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PVA/CA based electrospun nanofibers: Influence of processing parameters in the fiber diameter

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Abstract. Recently, the electrospinning technique has been explored as a natural and synthetic polymer processing tool due to its versatility and potential to generate complex structures at a nanoscale. In this work, non-woven nanofibrous mats were electrospun, with a structure resembling the extracellular matrix, for prospective biomedical uses. Poly (vinyl alcohol) (PVA) and cellulose acetate (CA) based electrospun nanofibrous meshes were prepared at different ratios 100/0, 90/10, 80/20 and 70/30 and characterized in terms of fiber diameter. The process was kept as green as possible by resorting to a combination of acetic acid and distilled water as solvents. Optimal conditions for PVA/CA processing were established at 29 kV, feeding rate of 0.8 mL/h and distance between needle and collector of 17 cm. These allowed for the most uniform fibers with the smallest diameters to be produced.

1. Introduction

Since the late 20th century, the electrospinning has been garnering increasing attention in the scientific community, as well as in the industry [1] due its relatively simple setup, cost-effectiveness, ease of process and versatility [2,3]. Electrospun nanofibrous mats are characterized by their large surface area, controllable fibre diameters and structures (i.e. dense, hollow, and porous) and unique surface morphologies, which can be obtained by varying for instance the molecular weight of the polymers and the polymeric solution properties (viscosity, conductivity, dielectric constant, and surface tension). Processing parameters such as voltage power supply, feeding rate, distance between needle and collecting plate, as well as the use of coaxial or triaxial needles for hollow, core–shell or multi-sheathed structures, and even the temperature and humidity during processing, are also of extreme importance during mats production, exerting much influence in the final product [4,5]. Electrospinning requires the application of a high electric field to generate nanofibers from a charged polymer solution. Random, aligned and core-shell fibers can be obtained from natural or synthetic polymers [6,7].

Synthetic polymers have great flexibility during synthesis. They exhibit excellent mechanical properties, thermal stability and an appropriated degradation profile, being desirable for many biomedical applications that require stable, reticulated, nanofibrous constructs [8]. Poly (vinyl alcohol) (PVA), for instance, is known for its high hydrophilic, nontoxic and biocompatible nature, possesses good physicochemical properties that account for their mechanical stability, flexibility and slow degradation kinetics, well above nanofibrous made of natural polymers, and presents high capacity of spinnability [8,9]. However, synthetic polymers, including PVA, lack cell affinity or cell recognition sites. To overcome this limitation, synthetic polymers have been conjugated with natural polymers, which exhibit superior biocompatibility and low immunogenicity, and some even display intrinsic

antibacterial properties. The acetate ester of cellulose, cellulose acetate (CA), has attracted wide interest in the production of nanofibers due to its biodegradability, chemical persistence, biocompatibility, and thermal constancy [10]. Regarding the CA low tensile strength, composites with synthetic polymers have been proposed. Here, the affinity of PVA/CA blends was explored in light of the electrospun processing parameters and their impact in the fiber's properties.

Most studies show the viscosity as a determinant factor for fiber diameter and morphology. However, the solution viscosity is not an independent variable and, as such, is intimately related to the concentration and molecular weight of the polymer, meaning that if one of these parameters increases the viscosity will also increase and, hence, larger diameter fibers are obtained. Still, for electrospinning processing, there is a critical value for each polymeric solution. If the viscosity is high, surpassing the polymeric solution critical value, the flow may be hindered and the droplet dries at the tip, blocking it. On the other hand, if the viscosity is low, the applied electric field and surface tension may cause the entangled polymer chains to break into fragments before reaching the collector, forming beaded nanofibers [11,12]. Regarding the solution conductivity, it not only affects the Taylor cone formation but also helps in controlling the diameter of the nanofibers. The increase of electrical conductivity of the solution, leads to a significant decrease in the diameter, whereas at low conductivities the jet elongation is not sufficient to produce uniform fibers. The conductivity is influenced by solvent type, polymer concentration and temperature [13].

