



# Silver/polysaccharide-based nanofibrous materials synthesized from green chemistry approach



M.A. Martínez-Rodríguez<sup>a</sup>, M.A. Garza-Navarro<sup>a,b,\*</sup>, I.E. Moreno-Cortez<sup>a,b</sup>,  
R. Lucio-Porto<sup>a,b</sup>, V.A. González-González<sup>a,b</sup>

<sup>a</sup> Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica, San Nicolás de los Garza, 66451 Nuevo León, Mexico

<sup>b</sup> Universidad Autónoma de Nuevo León, Centro de Innovación, Investigación y Desarrollo en Ingeniería y Tecnología, Apodaca, 66600 Nuevo León, Mexico

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## ABSTRACT

In this contribution a novel green chemistry approach for the synthesis of nanofibrous materials based on blends of carboxymethyl-cellulose (CMC)–silver nanoparticles (AgNPs) composite and polyvinyl-alcohol (PVA) is proposed. These nanofibrous materials were obtained from the electrospinning of blends of aqueous solutions of CMC–AgNPs composite and PVA, which were prepared at different CMC/PVA weight ratios in order to electrospin nanofibers applying a constant tension of 15 kV. The synthesized materials were characterized by means of transmission electron microscopy, scanning electron microscopy; as well as Fourier-transform infrared, ultraviolet and Raman spectroscopic techniques. Experimental evidence suggests that the diameter of the nanofibers is thinner than any other reported in the literature regarding the electrospinning of CMC. This feature is related to the interactions of AgNPs with carboxyl functional groups of the CMC, which diminish those between the later and acetyl groups of PVA.

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## 1. Introduction

Nanofibrous materials are defined in the literature as those composed of fibers with diameter less than 500 nm. These fibrous materials have several advantages in comparison with their bulk counterparts, since they present high area/volume ratio, as well as tunable porosity; which allows their use in specialized applications, such as multifunctional membranes, nanofilters, tissue engineering scaffolds, wound dressing, drug delivery systems, among others (Liang, Hsiao, & Chu, 2007; Venugopal & Ramakrishna, 2005). Polymeric materials are preferred for the preparation of nanofibrous materials due to their mechanical and solubility features, along with their relatively easiness of production and processing. Diverse techniques, such as phase separation, self-assembly and electrospinning have been suggested for the synthesis of nanofibrous materials (Chen et al., 2015; Huang, Wang, Qi, Su, & He, 2014; Ma & Zhang, 1999; Yang, Wu, Liang, Wan, & Xu, 2013). Among these approaches, the electrospinning technique emerges as the most attractive option due to it is low cost setting, versatility and single-step setup for the production of nanofibers. Accordingly, the electrospinning technique has been used to produce a

considerable amount of nanofibrous materials based on natural and synthetic polymers, with tunable fiber morphology and specific physicochemical properties.

In this contribution is reported the electrospinning of polysaccharides, which are natural homo- or co-polymers that can be found in many living organisms, such as the alginate in algal; cellulose and starch in plants; and chitin and chitosan in the exoskeleton of several insects and marine animals (Lee, Jeong, Kang, Lee, & Park, 2009; Sinha & Kumria, 2001). In relation to its origin, polysaccharides have diverse molecular structure, chemical composition, molecular weight and ionic character that determine their functionality and biological activity. In this context, the electrospinning technique has been used in the production of nanofibers from cellulose (Chen et al., 2015) and its derivatives, such as cellulose-acetate (Du et al., 2014), ethyl-cellulose (Kacmaz et al., 2013) and carboxymethyl-cellulose (Frenot, Henriksson, & Walkenström, 2007). The development of nanofibrous materials based on these polymers has been focused to the regenerative medicine, due to their biocompatibility and biodegradation (Lee et al., 2009; Sill & von Recum, 2008; Venugopal & Ramakrishna, 2005).

