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Electrospinning of Polycaprolactone in Dichloromethane/ Dimethylformamide Solvent System

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Abstract. Electrospinning of polycaprolactone (PCL) in a mixed solvent of dichloromethane (DCM)/dimethylformamide (DMF) with 1:1 volumetic mixing ratio was studied. The effects of solution concentration (5-30 %w/v), applied voltage (10-25 kV), solution flow rate (0.1-2.0 mL/h) and collecting distance (10, 20 cm) on fiber formation and morphology were investigated. The size of PCL fibers obtained were in the range of 10s nm-2.6 μm with either bead on string or smooth fiber morphology. In this study, the solution concentration strongly affected fiber size exponentially. The fiber size also increased with an increase in solution flow rate. The applied voltage and the collecting distance have no or minimal effect on PCL fiber size.

Introduction

Electrospinning is an established method of producing ultrafine continuous nanofibers of polymers and inorganic oxide materials. This fabrication method has been applied in various fields of application; such as biomedical, pharmaceutical, engineering and military [1-4]. For biomedical applications, electrospinning of biodegradable and biocompatible polymers from both natural and synthetic polymers; for example, collagen, silk fibroin, gelatin, polyglycolic acid (PGA), polylactic acid (PLA) and polycaprolactone (PCL) have been widely investigated. PCL, in particular, is an attractive material for large scale biomedical applications due to its biocompatibility, ease of fabrication and relatively low cost. Several research groups have fabricated PCL electrospun fibers using different solvents; such as, acetone, chloroform, formic acid, acetic acid, dichloromethane (DCM) and mixed solvent systems [5-9]. Their results indicated that solvent systems are an important factor governing morphology and size range of the fibers. A mixed solvent system of DCM and DMF was one of the most favorable solvent system for preparation of PCL electrospun fiber [10-12]. However, there is still not enough information on PCL electospining in 1:1 mixture of the DCM/DMF system.

Our main goal for this work was to investigate the effects of polymer concentration, applied voltage and collecting distance on the fiber size and morphology of PCL electrospun fibers in a 1:1 DCM/DMF solvent system. This complimentary data fills the existing information gap and benefits those who want to produce PCL electrospun fiber with morphology and size range suiting their desired application.

Experiment

Materials. Polycaprolactone (PCL) with an average molecular weight of 80,000 g mol^{-1} was purchased from Sigma-Aldrich (St. Louis, MO, USA). DCM and DMF were obtained from Carlo Erba (UK).

The electrospinning process set up. Our electrospinning system consisted of a high voltage power supply (Ormond beach, model ES30P-5w) with its positive polarity high voltage line connected to a metal spinneret made from a blunt needle (internal diameter of 0.337 mm) and its counter electrode connected to a rotating fiber collecting device. PCL polymer solution flow rate was regulated with a syringe pump (New Era Pump Systems, model NE-300).

