MAGNETIC SURFACE EFFECTS IN MAGHEMITE NANOPARTICLES

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Magnetic properties have been analyzed on maghemite-polymer nanocomposites with low size dispersion and a regular distribution of particles in the polymer matrix. We have used polyvinylpyridine (PVP) nanocomposite samples containing isolated particles with narrow size distribution, high crystalline perfection, and regular inter-particle separation. A representative number of samples have been studied with a diameter size ranging from 1.5 nm to 15 nm and ±10% of size dispersion. The samples have been characterized by XRD, IR, TEM and small angle x-ray scattering (SAXS). The use of SAXS for size determination has guaranteed statistical representativity and no changes in particles due to specimen preparation.

Magnetic properties in nanoparticles are greatly influenced by structural factors as mean size and particle size distribution. TEM and SAXS are used to analyze the particle size and shape. SAXS analysis produces a scattering curve that provide information about the distribution of the size and shape of the nanoparticles. Although the TEM analysis performed gives excellent insight into the particle shape, SAXS provide better insight into the nanoparticles size distribution in the polymer matrix since the x-rays pass through the sample. The scattered intensity from nanoparticles interrelates with the scattering from polymer structure so an extensive analysis has been performed for accurate size distribution determination. SAXS curves on nanocomposite powder pellet samples are compared with those of pure polymer as shown in Fig. 1. We have considered that, in the nanocomposite, the polymer structure is changed by the particles at their characteristic size. At the intermediate angle range the scattering from the polymer structural level decays while the scattering from the particle appears. We have considered the case where the polymer contribution is negligible above an angle defined by the particles size. Following an unified approach [1,2] it is possible to calculate the mean diameter and the standard deviation of the particle distribution [3] and to determine the distribution profiles. Particle distribution has been also estimated applying the program GNOM [4] to the scattering from the particles.

Magnetization against field measurements have been carried out on maghemite-polyvinylpyridine (PVP) nanocomposites. Plots of the magnetization against H/T for various maghemite nanocomposites with different particle sizes can be explained assuming a bulk-like ferrimagnetic core and a shell composed of disordered moments [5,6]. Fitting data to a Langevin modified equation including a linear term [7] allows us to estimate the core saturation magnetization. In this core-shell model, Ms is proportional to the volume fraction of the maghemite-like core, $M_S = M_{S0}\left(\frac{(D/2)-d}{D/2}\right)^3$, where d is shell thickness. The variation of the cubic root of the saturation magnetization, $Ms^{1/3}$, with the inverse of the particle diameter, 1/(D/2), is quite linear (Fig.2). This indicates that the layer thickness does not vary with the particle size. The extrapolation of 1/(D/2) to zero gives an estimation of the core saturation magnetization, close to the bulk value. For particles smaller than 3 nm, layer thickness increases rapidly, and M_S is already zero for 2.5 nm particle size. Then below a critical size of about 2.5 nm the ferrimagnetic ordering is apparently lost in the whole particle. This is in good accordance with published Monte Carlo simulations [8].

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Figures:

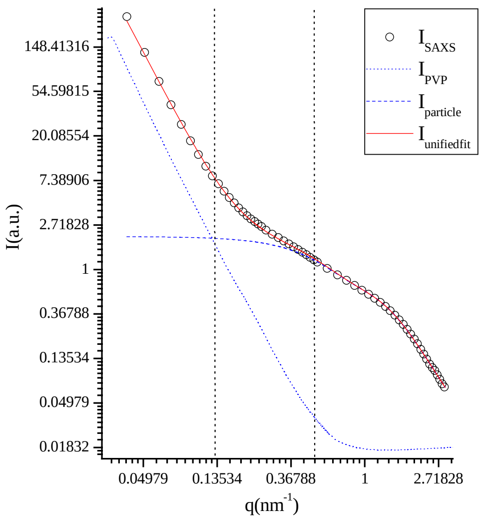

Figure 1. SAXS curve of a 6.84 nm sample.

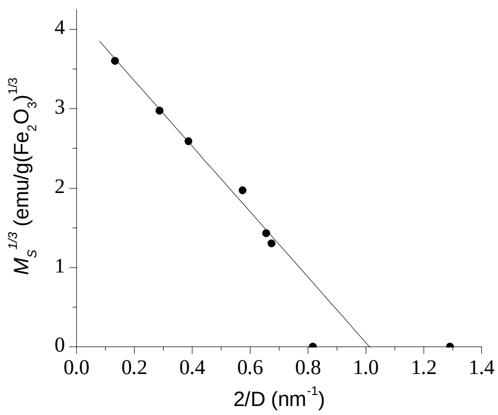

Figure 2. Linearization of Magnetization vs. size, where the constancy of thickness of the magnetically disordered layer d with the particles size can be observed.