



Magnetic nanofibrous materials based on CMC/PVA polymeric blends

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ABSTRACT

In this paper, the synthesis of magnetic nanofibrous materials with a soft ferromagnetic response based on magnetite nanoparticles (SMON) loaded to aqueous carboxymethyl-cellulose (CMC)/polyvinyl-alcohol (PVA) polymeric blends is reported. The nanofibrous materials were obtained from the electrospinning of SMON-CMC/PVA blends with different SMON content, applying a constant tension of 15 kV. The synthesized samples were analyzed by transmission electron microscopy, scanning electron microscopy, attenuated total reflectance Fourier transform infrared, Raman and X-Ray photoelectron spectroscopy, as well as static magnetic measuring. Our experimental findings indicate that nanofibers' diameter decreases as SMON content in the electrospun polymeric blends is increased, since these magnetic nanoparticles diminish the interactions between PVA and CMC molecules, which improves their spinnability. Moreover, the spatial distribution of SMON in the fibers provides to the synthesized nanofibrous materials a novel soft ferromagnetic response at room temperature. This phenomenon is attributed to the formation of nanoparticles' aggregates that are discretely distributed in the nanofibers.

1. Introduction

One-dimensional nanostructures, such as nanofibers, nanowires and nanotubes have gained interest among the scientific community due to their applications on the development of electronic, magnetic, sensing and biological technologies (Esmaili & Haseli, 2017; Wu, Zhang, Liu, Dandan Lin, & Pan, 2007; Luo, Wang, Wang, & Pan, 2016; Méndez et al., 2017; Reddy et al., 2009; Reddy, Jeong, Lee, & Raghu, 2010; Vimala et al., 2011; Wu et al., 2015; Zhang et al., 2017). The nanofibrous materials can be defined as those composed of fibers with diameter below 500 nm (nanofibers) and present several advantages over their bulk counterparts. It is known that even with the exact chemical compositions, these nanomaterials show dramatic changes on their physical properties due to the large surface-area/volume ratio (Esmaili & Beni, 2014; Esmaili & Haseli, 2017). Different approaches have been suggested for the synthesis of nanofibrous mats, that includes phase-separation, self-assembling and electrospinning (Chen et al., 2015; Huang, Wang, Qi, Su, & He, 2014; Ma & Zhang, 1999). Among these routes, electrospinning is the simplest, effective and low-cost technique to produce nanofibrous materials. The electrospinning technique has been successfully used to produce a large number of nanofibrous

materials based on natural and synthetic polymers, as well as composite nanomaterials, with tunable fiber morphology and specific physicochemical properties (An, Zhang, Wang, & Tang, 2008; Martínez-Rodríguez, Garza-Navarro, Moreno-Cortez, Lucio-Porto, & González-González, 2016; Sasikala, Unnithan, Yun, Park, & Kim, 2016).

In this report we deal with the electrospinning of magnetic polysaccharide-based nanofibrous materials. Depending on its origin, polysaccharides have distinct molecular structure, weight and ionic character that determinate their physicochemical properties. According to the literature, electrospinning technique has been used for the preparation of polysaccharide-based nanofibrous mats such as cellulose (Zhang et al., 2018), cellulose-acetate (Nair & Mathew, 2017), ethyl-cellulose (Lu, Wang, Li, Qiu, & Wei, 2017) and carboxymethyl-cellulose (Esmaili & Haseli, 2017; Martínez-Rodríguez et al., 2016). Among these polysaccharides, carboxymethyl-cellulose (CMC) emerges as an important polymer for the preparation of nanofibrous materials due to its polyelectrolyte nature (Lee, Jeong, Kang, Lee, & Park, 2009).

