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Effect of cycling on the magnetization of ion exchanged magnetic nanocomposite based on polystyrene

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Magnetic nanocomposites containing iron oxide particles embedded in a polymer matrix have been synthesized using the method of ion exchange. They have been characterized by using low temperature and room temperature magnetic measurements and Mössbauer spectroscopy. The iron content in these samples has also been determined. The results have been analysed and explained. The physical and chemical properties of these nanocomposite materials are different from those of the bulk. Some of the unique properties of these materials find application in information storage, color imaging, ferrofluids and magnetic refrigeration. © *2001 Kluwer Academic Publishers*

1. Introduction

Particles possessing nanometric dimensions lying in the range 1–10 nm are found to be exhibiting superior properties compared to their bulk counterparts [1–3]. It is also reported that for small particles the energy level spacing of quantised electronic states is comparable to kT at temperatures of 1 K and so it is possible to observe quantum size effects at finite temperatures in such small particles [4]. Also, the large reduction in linear dimensions and the boundary and surface conditions play an important role in moulding the physical properties of small particles. Magnetic properties of small particles are of immense importance because of their potential applications. Magnetic nanocomposites and magnetic nanomaterials have an important place among nanomaterials and they have the potential to replace many of the conventional magnetic materials.

Nanocomposites with magnetic nanoparticles dispersed in polymer matrices have gained considerable attention because of their wide ranging applications. Below a critical size they become single domain as against the multidomain in bulk. These composites exhibit remarkable properties like superparamagnetism, quantum tunneling of magnetization and magnetocaloric effect [5–7]. They also exhibit large coercivity values. Such changes in physical properties, brought about by the dimensional changes, make these materials attractive for many applications including magnetic recording, ceramics, catalysts, colour imaging and magnetic refrigeration [7, 8].

Studies carried out on nanometric magnetic particles include ultrafine metallic iron and iron alloy particles as well as nanometer sized iron oxide particles embedded in Al_2O_3, SiO_2, porous glass and nonmagnetic polymer matrices [9–12].

Attempts are made to acquire expertise on the preparation of nanostructured materials and gain control over physical properties, so as to tailor materials for potential applications. Synthesizing magnetic nanocomposites based on γ-Fe_2O_3 gives scope for the development of newer materials with improved magnetic and electrical properties. There are different methods like sol gel, gas phase condensation, high energy ball milling and ion exchange, for the preparation of magnetic nanocomposites.

It is well known that above a critical temperature called the blocking temperature (Tb) they do not exhibit any hysteresis loop. Reports as regard the Tb are also varied. For instance, some researchers have reported the Tb to be below room temperature [1, 12] while others have found the Tb of some nanocomposites to be above room temperature [13, 14]. So it is interesting to investigate the hysteresis behaviour of these nanocomposite samples as well.

In this paper the preparation of magnetic nanocomposites containing γ-Fe_2O_3 embedded in a polymer

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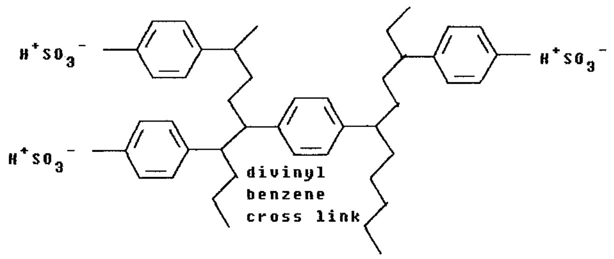

Figure 1 Structure of sulphonated polystyrene chain.

matrix of sulphonated polystyrene by the method of ion exchange is reported. Samples have been prepared using both weak and strong ion exchange resins. Different methods of preparation have also been tried. The prepared samples have been characterized by techniques like X-ray powder diffraction (XRD), vibrating sample magnetometry (VSM), chemical analysis and Mössbauer spectroscopy. An attempt is also made to investigate the exhibition of hysteresis behaviour by these samples at room temperature. Decomposition studies on these prepared samples were also carried out to study the effect of temperature on the particle size.

