Preparation of magnetic latexes using styrene monomer

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Abstract

The preparation of magnetic latexes using styrene monomer was carried out via the miniemulsion polymerization technique. Magnetite (Fe_3O_4), with an average size of 12 nmwas used as magnetic particles. An organic phasewas prepared dispersing the magnetite in styrene where bis(2-ethyl, hexyl) sulphosuccinate (AOT) was used as dispersant. The dispersion was then miniemulsified in water using cethyltrimethyl ammonium bromide (CTAB) as second emulsifier forming a stable emulsion. The miniemulsion polymerization was carried out at 60 °C and was initiated with 2,2-Azobisisobutyronitrile (AIBN). The latexes obtained were characterized by X-ray diffraction (XRD), magnetometry and transmission electron microscopy.

Keywords: Magnetic latexes, Polymers, Magnetic materials, Miniemulsion polymerization, Magnetic measurements.

Introduction

Magnetic particles are inorganic materials that can be embedded in a polymeric matrix. The mechanical properties of the composite are dictated by the polymeric phase and the magnetic properties by the magnetic material. Magnetic particles include ferrites and intermetalic compounds of rare earths. Magnetic materials have a wide range of application in our daily life, some in engineering and some in medicine, for example, as devices for automotive and communications systems, and thermosensitive magnetic materials for antibody purification [1].

The miniemulsion polymerization process requires a large amount of emulsifier agents, and a co-surfactant, such as a long chain alcohol. This process can be defined as the polymerization of all monomer droplets present in the initial emulsion, where the final particle size distribution will correspond to the initial droplet size distribution [2]. Droplets generally range in size from 50 to 500 nm and the emulsion can be stable for as little as days or as long as months. Few works has been reported related to the encapsulation of inorganic particles, for example titanium dioxide [3], calcium carbonate and barium carbonate [4] and others. However, the inorganic particles mentioned before are not magnetic; in a recent study Hoffmann et al. [5] used magnetite as inorganic particles and these were encapsulated in styrene using a miniemulsion process.

The purpose of this work is to obtain magnetic latexes using magnetite as a magnetic material and polystyrene as a polymer matrix, using a miniemulsion polymerization process with bis(2-ethyl hexyl) sulphosuccinate (AOT) as dispersing agent of magnetite in the monomer, cethyltrimethyl ammonium bromide (CTAB) as surfactant of the monomeric droplets in water in order to form the miniemulsion, and 2,2-azobisisobutyronitrile (AIBN) as initiator of the polymerization. The magnetic latexes obtained were studied by X-ray diffraction (XRD), magnetometry (VSM) and transmission electron microscopy (TEM).

Experimental

$FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$ and NH_4OH were used to obtain the magnetite particles by the coprecipitation method [6]. Styrene (St); AOT, hexadecane, CTAB, and AIBN, were used to prepare the polymer matrix.

The process to obtain the magnetic latexes was as follows: 12.5 g of magnetite styrene–AOT were added to a solution of 50.5 g of water with 0.2519 g of CTAB and 0.1209 g of AIBN. The mixture was sonificated for 1 min using an ultrasonic homogenizer (Branson W700). After the miniemulsion was formed, it was added into a flask reactor under nitrogen atmosphere to prevent possible oxidation. The reaction temperature was 60 °C and usually it was completed after 3 h.

The magnetite was characterized by XRD using a Siemens D-5000 X-ray diffractometer with Cu Kα (25 mA, 35 kV). The magnetic properties of the materials obtained were studied with a vibrational sample magnetometer (Lakeshore 7300). To determine the morphology and the size of the magnetite particles and the magnetic latexes, a TEM (JEOL 1200EXII) was used.

Results and discussion

The XRD pattern of magnetic particles obtained (Fig. 1) shows a spinel phase. The line positions and intensities were consistent with the presence of magnetite or maghemite. However, sufficient minor differences on the XRD patterns of magnetite and maghemite, such as the absence of the 210 and 211 lines of maghemite, indicate that a maghemite phase is not present [7]. The lattice parameter for the sample obtained from the main diffraction line 311 was 8.368 Å. This value lies between the lattice parameter corresponding to magnetite (8.396 Å) and the one corresponding to maghemite (8.345 Å). This is likely to be caused by the partial oxidation of the particles.

