Macromolecular Nanotechnology

An experimental study on the synthesis of poly(vinyl pivalate)-based magnetic nanocomposites through suspension polymerization process

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ABSTRACT

A new class of magnetopolymeric nanocomposites intended for biomedical applications such as vascular embolization and hyperthermia treatment has been synthesized by *in situ* incorporation oleic acid-modified Fe$_3$O$_4$ superparamagnetic nanoparticles into poly(vinyl pivalate) thermoplastic matrices through suspension polymerization. Spherical microparticles of poly(vinyl pivalate)/Fe$_3$O$_4$ with controlled morphology and size have been successfully obtained based on the proposed experimental methodology, showing good magnetic properties, which indicates that poly(vinyl pivalate) magnetic polymers might be employed as embolic agent. This new magneto-polymeric material presents as main advantage the *in situ* formation of the nanocomposites, which ensures the proper dispersion of the Fe$_3$O$_4$ superparamagnetic nanoparticles into the poly(vinyl pivalate) matrix, leading to a desired superparamagnetic behavior of the final material, observed via magnetization measurements. The chemical characterization of the inorganic filler into the nanocomposites through energy-dispersive X-ray spectroscopy showed that inorganic phase was composed mainly of Fe in the form of iron oxide, lying in the range of 92–99%. Thermal stability of the materials determined by thermogravimetry analyses showed a significant weight loss occurring in the range from 300 °C to 700 °C, exhibiting good thermal stability. In addition, the weight fraction of nanoparticles evaluated by thermogravimetric measurements was determined in the range from 2 wt.% to 16 wt.%.

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1. Introduction

Nanoparticles attract the interest of many scientists since the twentieth century. In recent years, several experimental techniques have been applied for the synthesis of new magnetic materials. A relatively large number of magnetic nanoparticles presenting different behavior when exposed to external magnetic fields is known, among them, it should be highlighted magnetite (Fe$_3$O$_4$), maghemite (γ-Fe$_2$O$_3$), cobalt ferrite (CoFe$_2$O$_4$), barium ferrite (BaFe$_{12}$O$_{19}$) [1]. Especially,

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when biomedical applications are considered, the presence of superparamagnetism makes the magnetic nanoparticles interesting for practical reasons [2,3].

Magnetite is a ferromagnetic mineral that can be found in sedimentary rocks, mollusks (radula), arthropods (bees), penguins, algae, fungi and bacteria [4,5]. Magnetite may be synthetically prepared by several experimental techniques, such as precipitation from mixtures of ferric and ferrous ions in an alkaline medium, oxidation of ferrous ion from ferrous hydroxide solutions, interaction of ferrous ions with hydrated iron oxide solutions or decomposition of organic precursors. Although chemical coprecipitation methods are widely used to the synthesis of ferrites nanoparticles [2,3,6–10], others important experimental techniques also deserve attention, such as hydrothermal [11,12], sonochemical [13,14], sol–gel [15,16], solvothermal [17–19], flow injection in tubular nanoreactors and electrochemical [20], aerosol [21] and precipitation from water-in-oil microemulsions [22].

Depending on the required necessity, magnetite nanoparticles can be employed in several applications, as for instance, (i) *biomedical*, where it is expected non-toxics and biocompatible magnetic nanoparticles, exhibiting high magnetization [20]; (ii) *sensors*, nanoparticles developed in order to improve detection limits in fluorimetric, electrical, magnetic and gravimetric methods of detection [23]; (iii) *drug delivery systems*, based on magnetic nanoparticles associated to biomolecules or (bio)polymers to enhance the pharmacokinetics features and biodistribution, since the drug release into the body may be properly controlled [24]; (iv) *hyperthermia*, nanoparticles are prepared to present a controllable thermal behavior when exposed to an external magnetic field [25–28]; (v) *contrast agents in magnetic resonance imaging (MRI)*, magnetic nanoparticles with average particles size below 20 nm and large magnetic moments contribute to provide very fast and detailed information about soft tissue and organisms [29,30]; (vi) *environmental*, nanoparticles are used as adsorbent materials in processes of removing metals ions in environmental remediation of gaseous and aqueous effluents and in wastewater treatment [31–33]; and (vii) *catalyst*, in this particular case, surface-modified magnetic nanoparticles presenting high surface area are properly dispersed in organic solvents. Due to the magnetic nature, magnetic nanoparticles are easily separated from the reaction medium after reaction, reducing operational costs. The use of ferrite nanoparticles as chiral catalyst systems for asymmetric hydrogenation of aromatic ketones [34], catalysts for H_2O_2 Fenton reaction [35] and oxidation of quinoline [36], styrene production by ethylbenzene dehydrogenation and Fischer–Tropsch processes [37,38] are typical examples.

