Colloid Polym Sci (2005) 283: 1253–1258
DOI 10.1007/s00396-005-1314-5

SHORT COMMUNICATION

S. P. Rwei
H. Y. Lee
S. D. Yoo
L. Y. Wang
J. G. Lin

Magnetorheological characteristics of aqueous suspensions that contain Fe_3O_4 nanoparticles

Received: 2 August 2004
Accepted: 10 December 2004
Published online: 11 May 2005

S. P. Rwei (✉) · H. Y. Lee · S. D. Yoo
Institute of Organic and Polymeric Materials, National Taipei University of Technology, #1, Sec 3, Chung-Hsiao E. Rd, Taipei, Taiwan, Republic of China
E-mail: f10714@ntut.edu.tw

L. Y. Wang · J. G. Lin
Center Condensed Matter Science, National Taiwan University, Taipei, Taiwan, Republic of China

Abstract This investigation examines the magnetorheological (MR) characteristics of Fe_3O_4 aqueous suspensions. Magnetite particles (Fe_3O_4) were synthesized using a colloidal process and their sizes were determined to be normally distributed with an average of 10 nm by TEM. Experimental results reveal that the MR effect increases with the magnetic field and suspension concentration. The yield stress increases by up to two orders of magnitude when the sample is subjected to a magnetic field of 146 Oe/mm. In comparison with other published results, concerning a concentration of approximately 10–15% v/v, this study demonstrates that the same increase can be obtained with a concentration of nano-scale particles as low as 0.04% by volume. The viscosity was increased by an order of magnitude while the shear rate remained low; however, the increase decayed rapidly as the shear rate was raised. Finally, the MR effect caused by DC outperformed that caused by AC at the same current.

Keywords Magnetorheological (MR) · Magnetite particles (Fe_3O_4) · Nano-scale particles · Yield stress · Fe_3O_4 suspensions

Introduction

Magnetorheological (MR) suspension is rapidly transformed from a Newtonian fluid-like structure to a solid-like structure with viscoelastic-plastic yielding, when subjected in an applied magnetic field. Rabinow [1] first identified these in 1948, soon after Winslow [2] discovered electrorheological (ER) fluids. Since then, numerous different metal or ceramic powders with magnetic characteristics have been dispersed in nonmagnetic carrier liquids (such as oil or aqueous liquids) to prepare MR fluids. The most frequently used MR fluid is made of particles derived by decomposing iron penta-carbonyl ($Fe(CO)_5$) in silicone oil. Notably, a serious problem associated with the dispersed MR-type is the lack of effective suspensions [3]. The most common MR fluid consists of particles on a micron-scale, normally 5–200 μm in size. The micron-scale particles are too weak to be stabilized by the Brownian motion, and using which, the reproducibility of MR characterization is difficult to achieve. Accordingly, the sedimentation of particles remains a critical problem to solve in relation to most designed MR fluids—even those that involve added surfactants.

Magnetorheological fluids can develop an apparent yield stress that depends on the compositions and the flux density when an external magnetic field is applied. Their mechanical characteristics can therefore be classified into two regions—pre-yield and post-yield—according to whether the applied stress is below or above the yield stress. MR fluids within the pre-yield region have viscoelastic characteristics and have been investigated in relation to a wide range of applications, including electromagnetic clutches, valves, controlled vibration dampers, sensors and electromechanical transducers [4–6].

Magnetorheological fluids in the post-yield region have another application in medical treatment. The idea of a drug delivery system in which magneto particles carry the drug through blood vessels to the target, was recently developed. The requirements of this application include a suspension with a low volume fraction of magnetic powder (0.1% v/v for medical application versus 10–30% v/v in engineering application), which can be stabilized in an aqueous system. Secondly, the particle size must be reduced to the nano-scale to prevent sedimentation. Nanoparticles can carry more medicine with a large surface area; they can be easily stabilized in a liquid with the aid of Brownian motion and the repulsive effect from the surfactant.

This work investigated the MR behavior of a suspension that contained Fe_3O_4 nanoparticles dispersed in an aqueous solution. A special synthetic approach was followed to produce nanoscale particles in a manner that eliminates the sedimentation problem.

