DOE/ER/45692-1

Final Technical Report

Studies of Particulates and Structural Transformations in Glass Using Synchrotron Radiation

(Grant # DE-FG02-98ER45692)

DOE Patent Clearance Granted
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Abstract

The intial study (reprint enclosed) on nanoparticles of magnetite was carried out in an epoxy matrix. The formation of agglomerates of Fe_3O_4 nanoparticles was studied by μ-XRF, magnetic, TEM and SEM techniques. A published paper with these results is included. Because of the elevated viscosity of epoxy resin and its effect on particle agglomeration, this study was extended using less viscous polyvinyl alcohol and some sol gels as a matrix. Unlike the results found in epoxy resin, spherical agglomerates were found in a PVA matrix even at Fe_3O_4 concentration of up to 50%.

Introduction

Although we have done considerable work in the past with glass specimens, it was early realized that the fabrication of the amorphous samples containing nanosize particles could be accomplished more quickly and more efficiently, if we initially used an organic non-crystalline material to simulate glass. In our initial studies epoxy resin was chosen as a working matrix. It was planned to use synchrotron x-ray radiation to penetrate these samples, and characterize the particle distribution in the samples. Subsequently, transmission and scanning electron microscopy (TEM and SEM) were used to corroborate the x-ray data. However, before any of these studies were initiated, the samples were examined magnetically to select those samples appropriate for synchrotron x-ray and electron microscopy analysis. It was hoped that the x-ray data coupled with the magnetic measurements could then be developed into a useful tool for future material science investigations of nano and submicron size magnetic and non-magnetic particles in an inert matrix. As detailed below, promising results have been obtained using these techniques, but further work is necessary in order to produce samples with tailored suspensions of the magnetic phase at high concentrations.

Accomplishments to Date

The initial study on nanoparticles was carried out entirely with an epoxy matrix into which nanosize magnetite particles were loaded[1]. Iron or magnetite (Fe_3O_4) particles of this size will oxidize quite rapidly, when exposed to air, and therefore it is not feasible to produce such small particles by simply grinding larger particles under dry conditions, and then incorporate the smaller ground particles into the polymeric matrix. To preclude oxidation, it is necessary to immerse the particles of this size in an inert matrix. A simple alternative is to start with magnetite ferrofluids containing particles nominally in the 10 nm range[2-5], and incorporate them into a non-magnetic matrix. Magnetite particles of this size do not oxidize in a ferrofluid because they are coated with a fluid-compatible surfactant, which prevents oxidation. Initially, low concentrations (0.03 to 0.5% Fe_3O_4) of 10 nm magnetite particles were incorporated into epoxy resin. It was noted that the Fe_3O_4

particles tended to cluster and be unevenly distributed, unless the samples were agitated by exposure to ultrasonics as the epoxy hardened. In this concentration range the micro-x-ray-fluorescence (μ-XRF) and transmission electron microscope studies showed the presence of spheroidal agglomerates of Fe_3O_4 particles. The agglomerates ranged in size from 100 to several thousand nanometers, and yielded smooth hysteresis curves with a coercive force corresponding to a particle size commensurate with 10 nm particles. The small coercive force indicated that, although the agglomerates were fairly dense, the individual particles did not interact magnetically. Electron micrographs also showed that the particles were not in physical contact. It was postulated that these agglomerates were formed by magnetostatic attraction prior to the epoxy hardening. The individual particles apparently maintained their coating of surfactant they had in the ferrofluid, which prevented physical contact.

The results can be summarized as follows:

Magnetite Concentration, wt.%	Mode of Agglomeration
<0.5	Spherical agglomerates, mostly in the 100 – 500 nm range
0.5 – 2	Combinations of spherical agglomerates
>2	Large, (10 – 20 μm), irregular coalesced agglomerates

Following the general explanation in the literature, it was conjectured that, due to their intrinsic magnetism, 10 nm particles of this size are attracted to each other in a fluid matrix. In the case of epoxy resin the matrix remains fluid for about 10 minutes or so before hardening. Therefore, densely packed spheroidal groups of particles (agglomerates) are formed. It would appear that, if the matrix is fluid for a longer period of time, or the concentration of particles is high, then the agglomerates tend to coalesce. The cause of the agglomeration was attributed to long-range magnetic forces. As shown in the table, the agglomerates are small at low concentrations (<0.5 %), and no strong magnetic interaction is observed between the particles. This would be the case, if the particles were separated by a film of surfactant on their surfaces. However at higher concentrations (>2.0 %) the greater magnetostatic forces, due to the larger agglomerates, could cause the particles to make physical contact in spite of the surfactant film on their surfaces. As a consequence the magnetic properties of the large structured agglomerates approach that of a single ferromagnetic particle. Along with the large agglomerates, smaller agglomerates were also observed. Scanning electron micrographs (SEM) showed that the large agglomerates were irregular in shape and about an order of magnitude larger than the spherical agglomerates observed at lower concentrations. It may be that, as the groups of agglomerates become larger, the magnetic attraction also becomes larger, and squeezes the surfactant out so that many of the initially isolated particles come into physical contact. A copy of a published paper with these results is included at the end of this report.

