Magnetic properties of conducting polymer doped with manganese–zinc ferrite nanoparticles

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Abstract

The magnetic properties of superparamagnetic particles are influenced by the supporting matrix. We have systematically studied the DC magnetic properties of loosely packed manganese–zinc ferrite ($Mn_{0.68}Zn_{0.25}Fe_{2.07}O_3$) nanoparticles synthesized using a reverse micelle technique. The results have been compared with those for particles suspended in paraffin wax and embedded in a polypyrrole matrix. The polypyrrole-doped particles were prepared using an *in situ* ultraviolet irradiation method and spin-coated into thin films. The loosely packed particles showed no resolvable coercivity even well below the blocking temperature. On the other hand, the same particles in wax showed the opening up of a large coercivity below the blocking temperature. However, both the samples showed characteristic superparamagnetic transition peaks in the temperature-dependent susceptibility nearly at the same temperature. The particles in the polypyrrole matrix showed a remarkable increase in the blocking temperature and large hysteresis at 300 K. The structural characterization of the polymer-doped sample showed clustering of the nanoparticles.

1. Introduction

The properties of magnetic nanoparticles are dramatically different from their bulk counterpart. When the size of the particles is reduced below the single domain limit (∼15–20 nm for iron and iron oxide), they show a number of novel properties like superparamagnetism, macroscopic quantum tunnelling, etc [1]. Since particles are generally dispersed in a non-magnetic matrix, it is important to investigate the influence of the carrier matrix on magnetism. Though the surface chemistry of the particles may not be directly affected by the matrix due of the coating of the particles by surfactant, matrix mediated particle agglomeration and magnetic interactions can affect the overall properties to a great extent. The main types of interactions that are prevalent in fine

magnetic particle assemblies are dipole–dipole interactions, exchange interactions, RKKY interactions through a metallic matrix when particles are also metallic, and super-exchange interactions when the matrix is insulating.

Polymers and paraffin wax have been traditionally considered as good carrier matrices for nanoparticles. Paraffin wax has been the carrier of choice for studies exploring relaxation phenomena with varying particle concentrations. On the other hand, several advanced polymer composites have been synthesized with a wide variety of inclusions like metals, semiconductors, carbon nanotubes and magnetic nanoparticles [2, 3]. Many attractive properties of polymers like non-corrosiveness, light weight, mechanical strength and dielectric tunability can be utilized along with novel magnetic and optical properties of nanoparticles to make multifunctional materials. The inclusion of ferromagnetic or superparamagnetic nanoparticles in polymers is especially

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important as magnetic nanoparticles have shown promise in various potential applications like spin-polarized devices, carriers for drug delivery, magnetic recording media, high-frequency applications, etc [4–6]. Recently, an effective industrial process for the mass production of polystyrene-coated iron nanoparticles was demonstrated using a microwave plasma method and the samples exhibited interesting magnetic switching characteristics [7, 8].

Conducting polymers have also found various applications due to their light weight, flexibility and ease of processing combined with high conductivity. Some of the potential applications include electromagnetic shielding in the form of coatings or sheaths [6, 9–11]. However, due to the high conductivity, eddy current losses in conducting polymers have been a problem. The composite system of conducting polymers and ferrite nanoparticles can be used as an effective coating for both magnetic and high frequency electromagnetic shielding. Ferrite particles have an added advantage of reducing the eddy current losses due to their high electrical resistance. Some of the soft ferrites like manganese zinc ferrites (MZFO) are also being extensively studied for RF applications such as inductors for resonant circuits, AC/DC converters, wide-band transformers, antennas, electromagnetic interference (EMI) suppression, etc [12–14]. Composite materials possessing both conducting and ferromagnetic properties are extremely useful due to their application potential in electrochemical display devices, sensors, broadband microwave absorbers and electromagnetic shields.

In this article we report on the magnetic properties of nanoparticles that are dispersed in various carrier matrices. To explore this issue we have compared the DC magnetic properties of manganese zinc ferrite (MZFO) nanoparticles with the particles suspended in paraffin wax and particles doped inside polypyrrole (PPy) synthesized using a UV-irradiation method.