In the processing parameters, the minimum voltage required to produce nanofibers increases with the solution's surface tension but this behavior is not always linear, its critical value varies from polymer to polymer [14]. High voltages lead to the formation of smaller fiber diameters attributed to the stretching of the polymer solution in correlation with the charge repulsion within the polymer jet [15]. Feeding rates and distances between the needle tip and the collector should be adjusted depending to the selected solvent. The solution feeding rate influences jet velocity and transfer rate. For proper solvent evaporation and to acquire well defined, solid nanofibers lower feeding rates are desirable. Ideally, the feeding rate must match the solution removing rate from the tip. Very low feeding rates may block the needle tip and prevent the polymer exit, while high feeding rates may result in beaded, large diameter fibers due to the short period allowed for solvent evaporation prior to fibers reaching the collector [16]. Large diameter nanofibers are also formed when the distance between needle and collector is kept small, since solvent evaporation is inefficient, whereas the diameter of the nanofibers decreases as the distance increases [17,18]. Environment parameters, such as relative humidity and temperature, also affect the diameter and morphology of the nanofibers. Humidity causes changes in the nanofibers diameter by controlling the solidification process of the charged jet. This phenomenon is, however, dependent on the chemical nature of polymer. It has been reported that the increase in the humidity may lead to a reduction in fibers diameter [19]. Temperature causes two opposing effects in the fibers diameter: (i) increases the rate of evaporation of solvent and (ii) decreases the viscosity of the solution. However, both have been shown to lead to the reduction of the nanofibers mean diameter [20,21].

In the present work, the previous parameters were altered and adapted in function of the concentration and polymeric ratios of PVA and CA. The goal was to determine their intimate relation and, in particular, their influence in the nanofiber's diameter.

2. Materials and methods

2.1. Materials

PVA with Mw 78,000 and 88% hydrolyzed was purchased from Polysciences, Warrington, USA. CA with Mw 30,000 was purchased from Sigma Aldrich, USA. The acetic acid (glacial) 100% was purchased from Merck, Darmstadt, Germany.

2.2. Fabrication of nanofibrous meshes

Polymeric solutions of PVA/CA were prepared at 11% and 9% (w/v) concentrations in acetic acid/distilled water at 60/40 v/v. PVA and CA were combined at varying ratios: 100/0 (or 100 PVA),

90/10, 80/20 and 70/30 (v/v). These solutions were continuously stirred at 80ºC for 3 h and were electrospun (figure 1) at specified processing conditions of applied voltage, feed rate, collection distance and needle inner diameter, which was established at 18 gauge (1.02 mm). After the electrospinning process, films were placed in a drying oven for 12 h at 40ºC, for a complete solvent evaporation. Four squared samples of 1x1 cm^2 were cut from each mesh and mounted on glass slides for microscopy observation. The microscope Leica DM750, with an integrated high definition digital camera, was used to verify the production of fibers. Five pictures were taken from each mesh and the respective fiber diameters were measured using the program Image J. Ten fibers were measured per picture and the average diameters reported.

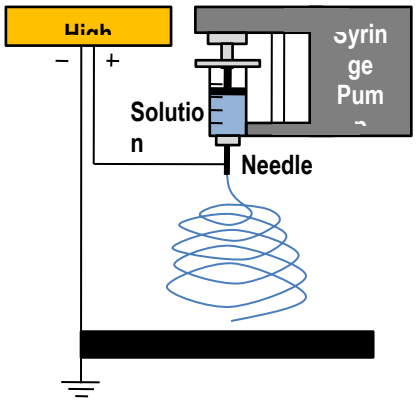

Figure 1. Schematic representation of the electrospinning setup.

3. Results and discussion

The main goal of this work was to produce nanofibrous meshes via electrospinning using green and sustainable methodologies. The polymers, PVA and CA, were selected based on their ease of process, biocompatibility and biodegradability. The solvents ratio of 60/40 v/v of acetic acid/distilled water was established as the most suitable to prevent polymer precipitation. Electrospun processing parameters, particularly voltages and feeding rates, which were found the most influential in the fibers diameter of this particular polymeric blend (PVA/CA), were altered to improve the fibers' features.

