

## Dipolar-driven formation of cobalt nanoparticle chains in polyethylene films



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### H I G H L I G H T S

- 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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### A B S T R A C T

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.

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## 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 assistance. In brief, 100  $\mu\text{L}$  of  $\text{CoCl}_2 \times \text{H}_2\text{O}$  (0.4 M) were added to 30 mL of aqueous solution of CTAB (0.1 mM). After this, 200  $\mu\text{L}$  of  $\text{N}_2\text{H}_4 \times \text{H}_2\text{O}$  was dropped in the solution and the pH value was adjusted to 9–10 using  $\text{NH}_4\text{OH}$ . 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  $\mu\text{L}$  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  $\text{Cu K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) 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  $1.72 \mu_B$ , where  $\mu_B$  is the Bohr magneton, placed on a fcc structure with lattice constant 0.352 nm. With these dimensions each particle has  $987 \times 10^6$  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

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

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  $J = 2946 \text{ kOe}/\mu_B$  where  $\mu_B$ . 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  $T = 300 \text{ K}$ .

### 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  $L_0 = 4.8 \times 10^2 \text{ nm}$ .

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  $M_s = 1380 \text{ emu/cm}^3$  for Cobalt. Also, we considered the presence of a constant external magnetic field  $H = 2.5 \text{ kOe}$ . The energy of system during chain formation is then written as

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

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  $r_{ij} < (d_i + d_j)/2$ .

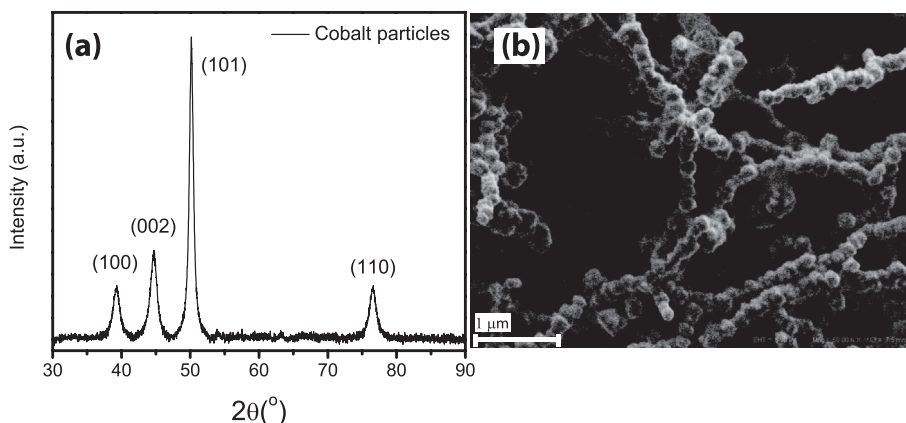


Fig. 1. (a) Powder XRD pattern of the Cobalt particles. (b) SEM image of the as-prepared Cobalt nanoparticles.

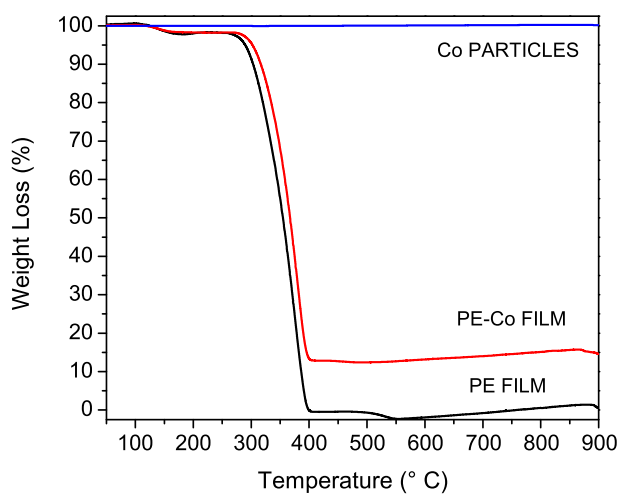


Fig. 2. Thermal degradation.

The dipolar term has a definition similar to the one in Eq. (1) with the substitution of  $\mu$  for  $m$ .