The CMC is a polyanionic and semi-synthetic polysaccharide derived from natural cellulose, which results from the partial substitution of cellulose native hydroxymethyl groups by carboxymethyl groups (Nadagouda & Varma, 2007). The degree of substitution (DS) of these

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functional groups is reported as an average of carboxymethyl groups per monomer unit. CMC is commercialized as water-soluble sodium salt, which in aqueous solutions can be loaded with metallic ions by the displacement of sodium cations (Liu, He, Gunn, Zhao, & Roberts, 2009; Nadagouda & Varma, 2007). Accordingly, it has been reported the synthesis of composite nanomaterials based on metallic particles such as Ag (Garza-Navarro et al., 2013), as well as magnetic spinel metal oxide nanoparticles (SMON), like magnetite, stabilized into CMC templates (Luna-Martínez et al., 2013; Torres-Martínez et al., 2014)

Nowadays one can find some reports regarding preparation of functional nanofibrous materials based on gelatin, polyimine, co-polymers as poly (D,L-lactide-co-glycolide) acid (PLGA) or tri-block copolymer like poly(ϵ -caprolactone)-poly(ethylene glycol)-poly(ϵ -caprolactone) (PCEC) nanofibers, where SMON like magnetite are used as fillers, due to its adequate magnetic response (Luo et al., 2016; Sasikala et al., 2016; Wang et al., 2014; Zhang et al., 2017). Thus, magnetite nanoparticles has been used in applications focused to therapeutic medicine and diagnosis, that includes MRI imaging, drug targeted delivery systems and hyperthermia inductors (Chakraborty, Dhakshinamurthy, & Misra, 2017; Ravichandran et al., 2016; Sasikala et al., 2016). For example, it has been reported that SMON incorporation to PLGA anticancer-drug-loaded nanofiber matrix is useful to induce the apoptosis-mediated tumoricidal effect when it is exposed to an alternating magnetic field (Sasikala et al., 2016).

Nonetheless, polysaccharides as CMC have an intricate distribution of polymeric chains, along with functional groups that promotes solutions with large surface tension and viscosity, which diminish its spinnability (Frenot, Henriksson, & Walkenström, 2007; Santos et al., 2014). Consequently, in our previously published work we propose the use of polyvinyl alcohol (PVA) with two different molecular weight and hydrolysis degree in order to obtain CMC/PVA polymeric blends with remarkable spinnability (Martínez-Rodríguez et al., 2016). Hence, the aim of this contribution is to present a first approach for the electrospinning of magnetic scaffolds based on CMC/PVA polymeric blends loaded with magnetite nanoparticles, that could be potentially focused to the develop of drug delivery systems and/or implantable hyperthermia inductors.

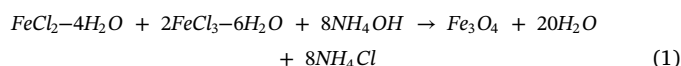
2. Materials and methods

2.1. Materials

For the synthesis of magnetic nanofibrous materials ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Mw = 198.85 g/mol), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Mw = 270.20 g/mol), polyvinyl alcohol with degree of hydrolysis of 99% and Mw = 130 kDa (HPVA), polyvinyl alcohol with degree of hydrolysis of 87–89% and Mw = 13–23 kDa (LPVA) and sodium carboxymethyl-cellulose with DS = 1.2 and Mw = 250 kDa (CMC), purchased from Sigma-Aldrich Co, Saint Louis, MO, USA; and ammonium hydroxide (NH_4OH , 29.5 v%) acquire from CTR-Scientific, San Nicolás de los Garza, NL, México, were used. All reagents were used as received without further treatment. Deionized water was used for the preparation of all solutions for this work (Barnstead EASYpure II system with $\rho = 13 \text{ M}\Omega \text{ cm}$).

2.2. Synthesis and characterization of magnetic nanoparticles

The synthesis of the magnetic nanoparticles was conducted following the route proposed by H. S. Lee et al. (Lee, Shao, Huang, & Kwak, 2005), with some modifications. Briefly, 0.99 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.43 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 80 mL of deionized water into a round-bottom flask (reactor), under magnetic stirring (350 RPM) at room conditions. Then, 6 mL of NH_4OH was poured into the reactor in order to obtain 1 g of magnetite ($\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$) with a Fe(II):Fe(III) molar ratio of 1:2, according to the following reaction:



It is worth to mention that solution turned blackish after NH_4OH addition, indicating the formation of a new phase. The reaction was left under continuous stirring conditions (350 rpm) for one hour at room conditions. Resultant product was centrifuged at 9000 rpm to precipitate the solid phase and washed with deionized water. This procedure was repeated until the dispersion reached a pH of 7. Finally, the dispersion was frozen with solid CO_2 and then lyophilized at a pressure of 0.160 mbar. This sample was named SMON.

