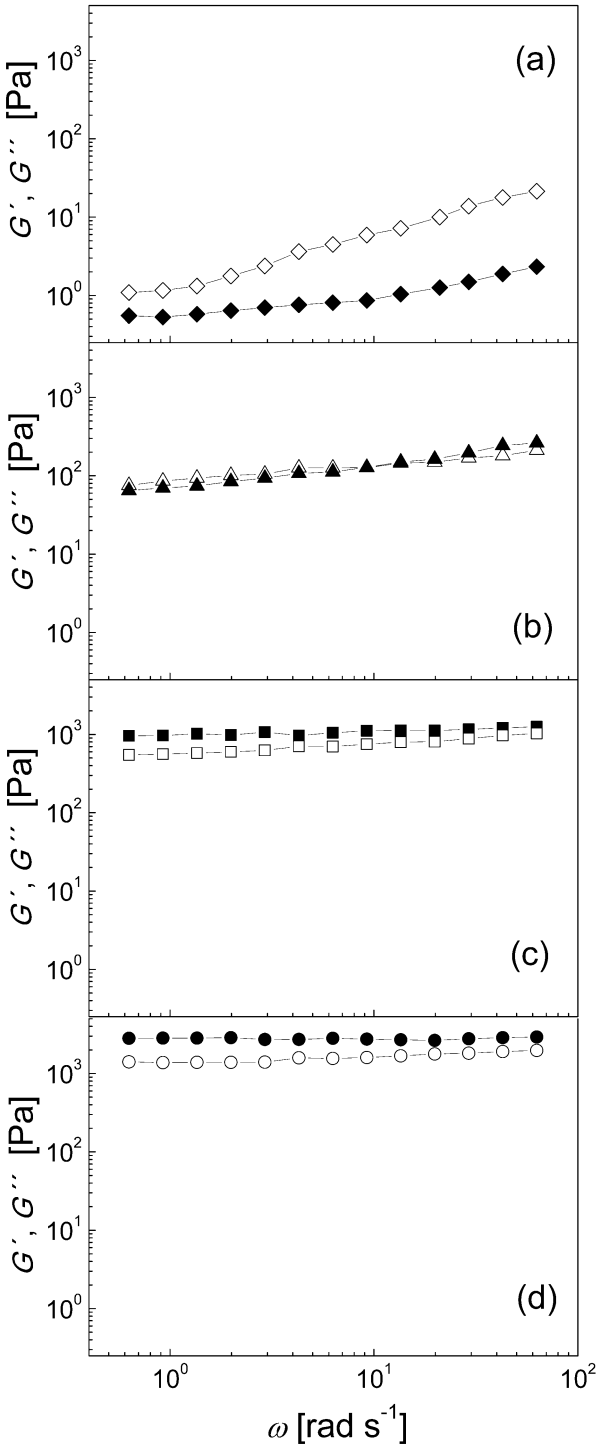

Figure 2. Dependence of elastic moduli , G', (solid symbols) and loss moduli, G'', (open symbols) on the angular frequency, ω, for 20 wt.% of CI/ZnO rod-like particles silicone oil suspensions under various magnetic flux densities (mT): (a) 0, (b) 44, (c) 126, (d) 213.

