Magneto-optical Faraday activity in transparent FeCo-sepiolite/polystyrene nanocomposites

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Abstract. FeCo nanoparticles synthesized on sepiolite microparticles were used for the preparation of nanocomposites by melt compounding with polystyrene. Both, the sepiolite fibers and the nanoparticles were free of agglomeration, which allowed preparing nanocomposites with a homogeneous dispersion of the second phases, avoiding the usual agglomeration of the nanoparticles and minimizing light scattering. As a consequence, transparent composites with a high magnetic susceptibility have been obtained. The magneto-optical Faraday activity of these nanocomposites has been studied, finding saturation rotations over $200 \text{ rad}\cdot\text{m}^{-1}$ in the visible range. The processing route presented in this work can be easily transferred to industry and allows preparing polymer matrix nanocomposites with no restriction on shape or size and opens the possibility of developing other highly transparent polymer based nanocomposites.

Keywords: Faraday rotation; ferromagnetic nanoparticles; nanocomposites; FeCo

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1. Introduction

The Faraday effect or Faraday rotation refers to the rotation of the polarization plane of an incident polarized light beam (Faraday, 1846). As all the magneto-optical effects, this is a quite useful phenomenon because it allows determining magnetic properties by optical measurements. Large Faraday rotations have been observed in metallic ferromagnetic materials, but due to their high absorption, Faraday rotation can only be measured in very thin films (Liu, 2005). On the other hand, large Faraday rotations have been observed in transparent compounds such as Terbium Gallium Garnett (Dentz et al., 1974), but they must be produced in the single crystal form in order to minimize light scattering. An alternative method to produce large Faraday rotations combined with a simple materials production has led to the preparation of nanocomposites with ferromagnetic nanoparticles dispersed in polymer and glass matrices (Ziolo et al., 1992). However, the large difference between the refractive indices of the matrix and the ferromagnetic particles leads to a large light scattering, which can only be minimized by using very small nanoparticles (well below 50 nm) evenly dispersed in pore-free matrix. Under these conditions, Rayleigh scattering is the dominant mechanism for light losses. This type of scattering has the advantage that directional effects are very limited, so that the material can be considered as a homogeneous effective phase. Additionally, it presents a linear concentration vs. thickness transmittance dependence (Hulst, 1957). Actually, the characterization of this scattering mechanism has been the main issue in most of the works published so far (Zayat et al., 2003; Dominguez et al., 2008). In this sense, magnetic nanoparticles have been dispersed in silica gels (Chanéac et al., 1996; del Monte et al., 1997; Cannas et al., 1998; Solinas et al., 2001), in polymer matrices (Mayer et al., 2000; Breulmann et al., 1998), or grown into porous colloidal silica particles (Bourlinos et al., 2001; Tartaj et al., 2001). Amongst the most attractive properties of the transparent magnetic compounds are those related to the magneto-optical effects and their scientific and industrial applications in such areas as: optical fiber sensor, optical isolators, modulators, optical circulators, information storage and magnetic field and electric current sensors based on the Faraday effect (Qiu et al., 1996).

In any case, the preparation of transparent magnetic suspensions is a complicated task. The magnetic interaction between particles favors clumping processes, so that specific additives or new dispersion methods should be used in order to notably increase the particle steric repulsion. In this work, we describe the preparation of a flexible, transparent and magnetic multiscale composite and its magnetic and magneto-optical activity, particularly the Faraday effect, in the range of 1.0-4.5 eV. The methodology relies on the possibility of embedding metallic magnetic nanoparticles inside sepiolite (Esteban-Cubillo et al., 2010; Esteban-Cubillo et al., 2008; Pecharroman et al., 2006) thus preserving them from agglomeration and

corrosion. It is also feasible to disperse sepiolite bearing metallic nanoparticles into an ad-hoc polymeric matrix and to produce materials behaving in all as plastics (light, tough, easy to process, transparent) while displaying specific properties endowed by the metallic nanoparticle. As an example, the preparation of “plasmonic plastics” has been recently reported (Tiemblo et al., 2012). The approach of this work is very similar though in this case the purpose is to prepare easy-to-handle optically transparent “magnetic plastics”. In the present case, the choice of FeCo as the ferromagnetic material is based on its large magnetic anisotropy and magneto-optical behavior, which make it interesting for different applications such as magneto-optical recording (Hwang et al., 1997; Stavrou et al., 2000) and photonic crystals (Chen et al., 2011).