2. Synthesis

2.1. Synthesis of manganese zinc ferrite nanoparticles

Monodisperse MZFO nanoparticles with an average size of 15 nm were synthesized using a reverse-micelle technique. For this sample, bis-(2-ethylhexl) sodium sulfosuccinate (AOT) was used as the surfactant and 2,2,4-trimethylpentane isooctane was used as the oil phase. The synthesis details are described elsewhere [13]. The stoichiometry of each sample was determined by ICP analysis to be $Mn_{0.68}Zn_{0.25}Fe_{2.07}O_3$. Powder x-ray diffraction confirmed the single phase and crystallinity of the material. The single domain nature of the as-prepared nanoparticles was also confirmed from magnetic susceptibility measurements that yielded a distinct peak in susceptibility at around 50 K separating the superparamagnetic state at high temperature from the blocked state at lower temperature. It should be noted that significant control of the micelle size in the 10–20 nm range achieved in this chemical method leads to the precipitation of monodisperse, single domain MZFO nanoparticles.

2.2. Synthesis of polypyrrole thin films doped with manganese zinc ferrite particles

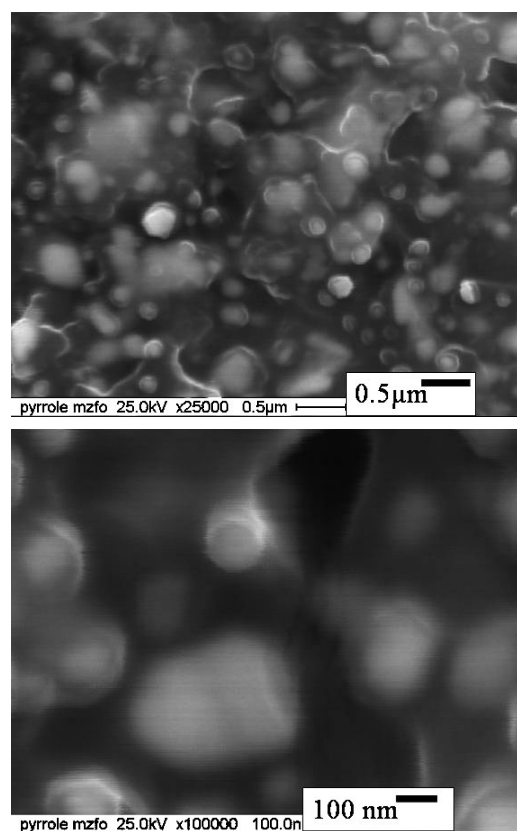PPy doped with MZFO nanoparticles was synthesized using a UV-irradiation technique [15]. This technique is considered

Figure 1. SEM images for two different resolutions of PPy doped with manganese zinc ferrite nanoparticles. Clustering of the nanoparticles can be seen.

as a simple single-pot room temperature reaction that can be scaled up to meet industrial requirements. In this technique, 10–15 molar% of silver nitrate ($AgNO_3$) is added to the pyrrole (C_4H_5N) as the electron acceptor for photo-polymerization, and the mixture is sonicated until the silver nitrate is completely dissolved. Though the pyrrole/salt solution polymerizes under UV light by itself, a photoinitiator was used to increase the rate and uniformity of polymerization. For this purpose, a cationic photoinitiator was chosen over radical photoinitiators due to its faster curing rates. CYRACURE UVI6992 from DOW Inc. was added to the pyrrole/salt solution in amounts of 0.3 wt%. MZFO nanoparticles in various concentrations were added to the solution and sonicated for five more minutes to achieve a uniform dispersion of nanoparticles. The solution was coated onto glass substrates using a commercial spin coater. The films were left overnight under UV light (365 nm) to allow polymerization, which resulted in films black in colour. The samples showed good room temperature electrical conductivity.