Among these polysaccharides, the carboxymethyl-cellulose (CMC) has become an important polymer for the preparation of nanofibrous materials due its polyelectrolyte nature and its biocompatibility (Frenot et al., 2007; Hatanaka, Yamamoto, & Kadokawa, 2014). The CMC is a semi-synthetic polysaccharide,

\* Corresponding author at: Av. Universidad s/n, Cd. Universitaria, San Nicolás de los Garza, Nuevo León 66451, Mexico.

E-mail address: [marco.garzanr@uanl.edu.mx](mailto:marco.garzanr@uanl.edu.mx) (M.A. Garza-Navarro).

derived from the natural polymer cellulose, which undergoes the partial substitution of cellulose native hydroxymethyl groups by carboxymethyl groups (Chakraborty, Chakraborty, & Ghosh, 2006). The degree of substitution (DS) of these functional groups is usually reported as an average of carboxymethyl groups per monomer unit. Due to this substitution, the CMC has a polyelectrolyte behavior, becoming a polyanion at pH above 4, whereas below this pH value carboxylic anions are protonated (Nadagouda & Varma, 2007).

The CMC is commercialized as water-soluble sodium salt, which in aqueous solution can be loaded with metallic ions by a simple displacement reaction of sodium cations (Nadagouda & Varma, 2007). Taking advantage of this feature, it has been possible the synthesis of hybrid materials based on Cu, Fe and Ag nanoparticles stabilized into CMC matrix, based on coordination complexes between carboxymethyl groups and the respective metal cation (He & Zhao, 2007; He, Zhao, Liu, & Roberts, 2007; Liu, He, Gunn, Zhao, & Roberts, 2009; Nadagouda & Varma, 2007). Moreover, due to the abundant hydroxyl groups on its molecular structure, CMC has been used as reducing agent for the preparation of nanocomposites based on metal nanoparticles like silver (AgNPs), following a green chemistry route (Garza-Navarro et al., 2013). Following this synthesis route, the use or production of toxic residues is totally avoided. Most importantly, it is possible to get an outstanding control over the size of the AgNPs and an improved efficiency over the silver ions reduction.

Nonetheless, the polysaccharides have intricate polymer chains and functional groups that promote solutions with large surface tension and viscosity (Homayoni, Ravandi, & Valizadeh, 2009; Santos et al., 2014). In order to deal with this scenario, it has been reported that polymers with a tensoactive behavior such as the polyvinyl alcohol (PVA) and the polyethylene oxide (PEO) improve the spinnability of polysaccharides solutions when they are added in different percentages in the blends (Frenot et al., 2007; Lee et al., 2009; Santos et al., 2014; Shalumon et al., 2009). However, nowadays the number of reports regarding to the electrospinning of CMC from polymeric blends is minimum, and most of the synthesized nanofibrous materials display large fiber diameter distribution (between 500 and 300 nm) and nanofibers morphology with bead-like defects; even when large tensions (above 40 kV) are applied for its electrospinning (Frenot et al., 2007).

Thus, considering the potential applications of CMC-based fibrous materials and their particular physicochemical properties, in this work we proposed a green chemistry approach for the electrospinning of nanofibrous materials based on blends of CMC–AgNPs nanocomposite and PVA. Following this approach it was possible to synthesize of nanofibrous materials composed by thinner nanofibers than any other reported in the literature regarding the electrospinning of CMC. Furthermore, it is the first time that this reduced diameter is obtained at CMC content as high as 32.3 wt% in the blend, with a defect free morphology.

## 2. Materials and methods

### 2.1. Materials

Polyvinyl alcohol with degree of hydrolysis of 98% and  $M_w = 126$  kDa (HMW-PVA), polyvinyl alcohol with degree of hydrolysis of 87–89% and  $M_w = 13$ –23 kDa (LMW-PVA) and sodium carboxymethyl-cellulose with DS = 1.2 and  $M_w = 250$  kDa (CMC) were purchased from Sigma–Aldrich Co. and silver nitrate was acquired from CTR-Scientific. 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  $\rho = 18$  M $\Omega$  cm).

