Journal of Mechanical Engineering *Vol SI 4(3), 246-254, 2017*

Electrospinning of Polycaprolactone (PCL) and Gelatin Polymeric Fibers

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ABSTRACT

Electrospinning is one of the commonly used polymeric fiber production technique, owing to its versatility and flexibility in spinning a wide range of polymers for various applications including tissue engineering. However, recent researches have been extensively focusing on exploring the electrospinnability of different polymers without fully realizing how the electrospinning parameters influence the electrospun fibrous structure, as the microstructure morphology will significantly affect the performance of electrospun membranes. The present work demonstrates the robustness of electrospinning technique in producing electrospun fibrous membranes with different microstructure morphology by altering the electrospinning parameters. Both PCL and gelatin solutions have been successfully transformed into electrospun fibrous membranes using an electrospinning machine. The PCL fibrous membranes consisted of beads and non-homogenous fibers while the gelatin membranes showed homogenous size of electrospun fibers. Results also revealed that the electrospinning parameters including solution and process parameters determined the microstructure morphology of electrospun membrane. The spindle-like beads in PCL membrane transformed into spherical size at higher solution concentration and applied voltage. Meanwhile, the gelatin membrane demonstrated similar morphology at different tip-collector distance. The size of gelatin fibers was also similar. Through this work, basic understanding on how the electrospinning parameters affect the morphology of different types of polymeric fibrous membrane can provide an insight for other researchers in facilitate production of electrospun membranes with desired microstructure morphology.

ISSN 1823- 5514, eISSN 2550-164X

Received for review: 2017-02-12
Accepted for publication: 2017-05-12
Published: 2017-10-15

Keywords: *electrospinning, polymeric fibers, polycaprolactone, gelatin, electrospun fibrous membrane*

Introduction

There are various techniques to fabricate polymeric fibers, including drawing, template synthesis, self-assembly (materials are assembled molecule by molecule), phase separation and electrospinning. Currently, electrospinning is the only technique that is able to produce continuous ultrafine fibers from micrometer to nanometer diameters [1]. Electrospun mat produced by electrospinning technique has totally different appearance and structures to those fabricated by self-assembly and phase separation technique. This simple yet versatile method is able to produce nanofibers in small quantity for laboratory research application and mass production for industrial use. Moreover, electrospinning is able to produce ultrathin fibers from a wide range of materials in various fibrous assemblies. The abovementioned unique features give rise to widely use of electrospinning technique in both academia and industry in recent years.

The idea of using electrostatic force to induce the formation of liquid drops was first introduced by Lord Rayleigh in 1882 [2]. He discovered that the droplet charged by high electricity was in a condition of unstable equilibrium, forming a cone shape and breaking down into smaller droplets when passed through a voltage gradient. In 1934, Formfals patented his first invention which was related with the process and apparatus for the production artificial filament by using electric charges [3]. The spinning process consists of a movable thread collecting to collect the threads in a stretched condition. By using this method, Formfals successfully collected cellulose acetate fibers using acetone/alcohol solution as the solvent. In 1939, Formfals has made some modifications in second patent to overcome incomplete solvent evaporation. In the new process, distance between the solution feeding nozzle and moving collector was increased in order to obtain greater space and sufficient time to evaporate the solvent and dry out the fibers before it reached the collector [4].

In 1969, Taylor published his work which relates to the shape of polymer droplet emerged at the tip of the needle when an electric field is applied [5]. The droplet at the tip needle changes into cone shape when surface tension is balanced by electrostatic force, and the fibers jets emitted from the vertices of the cone. This conical shape of the jet called “Taylor cone” by other researchers. Subsequently, in 1971, Baumgarten had started to investigate the effect of varying solution and process parameters including solution viscosity, applied voltage, flow rate and etc. on the structure properties of electrospun acrylic fibers [6].

Parameters of electrospinning

Working parameters were classified into three categories, which are (a) processing parameters such as applied voltage, distance between nozzle and collector, and flow rate, (b) solution parameters such as polymer concentration, solvent volatility and solution conductivity, and (c) ambient parameter such as solution temperature, humidity, and air velocity in the electrospinning chamber [7]. All of these parameters can affect the formation and structure of fibers [8].