Unfortunately, after the initial study with epoxy resin, we no longer had access to μ-XRF facilities, but continued the study using magnetic, TEM, and SEM techniques. These studies have been extended to polyvinyl alcohol (PVA) and recently to glasses prepared through a sol gel route. As the PVA was less viscous, it was found that the Fe_3O_4 mixed relatively uniformly without recourse to ultrasonic assistance. Also, it tended to remain fluid for a longer period of time compared to epoxy resin. The samples were prepared over a large concentration range (0.1 to 60 % Fe_3O_4). Up to 60 % Fe_3O_4, it was established from the hysteresis curves that there was no magnetic interaction among the individual particles. This further indicated that the individual magnetite particles were not in physical contact. However, before PVA dries out and hardens, there is sufficient time for the individual particles to move freely, and they may form agglomerates. As shown by the TEM in Figure 1, the presence of small loosely packed agglomerates (50 - 250 nm size) is observed both when 12 % magnetite is present and also when 53 % magnetite is present, but the agglomerates are larger and denser in the 53 % magnetite sample.

Figure 1a Sample:PVA 248
52.9% Fe_3O_4 100,000X

Figure 1b Sample 1b: PVA 250
11.97 % Fe_3O_4 100,000X

The presence of ionic iron in concentrations up to 10 percent did not influence the magnetic properties contributed by the 10 nm magnetite particles. However, the magnetic measurements indicate that about half of the ferric iron added to the PVA is reduced to ferrous iron. This reduction appears to be independent of the concentration up to about 10 % ionic iron.

The findings concerning the studies of PVA-based magnetic composites are included in a manuscript of a second paper, currently in preparation.

Sol gel glasses have a greater thermal stability than polymers, and also better chemical durability. Following an extensive and time-consuming investigation, with many initial failures, we have succeeded in incorporating ferrofluid suspensions into sol-gel matrices produced by carefully controlled, catalyzed hydrolysis of tetramethoxysilane. Characterization of these samples is still in progress. As in the case of PVA, it has proved possible to prepare sol-gel matrices incorporating both magnetite particles and dissolved iron ions introduced from aqueous solutions of the corresponding salts.

Breulman and Cölfen[6] have added nanosize Fe_3O_4 particles into a polymeric gel, but found that the gel attacked or etched the magnetite particles so that only a small core remained. Consequently the magnetite cores were smaller, and the authors were unable to obtain a hysteresis curve except by cooling the sample to about 5 K. We have been able to prepare samples in which the sol gel did not attack the 10 nm magnetite and we were able to obtain good hysteresis curves at room temperature (See Figure 2). The remanent magnetization, and coercive force are essentially the same values found for 10 nm particles in the ferrofluid. The fact that our sol gel did not attack the magnetite particles may be attributed to the mildly acidic, iron-based catalyst, which we used.

