Physica B 407 (2012) 3165–3167

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Anisotropy and relaxation processes of uniaxially oriented $CoFe_2O_4$ nanoparticles dispersed in PDMS

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ARTICLE INFO

Available online 17 December 2011

Keywords:
Magnetic anisotropy
Magnetoelastomers
Relaxation
Magnetic viscosity

ABSTRACT

When a uniaxial magnetic field is applied to a non-magnetic dispersive medium filled with magnetic nanoparticles, they auto-assemble into thin needles parallel to the field direction, due to the strong dipolar interaction among them. We have prepared in this way magnetically oriented nanocomposites of nanometer-size $CoFe_2O_4$ particles in a polydimethylsiloxane polymer matrix, with 10% w/w of magnetic particles. We present the characteristic magnetic relaxation curves measured after the application of a magnetic field forming an angle α with respect to the needle direction. We show that the magnetic viscosity (calculated from the logarithmic relaxation curves) as a function of α presents a minimum at $\alpha=0$, indicating slower relaxation processes associated with this configuration of fields. The results seems to point out that the local magnetic anisotropy of the nanoparticles is oriented along the needles, resulting in the macroscopic magnetic anisotropy observed in our measurements.

1. Introduction

In a suspension of magnetic particles dispersed in a viscous media, the individual magnetic moments of the particles are, in principle, oriented at random. When a magnetic field is applied, the magnetic moment of the particles orients along the direction of the field. In this configuration, the particles start migrating under the influence of the strong dipolar interaction among them, and form chain structures [1]. In this way it is possible to generate spatial texture on a magnetic suspension. An orientational texture is also possible to produce because the individual easy axis of anisotropy of the particles tends to align with the applied field. Hence, after a process of hardening of the solution, a topological and magnetic textured solid is obtained. In particular, textured magnetic elastomers are of great interest for their potential technological applications.

Even though the magnetic properties of textured fine particle systems have been studied [1,2], their phenomenology is far from being completely understood, particularly in reference to the anisotropic relaxation processes involved.

If a large magnetic field is applied to a fine particle system in the blocked state, and then removed, the magnetic remanence evolves logarithmically with time

$$M(t) = M(t_0) - S \ln t/t_0 \ (t > t_0) \quad (1)$$

where S is called magnetic viscosity, and is related to the dynamical behavior of the magnetic moment of the particles [3–5]. The magnetic viscosity will depend on the size, shape and anisotropy distribution of the system. In this way, S will be proportional to the thermal energy of the system, and inversely proportional to its mean energy barrier.

In this work, the relaxation behavior of a magnetic structured system of nanometer-size $CoFe_2O_4$ particles dispersed in a polymer are studied after curing in the presence of a uniform magnetic field. In the cured system, the magnetic nanoparticles are grouped forming needles oriented in the direction of the applied magnetic field. The aim of this work is to analyze the magnetic anisotropy induced by the morphologic structuration of the composite. For this purpose, the magnetic relaxation was measured and the magnetic viscosity recovered as a function of the angle (α) between the direction of the texturing magnetic field (H_T, applied during the preparation of the composite) and the probe magnetic field used for measuring the magnetization (H_a, for instance in VSM experiments).

2. Experimental

The method used to prepare $CoFe_2O_4$ nanocrystals was described elsewhere [6,7]. Briefly, a solution mixture (2:1) of $FeCl_3 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ in acid media was added to a solution of NaOH (80 °C), at high speed stirring. The obtained

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doi:10.1016/j.physb.2011.12.054

nanoparticles were washed by centrifugation and dried using a vacuum oven at 40 °C for 24 h. The obtained nanoparticles show Gaussian distribution of diameters with a maximum at 12 nm, as seen by TEM images.