2. Experimental

Sepiolite powder, purified and micronized by a wet process, and with a particle size below 1 μm was supplied by TOLSA, S.A (Spain). Polystyrene (PS, 143E from BASF) was used as received.

Cobalt-Iron nanoparticles embedded in a sepiolite matrix were obtained by a wet route. Sepiolite powder was dispersed at 10 wt.% concentration in water using high shear mixing and then the suspension was acidified with HCl at pH=0. Afterwards, 1.5 L of treated sepiolite suspension were mixed with 1.0 L of aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a molar Fe:Co rate of 1:1, so that the final relative metal concentration into sepiolite was 26 wt.%. Thereafter, the pH of the dispersion was adjusted with NaOH at 8.0, in order to precipitate the corresponding metal into the octahedral position of leached magnesium. The precipitation was carried out under high shear mixing. Finally, the dispersion was vacuum filtered and washed with water. The obtained precursors were reduced by a thermal treatment at 650°C in a H_2/N_2 (15/85) atmosphere.

Subsequently, sepiolite bearing FeCo (SepFeCo) nanoparticles were organically modified with methyl trimethoxysilane (MTMS) following a previously reported procedure (García et al. 2011). Basically, 3 g of FeCo sepiolite were dispersed in a solution of 16 mmol of MTMS in 72 mL of water by means of a lab dissolver (Dispermat® LC2) operating at 12000 rpm during 20 min. The resulting product (SepFeCo-MTMS) was dried overnight at 100 °C and afterwards purified by several washing cycles with dichloromethane.

The SepFeCo-MTMS/PS composite was prepared by melt compounding in a Haake MiniLab extruder (Tiemblo et al., 2012). 5.225 g of polymer and 0.275 g of SepFeCo-MTMS were physically mixed and directly introduced into the machine. The processing temperature, shear rate and residence time in the extrusion method were 160 °C, 120 rpm, and 20 min,

respectively. Finally, a subsequent extrusion step under the same conditions and lasting 10 min was performed. The composite was compression molded at 140 °C into 60 µm thick films.

X-ray diffraction patterns were recorded in a Bruker D8 Advance diffractometer with a Vantec detector and using Cu-K α radiation. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2100. The microparticle dispersion in the composite was characterized by scanning electron microscopy (SEM, Philips XL30ESEM).

The hysteresis loops were measured with an alternative gradient magnetometer (AGM, MicroMagTM, Princeton Measurements Corporation) with a maximum magnetic field of 0.5 T. The transmittance and Faraday spectra were taken with a SOPRA GES E5 ellipsometer in the energy range 1.5-4.5 eV in the normal configuration (magnetic field applied). For this, the polarizer was set to 0° (p-polarization) and transmittance measurements were carried out varying the analyzer between 85 and 95° in steps of 0.02°. These measurements were repeated, changing the sign of the applied field ± 3 kOe. For each wavelength, the difference in the analyzer positions that yield the minimum of transmission for positive and negative applied fields was calculated.