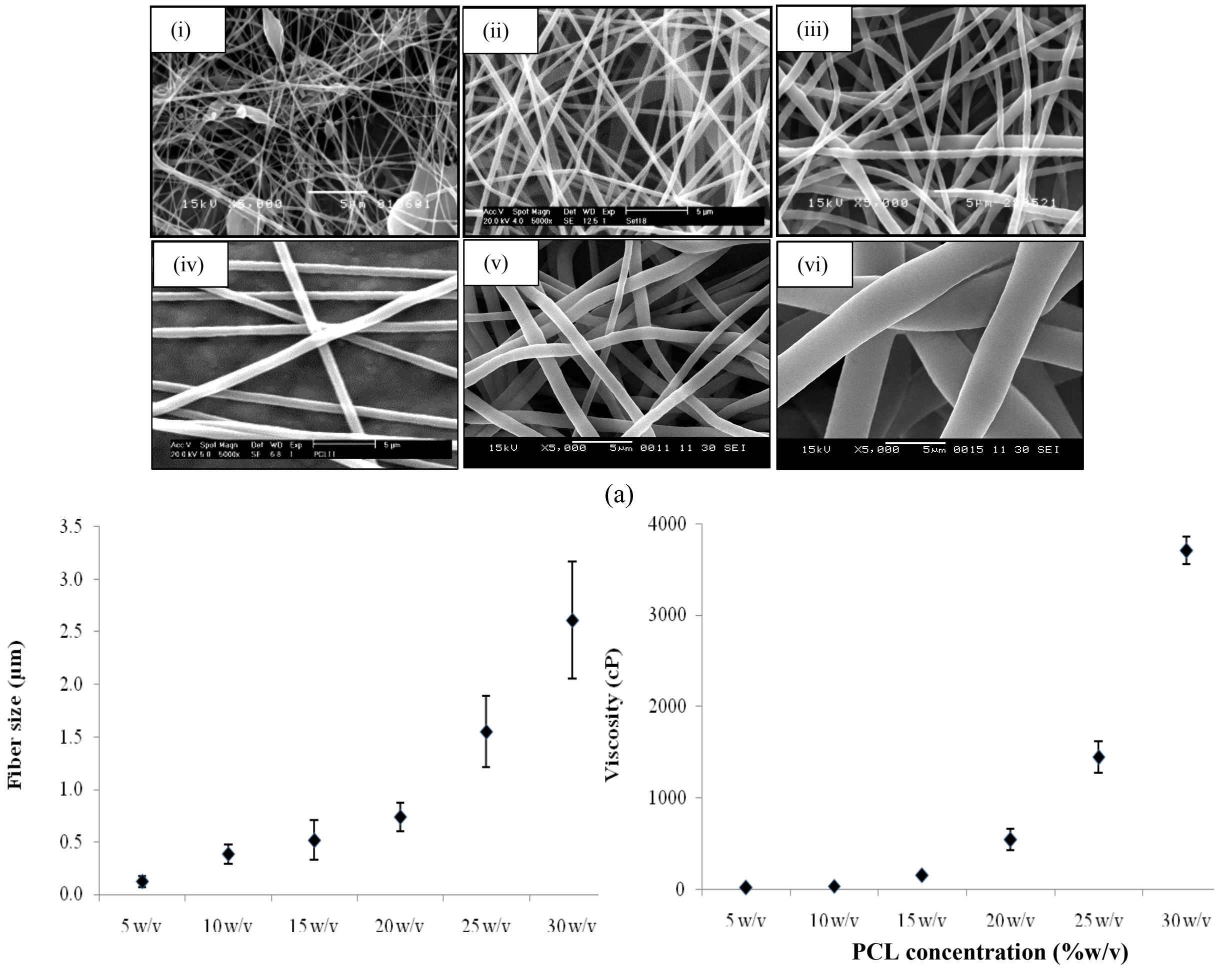
Preparation of PCL electrospun fiber. PCL solutions at different concentrations were prepared by dissolving an appropriate amount of PCL in a mixed solvent of DCM: DMF (1:1). The processing parameters were varied as follows to evaluate their effect on fiber formation and morphology: a polymer concentration (C) from 5 to 10, 15, 20, 25 and 30 %w/v, an applied voltage (V) from 10 to 15, 20 and 25 kV, a solution flow rate (F) from 0.1 to 0.5, 1.0 and 2.0 mL/h and a collecting distance between the syringe tip and ground collector (D) from 10 to 20 cm. The obtained fibers were kept in a desiccator for at least 24 h at room temperature to dissipate the remaining solvent prior to characterization.

PCL solution and fiber characterization. The viscosity and electrical conductivity of the PCL solution were measured using a Brookfield viscometer (Model DV-II+, USA) and a conductometer (Eutech Con510), respectively. The morphology of the spun fibers was assessed using a scanning electron microscope (SEM, Phillips series XL 20cp, USA). The fiber diameters were measured from at least fifty fiber segments using SEM micrographs using a Semafore 5.2.1.

Results and Discussions

Effects of solution concentration on fiber formation and morphology. PCL solutions with concentration of 5, 10, 15, 20, 25, and 30 %w/v were prepared and electrospun into fibers using applied voltage, solution flow rate and collecting distance of 15 kV, 0.5 mL/h, and 10 cm, respectively. The average size of fibers were found to be 0.12 ± 0.05, 0.38 ± 0.09, 0.51 ± 0.18, 0.74 ± 0.13, 1.54 ± 0.34 and 2.61 ± 0.55 μm, respectively. Fig. 1(a) and 1(b) show that the solution concentration strongly affects both fiber size and solution viscosity as both terms increased rapidly in an exponential fashion with an increase in solution concentration. Interestingly, relationships between fiber size and the concentration, as shown in Figure 1(b), and that of solution viscosity and the concentration, as shown in Figure 1(c), closely resembled one another. This similarity clearly elucidated the correlation between the fiber size and the solution viscosity.