Experimental

Synthesizing MR particles

Fe_3O_4 particles were prepared by treating 2.0 equiv. of $FeCl_2$ $4H_2O$ with 3.0 equiv. of $FeCl_3$ $6H_2O$ in 50 ml of deionized water, with stirring at a rate of 300 rpm at room temperature, before adding 100 ml of ammonium hydroxide. The particles thus generated were then washed in 5% NH_4OH solution, before an aqueous solution of poly(acrylic acid) (PAA, Mw 2000) was applied. Importantly, PAA acts as a dispersing agent that stabilizes the Fe_3O_4 suspension. The sizes of the particles were examined by transmission electron microscopy (Hitachi H-7100). Experimental results reveal that the mean particle size was approximately 10 nm (Fig.1). All chemicals used were supplied by ACROS Chemicals and used without further purification. Similar synthetic procedures are provided elsewhere [7].

Magnetorheological measurement

Rheological properties were measured using a Vilastic rheometer (Vilastic Scientific Inc.) [8], with which an oscillatory flow of the desired frequency and amplitude was generated, and instantaneous pressure and flow rate can be detected. Figure 2 demonstrates that MR-cell is made of aluminum in a cylindrical tubular configuration. A custom-designed coil wrapped around the MR cell generated the magnetic field. The coil had 900 turns of copper wire, with a diameter of 1 mm. The magnetic flux ran perpendicular to the longitudinal direction of the cell, and therefore ran through the capillary filled with MR fluids. The rheological behavior of the MR suspensions was investigated under dynamic shear and a static magnetic field.

Results and discussion

Figure 3a illustrates the dependence of shear stress on the frequency of oscillation under typical experimental conditions. At a specific amplitude of strain, normally under 5% to ensure that it was in the linear viscoelastic range, the dependence of stress on frequency can easily be converted to that on the shear rate (Fig. 3b). Figure 3b also shows that the yield stress can be determined by extrapolating the stress curve to the zero shear rate. Figure 4a–c plots the dependence of shear stress on the

