



Magnetic and magnetorheological properties of nanofiber suspensions

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composed of magnetic microfibers [6-10]. It has been reported that these new fiber-based MR fluids present an enhanced stability against particle settling and a higher yield stress as compared to conventional (based on spherical particles) MR fluids. In the present work magnetic nanofibers and nanospheres are used for the preparation of MR fluids. The effect of particle shape on both the magnetic and the MR response of MR fluids is investigated. An interesting effect of nanofiber orientation on the magnetic properties of the suspensions is found. Furthermore, an enhancement of the MR properties takes place when nanofibers are used instead of nanospheres as solid phase in MR suspensions. Such enhancement is considerably higher than that reported previously for the case of microparticles [6].

2. Experimental Methods

The CoNi particles used in this work, both nanofibers and nanospheres, were synthesized as described in Ref. [3] by means of the polyol process [11, 12]. Essentially, the synthesis process consisted of the reduction of cobalt and nickel ions in a polyol medium. The size of the particles was controlled by using an appropriate nucleating agent; in the case of nanofibers ruthenium was used, while platinum was employed for nanospheres. On the other hand, the shape of the particles was controlled by the concentration of NaOH in the medium. Figure 1 shows a high resolution transmission electron microscopy (HREM) picture of the particles synthesized.

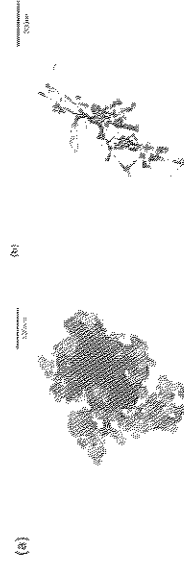


Figure 1. HREM picture of the synthesized nanoparticles. (a) nanospheres, (b) nanofibers.

The size distribution of the particles was obtained from HREM pictures. For nanospheres, the mean diameter was 24 nm, while for nanofibers the mean width and length were 6.6 nm and 56 nm, respectively. Note the high aspect ratio of fibers, which is higher than 8. Energy dispersive X-ray spectroscopy and X-ray diffraction were used to characterize the chemical composition and crystal structure of the particles. As a result of these experiments it could be concluded

MAGNETIC AND MAGNETORHEOLOGICAL PROPERTIES OF NANOFIBER SUSPENSIONS

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In this work the preparation and characterization of magnetorheological (MR) fluids constituted by CoNi nanofibers (56 nm length, 6.6 nm width) are reported. The properties of these new fluids were characterized by usual techniques (including magnetometry and magnetorheology). The results were compared with those obtained for conventional magnetic suspensions constituted by CoNi nanospheres. We found a remarkable effect of particle shape on the magnetic properties of the compressed powders: suspensions of nanofibers showed a weaker magnetic response than suspensions of nanospheres at low and medium applied field. This difference is probably due to the strong influence that nanofiber orientation could have on the demagnetizing field and, thus, on the internal field that governs the magnetization of the particles. This result was corroborated by means of finite element method simulations. Steady-state and oscillatory experiments were carried out in the presence of applied fields in order to characterize the MR response of the fluids. We found that the MR response of suspensions of nanofibers was considerably enhanced as compared to suspensions of nanospheres, in agreement with the results reported previously for microfibers.

1. Introduction

Due to their large potentiality for many technological [1] and biomedical [2] applications, there is an increasing scientific interest in the preparation of new magnetorheological (MR) fluids with novel properties. The synthesis of non-spherical magnetic particles and their use in the preparation of new MR fluids is one of the most recent approaches proposed in this direction [3-5]. For example, several works have been devoted in the last years to the preparation of MR fluids

that the chemical composition was $\text{Co}_{81}\text{Ni}_{19}$ for nanospheres and $\text{Co}_{71}\text{Ni}_{29}$ for nanofibers, and that in both cases cobalt presented a hexagonal structure, while nickel structure was a face-centered cubic one [3].

