Superparamagnetic Nanocomposites Based on the Dispersion of Oleic Acid-Stabilized Magnetite Nanoparticles in a Diglycidylether of Bisphenol A-Based Epoxy Matrix: Magnetic Hyperthermia and Shape Memory

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Supporting Information

ABSTRACT: Superparamagnetic nanocomposites were obtained by dispersion of oleic acid (OA)-coated magnetite NPs in an epoxy system based on diglycidylether of bisphenol A (DGEBA) modified with OA. Dispersion of conventional oleic acid-stabilized magnetite NPs in a typical epoxy matrix is not possible due to the dissimilar chemical structures of the organic coating and the reactive solvent. However, by modification of a DGEBA-based epoxy with 20 wt % OA, we obtained a suitable reactive solvent to disperse up to at least 8 wt % of OA-stabilized magnetite NPs. A tertiary amine was used to catalyze the epoxy–acid reaction and initiate the homopolymerization of the epoxy excess. Both reactions occurred practically in series, first the epoxy–acid and then the epoxy homopolymerization. It was necessary to complete the first reaction to attain a very good dispersion of magnetize NPs in the reactive solvent previous to the occurrence of the final reaction. Magnetization curves and TEM images revealed a uniform dispersion of individual nanoparticles in the



cross-linked epoxy. A sample containing 8 wt % OA-coated magnetite NPs exhibited a temperature increase of 25 $^{\circ}$ C at its surface when exposed to an alternating magnetic field. The temperature increase was enough to induce the shape memory effect of the nanocomposite.

INTRODUCTION

Nanocomposites based on the dispersion of magnetic nanoparticles (NPs) in a polymeric matrix are becoming an important class of advanced materials with varied medical and technological applications. A controlled increase in temperature can be produced in these nanocomposites by exposure to an alternating magnetic field, an effect known as magnetic hyperthermia. This increase in temperature is the basis of a variety of applications in medicine (cancer therapies, drug delivery), remote actuation of shape memory polymers, SMP (artificial muscles, space deployable structures, smart textiles), and many other fields.^{1–10} In addition, magnetic nanocomposites find applications for the shielding of high-frequency electromagnetic radiation.¹¹

On the other hand, due to their excellent thermomechanical properties associated with their chemical and solvent resistance, cross-linked epoxies are materials of choice for a variety of advanced applications,¹² including their use as SMP.^{13–20}

However, the use of epoxy matrices to disperse magnetic NPs has been scarcely reported.^{21–25} The main reason is the difficulty in generating uniform dispersions of NPs in a matrix, which precludes the benefits associated with the use of a nanometric phase. The use of uncoated Fe_3O_4 NPs leads to the formation of large aggregates in the cured materials.^{22–24} This is due to initial incompatibility or to phase separation of NPs during polymerization, a fact that has been theoretically predicted²⁶ and experimentally observed.²⁷

One way to avoid the phase separation process is to introduce functional groups in the organic ligands used to stabilize NPs. These groups participate in the chemical reaction and become part of the polymer network.²⁸ This strategy has been used with success employing epoxy-modified iron oxide

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magnetic NPs in a photocurable epoxy matrix.²⁵ A second possibility to generate uniform dispersions is to produce a close match of chemical structures of the epoxy matrix and the stabilizing organic ligands. Along this line, it would be interesting to use conventional oleic acid-stabilized magnetite NPs that can be synthesized by traditional coprecipitation or organic-phase methods.^{29–31} The main problem with this approach is the incompatibility of alkyl chains with the chemical structure of conventional epoxy monomers based on diglycidylether of bisphenol A (DGEBA, Figure 1). It has



Figure 1. (a) Chemical structures of the epoxy monomer diglycidyl ether of bisphenol A, oleic aci, and benzyldimethyamine; (b) epoxy–acid reaction; (c) propagation step of the epoxy polymerization.

been suggested that the use of hydrogenated DGEBA (HDGEBA) could afford an epoxy matrix more compatible with oleic acid-stabilized magnetite NPs;²¹ however, this approach was successful only for formulations containing up to 1 wt % magnetite NPs. Usually, the mass fraction of magnetic NPs required for obtaining magnetic heating is significantly higher.