3. Structural characterization

The MZFO particles were characterized using a transmission electron microscope. The average particle size was found to be ∼15 nm. PPy films doped with MZFO nanoparticles were characterized by a Hitachi-800 scanning electron microscope (SEM). In figure 1 we have shown SEM images at two different resolutions for the same sample. It can be observed that the

nanoparticles agglomerate to form large clusters with varying sizes. Recently we have observed the same type of clustering for polystyrene-coated iron nanoparticles in PPy matrix [16].

4. Magnetic properties

Magnetic moment measurements were performed using a physical property measurement system (PPMS) from Quantum Design. Zero-field-cooled (ZFC) and field-cooled (FC) measurements were done at 100 Oe magnetic fields. To study the magnetic properties of the as-synthesized MZFO particles (without any matrix), the particles were dried of solution to form surfactant-coated particles in powder form. This powder was filled in a gelatin capsule in loosely packed form that provided these particles with rotational as well as translational degrees of freedom under applied magnetic field. In another case, the particles were homogenously dispersed in paraffin wax. For this purpose, the nanoparticles-loaded solution was dispersed in molten wax and sonicated in a hot water bath to allow the solvent to evaporate leaving a uniform dispersion of particles in wax. We have also compared the magnetic properties of MZFO nanoparticles doped inside the polypyrrole matrix using the technique described in the previous section. Note that the magnetic moment values in all figures are for qualitative comparison only because of the varying loading factor of the magnetic nanoparticles into various matrices.

In figure 2 we have presented the ZFC–FC curves for loosely packed MZFO nanoparticles, particles dispersed in wax (top panel), and MZFO particles doped inside a PPy matrix (bottom panel). It can be observed that both the loosely packed particles and particles suspended in wax show a well defined peak at 48 K, typical of a superparamagnetic to blocking transition. In the case of loosely packed magnetic particles, an external field can cause rotational and translational motion of individual particles that would effectively contribute to the temperature and field dependence of the overall magnetization. However, in this case, the applied field of 100 Oe was sufficiently low for such contributions to be present. This is also confirmed by the qualitative similarity of the ZFC–FC curves in figure 2 between the loosely packed particles and the sample with particles dispersed in paraffin wax. In the case of particles in wax, of course, any physical motion due to external magnetic field is arrested because of the constraining matrix. Overall temperature profiles of ZFC–FC curves show no major difference between the loosely packed particles and particles in wax. Small differences may be due to the change in the strength of interactions from one case to another as the total effective energy of an interacting superparamagnetic particle system is given by the following expression:

$$E = \frac{\mu^2}{d^3} \sum_{i,j} \frac{(\hat{\mu}_i \cdot \hat{\mu}_j) - 3(\hat{\mu}_i \cdot \hat{R}_{ij})(\hat{\mu}_j \cdot \hat{R}_{ij})}{R_{ij}^3}$$
$$- KV \sum_i (\hat{\mu}_i \cdot \hat{e}_i)^2 - \mu H \sum_i (\hat{\mu}_i \cdot \hat{H}).$$

