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Production of magnetic nanoparticles in a polyvinylpyridine matrix

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Abstract

A commercial polyvinylpyridine polymer has been used for the in situ preparation of magnetic nanocomposites. Several procedures have been followed in the preparation of the nanoparticles based on the formation of polymer–metal complex gels. The use of mixtures of protic and aprotic solvents for the reaction of the polymer with the metal salts is discussed. Superparamagnetic nanoparticles of CoO and Fe_2O_3 have been obtained with an average size of 50 and 10 nm, respectively. The utility of nitrogen base polymers for the fabrication of magnetic nanocomposites is emphasized. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer nanocomposites; Magnetic nanoparticles; Metal oxides

1. Introduction

Magnetic nanocomposites have many possible technological applications [1,2]. Several solid matrixes have been used in this kind of material including gels, glasses, zeolites, metals, etc. Although, the most suitable matrix will always depend on the future application of the material, organic polymers have been often a suitable choice because of their high processability and versatility. The in situ precipitation of the magnetic particles in a polymeric matrix is an excellent method to control the mean size and size dispersion of a nanoparticle population. Polymers employed for this purpose in the past have been selected from various considerations. Sulfonated polymers have often been used due to the capability of the sulfonic groups to retain metal ions [3–5]. Polymers with a tridimensional structure, such as ion interchange resins, have rigid pores that set an upper limit to the size of particles that grow inside [6]. Diblock copolymers, composed of a part with charged radicals and another part with hydrophobic groups, contain polar nanoregions of a controllable size and shape [7] that serve as excellent sites for the encapsulation of inorganic particles [8]. Cross-linking iron ions in polysaccharide complex gels are known to act as nucleation centers for iron oxide nanoparticles [9]. Polypirrole polymers have been chosen as electrical conductive matrixes [10]. Phenolic polymers permit the fabrication of submicron spherical composites [11]. In general, polymers used as a matrix for the precipitation of magnetic nanoparticles are polyelectrolytes because of their capability to absorb metal ions. However, neutral polymers might be more advantageous concerning processability and versatility. Recently, we have successfully grown several kind of magnetic nanoparticles in N-based polymeric matrixes[12]. In this work, a commercial poly(4-vinylpyridine) (PVP) polymer has been used to produce nanocomposites of iron and cobalt oxides. As a precedent, Mössbauer spectroscopy studies had already revealed an anomalous magnetic behavior in polyvinylpyridine–iron-chloride compounds [13]. Later, magnetic nanoparticles were grown in a PVP matrix by a laborious method involving precipitation, reduction to metallic iron and further oxidation to magnetite [14]. Some of the advantages of PVP as a matrix for magnetic nanocomposites are the following: easily available; soluble in slightly acidic aqueous media and in polar organic solvents; resistant to degradation by acids, alkalis, reductors and oxidants; it melts congruently; and it is thermally stable. In this work, complexes of PVP with several metal ions have been prepared by various procedures.

2. Experimental

High purity reagents were purchased from Aldrich and Fluka. Solvents were dried following the standard procedure and deoxygenated under an argon flow. PVP, of average molecular weight of 50,000 Da was supplied by Sigma.

Polymer–metal coordination compounds were obtained

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Table 1
Characteristics of PVP-metal composite samples

Preparation			Composition		FTIR	DSC		Nanoparticles (TEM)			Superparamagnetism
Salt	Method	Color	[Pyr.]/[Me] ratio	n H_2O	ν (pyr.) (cm^{-1})	T_g (°C)	T_m (°C)		Structure	*Size* (nm)	
Blank		White			1600	77	173				
$CoCl_2{\cdot}6H_2O$	Heterog.	Dark blue	5.7	3.3	1600	103	159	No			No
$CoCl_2{\cdot}6H_2O$	Homog.	Pink	3.6	1.7	1613	90	196	Yes	CoO, $CoCl_2{\cdot}6H_2O$	50	Yes
$CoSO_4{\cdot}7H_2O$	Homog.	Red. Brown	1.9	5	1616			No			No
$FeCl_2{\cdot}4H_2O$	Homog.	Pale brown	5.2	2.1	1633			No			–
$FeCl_2{\cdot}4H_2O$	Re-precip.	Red. Brown	5.3	0.8	1598			Yes	a-Fe_2O_3	10	Yes
$FeSO_4{\cdot}7H_2O$	Homog.	Red. Brown	1.7	2.3	1637			No			–
$FeCl_3{\cdot}6H_2O$	Homog.	Pale brown	2.5	1.8	1636			No			–
$FeCl_3{\cdot}6H_2O$	Re-precip.	Red. Brown	4.1	0.7	1597			Yes	a-Fe_2O_3	7	Yes
$NiCl_2{\cdot}6H_2O$	Homog.	Pale green	3.6	4.7	1616			No			–
$Dy(NO_3)_3{\cdot}5H_2O$	Homog.	White	11.0	0	1602			No			–