2. Experimental

Nanometer sized γ-Fe_2O_3 particles were embedded in a polymer matrix by the method of ion exchange. The method adopted here is a modification of the preparation scheme reported by Ziolo *et al.* [15]. The polymer matrix employed is a cross linked polymer of sulphonated polystyrene and divinyl benzene, which have exchangeable H^+ ion containing $SO_3^-H^+$ groups. The schematic of a polystyrene structure is shown in Fig. 1.

The ion exchange resin was exchanged with Fe^{2+} ions from an aqueous solution of ferrous sulphate followed by thorough washings to remove excess Fe^{2+} ions. These exchanged Fe^{2+} ions were then converted into $Fe(OH)_2$ by the addition of alkali solution of NaOH. This was then oxidized to yield, presumably, γ-Fe_2O_3. Drop wise addition of dilute aqueous solution of H_2O_2 accelerated the conversion to oxide. The resin was then washed with water and then dried. Instead of adding H_2O_2, the addition of hydrazine hydrate solution was also tried which resulted in the same end product but with a lesser yield. The process of preparation up to the conversion to hydroxide was carried out in an oxygen free atmosphere. The reaction was carried out in a glass reactor set up with provisions for heating. The entire preparation scheme is depicted in Fig. 2.

Samples were prepared by using both weak and strong ion exchange resins, and were labeled as WRC and SRC9 respectively. Samples were also synthesized with H_2O_2 and with hydrazine hydrate and were coded as SRC9 and SRC6 respectively. Cycling of the preparation procedures was also done on one sample of strong ion exchange resin. These cycled samples are labeled as SA1, SA8 and SA12 for 1st, 8th and 12th cycled samples respectively.

Initial characterization of these samples was carried out by using XRD, room temperature Mössbauer spectroscopy and iron content estimation. Different sets of

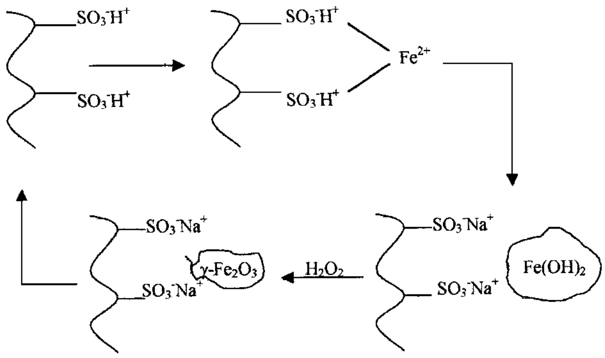

Figure 2 Schematic of the nanocomposite preparation procedure.

samples were further characterized by magnetic measurements by employing VSM.

XRD spectra of the samples were recorded using Rigaku Dmax C powder diffractometer using Cu K_α radiation. Room temperature magnetic measurements on all these samples were carried out by using VSM (model PARC 4500).

Fe content in the cycled samples was estimated by the same method used for estimation of iron in iron ores [16]. ^{57}Fe Mössbauer spectra of these samples were recorded at room temperature using a constant acceleration Mössbauer spectrometer and the spectrum was fitted to obtain the quadrupole splitting and isomer shift.

To study the effect of heating on the sample, decomposition studies on these samples were carried out. For this the sample was heated at different temperatures in air namely 200, 250 and 400°C and the XRD spectra were recorded afterwards.

3. Results and discussion

The XRD spectrum of a representative sample is shown in Fig. 3. The XRD pattern exhibits a broad peak centered at around $2\theta = 35.5^\circ$ which corresponds to a d value of 0.2528 nm which is characteristic of γ-Fe_2O_3 [17]. The reported d value for γ-Fe_2O_3 is 0.252 nm.

Magnetisation measurements on weak and strong ion exchange resins were carried out by using VSM and a representative hysteresis loop is shown in Fig. 4. The results are given in Table I. The results reveal that strong resins can exchange more Fe^{2+} ions than weak resins

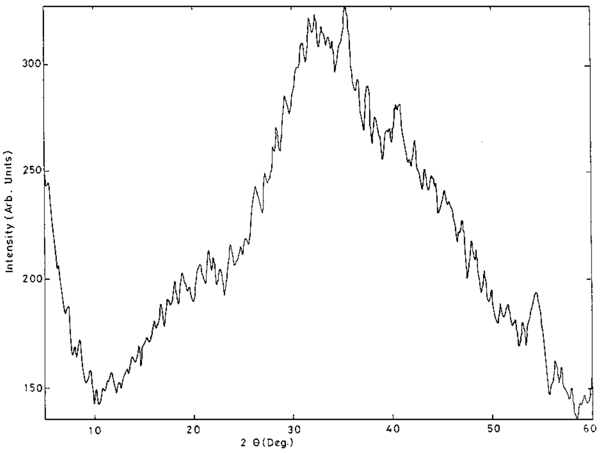

Figure 3 XRD spectrum of a representative sample.