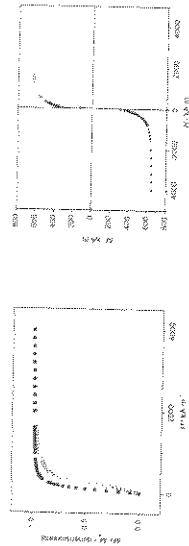


Figure 2. (a) First magnetization curve normalized by M_s (\square), nanospheres; \circ nanofibers. (b) hysteresis loop (\blacksquare) and first magnetization curve (\circ) for nanofibers. Taken from Ref [3].

The characterization of the properties of the particles was completed with their magnetic behavior, measured with a Squid Quantum Design Magnetometer. The first magnetization curve and the hysteresis loop were obtained (see Figure 2). From these curves the saturation magnetization (M_s) and the initial susceptibility (χ_0) were calculated. For nanofibers: $M_s = 626 \text{ kA/m}$, $\chi_0 = 2.7$; for nanospheres: $M_s = 743 \text{ kA/m}$, $\chi_0 = 9.2$. Besides, it is interesting to note (see Figure 2a) that the values of M/M_s are considerably lower for nanofibers than for nanospheres at low and medium field. In addition, it is seen in Figure 2b that for nanofibers, the first magnetization curve does not fall inside of the hysteresis loop. These interesting behaviors will be explained in the next section by means of a finite element method (FEM) simulation.

Both kinds of particles described above were used for the preparation of MR suspensions. For this purpose, mineral oil was used as carrier liquid and 1- α -phosphatidylcholine (PDC) as stabilizing additive (surfactant). All the suspension prepared contained 5 vol.% of solids.

The MR response of the suspensions was studied with a controlled-stress magnetorheometer (MCR300, Physica-Anton Paar). Steady-state and dynamic measurements were carried out. The system geometry was a plate-plate with a gap of 0.35 mm, and the temperature was set at 25 °C in all cases. All the suspensions were mechanically stirred before placing them on the magnetorheometer. A pre-shear of 30 s at a shear rate of 100 s^{-1} , and a waiting time of 30 s with no rate applied were allowed right before starting the measurements. During the waiting time the magnetic field was applied. In the case of steady state measurements a ramp of shear rates from 0 to 500 s^{-1} was applied. For oscillatory measures the amplitude of the stress was varied in

the range 0.1-2000 Pa with a frequency of 1Hz. From these experiments the viscosity, yield stress and viscoelastic moduli were obtained as a function of the applied magnetic field.

3. FEM Simulation of the Magnetic Properties

In the previous section it was shown that the values of M/M_s are smaller for nanofibers than for nanospheres at low and medium field. In addition, for nanofibers, the first magnetization curve does not fall inside of the hysteresis loop. In this section we justify these interesting behaviors by FEM simulation performed by using FEMM software package [13]. With this aim, we considered a fibers-in-air suspension of fibers aligned in the vertical direction (see Figure 3) containing a solid volume concentration of 13 %, similar to that estimated for the suspensions used in the magnetometry measurements. For each value of the intensity of the magnetic field, we considered two directions of application (of the field): perpendicular and parallel to the fiber axis. The magnetic induction in the fiber suspension was calculated (by FEM simulation) for each field intensity and direction of application. As an example, Figure 3 shows the results obtained for an applied magnetic field $B = 75 \text{ mT}$. As observed, when the magnetic field is parallel to the axis of the fibers, the magnetic induction in the fiber volume is higher than when it is applied perpendicularly. Similar results were obtained for the different magnetic field considered in the range 0 to 100 mT. Consequently, we can conclude that fiber orientation plays an important role in the magnetization of concentrated suspensions of fibers. This is a consequence of the fact that the demagnetizing field is higher when the external magnetic field is applied in the perpendicular direction to the fiber axis than when it is applied in the parallel one. Such simulation explains the results obtained experimentally (Figure 2). For the experimental measurements, the powders were poured in capsules and compressed with a plug. In the case of spheres the compression was very good, but for nanofibers it was rather poor due to their anisotropic shape. When the field was initially applied most of the fibers were misaligned with it, and consequently their demagnetizing field was considerably high, thus their magnetization considerably reduced. As the field was progressively increased, some of the fibers could align with it, but not all of them, justifying a lower magnetization in the fibers volume than for spheres at low and medium field (as observed in Figure 2a). This mechanism also explains that the first magnetization curve of nanofibers is not inside its hysteresis loop (Figure 2b): experimental measures of the magnetization loop began at the highest field and, consequently, most of fibers were immediately oriented with it. During the rest of the measure