Table 1 reports the variations in processing parameters considered, namely electric potential, feed rate and distance to collector as well as polymer concentration and polymeric blend ratio, and the respective average diameter obtained. Initial tests were conducted with a 100% solution of PVA. Various concentrations were tested, being the 9% and 11% (w/v) the most successful. Upon close analysis, larger fiber diameters were evidenced at 11% (w/v) concentration and as such all subsequent polymeric solutions (including blends) were prepared at 9%.

Table 1. Average fiber diameters in response to polymer concentration, blend ratio and electrospun processing parameters [average ± standard deviation (SD), with n=10].

PVA/CA Meshes	Processing Parameters			Fiber Diameter ± SD (nm)
	Voltage (kV)	Feed Rate (mL/h)	Distance (cm)	
11 % (w/v)				
100/0	28.0	1.2	17.0	705 ± 179
	29.0	0.8	17.0	851 ± 229
9 % (w/v)				
100/0	20.0	0.7	18.0	838 ± 246
	22.0	1.3	14.0	921 ± 155
	24.0	1.3	15.5	790 ± 188

	25.0	0.7	18.0	781 ± 190
	29.0	0.8	17.0	**665 ± 151**
	29.0	1.3	17.0	877 ± 227
	29.0	1.5	15.5	682 ± 188
	29.0	1.7	15.6	795 ± 170
90/10	20.0	0.8	17.0	788 ± 216
	22.0	0.8	17.0	772 ± 164
	29.0	0.8	17.0	**632 ± 117**
80/20	20.0	1.2	17.0	626 ± 149
	25.0	1.2	17.0	516 ± 128
	25.0	0.8	17.0	742 ± 181
	29.0	0.8	17.0	**665 ± 177**
70/30	29.0	0.8	17.0	**731 ± 156**