TABLE I Room temperature VSM results of nanocomposite samples

Sample ID	Saturation Magnetization (M_s) Am^2/kg	Coercivity (H_c) A/m	Remanent Magnetization (M_r) Am^2/kg
WRC	0.78	10270	0.066
SRC6	1.47	7165	0.14
SRC9	1.99	7165	0.15
SA1	4.55	4219	0.39
SA8	8.50	5254	1.10
SA12	9.18	4936	1.39

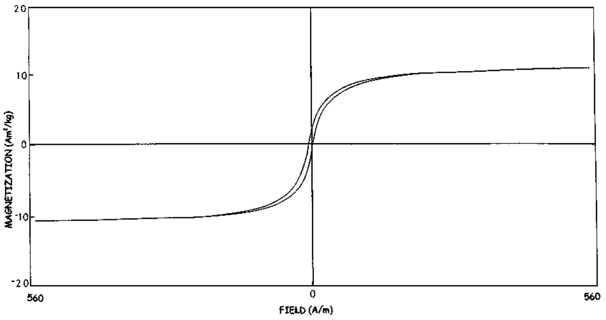

Figure 4 Hysteresis loop of a representative sample.

and hence yield more magnetic component in the matrix. This may be attributed to the existence of more ion exchange sites available in the strong ion exchange resin matrix. Magnetisation results on samples prepared with and without hydrogen peroxide show that addition of H_2O_2 increases the oxidation of $Fe(OH)_2$ to γ-Fe_2O_3 and hence creates more magnetic particles in the matrix. Thus the addition of H_2O_2 is found to give a better yield as far as the magnetic component is considered. Cycled samples show more magnetization compared with the uncycled ones and the saturation magnetization is found to increase with the increase in number of cycles. Thus cycling induces more magnetic component in the matrix as more sites are exchanged and the content of Fe_2O_3 is increased which is evidenced by the increase of Fe concentration in the nanocomposite. However, there exists a maximum value of the saturation magnetization (Ms) that could be obtained for the composite. This has been theoretically calculated to be around 16 emu/g [1]. It is to be noted that in our set of experiments a maximum of about 9 emu/g was obtained for the composite corresponding to 12 cycles.

Most of the reported literature indicates that magnetic nanocomposites do not show hysteresis at room temperature and hysteresis is observed only below the blocking temperature which is normally well below room temperature [1, 12]. But there also exist reports on nanocomposites with blocking temperature much above room temperature [13, 14]. Room temperature VSM measurements conducted on these samples exhibited hysteresis loop properties of a typical ferromagnetic system. This result is in conformity with the results obtained by various researchers [13, 14]. T. Ambrose *et al.* [13] have reported Tb to be much above room temperature in Fe-Al_2O_3 systems. Roy *et al.* [14] have also reported Tb to be above room temperature in Fe/SiO_2 system.

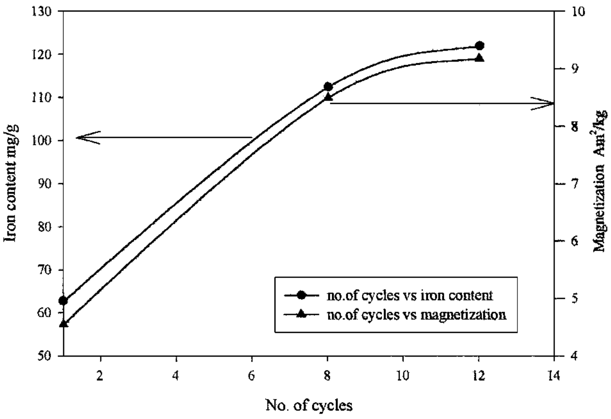

Figure 5 Fe content and saturation magnetization vs. number of cycles.