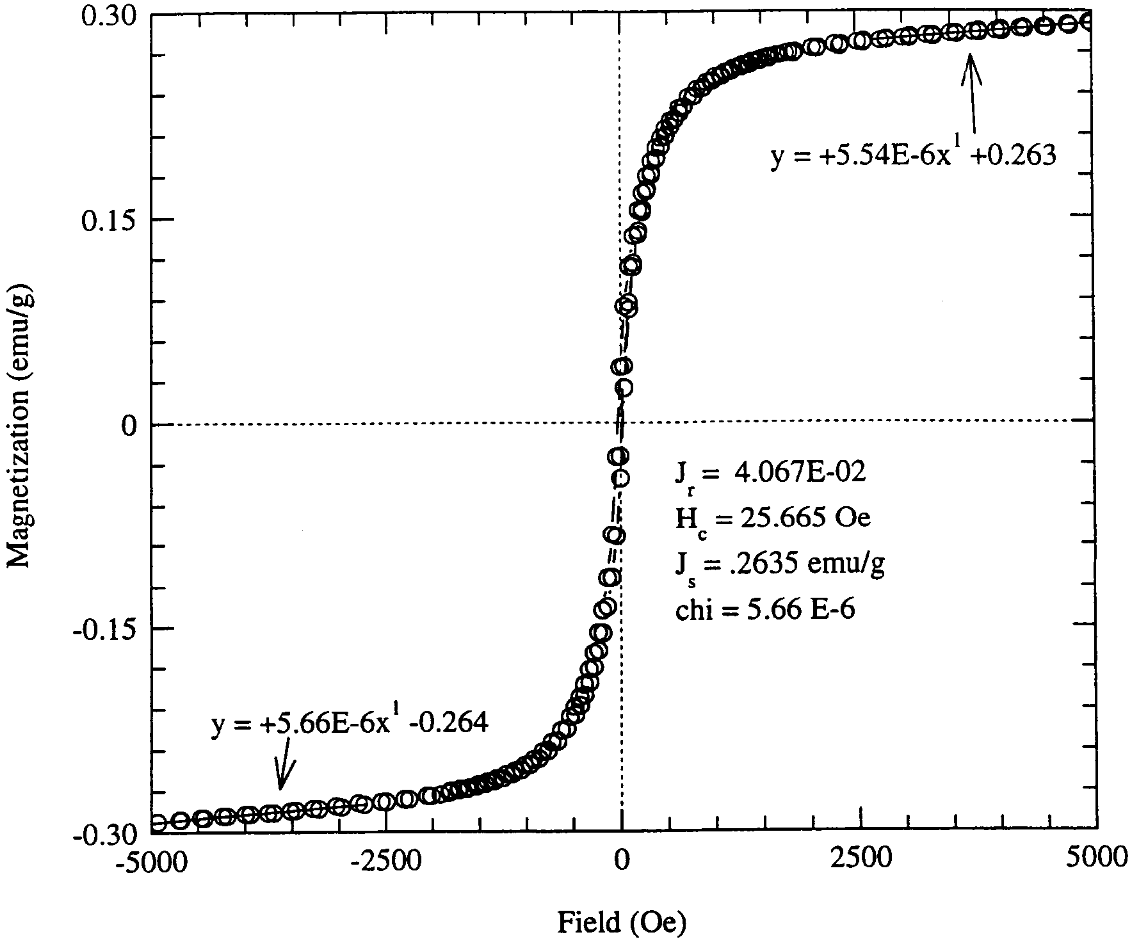

Figure 2 - 0.2 % $FeCl_3$ + 0.4 % Fe_3O_4

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Magnetization, micro-x-ray fluorescence, and transmission electron microscopy studies of low concentrations of nanoscale Fe_3O_4 particles in epoxy resin

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(Received 11 February 2000; accepted 14 August 2000)

Magnetization measurements, transmission electron microscopy (TEM), and high-resolution micro-x-ray fluorescence (μ-XRF) using a synchrotron radiation source (Advanced Photon Source) were used to examine Fe_3O_4 particle agglomerates of nominally 10-nm particles at low concentrations (down to 0.03%) in thick epoxy resin samples. The magnetization measurements showed that at low concentrations (<0.5%) the magnetite particles, although closely packed in the agglomerates, did not interact magnetically. Predicated on a 2-μm sample step scan, the μ-XRF results were compatible with the presence of spherical agglomerates due to magnetostatic attraction, and these ranged in size from 100 to several thousand nanometers, as observed in TEM measurements. At smaller step scans the resolution could be significantly improved. Thus, the synchroton μ-XRF method was very useful in detecting very small concentrations of particles in thick samples and could probably be used to detect particles in amounts as low as 10^{-16} g.

I. INTRODUCTION

A major trend in modern materials science and related fields is the fabrication, characterization, and application of materials containing nanoscale particles.[1,2] Much of the work to date has been performed with relatively high concentrations (>1 wt%) of such particles. At low concentrations the interparticle distances become so large that it is difficult to find and focus on individual particles or small agglomerates using a scanning electron microscope (SEM) or a transmission electron microscope (TEM). As there is no need to focus on individual particles when making magnetic measurements, magnetic studies are useful in studying low concentrations of particles, especially when coupled with other techniques. In this study commercial magnetite ferrofluids were used as a source of nanoscale Fe_3O_4 particles to prepare samples at low concentrations.

Superparamagnetic-size (single domain) magnetite particles behave as individual dipoles. In an aqueous solution they are free to move under the influence of thermal agitation, and therefore, due to dipole–dipole interactions, they tend to agglomerate.[3] In any event, the dipoles tend to neutralize each other so that the resultant remanent magnetization of the fluid is essentially zero.[4] In ferrofluids, the particles are generally coated with a surfactant that, because of its thickness, establishes a minimum interparticle distance, and prevents interactions (agglomeration) due to short-range van der Waals forces.[5] At first glance, in the absence of a magnetic field the magnetite particles in a water-based ferrofluid would be expected to be uniformly dispersed. However, as pointed out by Krueger,[3] agglomeration has been observed in ferrofluids in several types of experiments, particularly at high concentrations, even in the absence of an external magnetic field. Commercial water-based ferrofluids typically have concentrations of about 20 wt% Fe_3O_4, whereas kerosene-based ferrofluids have concentrations of about 14% magnetite.

In this investigation ferrofluids containing small particles of magnetite (nominally 10 nm, but with a size distribution of 2 to 30 nm) primarily at concentrations of

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less than 0.5 wt% were studied. A commercial water-based ferrofluid was therefore diluted by mixing it with epoxy resin. In this way a stable suspension was obtained, which could be used for subsequent studies. Such studies include magnetic measurements, micro-x-ray fluorescence (μ-XRF), and TEM.