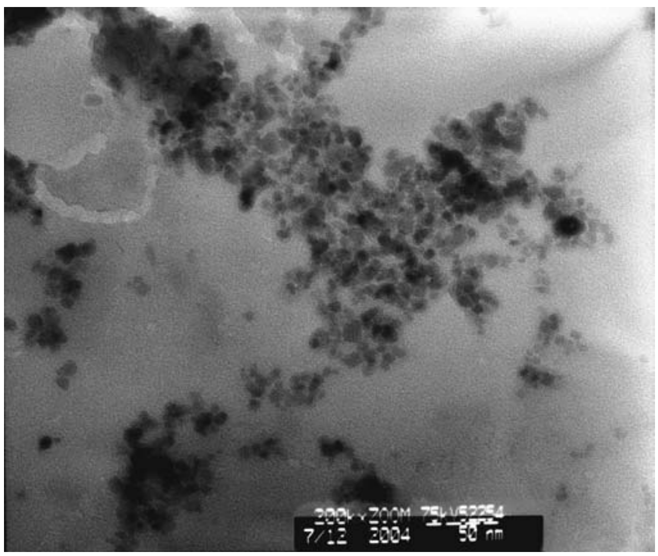

Fig. 1 TEM micrograph of magnetite nanoparticles

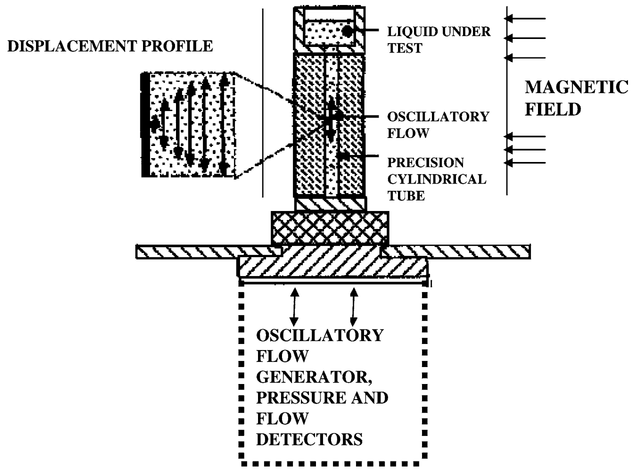

Fig. 2 Schematic of the device for measuring MR properties

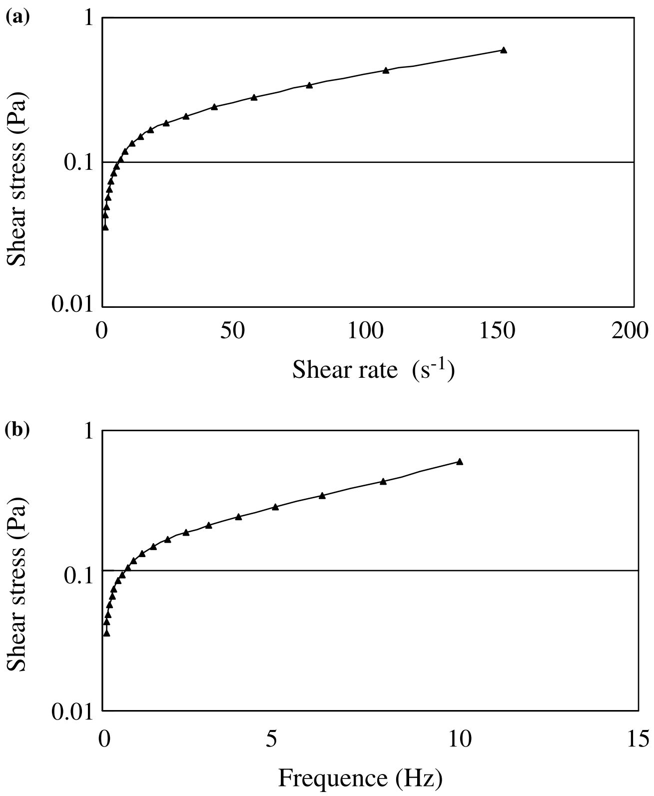

Fig. 3 Typical shear stress dependence on frequency (**a**) and on shear rate (**b**) for 0.3% w/w Fe_3O_4 suspension at a constant field strength of 146 Oe/mm

shear rate under different field strengths and particle concentrations obtained using the approach mentioned above. Applying magnetic fields across the MR suspensions raises their stress by orders of magnitude, at low shear rate (generally of under 10 s^{-1}). Each curve in Fig. 4a–c is traced to determine the yield stress, which is plotted in Fig. 5 against the magnetic field strength at various concentrations of iron particles. This plot reveals that the yield stress increases with the field strength and the concentration of particles. The iron particles form chain-like structures that are embedded in the matrix [9–11]. The origin of these liquid patterns is the attractive dipolar interaction induced by the magnetic field. In an external magnetic field, the particles in an MR suspension acquire dipole moments and aggregate into chains in the direction of the field. The presence of permanent dipole moments leads to the formation of one-dimensional structures, which are stable in applied fields of moderate strength. The yield stress is that required to break the alignment of particles. Restated, MR fluids act as a rigid solid until the stress has exceeded the threshold value. Notably, applying a magnetic field of 146 Oe/mm to a very dilute nano-iron suspension increased the yield stress by two orders of magnitude. In comparison with other published results, concerning a concentration of approximately 10–15% v/v [12], this study demonstrates that the same increase can be obtained with a concentration of nanoparticles as low as 0.3% by weight or 0.04% by volume. This concentration effect with respect to different particle sizes can be further elucidated by comparing the theoretical concentrations of the particle columns formed parallel to the magnetic field lines. For a suspension filled with 10 µm round-shaped particles, the critical concentration to initiate the MR behavior is approximately 10% by volume, which indicates that approximately 2.4×10^{3} columns per milliliter of suspension under a magnetic field of 1-mm thickness can be generated. In contrast, using 10-nm magnetic particles in a concentration of 0.01% v/v under the same field strength, the system can generate 2.4×10^{6} columns per milliliter of suspension. In general, the joint area between two spherical particles in a column is independent of the diameter of the particle. The denser distribution of the nano-particle column parallel to the magnetic field therefore initiates the MR behavior in an earlier stage. In short, the nano-size scale contributes most to dramatically reducing the suspension load, suggesting that, even at a concentration of Fe_3O_4 nanoparticles as low as 0.3% by weight, the MR effect does exist in an aqueous suspension.