The first term here represents the inter-particle dipolar interaction energy, where μ is the magnetic moment of each particle; R_{ij} is the centre to centre distance between the ith and jth particles measured in units of nearest neighbour distance d, and $\hat{\mu}_i$ and $\hat{\mu}_j$ are the spin directions of the ith
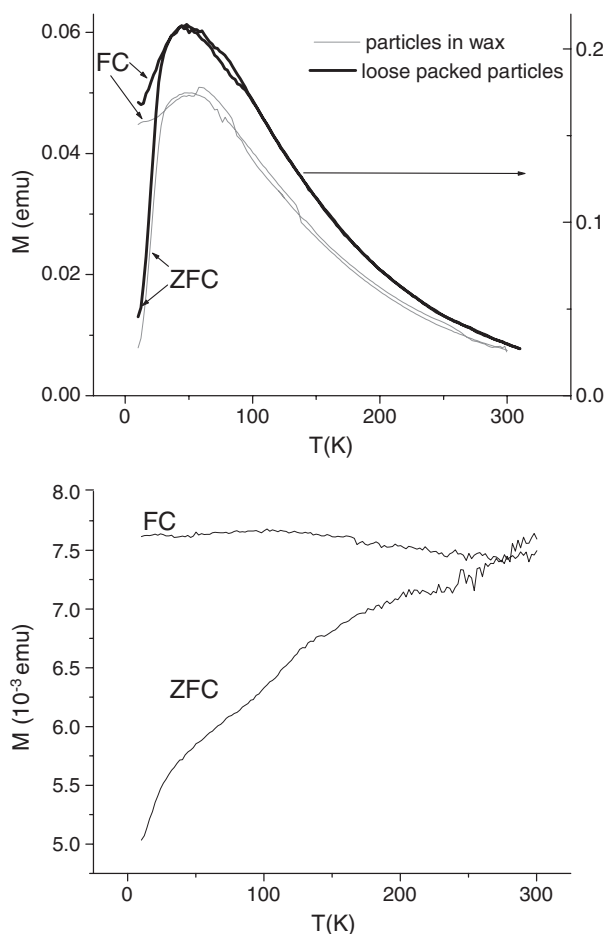
Figure 2. Zero-field-cooled and field-cooled measured magnetic moments for loosely packed manganese zinc ferrite particles, particles suspended in paraffin wax, and particles doped inside the polypyrrole matrix.

and jth spins. The second term represents the anisotropy energy, where K is the anisotropy constant and V is the volume of each particle; $\hat{e}_i$ is the easy axis direction. The third term represents the Zeeman energy, where $\hat{H}$ is the magnetic field direction. In this expression, dispersion in particle size has not been taken into account [17–20]. The dipolar interaction energy term in this expression depends upon the inter-particle separation. The width of the peak in the ZFC curve depends upon the distribution in effective anisotropy energy (KV) due to shape and size distribution. The sharpness of the ZFC peak in the upper panel of figure 2 reflects the highly monodisperse nature of the MZFO particles even after putting them in the wax matrix. This further demonstrates that suspension in wax is probably the best way to restrict agglomeration and have some variation over the inter-particle distance. On the other hand, it can be observed that the MZFO particles in the PPy matrix show a distinct change in the ZFC and FC behaviour. Here a large shift in the blocking temperature towards higher temperatures can be observed. The particles are coated by AOT, and even when agglomerated, it is likely that the surfactant coating around each particle is intact. Also, as is evident from the SEM images shown in figure 1, while being put in the PPy matrix, these particles tend to form clusters of various size ranges. The clustering

itself is due to steric forces in the polymer overcoming the natural tendency of the surfactant-coated particles to stay away from each other. These mechanisms contribute to the increase in the blocking temperature and broadening of the peak in susceptibility. Recently we have reported the synthesis and magnetic properties of polystyrene-coated iron nanoparticles doped inside a PPy matrix synthesized using photo-polymerization technique [16]. The polystyrene-coated nanoparticles for this study were synthesized using a microwave plasma technique. In this study too we saw evidence of clustering of polystyrene-coated nanoparticles in both microstructural as well as magnetic measurements. In the upper panel of figure 2, the FC magnetization data also show a downturn at low temperature. This signature is often seen in nanoparticle systems when the applied field (typically 50 or 100 Oe in ZFC, FC measurements) is not enough to overcome the effective anisotropy field of the system. At higher applied fields, this downturn is not seen, and one obtains the conventional FC variation in magnetic nanoparticles.

In figure 3, we have compared the $M-H$ loops at 300 K for three samples. It can be seen that the loosely packed particles as well as the particles in wax do not show any resolvable coercivity, but on the other hand, these particles doped in a PPy matrix show a significant difference with an opening up of hysteresis with coercivity of 272 Oe at 300 K. These results are consistent with the ZFC–FC and SEM results that show clustering of particles and an increase in the blocking temperature due to increased inter-particle interactions. While the presence of large clusters with agglomerated particles does favour enhanced magnetic coupling between particles in these clusters, there could be other contributions to the increase in blocking temperature in these polymer nanocomposite samples, such as effects due to shape anisotropy and matrix-mediated interactions. Systematic investigations in a variety of nanocomposite materials is needed to understand the various mechanisms that could contribute, and detailed discussions are beyond the scope of this paper.