#### 4. Results and discussion

The crystalline structure and purity of the as-prepared particles

were determined by powder XRD. A typical diffraction pattern is shown in Fig. 1(a). All the peaks were fully indexed to the hexagonal close packed phase (JCPDS 01–1278) as  $39.2^\circ$  (100),  $44.7^\circ$  (002),  $50.2^\circ$  (101), and  $76.5^\circ$  (110) planes. The broad peaks indicate that the size of the crystallites is small, being the average crystallite diameter, as calculated from the Scherrer equation,  $(25.3 \pm 1.7)$  nm. No impurity phases such as oxides, hydroxides or precursor compounds were detected, indicating that pure Cobalt particles can be synthesized by reduction method in aqueous medium under ultrasonic assistance. The morphology and size of the particles have been characterized by SEM as shown in Fig. 1(b). The image exhibits homogeneous regular and pseudo-spherical particles. It is also evident a small particle agglomeration and chain-like assembly of particles due to their strong magnetic interactions. Their size distribution was also determined by digital image processing of 100 particles in several SEM micrographs and has been adjusted by a Gaussian fit, leading to an average diameter of  $(255 \pm 22)$  nm. XRD and SEM results suggested the polycrystalline nature of the Cobalt particles and their size indicates that our Co nanoparticles are magnetic multidomains.

In order to generate the magnetic polymeric film, the Cobalt particles were supported on polyethylene using the solution blending method [18, 19]. The as-obtained film was first characterized by TGA to confirm and quantify the Cobalt incorporation into the polymer matrix. Fig. 2 presents the profile of the thermal degradation. The control sample of pure Cobalt particles showed practically no weight loss due to their high-thermal stability. From

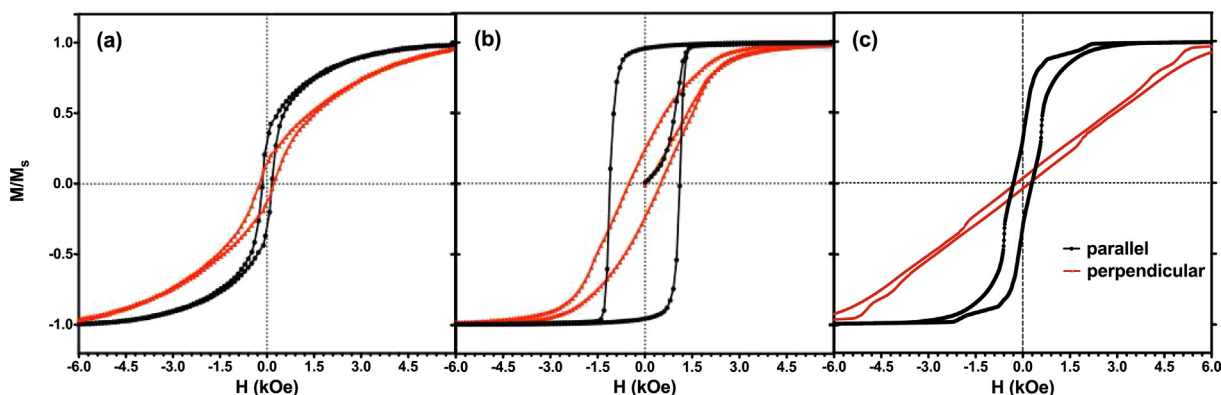


Fig. 3. Hysteresis curves with applied fields parallel (black line) and perpendicular (red dashed line) to the Cobalt chains. (a) Experimental system; (b) Simulated, monodomain chain; (c) Simulated multidomain chain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the thermogram of the pure polyethylene it was possible to observe the continuous decomposition process, started at about 80 °C and finished at 400 °C. The complete degradation is evident, as usually observed in samples with minimal residual mass. These results are usual for organic compounds [24–26]. It was also observed a similar situation for the Cobalt polyethylene film. However, in this analysis the residual mass is 15%, which can be associated to the Cobalt particle content in the material.