Figure 4a–c was converted into Fig. 6a–c by differentiation with respect to the shear rate, to examine the dependence of the viscosity on the shear rate. The viscosity was found to exhibit a shear thinning behavior at a low shear rate; however, such that the fluid became Newtonian as the shear rate exceeded 100 s^{-1}. Figure 7 was obtained by rearranging Fig. 6 to plot the viscosity versus magnetic strength at both low shear rate, 10 s^{-1}, and high shear rate, 100 s^{-1}. An order of magnitude increase was observed when the shear rate was kept low; however, the increase decayed quickly as the shear rate

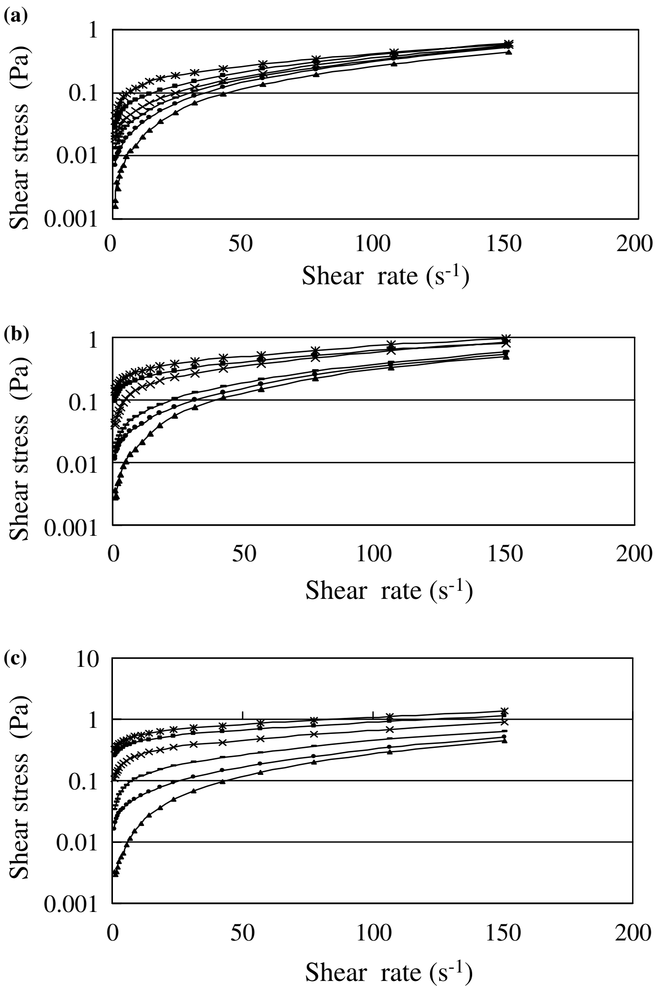

Fig. 4 Shear stress versus shear rate for **a** 0.3%, **b** 0.6%, and **c** 0.9% w/w of Fe_3O_4 suspension at a constant field strength (*filled triangle* 0 Oe/mm, *filled cricle* 35 Oe/mm, *continuous line* 69 Oe/mm, *crosses* 92 Oe/mm, *filled square* 121 Oe/mm, *asterisk*146 Oe/mm)