In figure 4, we have shown a comparison between the low temperature $M-H$ curves. It can be seen that the particles suspended in wax show an opening up of hysteresis with a coercivity of $\sim$270 Oe, indicating a ferromagnetic behaviour. On the other hand, the loosely packed powders of the same material did not exhibit any coercivity even at 10 K, which is well below the blocking temperature. In the inset of each panel of the figure we have shown a zoom view for clarity. We believe that this absence of coercivity even in the ferromagnetic regime may be due to mechanical rotation and translation of the nanoparticles in the external magnetic field. This behaviour was also shown by some other loosely packed magnetic nanoparticle systems. The mechanism by which the magnetic moment of a loosely packed particle below the blocking temperature may relax after removal of a magnetic field involves the bulk rotation of the particle as the magnetic moments of the particles are fixed relative to the crystal axes of the particles. This mechanism is similar to the Brownian relaxation of the particles in fluid [21]. On switching the field from positive to negative values, the particles tend to align with the magnetic field and thus the hysteresis effect is lost. On the other hand, for such a system, above the blocking temperature, the magnetic moment vector itself is free to rotate in response
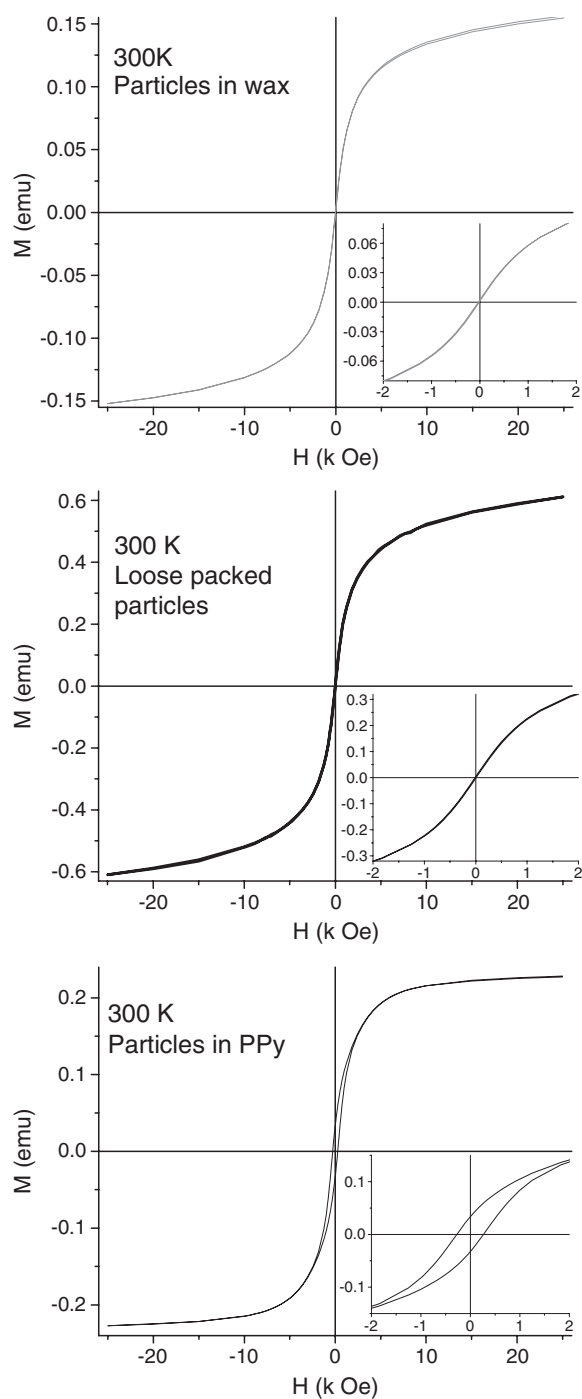

Figure 3. $M-H$ curves at 300 K of loosely packed manganese zinc ferrite particles, particles suspended in paraffin wax, and particles doped inside the polypyrrole matrix. The figure in the inset shows a zoom view.

to the applied field, while the particle remains stationary. This rotation is known as Néel relaxation. The response of the magnetization of such a system to alternating magnetic fields will be quite interesting.