In this manuscript, we show that it is possible to produce a homogeneous dispersion of large mass fractions of oleic acid (OA)-stabilized magnetite NPs (up to at least 8 wt %) in a DGEBA-based epoxy matrix. The key to our approach was to produce the end-capping of a fraction of DGEBA with OA, using a tertiary amine as catalyst (Figure 1). The tertiary amine also enabled the initiation of the homopolymerization of the epoxy excess (Figure 1), leading to an OA-modified epoxy network. The matching of chemical structures allowed the homogeneous dispersion of a large mass fraction of OAmodified magnetite NPs in the epoxy network. In addition, the glass transition temperature of the epoxy network could be tuned with the fraction of OA used in the formulation. This is convenient for applications as shape memory epoxies with remote activation. Magnetic properties and the hyperthermia effect of the resulting nanocomposites were analyzed.

EXPERIMENTAL METHODS

Materials. The diepoxy monomer was based on DGEBA (DER 332, Aldrich), with a mass per mole of epoxy groups equal to 174.3 g mol⁻¹ (n = 0.03 in the chemical structure shown in Figure 1). The fatty acid used was OA (Aldrich, 90% purity). BDMA (\geq 99%, Aldrich, boiling point 183 °C) was used as both catalyst of the epoxy-acid reaction and initiator of the homopolymerization reaction. The following chemical products (Aldrich) were used as received: ferric chloride (FeCl₃·6H₂O), ferrous sulfate (FeSO₄·7H₂O), and ammonium hydroxide (25% NH₃). Tetrahydrofurane (THF) and heptane, used as solvents, were P.A. grade.

Synthesis of NPs. Magnetite NPs with a size of 9.5 ± 2.6 nm and coated with oleic acid (Fe₃O₄@OA) were obtained by a chemical coprecipitation method.²⁹ Briefly, 0.09 mol of FeCl₃·6H₂O and 0.06 mol of FeSO₄·7H₂O were dissolved in 200 mL of distilled water and heated to 90 °C. Then 60 mL of ammonium hydroxide and 0.014 mol of oleic acid were sequentially and rapidly added. After 3 h, the sediment was washed with distilled water until neutrality was achieved. The solid was dispersed in heptane and stored for further use. Previously to their incorporation in the reactive formulation, NPs were precipitated with ethanol and dispersed in THF.

Synthesis of the Epoxy Networks. The epoxy networks were obtained by reaction of DGEBA with different amounts (0-20 wt %) of OA in the presence of BDMA (0.06 mol/mol) of epoxy groups). Selected amounts of OA and DGEBA were mixed at 100 °C until a homogeneous solution was obtained. After cooling to room temperature, an adequate amount of BDMA was added. The temperature was increased to 90 °C while stirring until a homogeneous solution was obtained. The mixture was placed between two Teflon-covered glass plates using a 1.4-mm-thickness rubber spacer. The reaction was performed at 90 °C for 6 h, leading to the final material.

Synthesis of Nanocomposites. Nanocomposites with 1.5, 7, and 8 wt % OA-coated magnetite NPs and 20 wt % OA in the blend with DGEBA (molar ratio OA/epoxy = 0.154), were synthesized. OA was mixed with an appropriate amount of the dispersion of NPs in THF. After evaporation of the solvent, required amounts of DGEBA and BDMA were added (mass ratio OA/DGEBA = 20:80, molar ratio BDMA/epoxy groups = 0.06). The blend was heated to 90 °C and held at this temperature for about 15–20 min while stirring until it became homogeneous. Then, it was placed between two Tefloncovered glass plates using a rubber spacer of 1.4 mm thickness. The cure was continued at 90 °C for 6 h, leading to the final nanocomposite.