II. EXPERIMENTAL

The samples were prepared by mixing known amounts of an aqueous suspension of nominally 10-nm magnetite particles (Ferrofluids Corp., Nashua, NH Cat. No. EMG 605) in bis-phenol-based epoxy matrix, using sonication to attain uniform dispersion, and then hardening the resin by means of a polyamine-based hardener. It was noted by examination at 126× (optical microscopy) that in the cases of samples containing >0.5% magnetite, the magnetite formed relatively large clumps. These clumps were irregular but somewhat spheroidal in shape and consisted of magnetite particles. These clumps were often several tens of microns across. Because the samples used in this study were at relatively low concentrations (<4%), large clumps were not anticipated in light of the work by Peterson and Kreuger.[6] At zero field they found no evidence of large agglomerates at high concentrations of Fe_3O_4. To break up the water-based ferrofluid, which is immiscible with the epoxy, each sample was exposed to ultrasonic vibration for about 1 min before addition of the hardener. To confirm the concentration of magnetite in the loaded epoxy, the samples were ashed and redissolved in HCl,[7] followed by the determination of the iron content using an inductively coupled plasma spectrometer (Perkin-Elmer Plasma 400, Norwalk, CT). In sonicated samples with <0.5% magnetite, no large clumps were observed. Instead, the samples contained spherically shaped aggregates, i.e., groups of particles no larger than 1–2 μm across.

The excited fluroescence lines of the sample were measured as the sample was scanned with a high-energy x-ray beam University of Michigan-Howard University-AT&T-Collective Access Team (MHATT-CAT) at the Advanced Photon Facility, Argonne National Laboratory, Argonne, Illinois.

The samples were further characterized by additional measurements. The transmission spectra of the samples in the ultraviolet (UV) and visible ranges were measured by means of a Perkin-Elmer Lambda 4 spectrophotometer. The magnetization of the samples was measured using a vibrating sample magnetometer (VSM). SEM was performed using a JEOL 5300 (Tokyo, Japan) instrument with a primary beam voltage of 20 kV and equipped with an energy-dispersive x-ray (EDX) spectrometer using a Kevex SiLi detector (San Carlos, CA). The samples were further examined with a transmission electron microscope (Hitachi 8700-HU11, Tokyo, Japan).

III. RESULTS

A series of epoxy resin samples containing various concentrations of magnetite were prepared. The UV-visible measurements gave largely featureless spectra, which are characteristic of particle scattering. The transmittance gradually decreased with decreasing wavelength, and the samples became opaque at the absorption edge around 320 nm. The predominant shape of the spectra was characterized of scattering by particles with sizes smaller than, or similar to, the wavelength range over which these spectra were taken. XRD measurements on samples with a high concentration of magnetite (approximately 5 wt%) confirmed that the predominant species in the epoxy matrix was magnetite.

It is pertinent to inquire whether the aggregates of magnetite contained water from the original ferrofluid. Heating the epoxy samples in a microwave oven did not cause any destruction or breakup of the aggregates. It was therefore tentatively concluded that there was no water present and that the spherical shape was due to magnetostatic forces as suggested by Chantrell *et al.*[5]

The magnetic properties of the loaded epoxy resin samples were determined with the VSM both at room temperature and at liquid nitrogen temperature. Hysteresis curves determined for samples containing Fe_3O_4 concentrations greater than about 1.5 wt% were somewhat irregular and not typical of 10-nm particles or bulk magnetite. However, at lower concentrations smooth hysteresis curves were observed at a relatively low magnetic field (<5000 Am^{-1}). These curves were more typical of hysteresis curves of 10-nm particles. For example, a typical curve for 0.39% magnetite in epoxy is shown in Fig. 1. The irregular hystersis curves found at the higher concentrations may be related to the results of Rosman *et al.*[8] who found that at low concentrations the agglom-

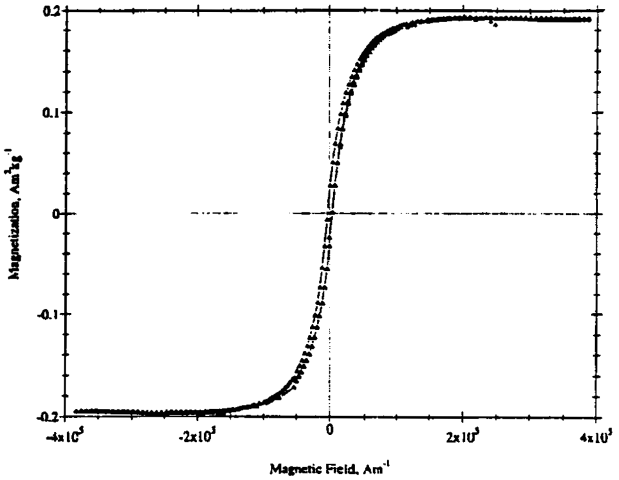

FIG. 1. Hysteresis curve for 0.39% magnetite as aqueous globules in epoxy resin.

erates tend to be two-dimensional, whereas at higher concentrations the agglomerates start to develop a three-dimensional or bulk structure. For example, a 3.4% magnetite epoxy sample, which showed abundant evidence of clumping, as observed by scanning electron microscope, also gave a very irregular hysteresis loop.

