

Effect of Submicrometer Clustering on the Magnetic Properties of Free-Standing Superparamagnetic Nanocomposites

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Superparamagnetic polymer nanocomposites with well differenced distribution of the nanofiller in the matrix were obtained by using oleic acid-coated maghemite nanoparticles. Both homogeneously dispersed magnetic films and dispersions constituted by a distribution of submicrometric nanoparticle (NP) clusters could be obtained starting from the same batch of magnetic NPs. We demonstrated that differences in the magnetic behavior of these materials are solely due to changes in the NP spatial distribution not involving changes in their size or total volume fraction. The experimental behavior of random distributions of NPs was consistent with Monte Carlo (MC) simulations performed on equivalent systems. On the contrary, the presence of aggregates produced higher values of the blocking temperatures (T_B) due to an increase in the strength of dipolar interactions produced by an increase of the local concentration of NPs in the aggregates. In this way, we determined that clustering, even in the submicrometric range, strongly controls the magnetic behavior of nanocomposites. This is of fundamental importance in the design of new magnetic materials with technological applications.

Introduction

Nanocomposites are very versatile materials, as their properties strongly depend on the selected matrix, the nature of the nanofiller, and the geometrical way in which they are arranged.¹ In fact, the strong dependence between the performance of these materials and the distribution and geometrical arrangement of the particles in the matrix have stimulated the development of new strategies of controlled assembly.¹ In recent years, nanocomposites obtained by combination of magnetic nanoparticles (NPs) and polymers have deserved increasing attention because of their excellent potential for applications in the fields of information storage, biomedicine, sensing, actuation, magnetic separation, etc.² Several examples of magnetic nanocomposites with special morphologies as magnetic mesoporous capsules,³ colloidosomes,⁴ and one-dimensional arrangements⁵ have recently appeared, showing new and promising applications in diverse fields.

Single-domain magnetic particles (usually in the nanometer range) show unique properties compared to the bulk. For these particles, the energy barrier for magnetization relaxation is proportional to the volume. Below a certain size and above a characteristic temperature T_B (called blocking temperature), NPs can achieve thermal equilibrium in the time of measurement (100 s in common dc magnetization experiments). For larger particles (or below this temperature), the whole magnetic moment is blocked.

Interparticle interactions (dipolar and exchange) modify the energy barrier, changing the global magnetic behavior of fine particle systems.⁶ In the case of homogeneous, randomly

distributed superparamagnetic dispersions of NPs, experimental and modeling results indicate that an increase in dipolar interactions produce an increase in the blocking temperature of the system, a decrease in the magnetic susceptibility of the dispersions, and a decrease in the magnetic relaxation rate.^{6a,7} In concentrated and/or strongly interacting systems, formation of random dispersions of NPs becomes more difficult and the probability of generation of clusters increases.⁸ In this case, both particle–particle and cluster–cluster interactions are expected to play a role in the final response of the material. Complex behaviors can also be expected for nanocomposites with special morphologies as those mentioned above, in which concentrated and dilute regions of magnetic NPs can simultaneously coexist.

The general nature of clustering and its importance in the understanding of the physics of superparamagnetic systems has recently been addressed.^{8b} However, prediction of the magnetic response of these systems is not trivial, and clarification of the effect of cluster–cluster interactions on the final magnetic properties of the materials is still a great challenge.^{7d,8a} Undoubtedly, the first step toward the understanding of this effect is the analysis of experimental evidence in well-controlled systems.

In this work we propose a first approximation to the problem through the determination of the effect of submicrometer clustering on the superparamagnetic behavior of free-standing polymer magnetic nanocomposites. The common challenge associated with the analysis of clustering relies on the hard experimental task of controlling the dispersion level of magnetic nanoparticles without changing their size or coating. Here we show that by combining oleic acid-coated maghemite NPs with polymers of different polarity, freestanding nanocomposites with completely different morphological distribution and well differenced magnetic response can be obtained.

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Experimental Methods

Materials. Poly(ethylene oxide) (PEO), with a molecular weight, $M_w \approx 300\,000$, and poly(vinyl butyral) (PVB) with $M_w = 50\,000$ – $80\,000$ (both from Aldrich) were used as polymeric matrices. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), cyclohexane, dichloromethane, and poly(oxy-ethylen-10-oleyl ether) (Brij-97) were purchased from Aldrich. Oleylamine was provided by Fluka while oleic acid was purchased from Merck. Heptane was from Riedel-de Haën. All the reagents were used as received. Deionized water was used in all the preparations.

