



Magnetic silica:epoxy composites with a nano- and micro-scale control



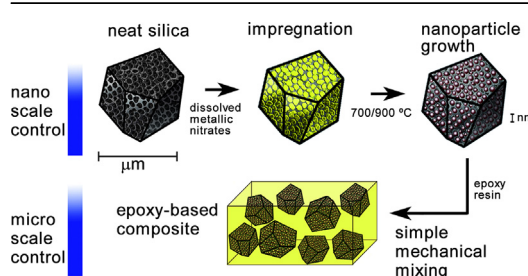
María Crespo, María González, Javier Pozuelo*

Departamento de Ciencia e Ingeniería de Materiales e Ingeniería Química (IAAB), Universidad Carlos III de Madrid, 28911 Leganés, Madrid, Spain

HIGHLIGHTS

- We present a strategy that permits the nanoscale and micro-scale control through a simple protocol.
- Cu–Ni ferrites were prepared into the structure pores if commercial silica with a size control by annealing temperature.
- Composites with epoxy matrix were prepared.
- The reinforcements provided an increase in glass transition temperature and decomposition temperature of the composites.

GRAPHICAL ABSTRACT



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ABSTRACT

Multiscale composites with magnetic properties were prepared by incorporating Cu–Ni nanoferrites filled silica microparticles in an epoxy matrix. The size of the nanoferrites was controlled both by the structure of the silica template and the annealing temperature (700 and 900 °C) used during the synthesis procedure. The ferrite:silica particles prepared at 700 °C showed a narrow size distribution close to 8.3 nm with a superparamagnetic behaviour. A less symmetric size distribution was obtained when annealing was performed at 900 °C, with diameters ranging from 15 to 80 nm. The reinforcement incorporation increased up to 7 °C the glass transition temperature and 30 °C the decomposition temperatures of the composites. The proposed strategy permits the nanoscale control, by the trapping effect of the silica on the magnetic nanoparticles, as well as the control of the micro-scale distribution through a simple protocol. These composites could have potential applicability as EMI shielding materials, owing to their magnetic nature, lightweight and enhanced thermal stability.

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1. Introduction

Research on materials with specific functional properties is an active field nowadays. Combining low density polymers with nanoparticles seems to be a good strategy to transfer the properties of the reinforcement (mechanical, electrical, magnetic, thermal, etc) to the global material. For example, improved electrical and

mechanical properties have been achieved when introducing small amounts of carbon nanotubes in polymer matrices [1,2], epoxies loaded with nano- and micro-silica particles have shown enhanced mechanical properties and wear resistance [3,4], and multifunctional nanostructured core–shell magnetic nanoparticles having giant magnetoresistance sensing ability or microwave absorption properties [5] could lead to composites with potential applications as magneto-optical modulators [6], biocompatible membranes for sensing [7] or as electromagnetic (EMI) shielding materials [8] when embedded in polymer matrices.

* Corresponding author. Tel.: +34 91 6249940; fax: +34 91 6249430.
E-mail address: jpozue@ing.uc3m.es (J. Pozuelo).

In all cases, the properties of the nanocomposites seem to depend mainly on the aspect ratio of the particles and their dispersion degree in the matrix. Thus, two main aspects must be controlled when designing such materials: the size and shape of nanoparticles and the homogeneity of their dispersion. For magnetic particles, the size of the magnetic domains and its dispersion will strongly determine the magnetic properties of the final material, e.g. soft or hard magnetic behaviour [9]. Thus, in order to achieve monodomain superparamagnetic nanoparticles, it is essential to avoid the coalescence of nanoparticles during its growth and to restrict their maximal dimensions [10].

The synthesis of size-controlled magnetic nanoparticles within polymer matrixes may be accomplished either by in-situ polymerization while particle formation [9,11] or by dispersing pre-formed magnetic nanoparticles in the polymer matrix. In this latter case, many routes for synthesizing size-controlled nanoparticles involve the use of capping agents [12], precipitation in reverse microemulsions [13], or sol–gel processing [14] to avoid the coalescence and further growth of the particles. But, since geometry is also important, other methods that allow the synthesis of shape-controlled particles are being explored [15]. Nanocasting is a useful technique that involves using a template (either soft or hard) which is impregnated by liquid precursors of the particles [16]. Finally, homogeneously dispersed nanoparticles within the template are obtained as the negative image of it. Silica is may be the most widely used hard template, since its geometry is stable and can be obtained with different pore shapes and sizes via sol–gel [17]. Nanocasting using hard templates has been successfully employed for the preparation of ferrites with several transition metals as Cu, Co, Ni, Pd, Zn [18–21]. Ferrites have attracted much attention in EMI shielding applications because of their strong magnetic losses [22]. The electromagnetic absorption process by magnetic particles induces magnetic spin rotation and the magnetic energy can be dissipated by heat transfer to the matrix. This mechanism could be the most appropriate for protecting the internal elements of electronic devices. Among spinel ferrites, inverse spinels are particularly interesting because of their high magnetocrystalline anisotropy and permeability. Ni ferrites correspond to these types of ferrites and their substituted counterparts have shown increased attention due to their promising high-frequency applications [23]. Moreover, Cu-Ferrites have shown enhanced thermal, magnetic and dielectric properties [24,25] and its substitution with Ni, e.g. $\text{Cu}_{1-x}\text{Ni}_x\text{Fe}_2\text{O}_4$, has lead to EMI shielding materials having the maximum reflection loss (–25 dB) for the composition of $x = 0.5$ [26].