This result was similar to many previous reports such as those from P. Gupta *et al.*, N. Bhardwaj *et al.*, and S. Sukigara *et al.* [13-15]. The SEM images also showed significant changes of fiber morphology when the concentration of the polymer solution was varied. At low concentration, (5 %w/v,) a number of beads with spindle like shape of various sizes appeared on the straight segment of the fibers. The smooth and uniform fibers were formed at the concentration of 10 to 30 %w/v. The bead formation at low concentration suggested that while the entanglement between PCL polymer chains, which related to a viscoelastic force presented in the PCL charged jet, was sufficient to prevent the jet from breaking up into droplets, it was not enough to restrain the occurrence of the capillary instability on the charged jet; this led to a bead formation on the fibers. On the other hand, at higher concentration, there was adequate molecular entanglement to suppress the instability from happening in a scale large enough to be detected, and thus a formation of bead free fibers.

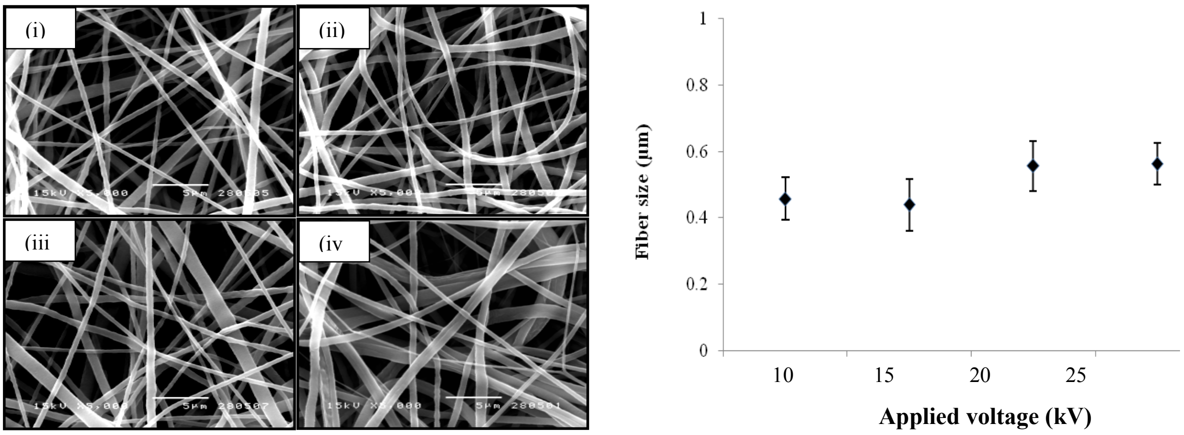


(a)

(b) (c)

Fig. 1 (a) SEM micrograph, (b) fiber diameter of PCL electrospun fiber and (c) viscosity of PCL solution obtained from different concentrations (i) 5, (ii) 10, (iii) 15, (iv) 20, (v) 25 and (vi) 30 %w/v. [V = 15 kV, D = 10 cm, and F = 0.5 mL/h]

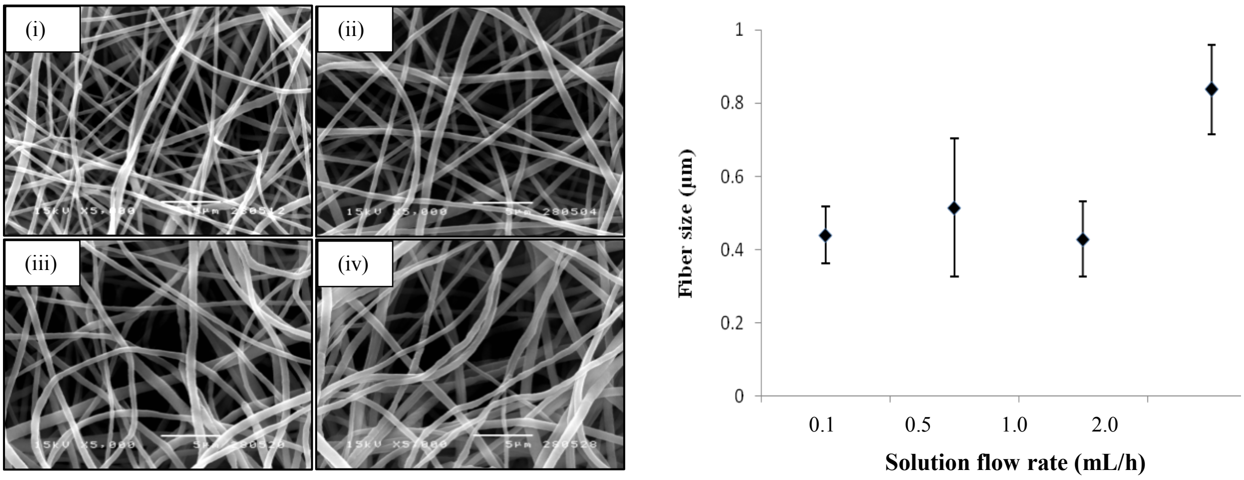
Effect of applied voltage on fiber formation and morphology. Fig. 2(a) and 2(b) shows the SEM micrograph and fiber diameter of PCL fibers, respectively as a function of applied voltage (ranging from 10, 15, 20 to 25 kV) using the polymer concentration of 15 %w/v with a collecting distance of 10 cm and 0.5 mL/h solution flow rate. The fiber diameters were found to be 0.45 ± 0.06, 0.44 ± 0.07, 0.55 ± 0.07 and 0.56 ± 0.06 µm, respectively. In general, the applied voltage affected the fiber formation process in two opposite ways at the same time. It increased the repulsive force between surface charges on the polymer charged jet, which led to fiber size reduction, and increased local mass flow of the charged jet at the spinneret, which led to an increase in fiber size. Within the scope of this study, however, the applied voltage appeared to have no or minimal effect on fiber size. This suggested that as the applied voltage increased, the influence from the repulsive force enhancement and the increase in local mass flow were in the same order. A slight increase in fiber size as the applied voltage rose might indicate that the latter factor had more influence than the former one.



