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Electrospinning of Gelatin/PEO Blends: Influence of Process Parameters in the Nanofiber Properties

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Summary: Results of electrospinning of gelatin/PEO blends from aqueous solutions are presented. The effects of applied electric field (15–25 kV), flow rate (0.25–0.75 mL/h) and gelatin concentration in the final fiber diameter were studied. It was observed that the resulting fiber system presented high polydispersity, where fiber diameters ranged from 150 nm to 1.3 μm. In some cases an adequate fibrous system were not obtained. It was observed that the average diameter decreased mainly when the flow rate and gelatin concentration decreased.

Keywords: blends; electrospinning; gelatin; nanofibers; PEO

Introduction

Electrospinning is a technique used for obtaining polymer nanofibers through the application of a high intensity electrostatic field. Electrospun nanofibers of biopolymers have found great potential in bioengineering applications, such as drug delivery and tissue engineering.[1–3] Fibrous systems from electrospinning can be obtained from polymer melt or solution in single polymer systems or as blends.[4,5] Usually, polymer solutions are used for obtaining fibers with diameter in the nanometer scale.

In the process, electric potentials in the order of 10^1 kV are applied in the polymeric fluid in such a way that the electrostatic force stretches the polymer solution which is pumped at a constant flow rate through a capillary; the solvent dries during the stretching and the fibers are collected on a plate or other collecting system.[5–7] A scheme of the process is shown in Figure 1. Usually, the resulting fibrous system consists of a highly porous non-woven mesh, where it is recognized that this structure mimics physically the structural dimensions of extracellular matrix of various human tissues.[8–10] Therefore, they have great potential for biomedical applications such as tissue growth and regeneration.[11] The porous matrix formed by the spatial distribution of the fibers and high surface area motivates research related to the applications of nanofibers as wound dressing.[12,13]

Gelatin is a biopolymer which its use as wound dressing has been studied, since it is a biocompatible and low cost natural polymer. This material is a derivative from collagen through controlled hydrolysis,[11] and both have similar biological properties.[8] However, the electrospinning of gelatin is difficult since at room temperature and without any treatment, the aqueous gelatin solution is a colloidal sol which cannot be electrospun.[8] One way to obtain electrospun fibers from gelatin aqueous solutions is to use another polymer in the system in order to improve gelatin spinnability without losing its original properties.[14]

In the present work, poly(ethylene oxide) (PEO) was used in order to form a blend of gelatin/PEO. Aqueous solutions of gelatin/PEO blends with different gelatin concentrations were prepared and electrospun under different conditions. The influence of the solution properties and processing conditions in the final product was

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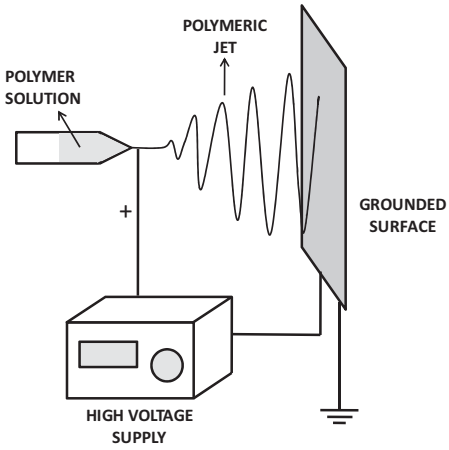

Figure 1.
Scheme of the electrospinning apparatus.

evaluated through scanning electron microscopy (SEM) images. It was found that for some conditions it was possible to obtain non-woven fibrous membranes.

Experimental Part

PEO with molar mass of 900 000 and 100 000 g/mol, and type A bovine gelatin were obtained from Sigma-Aldrich®. Aqueous solution using distilled water with 4.5%wt of PEO and different gelatin concentrations with 2.8, 4.6 and 5.9%wt were prepared by dissolving both polymers at room temperature with stirring for 4 hours. These solutions were named as solution A, B and C, respectively. Additionally, 0.5%wt of NaCl was added to the solution, following the procedure described by Butaffoco et al.[15]

For the electrospinning, the distance between the syringe needle (0.5 mm of internal diameter) and the collecting plate was 10 cm and the process were performed at voltages of 20, 25 and 30 kV using a high voltage supply from Testtech, Ltd. Flow rates of 0.25, 0.50 and 0.75 mL/h were set using a syringe pump (KD-100, KD Scientific).

