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Electrospinning of poly (2-ethyl-2-oxazoline)

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Abstract Poly (2-ethyl-2-oxazoline) (PEOZ) is one of the commercial members of a family of materials that have shown significant application potential in a large number of technological contexts, most of them related with biomedical problems where water-soluble polymer systems are highly desirable. Polymeric fibers with diameters in the 200–800 nm range of PEOZ were prepared by electrospinning of its water solutions. Processing and solution parameters effects on the morphology and the diameter of the fibers were investigated. SEM results showed that the polymer concentration and the applied voltage might be used as variables to control the morphology and the diameter of the electrospun fibers. Solutions of the same polymer in other two organic solvents (*N*,*N*-dimethylformamide (DMF) and tetrahydrofurane (THF)) were also processed by the same technique but without the promising results of the water solutions.

Introduction

Electrospinning of polymer solutions is a long known process used to generate very fine diameter polymeric fibers with high surface area-to-volume ratios. As a result of this property, micro- and nanofibers so obtained are being studied for applications in fields of great interest, such as filtration, membrane technology, controlled drug release, and tissue engineering [1]. In these last medical applications in particular, water-soluble polymers are especially important. Many drugs will lose their bioactivity if electrospun in organic solvents and, therefore, they must be preferably spun in water-soluble polymer systems. In addition, residual solvents remaining in the electrospun mat are difficult to remove completely and could result in toxicity issues. Finally, the evaporation of an organic solvent, during the electrospinning process results in the generation of volatile organic compounds (VOCs). Therefore, water-based electrospinning systems are highly desirable.

Unfortunately, only a limited number of polymers are soluble in water. Poly (2-ethyl-2-oxazoline) (PEOZ) is one of these unusual polymers. It is one of the members of a family that includes some commercially available 2-oxazolines (2-methyl, 2-isopropyl, 2-phenyl) from which other polyoxazoline-based or polyoxazoline-derived polymers have been prepared and reported [2]. They have shown significant application potential in a large number of technological contexts, such as the formation of liposomes, membrane structures and containers which allow the incorporation of functional proteins. They can be used as carriers of drugs or as synthetic vectors and antimicrobial materials. This broad application range is coupled with properties such as responsiveness to external stimuli. Furthermore, the fact that polyoxazolines can be prepared via living polymerization processes, affords extraordinary control and definition, a factor that is tremendously important, particularly when dealing with regulatory authorities.

However, while the research literature concerning the fundamental properties and applications of other water-soluble polymers, such as poly (ethylene oxide) or poly(ethylene imine) [3, 4] in biological application

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contexts is vast, polyoxazolines are only now beginning to be explored by the scientific community. However, as pointed out in a recent and specific review [2], polyoxazolines properties, such as solubility control, toxicity, etc., are in many cases equivalent to or even exceed those of other polymers traditionally used in the above mentioned applications.

From a biological viewpoint, almost all of the human tissues and organs are deposited in nanofibrous forms or structures. Examples include bone, dentin, collagen, cartilage, and skin. All of them are characterized by well-organized hierarchical fibrous structures realigning in nanometer scale. As such, current research in electrospun polymer nanofibers is been focused on bioengineering applications [5]. However, as far as we know, there are not exhaustive experimental studies about the effect of processing variables on the morphology of electrospun PEOZ nanofibers and other related polymers, whereas poly (ethylene oxide) is one of the most popular materials in obtaining electrospun fibers. Reneker et al. [6] studied the preservation of RNase and trypsin enzymes in electrospun PEOZ nanofibers. The enzymes were added to an aqueous solution containing 26 wt% of PEOZ. The solutions were electrospun generating nanofibers with uniformly distributed enzyme. Khanam et al. [7], electrospun L-PEI/SBA-15 composite fibers and PEO/ferrofluid magnetic fibers. In that case, PEOZ was used to synthesize a linear PEI, which is an effective proton conductor.