Techniques. Transmission electron microscopy (TEM) images were obtained using a Philips CM-12 microscope operated at an accelerating voltage of 100 kV. NP samples were prepared by dropping 6 μ L of the dispersion onto a copper grid coated with Formvar and a carbon film. The average size of the magnetite core was determined using several images and employing more than 100 particles/image. TEM images of nanocomposites were obtained from ultrathin sections that were cut with a cryo-ultramicrotome.

X-ray diffraction (XRD) spectra of NPs were obtained with a PANalytical X'Pert Pro diffractometer using a Cu K α radiation source (λ = 0.1546 nm) operating at 45 kV and 30 mA.

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Thermogravimetric analysis (Shimadzu TGA-50) was carried out for powder samples (5 mg) with a heating rate of 10 $^{\circ}C/$ min under air flow, up to 900 $^{\circ}C$. TGA thermograms were used to determine the amount of NPs in the nanocomposite and the fraction of oleic acid coating the NPs.

Fourier-transformed middle infrared spectroscopy (FT-MIR, Nicolet 6700) was used to characterize the organic ligands stabilizing the NPs. KBr was impregnated with a few drops of the dispersion of NPs in heptane and compressed forming a pellet. The IR spectrum was recorded after solvent evaporation. FT-MIR was also used to follow the decrease of the epoxy peak at 915 cm⁻¹ and the carbonyl group of oleic acid at 1710 cm⁻¹ during reaction at 90 °C. The device was provided with a heated transmission cell (HT-32, Spectra Tech, KBr windows of 32 mm diameter and a 0.025 mm copper spacer) and a temperature controller (CAL 9500P, Spectra Tech). The sample was placed in a polyethylene bag between KBr windows (PE did not exhibit peaks in the spectral range of interest). Fourier-transformed near-infrared spectroscopy (FT-NIR, Nicolet 6700) was used to determine the conversion of the epoxy groups as a function of time. The sample was placed between glass windows using a rubber spacer of 1.4 mm. The reaction was carried out at 90 °C, following the height of the absorption band at 4530 cm⁻¹ (assigned to the conjugated epoxy CH₂ deformation band with the aromatic CH fundamental stretch) with respect to the height of a reference band at 4621 cm⁻¹ (assigned to a combination band of the aromatic conjugated C=C stretch with aromatic CH fundamental stretch).³²

An Anton Paar rheometer (model Physica MCR-301) equipped with a CTD 600 thermo chamber was used to determine the variation of the storage (G') and loss moduli (G'') with temperature. Glass transition temperatures (T_g) were determined as the maxima of the damping peak (tan δ). A rectangular–solid configuration with probes of 40 × 5 × 1.4 mm³ was used in oscillatory mode with 0.1% amplitude at a frequency of 1 Hz. Temperature scans were performed at 5 °C/ min from -30 to 120 °C.

A Leica DMLB microscope provided with a hot stage (Linkam THMS 600) was employed to determine the time required to obtain a homogeneous dispersion in blends containing NPs during reaction at 90 °C. Optical transmittance measurements in the wavelength of visible light were made at 90 °C using a photodetector incorporated into the optical path of the microscope.

Magnetic properties were measured at 5 and 300 K in a superconducting quantum interferometer device (SQUID) with vibrant measuring sample technology (VSM) under a maximum applied magnetic field of 2 T. A vibrant sample magnetometer (VSM) was also used to perform the hysteresis loops at room temperature.

The heating response of nanocomposites exposed to an alternating magnetic field was characterized using inductive heating equipment with a field strength of 30 mT and a frequency of 293 kHz. Measurements were carried out placing a small piece of the nanocomposite in the sample holder and recording the temperature increase versus time with a fiber optic thermometer.

RESULTS AND DISCUSSION

Characterization of Oleic Acid-Stabilized Magnetite Nanoparticles. Figure 2 shows a TEM image of the





Figure 2. TEM image of oleic acid-stabilized magnetite NPs. The inset shows the size distribution of the magnetite cores.



