Journal of Magnetism and Magnetic Materials 380 (2015) 221–226

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Effective particle magnetic moment of multi-core particles

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ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form
24 September 2014
Accepted 28 September 2014
Available online 6 October 2014

Keywords:
Magnetic nanoparticles
Magnetic relaxation
Multi-core particles
Single-core particles

ABSTRACT

In this study we investigate the magnetic behavior of magnetic multi-core particles and the differences in the magnetic properties of multi-core and single-core nanoparticles and correlate the results with the nanostructure of the different particles as determined from transmission electron microscopy (TEM). We also investigate how the effective particle magnetic moment is coupled to the individual moments of the single-domain nanocrystals by using different measurement techniques: DC magnetometry, AC susceptometry, dynamic light scattering and TEM. We have studied two magnetic multi-core particle systems – BNF Starch from Micromod with a median particle diameter of 100 nm and FeraSpin R from nanoPET with a median particle diameter of 70 nm – and one single-core particle system – SHP25 from Ocean NanoTech with a median particle core diameter of 25 nm.

1. Introduction

In biomedical applications where magnetic nanoparticles are used, both magnetic multi-core and single-core particles can be found [1,2]. Magnetic multi-core particles consist of several magnetic single-domain nanocrystals, geometrically positioned in different types of configurations while single-core particles only consist of one single-domain nanocrystal. Depending on the size distribution and configuration of the nanocrystals inside the multi-core particle and the hydrodynamic particle size distribution, different types of magnetic behavior can be obtained. The magnetization process of the magnetic multi-core ensemble will depend on both the individual magnetic moments of the nanocrystals as well as on the total effective magnetic moment of the particle (which in turn depends on both the magnetic moment values and moment orientations of the individual nanocrystals). Magnetic nanocrystals can be coarsely divided into small crystals that show internal magnetic relaxation, Néel relaxation, and larger crystals with thermally blocked magnetic moment where the nanocrystal magnetic moment is locked in a specific direction in the nanocrystal. If the magnetic nanocrystals are dispersed in a carrier liquid the nanocrystal magnetic moment can be decoupled from the physical particle rotation in the liquid and give rise to Néel relaxation, or the nanocrystal magnetic moment can be physically locked in the nanocrystal. In the latter case, magnetic relaxation occurs at the same rate as the rate of particle rotation in the liquid and gives rise to Brownian relaxation. The parameters that determine whether we have Néel or Brownian relaxation at a given temperature are the size distribution of the nanocrystals, the magnetic material properties (through the magnetic anisotropy), the viscous properties of the liquid and magnetic interactions between the nanocrystals (for instance the interactions between the nanocrystals in a magnetic multi-core particle system). In order to study the magnetic interaction effects in multi-core particles Monte Carlo simulations can be used [3,4]. In these simulations the effects of magnetic interactions between the nanocrystals in the multi-core structure, the nanocrystal size distribution and the magnetic anisotropy can be studied independently from each other. It is seen from these results that in order to

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http://dx.doi.org/10.1016/j.jmmm.2014.09.070
0304-8853/

fully understand the magnetic properties of magnetic multi-core particles it is important to include all of these effects.

2. Material and methods

The BNF Starch particles from Micromod are iron oxide based multi-core structured particles with a median particle size of about 100 nm. The particles are prepared by high-pressure homogenization according to the core–shell method [5]. The core of the multiple magnetite nanocrystals is coated with a shell of hydroxyethyl starch. The particles are supplied as suspension in water. The BNF particles are widely used in hyperthermia studies for cancer treatment [6–8] and show interesting properties as contrast agent for magnetic resonance imaging [9]. The FeraSpin R particle system from nanoPET is also an iron oxide multi-core particle system with a median particle size of about 70 nm. The FeraSpin R particles are carboxydextran coated multicore particles, i.e. the multi-core particles consist of clusters composed of smaller nanocrystals of about 5–8 nm [10,11]. The multi-core particles exhibit a size distribution with the smallest one comprising only one nanocrystal per multi-core particle and the larger ones containing multiple nanocrystals per multi-core particle. The Feraspin R multi-core particles are dispersed in water. In the case of the multi-core particles, the particle sizes are defined as the size of the clustered nanocrystals. One major application of FeraSpin R is its use as MRI contrast agent for small animal imaging for pharmaceutical research purposes. The SHP25 particle system from Ocean NanoTech is an iron oxide based single-core particle system (with only one core per particle) with a median particle size of 25 nm. The SHP25 particles are dispersed in water with amphiphilic polymer coating.

In order to study the dynamic magnetic properties, three AC susceptometers were used. The DynoMag system [12] was utilized between 1 Hz and 500 kHz, a lab high frequency AC susceptometer [13] was used in the frequency range between 10 kHz and 10 MHz and an additional lab high frequency susceptometer up to 1 MHz [14]. Measurements were carried out at 300 K.

Magnetization versus field was measured with a MPMS SQUID magnetometer from Quantum Design. The ultra-low field mode utility was used in order to optimize the low field magnetic measurements.