the demagnetizing field was lower than that induced in the measurements of the first magnetization curve, which started at zero field, thus with most of the fibers misaligned with the field.

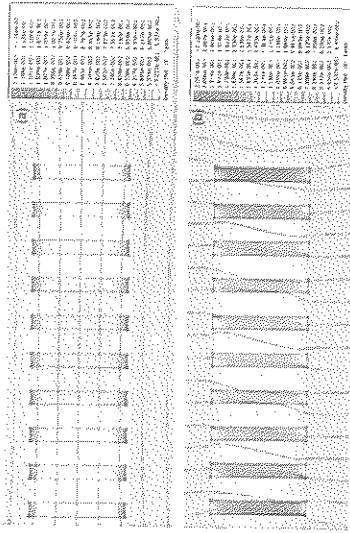


Figure 3. FEM simulation. Distribution of the magnetic field B in the fiber suspension, when an external field of 75 mT is applied perpendicular (a) and parallel (b) to the axis of fibers. Fibers are depicted by the vertical rectangles.

4. Experimental Results of the MR Tests

From shear stress vs. shear rate curves (not shown here for brevity), it could be concluded that these kinds of suspensions (both suspensions of nanofibers and suspensions of nanospheres) presented a typical MR behavior: increase of the shear stress with the magnetic field and appearance of field-dependent yield stress. The curves of the storage (G') and loss (G'') moduli vs. the amplitude of the shear stress, obtained by oscillatory measurements, were also typical of MR fluids: a pseudoplateau, which could be associated to the viscoelastic linear region (VLR), was observed at low shear amplitude, followed by a sharp drop at higher amplitudes. The values of both G' and G'' increased as the magnetic field was increased.

In order to focus on the differences in the MR behavior due to particle shape, it is convenient to normalize the characteristic MR magnitudes (yield stress, and G' and G'' corresponding to the VLR) by the square of the magnetization of the suspensions, since nanofibers and nanospheres present different magnetic properties (see Figure 2). Figure 4a shows the normalized

yield stress as a function of the external field. From this figure it could be concluded that the yield stress of the nanofiber suspension is much higher than that of the nanosphere suspension, probably due to the existence of solid friction between fibers, as it is the case for suspensions of microparticles [14]. Nevertheless, the enhancement of the yield stress attributed to the fiber-like shape in the case of nanoparticles is more important than that reported for microparticles [15].

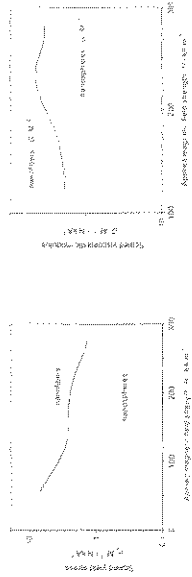


Figure 4. Normalized yield stress (a) and storage modulus (b) as function of the applied magnetic field strength, for nanofiber and nanosphere suspensions containing 5 vol.% of solids.

In Figure 4b the normalized storage modulus corresponding to the VLR is plotted against the intensity of the applied field. A similar behavior is obtained for the loss modulus, not shown here. As observed, as it was the case for the yield stress (Figure 4a), there is an important enhancement of the storage modulus when nanofibers are used instead of nanospheres.

5. Conclusions

It can be concluded that an interesting magnetic behavior arises in suspensions of nanofibers, based on the effect of fiber orientation on the demagnetizing field. In addition, an enhancement of the yield stress and the viscoelastic moduli is found when nanofibers are used instead of nanospheres, as solid phase in MR fluids.

Acknowledgments

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