If there were no magnetic interactions between the particles within the agglomerates, there would be no increase in the coercive force due to packing,[9] and therefore the coercive force would be a function of particle size only. The coercive force of small noninteracting particles is known to increase with particle size up to a maximum value. For example, Ebisawa *et al.*[10] found that the coercive force of noninteracting magnetite particles increased with particle size up to a maximum value of about 200 Am^{-1} for particle sizes of about 5 nm or greater. The coercive force for our loaded epoxy resin samples ranged from 40 to 60 Am^{-1}, a relatively narrow range, with a mean value of about 51 Am^{-1}. The nearly constant value of the coercive force suggested that the particles were all about the same size. From the general shape of the coercive force versus particle-size curves reported by Tanaka *et al.*,[11] the particles in the resin should be of the order of 10–20 nm, i.e., essentially the same size as that specified for the particles in these ferrofluids.

For a given set of noninteracting subdomain size particles, such as in the agglomerates in this study, the coercive force of each particle is a function of the square root of the absolute temperature, $T^{1/2}$. The measured hystersis curve is a summation of the magnetic properties of all the particles. Qualitatively, the change with temperature can be seen in Fig. 1 showing the hysteresis curves for the 0.39% sample at 77 and 298 K. Bean and Livingston[12] derived the following expression for the coercive force of a sub-domain particle:

$$H_c = 2KV \cdot [1 - 5\,(\mathrm{k}T/KV)^{1/2}]/\mu \quad , \tag{1}$$

where K is the magnetic anisotropy, V is the particle volume, μ is the magnetic moment, T is the absolute temperature, and k the Boltzmann constant. Based on this relationship, Bean and Livingston[12] showed that at the onset of superparamagnetism and at temperatures below the blocking temperature, T_B the coercive force becomes zero. Thus

$$KV = 25\mathrm{k}T_B \quad . \tag{2}$$

For a plot of H_c versus $T^{1/2}$, the intercept I at $T = 0$ is

$$I = 2KV/\mu \quad . \tag{3}$$

Candela and Haines[13] have shown that for a size range distribution of superparamagnetic particles, a linear plot is obtained, which verifies Eqs. (1) and (2). If we plot H_c versus $T^{1/2}$ for the sample shown in Fig. 1 (plot not shown), the data fall on a straight line where $I = 167$ for $T = 0$, and $H_c = 0$ for $T = 576$ K (the blocking temperature). From Eq. (1), the slope S of this line is $[-10\,(\mathrm{k}KV)^{1/2}]/\mu$, and therefore

$$\mu = 50\mathrm{k}I/S^2 \quad . \tag{4}$$

It can be shown that by dividing the total magnetic moment in Eq. (4) by the saturation magnetization σ and the density ρ of magnetite, the volume V per particle of magnetite can be estimated as

$$V = 50\mathrm{k}I/(\sigma\rho S^2) \quad . \tag{5}$$

For the sample in Fig. 1, and using $\sigma = 92$ A m^2/kg and $\rho = 5.18$ g/cm^3 for magnetite, one can calculate the volume per particle to be 5×10^{-17} cm^3. Assuming that the particles are spherical, this volume corresponds to a diameter of about 23 nm. Keeping in mind that coercive force goes up rapidly with particle size,[10] this is a reasonable value.

In general, the saturation magnetization of the samples at low concentrations increased linearly with the concentration of magnetite in the epoxy matrix. The individual particles were less than a single domain in size (superparamagnetic), and therefore it appeared that there was little interaction of particles below a concentration of 0.5 to 1 wt%. Above this concentration, and for reasons described above, there was no longer a regular relationship between magnetization and concentration, although in general, the saturation magnetization increased as the concentration increased.