Low temperature magnetic measurements were conducted on SA12 sample and the results show an expected increase in magnetization with decrease in temperature.

The Fe contents on cycled samples were also estimated. Fe content and saturation magnetization versus number of cycles were also plotted for SA1, SA8 and SA12 and is shown in Fig. 5. The results indicate an increase in Fe content with the increase in number of cycles. It can be noticed that as cycling increases the iron content also increases which in turn increases the saturation magnetization. This is evident from the graph showing Ms/Fe content versus number of cycles. Differentiation between Fe^{2+}/Fe^{3+} is not possible by these techniques and only the total amount of Fe present in the composite is evaluated. Moreover it cannot be said for sure whether these reactions have resulted in Fe_3O_4 or γ-Fe_2O_3 in the matrix. However, the method of preparation adopted can result in only γ-Fe_2O_3.

The superparamagnetic behaviour of the samples is due to their small grain size. The Fe^{57} Mössbauer spectrum of a representative sample (SRC4) recorded at room temperature is shown in Fig. 6. The Mössbauer spectrum could satisfactorily be fitted, based on a computer program code developed by Bent *et al.* [18], with two doublets corresponding to Fe^{3+} in A and B sites. The relative intensities of the A and B site spectra are in the ratio 85 : 15. The Mössbauer parameters from the

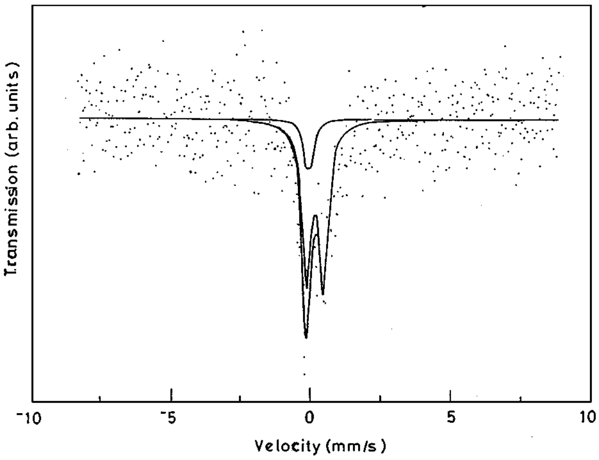

Figure 6 Mössbauer spectrum of the sample SRC4 at room temperature.

TABLE II Mössbauer results on SA4 sample

Doublet	C.S. mm/s$^+$	Q.S. mm/s	Linewidth mm/s	Relative intensity
I	0.26	0.60	0.40	85
II	0.02	0.20	0.30	15

$^+$relative to Fe at room temperature.

fittings are shown in Table II. The values reported here are in agreement with the values reported by Shull *et al.* [12]. The room temperature Mössbauer spectrum for γ-Fe_2O_3/polymer nanocomposite reported by Shull *et al.* corresponds to a central doublet with an isomer shift of 0.3 mm/s and a quadrapole splitting of 0.6 mm/s.

Subsequent XRD analysis conducted on the decomposed samples reveal that as firing temperature is increased the alpha phase of the iron oxide becomes predominant and the composite loses its magnetic characteristics. It may also be noted that the degree of crystallinity also increases. The average particle size evaluated by employing Scherrer's formula indicates that the decomposed samples exhibit an average particle size lying in the range 30–50 nm. Traces of FeO also have been detected.

4. Conclusion

Magnetic nanocomposites containing γ-Fe_2O_3 nanocrystals embedded in a polymer matrix have been synthesized by ion exchange by using both weak and strong resins and precipitation reaction. The polymer matrix provides localized nucleation sites and imposes an upper limit to the particle size, thereby minimizing the degree of aggregation. These studies indicate that by cycling the preparation steps and by the addition of dilute H_2O_2 one can achieve good yield as far as the magnetic component is considered. Fe content enhancement with cycling tallies well with the magnetization measurements. Further studies on these samples using low temperature and high temperature magnetization measurements and low temperature and high temperature Mössbauer spectroscopy are in progress.

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