Now we examine the magnetic response of the system by means of the hysteresis loops with in-plane fields parallel and perpendicular to the chains. The experimental and numerical curves can be seen in Fig. 3. From the experimental curves in Fig. 3(a) we observe that the coercivity is similar for both field directions. When one thinks about a long linear particle chain, similar to a wire, one immediately expects a larger parallel coercivity, together with a high remanence cycle. This is exactly what happens if we simulate the hysteresis cycle of a chain of monodomain particles, as seen in Fig. 3(b). The point is the assumption that the particles are monodomain, a necessary simplification when dealing with the large number of particles needed in the chain formation process. In order to consider the existence of an internal structure in each particle one needs to use the scaling technique and even with that, the number of particles in the chain must be small. The curves for a chain of seven multidomain particles can be seen in Fig. 3(c). In spite the small size of the simulated chain prevents us to get a perfect agreement with experimental results, a qualitative comparison of Fig. 3(a) and (c) lead us to the conclusion the particles synthesized are multidomain and that the internal structure of each particle is fundamental for obtaining small coercivities for both field directions.

The effect of a magnetic field during the chain formation is evident as can be seen in Fig. 4 where SEM images of the chain formation without field (Fig. 4(a)) and with an external magnetic

field of 2.5 kOe (Fig. 4(b)). The same effect appears in the Monte Carlo simulations, as can be seen in Fig. 5(a) and (b) obtained with the procedure described in Section 3.2.

## 5. Conclusions

Polymeric films with magnetic nanoparticle have been studied from theoretical and experimental sides. By means of Monte Carlo simulations we demonstrated that the organization of the spheres into chains is due to inter-particle dipolar interactions. When an external magnetic field is applied during the film fabrication the chains become aligned with the field direction, but with no significant effect on the length of the chains. The hysteresis loops of such system exhibit similar coercivities for fields applied along and perpendicular to the chains. To explain this behavior it was needed to develop numerical simulations considering the internal structure of the particles. These simulations confirm that the multidomain character of the particles is responsible for the lack of squareness and low coercivity of the parallel field hysteresis. Using this approach one can tune mechanical, morphological, and magnetic properties of nanoparticle-embedded polymeric films in order to attain the desired behavior, using a simple chemical route and the application of an external magnetic field. Due to the simple and low-cost fabrication process of these polymeric magnetic films, they have a great potential for industrial and technological applications.

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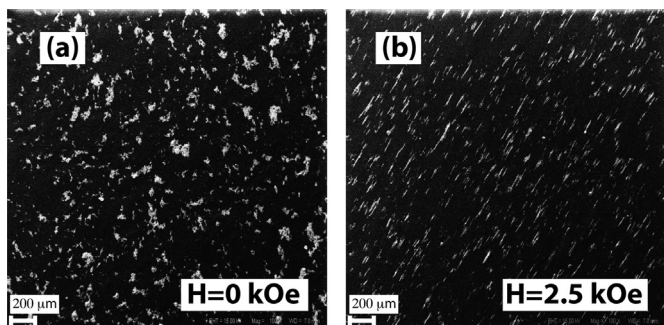


Fig. 4. SEM images of the system without (a) and under (b) an external field of 2.5 kOe.

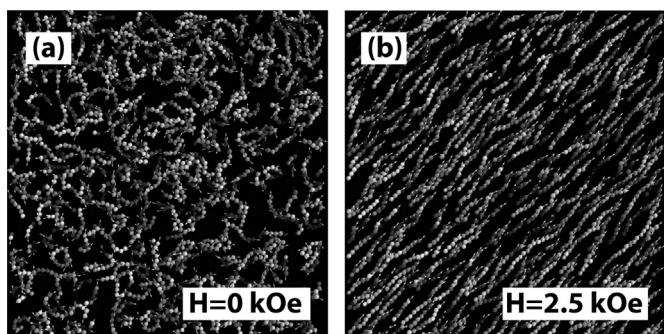


Fig. 5. Images of the system without (a) and under (b) an external magnetic field of 2.5 kOe from Monte Carlo simulations.

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