NP Synthesis. A ferrofluid of oleic acid-capped maghemite ($\gamma\text{-Fe}_2\text{O}_3$) NPs, with a mean average size of 3.5 nm, was synthesized by a microemulsion method previously described in the literature.⁹ Briefly, a (cyclohexane/Brij 97/aqueous phase) system was used with an aqueous phase formed by a 2:1 ferric-ferrous solution. To form the NPs, oleylamine was added to the microemulsion with magnetic stirring. Final stabilization was attained by adding a 50/50 molar mixture of oleic acid and oleylamine on the reaction media. The obtained oleic acid-coated NPs were separated, washed, and finally dispersed in heptane to form a stable ferrofluid.

Nanocomposite Synthesis. Magnetic nanocomposites were obtained by dispersion of maghemite NPs in PVB and PEO matrices. PVB-based nanocomposites were prepared by mixing selected amounts of the ferrofluid and the polymer using CH_2Cl_2 as common solvent. The obtained homogeneous dispersions (concentration of dispersions ~ 1 wt %) were cast on glass or Teflon molds and evaporated for 24 h at room temperature to obtain films with different concentrations of NPs. Concentration of maghemite in the final samples was varied between 0.3 wt% and 30 wt%.

Techniques. Transmission electron microscopy (TEM) was performed with a Philips CM-12 microscope operated at an accelerating voltage of 100 kV. Ferrofluid samples were prepared by dropping a dispersion of the particles on copper grid-supported Formvar films. TEM of ultrathin sections of the nanocomposites and high resolution transmission electron microscopy (HRTEM) of maghemite crystals were carried out with a JEOL JEM-2010 FEG microscope. The final concentration of iron oxide in the nanocomposites was determined by atomic absorption spectrophotometry (Varian SpectraAA-250 Plus spectrophotometer, in PVB nanocomposites) and thermogravimetric analysis (TGA 7, Perkin-Elmer, in PEO nanocomposites). Magnetic properties of the samples in the temperature range 1.9–300 K were obtained using a commercial SQUID magnetometer ($H_{\text{max}} = 5$ T).

Results and Discussion

Both homogeneously dispersed magnetic films and dispersions constituted by a distribution of submicrometric NPs clusters were obtained starting from the same batch of magnetic NPs. We will next show that differences in the magnetic behavior of these materials were solely due to changes in the NP spatial distribution not involving changes in their size or total volume fraction. Several points have been carefully considered in order to control the reliability of the results. First, nanoparticles with a narrow size distribution were used in order to avoid effects associated with a wide distribution of particle energy barriers. Second, selected comparative analysis were done on samples prepared using the same batch of NPs, in order to keep the particle size distribution constant. Finally, exchange interactions, that could also affect the magnetic response of nanocomposites,¹⁰ were negligible because of a spacer attached

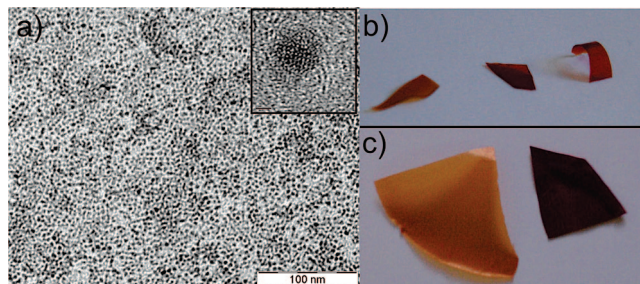


Figure 1. (a) TEM micrograph of the obtained nanoparticles. The inset in a demonstrates the single-crystal nature of the nanocrystals. Photographs of representative PVB (b) and PEO nanocomposites (c).

to the particles (oleic acid) that precluded sticking and introduced a small, constant separation between them.^{8a}

Figure 1a shows a TEM image of the synthesized NPs. As can be observed, individuality of NPs is preserved after evaporation of the solvent as a consequence of oleic acid capping. The inset shows a HRTEM image of one of the individual maghemite crystals.