The first patent describing electrospinning was granted in 1934 [8], when Formals described the process of using an electric field to produce fibers from solutions of “dissolved material”. In most of the electrospinning equipments, a high electrostatic voltage is imposed on a drop of polymer solution held by its surface tension at the end of a capillary. The surface of the liquid is distorted into a conical shape known as the Taylor cone. Once the voltage exceeds a critical value, the electrostatic force overcomes the solution surface tension and a stable liquid jet is ejected from the cone tip. Solvent evaporates as the jet travels through the air, leaving behind ultrafine polymeric fibers collected on an electrically grounded target [9]. Till date, many polymers have been successfully electrospun into micro- and nanofibers, in some cases with diameters as small as 5 nm [10].

It has been found that morphological characteristics, such as the fiber diameter or its uniformity are dependent on many processing parameters. These parameters can be divided into three main groups: solution properties such as polymer concentration, surface tension, and electrical conductivity, processing conditions such as applied voltage or volume feed rate and, finally, ambient conditions such as humidity. Numerous reports studying the effects of these parameters have been reported and each of them has been found to affect the morphology of the electrospun fiber. Under certain conditions, not only uniform fibers but also beads-like formed fibers can be produced by electrospinning [11–14].

In the present work, we study the electrospinning properties of PEOZ mainly in water solutions (although tetrahydrofurane (THF) and *N*,*N*-dimethylformamide (DMF) have been also used as solvents). The study may be representative of a vast family of polymers with interesting abilities to form functional materials and nanostructures for biological and biomedical application areas. We present the effect of some process variables such as the applied voltage and the volume feed rate, as well as some solution properties such as the polymer concentration. We interpret the results of observations made by scanning electron microscope (SEM) and compare them with previous literature results on the electrospinning of other polymer/solvent systems.

Experimental

The polymer used in the study was PEOZ (Aldrich) with an average molecular weight (M_W) of 500.000 g/mol. This polymer was dissolved in different concentrations (15, 20, and 25 wt%) in three different solvents, i.e., water, DMF, and THF by gently stirring with a magnetic bar at room temperature and atmospheric pressure. In order to observe the voltage effect on the fiber diameter, PEOZ solutions were electrospun at different applied voltages to produce a single jet without clogging or splitting. Different flow rates were also used to analyze its influence in fiber diameter.

For the electrospinning process, polymer solutions were placed into a syringe with an 18-gauge blunt-end needle that was mounted in a syringe pump (Cole-Parmer). Randomly oriented nanofibers were electrospun by applying a voltage of 10–21 kV to the needle using a Spellman CZE1000R high voltage supply (0–30 kV CZE1000R; Spellman High Voltage Electronics Corp.), with a low current output (limited to a few μA). The ground plate (stainless steel sheet on a screen) was placed at 15–35 cm from the needle tip. The syringe pump delivered the polymer solutions at a controlled flow rate, which ranged from 0.05 to 0.50 mL/h. All the experiments were performed at least twice. The resulting fibers were collected on the screen, in order to produce a sheet of non-woven fabric. Finally, electrospun fiber morphology was analyzed using a Hitachi S-2700 SEM, after drying in air for 24 h and putting the samples on a SEM disk and sputter-coated with an 8 nm Pt/Au layer to reduce electron charging effects. Fiber diameters were obtained by different measurements on random fibers resulting from the different experiments. In all cases the standard deviation was between 40 and 300 nm.

Results and discussion

A series of polymer solutions with different concentrations of PEOZ dissolved in water were electrospun, resulting in various fiber morphologies, as shown in Fig. 1. At 15 wt%, spindle-like beads were seen. With increasing concentration, the morphology changed from beaded fiber to uniform fiber structure. A minimum polymer concentration for electrospinning uniform fibers was found to be 15 wt% and beaded morphology would be formed with further decreased polymer concentration. As it is well-known, a critical concentration of the polymer solution requires to be exceeded in electrospinning, as extensive chain entanglements are necessary to produce electrospun fibers [15].