Fig. 2 shows a typical magnetization curve for the particles obtained. The saturation magnetization of the particles was 75.4 emu/g. This value is lower than the theoretical value of the bulk magnetite (92 emu/g) [8]. The decrease in the magnetization is reported to occur when the particle size of magnetite decreases below 30 or 20 nm due to superparamagnetism [9].

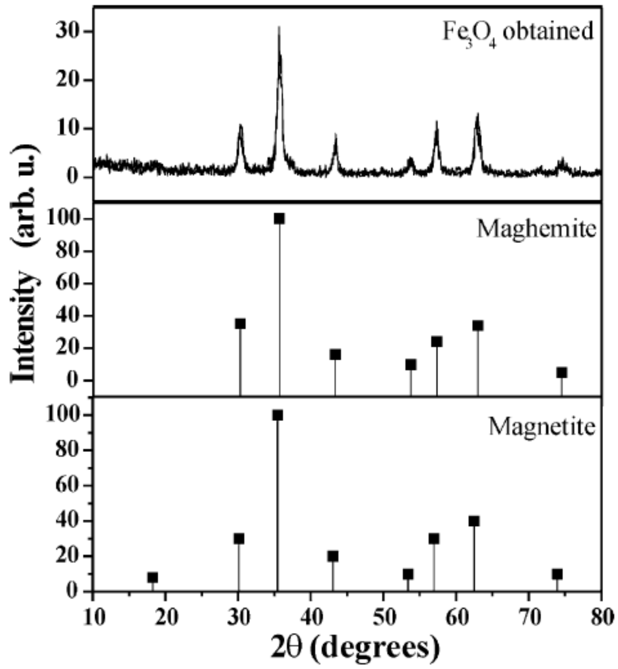

Fig. 1. X-ray diffraction pattern of Fe_3O_4 obtained and for magnetite and maghemite standards.

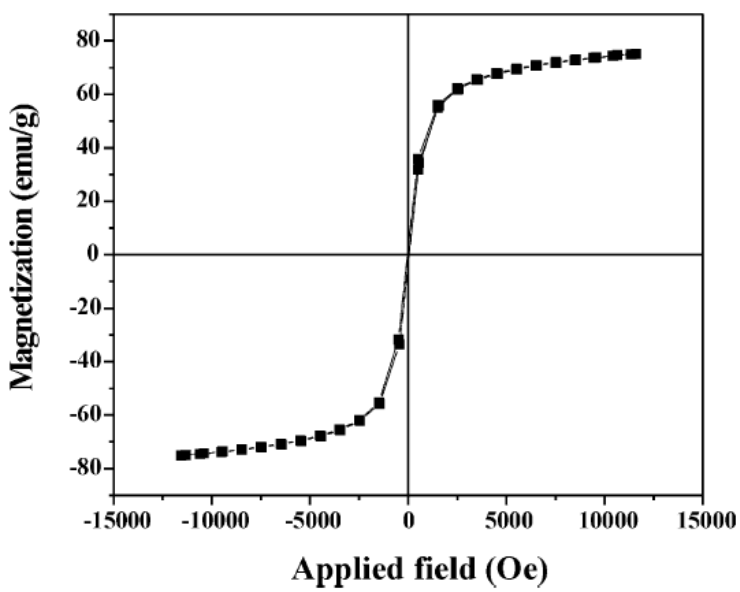

Fig. 2. Magnetization curve for magnetite.

The magnetization curve for the magnetic latex is shown in Fig. 3. The saturation magnetization of the magnetic latex was found to be 0.44 emu/g, this value depends on the weight fraction of magnetite in the latex, which for our system corresponds to 0.0036. The magnetization curve shows a small negative slope at high magnetic field. This is possibly caused by the diamagnetic background signal of water in the sample, the plastic sample holder or the polymeric shell. This same behavior has been reported [10,11] when using similar materials obtained also by the miniemulsion polymerization process.