As noted above, relatively large elongated clumps of magnetite particles were observed with an optical microscope in samples containing more than 0.5% magnetite but were not visible in samples of lower concentrations. Using an SEM, clumps of the order of 50 μm were observed in the 2% samples, but no clumps were seen in the 0.39% magnetite sample. This is consistent with the magnetic data. TEM measurements on thin sections of the 0.39% and 0.03% samples showed the presence of small particle agglomerates [see Figs. 2(a) and 2(b)]. A typical low-concentration sample (<0.4%) observed with a TEM contained a relatively large number of empty bubbles produced by the ultrasonic agitation, and a relatively small number of opaque agglomerates. By changing the focus, these agglomerates appeared to be roughly spherical and ranged in size from about 100 nm up to several thousand nanometers. The 10–25-nm particles observed in the present study were similar to those previously reported.[14] However, the present study indicated that these particles were much more loosely dispersed as shown by Rosensweig.[14] To shed some light on the magnetostatic explanation, very fine dry ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), a nonferromagnetic iron compound, was mixed in epoxy, sonicated, and hardened. Subse-

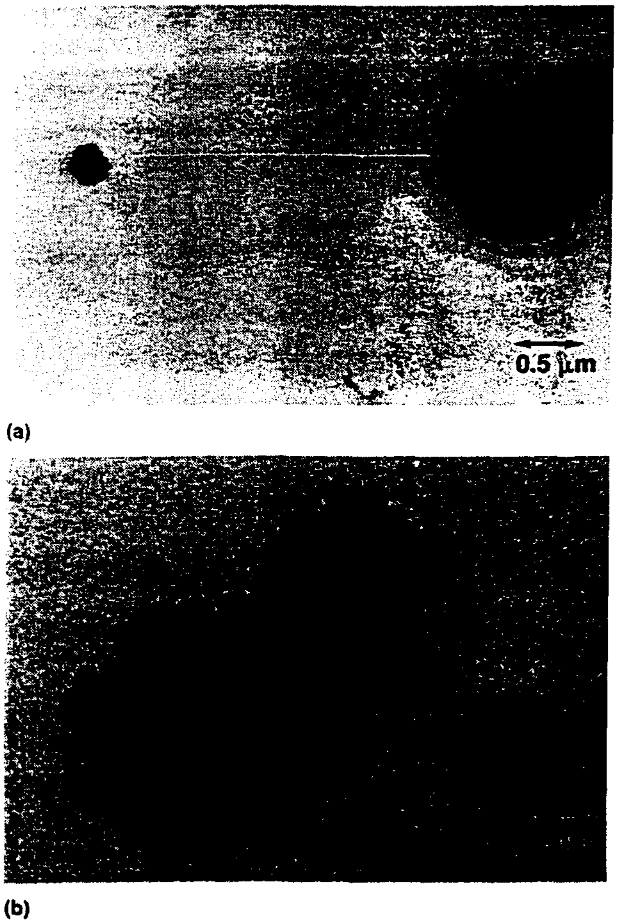

FIG. 2. TEM photographs of the agglomerates. Partially filled globules are shown in (a), and at higher magnification the individual magnetite particles can be seen at (b).

quent examination revealed the presence of empty air bubbles and a few nonspherical agglomerates (probably as a result of electrostatic forces). Following sonication, the water disappeared during the hardening stage, probably by diffusion into the epoxy. Therefore, in the case of the magnetite dispersions the magnetostatic forces produced the spherical agglomerates of magnetite particles while still in the aqueous phase. After and during the hardening stage the water was displaced by epoxy and the magnetite agglomerates maintained their spherical shape.

One also needs to consider the fate of the surfactant initially present in the aqueous dispersion. As the surfactant effectively kept the individual particles separated in water, magnetic particle interaction was small, and the coercive force was relatively low. During incorporation of the ferrofluid into the epoxy, the surfactant appeared to remain on the surface of the magnetite particles, and kept the individual particles separated. This was evident by the lack of change in the coercive force when the ferrofluids were incorporated into the epoxy. In the TEM photograph of Fig. 2(a), the opaque inclusions are actually spherical agglomerates. There are two close-packed agglomerates and also two regions containing only a few particles. The particles appeared to be lying on a spherical surface such as the inside of a globule. From Figure 2(b) one can see that the individual particles in the agglomerates are about 10–25 nm in size. The typical size is around 20 nm. This observation is in good agreement with the value deduced on the basis of applying Eq. (5) to the results of the magnetic measurements (see above). Furthermore, the individual particles in the agglomerates are far enough apart to preclude any significant magnetic interaction. No individual 10-nm particles were observed outside of the boundary of the agglomerates. Again, the observation of the subnanometer particle separation was in good agreement with the conclusions of the magnetic studies. From the nominal size of the individual particles one can calculate their volume and mass. For the 0.39% sample, we estimate about 5×10^{15} particles per cc. For a full aggregate 1 μm in diameter, there would be about 10^6 particles per aggregate.

A study using similar concentrations of magnetite, originally present in kerosene-based ferrofluid, also produced spherically-shaped aggregates in the epoxy, strengthening the evidence for magnetostatic forces being the cause of the formation of spherical aggregates.