by three different methods: (I) In a typical heterogeneous procedure, an amount of 9.51 mmol of PVP powders were suspended in 20 ml of a 1.6 mM $CoCl_2{\cdot}6H_2O$ solution in methanol. The suspension was kept 12 h under stirring, at room temperature, and then it was filtered, washed and vacuum dried. (II) In a typical homogeneous procedure, 20 ml of a 4.83 mM $CoCl_2{\cdot}6H_2O$ solution in methanol was mixed with 30 ml of methanol solution containing 9.51 mmol of PVP. The mixture was stirred during 5 h and the resulting precipitate was filtered, washed and vacuum dried. (III) In a typical re-precipitation procedure, an amount of material obtained by procedure I was dissolved in 1 M HCl and re-precipitated by a controlled addition of a 1 M NaOH solution. Ethanol, and water–acetone mixtures were also used as solvents in procedures I and II.

The following apparatus were used for the characterization of the materials: a Perkin–Elmer 248B analyzer for elemental analysis of carbon, hydrogen and nitrogen, a plasma analyzer Perkin–Elmer Plasma 40 for determination of metal content, a Perkin–Elmer 1600 for FTIR spectroscopy, a Varian XL200 MHz or a Variant Unity 300 MHz for NMR spectroscopy, a Perkin–Elmer TGS2 and DSC instruments for thermogravimetric and differential thermal analysis, a Siemens D501 instrument with a CuKα source for X-ray powder diffraction studies, a MPMS Quantum Design SQUID magnetometer for the measurements of the ac magnetic susceptibility and a JEOL 2000FXIII microscope equipped with a Link Analytical EXL system for EDS analysis in the TEM observation. Samples for TEM were prepared by milling the grains, dispersing in *n*-butanol and extending the suspension on a copper grid coated with carbon. Occasionally, samples were embedded in an epoxy block and cut into ultrathin sections before examination. The structure of the nanoparticles was studied by electron diffraction.

3. Results and discussion

Details about the preparation, characterization and magnetic properties of the samples are presented in Table 1. A FTIR examination of the product shows that the pyridine stretching band at 1600 cm^{-1} is displaced to higher wavenumbers (Table 1), indicating the onset of nitrogen–metal coordination bonds. The amount of the shift was larger for PVP–iron in comparison with Co and Ni compounds, thus the pyridine–metal interactions are stronger in this case. The PVP–cobalt complex has been described as tetrahedrally coordinated [15]. The reaction involves a significant change in the X-ray diffraction pattern of the polymer that was used to establish the end of the reaction (Fig. 1). The complex formation reaction was tried using several metal salts. The polymer reacts relatively fast with Fe(II), Fe(III), Co(II) and Ni(II) but it hardly reacts with rare earth salts. Optical microscopy observations show

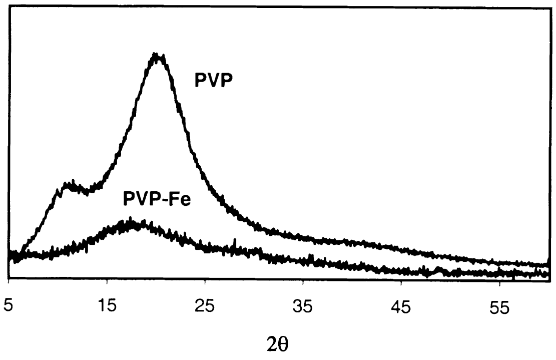

Fig. 1. X-ray powder diffraction spectra of PVP and PVP–Fe(III) polymer complex.

a narrow front of reaction separating the white transparent PVP block from the colorful complex grains. This is suggesting a surface reaction mechanism for the process rather than ion diffusion. The polymer swells extensively when forming the complex material resulting in a soft gel. The reaction is very slow in water; it is faster in ethanol or acetone and much faster in water–acetone mixtures. Such a behavior of the solubility can be explained considering that the polymer–metal complex chains have ionic and apolar parts. Acetone molecules can solvate the apolar parts but metal ions are better solvated by water. Thus, it is obvious that mixed solvents should enhance the process. Chemical analysis of polymer complex samples shows that they all contain water and the metal salt in variable amounts. However, samples prepared from sulfate salts contain higher amounts of both water and metal ions than those prepared from chloride salts, probably because sulfate ions are better solvated than chloride ions so they get easier into the intermediate polymer gel. Magnetic susceptibility measurements of dry samples showed that PVP–cobalt materials prepared by the homogeneous method are superparamagnetic. However, only the PVP–iron samples obtained by re-precipitation have a superparamagnetic behavior. Fig. 2 shows the dependence of the ac magnetic susceptibility with the temperature for a PVP–Co sample. The change of the susceptibility curves with the frequency of the alternating field reveals the presence of relaxation effects that are typical of superparamagnetic materials. Only the susceptibility maximum for the out-of-phase susceptibility is clearly shown since the in-phase maximum is hidden by the strong paramagnetic background at that low temperatures due to coordinated Co(II) ions. Nevertheless a blocking temperature of about 5 K can be anticipated. Fig. 3 shows a similar plot for a re-precipitated PVP-Fe sample. In this case the susceptibility maximum falls well in the measured temperature range and a blocking temperature (T_B) around 7 K can be deduced from this plot. This T_B value is also quite low suggesting a very small particle size. Samples of re-precipitated PVP–Fe(III) yielded similar susceptibility plots with T_B around 5 K. TEM images of PVP–Fe(II) (Fig. 4A) and PVP–Fe(III) (Fig. 4B) samples