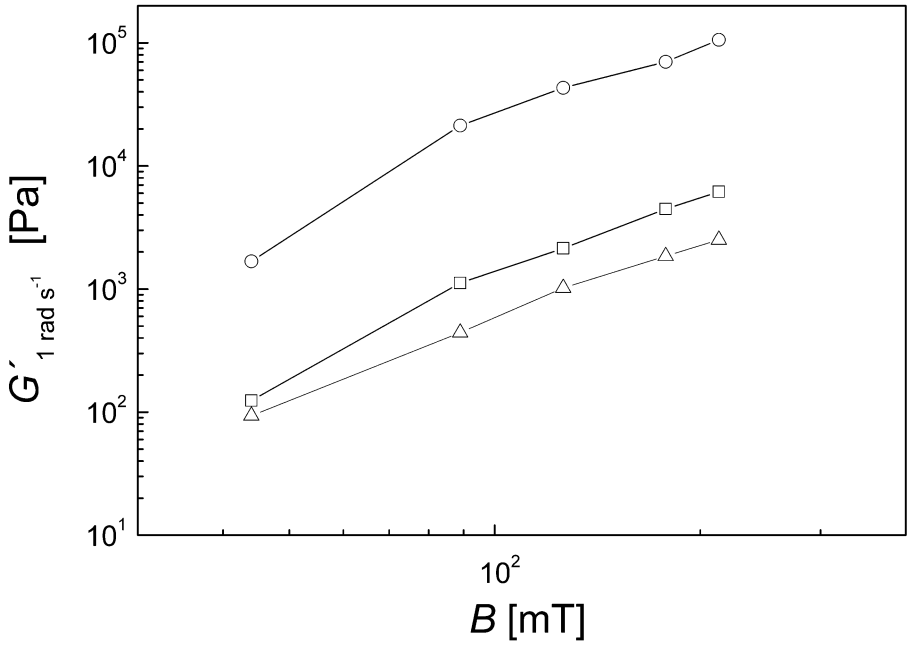

Figure 2. Dependence of the elastic modulus G´, at $\omega = 1$ rad s^{-1}, on the magnetic flux density for silicon oil suspensions with various concentrations of CI/ZnO rod-like particles (wt. %): (△) 20, (□) 40 and (○) 60.

4. Conclusion

In the present study, the simple preparation of the CI/ZnO rod-like particles was introduced. The coating of CI particles was realized via solvothermal synthesis. Magnetic properties of prepared particles are lower in comparison with the bare ones due to coating of CI particles with inorganic ZnO layer. Viscoelastic investigation elucidated the suitable dynamic behaviour of the presented system. Moreover, with increasing particle wt. % fraction the MR performance of such system considerably enhanced and thus can be utilized in their potential applications.

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References

[1] de Vicente J, Klingenberg D J and Hidalgo-Alvarez R 2011 *Soft Matter* **7** 3701
[2] Bica I 2006 *J. Ind. Eng. Chem.* **12** 501
[3] Bossis G, Lacis S, Meunier A and Volkova O 2002 *J. Magn. Magn. Mater.* **252** 224
[4] Park B J, Fang, F F and Choi H J 2010 *Soft Matter* **6** 5246
[5] Wang D H and Liao W H 2011 *Smart Mater. Struct.* **20** 023001
[6] Sedlacik M, Pavlinek V, Lehocky M, Mracek A, Grulich O, Svrcinova P, Filip P and Vesel A 2011 *Colloid Surf. A-Physicochem. Eng. Asp.* **387** 99
[7] Mrlik M, Sedlacik M, Pavlinek V, Bazant P, Saha P, Peer P and Filip P 2013 *J. Appl. Polym. Sci.* **128** 2977

[8] Mrlik M, Ilcikova M, Pavlinek V, Mosnacek J, Peer P and Filip P 2013 *J. Colloid Interface Sci.* **396** 146
[9] Sedlacik M, Pavlinek V, Saha P, Svrcinova P and Filip P 2012 *Mod. Phys. Lett. B* **26** 6.
[10] Sedlacik M, Moucka R, Kozakova Z, Kazantseva NE, Pavlinek V, Kuritka I, Kaman O and Peer P 2013 *J. Magn. Magn. Mater.* **326** 7
[11] Lopez-Lopez M T, de Vicente J, Gonzalez-Caballero F and Duran J D G 2005 *Colloid Surf. A-Physicochem. Eng. Asp.* **264** 75
[12] Sedlacik M, Pavlinek V, Saha P, Svrcinova P, Filip P and Stejskal J 2010 *Smart Mater. Struct.* **19** 115008
[13] Fang F F, Choi H J and Jhon M S 2009 *Colloid Surf. A-Physicochem. Eng. Asp.* **351** 46
[14] Wereley N M, Chaudhuri A, Yoo J H, John S, Kotha S, Suggs A, Radhakrishnan R, Loven B J and Sudarshan T S 2006 *J. Intell. Mater. Syst. Struct.* **17** 393
[15] Sedlacik M, Pavlinek V, Vyroubal R, Peer P ,Filip P 2013 *Smart Mater. Struct.* **22** 035011
[16] Fang F F, Choi H J and Seo Y 2010 *ACS Appl. Mater. Interfaces* **2** 54
[17] Fang F F, Choi H J and Choi W S 2010 *Colloid Polym. Sci.* **288** 359
[18] Machovsky M, Mrlik M, Kuritka I, Pavlinek V and Babayan V 2014 *RSC Adv.* DOI:10.1039/C3RA44982C.