### 2.2. Synthesis and characterization of CMC–AgNPs composite

Synthesis of CMC–AgNPs composite was performed following a previously reported route, with some modifications (Garza-Navarro et al., 2013). Briefly, aqueous CMC and silver nitrate solutions were prepared at concentrations of 15 and 0.24 mg/mL, respectively, using deionized water. Then, 20 mL of CMC was poured at room temperature into a round-bottom three-neck flask and stirred for 10 min. Later, 10 mL of silver nitrate solution was added to the reactor and the temperature was quickly raised to 90 °C. Reaction was kept at this temperature for 24 h, under reflux conditions. Once the reaction time has elapsed, the resultant yellowish solution was rapidly poured in a previously cooled round-bottom flask, in order cool the solution down to room temperature; this solution was frozen in the flask and then lyophilized. Dried sample was weighted and finally dissolved in deionized water to obtain a CMC–AgNPs solution with a concentration of 5.3 (w/v%) (g/mL). It is worth to mention that this concentration shows best miscibility during the preparation of the blends with PVA.

The crystalline and morphological features of CMC–AgNPs composite were examined by transmission electron microscopy (TEM) in a Field Emission Gun, FEI Titan G<sup>2</sup> 80–300 microscope, using electron microscopy (EM) techniques as bright field (BF) and Z-contrast (HAADF-STEM) imaging, as well as selected area electron diffraction (SAED). Particle size distribution of AgNPs was obtained from the measuring of at least 700 randomly selected particles. Ultraviolet-visible (UV–vis) spectroscopy studies of CMC–AgNPs composite as well as AgNO<sub>3</sub> precursor solution were performed in a Perkin-Elmer, Lambda 35, spectrometer. Fourier transform infrared spectroscopy (FTIR) analyzes of pure CMC, as well as CMC–AgNPs composite was recorded from a Thermo-Scientific, Nicolet 6700, spectrometer.

### 2.3. Synthesis and characterization of CMC–AgNPs/PVA nanofibrous materials

In order to obtain the CMC–AgNPs/PVA nanofibrous materials, a PVA solution was prepared with a concentration of 11 (w/v%) (g/mL), mixing HMW-PVA and LMW-PVA powders at a weight ratio of 1:1. Our research group previously reported that this mixture gets an improvement on the mechanical properties, solution stability and spinnability of PVA solutions, avoiding the use of toxic tensoactive surfactants (Moreno-Cortez et al., 2015). Accordingly, this mixture was dissolved in deionized water with a moderate magnetic stirring at 90 °C for 1 h. Resultant PVA solution was mixed with that previously prepared of CMC–AgNPs at 5.3 (w/v%) (see Section 2.2) in order to obtain 5 mL of blend at five different CMC:PVA ratios of 10:90, 20:80, 30:70, 40:60 and 50:50 (v%); so as we get CMC/PVA weight ratios of 0.05, 0.12, 0.20, 0.32 and 0.48, respectively. Accordingly, the CMC content in the blends goes from 4.6 to 32.3 wt% with respect the total polymer weight in the blends. These blends were stirred in a round-bottom flask for 30 min, in order to get homogenous solutions. It is worth to mention that it was observed a phase separation (not gelation) when the solutions starts to mixing, but it disappears after stirring of the blend for the aforementioned time (see Fig. S1 of the supplementary material). Then, the blends were poured into a 5 mL syringe with a blunt ended needle of 21 gauge. Electrospinning of the blends were carried out at room temperature at an applied voltage of 15 kV (high voltage DC power supply, 0–30 kV, Gamma High Voltage Research Inc., USA), using a spinning rate of 1 mL/h (syringe pump, New Era Pump System, Inc., USA). The electrospun nanofibers were collected on a grounded aluminum foil placed at 8 cm from syringe needle.

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