Chemical Physics Letters 693 (2018) 183–187

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

Nanocomposites based on self-assembly poly(hydroxypropyl methacrylate)-*block*-poly(N-phenylmaleimide) and Fe_3O_4-NPs. Thermal stability, morphological characterization and optical properties

Guadalupe del C. Pizarro [a,*], Oscar G. Marambio [a], Manuel Jeria-Orell [a], Julio Sánchez [b], Diego P. Oyarzún [c]

[a] *Departamento de Química, Universidad Tecnológica Metropolitana, J. P. Alessandri 1242, Santiago, Chile*
[b] *Departamento de Ciencias del Ambiente, Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, Casilla 40, Correo 33, Santiago, Chile*
[c] *Center of Applied Nanosciences (CANS), Facultad de Ciencias Exactas, Universidad Andres Bello, Avda. República 275, Santiago, Chile*

ARTICLE INFO

Article history:
Received 13 November 2017
In final form 14 January 2018

Keywords:
Self-assembled polymer
Nanocomposites
Optical properties
Thermal stability
Morphological behavior
Photodegradation

ABSTRACT

The current work presents the synthesis, characterization and preparation of organic–inorganic hybrid polymer films that contain inorganic magnetic nanoparticles (NPs). The block copolymer, prepared by Atom-Transfer Radical Polymerization (ATRP), was used as a nanoreactor for iron oxide NPs. The NPs were embedded in poly(hydroxypropyl methacrylate)-*block*-poly(N-phenylmaleimide) matrix. The following topographical modifications of the surface of the film were specially analyzed: control of pore features and changes in surface roughness. Finally, the NPs functionality inside the polymer matrix and how it may affect the thermal and optical properties of the films were assessed.

1. Introduction

Iron oxide nanoparticles, such as maghemite and magnetite, have been of technological and scientific interest due to their unique electric and magnetic properties. These nanoparticles can be used in numerous fields, such as in high-density information storage and electronic devices [1–4]. The simplest synthetic route to manufacture nanomaterials is probably self-aggregation, in which ordered aggregates are formed by a spontaneous process [5]. However, there is a permanent challenge of developing simple and reliable synthetic ways for low-dimensional metal oxide nanostructures. The designed chemical components and controlled morphologies strongly affect the properties of nano-materials. [6]. In recent years, nanostructures of super-paramagnetic iron oxides have been extensively investigated because they offer several potential biomaterials, as well as biomedical applications in magnetically-controlled drug delivery, magnetic resonance imaging as a contrast agent, and tissue repair [7–9]. Reducing the crystal dimension and enhancing the surface area of the sensing materials are optical approaches used to improve the responses, since the reduction/oxidation reactions are mainly activated by the active surface areas.

In nanotechnology, iron oxide NPs are defined as small particles that behave as a whole unit in terms of their transport and properties. Nanoparticles may or may not exhibit size-related properties that differ significantly from those in fine particles or bulk materials [10].

In the case of maghemite, γ-Fe_2O_3, an allotropic form of magnetite, Fe_3O_4, while the Fe_3O_4 properties are superior, γ-Fe_2O_3 is more stable, since iron cannot be further oxidized under ambient conditions [11].

The viability to form a variety of structural morphologies from metal oxide NPs offers many opportunities of tuning these chemical sensing properties.

The aim of this work was to prepare organic-inorganic hybrid porous films that contain inorganic magnetic NPs, in which the percentage variation of metal oxide (1.0%-3.0% wt.% of NPs) was evaluated on thermal stability, optical and morphological properties. The self-assembly block copolymer matrix was synthesized by Atom-Transfer Radical Polymerization (ATRP) [12,13]. The advantage of using this self-assembled block copolymer as a matrix is the immiscibility of the blocks that creates a microphase separation, thus promoting the formation of nanosized spherical domains. Besides, the introduction of the functional NPs is crucial to the applicability of these porous composite structured films.

---

[*] Corresponding author.
E-mail addresses: gpizarro@utem.cl, pizarroguadalupe048@gmail.com (Guadalupe del C. Pizarro).

https://doi.org/10.1016/j.cplett.2018.01.030
0009-2614/

This is an important approach when extending the potential practical applications of the nanocomposite systems to advanced technologies, such as nanoscale devices and biomedical materials [14,15].

2. Materials and methods

The nanocomposite system was characterized by Fourier transform infrared (FTIR) spectra recorded using a Bruker Vector 22 (Bruker Optics GmbH, Inc., Ettlingen, Germany). Optical absorption spectra and diffuse reflectance were measured with a UV–visible spectrometer Perkin Elmer model Lambda 35 with an integrator sphere. The measurements were recorded within the range 200–800 nm, at room temperature, medium scan rate and slit 0.0 nm. Photoluminescence (PL) measurements were performed by a fluorescence spectrometer system (Perkin Elmer, model L 55) at room temperature, using an excitation wavelength of 320 nm. Thermal studies were performed using a thermogravimetric analyzer (TG) Star System 1, Mettler Toledo, at a heating rate of 10 °C min^{-1}. The morphology (1 mg polymer/mL solvent) was examined by scanning electron microscopy (SEM; JEOL, GSM-6380LV), and by transmission electron microscopy (TEM) (JEOL JEM 1200EX, operating at 120 kV, with a point resolution of approx. 4 Å). The TEM images were taken by placing a drop of the block copolymer solutions in THF onto a carbon-coated copper grid. Surface characterization of the block copolymers was carried out using atomic force microscopy (AFM) (Digital Instruments Scanner SFM NT-MDT NANOEDUCATOR; tapping mode, at scan rate of 10.0 mm s^{-1}).

