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Dipolar-driven formation of cobalt nanoparticle chains in polyethylene films

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HIGHLIGHTS

- We use a simple method for the production of a film with embedded cobalt particles.
- We studied the morphology and magnetic properties of the Co nanoparticle aggregates.
- The low-cost of the fabrication offers a strong potential for industrial applications.

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ABSTRACT

Using a simple method we produce polyethylene film with embedded chains of cobalt nanoparticles. The crystalline magnetic nanoparticles were synthesized through a simple chemical reduction method at room temperature using ultrasonic assistance. These particles were incorporated in a polyethylene matrix using a solution blending mechanism under an external magnetic field. The morphology and magnetic properties of Co nanoparticle aggregates were studied experimentally and by means of Monte Carlo simulations, showing a chain-like structures due to the strong dipolar interaction between aggregates. The hysteresis loops reveal typical ferromagnetic behavior at room temperature and magnetic anisotropy associated to a linear ordering of particles into the polymeric matrix. Numerical results confirmed the chain-like character of the aggregates and that an external magnetic field aligns them along its direction. The low-cost of the fabrication process of these polymeric magnetic films give them a strong potential for industrial and technological applications.

1. Introduction

Magnetic particles in regular arrays have become of increasing importance in material science due to their potential for industrial and technological applications [1,2]. Small magnetic particles based on Fe, Co, and Ni have been used for specific performances in micromechanical sensors [3], microwave absorbers [4], magnetic recording systems [5], and others. As example, Ni hollow powders have been developed by electroless plating and considered as military radar-absorbing material [6]. Iron-oxide nanoparticles prepared through solvothermal routes have been dispersed in different organic solvents and studied in photonic-crystals with magnetic-responsive capacity [7]. Besides, they have been used as reinforcing agent in multifunctional nanocomposites [8]. Similarly, Cobalt particles have been supported on semiconducting polymer and evaluated for organic electronics applications, such as transistors, diodes, and photovoltaic devices [9].

In general, experimental results have revealed that the performance of these hybrid materials depends on the collaborative and specific combination of physico-chemical properties of the organic phase and the polymer matrix. Besides, experiments have shown that efficiency depends strongly on the spatial organization of

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particles since, from the physical point of view, disordered systems usually exhibit weak response to external fields. Therefore, several studies focus on the simple and large scale synthesis of regular and periodic magnetic structures.

In this context and up to now, magnetic linear chain-like structures have been developed by induced assembly [10–12] and direct dipolar assembly [13,14] methods. Li et al. [15] developed magnetite particle-chain microwires by coprecipitation method under a magnetic field gradient. Also, Wang et al. [16] described a hydrothermal process to prepare chains of Cobalt spheres; and Iron–Nickel alloy nanochains have been reported by Lu et al. [17]. However those synthesis techniques are expensive and the resulting nanoparticles usually present undesired agglomeration and polydispersion in size and shape with the formation of complex structures.

In this work we report the preparation of a polyethylene magnetic film using a simple chemical process. A large scale homogeneous Cobalt particles were obtained by chemical reduction method at room temperature using ultrasonic assistance. These particles were incorporated in a polyethylene matrix using a solution blending method under an external magnetic field. The formation and the magnetic properties of chain-like agglomerates of Co particles were studied by means of electronic microscopy, magnetic characterization and Monte Carlo simulations.

2. Experiment

2.1. Ultrasonic assisted synthesis of cobalt particles

The cobalt particles were produced by chemical reduction process under ultrasonic assiatance. In brief, 100 uL of $CoCl_2 \times H_2O$ (0.4 M) were added to 30 mL of aqueous solution of CTAB (0.1 mM). After this, 200 μL of $N_2H_4 \times H_2O$ was dropped in the solution and the pH value was adjusted to 9–10 using NH_4OH. A gradual color change from sky blue to black indicated the formation of metallic particles. As-prepared particles were purified by magnetic decantation, washed several times using a mixture of ethanol and water, and vacuum dried.

2.2. Preparation of cobalt-polyethylene film

The magnetic polymeric film was produced by solution blending method [18,19]. First, the Co particles were re-dispersed into 1 mL of toluene. After that, 100 μL of the Cobalt black suspension was incorporated into the dilution of polyethylene-toluene (10% wt). Finally, the mixture was supported on a glass slide and vacuum dried under an external magnetic field of 2.5 kOe parallel to the glass plate.