Figures 1b and 1c show representative images of the obtained free-standing films with typical thicknesses in the range of 50–100 μm and areas of several centimeters. A first view of the obtained materials and their optical homogeneity pointed to the absence of macrophase separation. This was confirmed by transmission optical microscopy (TOM). Both kinds of nanocomposites (PEO- and PVB-based) looked microscopically homogeneous at the highest magnifications used ($500\times$). Because of the high crystallinity of PEO composites, films were observed both at room temperature and above their melting temperature. Room temperature TOM images of a sample containing 6.6 wt% of iron oxide showed the presence of spherulitic crystals without evidence of NP phase separation. Above the melting temperature, a homogeneous field was observed confirming the absence of macroclusters. Only after prolonged heating at 80 $^{\circ}\text{C}$ were aggregates observed to form, possibly as a consequence of the low viscosity of the system under these conditions.

The possible presence of submicrometric clusters of NPs (not observable by TOM) was investigated by TEM. A comparative analysis of samples obtained with identical contents of NPs was carried out by direct evaporation of dispersions on carbon-coated TEM grids. Figure 2 shows TEM micrographs obtained for samples with 1.3 wt% and 6.6 wt% of NPs in PVB and PEO. Differences between both kinds of arrangements can be clearly observed. In PVB nanocomposites (Figures 2a and 2b) NPs were homogeneously distributed, and only a decrease in the mean interparticle distance was observed by increasing the volume fraction of particles. It is worth noting that although a low level of clustering cannot be completely discarded, most of the imaged grid showed a homogeneous appearance. This was also confirmed by directly imaging ultrathin cuts of PVB films with low concentrations of NPs (Figures 2c and 2d). On the contrary, formation of clusters was clearly observed in PEO matrices (Figure 3) even for the lower NP concentration used. An increase in the volume fraction produced an increase in the mean size of clusters, which in some regions reached several hundreds of nanometers (Figures 3b and 3c). The presence of clusters was also clearly observed in TEM images obtained from ultrathin cuts of PEO composites (Figure 3d). From this image it is also clear that magnetic cores are not directly in contact but preserve their individuality, forming an assembled arrangement. This is

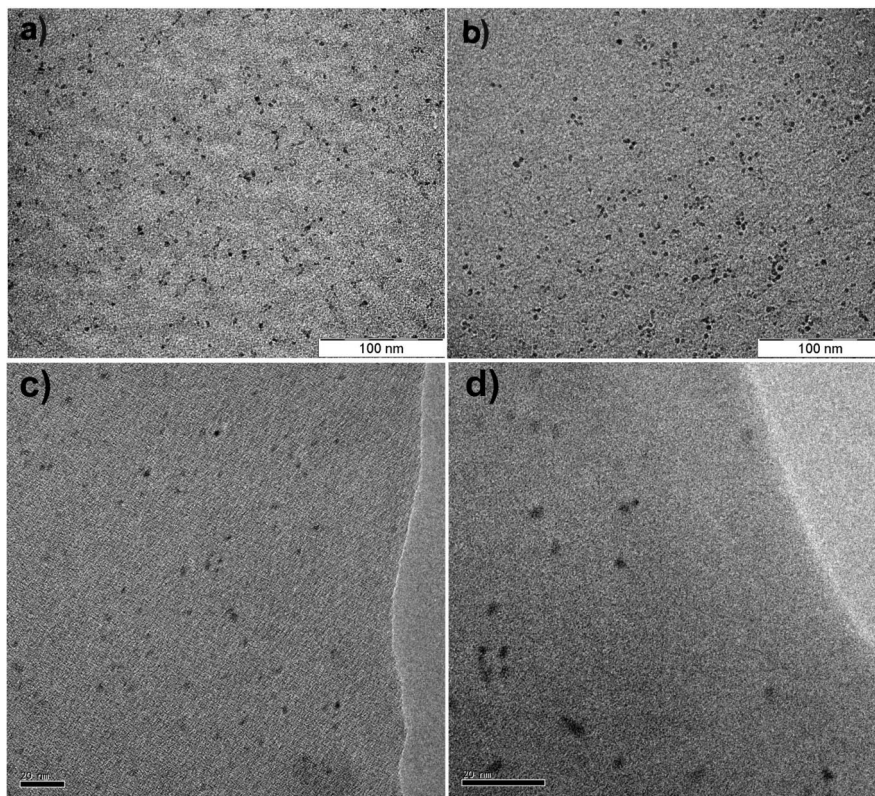


Figure 2. TEM micrographs of films obtained by direct evaporation of stable dispersions onto TEM grids: (a) 1.3 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PVB; (b) 6.6 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PVB; (c, d) TEM images of an ultrathin cut corresponding to a sample with 0.3 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PVB.