Our measurements also showed that the diameter of the electrospun fibers substantially decreased with decreasing polymer concentration, as it can be seen in Fig. 2.

Figure 3 shows the trend of voltage effect on the diameter of the electrospun nanofibers. It was observed that, depending on the solution concentration, the diameter of the electrospun fibers exhibits different trends with the varied applied voltage. Too high voltages were not favorable as they result in the production of multiple jets, which would provide smaller diameters of the electrospun fibers, but non-uniform fiber diameter.

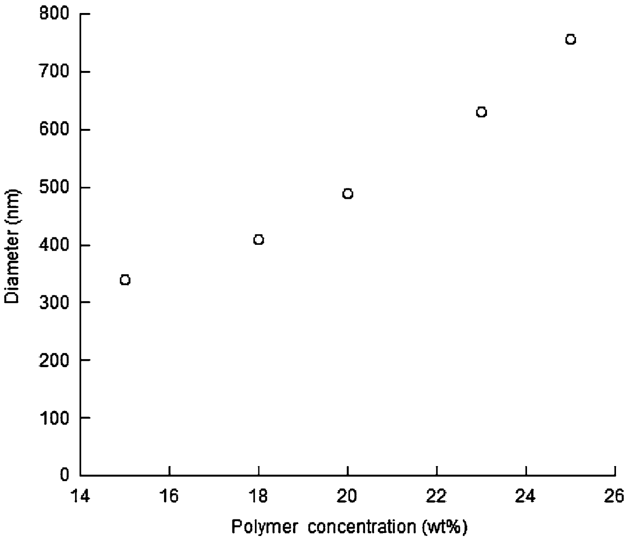
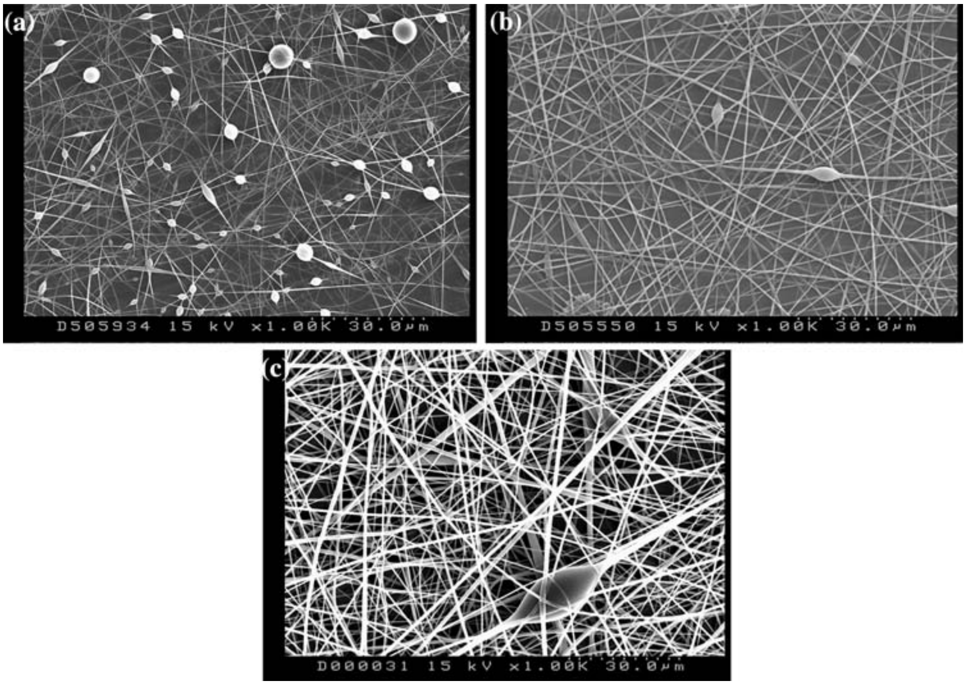


Fig. 2 Polymer concentration effect on the diameter of PEOZ fibers obtained from water solutions

The results are in agreement with other previous works, where the use of a high voltage was reported to induce not only larger diameters but also smaller diameters [16, 17]. This is a consequence of the effect of the applied voltage in the different factors affecting the final fiber morphology. Applied voltage may affect some factors such as mass of polymer fed out from a tip of needle, elongation level of a jet by an electrical force, morphology of a jet (a single or multiple jets), and others.

