The Influence of Process Parameters on the Characteristics of Electrospun 3D Nanostructures

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Abstract. Electrospinning is a fast developing technique that employs electrostatic repulsive forces to produce ultrafine fibres with application in fields like environment protection, medicine, sensors and many others. The characteristics of the polymer jet and the properties of the electrospun nanofibres are highly influenced by technological and environmental parameters. This paper offers a report on the main processing parameters that may influence the characteristics of the obtained nanofibres. The influence of flow rate, spinneret to collector distance and applied voltage on maximum fibre length, average fibre diameter, diameter uniformity and nanofibre quality is reviewed.

1. Introduction
Electrospinning is an economical and uncomplicated method to produce polymer fibres at low basis weight and at a small fibre diameter and pore size [1-5]. Electrospinning is different from traditional wet/dry fibre spinning; if in the traditional methods mechanical pulling forces lead to fibres in the micrometre range, in electrospinning electrical pulling forces enable the production of nanofibres. A representation a typical electrospinning setup is shown in figure 1.

![Figure 1. Schematic electrospinning setup [1].](image)

High voltage is linked to the end of a capillary that contains the polymer solution, forcing the extinction of the hemispherical surface of the solution from the end of the capillary and creating a Taylor cone. When the electric field is increased, the repulsive electrostatic force overwhelms the
surface tension and the charged strand emerges out of the end of the Taylor cone [6-9]. The polymer jet elongates and the solvent evaporates, forming fibres that are deposited on the collector (figure 2).

Figure 2. The mechanism of the effect of charges on the polymeric droplets [10].

The process can be tuned by controlling three main groups of parameters: solution properties, processing conditions and ambient conditions. Process variables, such as fluid flow rate, spinneret to collector distance and electric field strength have a significant influence on the properties of the obtained nanofibres [11-14].

2. Fluid flow rate

Flow rate is considered to be as one of the main parameters that control the diameter of the fibre and its distribution, the initial shape of the droplet, the trajectory of the jet, the persistence of Taylor cone and deposition area [15-18]. The polymer solution flow rate within the syringe is an important process parameter; generally a lower polymer solution flow rate is recommended to have enough time for polarization [19-22]. If the feed rate is very high, exceeding a critical value, which varies with the polymer system, the delivery rate of the polymer solution jet to the capillary tip surpasses the rate at which the solution is detached from the tip by electric forces [1], larger droplets are formed, and polymer fibres with a high density of beads are formed, because of the reduced solidification time of the polymer filament before reaching the collector and of low tension forces.

Figure 3. Morphology of electrospun polysulfide fibres at different flow rates – a) 40 mL/h; b) 66 mL/h [23].

The way the shape of the polymer cone changes with increasing flow rate is shown in figure 4. In a study on the influence of flow rate on the polystyrene fibre morphology and size it was observed that bead formation occurs when the flow rate is higher than 0.1 mL/min, and the pore size and diameter of fibres increases [26]. An investigation on the effect of the flow rate on morphologies of the polysulfone fibres from 20% polysulfone/ N,N-dimethylacetamide solution at 10 kV showed that bead fibres with thicker diameters were obtained by the flow rate of 0.66 mL/h [27].
Figure 4. Formation of various jets with increasing flow rate [24, 25].

Similar results have been reported for nylon 6, where bead fibres formed when the feeding rate exceeded 4 mL/min [28]. To increase the productivity of electrospinning, the feed rate can be increased as the applied stress increases, which usually leads to smaller diameter of the nanofibres [29], but when the flow rate is too high, as larger volume of solution is drawn from the needle tip, which needs a longer time to dry, there is the possibility that fibres merge together and make webs instead of fibres [15].

Furthermore, when the flow rate increases, fibre diameter distribution becomes wider. Since increases and decreases in the polymer solution flow rate influence the nanofibre formation and diameter, it is preferable to maintain a minimum flow rate which ensure a balance between the leaving polymeric solution and its replacement with a new one during jet formation [10].

Figure 5. Effect of Solution Flow Rate on the morphology and diameters of nanofibres - Variation of average fibre diameters with flow rate [30].

