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Superparamagnetic magnetite–divinylbenzene–maleic anhydride copolymer nanocomposites obtained by dispersion polymerization

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ABSTRACT

Magnetite alternating copolymers divinylbenzene–maleic anhydride (DVB–MA) composites were prepared by dispersion polymerization. Because magnetite is used as a complex with oleic acid (Fe_3O_4OLA), the final hybrids show good dispersion of inorganic nanofillers in the polymer matrix. The obtained composites were analyzed by infrared absorption spectrometry, diffuse reflectance in visible light, thermogravimetry, X-ray fluorescence, X-ray diffraction, dynamic light scattering, scanning electron microscopy and vibrating sample magnetometry. The obtained results indicate the successful preparation of magnetite nanoparticles with an average size of about 23 nm dispersed in micrometer size copolymer spherical particles, which relative content can be controlled via the processing parameters. A relationship between the relative content of magnetite nanoparticles and the size of the polymer particles, with direct influence on the diffuse reflectance in the visible domain, was observed. A superparamagnetic behavior was evidenced at room temperature with a blocking temperature lower than as expected from the bulk anisotropy constant and the average size of the magnetite nanoparticles. Both the unexpected low blocking temperature and the observed low specific magnetizations were explained by a defected and poor crystalline structure of the magnetite nanoparticles, giving rise to spin disorder and diminished crystalline anisotropy constant.

1. Introduction

Polymer nanocomposites containing magnetic particles as fillers have shown a particular interest in the last three decades [1,2]. Such materials that offer many possibilities of modeling magnetic and physicochemical properties were obtained for different targeted applications.

The main concerns were directed towards the possibility of more advanced dispersion of magnetic filler in the polymer matrix [1,2]. One important direction is the polymerization of monomers in disperses media: emulsion, miniemulsion, suspension, dispersion [2]. Depending on the polarity of the monomers and the dispersion medium, nanocomposite systems containing magnetic nanoparticles of core–shell structure, homogeneously dispersed in micrometer size polymeric particles/or fixed on the surface of the polymeric particles, can be obtained [2].

A good compatibility of the magnetic nanoparticles (magnetite, in this report), can be obtained by organophilization with oleic acid (OLA). Using such organophilizated magnetite (Fe_3O_4OLA), various nanocomposites can be prepared by emulsion polymerization [3], miniemulsion

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[4–6], microemulsion [7] and dispersion [8,9]. As already proven in previous reports, the liophilic complex Fe_3O_4OLA is dispersible in monomer [6] or in organic solvents [3,10–17]. In water–oil mixtures, depending on working conditions (pH), it can be distributed in the oil (*o*) phase, in the aqueous (*w*) phase or at the o/w interface [18].

Based on the above mentioned information, we consider that a good dispersion of magnetic filler can be obtained by dispersion polymerization [8]. The system is initially homogeneous under these conditions and the obtained polymeric particles can disperse more efficiently Fe_3O_4OLA magnetic nanoparticles, due to the copolymerization ability of OLA with the existing monomers [7]. In this work, the Fe_3O_4OLA complex was prepared as in [10]. A subsequent dispersion polymerization was aimed to obtain alternanting copolymers divinylbenzene–maleic anhydride [19]. Heptane-methyl ethyl ketone (C7-MEK) mixture [19] was used as a dispersion medium, and decaethylene glycol oleyl ether (Brij® 96V) ($OLAEO_{10}$) as a reactive surfactant. The influence of Fe_3O_4OLA concentration on particle size of alternanting copolymers DVB–MA, thermal stability and optical and magnetic properties of the composites was analyzed. The reported copolymers are interesting because the hydrolysis in alkaline aqueous medium [19] can transform them into polyelectrolyte dispersed in water, of importance in fixing some biologically active compounds.

2. Experimental

2.1. Materials

Divinylbenzene (Fluka) (DVB) and maleic anhydride (Fluka) (MA), were purified by distilation, respectively by sublimation. Heptane (Fluka), methyl ethyl ketone (Chimopar) were purified by distilation. Decaethylene glycol oleyl ether (Brij® 96V) ($OLAEO_{10}$) (Fluka), azo iso butyronitrile (AIBN) (Amos Organica) and oleic acid (Fluka) (OLA) were used without further purification. Also $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ (Merck) were used as they were received.