Fiber diameters were determined from scanning electron microscopy (SEM) images obtained using a SEM Jeol, JXA-840A (Accel Voltage: 15 kV, Probe Current: 2×10^{-11} A) using the software Autocad. Average diameter and standard deviation were obtained from a sample of at least 50 fibers.

Results and Discussion

Fiber Size

Fiber diameter results for different voltages and flow rates are shown in Table 1 and Table 2 for fibers obtained from solutions A and B, respectively. The values correspond to the average diameter whereas the number in parenthesis is the standard deviation, both in nanometers.

Scanning Electron Microscopy

Figure 2 shows SEM images of some samples with three different gelatin concentrations. It can be observed that the samples with high gelatin concentrations did not form a fibrous system (figures 2g, 2h and 2i). Although it is possible to observe fibers, they were not adequately formed and seem to be partially dissolved in a non-fibrous matrix. Therefore, in this case fiber diameters were not measured. The SEM images also show that nanofibers were successfully obtained from aqueous solutions of PEO/gelatin for different experimental conditions.

Voltage Effects

It can be seen from Table 1 that for most cases a higher voltage leads to a higher fiber average diameter and standard deviation. Also, it can be seen from SEM images that at higher voltages there is an increase of the

Table 1.
Average fiber diameter and standard deviation in nanometers for the fiber mats obtained from solution A at different voltages and flow rates.

Voltage (kV)		20	25	30
Flow rate (mL/h)	**0.25**	167 (51)	146 (34)	283 (119)
	0.50	190 (53)	216 (108)	250 (83)
	0.75	168 (46)	233 (84)	329 (134)

Table 2.
Average fiber diameter and standard deviation in nanometers for the fiber mats obtained from solution B at different voltages and flow rates.

Voltage (kV)		20	25	30
Flow rate (mL/h)	**0.25**	212 (78)	455 (160)	269 (69)
	0.50	223 (58)	326 (93)	361 (149)
	0.75	354 (141)	1345 (877)	721 (223)

presence of non-fibrous structures. The effect obtained is opposite to what was expected, that means, that the higher the applied electric field, the lower the diameter. Also, the high size dispersion was observed by Ki et al.[16] in their work on electrospinning of gelatin. The explanation for this fact is that when high electric fields are applied, there is an increase in the jet instabilities leading to higher non-uniformity in the fibers. The effects of flow instabilities are evidenced in the appearance of non-fibrous particles at higher voltages. However, it was not possible to electrospin at lower values of voltage since the electric field was not sufficiently strong in order to supersede the surface tension of the droplet at the tip of the syringe.[17]

Effect of the Flow Rate

From Table 1, it can be observed that the average diameter increases with the increase of the flow rate. This tendency can be associated by the fact that the charge density for low flow rates will be higher than for higher flow rates. In the electrospinning process, the charge excess at the tip of the syringe needle leads to the formation of the Taylor cone and a subsequent jet that flows to the collector plate. It has been pointed