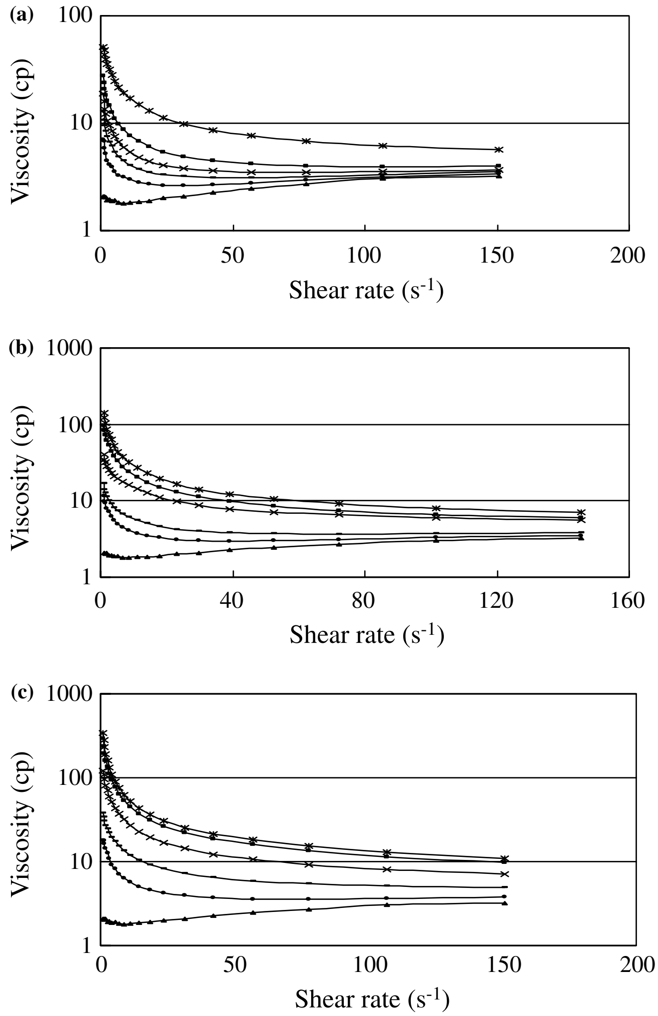

Fig. 6 Viscosity versus shear rate for **a** 0.3%, **b** 0.6%, and **c** 0.9% w/w of Fe_3O_4 suspension at various field strengths (*filled triangle* 0 Oe/mm, *filled cricle* 35 Oe/mm, *continuous line* 69 Oe/mm, *crosses* 92 Oe/mm, *filled square* 121 Oe/mm, *asterisk* 146 Oe/mm)

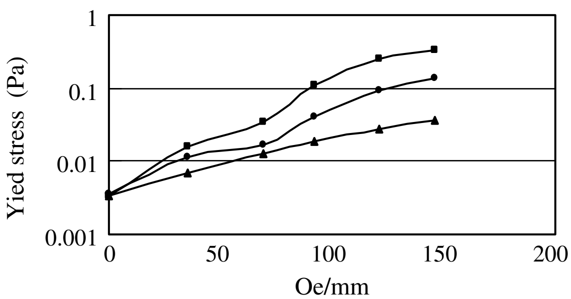

Fig. 5 The dependence of yield stress on the field strength for Fe_3O_4 suspension at various concentrations (*filled triangle* 0.3%, *filled cricle* 0.6%, *filled square* 0.9% w/w)

was increased. This result again further verifies that the microstructure was established at a low shear rate and was disrupted at a high shear rate, as presented above.

Whereas the viscosity data yielded information only on energy losses due to the disruption of the structure, viscoelasticity data provide information on the microstrucutre's capacity to store energy and its energy loss. Structural enhancement and breakdown increase and reduce the storage modulus, respectively. Figure 8 reveals that the storage modulus increases with the magnetic field strength. Interestingly, the storage modulus falls sharply to a constant value as the amplitude of the applied stain is increased, indicating that MR fluids are predominantly elastic at very small displacements. The elasticity is related to the built-up structure as stated previously, and becomes dramatically weaker as the structure is broken. However, a small but steady G′ can be reached at higher amplitude, indicating that a weak structure remains; the steady G′ is proportional to the

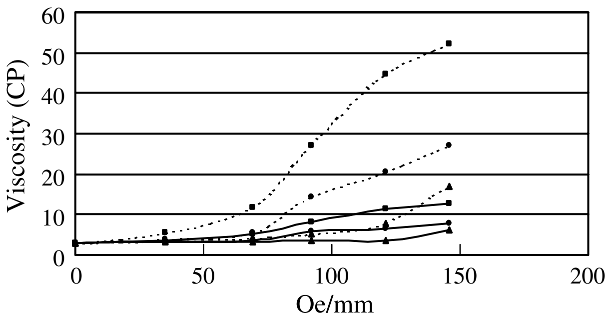

Fig. 7 The dependence of viscosity on the field strength for Fe_3O_4 suspension at various concentrations (*filled triangle* 0.3%, *filled cricle* 0.6%, *filled square* 0.9% w/w) and different shear rates (*dotted* 10 s^{-1}, *solid* 100 s^{-1})