3. Results and discussion

In figure 1a) SepFeCo microparticles bearing FeCo nanoparticles of diameters below 20 nm are shown. Further organic modification of sepiolite with MTMS nanotexturises the surface as shown in figure 1b). The nanotexturization consists on evenly dispersed spheres arising from the MTMS self-condensation onto the sepiolite surface (Tiemblo et al., 2011). This nanotexturization of the sepiolite surface enables a fine dispersion of the particles into the polymer matrix by one-step conventional melt extrusion processing. Figure 1c) shows the frequency distribution of the size of FeCo nanoparticles. The TEM images and histogram show that, very remarkably, this processing method prevents the nanoparticles from agglomerating, making processing easier. Finally, a SEM image of the PS composite is provided in figure 1d), where homogeneously dispersed white spots corresponding to individualized sepiolite particles are detected. No aggregates larger than 1 µm in size were detected.

Figure 1. a) TEM image of FeCo nanoparticles embedded into dehydrated sepiolite fibres. b) Sepiolite FeCo particles functionalized with MTMS; c) histogram showing the size distribution of FeCo nanoparticles; d) SEM image of SepFeCo-MTMS/PS composite.

As a matter of fact, the one step extrusion processing produces a material which is easily molded and shapeable, and behaves mechanically as PS, while being quite transparent, as shown in figure 2. The transparency of the final composites relies on both, the excellent dispersion of the nanometallic sepiolite and on the matching of the refractive indexes between the phases. Sepiolite particles present a refractive index ($n=1.62$) in the range of that of most used thermoplastics, in particular PS ($n=1.59$) so that the scattering induced by the silicate particles is minimized (Hulst, 1957).

Figure 2. Handiness and transparency of a 60 μm thick film of SepFeCo-MTMS /PS composite.

In order to determine the presence of the Fe-Co alloy, X-ray diffraction patterns (figure 3) were taken on as received powder: curve *i*), functionalized powder, curve *ii*), polymeric film, curve *iii*) and polymer-powder composite, curve *iv*). In the case of powdered samples, curves *i*)

and *ii*), a large number of peaks corresponding to anhydrous sepiolite can be seen in both samples (indicated with *s*). Due to the amorphous character of the MTMS, no new peak appears in the treated sample, as shown in curve *ii*). Additionally, two peaks at 45 and 63°, corresponding to the FeCo (1:1) can be observed. It should be noted that these peaks appear at a position very close to those of α -Fe but slightly shifted. This fact is in good agreement with the proposed crystalline structure of FeCo alloy (Sorescu et al., 2002). Finally, in the case of the SepFeCo-MTMS/PS composite, curve *iv*), the diffractogram is dominated by two broad bands at $2\theta=10$ and 20° corresponding to the amorphous Polystyrene, as it can be checked out in the curve *iii*). Over these, some peaks corresponding to anhydrous sepiolite as well as the strongest FeCo maximum are still visible.

Figure 3. X-Ray diffractograms corresponding to *i*) SepFeCo, *ii*) SepFeCo-MTMS, *iii*) PS and *iv*) SepFeCo-MTMS/PS composite. Peaks corresponding to dehydrated sepiolite, FeCo Alloy and Polysterene have been labeled a *s*, *FeCo* and *PS* respectively.

The magnetic hysteresis loop (figure 4) shows that the SepFeCo-MTMS/PS composite is magnetically soft, with a coercivity $H_c = 345$ Oe, and it is already saturated around 4 kOe. No indication of superparamagnetism has been found in the hysteresis loop. This result is in agreement with the theoretical condition of superparamagnetism at room temperature. Thus, by taking $\gamma = (6.9 \pm 0.5) \cdot 10^5 \text{ J} \cdot \text{m}^{-3}$ as the value of the uniaxial magnetic anisotropy (Zuberek et al., 2000), it can be deduced that spherical particles with diameters over 5 nm, as it appears in figure

1a-c, will not behave superparamagnetically at room temperature (Dentz et al., 1974). In particular, the histogram in Fig 1c shows that the diameters of the particles range between 5 and 17 nm and, therefore a single domain behavior is expected. It is very important to note that at 3 kOe, the system is already very close to the magnetic saturation; this is important because the Faraday effect spectrum (figure 5) was taken at ± 3 kOe and, therefore, the rotations measured can be taken as the Faraday effect at saturation.