Choosing an appropriate flow rate leads to a limitation of the formation of any defects such as blobs, splitting and branched fibres. In addition, a stable and constant flow rate is required [31]

3. Spinneret to collector distance

By proper setting of the distance between the metallic needle tip and the collector it can be controlled the morphology and the diameter of the electrospun fibres. If the distance is too small, the fibre will not have enough time to solidify before it reaches the collector, while if the distance is too high, it is possible to obtain fibre with droplets at the surface [19,32]. The solvent removal capacity being an essential factor in obtaining high quality fibres, it is advisable to carefully set the distance to the collector. It has been shown that a small change in this distance significantly influences the characteristics of the fibres. Furthermore, as the distance between the charged nozzle and the collector increases, the level of the electric field between the two decreases, forming fewer charged ions, allowing bending instabilities and whipping action to elongate and decreases the diameter of the polymer jet [31, 33]. Most studies concluded that defective and large-diameter nanofibres are obtained when the spinneret to collector distance is small, while the diameter of the nanofibre is reduced as the distance was increased [34]. Electrospun poly (vinylene fluoride) nanofibres obtained from a 28 wt% solution at 12 kV showed a decrease in diameter from 397 nm to 314 nm when the distance between the nozzle and the collector increased from 15 cm to 16 cm (figure 6), as well as improved uniformity [35]. A study of the influence of the spinneret to collector distance D on the diameter of the fibres electrospun from 12% polyetherimide solution (PEI), using as solvents a mixture of
dimethylacetamide / tetrahydrofuran 1:1 came to the conclusion that the smallest values of the diameter are obtained for a distance of 45 mm [36].

![Figure 6. SEM micrographs of poly(vinylidene fluoride) fibres at spinning distance of: a. 15 cm; b. 16 cm [35].](image)

Usually the appropriate distance between the metallic needle tip and collector varies with the polymer system, but there were cases when no effect on the morphology of the nanofibre occurred when changing the distance between the metallic needle and collector [37].

4. Applied voltage
The applied electrical potential is one of the most important parameters of the electrospinning process because it influences directly both the dynamics of the fluid flow and the morphological characteristics of the electrospun fibres, but its degree of significances varies with the polymer solution concentration and the distance between the nozzle and the collector [38]. Only when the applied voltage exceeds a threshold value, the charged polymer jets are ejected from the Taylor cone [39]. The size of the threshold voltage is dependent on the nature of the polymer and the polymer-solvent system [10]. The applied voltage is the most contradictory parameter in affecting nanofibres morphology. There are studies showing that an increase in applied voltage leads to the formation of smaller diameter nanofibres due to the extent of the polymer solution in correlation with the increased rejection forces in the polymer jet [40, 41], but also studies which have demonstrated that there is no essential influence of the electric field on the diameter of electrophilic polyethylene oxide (PEO) nanofibres [42, 43]. There are studies that highlight the fact that higher voltage facilitate the formation of high diameter fibres, such as poly (vinyl alcohol) (PVA) / water [37]. Therefore, the applied voltage influences the diameter of the fibre, but the level of significance varies depending on the nature and concentration of the polymer solution and the distance between the electrode and the collector [44]. It is generally accepted that an increase in the applied voltage leads to an increase in the deposition rate, therefore there is a greater probability of defect formation [40, 45]. The length and diameter of the electrospun fibre decrease with the increase in applied voltage without any change in pore size [46, 47]. For nanofibres obtained with low electrical voltage a uniform morphology with lesser defects and drops is obtained [48-53]. The study on a mixture of PANI-HCSA / PEO highlighted the fact that higher voltage leads to thinner nanofibres, but also a greater diversity of diameters and a wider distribution of diameters, as it can be seen in figure 7 [29].

![Figure 7. Applied voltage influence: a) 13.5 kV; b) 9.2 kV; c) 5 kV [29].](image)
5. Conclusions
This paper offers an overview of the electrospinning process parameters (applied electric field strength, distance between the spinneret and collector and fluid flow rate) that influence the nanofibres production. All these parameters significantly affect the morphology of the electrospun nanofibres, and by controlling them it is possible to produce nanofibres for specific functions. The fluid flow rate influence the droplet size and its initiating shape at the capillary tip, the trajectory of the jet and the maintenance of Taylor cone, the fibre diameter distribution and the morphology of the nanofibres. The correct distance between the nozzle and collector varies with the polymer system, but most frequently a slight decrease in the average fibre diameter is noticed by the distance increases. The applied voltage has a contradictory influence on nanofibres morphology, as there are studies that found that average fibre diameters is directly proportional to the applied voltage, but many studied that reported a inverse proportionality.

6. References
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