Applied voltage reflects the force to pull a solution out from the needle. Consequently, higher voltage causes more solution coming out and an increase in the fiber diameter. On the other hand, applied voltage affects the charge density, thus an electrical force that acts to elongate the jet during electrospinning. Hence, higher applied voltages increase the jet elongation and, consequently, decrease the fiber diameter. As a consequence, and depending on the

Fig. 1 Concentration effects on the morphology of electrospun PEOZ fibers from water solutions; **a** 15 wt%, **b** 20 wt%, and **c** 25 wt%



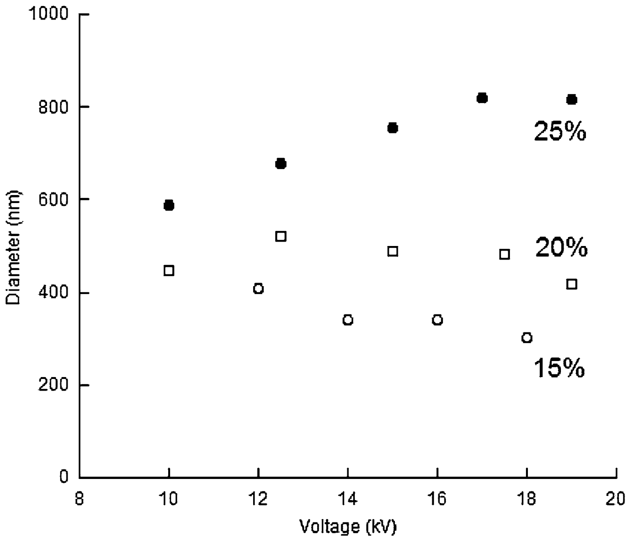


Fig. 3 Applied voltage effects on the diameter of the PEOZ fibers electrospun from water solutions with different polymer concentration

electrospun solution characteristics, a balance among these factors will determine the final diameter of electrospun fibers [18].

A similar trend was observed for the effect of the volume feed rate on the morphology of electrospun fibers. Figure 4 shows that the diameter of the electrospun PEOZ fibers changed with varied volume feed rate. The flow rate is a parameter which could affect electrospinning process. When the flow rate exceeded a critical value, the delivery rate of the solution jet to the capillary tip exceeded the rate at which the solution was removed from the tip by electric forces. This shift in the mass-balance resulted in sustained but unstable jet and fibers with big beads are formed [19].

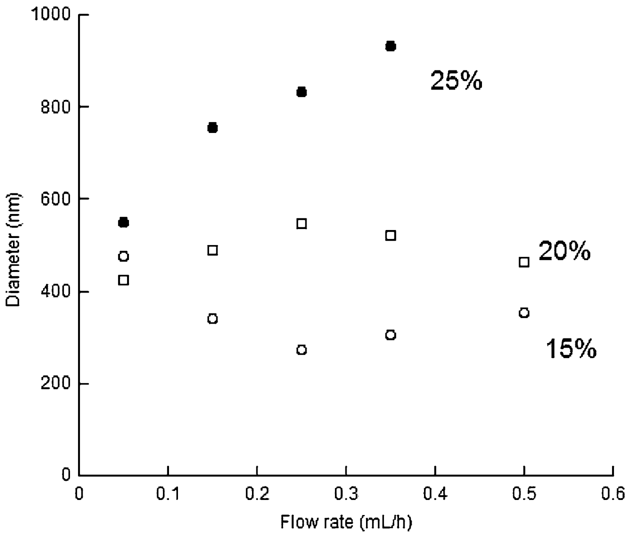


Fig. 4 Volume feed rate effects on the diameter of the PEOZ fibers electrospun from water solutions with different polymer concentrations