Figure 3. XRD spectrum of magnetite NPs.



Figure 4. FTIR spectra in the $1000-2000 \text{ cm}^{-1}$ range of (a) magnetite NPs and (b) oleic acid.

synthesized NPs while the inset shows the size distribution of the magnetite cores (average diameter = 9.5 ± 2.6 nm).

The XRD spectrum matches well with standard magnetite (Fe_3O_4) powder diffraction data (Figure 3). The Scherrer's equation was used to determine the crystal size,

$$D = k\lambda/B\cos\theta$$

where k = 0.9 was used as Scherrer's constant,²¹ λ is the radiation wavelength, and *B* is the width of the selected peak at



Figure 5. FTIR spectra as a function of reaction time at 90 °C for a DGEBA/OA formulation with 20 wt % OA (a) region of the epoxy ring, (b) region of the C=O group.



Figure 6. Conversion of epoxy groups as a function of time, derived from the evolution of FT-NIR spectra, for the formulation containing 20 wt % OA, at 90 $^{\circ}$ C.

half height, in radians. Using the most intense (311) reflection gives an average crystal size of 10.4 nm, in good agreement with the value calculated from TEM images.

FTIR spectra in the 1000–2000 cm⁻¹ range of magnetite NPs and oleic acid are compared in Figure 4. The intense peak present at 1710 cm⁻¹, characteristic of the C=O stretch of the COOH group of OA, practically disappeared from the spectrum of the OA-stabilized NPs. Instead, two peaks at



Figure 8. Sequence of photographs of a predeformed bar of the 20 wt %-modified epoxy network immersed in a water bath held at 70 $^{\circ}$ C.



Figure 9. Optical transmittance of a 20 wt % OA-modified DGEBA with 1 wt % magnetite NPs during reaction at 90 °C.



Figure 7. Damping peaks (tan δ) and glass transition temperatures of formulations containing different amounts of OA.



Figure 10. TEM images from ultrathin cuts of nanocomposites with different weight percents of NPs.



Figure 11. Damping peaks $(\tan \delta)$ for a cured 20 wt % OA-modified DGEBA matrix with different amounts of NPs.

about 1541 and 1635 cm⁻¹, characteristic of the carboxylate anion (COO⁻),³³ are present in the FTIR spectrum. The broad

band at about 1060 cm^{-1} arises from C–O single bond stretching.³³ Therefore, most of the OA stabilizing the NPs was chemically bonded to the surface as carboxylate anions. The total amount of the organic stabilizing groups was 22.4%, as determined from TGA thermograms.

OA-Modified Epoxy Networks. The main reactions taking place in the OA-DGEBA system in the presence of a tertiary amine (BDMA) are the epoxy–acid reaction and epoxy homopolymerization (Figure 1). Secondary reaction such as alcoholysis of ester groups and transesterification reactions also take place.³⁴ Initiation, termination, and chain transfer reactions taking place in the epoxy homopolymerization^{34,35} are not indicated.

The competition between epoxy-acid and epoxy homopolymerization was analyzed following the reaction by FTIR. Figure 5 shows the evolution of FTIR spectra in two different regions, at 90 °C, for a DGEBA/OA formulation with 20 wt % OA. After about 300 min, no trace of the epoxy peak at 915 cm⁻¹ remained in the FTIR spectra (this was the selected cure time at 90 °C). The other spectral region shows the disappearance of the carboxylic acid peak at about 1710 cm⁻¹ and the appearance of the reaction product (ester band) at 1740 cm⁻¹. The epoxy-acid reaction is very fast and is practically completed after about 20 min at 90 °C; therefore, it may be concluded that both reactions occur in series: first the epoxy-acid and then the epoxy homopolymerization. This was also confirmed following the rate of consumption of epoxy groups from the evolution of FT-NIR spectra. Figure 6 shows the conversion of epoxy groups as a function of time, at 90 °C, for the formulation containing 20 wt % OA (molar ratio OA/ epoxy groups = 0.154). The kinetic curve exhibits a clear discontinuity of the derivative at a conversion of epoxy groups close to 20%. Because the maximum conversion of epoxy groups in the reaction with OA is 15.4%, the extra conversion might be assigned to the initiation step of the homopolymerization (molar ratio BDMA/epoxy groups = 0.06). Therefore, during the first 20 min reaction, the epoxy-acid reaction was completed, and a significant fraction of the tertiary amine reacted with epoxy rings forming alkoxide anions that initiate the slow homopolymerization reaction. After 6 h, the final conversion of epoxy groups was close to 0.99.

