Optimal fabrication of nanofiber membranes from ionized-bicomponent cellulose/polyethyleneoxide solutions

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ABSTRACT

The effect of cellulose acetate (CA)/polyethyleneoxide (PEO) ratio (0.5–1.5 wt%) and lithium chloride (LiCl) content (0.25–0.75%, w/v) on the viscosity, surface tension and electrical conductivity (EC) of the solutions and diameter of the fabricated nanofiber membranes (NFMs) were optimized using response surface methodology-central composite rotatable design (RSM-CCRD). The NFMs were composed of non-woven fibers with maximum diameter of 121.70 ± 33.40. Second-order polynomial models with high R^2 values (0.977–0.998) were developed using multiple linear regression analysis. Results showed that the NFMs diameter and morphology were significantly affected by CA and LiCl contents ($p < 0.0001$). The overall optimum region was found to be at the combined level of CA to PEO ratio of 1.5 wt% and LiCl content of 0.5% (w/v). At the optimum point, the viscosity, surface tension, EC and diameter were 0.425 ± 0.036 Pa s, 36.21 ± 1.25 mN/m, 0.383 ± 0.014 ms/cm, and 82.19 ± 3.01 nm, respectively. The most uniform and bead-free NFMs were fabricated from the solution formulated with 1 wt% CA/PEO and 0.85% (w/v) of LiCl content.

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1. Introduction

Recently, electrospun nanofibers (ENFs) have received great attentions due to their unique properties such as high aspect ratio, specific surface area, flexibility, porosity and tensile strength [1,2]. ENFs have considerable impacts on the different industrial areas such as affinity membranes, biosensors, tissue engineering scaffold, chemosensors, military protective clothing, cosmetic skin masks, air filtration, reinforced nanocomposites, drug delivery carrier, etc. [3,4]. Fibers can be obtained using different methods such as drawing, template synthesis, phase separation and self-assembly but electrospinning process (ESP) has many advantages such as high suitability and flexibility, cost efficiency and being easy to handle. Thus, this technique during recent decade was highly appreciated by different research groups to produce fibers with very thin diameters from a nanometer to a micrometer scale using the various types of materials or polymers [4,5].

ESP is based on the application of a high voltage to the end of a capillary containing a polymer liquid (i.e., solution or melt), causing an accumulation of charges on the liquid surface [5,6]. When the voltage reaches to a critical level where the coulombic repulsion of the charges overcomes surface tension of the polymer droplet at the capillary tip, a charged jet is ejected. Acceleration through the electric field causes the charged jet to thin down. Finally, ultra-fine fibers are collected on a grounded electrode due to the evaporation of the solvent or the cooling of the charged jet [7].

Nanofibers could be made uni-directionally aligned or non-woven. A non-woven network of polymeric nanofibers is characterized by the presence of highly interconnected pores which makes them feasible for filtration industry [8]. Meanwhile, ENFs have been also applied for creating self-cleaning and antimicrobial membranes [5,9].

The formation process of ESNs from polymer solutions is highly depended on the solution properties such as viscosity, surface tension and net-charge density. One of the most important factors is the viscosity which depends on the polymer concentration and the type of used solvent [10]. ESP at high viscosity was inhibited because of the flow instability caused by high cohesiveness of the solution [11]. Surface tension of a polymer solution may be favored

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to form of the beads instead of the fibers [12]. Thus, modifying the surface tension of the solutions has been shown to cause positive effects on fiber morphology. On the other hand, an increase in the charges density of the solution which can be obtained by the addition of ionic salts or poly-electrolytes, improves the conditions of fiber formation [13]. In this case, more charges are carried out along the jet resulting in strong elongation forces due to the mutual charge repulsion within the jet [10].

Cellulose as one of the most abundant renewable polymer resources has been widely used for the production of fibers and films. Recently, the fabrication of nanofibers from cellulose has attracted a high interest due to their good chemical resistance, thermal stability and biodegradability [14]. However, ESP of cellulose is not an easy process because of its low solubility in traditional solvents [15,16]. Many solvents have been recently used to fabricate of good ENFs based on cellulose [14–18].

