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Fabrication of Poly(Caprolactone) Nanofibers by Electrospinning

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Abstract Nanofibers at 466 ± 242 nm average diameter were fabricated due to phase separation caused by polarizability difference under static electric field. Fibre morphology was observed under a scanning electron microscopy. An insight into the process of electrospinning of the polymer, poly(caprolactone) was systematically evaluated and discussed the effects of the solution parameter of concentration of the polymer solution and process parameters of voltage, flow rate and drop height to fabricate poly(caprolactone) electrospun fibers with desired morphologies in this manuscript. Of all combinations, the best nanofibres with the fewest beads and finest fibers could be electrospun with a more uniform distribution in with a 15 kV applied voltage of on poly(caprolactone) solution of 12 per cent concentration at a 0.5 ml/h flow rate, from a drop height of 15 cm and the structure of nanofibres was found completely dry and stabilized.

Keywords: *electrospinning, polymer, solution parameters, process parameters, Poly(caprolactone), nanofiber*

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1. Introduction

Electrospinning is one of the most recognized techniques to make polymer nanofibers. These non-woven sub-micron range spun fibers mimics extracellular matrix components much closely and possess high surface area to volume ratio and tunable porosity. These nanofibers, made from electrostatically driven jet of polymer solution (polymer melt) delivered through a millimeter-scale nozzle by the application of strong electric field is widely used as tissue engineering scaffolds, drug delivery, wound dressings, filtration, enzyme immobilization and biosensors. Fabrication of suitable scaffolds is critical for successful application of tissue engineering (TE) in regenerative medicine. Among various techniques to fabricate TE scaffolds, electrospinning is a widely used technique to create nanofibers from a natural or synthetic polymer solution. There are three main components in the apparatus used for the process (Figure 1). A spinneret, a high voltage power source and a grounded collector. In this process, the polymer solution is taken in a syringe and it is ejected out through the needle very slowly. So, a small drop is formed at the tip of the needle. Then, a very high voltage is applied. The electric field induces an electric charge on the liquid droplet. The electrostatic repulsion counteracts the surface tension, and at a critical point, a stream of liquid erupts from the surface. This point of eruption is called Taylor cone. The charged liquid jet migrate towards the collector. As it migrates, it dries up and the charges moves to the surface of the fiber. The fiber then elongates and finally deposits at the collector. The machine used for electrospinning is shown in Figure 2.

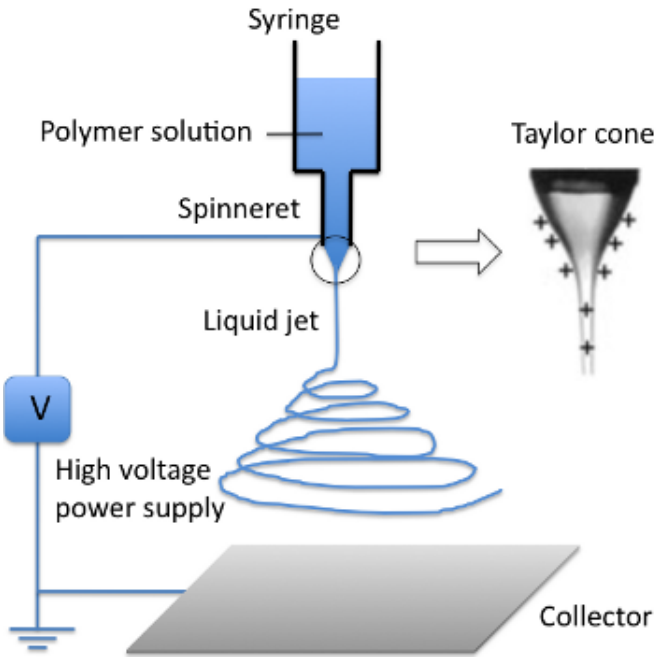

Figure 1. A schematic diagram showing the process of electrospinning

1.1. Parameters Affecting Electrospinning

There are many factors affecting the process of electrospinning. They have been broadly classified into two: Solution parameters and Processing parameters. Solution parameters include concentration of the polymer

solution, viscosity, surface tension, etc. Processing parameters include voltage applied, flow rate, and drop height. Some of the major parameters affecting the process of electrospinning and controlling the fiber morphology have been discussed here.