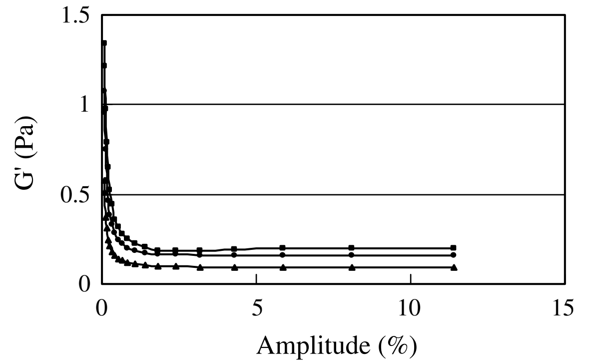

Fig. 8 The storage modulus as a function of strain amplitude under 1 Hz for 0.3% w/w of Fe_3O_4 suspension at various field strengths (*filled triangle* 35 Oe/mm, *filled cricle* 69 Oe/mm, *filled square* 92 Oe/mm)

strength of the applied field. This information will be useful in the future, when the magnetic particles are adopted as smart carriers in medical applications for delivering a cure to a specific location in the body. Two issues are critical to fulfill this adoption. First, how can this particle-structure survive inside the blood vessel at a high shear rate of normally around 1,000 s^{-1}? Second, how can the built-up structure not block the blood transportation? This study demonstrates that both problems associated with the sturdiness of the structure may be solved by carefully changing the strength of the magnetic field.

Experiments were conducted to compare the results of imposing a magnetic field induced by DC power with those of a field induced by 60 Hz AC power. The fluid was 0.6% by weight of iron particles in an aqueous solution. Figure 9 plots the shear stress against shear rate under various magnetic conditions, using DC (0.11 A), AC (0.11 A) and without any current. The magnetic field generated with DC produces higher stress than that produced by AC. DC power is expected to induce stronger dipole interaction to align the particles and so form a sturdy microstructure. In contrast, when AC power is applied, the direction of the magnetic field switches too frequently to stabilize the microstructure.

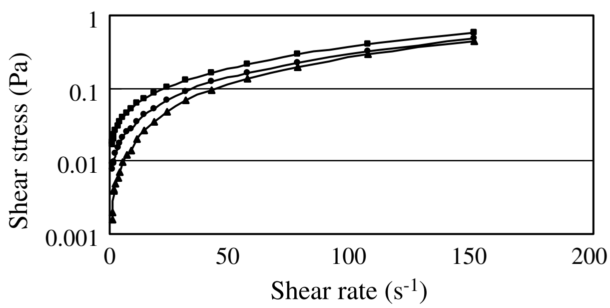

Fig. 9 Comparison of effects of the magnetic fields induced by AC or DC powers for a 0.6% (w/w) Fe_3O_4 aqueous suspension. (*filled triangle* 0 A, *filled cricle* AC 0.11 A, *filled square* DC 0.11 A)

Conclusion

This study investigates the MR characteristics of Fe_3O_4 suspensions. Magnetite particles (Fe_3O_4) were synthesized using a colloidal process and their sizes determined to be normally distributed with an average of 10 nm by TEM. Experimental results reveal that the MR effect increases with the magnetic field and suspension concentration. The yield stress increases in proportion to the magnetic field strength. Moreover, adding less than 1% by weight of Fe_3O_4 particles to the MR suspension can significantly increase the yield stress by up to two orders of magnitude when the sample is subjected to a magnetic field of 146 Oe/mm. The viscosity was increased by an order of magnitude while the shear rate remained low; however, the increase decayed rapidly as the shear rate was raised. Finally, the MR effect caused by DC outperformed that caused by AC at the same current.

Acknowledgements The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC-92-2622-E-027-009-CC3.

References

1. Winslow MW (1947) US Patent 2:417–850
2. Rabinow J (1948) AIEE Trans 67:1308
3. Stangroom JE (1983) Phys Technol 14:290
4. Weiss KD, Carlson JD, Nixon DA (1994) J Intell Mater Syst Struct 5:772
5. Guozhi Y, Guang M., Tong F (1995) Mech Vib 4:232
6. Hartsock DL, Novak RF, Chaundy GJ (1991) J Rheol 35:1305
7. Chu CC, Yeh CF, Wang L, Ho TI, Rwei SP (2003) Synth Metal 135(136):109
8. Thurston GB (1991) J Rheol 35(7):1327
9. Park JH, Chin BD, Park OO (2001) J Colloid Interface Sci 240:349
10. Volkova O, Cutillas S, Carletto P, Bossis G, Cebers A, Meunier A (1999) J Magnetism Magn Mater 201:66
11. Bednarek S (1999) J Magnetism Magn Mater 202:574
12. Li WH, Chen G, Yeo SH (1999) Smart Mater Struct 8:460