

Synthesis and Magnetorheological Characteristics of Ribbon-Like, Polypyrrole-Coated Carbonyl Iron Suspensions under Oscillatory Shear

Miroslav Mrlik,^{1,2} Michal Sedlacik,^{1,2} Vladimir Pavlinek,^{1,2} Pavel Bazant,^{1,2}
Petr Saha,^{1,2} Petra Peer,³ Petr Filip³

¹Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic

²Polymer Centre, Faculty of Technology, Tomas Bata University in Zlin, nam. TGM 275, 762 72 Zlin, Czech Republic

³Institute of Hydrodynamics, Academy of Sciences of the Czech Republic, 166 12 Prague 6, Czech Republic

Correspondence to: M. Sedlacik (E-mail: msedlacik@ft.utb.cz)

ABSTRACT: One of the crucial problems of classical magnetorheological (MR) fluids is their high rate of sedimentation. This disadvantage may be substantially eliminated using core-shell particles. The aim of this study is to prepare spherical carbonyl iron (CI) particles coated with conducting polymer polypyrrole (PPy) with ribbon-like morphology. Scanning electron microscopy proved the formation of the ribbon-like layer onto CI particles while Fourier transform infrared spectroscopy confirmed the chemical structure of PPy. The magnetic properties observed via vibrating sample magnetometer showed decreased magnetization saturation of core-shell-structured particles due to the existence of non-magnetic surface layer. MR measurements performed under oscillatory shear flow as a function of the applied magnetic flux density, temperature, and particle concentration showed that core-shell particle-based MR suspension exhibits sufficient MR performance for practical applications. Moreover, the suspension stability is promoted significantly when core-shell particles are used as a dispersed phase. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: carbonyl iron; core-shell; magnetorheological fluid; polypyrrole; viscoelasticity; ribbon-like particles

Received 29 May 2012; accepted 16 August 2012; published online

DOI: 10.1002/app.38473

INTRODUCTION

Magnetorheological (MR) fluids are multicomponent systems consisting basically of ferromagnetic particles usually within the size range of 100 nm–10 μ m in diameter with high-magnetic permeability and low levels of magnetic coercivity dispersed in a non-magnetizable medium such as mineral oils or hydrocarbons. A survey of systems studied in the past can be found in reviews.^{1,2} When a certain external static magnetic field is imposed, magnetic dipole and multipole moments are induced on each particle because of the multidomain particle's structure. The anisotropic magnetic forces between pairs of magnetized particles promote the structuration into chain-like or columnar particulate structures aligned with the direction of the magnetic field applied. Such internal structure development causes the liquid to solid-like state transition in milliseconds, which is accompanied with the increase in viscosity within the MR fluids by several orders of magnitude and, hence, is able to support shear stresses resulting in large field-dependent viscoelastic moduli and a yield stress generation.^{3,4} The stiffness of MR structures may be further controlled via the magnetic field

intensity. The chain-like structures are destroyed due to shear forces at high deformations, and viscosity of suspension decreases to a value observed in the absence of magnetic field. Moreover, the system returns to initially Newtonian-like fluid when the external magnetic field is switched off. Described field-responsive physical phenomenon ranks MR fluids among smart materials. Comparable behavior can also be observed in electrorheological (ER) fluids, where external stimulus is external electric field.^{5,6} However, ER fluids do not exhibit appropriate values of the yield stress as well as viscoelastic moduli. Hence, the MR fluids are more commercialized systems providing applicability as various active damping systems, torque transducers, brakes and valve devices, shock absorbers, and elastomeric mounts.^{7–11}

However, the magnetic particles tend to settle rapidly due to their high density compared to that of the suspending medium. The particle's sedimentation consequently affects the efficiency of MR fluids as well as their redispersion. A series of methods have been adopted in the past to improve the low long-term stability of MR fluids, for example, the addition of various