Figure 2. Electrospinning machine used for present study

1.1.1. Concentration of the Polymer Solution

The concentration of the polymer solution used is a very important parameter that affects the process. At very low concentrations, fibers may not form evenly due to low viscosity, resulting in the formation of droplets – a phenomenon known as spraying. On the other hand, at high concentrations also, formation of fibers are prohibited, due to high viscosity. Thus, there will be an optimal concentration range for each polymer at which good fibers will be obtained.

1.1.2. Voltage

Voltage applied is a very important factor in the process. Only if a minimum voltage is applied, the process of fiber formation occurs. However, there exist some disputes about the effects of applied voltage in the process.

1.1.3. Flow Rate

The flow rate determines how much amount of polymer comes out in a certain time. It is an important factor in the process. Lower flow rates are preferred to allow enough time for evaporation of the solvent. Researchers have observed an increase in the fiber diameter with increase in flow rate. But higher rates results in the formation of beads due to non-evaporation of the solvent.

1.1.4. Drop Height

The height of the tip from the collector also plays a role in the process. There should be a minimum distance so that the solvent gets time to get dried up before reaching the collector. The drop height does not play as significant role as the other parameters in the fiber morphology within certain limits. But if the height is too small or too large, beads are often obtained.

In the present study, nanofibrous mats were prepared from poly(caprolactone) (PCL) solution by electrospinning technique. PCL is a biodegradable polyester with a low melting point (60°C). Due to hydrolysis of its ester linkages in physiological conditions, PCL has received much attention for use as an implantable biomaterial. Food and Drug Administration (FDA) has already approved the use of PCL in drug delivery device and suture applications.

2. Material and Methods

2.1. Preparation of Polymer Solution

PCL solution was using tri-fluoroethanol (TFE) as a solvent. In brief, for 10% (w/v) solution, 300 mg PCL was taken in a glass vial and 3 ml of TFE was added to it. A magnetic bead was put into the vial, the vial was closed, wrapped with parafilm tape (as the solvent is volatile) and kept on a magnetic stirrer and left overnight. Similarly, 12% (w/v) and 15% (w/v) PCL solution were also prepared.

2.2. Electrospinning

The polymer solution is taken in a 2 ml disposable syringe. The syringe needle tip was cut to produce a blunt end which helps to form uniform fibers. After mounting the syringe into the set-up, the electrospinning machine as well as the computer connected to it were switched on. The syringe pump was switched on and the flow rate was set by using the software in the computer. Finally the voltage (set to required value) was applied and formation of nanofibers started. A glass slide was placed over the collector to check the formation of electrospun fibers under the microscope. Also, aluminium foils were placed

onto the collector to collect nanofibers for examining under electron microscope.

Electrospinning was done for the different concentrations and fiber formation was observed changing some of the parameters. For 10% PCL solution, fiber formation was observed for the following parameters: drop height of 15 cm, flow rate of 0.1ml/h, 0.5ml/h and 1ml/h, voltages of 8kV, 10kV, 12kV and 15kV. For 12% PCL, fiber formation was observed for the following parameters: drop height of 15 cm and 10 cm, flow rate of 0.5 ml/h, voltage of 10kV and 15kV. For 15% PCL, fiber formation was observed for the following parameters: drop height of 15 cm, flow rate of 1ml/h, voltages of 10kV, 12kV, and 15kV. Some of the electrospun fibers were observed under a scanning electron microscope (SEM).