X-ray fluroescence experiments were carried out at the MHATT-CAT Sector at the Advanced Photon Source (APS). A microfocus x-ray beam from an undulator source was used to explore the effectiveness of using μ-XRF in characterizing small particles present at low concentrations in polymeric or glassy matrices. Two typical small rectangles of the loaded epoxy resin samples (0.39% and 0.03% magnetite), on which magnetic studies have been made, were further studied by μ-XRF using the APS synchrotron. The dimensions of the 0.39% and 0.03% magnetite samples were 2.71 × 2.13 × 7.33 mm and 3.13 × 3.16 × 4.96 mm, respectively. The two samples were placed side by side in the sample holder with the 0.03% sample on the left and the 0.39% sample on the right. Using a Newport PM-500 motion controller the combined samples were scanned in the *x*-direction along the 2.71- and 3.13-mm sides, respectively. The x-ray beam (white radiation) had a spot size 1.2 μm wide and 2.5 μm high, i.e., slightly smaller than that reported by Lechtenberg *et al.*[15] An Amptek 13 mm^2 solid-state detector (Stafford, TX) was used to measure the fluorescent radiation. About 400 discrete data points (about 20 μm apart) were recorded across each spectrum. Data for each point were typically collected for 20 s by delaying subsequent steps. The detector was gated and cleared between steps. Figure 3(a) shows a single scan for both samples (contact between samples is at 6200

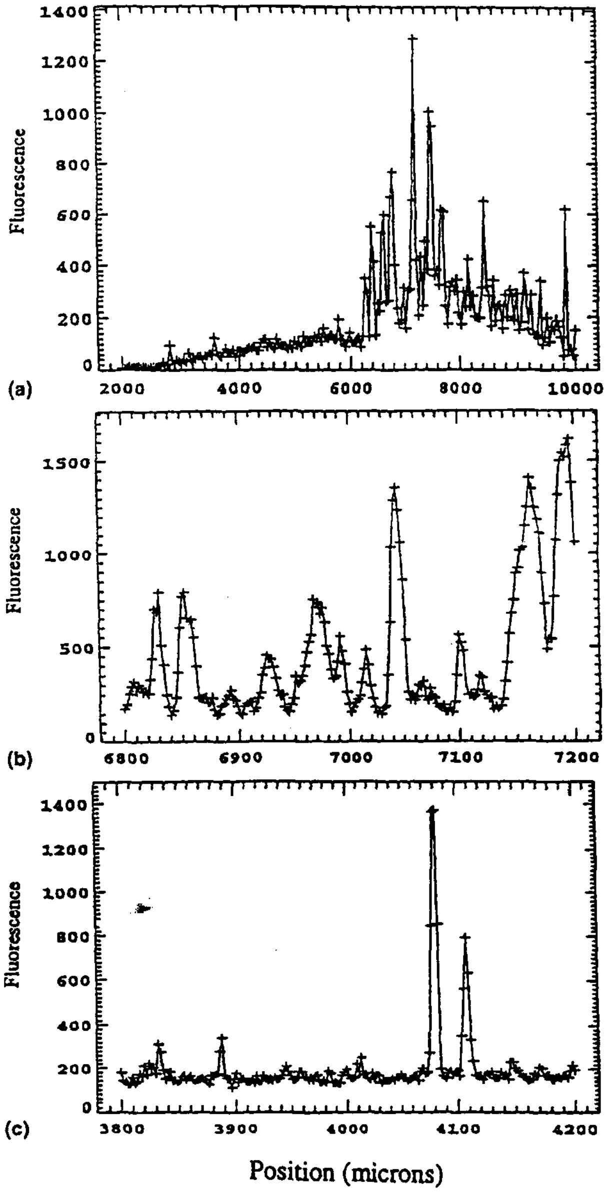

FIG. 3. (a) Fluorescence as a function of position for the 0.03% (left of 6200 μm) and the 0.39% (right of 6200 μm) magnetite (epoxy samples) using 200 scan points. (b) Expanded portion of the spectrum of the 0.39% magnetite/epoxy sample only. (c) Expanded portion of the spectrum of the 0.03% magnetite/epoxy sample with a discriminatory level set to filter out background noise.

μm) and Figs. 3(b) and 3(c) are subsequent scans (in a different position) for each sample on an expanded scale. The difference in concentration is evident from the number of peaks in each sample in Fig. 3(a). The spectrum in Fig. 3(c) is the best of the three spectra, as some of the background interference was filtered out.

Clearly, the TEM photographs showed that aggregates of magnetite particles were formed, which correspond to the peaks observed in the μ-XRF spectra. In samples with magnetite concentrations below 0.5% magnetite, the magnetic measurements showed that the individual particles within an aggregate did not interact with one another (see above). The separation among particles could be clearly seen in the TEM photographs. Care must be exercised in the determination of the size of the aggregates observed by the μ-XRF method, since the radiation completely penetrates the sample, and aggregates at different depths in the sample may be observed simultaneously. From Fig. 3(c) it appears that most of the peaks in the filtered spectrum fall into two categories, namely, the narrowest peaks with a base of about 7 μm, and the rest with considerably wider bases. The narrowest peaks probably correspond to single aggregates, whereas the wider peaks may be caused by a combination of aggregates at various depths. As expected, the base of the narrowest peaks are larger than any of the aggregates observed by TEM. This is due to the size of the beam and dispersion of the x-rays in the sample. Thus, the μ-XRF method may appear to yield aggregate sizes larger than the actual size, but the size could be consistent with the TEM results when corrected for beam size and dispersion effects.