Transmission electron microscopy (TEM) was performed using two different instruments: (1) A FEI Tecnai F20 equipped with a LaB6 electron gun and operated at 200 kV and (2) a FEI Titan 80-300 equipped with a field emission gun and operating at 80 or 300 kV.

3. Results and discussion

In Fig. 1, TEM images of the BNF Starch and FeraSpin R multi-core particle systems and the SHP25 single-core particle system can be seen.

The median value of the multi-core particle size of the BNF Starch particle system is 100 nm with a distribution in diameters of ± 50 nm, by defining circles around the multi-core structures and determining the diameters of these circles. The multi-core particle size is defined as the total size of the clustered nanocrystals (see Fig. 4). An evaluation of 200 multi-core structures was carried out to determine the distribution of the particle sizes. The individual nanocrystal size in the multi-core structure is in the range of 10 nm–20 nm. For the FeraSpin R system the median total particle diameter was determined to be in the range of 70 nm with a distribution in diameters in the range of ± 50 nm and with individual nanocrystal sizes in the range of 5–10 nm. The

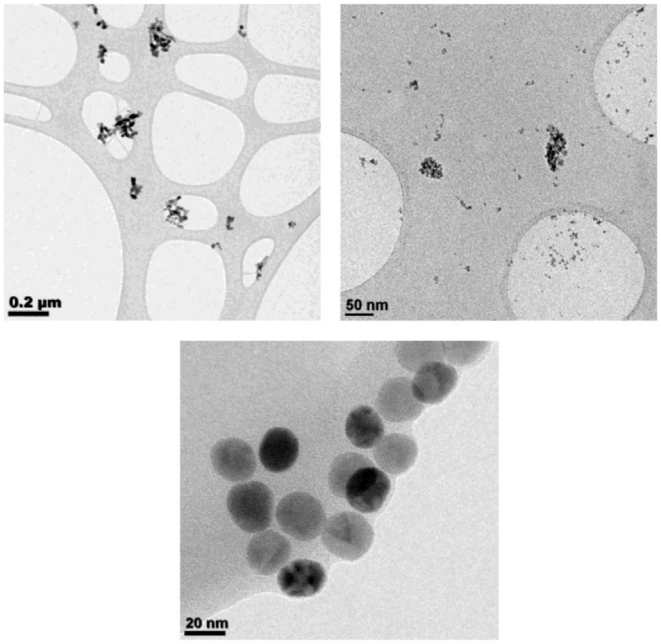

Fig. 1. TEM images showing the BNF Starch (left top) and FeraSpin R (right top) multi-core particles and SHP25 single-core particles (bottom). All particles in the images are dispersed on holey carbon films. In the two upper TEM pictures some of the multi-core structures are shown for the BNF Starch and FeraSpin R particle systems, together with free nanocrystals in the FeraSpin R particle system. Contrast variations among the individual single core particles are due to diffraction contrast in the TEM. The median diameter of the BNF Starch particle system is about 100 nm and 70 nm for the FeraSpin R particle system. The median diameter of the single-core SHP25 particle system is about 25 nm. The clustering of the SHP25 particles as seen in the TEM picture is due to the TEM sample preparation.

determined nanocrystal median diameter of the single-core particle system SHP25 is 25 nm with a distribution in diameters of about ± 5 nm.

In Fig. 2, AC susceptometry data of the three particle systems can be seen. From measurements on dilutions of the samples we found no evidence of interactions between the particles in the dynamic magnetic response (the concentration normalized AC susceptibility curves overlapped and the Brownian relaxation frequencies were constant with particle concentration). Therefore we give the dynamic susceptibility data given in Fig. 2 for the original particle concentrations.

In the AC susceptibility versus frequency data in Fig. 2b we can see three peaks in the imaginary part of the AC susceptibility at 460 Hz for the BNF Starch system, 1 kHz for the FeraSpin R system and 11 kHz for the SHP particle system. As was mentioned in the introduction chapter, magnetic particle systems (multi-core and single-core) can show Brownian or Néel relaxation when they are dispersed in carrier liquid. The type of relaxation depends on particle size parameters (hydrodynamic diameter D_H and nanocrystal diameter D_C), magnetic anisotropy (K), temperature (T) and viscosity (η) of the carrier liquid. From the Brownian relaxation time ($\tau_B = \pi D_H^3 \eta / 2kT$) and the Néel relaxation time ($\tau_N = \tau_0 \exp(K\pi D_C^3/6kT)$) where k is the Boltzmann constant and τ_0 the Néel relaxation pre-factor, it is possible to estimate the effective relaxation times for a specific particle system. If we take the BNF Starch system as an example (with $D_H = 97$ nm, $D_C = 20$ nm, $\eta = 10^{-3}$ Pa s, $T = 300$ K, $K = 2.10^4$ J/m^3 and $\tau_0 = 10^{-9}$ s) we get $\tau_B = 346$ µs and $\tau_N = 0.6$ s. Due to that $\tau_B << \tau_N$ the Brownian relaxation will dominate with a relaxation frequency of about 460 Hz ($=1/2\pi\tau_B$) which is the lowest relaxation frequency that can be obtained for this particle system. The same discussion has been carried out for the other two studied particle systems with the conclusion that they also relax substantially via the