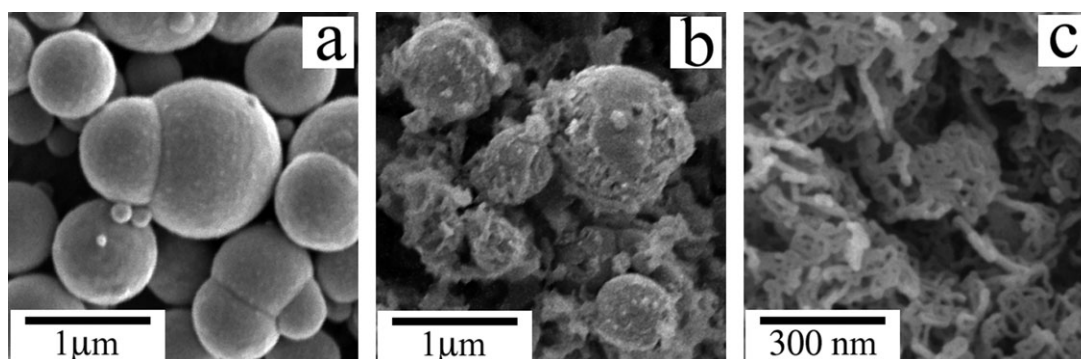


Figure 1. SEM images of (a) bare CI particles, (b) CI/PPy ribbon-like particles, and (c) zoomed surface of coated CI particle.

additives (surfactants, thixotropic agents, or fillers), the usage of viscoplastic or stabilized suspending media, or the use of bidispersed or bimorphic MR fluids.^{11–13} Recently, core-shell-structured particles with a magnetic agent as a core and polymeric layer as a shell have attracted much attention, because such particles exhibit decreased density compared to bare magnetic ones, which results in improved long-term stability.^{14,15} Simultaneously, the surface layer may also promote the MR effect via better mutual compatibility between particles and the suspending medium, because bare metal particles used as a dispersed phase have high-surface energy while various oils used as a suspending medium have low-surface tension.¹⁶

In the present study, core-shell structured particles with a carbonyl iron (CI) magnetic core and a ribbon-like polypyrrole (PPy) conducting shell were prepared by incorporating *in situ* polymerization of PPy onto CI particles.¹⁷ Viscoelastic properties as important characteristics reflecting the change of the microstructure within the MR fluid as well as the long-term stability of the prepared system were evaluated.

EXPERIMENTAL

Materials

CI particles (HS grade) greater than 97% in purity are a product of the BASF Company (Germany). Before use, pyrrole (Py, 98%, Aldrich Chemicals, USA) was twice distilled under reduced pressure. The oxidizing agent ammonium persulfate [APS, (NH₄)₂S₂O₈, 98%, Aldrich Chemicals] and surfactant cetyltrimethylammonium bromide (CTAB, Lach-Ner, Czech Republic) were used as received.

Coating of CI Particles with PPy-Ribbons

First, CI particles were treated with 0.5 M HCl following the instructions,¹⁸ creating hydroxyl groups on the surface of the particles. The modified particles were then sonicated with the surfactant CTAB water solution for 1 h. Then the dispersion of CI particles was transferred to a three-necked flask cooled to 0–5°C, and monomer Py was added under vigorous stirring. After 20 min, the oxidizing agent APS was added in drops. The reaction was carried out for an additional 18 h.¹⁷

Characterization of Prepared Particles

The morphologies of bare CI microparticles and PPy ribbon-like coated ones were studied using a scanning electron microscopy (SEM, VEGA II LMU, Tescan, Czech Republic), with an

operating voltage of 5 kV. FTIR spectra of the prepared samples were obtained using a Nicolet magna-550 spectrometer, USA, in the range of 4000–700 cm⁻¹. Furthermore, the magnetic properties of the particles were examined using a vibration sample magnetometer (EG&G PARC 704, Lake Shore, USA) at room temperature.

Suspension Preparation and Rheological Measurements

Bare and coated particles were suspended in silicone oil (Dow Corning, Fluid 200, USA, $\eta \approx 100$ mPa·s) with 20, 30, and 40 wt % particle concentrations. The suspensions were mechanically stirred before each measurement. The viscoelastic properties under an external magnetic field in the range 0–300 mT were investigated using a rotational rheometer Physica MCR501 (Anton Paar GmbH, Austria) with a Physica MRD 180/1 T magnetocell. The true magnetic flux density was measured using a Hall probe, and the temperature was checked with the help of an inserted thermocouple.¹⁹ Rheological measurements at temperatures 25, 45, and 65°C were performed using a Viscotherm VT2 circulator with a temperature stability of $\pm 0.02^\circ\text{C}$.