3. Results and Discussion

3.1. Polymer Solution Concentration

It was found that fiber formation occurred in solution concentration of 10 - 15%. Beads or spherical shaped fibers could not be observed in any of these concentrations. Fibers obtained from a concentration of 12% was observed under a SEM and uniform fibers with porosity were observed (Figure 3). Higher viscosity resistance might be the reason for this as already reported [1,2]. It has been already reported that when the concentration is very low, polymeric micro (nano)-particles will be obtained as electrospray occurs instead of electrospinning owing to the low viscosity and high surface tensions of the solution; when the concentration is little higher, a mixture of beads and fibers will be obtained; when the concentration is suitable, smooth nanofibers will be obtained; If the concentration is very high, not nanoscaled fibers, helix- shaped micro- ribbons will be observed [3]. Using the typical SEM images obtained in this study, all concentration treatments resulted smooth nanofibers only (Figure 3). Higher fiber diameter was obtained upon increasing the concentration of solution with gelatin electrospinning [4]. Solution surface tension and viscosity also play important roles in determining the range of concentrations from which continuous fibers can be obtained in electrospinning [5].

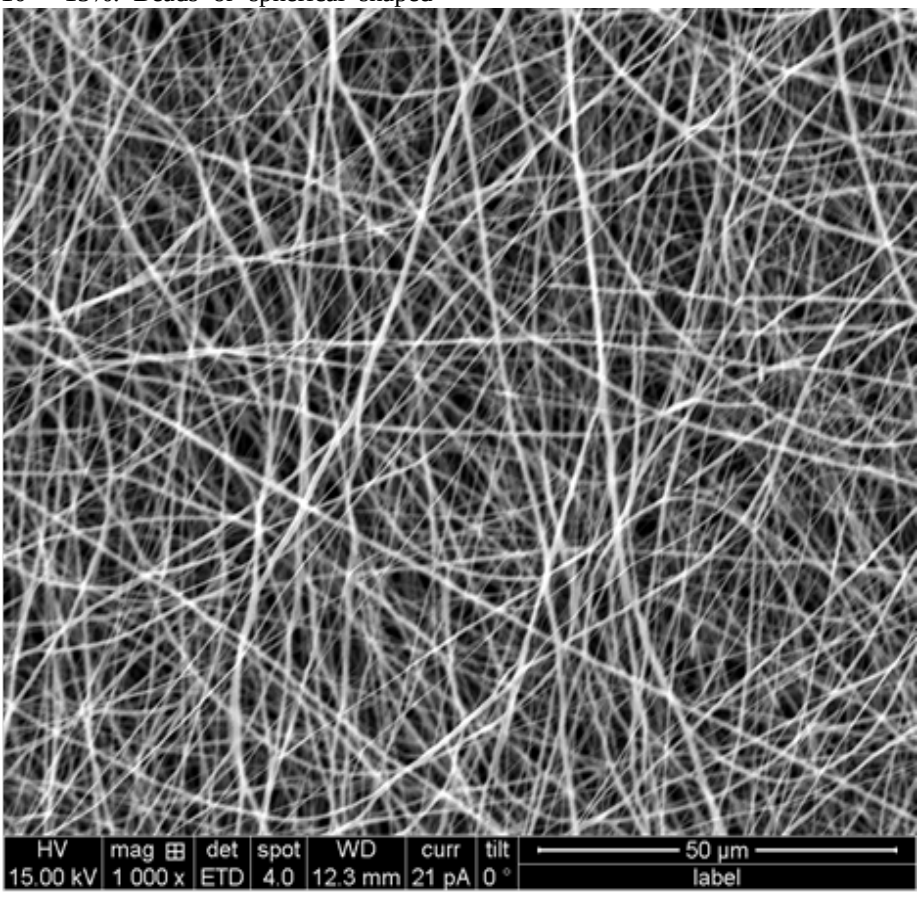

Figure 3. SEM image of PCL electrospun fibers of 12% polymer solution (Average fiber diameter: 466 ± 242 nm)

If the solution concentration is suitable for electrospinning, by increasing the concentration of solution, usually, the fiber diameter will increase as solution viscosity can be tuned by adjusting the solution concentration and surface tension being the dominant factor [3]. But, such differences were not significant in the present study.