2.2. Samples preparation

2.2.1. Preparation of Fe_3O_4OLA

The procedure previously published in [10] has been used for preparation of magnetite nanoparticles stabilized with OLA. Briefly, it was proceeded as follows: 240 cm^3 25 wt.% NH_4OH and 260 cm^3 distilled water were introduced in a three necked flask equipped with mechanical stirring (350 rpm). After purging with nitrogen while stirring at room temperature, a mixture of 4 g $FeCl_2{\cdot}4H_2O$ dissolved in 10 cm^3 2 N HCl and 10.8 g $FeCl_3{\cdot}6H_2O$ dissolved in 40 cm^3 distilled water was added. The mixture, which immediately turns colored was kept stirring for one hour. After stopping the stirring ferrite precipitate can be quickly decant magnetically. After removing, the aqueous layer precipitate was washed twice, with 100 cm^3 H_2O. The black-brown mixture separated by magnetic field was decanting from the aqueous phase and over the wet precipitate were added 250 cm^3 CH_2Cl_2 containing 1.5 g OLA. After an additional 0.5 h stirring, the mixture was left to stand. A bottom highly colored organic layer and a superior highly transparent and colorless aqueous phase, were obtained. The aqueous layer was separated and then the organic layer was transferred in a polyethylene container after removal of water and the CH_2Cl_2 was evaporated at room temperature. After drying, good quality Fe_3O_4OLA nanoparticles (similar to the ones reported by [10]), with 24.5% OLA/1 g solid mixture (according to the thermogravimetry measurements) were obtained.

2.2.2. Preparation of DVB–MA/Fe_3O_4OLA hybrids in dispersion

A similar methodology as previously published in [19], but adapted to our target, has been used. The obtained samples (together with their labeling) as well as the corresponding concentrations of reactants are listed in Table 1. An example of synthesis is provided in the following for the case of sample D47: In a three necked flask equipped with a mechanical stirrer (300 rpm) and a condenser, 40 cm^3 MEK and 60 cm^3 heptane as well as 4 g DVB and 4 g MA were successively introduced. After stirring, the mixture was homogeneous and transparent. Under nitrogen and stirring, there were introduced 0.8 g $OLAEO_{10}$ and 0.4 g Fe_3O_4OLA. After 15 min of stirring and 30 min of ultrasonic disaggregation, the mixture was homogeneously colored. The whole mixture was heated at 70 °C while stirring. After reaching this temperature, 0.2 g AIBN were firstly added and another 0.2 g after 2 h. The mixture was cooled after 4 h of reaction. A part of the mixture was transferred to a glass vial and sealed, and another part in polyethylene containers for solvent evaporation. After drying in vacuum at 40 °C, the resulting composite was weighted (Table 1).

2.3. Methods

Conversions were estimated gravimetrically. Thermal analysis was conducted with a TA Q5000 IR instrument under nitrogen at a heating rate of 10 °C/min. Infrared (IR) spectra were obtained directly on the copolymer powders by using a Specac Golden Gate ATR device (KRS5) with a Jasco FT-IR 6300 instrument, in the range 400–4000 cm^{-1} (30 scans at a resolution 4 cm^{-1}).

The particle size distribution was measured by Dynamic Light Scattering (DLS) in the mixture of solvents used in polymerization or in 0.1 N HCl aqueous solutions. The polymer concentration in the dispersion medium was 0.01% by weight. Measurements were made with an instrument Nanosizer ZS (Malvern) after ultrasonic disaggregation for 10 min. The Scanning Electron Microscopy (SEM) was performed with a FEI Quanta 200 instrument. Diffuse reflectance spectra were recorded on solid samples (as powders) with Spectralon as a reference, on a Jasco UV–Vis–NIR V 570 spectrometer equipped with a 472 ILN integrating sphere (150 mm).

X-ray diffraction (XRD) analysis was performed using an X-ray diffractometer DRON-UM with horizontal goniometer in Bragg–Brentano geometry, at room temperature using an iron filtered Co Kα radiation (λ = 1.79021 Å). X-ray fluorescence analysis was performed on a PW4025-MiniPal-Panalytical EDXRF Spectrometer. Measurements were