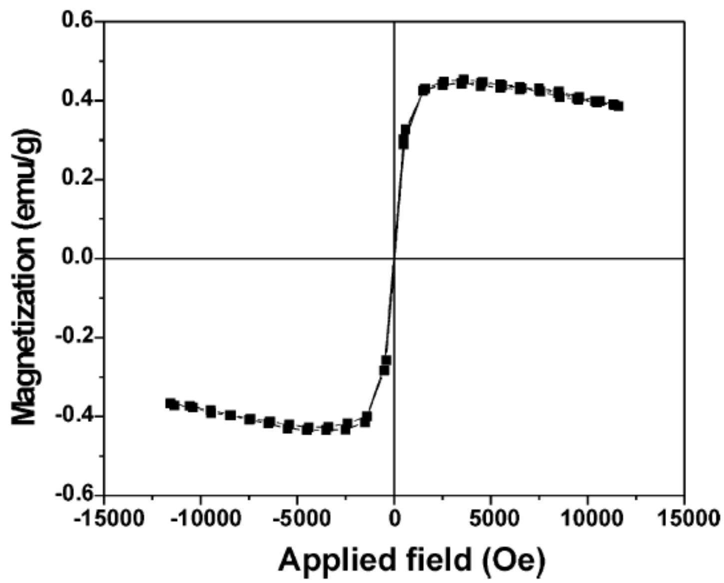

Fig. 3. Magnetization curve of magnetic latexes.

Fig. 4 shows a micrograph of the magnetic latexes obtained by TEM. We observed polymer particles of around 300 nm containing magnetite. The distribution of magnetite seems to be rather inhomogeneous, some polymer particles contain large amounts of magnetite, whereas some others are practically void of magnetic particles. This effect can be explained considering the ionic interactions between the different surfactants used; CTAB is a cationic surfactant used to produce micelles and to stabilize the monomer droplets and AOT is the anionic surfactant used to stabilize the magnetite in the monomer. It is possible that these ionic interactions helped to maintain the magnetite within the monomer droplets once polymerization has initiated.

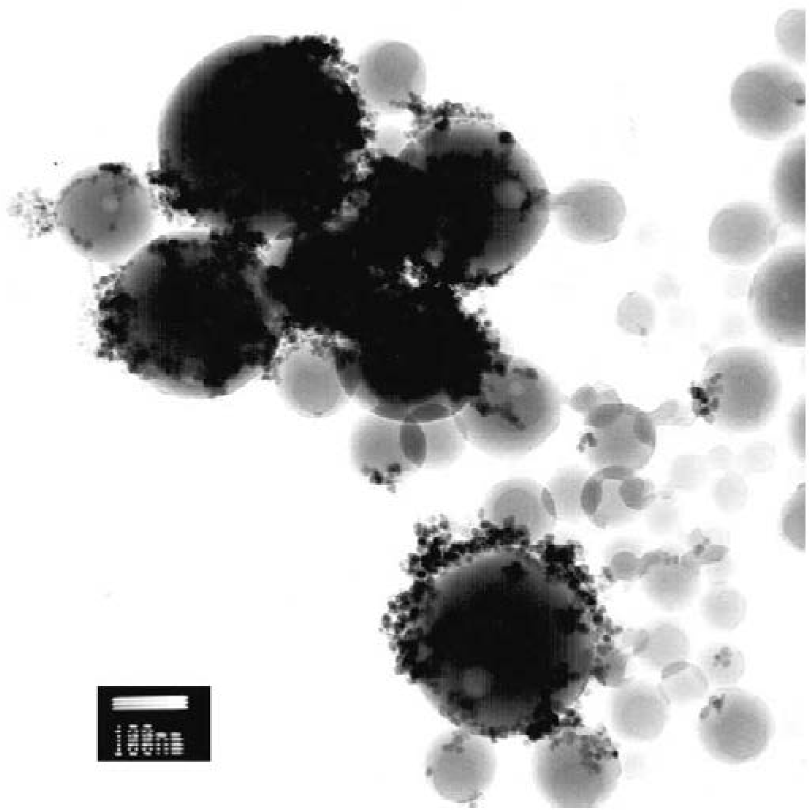

Fig. 4. TEM micrograph for the magnetic latexes.

Conclusions

Magnetic particles of nanometric size showing superparamagnetic behavior were partially encapsulated with polystyrene via the miniemulsion polymerization process. Ionic interactions between the surfactant used to stabilize the magnetic particles within the monomer and the surfactant used to produce the miniemulsion are important in order to obtain magnetic latexes.

Acknowledgments

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