



# Epoxy nanocomposites functionalized with *in situ* generated magnetite nanocrystals: Microstructure, magnetic properties, interaction among magnetic particles



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## ABSTRACT

Magnetite nanoparticles in the range 7–10.5 nm were prepared by non hydrolytic sol–gel (NHSG) process in the presence of benzyl alcohol in different concentrations. The suspensions were mixed with bisphenol A diglycidyl ether (DGEBA) and cured in the presence of ytterbium(III) trifluoromethanesulfonate as cationic initiator. Magnetite nanoparticles and epoxy nanocomposites were characterized by structural, chemical and magnetic techniques. A procedure of data analysis is proposed to determine value, sign and surface contribution of the magnetic anisotropy of nanoparticles by comparing the information gained from field-cooled/zero-field-cooled magnetization curves and TEM images. Above blocking temperature, the nanoparticles dispersed in the epoxy resin give rise to an interacting superparamagnetic system and follow the corresponding scaling law. A model explains why the magnetic interaction energy depends not only on nanoparticle concentration in the epoxy but also on concentration fluctuations, being larger in samples where the nanoparticle dispersion is not uniform.

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## 1. Introduction

In recent years, considerable efforts have been devoted to the design and controlled fabrication of nanostructured materials having definite physico-chemical properties [1]. Nanocomposites combining inorganic nanoparticles (NPs) and organic polymeric matrices show not only a dramatic improvement of mechanical properties [2] but also innovative functional properties [3]. The magnetic behaviour of polymeric nanocomposites has been recently investigated for potential application in electronic, magnetic and photonic devices, gas and vapour sensors, non linear optic systems, photovoltaic solar cells and biomedical applications [4–6]. In most of the existing literature a polymeric phase is used to modify the surface chemistry of magnetic NPs in order to prevent their aggregation in large clusters; recent studies have been rather aimed to obtain *bona-fide* magnetic nanocomposite materials. The

main approach involves the use of preformed magnetite NPs obtained by chemical precipitation starting from ferric chloride [7]. In order to prevent NP agglomeration and to ensure compatibility between the nanoparticles and the polymer matrix, oleic acid is generally used as a surfactant. In this way magnetite NPs have been incorporated in poly(methyl methacrylate) (PMMA) [8,9] or in hydrogenated epoxy resin (HDGBA) [10]. Recently, Guo et al. [11] used a conductive polypyrrole coating on nanomagnetite as a coupling agent to obtain reinforced magnetic epoxy nanocomposites.

An alternative strategy is represented by *in situ* synthesis that uses chemical reactions in a liquid [12]. Nanoparticles are first synthesized either as a sol or dispersed in a solution; in a second step a monomer or resin is added and brought to polymerization. The sol–gel chemistry represents one of the preferred preparation routes, thanks to its mild conditions that become strategic when organic materials are involved, avoiding their thermal degradation. Typical precursors are metal alkoxides which reacting with water give rise to NPs having narrow grain size distribution with dimensions ranging from 5 to 100 nm [13]. Alternatively to the aqueous route, the so-called non-hydrolytic sol–gel (NHSG)

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reaction can also be used to obtain pure, crystalline metal oxides [14–17]. As well as the aqueous route, the NHSG process is divided in two steps. The first step involves the reaction of a metal halide, alkoxide or acetylacetonate with an organic oxygen donor (such as alcohols, ether, etc.). The second step (condensation) can follow different pathways depending on the selected precursor. The presence in the reactive system of a suitable organic oligomer or polymer leads to the formation of organic-inorganic hybrid structures composed of metal oxide and organic phases intimately mixed with each other. In principle, the NHSG route gives access to a wide range of organic-inorganic nanocomposite products similar to those accessible using the hydrolytic route [18–20]. In practice, however, differences arising from the nature of the precursors, the choice of possible solvents and the different reaction mechanisms may dictate the type of hybrid material which can be prepared by either route. It is generally recognized [21] that the NHSG process is potentially solvent-free, without problems with hydrophobic substances, and particularly suitable for water-sensitive species. On the other hand, the formation of by-products and their potential incompatibility with O-containing species have to be taken into account as possible negative aspects.

Most chemical routes to synthesize ferrimagnetic Fe-oxide NPs [22] have a reproducible output and lead to a well-defined chemical composition and structure together with a narrow spread of NP sizes/shapes. Magnetic nanocomposites containing Fe-oxide NPs are attracting widespread attention because of their prospective applications, mostly related to the physical properties resulting from the combination of a magnetic dispersoid and a host matrix [23] and including functionally graded materials [24] and/or sensing elements in the area of information and communication technologies (ICTs) [25].

Spontaneous magnetization, coercive field and magnetic interactions of magnetite NPs are affected by the surroundings [22]. The experimental evidence points to a substantial role played by magnetic interactions among particles, which is remarkably modified by NP concentration and/or by the hosting material. In systems where contact interactions are minimized, magnetic dipolar interaction plays a central role up to room temperature and above [26]. Departures from the superparamagnetic scaling law are typically observed in many nanoparticle systems; these can be satisfactorily accounted for by a model of interacting superparamagnetism (the ISP model) [27], a mean-field theory applied to temperatures where the dipolar interaction energy is comparable in magnitude to the thermal energy  $k_B T$ . The region where this condition holds extends up to room temperature in several systems.