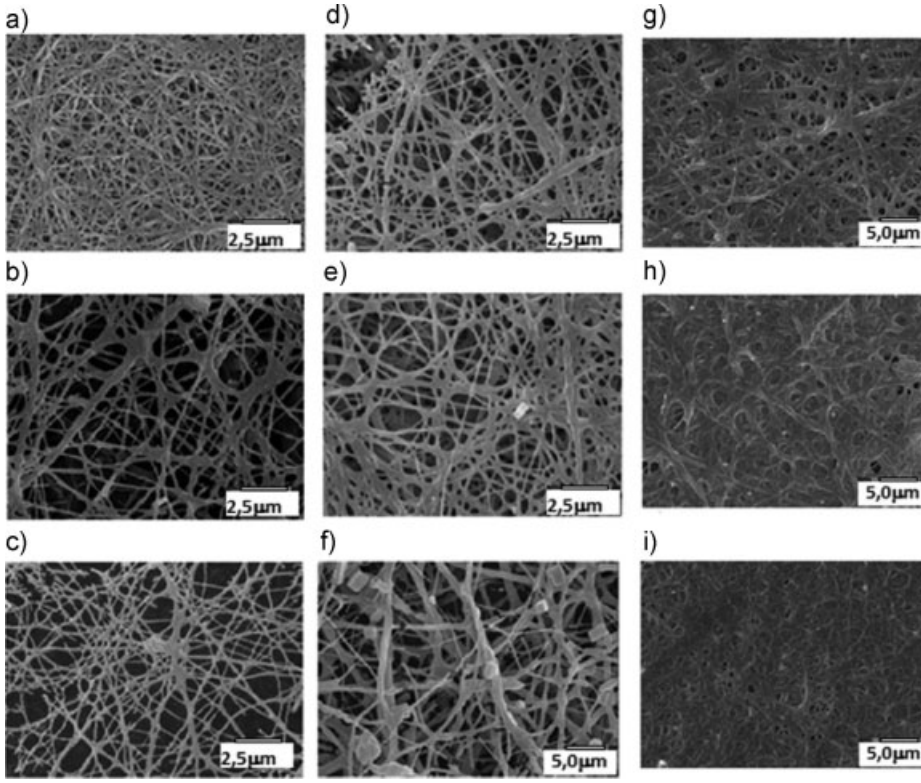

Figure 2.
SEM images from tests with the following conditions for solutions A, B and C: (a) A, 25 kV, 0.25 mL/h; (b) A, 30 kV, 0.50 mL/h; (c) A, 20 kV, 0.75 mL/h; (d) B, 20 kV, 0.25 mL/h; (e) B, 25 kV, 0.50 mL/h; (f) B, 30 kV, 0.75 mL/h; (g) C, 25 kV, 0.50 mL/h; (h) C, 30 kV, 0.75 mL/h; (i) C, 20 kV, 0.25 mL/h.

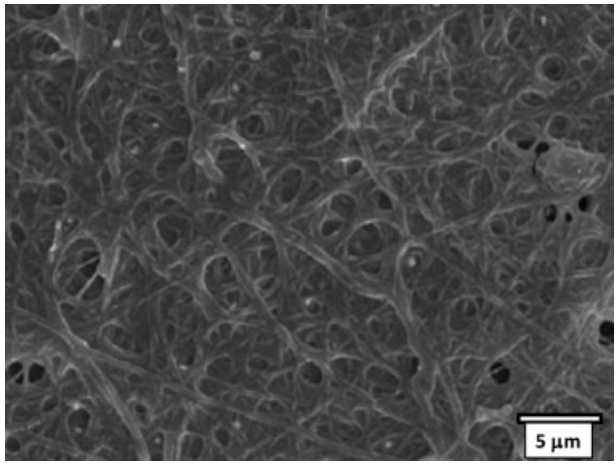

Figure 3.
SEM image obtained from gelatin/PEO blend using a low molecular weight PEO.

out in the literature that the electric charge excess at the tip of the syringe leads to the decrease of the fiber diameter.[12]

Gelatin Concentration Effects

From Tables 1 and 2 and Figure 2, it can be observed that the concentration of gelatin has an important role in the resulting fibers. It can be noted that in almost all cases smaller average fiber diameters were observed for lower gelatin concentration (solution A). It also has been observed that for high gelatin concentration it was not possible to obtain fibers (solution C). This effect was expected since gelatin tends to form a colloidal sol in aqueous solution. This is due to the fact that gelatin is a polyelectrolyte with ionizing groups.[8,11] This characteristic, together with the high number of hydrogen bonds, leads to a rigid chain conformation. Therefore, the gelatin spinnability is low and adding another polymer such as PEO is necessary in order to obtain fibers. This agrees with the results obtained in this work, where the fiber quality improved when the ratio gelatin/PEO content decreased.

PEO Molecular Weight Effect

A gelatin/PEO blend solution with 4.1 and 4.3%wt of PEO and gelatin, respectively, were prepared using a lower molecular weight PEO (Mw = 100000). It can be seen from Figure 3 that the fibers were not formed appropriately and seem to be partially dissolved forming a non-fibrous matrix. Other tests were also performed with the same PEO content as the ones presented in Table 1 and it was not observed the formation of fibers. This shows that the PEO molecular weight has a strong influence in the fiber formation. This result suggests that the PEO chain entanglements are responsible for avoiding jet breakup during the process.

Conclusion

Nanofibers were obtained using electrospinning from gelatin/PEO aqueous solutions. The present study allowed the determination of a range of parameters where this technique can be used in order to obtain nanofibers of this polymeric system. In the range studied, the conditions that lead to smaller fiber diameters were for the cases of low gelatin concentration, voltage and flow rate. It also has been shown that the use of low molecular weight PEO did not lead to the formation of fibers with good quality.

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