RESULTS AND DISCUSSION

Morphology and Magnetic Properties

SEM images of the bare CI (a) and coated CI/PPy ribbon-like particles (b) are depicted in Figure 1. As can be seen, the coating of the CI particles with PPy ribbons does not significantly increase the particle size. The diameter for both bare and coated particles is around 1 μm or less. Moreover, under higher magnification, the ribbon-like structures (c) are clearly visible on the surface of CI particles.

The influence of coating on the magnetic properties of CI is presented in Figure 2. The magnetization curves of bare CI and the core-shell composite show negligible remanence. The magnetization saturation of coated CI/PPy ribbon-like particles is lowered due to the coating of CI with the non-magnetic polymer PPy. However, this slight reduction has no impact on real applications as the values of magnetization of such particles are still sufficient.

Structure Characterization

Figure 3 shows the FTIR spectra of the bare CI, PPy ribbon-like particles, and coated CI/PPy. As expected, there are no visible characteristic bands for the bare CI due to their composition >97% of iron particles. This contrasts to PPy where

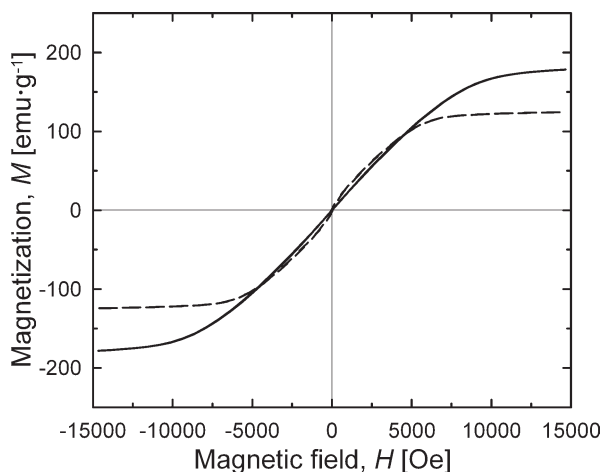


Figure 2. Magnetization curves of bare CI (solid line) and CI/PPy ribbon-like particles (dashed line).

characteristic bands are as N—H at 3300 cm^{-1} , 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.²⁰ Finally, the successful coating of the bare CI with PPy ribbons is observed in Figure 3(c). The broad band at 3170 cm^{-1} is related to the N—H stretching mode from PPy. However, the bands become weaker due to bare CI in the CI/PPy ribbon-like system. Furthermore, analogically to the reference,²¹ some of the vibrations are shifted to lower wave numbers, probably due to the polymerization of the PPy in the presence of the CI particles.

Rheological Properties

Generally, MR suspensions are represented by two-phase fluids enabling the transition from a liquid to solid-like state under application of an external magnetic field. This behavior is usually examined through measurement in the steady shear mode.^{22–25} However, in real applications, the MR suspensions are mostly stressed dynamically. This indicates that oscillatory

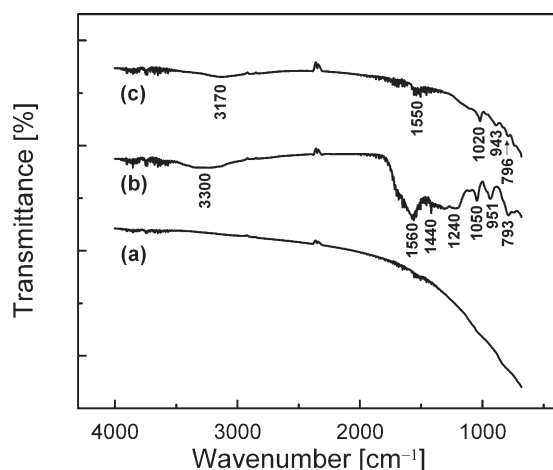


Figure 3. FTIR spectra of (a) bare CI, (b) PPy ribbon-like particles, and (c) coated CI particles.