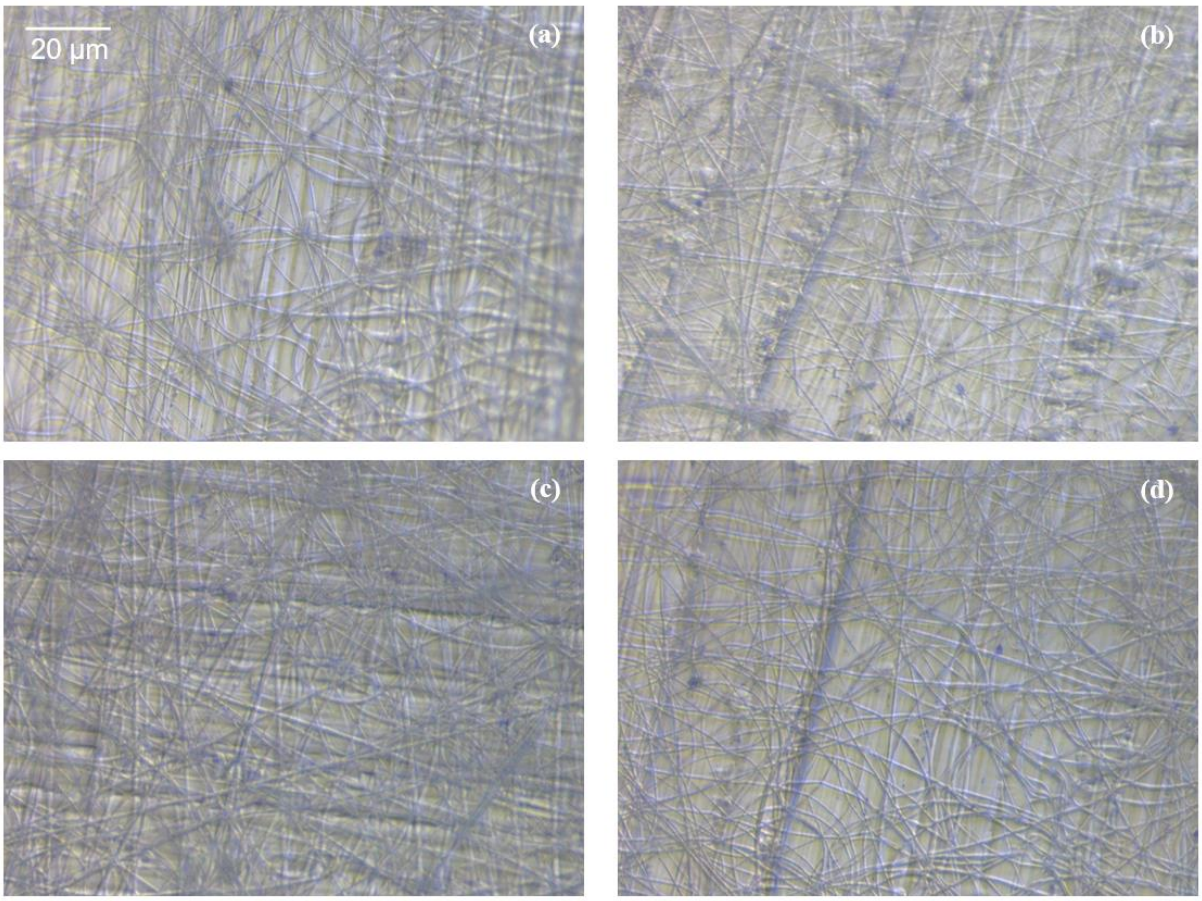

Figure 2. Optic micrographs (bright field) of (a) 100/0, (b) 90/10, (c) 80/20 and (d) 70/30 PVA/CA nanofibrous electrospun meshes, processed at 29 kV, 0.8 mL/h and 17 cm distance. All imagens were collected with the objective magnification of 100x and ocular magnification of 10x (scale bar of 20 µm).

Optimal processing conditions were selected based on gradual alterations in voltage. Extremes were defined between 20 kV (lowest) and 29 kV (highest). According to the literature, higher voltages are more likely to give rise to smaller diameters [13]. Data from 100 PVA showed that by increasing the voltage, the mean fibers diameter decreased. Changes in the feeding rate were also decisive to obtain diameters close to those required for biomedical applications (mimicking the extracellular matrix). It is clear that by increasing the feeding rate the fiber diameters also increased since the solvent did not have enough time to evaporate, becoming entrapped within the polymeric matrix. As such high voltages and

low feeding rates were found more appropriated to process the PVA/CA meshes. Higher distances were also observed to promote the formation of continuous, beadless fibers with small diameters. To confirm these conclusions random processing parameters were applied both to 90/10 and 80/20 PVA/CA blends. In general, data collected confirmed our latest premise. A reduction of almost 200 nm in average diameter was registered when passing from a low voltage of 20 kV (838 nm) to a high voltage of 29 kV (665 nm), for 100 PVA, with similar observations being made for the combination 90/10. In the 80/20 ratio this linearity was not completely verified; in fact, the most successful combination of parameters required the lowest potential and the highest feeding rate. In light of previous reports, it is likely this to be an anomaly and a result of environmental conditions interference, such as temperature and humidity; this specific test is carried out in a different month than the rest. The blend 70/30 was only tested with the parameters defined as ideal.

In this research, it is proven the stability of the polymeric blend and the homogeneity of the solution, since optimal processing parameters were found for all mixtures at 29 kV, 0.8 mL/h and 17 cm distance, with resulting average diameters in the same ranges (figure 2).

4. Conclusion

Our main goal was to generate polymeric mats from PVA/CA with the minimal diameter possible using the most environmentally friendly and sustainable processes and materials. After several attempts, PVA and CA solvents were established at 60/40 acetic acid/distilled water, and the electrospinning processing conditions at 29 kV, 0.8 mL/h and 17 cm. These were the most successful in giving rise to continuous, beadles, small diameter nanofibers for all polymeric combinations. Further tests will be conducted to ensure the reproducibility of these results in different environment conditions. Still, preliminary data are very promising, revealing the potential of this polymeric combination, PVA/CA, to promote the formation of intricate and complex nanofibrous meshes for prospective biomedical uses.

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