This work is focussed on the preparation of innovative nanocomposites through the *in situ* generation of magnetite nanoparticles within a suspending medium which undergoes a subsequent polymerization in the presence of aliphatic epoxy resin (bisphenol A diglycidyl ether, DGEBA). The so-called 'benzyl alcohol route' [15] was used to prepare magnetite nanoparticles suspended in benzyl alcohol which was also reactive towards the polymerization of epoxy resins induced by cationic initiators. Recently, this innovative procedure has been shown to be expedient in obtaining magnetic composites using a UV-curable cycloaliphatic epoxy resin [28]. Here, the same method is used to incorporate magnetite suspensions in benzyl alcohol with epoxy resin by means of a thermally activated cationic polymerization instead of the UV-curing process. The prepared magnetite NPs and epoxy composites are fully characterized in order to correlate the composite microstructure with the magnetic properties. The static magnetic properties are measured on four dried nanopowders differing by a single preparation parameter (the  $\text{Fe}(\text{AcAc})_3:\text{BzOH}$  ratio) and on four nanocomposites containing the same as-prepared

nanoparticles in different amounts. The measurements are combined with structural/morphological results. In this way, the effective magnetic anisotropy of the nanoparticles can be determined singling out the contribution from the surface and the effects of dipolar interaction in nanocomposites can be measured and explained.

## 2. Experimental

### 2.1. Materials

Bisphenol A diglycidyl ether (DGEBA, Dow D.E.R.<sup>TM</sup> 332 with an epoxide equivalent weight of 172–176), benzyl alcohol (BzOH), ytterbium(III) trifluoromethanesulfonate hydrate ( $\text{Yb}(\text{OTf})_3$ ), and ethanol (EtOH) were purchased by Sigma Aldrich (Milan, Italy).

Acetylacetonate (AcAcH) and iron(III)chloride exahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were purchased from Carlo Erba (Milan, Italy).

All materials were high purity reactants and were used as received without any further purification.

### 2.2. Synthesis of magnetite alcoholic suspensions

In a 100 mL Schlenk tube 1.00 g (2.83 mmol) of Iron(III)-acetylacetonate ( $\text{Fe}(\text{AcAc})_3$ ), synthesized as reported in Bondioli et al., [13] was dissolved in different amounts of BzOH in order to evaluate the effect of the  $\text{Fe}(\text{AcAc})_3:\text{BzOH}$  ratio on the powder properties (see composition details in Table 1). The reaction was left stirring at room temperature for 15 min and then heated to 200 °C in an oil bath for 48 h. The main reaction occurring in the solvothermal treatment of Iron(III)-acetylacetonate in benzyl alcohol is summarized in the scheme of Fig. 1. After reaction a stable suspension was obtained. To better characterize the inorganic phase, the obtained powders were dispersed in methanol with an ultrasonic bath and centrifuged at 4000 rpm for 60 min; the powders were washed, centrifuged till the obtainment of a colourless liquid phase and finally dried under reduced pressure.

### 2.3. Characterization of magnetite powders

Crystalline phase of the synthesized powders were analysed by X-ray powder diffraction technique using an X'Pert PRO diffractometer (PANalytical, Netherlands), powered by a Philips PW3373/10 Cu LFF DK388689 X-ray generator and fitted with an X'Celerator detector. Diffraction data were acquired by exposing powder samples to  $\text{Cu-K}\alpha$  X-ray radiation with a characteristic wavelength ( $\lambda$ ) of 1.5418 Å. X-rays were generated from a Cu anode supplied with 40 kV and a current of 40 mA. The X-ray diffraction (XRD) patterns were collected at room temperature in 10–70°  $2\theta$  range, with a step size of 0.0167° and a nominal time per step of 0.008 s<sup>-1</sup>. Fixed anti-scatter and divergence slits of 1/2° were used together with a beam mask of 10 mm and all scans were carried out in 'continuous' scanning mode. The average crystallite size was calculated using the Scherrer method [29], based on the calculus of the integral breadth of the X-ray diffraction peaks.

**Table 1**

Composition of the NHSG reaction batches and morphology of the obtained powders.

$\text{Fe}_2\text{O}_3$ powder code	$\text{Fe}(\text{AcAc})_3$ (g)	BzOH (g)	$\text{Fe}(\text{AcAc})_3:\text{BzOH}$ ratio	TEM size (nm)	Aspect ratio
Fe1	1.00	31.1	0.03	7.2 ± 0.9	1.13 ± 0.09
Fe2		15.6	0.06	8.4 ± 1	1.12 ± 0.07
Fe3		7.77	0.12	9.6 ± 1.6	1.20 ± 0.10
Fe4		3.87	0.24	10.2 ± 1.7	1.18 ± 0.15

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