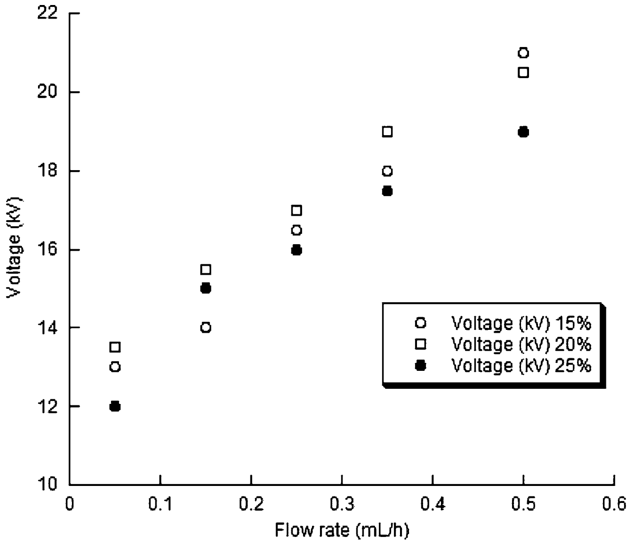


Fig. 5 Volume flow rate effects on applied voltage of the PEOZ fibers electrospun from water solutions with different polymer concentrations

On the other hand, as can be seen in Fig. 5, an increase on the feed rate supposes an increase in voltage to maintain the conical shape of the surface in the tip of the needle.

The use of water solutions for electrospinning PEOZ fibers was not the only alternative when the PEOZ electrospinning was considered. In fact, two other solvents, THF and DMF, were tentatively considered. It is well-known that the solvent properties can also affect the best conditions for the electrospinning of a given polymer and, consequently, the characteristics of the fibers finally obtained. As previously mentioned, electrospinning involves stretching of the solution caused by repulsion of the charges at its surface. Thus, if the conductivity of the solution is increased, more charges can be carried by the electrospinning jet and, in general, there are more chances to get fibers without beads. Organic solvents are known to be generally non-conductive, although many of them do exhibit a certain level of conductivity. With these ideas in mind, PEOZ solutions in DMF and THF were also tested. Table 1 shows the electrical conductivity and dielectric constant of the three solvents used in our work [20]. The conductivity in a polymer solution may be related with the dielectric constant of the solvent.

As a way to compare the role of the solvent characteristics in the final fibers, 20 wt% solutions of water, THF, and DMF were electrospun. As Fig. 6 shows, water was the best solvent in providing PEOZ fibers with highest productivity (the numbers of fibers webs per unit area per unit time) and optimal morphological characteristic (uniform fibers). The beadless PEOZ fibers with a diameter of

Table 1 Electrical conductivity and dielectric constant of the solvents used to electrospun PEOZ fibers

Solvent	Conductivity (mS/m)	Reference	Dielectric constant	Reference
Dimethylformamide (DMF)	1.09	Jarusuwannapoom et al. [21]	36.7	Yang et al. [23]
Distilled water	0.45	Theron et al. [13]	80.2	Merck Chemical data sheet
Tetrahydrofuran (THF)	0.00	Wannatong et al. [22]	7.5	Wannatong et al. [22]