The magnetic nanoparticles were then used to prepare the textured composite. First, the polydimethylsiloxane (PDMS) base and crosslinker agent (Sylgar 184, Dow Corning) were mixed in proportions of 10:1 (w/w) at room temperature. The nanoparticles were dispersed in the uncured PDMS at 10% w/w concentration (we also made composites at 5% w/w, in which the observed phenomenology is the same). The mixture was poured into an aluminum cylindrical cast, provided with an electronic-controlled oven. The system was placed between the pole pieces of an electromagnet. The cylindrical cast could spin around its axis by means of an electrical motor to promote homogenization. A magnetic field of 0.35 T (the texturing field, H_T) was applied along the cylinder axis. The polymer was cured with the field applied during 4 h at 75 °C. A control sample was also fabricated without applied field (random sample). As a result of this process, a cylindrical polymer is obtained, with a set of thin particle chains (or "needles") parallel to the cylinder axis (see the diagram in Fig. 2).

The magnetization measurements were performed in a Vibrating Sample Magnetometer (VSM, LakeShore model 7400) provided with an electromagnet. Relaxation of the magnetization at zero magnetic field measured after applying a field at the angle α, was recorded with the following protocol: The sample was first positioned at the measuring angle at zero field. Then, a maximum field of 1 T was applied to the sample, and suddenly removed at a rate of 1.5 T/min. The VSM control unit automatically performed the shutdown ramp and started taking magnetic moment data aprox. 5 s after the field reached zero value. A time window of 300 s was measured for each angle.

3. Results and discussions

As mentioned in the Introduction, morphologic structuration appears in the cured composite, given by the formation of chains (needles-like shaped) of grouped nanoparticles, aligned in the direction of the field H_a. These needles are observed by the naked eye, and SEM images confirmed that are formed by the individual nanoparticles [7].

We measured the remanent magnetization as a function of time for different values of the angle α between the applied field H_a and the direction of the texturing field H_T (see the diagram in Fig. 2). The time-dependent remanence (relative to its value at $t=0$) for three specific angles is shown in Fig. 1a. The curves display the characteristic logarithmic decay dependence of Eq. (1). In Fig. 1b we regraph the same data with a logarithmic scale in the time axis. The linear tendency of the data confirms the scenario of logarithmic relaxation, characteristic of a system with a wide energy barrier distribution. The slope of the curves in Fig. 1b is the magnetic viscosity S of the system.

The relaxation curves were taken with $-20^\circ < \alpha < 100^\circ$, in steps of 10°. Taking S for each curve, we can construct a map of magnetic viscosity as a function of angle, shown in Fig. 2. The values of S are measured relatives to the magnetic viscosity of a random sample. A minimum is present for S at $\alpha=0$, i.e., when the applied field is paralell to the texturing field. The curve monolitically rises from $\alpha=0$ and presents a maximum at $\alpha=90^\circ$, when the fields are perpendicular one another. The minimum value is reduced about a 25% of its maximum value.

As the magnetic viscosity is directly related to the energy barriers for the magnetic moment to rotate to a lower-energy state, the results indicate that the mean energy barrier is highers

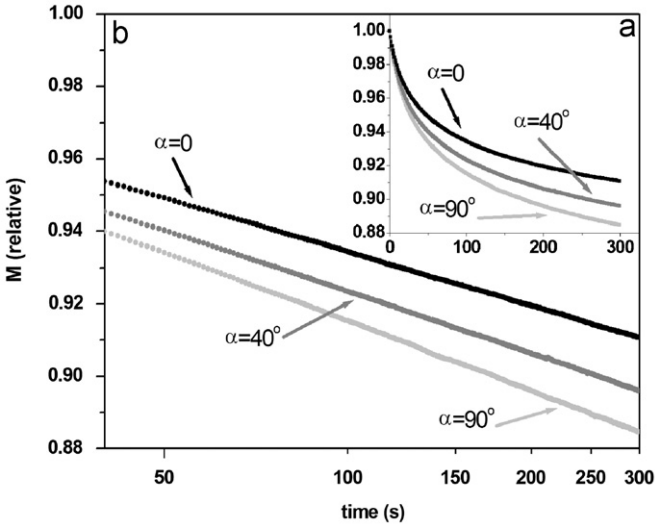

Fig. 1. (a) Magnetic remanence (relative to its maximum value) as a function of time for different orientations of the applied magnetic field. (**b**) The same data of (a) with a logarithmic time axis, the slope of the curves is the magnetic viscosity S.