2.3. Morphological and magnetic characterization

The particles crystalline structure was identified by powder X-ray diffraction (XRD, Philips PW 1830) in a powder diffraction mode, using the Cu Kα ($\lambda = 1.5418$ Å) radiation source of a Philips PW 1830 diffractometer. The morphology, size and distribution of particles in the film were obtained by scanning electron microscopy (SEM, Zeiss EVO MA10). The incorporation of particles in the polymeric matrix was quantified by thermogravimetric analysis (TGA, SDT 2960 Simultaneous DSC-TGA). The magnetic properties of the sample were measured with a homemade Alternating Gradient Force Magnetometer (AGFM) at room temperature.

3. Numerical simulation

In order to understand our experimental results and to identify the relevant parameters for chain formation, we performed Monte Carlo simulations comprising two parts: magnetization process and the chain formation.

3.1. Magnetization process

For the hysteresis curves we considered a single chain formed by seven quasi-spherical particles each with 260 nm of width and 208 nm of height (80% of the width), formed by Co atoms with magnetic moment 1,72 μ_B, where μ_B is the Bohr magneton, placed on a fcc structure with lattice constant 0.352 nm. With these dimensions each particle has 987×10^6 Co atoms, leading to a total of about 10^9 atoms in the system, which is out of reach for a regular Monte Carlo simulation with dipolar interactions. In order to circumvent this problem we used a scaling technique previously reported [20–22].

The energy of the i-th Co atom is

$$E_{\text{atom},i} = -\vec{H}\cdot\vec{m}_i - \frac{J}{2}\sum_{\langle ij\rangle}\vec{m}_i\cdot\vec{m}_j + \sum_{i<j}\frac{\vec{m}_i\cdot\vec{m}_j - 3(\vec{m}_i\cdot\hat{n}_{ij})(\vec{m}_j\cdot\hat{n}_{ij})}{r_{ij}^3}, \tag{1}$$

where $\vec{H}$ is the applied field, $\vec{m}_i$ is the Co atomic magnetic moment, J is the exchange coupling constant and $\langle ij\rangle$ means "sum over nearest neighbors pairs". We used $J = 2946$ kOe/μ_B where μ_B. In the dipolar term, r_{ij} is the distance between atomic magnetic moments $\vec{m}_i$ and $\vec{m}_j$, and $\hat{n}_{ij}$ is the unit vector along the direction that connects these two magnetic moments. In all simulations the temperature was $T = 300$ K.

3.2. Chain formation

In order to understand the origin of the linear chain formation observed in the SEM images shown in Fig. 1 (b), we considered a system composed by 2048 spherical particles, with diameters $\{d_i\}$ distributed according to a Gaussian function centered at 255 nm and standard deviation of 22 nm. The chain formation was simulated with the standard Monte Carlo method using the single-flip Metropolis algorithm [23] in a rectangular box of volume $V = (\sqrt{\alpha}L_0)_x \times (\sqrt{\alpha}L_0)_y \times (L_0/\alpha)_z$ with $L_0 = \left(\sum_i \frac{\pi d_i^3}{6C}\right)^{1/3}$, $\alpha = 10$, and volume concentration $C = 0.1$, where the initial particles positions were chosen at random within the box. For the specific values of $\{d_i\}$ used in the simulations we have $L_0 = 4.8 \times 10^2$ nm.

Due to the large number of elements and, consequently, of magnetic moments, it was not possible to consider the internal atomic structure of each particle with standard computational facilities. However, since under an external field each particle saturates into a single domain, we used this simplification in the chain formation process. With this approximation each particle can be represented by its total magnetic moment $\vec{\mu}_i$ calculated using its diameter d_i and the saturation magnetization $M_s = 1380$ emu/cm^3 for Cobalt. Also, we considered the presence of a constant external magnetic field H = 2.5 kOe. The energy of system during chain formation is then written as

$$E_{\text{for}} = -\sum_i \vec{\mu}_i\cdot\vec{H} + \sum_{i<j}\frac{\vec{\mu}_i\cdot\vec{\mu}_j - 3\left(\vec{\mu}_i\cdot\hat{n}_{ij}\right)\left(\vec{\mu}_j\cdot\hat{n}_{ij}\right)}{r_{ij}^3} + \sum_{i\neq j}V_{ij}, \tag{2}$$

where V_{ij} is a hard core potential, added to avoid particle overlap, defined as $V_{ij} = 0$ if $r_{ij} \geq (d_i + d_j)/2$ and $V_{ij} = \infty$ if $r_{ij} < (d_i + d_j)/2$.