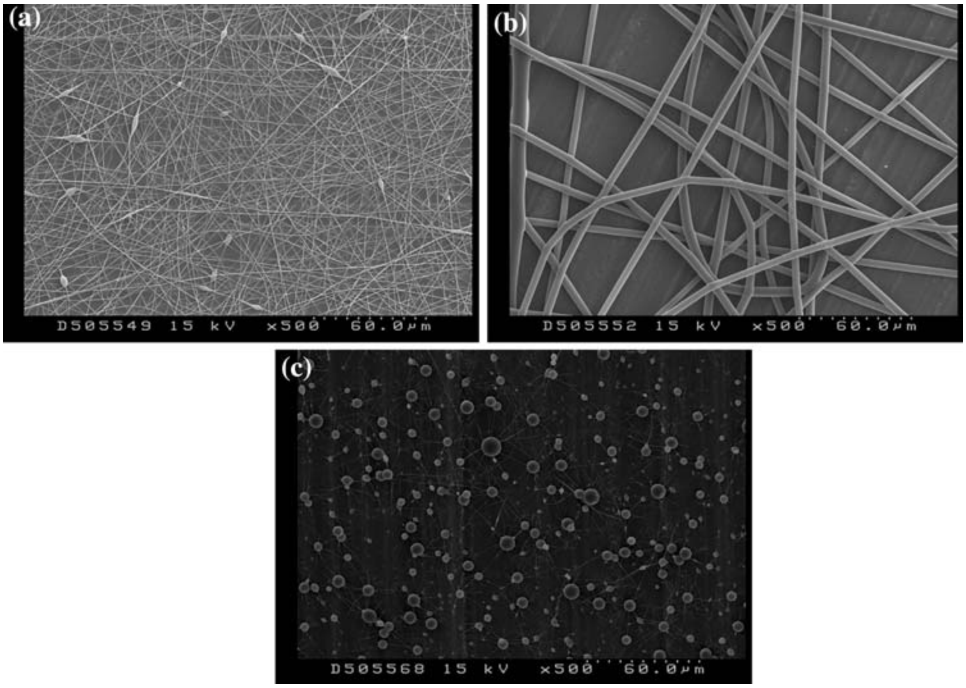


Fig. 6 Solvent effects on the electrospinning of 20 wt% PEOZ solutions; **a** Distilled water, **b** THF, **c** DMF

~500 nm were produced from 20 wt% PEOZ solution in water at an applied voltage of 15–16 kV and a volume flow rate of 0.15 mL/h.

The electrospinning of the 20 wt% PEOZ solutions in THF was quite difficult due to its fast evaporation in the hanging droplets. This induced high viscosity of the solution and the clogging of the spinneret at the tip. In order to circumvent these problems, it was necessary to use higher volume flow rates (0.35 mL/h) that, at its turn, generated PEOZ fibers with diameters substantially larger than those obtained with the water solutions.

Finally, DMF solutions, at the same concentrations, gave a bead-on-string morphology, in spite of the inherent conductivity of the solvent. In a recent paper investigating the role of the solvent in the electrospinning of polystyrene solutions, Wannatong et al. [22] found similar results in using DMF. They attributed the results to the limited solubility of polystyrene (PS) in DMF, characterized in terms of dissimilar solubility parameters. In a poor solvent, the polymer random coils prefer to interact with themselves, decreasing the number the entanglements and, consequently the possibilities of forming fibers. This could be the case in the PEOZ/DMF solutions. According to the Polymer Handbook [24], DMF has a solubility parameter of 12.1 $(\mathrm{cal/cm^3})^{1/2}$, whereas according to the Painter and Coleman group contribution method [25], PEOZ solubility parameter would be 10.0 not far from the 9.5 value obtained for polystyrene by the same group contribution method.

Conclusions

In the present work, fibers of micron diameters have been successfully produced by electrospinning of different PEOZ water solutions. THF and DMF solutions have been also tested. According to the results above summarized, the properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber. Polymer concentration and electrical conductivity of solvents were found to play (although not always) a significant role in controlling the morphology and the diameter of the electrospun nanofibers. The external factors exerting on the electrospinning jet such as voltage supplied or feed rate have also an influence in the fiber morphology, although, in this case, the final effect is more difficult to predict.

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