The viscoelastic characterization of OA-modified epoxy networks showed a decrease in the glass transition temperature with the increase in OA in the formulation. Figure 7 shows the damping peaks (tan δ) for formulations containing different amounts of OA and the glass transition temperature, defined at the maximum of the damping peak, plotted as a function of the wt % OA. The interesting fact is that controlling the amount of OA added to the formulation enables tuning the glass transition temperature of the epoxy network. To prepare nanocomposites with magnetic NPs for shape memory applications, it is convenient to select a glass transition temperature higher than but close to room temperature to facilitate the magnetic hyperthermia effect. The formulation containing 20 wt % OA, with a maximum damping peak at 51 °C, was selected for this purpose.

The shape memory behavior of the 20 wt % OA-modified epoxy network was investigated. A rectangular bar (permanent shape) was deformed into a secondary shape by twisting at 70 °C (in the rubbery state). Upon cooling under loading, the temporary shape was fixed. Subsequent immersion in a water bath held at 70 °C allowed complete recovery of the original rectangular shape in 2.3 s (Figure 8).



Figure 12. Hysteresis loops for three different concentrations of magnetite cores, at (left) T = 300 K and (right) T = 5 K. Inset shows zoom at low magnetic field.



Figure 13. Temperature increase for nanocomposites with different wt % NPs under application of an alternating magnetic field (f = 293 kHz, field strength 30 mT).



Figure 14. Photographs of a predeformed bar of the nanocomposite containing 8 wt % of OA-stabilized NPs before (left) and after (right) exposure to the alternating magnetic field for 60 s.

Magnetic Nanocomposites. At 90 °C, the reactive mixture of DGEBA, OA, and magnetite NPs showed the formation of large aggregates of NPs. The presence of the alkyl chains of OA did not help to produce a homogeneous dispersion. However, the sample became progressively clear, and after about 650 s, it was transparent, meaning that aggregates of NPs attained dimensions much lower than the wavelength of visible light. Figure 9 shows the optical transmittance of a 20 wt % OA-modified DGEBA with 1 wt % magnetite NPs during reaction at 90 °C. The time scale at which the sample became transparent corresponds to a high conversion in the epoxy–acid reaction. This means that once OA reacted with DGEBA, the resulting solvent was good enough to produce the dispersion of OA-stabilized magnetite NPs. Moreover, transparency was kept after completion of the

epoxy homopolymerization. This implies that magnetite NPs were effectively dispersed in the cross-linked epoxy.

TEM images of the cured nanocomposites show a uniform dispersion of NPs in the matrix (Figure 10). In the image with the largest magnification, a dispersion of individual NPs and very small clusters containing few NPs is observed. This clearly demonstrates that OA-modified DGEBA is an excellent solvent to disperse OA-coated NPs.

A viscoelastic characterization of nanocomposites was performed. Figure 11 shows the damping peaks (tan δ) for nanocomposites with different amounts of NPs. A slight increase in the maximum of the peak with the concentration of NPs was observed (from 51 °C for the neat matrix to 58 °C for the sample with 8 wt % NPs).