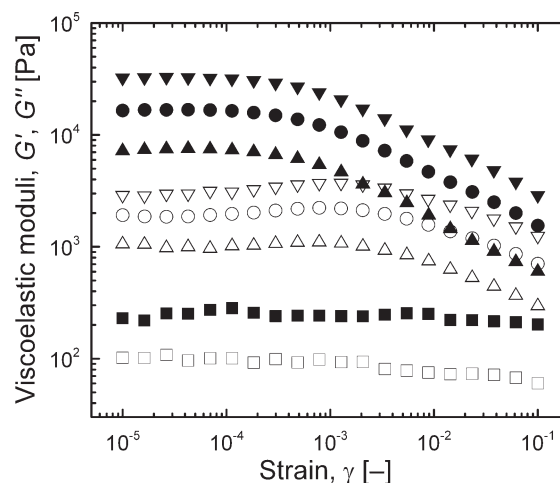


Figure 4. Dependence of elastic modulus, G' (solid symbols), and loss modulus, G'' (open symbols), on the strain, γ , for 40 wt % suspension of CI/PPy ribbon-like particles in silicone oil, at temperature 25°C , under various magnetic flux densities (mT): (\square, \blacksquare) 0, ($\triangle, \blacktriangle$) 84, (\circ, \bullet) 174, ($\nabla, \blacktriangledown$) 263.

shear measurement is an adequate method for performance evaluation.

Liquid to solid-like state transition is interlaced with the development of the internal structures when the magnetic field is applied. This behavior is well documented by the courses of viscoelastic moduli (storage modulus G' and loss modulus G'') and complex viscosity η^* as representative quantities of the dynamic rheological measurement.

An increase of both moduli with increasing magnetic flux density (Figure 4) implies the formation of internal structures between parallel plates of the rotational rheometer. The plateau for G' terminates at $\gamma \sim 3 \times 10^{-4}$, and as for higher values of

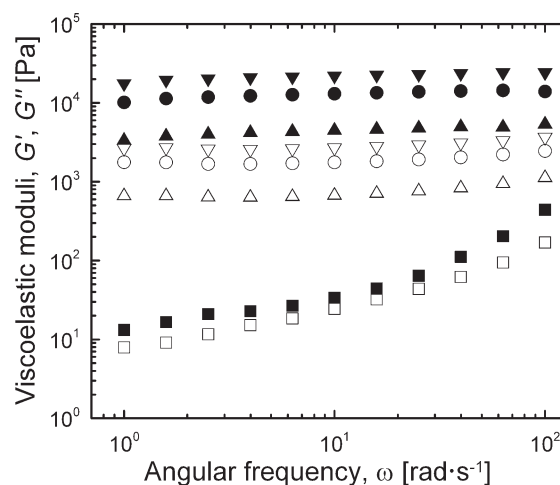


Figure 5. Dependence of elastic modulus, G' (solid symbols), and loss modulus, G'' (open symbols), on the angular frequency, ω , for 40 wt % suspensions of CI/PPy ribbon-like particles in silicone oil, at temperature 25°C , under various magnetic flux densities (mT): (\square, \blacksquare) 0, ($\triangle, \blacktriangle$) 84, (\circ, \bullet) 174, ($\nabla, \blacktriangledown$) 263.

strain, the hydrodynamic forces dominate the magnetic ones. This reflects an irreversible destruction of the internal structures. The plateau indicates the linear viscoelastic region (LVR) in which both moduli are independent of the strain. Further investigation of viscoelastic properties was carried out in the range of strain characterizing the LVR.

The angular frequency dependence of the viscoelastic moduli (Figure 5) in the absence of the external magnetic field shows elastic behavior, when G' is slightly higher than G'' , probably due to higher suspension concentration. In the presence of the magnetic field, both moduli dramatically increase, but G' dominates G'' in the whole range of the measured angular frequency, indicating relatively stiff three-dimensional structures created by the CI particles coated with PPy ribbons.²⁶

Applications of the MR suspension in the industry are usually in coherence with their use at elevated temperatures. Therefore, the investigation of the complex viscosity in the absence (0 mT) and presence (263 mT) of the magnetic field at different temperatures was performed (see Figure 6). This figure documents a decrease in viscosity of the suspension with increasing temperature both in the absence and presence of an external magnetic field. The viscosity of CI/PPy ribbon-like particle suspensions,