The applied voltage can control the fiber diameter from several microns to tens of nanometers. It could also result bead defects in the spun fibers. Increasing the applied voltage causes the Taylor cone to recede and lead to appearance of bead defects [9]. Lesser nozzle-collector distance also produces beaded structure. This is caused by the solvent does not has enough time to evaporate before the electrospun fibers reaching the collector [10]. In contrast, larger nozzle-collector distance enhances the evaporation rate of solvent, so that smooth and thinner fibers can be obtained. Lower flow rate yields fibers with smaller diameter and free from beads. The fiber diameter and pore size increase with the increasing of flow rate [11]. At the same time, bead defect emerged due to the solvent did not evaporate completely before reaching the collector.

Polymer concentration has strong influence on structure of electrospun mat. At a very low polymer concentration, electrospun nanofibers could not be found [12]. With a slight increase of polymer concentration, a lot of beads and droplets were formed. This phenomenon was attributed to the low viscosity and relatively high surface tension [13]. With further increase in polymer concentration, uniform and smooth fibers can be obtained. Beside polymer concentration, a volatile solvent is needed for sufficient solvent evaporation between the needle nozzle and collector. The electrical conductivity of solution also greatly influences the formation of fibers. Adding charges on the surface mean higher conductivity of the solution under the higher electric field and thus the movement of charged jets increase, resulting in greater elongation.

Another parameter that can influence the fibers structure and morphology is ambient parameters. The ambient parameters include ambient humidity, ambient temperature, and air velocity in an electrospinning chamber. Higher temperature resulted in smaller size of fibers diameter due to decrease of polymer solution viscosity [14]. Small circular pores were found to appear on fiber surface at high ambient humidity, with increasing the humidity further lead to pore coalescing [15].

Although the electrospinning parameters were found to significantly affect the formation and structure properties of fibers, recent researches are more focus on exploring the electrospinnability of different polymers for wider range of applications without fully realizing how the electrospinning parameters influence the electrospun fibrous structure, as the microstructure morphology will bring significant effect on performance of electrospun membrane. Therefore, the objective of this work is to explore how the solution and process parameters affect the microstructure morphology of electrospun fibrous membranes. Two distinct types of polymers, PCL and gelatin, were spun into fibrous membranes under different electrospinning settings. Their morphology was then visualized using scanning electron microscopy (SEM).

Methodology

Materials

Polycaprolactone pellets (PCL) with average molecular weight of 80,000 kDa and gelatin from cold water fish skin were purchased from Sigma Aldrich. Solvent of glacial acetic acid (AA) was supplied from Merck. All the materials were used without further purification.

Electrospinning setup

The electrospinning setup consists of three main components, which are high voltage power supply, syringe pump and metal collector. The high voltage power supply is used to generate the electrostatic force while the syringe pump is used to control the polymer solution feed rate. A metal collector is used to deposit the electrospun polymeric fibers. Schematic diagram of the electrospinning setup is shown in Figure 1.

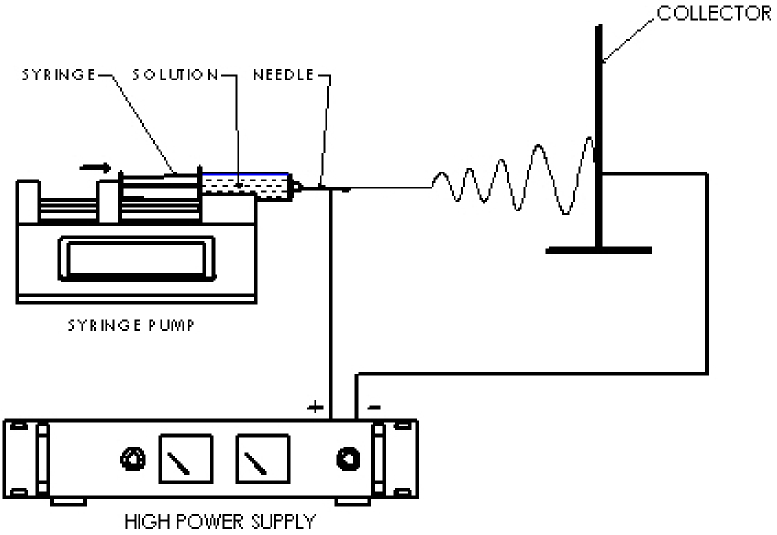

Figure 1: Schematic diagram of the electrospinning setup.