(a) (b)

Fig. 2 (a) SEM micrograph and (b) fiber diameter of PCL electrospun fiber mats obtained from different applied voltage (i) 5, (ii) 10, (iii) 15 and (iv) 20 kV. [C= 15 %w/v, D = 10 cm. and F = 0.1 mL/h]

Effects of polymer flow rate on fiber formation and morphology. Fig. 3 showed SEM micrograph of PCL fibers electrospun from different flow rates at 0.1, 0.5, 1.0 and 2.0 mL/h from 15 %w/v solution concentration under 15 kV applied voltage and 10 cm collecting distance. The size of spun fibers were 0.44 ± 0.07, 0.51 ± 0.18, 0.43 ± 0.10 and 0.83 ± 0.12 μm, respectively. The results show that fiber size increased as the solution flow rate increased. Fibers appeared to be bead free with a smooth surface. However, at 2.0 mL/h flow rate, fibers started to have an uneven surface and minor non-uniformity in morphological appearance suggesting too high a flow rate to produce uniform PCL fibers.



(a) (b)

Fig. 3 (a) SEM micrograph and (b) fiber diameter of PCL electrospun fiber mats obtained from different flow rate (i) 0.1, (ii) 0.5, (iii) 1.0 and (iv) 2.0 mL/h. [C = 15 %w/v, V = 15 kV and D = 10 cm.]

Effects of collecting distance on fiber formation and morphology. The effect of collecting distance on the fiber size was tested by comparing the size of fibers electrospun from 15 %w/v PCL solution under a constant of flow rate of 0.1 mL/h, applied voltage 15 kV under concentration 15 %w/v with 10 and 20 cm collecting distance (Fig. 4). We found that the collecting distance had no effect on fiber size as the size of the fibers obtained from 10 and 20 cm collecting distance were 0.57 ± 0.22 μm and 0.58 ± 0.18 μm, respectively.

In general, an increase in fiber collecting distance had two effects on the process. Firstly, it reduced electric field strength which in turn reduced the amount of surface charge induction, which lowered repulsive force and hence a formation of a bigger fibers. Conversely, it would also provide more time and space for the charged injected segment to elongate more, given there was still enough repulsive force on the fiber for the elongation process to continue, which would reduce fiber size. Since the fiber size remained the same for both collecting distance and the fibers showed no interfiber fusion. This indicated that the fibers were fully solidified prior to collection on the device. This finding suggests that solvent evaporation was completed quickly, long before the fibers reached the collector. Therefore, no additional elongation occurred when the collecting distance increased, even if the charged jet still had sufficient surface charges and ample space to do so.

Conclusions

PCL fibers with diameters ranging from 10s nm to 2.6 μm, with bead on string and smooth fiber morphology were successfully prepared via electrospinning using a mixed solvent system of DCM/DMF (1:1). The solution concentration strongly affected fiber size exponentially. The fiber size also increased with an increase in solution flow rate. In contrast, the applied voltage and the collecting distance appeared to have no or minimal effect on PCL fiber size.

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