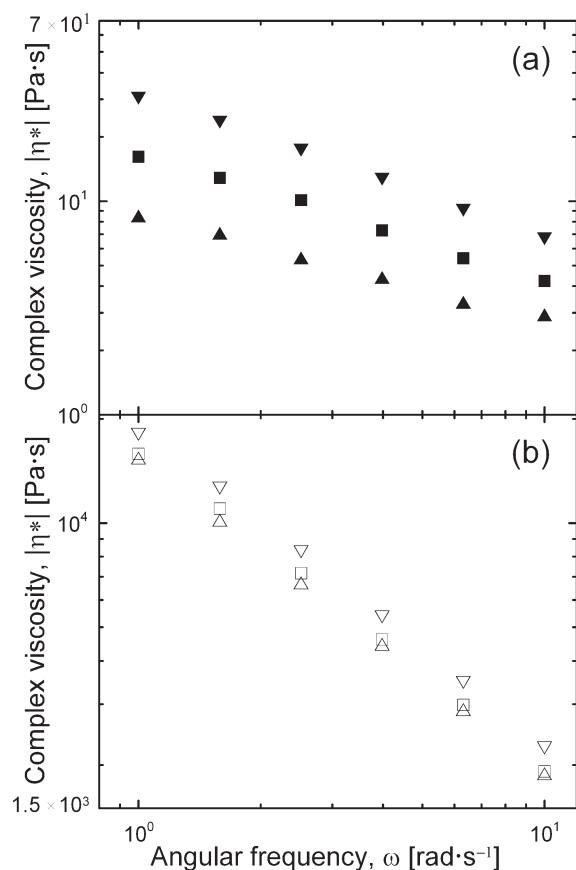


Figure 6. Dependence of complex viscosity, η^* , on angular frequency, ω , for 40 wt % suspension of CI/PPy ribbon-like particles in silicone oil in the absence (solid symbols) and in the presence (open symbols) of the magnetic flux density (263 mT) at various temperatures: ($\nabla, \blacktriangledown$) 25, (\square, \blacksquare) 45, ($\triangle, \blacktriangle$) 65°C.

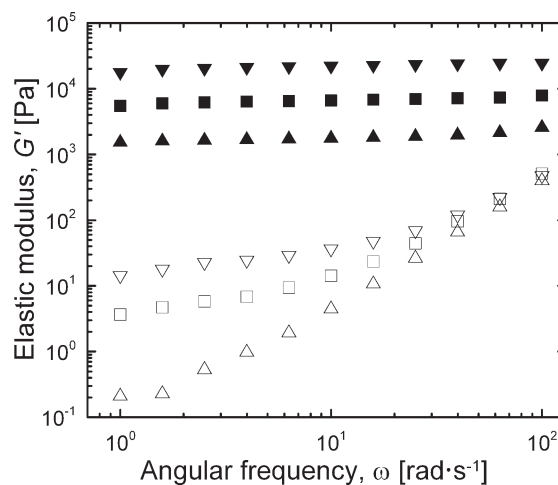


Figure 7. Dependence of elastic modulus, G' , on angular frequency, ω , in the absence (open symbols) and in the presence (solid symbols) of the magnetic flux density (263 mT) at temperature 25°C, for various concentrations (wt %): ($\triangle, \blacktriangle$) 20, (\square, \blacksquare) 30, ($\nabla, \blacktriangledown$) 40 of CI/PPy ribbon-like particles in silicone oil.

when the magnetic flux density attains 263 mT, rises over four orders of magnitude in comparison with 0 mT due to the formation of internal chain structures exhibiting similar viscosity values regardless of temperature. Finally, more pronounced shear-thinning behavior was observed due to increasing angular frequency, which contributes to the partial deformation of the structures created in the presence of the external magnetic field.