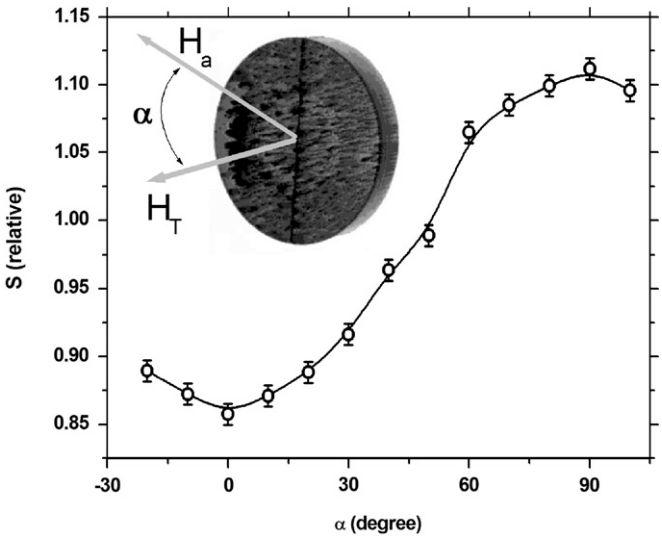

Fig. 2. Magnetic viscosity S as a function of the angle α. Values of S are relative to the random sample relaxation coefficient. The diagram shows the definition of α, as well as a photograph of the sample.

when the field is applied parallel to the uniaxial texture. In this configuration, the local magnetization has a slower dynamics, with the local magnetic moments interacting stronger with their neighbors. As we rotate the applied field away $\alpha=0$, the barriers decrease and present a minimum at $\alpha=90^\circ$. In this configuration, the local moments are perpendicular to the texture direction. It should be also noted that the value of S at the minimum of the curve is lower than the corresponding value for the random sample ($S=0.86$), and is higher at the maximum value ($S=1.11$).

The above effect is an indication of magnetic orientational texture, since the relaxation processes of a fine particle system is governed by the magnetic anisotropy energy [8]. The particles not only aggregates spatially into needles, but also orientate its easy axis of anisotropy along the needle direction. The anisotropy could come from crystalline origin, as well as shape anisotropy. Similarly, the measured value of the remanence at a given time has a similar behavior as the energy barriers, having a maximum value at $\alpha=0$, and a minimum for $\alpha=90^\circ$ (the anisotropy of the remanence is studied in a forthcoming paper) [7]. The anisotropic

behavior of the magnetic relaxation is apparently not studied for textured fine particle systems, up to our knowledge. The slower dynamics of relaxation when moments are oriented parallel to the needles is apparently caused by enhanced interparticle interaction due to the orientational texture of the sample.

4. Conclusion

We have prepared textured magnetic composites of $CoFe_2O_4$ nanocrystals immersed in a PDMS matrix. During the polymerization process we applied a magnetic field that produced a spatial texture, with the particles aggregating into chains or needles. We performed a study of the magnetic viscosity as a function of the angle between the remanent magnetization and the uniaxial texture. We found that that parameter have an orientational modulation, presenting a minimum when the applied field is parallel to the needles. We associate this modulation with enhanced energy barriers in this configuration, due to stronger dipole–dipole interactions when the easy axis of anisotropy of individual particles are oriented along the needles.

Acknowledgements

This work was supported by ANPCyT (PICT2006-568, PICT2006-1201), CONICET and UBA (UBACYT 2008-2010 $\times$ 157).

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