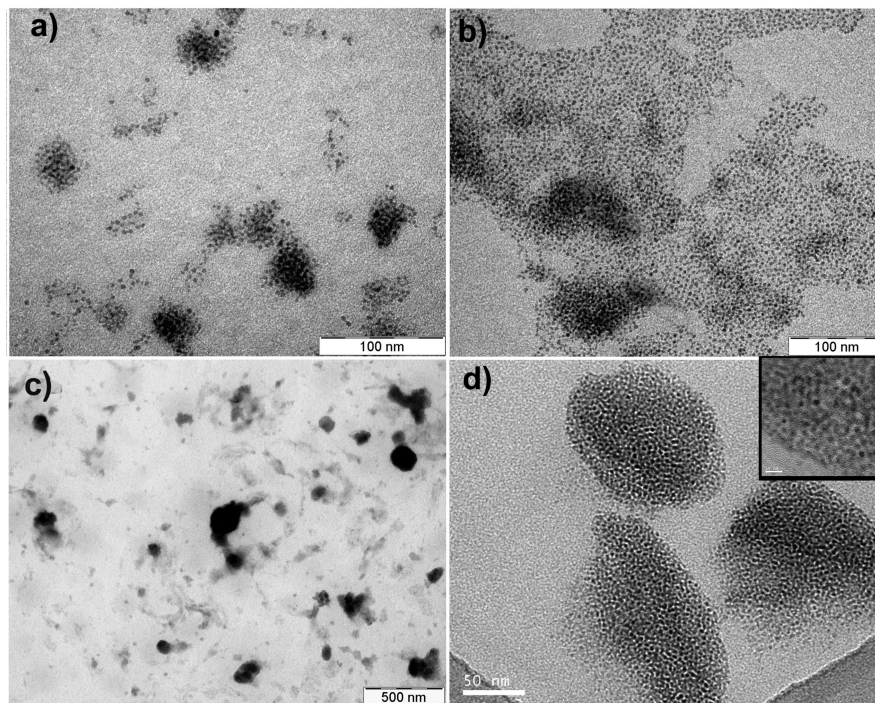


Figure 3. TEM micrographs of films obtained by direct evaporation of stable dispersions onto TEM grids: (a) 1.3 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PEO; (b) 6.6 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PEO; c is a lower magnification of b. (d) A TEM image of an ultrathin cut corresponding to a sample with 6.6 wt% of $\gamma\text{-Fe}_2\text{O}_3$ in PEO. The inset shows a higher magnification of one of the aggregates in which individual magnetic NPs can be identified.

a consequence of the oleic acid coating that acts as a physical spacer that precludes sticking of the particles.

The different tendency to aggregation of NPs in both matrices can be understood taking into account the differences in the nature of the polymers. PEO is a hydrophilic polymer with a low affinity for the hydrocarbon chains of oleic acid

(used as NP capping). On the contrary, hydrophobic methylene units of the main chain of PVB confer a certain level of hydrophobicity to the matrix which increases the compatibility with the capped NPs. Higher molecular weight and crystallinity of PEO with respect to PVB is also expected to favor segregation of the NPs.

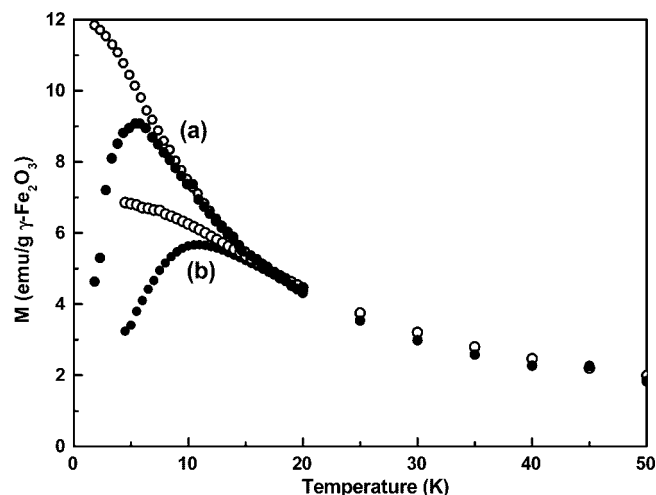


Figure 4. Magnetization versus temperature measured at 100 Oe under zero field cooling, ZFC (solid circles) and field cooling, FC (open circles) conditions. Content of γ -Fe $_2$ O $_3$ (from an identical synthesis batch) is 6.6 wt% for both PVB (a) and PEO (b) matrices.