2.1. Synthesis of block copolymers

The macroinitiator P(HPMA-TBDMS)-Br was polymerized with N-phenylmaleimide (N-PhMI) using the CuBr /PMDETA initiating system, and synthesized according to a previously reported procedure [12,13]. The final block copolymer, abbreviated as $P(HPMA)_m$-b-$P(N\text{-}PhMI)_n$ was obtained by the hydrolysis of the tert-butyl group by treatment with tetrabutylammonium fluoride $(C_4H_9)_4NF$, as described in the literature [13].

2.2. Preparation of nanocomposites block copolymer

As a common procedure, the self-assembled poly(hydroxypropylmethacrylate)-*block*-poly(N-phenylmaleimide) (denoted **HPP-3)** was dissolved in THF at concentration of 0.2% (P/V) followed by adjusting the pH by drop-wise addition of 1 M NaOH. The pH of the solution was adjusted at 9.0 and then, the iron oxide NPs produced (contents from 1.0 to 3.0 wt%) were incorporated. The solution was left stirring for 6 h, so that the system could reach balance with the functional groups of the polymer matrix that were participating in the complex process [16].

3. Results and discussion

3.1. Structural and thermal analysis

The infrared spectroscopy is used for the identification of the iron oxide phase as a result of divalent and trivalent cations interaction with electromagnetic radiation. The $\mathbf{HPP\text{-}3_{1.0\%–3.0\%}}$ nanocomposites were examined by FTIR spectroscopy in order to verify precursor association with functional groups of the block domains. The FTIR spectrum recorded for the HPP-3 in presence of Fe_3O_4 NPs (Fig. 1a) shows a band at 582 cm^{-1} (Fig. 1a, right-zoom) that increases, as the percentage of the nanoparticles grows, and that is absent in the spectrum of the polymer alone. The presence of this band is associated to the Fe—O vibration modes in tetrahedral sites of the Fe_3O_4 and evidences the incorporation of the nanoparticles to the polymer. It is known that due to their hydrophilic character of PHPMA, the iron oxide nanoparticles have a higher affinity for the hydrophilic phase, specifically with the hydroxyl group in hydroxypropyl moiety, and a much lower one for the hydrophobic phase, (PN-PhMI) domain. As can be noted, the FT-IR spectrum of the polymer, in absence of Fe_3O_4 NPs (Fig. 1(a)), shows a broad band with a pronounced peak at 3475 cm^{-1} that corresponds to the O—H stretch of the hydroxyl group in the hydrophilic domain. In presence of Fe_3O_4 NPs, the intensity of this band decreases as the nanoparticle content increases (1–3%). Therefore, the decrease of this band should be associated to the coordination of the hydroxyl group either to Fe^{2+} or Fe^{3+}, at the nanoparticle surface. Additionally, it was observed that when the copolymer had a large amount of iron oxide NPs in the system, the vibration mode of other functional groups was clearly affected. Consequently, some bands in the block copolymer considerably decrease in intensity for example, in the 3060–2950 cm^{-1} range (antisymmetric CH_3, antisymmetric CH_2 and aromatic CH stretch), see Fig. 1(a) [17].

Raman spectrum shows the main features of the wave number present at about 225, 290, 410, 500, and 620 cm^{-1} for Fe—O stretching vibration. These large bands may be assigned to a magnetite phase (Fe_3O_4) of iron oxide NPs.

The TGA results revealed good thermal stability of the block copolymer; higher than both the macroinitiator and their block copolymer nanocomposites, shown in Fig. 1(c and d). The block copolymer (**HPP-3)** and its $\mathbf{HPP\text{-}3Fe_3O_{4(1.0–3.0\%)}}$ composites exhibited one-step degradation at 350, 280, 270 and 260 °C, respectively. The $\mathbf{HPP\text{-}3Fe_3O_{4(1.0\%)}}$ composite, with lower nanoparticles percentage, showed a higher thermal decomposition temperature. According to these results, the incorporation of $\mathbf{Fe_3O_4}$ NPs, in the block copolymer matrix, strongly affected the thermal stability of the system, decreasing with respect to the block copolymer, and slightly increasing when the amount of Fe_3O_4 incorporated into the matrix was higher; see Fig. 1(d). The residual mass was over 50%, as the amount of Fe_3O_4 into the polymeric matrix increased too.

3.2. Optical properties

The optical properties of the Fe_3O_4 NPs were determined by UV–Vis and fluorescence. The UV–Vis absorption spectra for the system **HPP-3** $Fe_3O_{4\mathbf{1.0–3.0\%}}$ composites exhibited exciton peaks ranging from 236 to 232 nm, which were slightly blue-shifted. These absorption bands were larger than the ones at 239 nm and were attributed to the polymer matrix. This blue shift is characteristic of a strong quantum confinement (QDs) effect, arising from particle size reduction.

Fig. 2(a) shows the representative electronic absorption spectra of Fe_3O_4/NPs in THF. Photo-catalytic degradation of the polymer matrix was caused by the absorption of photons in wavelengths found via ultraviolet light. The photo-degradation of the polymer matrix predominantly occurred on the iron oxide NPs surface at different concentrations. This degradation was measured by monitoring its concentration, with and without NPs, after reaching degradation [18]. Fig. 2(a) shows the gradual decrease in absorption spectra for the nanocomposite films as a function of photoirradiation time (maximum of 2 h). The presence of a higher concentration of iron oxide NPs, leading to a decrease in absorption bands and a blue shifting ranging from 232 to 239 nm, was observed.

The UV–vis absorption spectra of grown iron oxide NPs (Fe_3O_4) solution is at room temperature, shown in Fig. 2(b). In this procedure, the spectrum obtained from optical absorption, was analyzed to acquire the energy band gap of semiconductor nanomaterials. This gap displays an onset of absorption maxima at 390 nm, in a