Cellulose acetate (CA) has been used in different solvent systems to produce nanofibers. It converts into cellulose by de-acetylation [19–23]. Electrospun CA-fiber mats have been explored as affinity membranes [24], antimicrobial membranes [13], three-dimensional (3D) structures resembling the urinary bladder matrix (UBM) [25], and drug-delivery membranes [26]. Many researchers have found that a proper solvent system for CA should be a mixture of polar and non-polar solvents. Liu and Hsieh [20] investigated solvent parameters to obtain some of solution properties which can facilitate the continuous ESP of ultrafine and uniform CA-fibers. They used a wide range of solvents such as acetone, acetic acid, N,N-dimethylacetamide (DMAc) and their mixtures. These solvents together can generate a series of solvent systems with wide-ranging solution properties. The results showed that several mixtures of DMAc with either acetone or acetic acid provide suitable solvent systems for CA-ESP [20]. In a recent study conducted by Aliabadi et al. [1] a polyethylene oxide (PEO)/chitosan nanofiber membrane (NFM) using ESP was successfully fabricated. Desai and Kit [27] investigated the effect of spinning temperature and mixing ratios on the electrospun NFM formed from chitosan/poly acrylamide. They indicated that fiber formation and size were strongly influenced by the blend ratio of two polymers and also hot-air blowing conditions. Uniform bead-less fibers in the sub-micron range (250–300 nm) were obtained using blend solutions with 90% chitosan [27]. Zhang and Hsieh [28] investigated structural properties of CA and PEO in N,N-dimethylformamide (DMF)/dioxane (DOX) solvent system by ESP. They reported that the formation of bicomponent NFM was strongly influenced by their chain length, concentration and the mixture ratios as well as the applied solvent [28].

The optimization of solution properties in relation to their composition and structure by response surface methodology (RSM) could be a promising method to fabricate electrospun NFM. RSM is a collection of mathematical and empirical techniques useful for establishing models optimizing processes even in the presence of complex interactions [29]. Central composite design has been found to be the most successful factorial design for the parameter optimization with a limited number of experiments and estimates the response surface [30,31]. The advantage of this statistical design of experiments compared to conventional methods is the reduction in the experiments number.

Many studies have been carried out on ESP of polymers/biopolymers. However, to the best of our knowledge, there is no study about the effect of simultaneous optimization of two important structural factors of polymer mixing ratio and solution charge density on the fabrication, morphology and homogeneity of the obtained NFM. In the most previous studies, researchers had been focused on the fiber formation from single systems and investigated just one process variable. The modeling of the nanofiber fabrication using a binary composited system (two polymers) has

not been investigated. In this work, the fabrication of nanofibers from CA/PEO and lithium chloride (LiCl) as an ionizing agent in a DMF/DOX solvent system was investigated to use in many industrial fields.

2. Materials and methods

2.1. Materials

CA (Mn = 50 kDa, 39.7 wt% acetyl content) and PEO (Mn = 100 kDa) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). DMF and DOX were provided by Panreac (Barcelona, Spain), and Chem-Lab NV (Zedelgem, Belgium), respectively. LiCl was also obtained from Merck Chemical Co. (Darmstadt, Germany).

2.2. Solutions preparation

The homogenous and clear solutions were prepared by the desolation of certain proportion of each polymer and also a determined amount of LiCl (Table 1). A 1:1 DMF/DOX binary mixture was used as solvent. The central composite rotatable design (CCRD) was used for preparing the solutions (Table 1). 1:1 DMF/DOX mixture was a versatile solvent system to afford highly fiber generation from CA/PEO at a wide range of ratio. The total concentration of the polymers in the solvents was 12% (w/v). These mixtures were stirred for 4 h at $40 \pm 1\,^\circ$C under a constant stirring speed (300 ± 1 rpm) in order to obtain the clear solutions. Then, the solutions were transferred to sealable opaque bottles and stored at room temperature ($23 \pm 2\,^\circ$C) before the performing ESP and subsequent analyses.

2.3. Electrospinning process

Electrospinning of each solution was performed at a feed rate of 0.4 mL/h under ambient temperature. A needle tip-to-collector distance of 23 cm and a voltage of 25 kV were applied. The flow rate of solutions was controlled using a syringe pump (JMS, model SP 500/Japan). Mixed solutions were placed in a plastic syringe (1 mL, Gage 23, inner diameter 337 μm), which was connected to a high-voltage power supply. The grounded counter electrode was connected to a collector covered by an aluminum foil. Then, aluminum foil was detached from the collector and was used for the analysis of scanning electron microscopy (SEM).

2.4. Analytical methods

2.4.1. Viscosity measurement
The viscosity measurements were performed with a constant shear rate of 36.69 s^{-1} at $40 \pm 1\,^\circ$C by using a steady stress rheometer (Brookfield DV-II, LV Viscometer, USA).

2.4.2. Surface tension determination
Surface tension of the solutions was measured by the plate method using a Krüss K100 tensiometer (Krüss, Germany) at $40 \pm 1\,^\circ$C. Ten measurements were carried out for each solution in 2 min and the mean value was used for data analysis.

2.4.3. Electrical conductivity measurement
Electrical conductivity (EC) of the solutions was triplicately measured at ambient temperature using a digital conductometer (Metrohm model 660, Switzerland).

2.4.4. Morphology analysis
The morphology of the NFMs was observed using a SEM apparatus (KYKY-EM3200 SN:0056, China). For this experiment, the mounted samples were sputtered with a thin layer of gold using a