Figure 4 shows curves of dc magnetization as a function of temperature for samples prepared with identical amounts of NPs (from the same batch) in PEO and PVB. Experiments were done under zero field cooling (ZFC) and field cooling (FC) conditions at $H = 100$ Oe. Both curves show the typical behavior associated with arrangements of superparamagnetic nanoparticles, with a maximum in the curve of ZFC (the blocking temperature, T_B) separating the blocked from the superparamagnetic state. Below T_B the free movement of the moment of the particle is blocked by the anisotropy; above T_B , thermal energy induces rapid fluctuations of the magnetic moment of the whole particle compared to the observation time so that the system appears superparamagnetic.¹¹ Although both systems are superparamagnetic at room temperature, several differences are obvious. First, in PEO-based samples the blocking temperature, T_B , was about 6 K higher than in PVB nanocomposites. Second, the maximum of the ZFC curve was broader and showed lower magnetic susceptibility. Finally, low temperature saturation becomes evident in the FC curves in the case of PEO. All these features indicate that magnetic dipolar interactions are stronger in PEO-based composites compared with dispersions in PVB. As a consequence of the presence of aggregates, the local concentration and hence dipolar interparticle interactions increase from the expected nominal value, determining the collective magnetic behavior of the samples. From an experimental point of view, the fact that even very small clusters (nonvisible by optical microscopy) could exert this high influence on the final magnetic response of the films is of fundamental and practical importance and suggests a new way to tune the magnetic response of magnetic nanocomposites.

Another interesting point to analyze is the effect that an increase in the global concentration of filler has on the magnetization curves for samples with and without clustering. ZFC-FC curves for different concentrations of maghemite in the PEO matrix were obtained by dc magnetometry. Figure 5a shows the obtained curves. A clear increase in T_B with the increase in NP content can be clearly observed. This change occurred along with a decrease in the magnetic susceptibility and a progressive saturation at lower temperatures in FC curves. A plot of the T_B vs maghemite concentration is presented in Figure 5b. A gradual increase in T_B can be observed between 7 K, corresponding to a sample with 1.3 wt% of maghemite, and 15.5 K, the maximum value attained for a dried NP sample (57

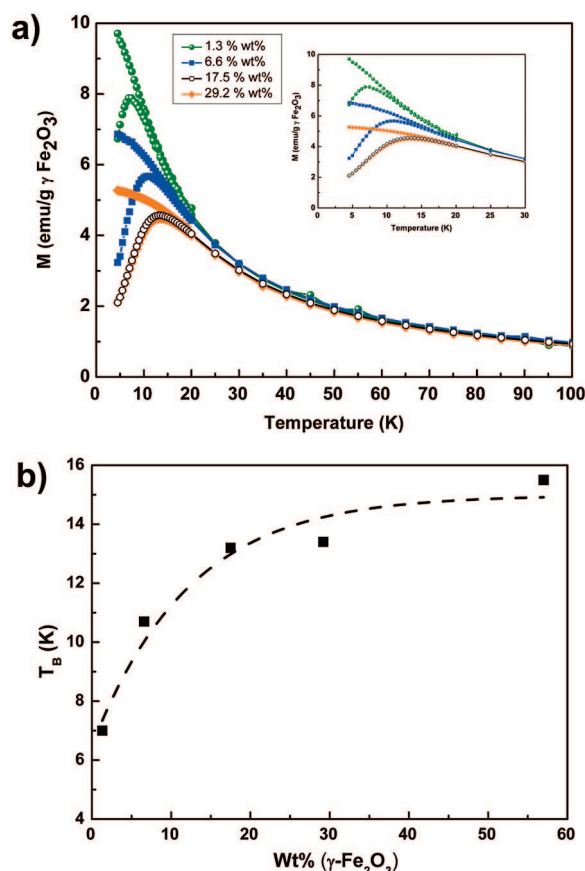


Figure 5. (a) Magnetization versus temperature measured at 100 Oe under ZFC and FC conditions for samples containing different concentrations of γ -Fe $_2$ O $_3$ NPs. The inset is an enlarged plot of the low temperature region. (b) Blocking temperature as a function of the total γ -Fe $_2$ O $_3$ content for PEO nanocomposites. The line serves only to guide the eye.