To examine the influence of particle concentration on the MR behavior under an external magnetic field, the G' was plotted against the angular frequency ω (see Figure 7). In the absence of the magnetic field, the suspension consisting of 20 wt % of the coated CI particles attains the lowest values of the elastic modulus. With increasing particle concentration, the G' increases, and a suspension containing 40 wt % of coated particles reaches the highest values. However, G' above an angular

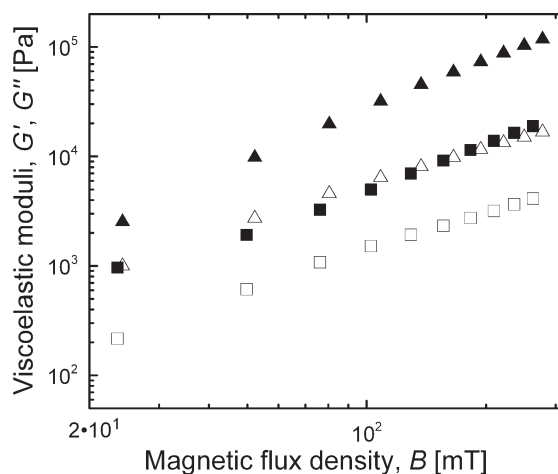


Figure 8. Dependence of elastic modulus, G' (solid symbols), and loss modulus G'' (open symbols), on the magnetic flux density, B , for 40 wt % suspension at temperature 25°C, where (\square, \blacksquare) are CI/PPy ribbons, ($\triangle, \blacktriangle$) are bare CI.

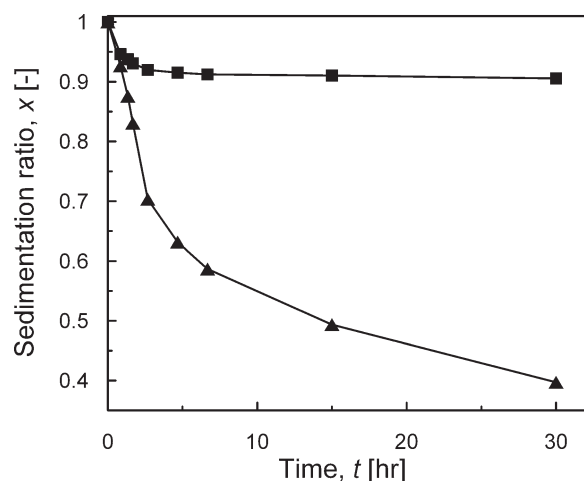


Figure 9. Sedimentation ratio of 40 wt % particles in silicone oil at temperature 25°C, for bare CI (▲) and CI/PPy ribbon-like particles (■).

frequency of about $30 \text{ rad}\cdot\text{s}^{-1}$ is nearly identical for all samples. High-frequency application contributes to an increase in the elastic behavior of the suspensions. Increase the frequency and shorten the time, and the response to this stimulus results in an enhanced elasticity of the suspensions in comparison with that of a low-frequency application indicating mainly viscous behavior. On the other hand, in the presence of the magnetic field, G' increases with increasing particle concentration and becomes independent of ω in the whole frequency range. This confirms the inherence of strong chain-like structures developed in the suspension.

The dependence of the viscoelastic moduli on the magnetic flux density (Figure 8) proves the good MR behavior of the prepared material. The viscoelastic moduli of both materials, CI and coated CI with PPy ribbons, increase with increasing magnetic flux density. The partially lower values of the viscoelastic moduli for the suspensions with CI/PPy ribbon-like particles in comparison with bare CI are more than balanced out by their much better sedimentation stability as shown below.

Sedimentation Stability

Sedimentation is a key factor influencing the use of MR suspensions in many applications. The sedimentation test measured by naked-eye method reveals that the stability of bare CI particle suspension is insufficient (Figure 9). On the other hand, with the PPy ribbon-like structures synthesized on the surface of CI, the sedimentation stability increases, and the particles showed stable behavior during the 30-h test. The polymer coating on the CI particles with PPy ribbons partially decreases the particle density and probably increases the particle-silicone oil interactions²⁶ that contribute to the enhancement of the sedimentation stability.

CONCLUSIONS

A simple way to prepare coated CI particles with PPy ribbons was presented. CI/PPy ribbon-like particles showed lower magnetization saturation in comparison with bare CI particles due to the coating of the surface with a nonmagnetic polymer. Furthermore, the MR efficiency of the suspension of coated CI rapidly increases

with increasing temperature. This efficiency is lower than that of suspensions of bare CI particles; nevertheless, the sedimentation stability of the suspension with coated particles is enhanced and stable for tens of hours, whereas the suspension consisting of bare CI rapidly decreases within the same time period.

ACKNOWLEDGMENTS

This article was written with the support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of the Czech Republic, within the framework of the project of the Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111). The authors further thank the internal grant of TBU in Zlin No. IGA/1/FT/11/D funded from specific university research resources.