3.2. Applied Voltage

Under the optical microscope, no beads formation could be noticed when 8 to 15 kV voltage applied to the polymer solution and fibers were formed in all the treatments. This has proved that the treatments were in the range of threshold voltage that initiated electrospinning process. It has been proved experimentally that the shape of the initiating drop changes with spinning conditions of voltage, viscosity, and feed rate [6]. There is not much effect of electric field on the fiber diameter with electrospinning of polyethylene oxide and the present

investigation support this finding [7]. When higher voltages are applied, there is more polymer ejection and this facilitates the formation of a larger diameter fiber [8], [9]. An increase in the applied voltage by increasing the electric field strength, increases the electrostatic repulsive force on the fluid jet which ultimately favors the narrowing of fiber diameter [10]. In most cases, a higher voltage causes greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter and also rapid evaporation of solvent from the fibers results. At a higher voltage there is also greater probability of beads formation [2]. Thus, voltage influences fiber diameter, but the level of significance varies with the polymer solution concentration and on the distance between the tip and the collector [11].

Within the electrospinning process, applied voltage is the crucial factor. Only the applied voltage higher than the threshold voltage, charged jets ejected from Taylor Cone, can occur. There is not much effect of electric field on the diameter of electrospun polyethylene oxide (PEO) nanofibers [7]. Higher voltages facilitated the formation of large diameter fiber with poly (vinyl alcohol) (PVA)/water solution as mode [8]. Higher voltage offers the greater probability of beads formation [11]. Higher voltages can increase the electrostatic repulsive force on the charged jet, favoring the narrowing of fiber diameter with polysulfone (PSF)/DMAC/acetone as model [12]. Thus, voltage does influence fiber diameter, but the level of significances varies with the polymer solution concentration and on the drop height [3]. None of the applied voltage had significant differences in resultant fiber morphologies of poly(caprolactone).

3.3. Flow Rate of Polymer Solution

All the treatments from 0.1 ml/h to 1 ml/h yielded fibers. None of the polymer flow rates from 0.1 ml/h to 1 ml/h yielded beaded fibers. This shows that all treatments had a minimum flow rate of the spinning solution. A lower feed rate is more desirable as the solvent will get enough time for evaporation [12] and high flow rates result in beaded fibers [13]. The fiber diameter and the pore diameter increases with an increase in the polymer flow rate in the case of polystyrene fibers by influencing the jet velocity and the material transfer rate [14].

The flow rate of the polymer solution within the syringe is another important process parameter. Generally, lower flow rate is more recommended as the polymer solution will get enough time for polarization. If the flow rate is very high, bead fibers with thick diameter will form rather than the smooth fiber with thin diameter owing to the short drying time prior to reaching the collector and low stretching forces. Bead fibers with thicker diameters were obtained as the flow rate is 0.66 ml/h with the PSF fibers from 20 % PSF/DMAC solution at 10 kV [12].

3.4. Drop Height

No beads have been observed in either of the drop height of 10 cm or 15 cm and hence both the treatments resulted sufficient time to dry before reaching the collector from the tip and could be regarded as optimum distance that favors the evaporation of solvent from the nanofibers [15].

Beads have been observed, if the distances are either too close or too far [16]. It has been reported that flatter fibers can be produced at closer distances but with increase in distance rounder fibers have been observed with the spinning of silk-like polymer with fibronectin functionality [17]. For polysulfone, closer distances between the tip and collector has yielded smaller fibers [18]. The effect of tip and the collector distance on fiber morphology is not as significant as other parameters as already reported with electrospinning of poly(vinylidene fluoride) [19].

It has been proven that the drop height can also affect the fiber diameter and morphologies [3]. If the drop height is too short, the fiber will not have enough time to solidify before reaching the collector, whereas if the drop height is too long, bead fiber can be obtained. It is well known that one important physical aspect of the electrospun fiber is the dryness from the solvent, so optimum distance is recommended. A little long distance favors the thinner fiber diameter [12].

4. Conclusions

The electrospun fibers produced in the present study have a diameter in the nano meter range. Their random alignment creates very small pores in them which help their application as a biomaterial scaffold. Solution and processing parameters such as concentration of the polymer, applied voltage, drop height, flow rate of polymer solution etc. significantly affect the fiber morphology and by manipulation of these parameters, one can get desired properties.

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