In the lower panel of figure 4, we have shown the 10 K $M-H$ loop measurements on PPy-doped MZFO particles. We can see an increase in the coercivity from 272 Oe (at 300 K) to 540 Oe. The presence of variable size clusters ranging from single domain particles to possible multidomain agglomerates
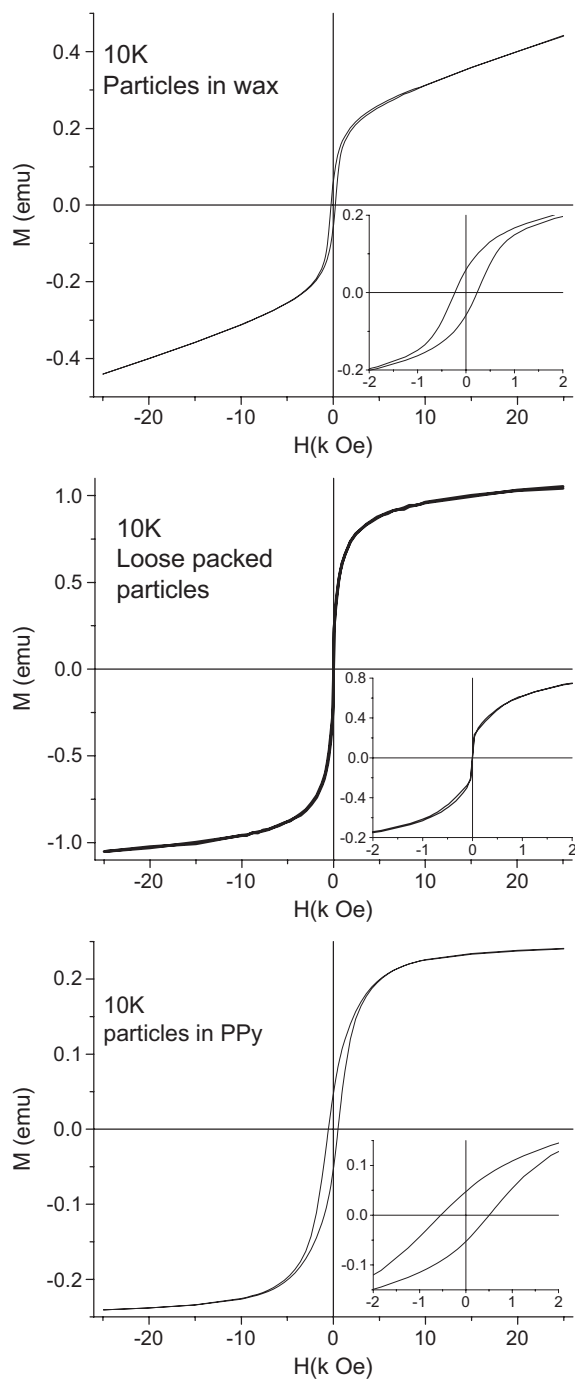
Figure 4. *M–H* curves at 10 K of loosely packed manganese zinc ferrite particles, particles suspended in paraffin wax, and particles doped inside a PPy matrix. The figure in the inset shows a zoom view.

makes the interpretation of the magnetization data somewhat complicated, as there would be a collective response from these different regions. However, our comparative experimental studies with particles in the paraffin wax matrix do clearly correlate the increase in blocking temperature in the case of the PPy-doped particle system to the presence of larger clusters and the associated increase in inter-particle interactions.

5. Conclusion

In this article we have studied in detail the effect of inter-particle dipolar and exchange interactions, physical motion of particles under applied magnetic field and clustering on the blocking temperature and coercivity at various temperatures. We have observed that the particles doped in wax do not agglomerate but the particles in a conducing polymer matrix form clusters of various size ranges. Loosely packed particles free to move about show no coercivity even below the blocking temperature, due to the instant rotation of the entire particle in response to the switching field.

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