The crystalline and morphological feature of SMON was examined by X-Ray diffraction (XRD) technique in a Bruker D8 Advance, with a Cu anode ($\lambda_{\text{K}\alpha} = 1.54 \text{ \AA}$); and by transmission electron microscopy (TEM) in a Field Emission Gun, FEI Titan G2 80-300 microscope, using electron microscopy (EM) techniques as bright field (BF) and Z-contrast (HAADF-STEM) imaging, selected area electron diffraction (SAED), as well as energy-dispersive X-ray spectroscopy (EDS). Particle size distribution was obtained from the measuring of at least 700 randomly selected particles. Finally, X-Ray photoelectron spectroscopy (XPS) was carried out in a Thermo-Scientific, K-Alpha spectrometer (with X-ray spot of 400 μm and flood gun for charge compensation), in order to identify the formation of pure magnetite phase for SMON sample. For this analysis, the C1s was taken as reference (284.83 eV).

2.3. Synthesis and characterization of CMC/PVA-based magnetic nanofibrous materials

Synthesis of magnetic nanofibrous materials was perform as follows. First, a PVA solution with a concentration of 11 w/v% was prepared mixing HPVA:LPVA using a weight ratio of 1:1. In order to prepare this solution 2.75 g of each kind of PVA, HPVA and LPVA, were dissolved in 50 mL of deionized water under magnetic stirring at 90 °C for 1.5 h. According to the literature, the mixture of PVA with different molecular weight and hydrolysis degree improves the spinnability of their aqueous solutions, without the need of adding any tensoactive reagent (Martínez-Rodríguez et al., 2016). In addition, a CMC aqueous solution was prepared dissolving 5.3 g of the polysaccharide in 100 mL of deionized water under magnetic stirring at room conditions, in order to obtain a concentration of 5.3 w/v%.

Then, PVA and CMC solution were mixed at a CMC:PVA volume ratio of 1:9, adding 1 mL of CMC solution to 9 mL of PVA solution, so that we obtain almost 10 mL of CMC/PVA polymeric blend. The sample that was obtained from the electrospinning of this blend was named as M10. The loading of synthesized SMON to the CMC/PVA blend was carried out by the addition of five different quantities of powdered sample into a flask with the CMC/PVA polymeric blend. The mixtures were homogenized performing three cycles of 5 min (each) of sonication to avoid excessive heating of the blend; using a stainless-steel-tipped dismember, controlled by an ultrasonic homogenizer; so that we get a weight ratio (CMC/PVA)/SMON of 500, 250, 167, 125 or 100 for each SMON-CMC/PVA blend, after the addition of 2, 4, 6, 8 or 10 mg of SMON, respectively. The samples that were obtained from the electrospinning of these five blends were named as MNF1, MNF2, MNF3, MNF4 and MNF5, respectively.

Then, 5 mL of CMC/PVA or SMON-CMC/PVA polymeric blends were transferred to a 5 mL syringe with a 21 gauge blunt-ended needle. Electrospinning of the blends was achieved under room conditions, using an applied voltage of 15 kV (high voltage DC power supply, 0–30 kV, Gamma High Voltage Research Inc., USA) and spinning rate of 0.5 mL/h (syringe pump, New Era Pump System, Inc., USA). The electrospun mats were collected on a grounded aluminum foil placed at 10 cm from the syringe needle.

Morphological features of the magnetic nanofibrous materials were evaluated by scanning electron microscopy in a Field Emission Gun (FEG), FEI, Nova NanoSEM microscope, as well as in a Cold-FEG,

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