Figure 12 shows the magnetization curves for three samples containing different amounts of magnetite NPs, (1.5, 7, and 8% w/w of coated NPs), as a function of an applied reversal magnetic field up to 2 T. M-vs-H curves were obtained at two different temperatures, 300 and 5 K. The data were normalized to the total sample mass to obtain comparable results. Magnetic curves show a typical superparamagnetic behavior at room temperature, consistent with an assembly of magnetic single domain particles. As expected, coercive forces and remanence appear as the temperature decreases below the blocking magnetic temperature (defined as the maximum of the M(T)curve in zero-field-cooled (ZFC) conditions), as evidenced in curves obtained at 5 K. ZFC-FC magnetization curves as a function of temperature evidenced a shift of the blocking temperature to higher temperatures with an increasing particle concentration in the samples, pointing to the existence of magnetic coupling between nanoparticles, as has also been reported for other well dispersed but concentrated magnetic nanocomposites $^{36-39}$ (see Figure S1).

The magnetic hyperthermia effect of the synthesized nanocomposites was analyzed using values of frequency and field strength in the range commonly used for biomedical applications. For industrial applications (with less restrictive safety regulations), larger and faster responses can be achieved by using stronger magnetic sources properly designed for each application. The increase in temperature induced by the alternating magnetic field (range for biomedical applications) is shown in Figure 13 for nanocomposites with different contents of NPs. As soon as the magnetic field was switched on, the temperature recorded by the fiber optic thermometer began to increase. A $\Delta T \sim 25$ °C was recorded for nanocomposites with 7 and 8 wt % OA-stabilized NPs after about 60 s of

inductive heating. The temperature increase was much smaller $(\Delta T \sim 4 \ ^\circ\text{C})$ for the nanocomposite with 1.5 wt % OA-stabilized NPs. It must be pointed out that strictly speaking, the temperature recorded by the fiber optic thermometer represents conditions at the surface of the nanocomposite. Because of the heat dissipation to the surrounding atmosphere, temperature at the bulk might be slightly higher than the one actually measured.

It is also worth noting that saturation magnetization of NPs used in this work was about 70 emu/g. This is almost 25% lower than expected for bulk magnetite, which is possibly a consequence of the defective crystalline structure commonly obtained by coprecipitation of iron salts. The use of alternative synthesis methods yielding particles of better crystal quality and higher saturation magnetization (for instance, thermal decomposition of an organic iron precursor) could help to improve the magnetic response of the obtained nanocomposites.

The next step was to investigate if the temperature increase was enough to induce the shape memory of the material. A bar of the nanocomposite containing 8 wt % of OA-stabilized NPs was immersed in a water bath held at 60 $^{\circ}$ C, twisted and cooled while keeping the twisted shape. It was then introduced in the chamber of the inductive heating device and exposed to the alternating magnetic field for 60 s. After this process, the specimen recovered its initial shape, meaning that the actual temperature increase produced by the inductive heating was enough to attain the rubbery state. Initial and final shapes can be seen in Figure 14.

CONCLUSIONS

Modification of a DGEBA-based epoxy with 20 wt % oleic acid enabled us to obtain a suitable reactive solvent to disperse conventional oleic acid-stabilized magnetite NPs. A tertiary amine (BDMA) was used to catalyze the epoxy-acid reaction and initiate the homopolymerization of the epoxy excess. Both reactions occurred practically in series, first the epoxy-acid and then the epoxy homopolymerization. It was necessary to advance the first reaction to attain a very good dispersion of magnetite NPs in the reactive solvent previous to the occurrence of the final reaction. TEM images revealed a nice dispersion of individual NPs in the cross-linked epoxy. A sample containing 8 wt % OA-stabilized magnetite NPs exhibited a temperature increase of 25 °C at its surface when exposed to an alternating magnetic field allowed for biomedical applications. The temperature increase was enough to induce the shape memory of the nanocomposite.

ASSOCIATED CONTENT

S Supporting Information

ZFC-FC magnetization curves as a function of temperature for three different concentrations of magnetite NPs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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