wt% of maghemite in the dried sample). The shape of the curve is similar to that obtained for Vestal et al.^{8a} for MnFe $_2$ O $_3$ distributed in eicosane and agrees with the general experimental observation of a progressive increase in T_B with concentration, obtained for dispersions of maghemite particles in a polymer.^{6a}

We analyzed a similar curve obtained for a set of PVB-based materials with variable NP concentrations.^{7a} In this case the absolute values of T_B cannot be directly compared with that of PEO composites because of slight differences in the size distribution of NPs used in both experiments. However, similarity of the samples still allows comparison of the curve shape of T_B vs concentration. As observed in Figure 6a, the shape of the curve differs from that found for PEO composites: T_B remains almost constant until about 10 wt%, indicating that dipolar interactions are negligible at high dilution; above this concentration, T_B shifts to higher temperatures as expected for an increase in the dipolar interactions. These results would show that below a critical concentration, dipolar interactions become negligible and the relaxation rate of the particles is independent of one another. A similar behavior has been reported by Frankamp et al., who determined the existence of two regimes in the curve of T_B vs interparticle spacing, d , for assemblies of magnetic NPs and polyamidoamine (PAMAM) dendrimers. In this work, they found a critical value of d above which very little interaction penalty was present, and T_B remained almost constant.¹² A similar “noninteracting” region was also observed by Jonsson and co-workers for highly diluted samples of a frozen ferrofluid of maghemite nanoparticles.¹³ Hence, both

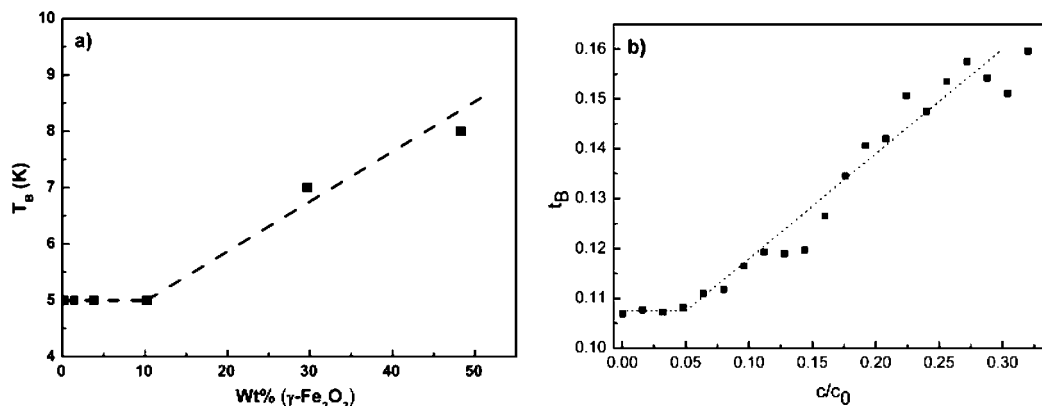


Figure 6. (a) Evolution of the blocking temperature with the volume fraction of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles for PVB nanocomposites. The line serves only to guide the eye. (b) Reduced blocking temperature versus the reduced sample concentration obtained from MC simulation.

kinds of nanocomposites are consistent with different experimental results observed in similar superparamagnetic arrangements of NPs. At this point it becomes useful to compare the experimental results with the expected behavior obtained using a computational simulation of the physical conditions of these systems.

MC Simulation. The behavior of a random arrangement of superparamagnetic NPs can be simulated using numerical methods. In this case, a Monte Carlo method¹⁴ was used to treat the influence of the dipolar interaction on the blocking temperature of a random distribution of superparamagnetic NPs with similar size (3.5 nm), anisotropy constant ($K = 6 \times 10^5$ emu/cm³), and saturation magnetization ($M_S = 203.4$ emu/cm³) than those corresponding to the experimental NPs used in this work.¹⁵ The experimental situation of a frozen ferrofluid without aggregations in which the positions of the particles and their anisotropy axes are kept fixed has been resembled. All the particles are considered identical (same size, anisotropy, and magnetization). In the superparamagnetic frame, monodomain particles with inner coherent magnetization rotation of the atomic moments are assumed. Hence, the total magnetic moment of the i -particle is $|\vec{\mu}_i| = M_S V$, where M_S is the saturation magnetization and V is the volume of each particle. The anisotropy of every particle is assumed to be uniaxial, with the anisotropy easy axes distributed at random.