Polymer solutions preparation

For electrospinning of PCL fibrous membrane, the PCL pellets were dissolved in two different solvents at different concentration. The solvents were glacial acetic acid and mixture of glacial acetic acid/distilled water. The first PCL solution was prepared following a similar method to that of [16]. Briefly, the PCL pellets were dissolved in glacial acetic acid to create solutions of concentrations 20 and 23 wt. %. The second PCL solution contains 20 wt. % PCL in a mixture of 90 wt. % acetic acid and 10 wt. % distilled water.

For gelatin solution preparation, method described in previous study [17] was followed. Briefly, a 25 wt. % of gelatin wa %s dissolved in a mixture of glacial acetic acid and water with a ratio of 90 wt. % :10 wt. %.

All the PCL and gelatin solutions were stirred overnight at room temperature.

Electrospun fibrous membranes preparation

All electrospun fibrous membranes were produced in the electrospinning chamber with horizontal setup (Figure 1). The polymer solution was loaded in a plastic syringe and connected with a blunt tip needle. Electrospinning parameters that used in preparation of electrospun fibrous scaffolds for different polymer solutions were summarized in Table 1. The relative humidity in the electrospinning chamber was maintained at 50 ± 10 % throughout the electrospinning process.

Table 1: Summary of electrospinning parameters in preparation of electropsun fibrous scaffolds.

Case study	Polymer	Solvent	Solution concentration (%)	Tip-collector distance (cm)	Solution feed rate (ml/h)	Applied voltage (kV)
1	PCL	AA	20 wt.	10	0.30	6
2	PCL	AA	20 wt.	10	0.30	12
3	PCL	AA	23 wt.	10	0.30	6
4	PCL	AA/Water	20 wt.	15	0.30	11
5	Gelatin	AA/Water	25 wt.	20	0.30	9
6	Gelatin	AA/Water	25 wt.	30	0.30	9

Electrospun scaffold morphology observation

Samples with size approximate 1 x 1 cm were cut from each electrospun fibrous membrane. The morphology of samples was visualized by scanning electron microscopy (SEM, Hitachi, USA). Prior to SEM observation, a thin layer of gold was sputter coated on the samples using a sputter coating unit.

Results And Discussion

Influence of solution parameters

The PCL solutions with different polymer concentration and solvent system were prepared to study the influence of solution parameters on microstructure morphology of electrospun membranes. Figure 2a and 2b illustrate the SEM images of electrospun PCL membranes obtained from two different solution concentrations which are 20 wt. % and 23 wt. %, respectively. At solution concentration of 20 wt. %, formation of non-homogenous fibers and spindle-like beads were observed (Figure 2a). As the concentration increased to 23 wt. %, no reduction or elimination of bead defect was found. The spindle-like beads was transformed into spherical shape at higher solution concentration (Figure 2b).

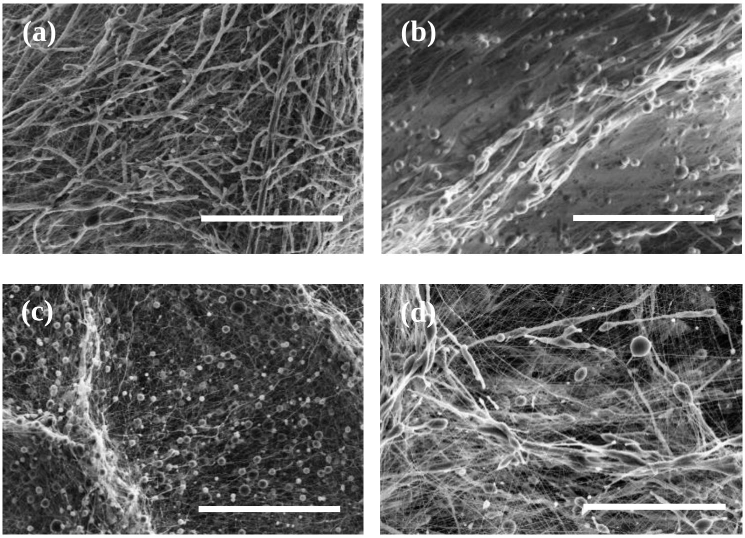

Figure 2: SEM images of electrospun PCL membranes obtained from different solution concentration and process parameters.
All scale bars are 50 µm.