REFERENCES

1. de Vicente, J.; Klingenberg, D. J.; Hidalgo-Alvarez, R. *Soft Matter* **2011**, *7*, 3701.
2. Park, B. J.; Fang, F. F.; Choi, H. J. *Soft Matter* **2010**, *6*, 5246.
3. Bica, I. *J. Ind. Eng. Chem.* **2006**, *12*, 501.
4. Bossis, G.; Lacis, S.; Meunier, A.; Volkova, O. *J. Magn. Mater.* **2002**, *252*, 224.
5. Choi, H. J.; Jhon, M. S. *Soft Matter* **2009**, *5*, 1562.
6. Sedlacik, M.; Mrlik, M.; Pavlinek, V.; Saha, P.; Quadrat, O. *Colloid Polym. Sci.* **2011**, *290*, 41.
7. Wang, D. H.; Liao, W. H. *Smart Mater. Struct.* **2011**, *20*, 023001.
8. Carlson, J. D. *J. Intell. Mater. Syst. Struct.* **2002**, *13*, 431.
9. Kuzhir, P.; Bossis, G.; Bashtovoi, V. *Int. J. Mod. Phys. B* **2005**, *19*.
10. Park, J. H.; Chin, B. D.; Park, O. O. *J. Colloid Interface Sci.* **2001**, *240*, 349.
11. Wereley, N. M.; Chaudhuri, A.; Yoo, J. H.; John, S.; Kotha, S.; Suggs, A.; Radhakrishnan, R.; Love, B. J.; Sudarshan, T. S. *J. Intell. Mater. Syst. Struct.* **2006**, *17*, 393.
12. Fang, F. F.; Choi, H. J.; Jhon, M. S. *Colloid Surf. A-Physicochem. Eng. Asp.* **2009**, *351*, 46.
13. Lopez-Lopez, M. T.; de Vicente, J.; Gonzalez-Caballero, F.; Duran, J. D. G. *Colloid Surf. A-Physicochem. Eng. Asp.* **2005**, *264*, 75.
14. Fang, F. F.; Choi, H. J.; Choi, W. S. *Colloid Polym. Sci.* **2010**, *288*, 359.
15. Fang, F. F.; Choi, H. J.; Seo, Y. *ACS Appl. Mater. Interfaces* **2010**, *2*, 54.
16. Sedlacik, M.; Pavlinek, V.; Saha, P.; Svrčinová, P.; Filip, P.; Stejskal, J. *Smart Mater. Struct.* **2010**, *19*, 115008.
17. Zhang, X. T.; Zhang, J.; Song, W. H.; Liu, Z. F. *J. Phys. Chem. B* **2006**, *110*, 1158.
18. Belyavskii, S. G.; Mingalyov, P. G.; Giulieri, F.; Combarrieau, R.; Lisichkin, G. V. *Protect. Met.* **2006**, *42*, 244.
19. Laun, H. M.; Gabriel, C. *Rheol. Acta* **2007**, *46*.
20. Cheng, Q. L.; He, Y.; Pavlinek, V.; Li, C. Z.; Saha, P. *Synth. Met.* **2008**, *158*, 953.

21. Somani, P. R.; Marimuthu, R.; Mulik, U. P.; Sainkar, S. R.; Amalnerkar, D. P. *Synth. Met.* **1999**, *106*, 45.
22. Kim, I. G.; Song, K. H.; Park, B. O.; Choi, B. I.; Choi, H. *J. Colloid Polym. Sci.* **2011**, *289*, 79.
23. Liu, Y. D.; Fang, F. F.; Choi, H. *J. Colloid Polym. Sci.* **2011**, *289*, 1295.
24. Lopez-Lopez, M. T.; Kuzhir, P.; Meunier, A.; Bossis, G. *J. Phys.-Condes. Matter* **2010**, *22*, 324106.
25. Shambharkar, B. H.; Umare, S. S. *J. Appl. Polym. Sci.* **2011**, *122*, 1905.
26. Tsuda, K.; Takeda, Y.; Ogura, H.; Otsubo, Y. *Colloid Surf. A-Physicochem. Eng. Asp.* **2007**, *299*, 262.