Polymers can be designed to provide different responses to external factors such as temperature changes, pH, magnetic field, solvent medium, among others [39]. Because of the intrinsic magnetic properties, magneto-polymeric materials (MPM) are easy to handle and therefore they can be applied, as for example, in the automation of analytical equipment, allowing for rapid separation and stabilization of the nanoparticles. In addition, MPM can also undergo chemical functionalization, which enables their use as specific ligands for immunoassays, sequencing of nucleic acids, cells, microorganisms and others [40]. In the biomedical field, the polymeric materials presenting bifunctionality are commonly used in applications such as cell separation, drug delivery systems, proteins and enzymes carriers, immunology and purification of nucleic acids [41].

Polymer magnetization is strongly dependent on factors such as chemical composition, morphology, size, crystal structure, crystallinity, among others. In the context of embolotherapy, it is preferable to disperse nanocharges whose monodomains lead to a superparamagnetic behavior into the thermoplastic polymer matrix.

Embolotherapy consist of an intentional occlusion of a vessel due to the introduction of material with the intent of reducing the vessel size in order to decrease or avoid the blood (and nutrients) flow through vessels to the injured area [37,42,43]. This medical procedure can be employed combining ischemia and chemoembolization [42]. Due to the micrometer diameter of the capillaries, it is strongly recommended the use of micrometer embolic particles to enhance the treatment efficiency [44]. It is also interesting that an embolic material presents regular morphology, preferentially spherical to minimize the undesirable agglomeration into the catheter during the medical procedure [2,3,45].

This work aims to develop a new class of magneto-polymeric materials intended for biomedical applications, such as intravascular embolization treatment. This polymeric nanocomposite is basically composed of nanostructured Fe_3O_4 magnetic particles homogeneously dispersed into a thermoplastic matrix of poly(vinyl pivalate). To the best of our knowledge, poly(vinyl pivalate)-based magnetic nanocomposites are produced for the first time by *in situ* incorporation of surface-modified superparamagnetic Fe_3O_4 nanoparticles in batch suspension polymerization process. The resulting materials have been characterized in order to provide information on the effect of the operating process variables on the polymer properties.

2. Experimental section

2.1. Materials

2.1.1. Formation and modification of Fe_3O_4 nanoparticles

Nitrogen, used in the reactions to keep an inert atmosphere, was supplied by White Martins Ltda (Rio de Janeiro, Brazil) with purity of 99.5%. Ethanol (C_2H_5OH) with 99% purity, acetone [$(CH_3)_2CO$] with purity of 99.5%, aluminum sulfate hydrate [$Al_2(SO_4)_3 \cdot xH_2O$] with purity of 98%, ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) with purity of 97%, ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) with purity of 99% and sodium hydroxide (NaOH) with purity of 99%, were provided by VETEC Química Fina Ltda (Rio de Janeiro, Brazil). Ultrapure water was used as the reaction medium. Hydrochloric acid (HCl, 37% w/w) was supplied by ISOFAR (São Paulo, Brazil). Oleic acid extra pure was supplied by Merck (Rio de Janeiro, Brazil). All chemicals were used as received without additional purification.