Figure 2c illustrates the SEM micrograph of electrospun PCL membrane obtained from 20 wt. % of PCL dissolved in mixture of glacial acetic acid and distilled water. The beads defects were still formed in the PCL membrane. However, the appearances of fibers and beads were different from the 20 wt. % of PCL membrane obtained from single solvent system (glacial acetic acid), as illustrated in Figure 2a. The beads became in spherical shape and lots of thinner fibers were observed.

Influence of process parameters

The effect of varying the electrospinning process parameters on microstructure morphology of both PCL and gelatin fibrous membranes have been conducted.

The applied voltage and tip-collector distance were varied in electrospinning of PCL and gelatin membrane, respectively.

Figure 2d illustrates the SEM image of electrospun PCL membranes obtained at tip-collector distance, solution feed rate and applied of voltage of 10 cm, 0.30 ml/h and 12 kV, respectively. As compared to Figure 2a, no significant change was observed in morphology of fibrous membrane as the applied voltage is varied. Beads formation continues to exist in the PCL membrane.

Figure 3 illustrates the SEM images of electrospun gelatin membranes obtained at tip-collector distance of (a) 20 cm and (b) 30 cm. In contrast to morphology of PCL membranes, the gelatin fibrous membrane with defect free was collected at different electrospinning process parameters. Electrospun gelatin fibers with homogenous size were randomly distributed throughout the membrane.

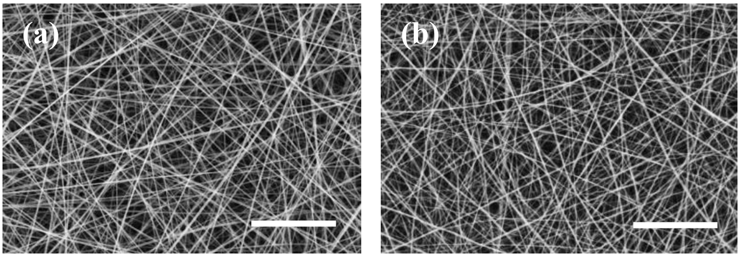

Figure 3: SEM images of electrospun gelatin membranes produced at tip-collector distance of (a) 20 cm and (b) 30 cm. The gelatin solution feed rate and applied of voltage for both membranes was kept constant at 0.30 ml/h and 9 kV, respectively. All scale bars are 10 µm.

Conclusion

This work demonstrates the electrospinning setup with its robust capability in producing electrospun fibrous membranes with different microstructure morphology. The PCL mats showed its morphology with non-homogenous size of electrospun fibers and lots of beads. Meanwhile, the gelatin membrane exhibited fibers with homogenous size. Results also revealed that the electrospinning parameters like solution and process parameters determined the microstructure morphology of electrospun fibrous membrane. Varying the PCL solution properties and process parameters had resulted in changes in the appearance of beads. The spindle-like beads was transformed into spherical shape at higher solution concentration and applied voltage. Meanwhile, in contrast to PCL fibrous membrane, the electrospun gelatin membrane demonstrates similar morphology at different electrospinning process parameters. The electrospun gelatin fibers size was also similar. Through this work, the fundamental understanding on how the electrospinning parameters affect the fibrous membrane morphology provides an insight for other researchers in producing membranes with desired microstructure morphology, as different types of microstructure morphology require more specific solution properties and process parameters.

Acknowledgment

The authors would like to express their greatest gratitude to Ministry of Science, Technology and Innovation Malaysia [03-01-13-SF0112-S026] and the Ministry of Education Malaysia [FRGS/1/2014/TK01/UTHM/02/2-1462] for funding the research work. This paper was partly sponsored by the Centre for Graduate Studies UTHM.

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