However, ferrites are quite heavy and, although promising results have been published, EMI shielding materials are advocated to find lighter counterparts that may replace heavy, nor easily processable or chemically resistant materials that have been traditionally used as microwave shields/absorbers. Consequently, for this application, polymer-based composites, having low densities, are attractive matrixes for the incorporation of high magnetic loss constituents. Ferrite powders mixed with non-magnetic polymers have been proposed as tentative materials that may overcome the high frequency loss that ferrites, by themselves, present at frequencies above 100 MHz, enabling their use in electromagnetic absorption applications even at GHz range [27].

Preparation and characterization of nanocomposites by incorporation of magnetic nanoparticles within thermosetting polymers has been pursued by different approaches [28–31], and, in most cases, being able to disperse the nanoparticles remains challenging since their high surface energy favours agglomeration [32,33] even at low loadings. To overcome this problem several routes have been proposed, such as surface modification of the nanoparticles, which is expected to improve nanoparticle–polymer matrix interactions

either through weak Van der Waals interactions or strong chemical bonds [34,35]. Silica coated magnetic nanoparticles have also been proposed as an alternative to increase compatibility and to avoid further oxidation of the particles [36,37]. Additionally, enhanced EMI shielding of such core–shell type structures has been reported, owing to multiple-interfacial polarization mechanisms and to a better impedance matching due to the unique structure of silica [38,39].

Though all these promising findings, as it was mentioned previously, dispersing inclusions having nanometric sizes is physically unfavourable even having the best possible scenario. High-energy mixing techniques are necessary and time-consuming surface modifications are still needed to partially overcome nanoparticle agglomeration. To circumvent this situation and still being able to combine the specific properties of individual magnetic nanoparticles with the lightweight of polymers, a possible approach could be to pre-disperse the nanoparticles inside micron-sized porous particles, which are by far more easily dispersible in polymers. Inclusion of magnetic nanoparticles within micron-sized mesoporous silica has diverse applications such as separation of biomolecules [40], adsorption of pollutants in water [41] and as catalysts for chemical reactions [42], although, as far as our knowledge, no preparation of polymer-based composites has been reported with this type of hybrid structures. Moreover, this type of combination could eventually lead to strengthened multifunctional polymer-based materials, besides magnetism, as it has been reported that pristine porous micron sized-silica improves the mechanical properties (fracture toughness, modulus, and deformation at break) of polymer based composites [43,44] and increased thermal stability is also expected. Besides, when considering magnetically loaded polymer composites for EMI shielding, it is well established that electromagnetic absorbers dissipate electromagnetic energy into heat and thus, materials which combine enhanced thermal stability, magnetic activity and lightweight, could be prospective candidates for this application.

In this work a high surface micron-sized silica template has been selected as host structure of magnetic CuNi-ferrite nanoparticles. The hybrid silica–ferrite material has been synthesized by a simple and cheap nanocasting procedure that enables the homogeneous and individual spatial distribution of the magnetic cores within the silica pores. The hybrid micro-reinforcement has been homogeneously dispersed in an epoxy resin by low-energy mixing while the ferrite nanoparticles remained unaltered within the micron-sized silica particles. The employed strategy permits to disperse magnetic nanoparticles in an epoxy matrix in a simplified way due to the fact that they are already dispersed within easily-dispersible micron-sized silica particles. The prepared composites could have potential applicability as EMI shielding materials, owing to their magnetic nature, lightweight and enhanced thermal stability.

2. Materials and methods

2.1. Synthesis of nanoparticles and preparation of composites

$\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_2\text{O}_4$ ferrite nanoparticles were synthesized using silica gel (Aldrich Ref. 288500, particle size: 2–25 μm and pore size: 60 Å) as hard template. The general casting procedure developed by Fuentès et al. was followed [21]. Appropriate amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (purchased from Sigma Aldrich) were mixed in order to get a Cu:Ni:Fe ratio of 1:1:4. The nitrates were dissolved in 16 g of ethanol and the solution was used for impregnating the silica gel. The wet nitrate–silica was dried at 90 °C overnight and the impregnation–drying process was repeated once in order to increase the metal ion content inside the silica pores. The thermal decomposition of the nitrates was

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