For the simulation procedure, the energy of each particle is considered to have three main sources: anisotropy (E_A), Zeeman (E_H), and dipolar interaction (E_D). For the i -particle the anisotropy energy is given by $E_A^{(i)} = -KV(\vec{\mu}_i \cdot \hat{n}_i/|\vec{\mu}_i|)^2$, where K is the anisotropy constant and $\hat{n}_i$ is the unit vector that denotes the easy direction. The Zeeman energy for the coupling of the magnetic moment to an external magnetic field $\vec{H}$ is described by the usual way, $E_H^{(i)} = -\vec{\mu}_i \cdot \vec{H}$. The dipolar interaction energy between two particles i and j located at $\vec{r}_i$ and $\vec{r}_j$, respectively, is given by $E_D^{(ij)} = (\vec{\mu}_i \cdot \vec{\mu}_j)/r_{ij}^3 - 3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})/r_{ij}^5$, where $\vec{r}_{ij}$ is the interparticle distance. To take into account the long-range interactions, periodic boundary conditions have been applied in the same way as it was done in ref 14. The total energy of the system (E_T) is represented as

$$E_T = \sum_i E_i = \sum_i \left(E_A^{(i)} + E_H^{(i)} + \frac{1}{2} \sum_{j \neq i} E_D^{(ij)} \right) \quad (1)$$

To compute the energetic evolution of the system, the Metropolis algorithm has been used to drive the motion of the individual moments of the particles. In every MC step (that accounts for one time unit), a particle i is chosen at random, and a new possible orientation of its magnetic moment is

generated. The new orientation is accepted with probability $\min[1, \exp(-\Delta E/k_B T)]$, where ΔE is the difference in energy between the attempted and the current orientation, T is the temperature, and k_B is the Boltzmann factor. After each trial the time is incremented by N^{-1} (where N is the number of particles in the simulated sample) so that in one MC step N attempts are made. Simulations were made with $N = 125$, and the calculus was performed averaging over 500 different configurations of the sample. All results were calculated by using reduced units. The parameter varied is the unitless sample concentration c , defined as the ratio between the total volume occupied by the particles and the volume of the cell. It is treated by means of the related parameter c/c_0 , where $c_0 = 2K/M_S^2$ is a unitless material constant that characterizes the material. The temperature is introduced by $t = k_B T/2KV$, and the magnetic field by $h = H/H_A$. The temperature variation ratio was $0.001225KV/k_B$ every 200 Monte Carlo steps, under a small magnetic field of value $h = 0.1$. The magnetization to obtain the maxima of the ZFC curves was given in normalized units of M/M_S .

In Figure 6b the reduced blocking temperature ($t_B = k_B T/2KV$ where k_B is the Boltzmann factor, T is the temperature, and V the volume of the particle) is plotted against the reduced sample concentration (c/c_0). As can be seen, at low sample concentrations t_B remains almost constant, suggesting that particles behave independently of each other as a noninteracting system; at higher sample concentrations the blocking temperature increases clearly with the volume fraction. Hence, simulation results obtained for a random distribution of NPs are in good agreement with the behavior observed for PVB-based nanocomposites and confirm that curves obtained for PEO-based nanocomposites were strongly influenced by the presence of clustering. This is especially remarkable at low concentrations, where the increase in T_B observed for PEO-based nanocomposites is clearly provoked by the presence of very small clusters.

Conclusions

We have obtained free-standing superparamagnetic nanocomposites with well differentiated magnetic behavior by controlling the degree of dispersion of the magnetic NPs in the matrix. We also demonstrated that clustering, even in the submicrometric range, strongly controls the magnetic behavior of nanocomposites. This is an important point to be considered when T_B values coming from different works are compared and could explain contradictory results obtained in the literature for dispersions of the same kind of magnetic NPs. The increase in

the strength of dipolar interactions produced by the increase of the local concentration of NPs in the aggregated domains resulted in higher T_B values, lower magnetic susceptibilities, and broader peaks. From the application point of view, it is clear that the presence of NP clusters can affect, to a high extent, the magnetic behavior of the materials. However, it is important to note that changes in the magnetic response of PEO-based nanocomposites were not random but followed a coherent increasing tendency with concentration that could be used to tune the final behavior of nanocomposites. Our results also showed that the polymeric matrix is not a mere supporting media for the NPs of the composite, but its careful selection could be an important and versatile tool for the design of materials with new and improved magnetic properties.

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