Figure 4. Hysteresis loop corresponding to the SepFeCo-MTMS /PS composite.

Both transmittance and Faraday rotation are shown in figure 5, where it can be seen that the 60 μm thick films of the SepFeCo-MTMS/PS composite present a broad peak of the Faraday activity between 2.5 and 3.5 eV, with a maximum of 1° close to 3 eV for applied magnetic fields of $\pm 0.3\text{T}$, which corresponds to a specific saturation rotation of $290 \text{ rad}\cdot\text{m}^{-1}$. FeCo nanoparticles shows an absorption band around 2 eV that was interpreted by Kim et al. (2000) as due to the overlap of the d-states from Co sites with those from Fe sites. According to Becquerel's formula, the Verdet constant and, therefore, the Faraday rotation depends on a variation of the refractive index with the photon energy, which takes place, for example, in the absorption

regions. For this reason, this transition can be considered as the origin of the Faraday peak observed around 2 eV.

Other works have shown the potential of pure FeCo alloys for magneto-optical recording and the high Faraday rotations obtained in this system, reaching $10^5 \text{ rad}\cdot\text{m}^{-1}$. However, due to their high absorption, they have only been studied in the thin film form (Reim et al., 1987). More recently, Co:TiO₂ composite thin films have also shown a large Faraday activity combined with a high transmittance. However, due to the thickness the total measured Faraday ellipticity was only 0.05 deg (Ikemiya et al., 2011).

The herewith obtained magneto-optical effects are even more remarkable if we take into account that samples do not need any substrate and they can be handled without any special precaution. This is so because their mechanical properties are very similar to those of the polymeric matrix but keeping a very good degree of transparency. In this regard, most of previous reported magneto-optical materials have been deposited on a thick substrate and/or show a poor transmittance due to a large scattering originated from the presence of agglomerated particles in the system.

In this particular work we have focused on Fe-Co nanoparticles alloy due to its large magneto-optical activity, but the same experimental procedure could be used for other metallic or dielectric magnetic nanoparticles, such as Fe, Ni, Co, Fe₃O₄ or γ -Fe₂O₃, Co₃O₄, etc.

In fact, the versatility of this procedure is based on the fact that it avoids the agglomeration of the particles, either the nanometallic or the microsepiolite ones. Sepiolite acts as a microcarrier on which metallic nanoparticles are supported and hence they have no mobility of their own; sepiolite on its turn is chemically modified to avoid its reaggregation. Processing in PS is then very simple. At the same time, the fine dispersion of both types of particles and the adequate choice of materials permits the preparation of flexible, handy and highly transparent films. Transparency is well illustrated in the real in-line transmittance spectrum in figure 5. In the infrared range studied, the transmittance reaches 60%, whereas in the visible range, the transmittance decays from 0.4 at 2 eV to 0.1 at 3 eV. Actually, this method is highly convenient for a number of reasons: i) it allows a robust control of the optical and magnetic properties of the whole composite, ii) it renders stable composites, ii) it is easy to reproduce and iv) it can be easily scaled up for possible industrial applications.

Figure 5: Faraday rotation and transmittance of the SepFeCo-MTMS /PS composite in the 1.0-4.5 eV range. Inset: Picture of the transparent SepFeCo-MTMS /PS magnetic composite.

4. Conclusions

This work describes the preparation of flexible and robust SepFeCo-MTMS /PS composites. The processing method enables a homogeneous dispersion of the FeCo nanoparticles in the polymer matrix and the composites show a high real in-line transmittance. The Faraday activity of the system presents a broad peak with a maximum close to 3 eV, leading to a saturation rotation of $290 \text{ rad} \cdot \text{m}^{-1}$ at this energy, making it useful for applications as a magneto-optical sensor. The stability and low cost of the fabrication method make this method a good candidate for a potential scale up for industrial production of magneto-optical composites at low cost.

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