Alternatively, the peaks can be analyzed in terms of the total counts. For example, the peak at about 4080 μm [Fig. 3(c)] has a width of about 20 μm, and has about 1100 counts. For this size range the beam size and dispersion effects should be negligible and can be compared to the smallest peaks of about 50 counts. Thus, by proportion the smallest peaks in the spectrum [Fig. 3(c)] correspond to an agglomerate diameter of the order of 1 μm (1000 nm). This estimate, of course, assumes that a single aggregate is being observed, and could be misleading if there are additional overlapping particle aggregates at different depths in the sample. The broader peaks in Fig. 3(c) are undoubtedly due to overlapping of the signals of one or more aggregates at a certain depth with additional signals due to the presence of further aggregates deeper in the sample. Considering that the results obtained in this study were obtained with a single detector and considering the small x-ray detection angle subtended, larger and/or multiple detectors should be able to examine aggregates or single particles down to the order of 0.01 μm (10 nm) or better.

IV. DISCUSSION AND CONCLUSIONS

A water-based ferrofluid was used as a source of small magnetite particles (10 nm); it was loaded into epoxy resin as an aqueous slurry, dispersed ultrasonically, and finally hardened with a catalyst. TEM observations showed that in samples with magnetite concentrations below 0.5%, individual magnetite particles, 10–25 nm in diameter, formed mainly close-packed aggregates. Magnetization measurements confirmed that (i) the particles were close to an average diameter of approximately 20 nm; (ii) the particles within each aggregate were separated from one another and did not interact magnetically; and (iii) at high concentrations the hysteresis curves were erratic. The TEM and magnetic data, in agreement with the results of SEM and μ-XRF measurements, indicated that the spherical agglomerates at low concentrations were probably close packed and confined to the space of the original aqueous globule (with the water subsequently removed and replaced by the epoxy). On the other hand, at high concentrations, the larger amount of the aqueous ferrofluid was not as finely dispersed by the ultrasonic waves, and resulted in larger, nonspherical inclusions in the epoxy, as observed by TEM and SEM. The magnetite particles could move within these inclusions under the influence of a magnetic field. (It should be noted that according to Chikazumi *et al.*[4] motion of magnetic moments does not necessitate free motion of the net volume of the particles.) For this reason, the hysteresis curves at high magnetite concentrations tended to be erratic, whereas at low concentrations normal smooth hysteresis curves were obtained.

Our results show that μ-XRF with its high intensity microbeam is capable of detecting magnetite agglomerates at much lower concentrations in thick samples. The large amount of power in the APS undulator beam was reduced to only a few watts by the white beam slits upstream of the focussing mirrors, thus reducing the incident power on the sample to less than a watt.[16] There were no observed changes in subsequent TEM measurements on the samples to indicate thermal or radiation damage from the synchrotron x-ray microbeam. This finding could be particularly important because of the potential application of the technique to opaque samples and nonmagnetic small particles. Since the samples can be positioned in the beam arbitrarily they can be of any geometry with a wide range of thickness. Choosing different sample orientations and scan directions, directional information could be derived in some cases.

Although additional work is required, the initial results reported here indicate that μ-XRF measurements using the high-intensity APS beam provide a powerful tool for the characterization of solid nanodispersions at very low concentrations. TEM can be used to detect nanodispersions, but only in thin samples (up to 200 nm) at concentrations of >0.1%. At low concentrations TEM measurements become difficult because of the large inter-agglomerate distances. The synchrotron μ-XRF extends the range of sample size to samples several orders of magnitude greater in thickness than those that can be characterized by TEM. Because of the capability of the μ-XRF to detect small concentrations of particles in thick opaque samples, the absolute detection limit provided by the method is extremely low, and is about 10^{-16} grams.[17] The results of these experiments, using various direct-observation techniques to study the magnetite/epoxy nanodispersions, confirm the conclusions based on the magnetic measurements.

ACKNOWLEDGMENTS

The authors are very grateful for the measurements made by the MHATT-CAT group at the Advanced Photon Source facility at the Argonne National Laboratory. MHATT-CAT is supported by the United States Department of Energy (DOE) Grant No. DE-FG02-94ER45513. This work was funded in part by the DOE under Grant No. DE-FG02-98ER45692. The authors are indebted to Dr. M.A. Adel-Hadadi for his assistance in analyzing the chemical composition of the samples, to E. Gresham for assistance with the TEM measurements, and to S. Magee for help with the SEM observations.

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