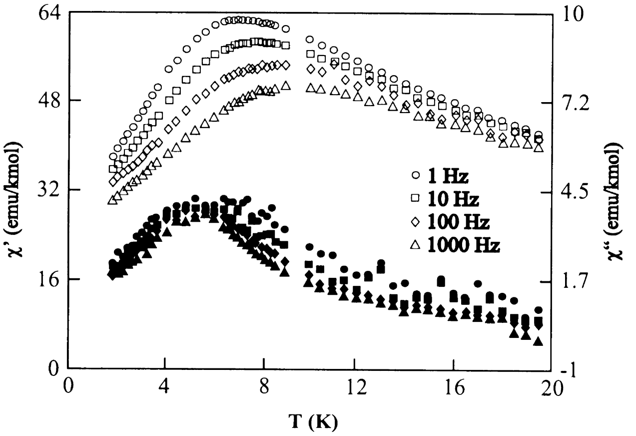

Fig. 3. Temperature dependence of the in-phase, χ', and the out-of-phase, χ'', components of the ac magnetic susceptibility for a PVP–Fe(II) sample obtained by re-precipitation, at several frequencies of the alternating field.

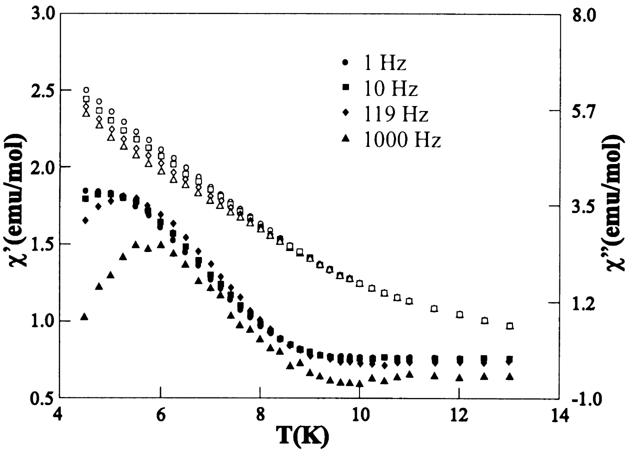

Fig. 2. Temperature dependence of the in-phase, χ', and the out-of-phase, χ'', components of the ac magnetic susceptibility for a PVP-Co sample, at several frequencies of the alternating field.

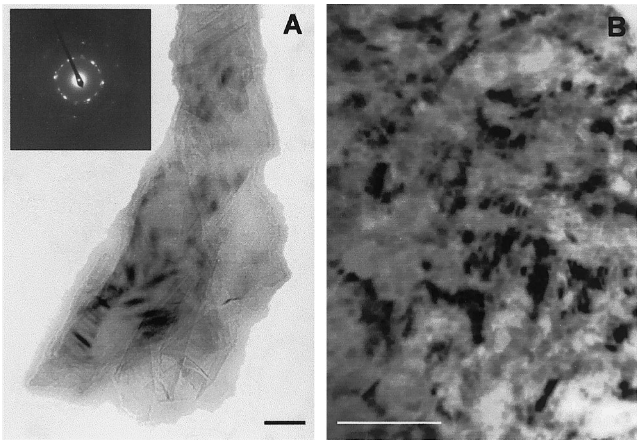

Fig. 4. TEM images of re-precipitated PVP-metal samples: (A) PVP–Fe(II) sample; and (B) PVP–Fe(III) sample. Bars at the bottom are 100 and 50 nm, respectively. The upper left part of the picture shows an electron diffraction pattern of a polycrystalline area of the PVP–Fe(II) sample.

reveal the presence of nanoparticles that were more abundant in the Fe(III) polymer complex. The electron diffraction pattern of these particles, shown in the upper left part of Fig. 4 is consistent with a hematite (α-Fe_2O_3) structure. The presence of nanoparticles was also observed in PVP-Co samples and their electron diffraction pattern showed some spots that correspond to CoO and some others corresponding to $CoCl_2 \cdot 6H_2O$ structure. On the other hand, samples with a non-superparamagnetic behavior were clean of particles. In a previous work about polyimine–metal composites it was argued that the precipitated nanoparticles arise from solvated ions trapped in the polymer gel, rather than from coordinated metal ions [12,16]. This is probably the case in PVP composites also. However, unlike polyimine–metal composites that yield cobalt and iron oxide nanoparticles without a prior alkali treatment, PVP requires the use of a basic reaction medium for the hydrolysis of iron ions. This is indicative of the participation of the imine groups in the process of formation of the hydroxide phase. Whereas, the basicity of the pyridine groups is hardly enough to induce the hydrolysis of cobalt ions.

Acknowledgements

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