

TUNING SURFACE ROUGHNESS OF ELECTROSPUN POLY CAPROLACTONE FIBRES BY SINGLE SOLVENT ELECTROSPINNING SYSTEM

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Secondary surface texture or surface roughness is having a powerful impact on morphological variety and magnifies the application areas of electrospun fibres. This paper for the first time assesses the formation of varying degrees of surface pores on electrospun poly caprolactone (PCL) fibres by using a single solvent system. PCL solutions were prepared by dissolving PCL granules in dichloromethane (DCM) at the concentration of 5, 10, 15 and 20% (w/v), before being subjected to the electrospinning process at lower kV values of 5, 10 and 15, respectively. The morphology of electrospun fibres was characterised by field emission scanning electron microscope (FESEM). The resultant PCL fibres showed a highly porous surface was formed at lower PCL concentration. The surface roughness of PCL fibres was increased gradually with the increment of PCL concentration. The formation of porous surface was mainly due to the fast phase separation process while pore size and pore size distribution was found to depend on the blend composition.

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1. Introduction

Electrospinning is an electrohydrodynamic technique that uses electrostatic forces to induce fluid ejection and intense stretching of polymer jets into fibrous form. The electrospinning process presently produces fibres within diameter range of few nanometers to several micrometers [1]. Various morphologies of electrospun fibres including bead-on-string fibres [2], porous fibres [3], grooved fibres [4], multichannel fibres [5], ribbon fibres [6], hollow fibres [7] and core-sheath fibres [8] are able to be formed through electrospinning. Electrospun nanofibres have shown remarkable properties such as high specific surface area, flexibility, variety of morphology and architecture, superior directional strength, excellent pore interconnectivity, and ease of functionalization and is currently attractive for diverse applications especially in filtration [9], scaffolds [10] and biosensors [11]. Studies have demonstrated that by regulating the secondary morphologies (e.g., porous surfaces, grooved surfaces, rough surfaces, and interior porosity) of electrospun fibres, their properties could be greatly enhanced, due to the increase in their specific surface areas through the introduction of intra fibre pores [12].

At present, various complex techniques are required for the distinctive fabrication of surface texture electrospun PCL fibres. These methods include the subsequent removal of secondary polymers, the use of additives and others post electrospinning treatment [13-15]. The highlight of this study is to demonstrate the fabrication of electrospun PCL fibres in different surface roughness and interior porosity using single solvent of dichloromethane (DCM), a geminal organic compound with the chemical formula CH_2Cl_2 , colourless, highly volatile fluid with moderate sweet smell via electrospinning. This study provides the simplest technique for the preparation of porosity formation on the surface of PCL fibres through electrospinning, neither involving any special collection method nor post-spinning treatment.

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2. Experimental

2.1. Electrospinning process

Poly (ϵ -caprolactone) (PCL) granules with the molecular weight average 80,000 g/mol (Mw) were dissolved in dichloromethane (DCM), anhydrous, \geq 99.8% solution and stirred 24 hours at room temperature. The concentration of PCL was varied at 5, 10, 15 and 20wt%, respectively. The prepared PCL solution was then loaded into a plastic syringe equipped with a 0.4-mm internal diameter of blunt needle, with a needle-collector distance of 10 cm, attached to a high voltage power supply and the ground connected collector. A high voltage value of 5-15 kV was applied to an end needle to create voltage differences between the needle and a ground collector. A syringe pump was used to deliver the polymer solution from a syringe to the needle at a fixed rate of 0.5 ml/hr. All the electrospinning processes have been performed using a custom-built electrospinning reactor in a dedicated cabin, outfitted with a control operating panel, to protect the user from a number of risks.

2.2. Fibre characterization

The surface morphology of electrospun PCL fibres was characterized using FESEM (Carl Zeiss, Supra 40vp). Electrospun fibres specimens were gold coated using a sputter coater (Sputter Coater 108; Cressington Scientific Instruments) prior to FESEM analysis. For fibre diameter measurement, 50 measurements from FESEM micrographs were taken randomly and measured using an image analysis software (Image J, National Institutes of Health, USA). A rotating viscometer (PCE_RVI 3 PCE Instruments) was used to measure the solution viscosity of each polymer concentration. All the solution viscosity tests were conducted at room temperature and performed in five repeats for each PCL solution.

3. Results

3.1. FESEM of electrospun PCL fibres

Fig. 1 shows FESEM micrographs of electrospun PCL fibres from 5 to 15wt% polymer concentration. The fibre morphology of 5wt% PCL concentration was depicted in a long, continuous and interconnected fibrous structure, with bead-on-string and porosity formation. The mean fibre diameter of 5wt% PCL concentration was measured to be 450 ± 147 nm, with the porosity diameter of approximately 190 ± 32 nm (Fig.1 (A-C)). Lower PCL concentration resulted in low internal resistance of a fluid to flow. Therefore, the applied voltage started to induce the formation of secondary jets, which caused the variation of fibre diameter between deposited fibres. However, the mean fibre diameter of electrospun PCL fibres increased gradually to $2260 \text{ nm} \pm 124$ nm when the PCL concentration was increased to 10wt% (Fig.1 (D-F)). The FESEM micrographs signify the presence of larger pore formation with the increase of polymer concentration. The measured pore diameter was measured to be 250 ± 55 nm. As the PCL concentration was increased to 15wt%, the fibres morphology obviously appeared in a groovy surface, with less porosity. The mean fibre diameter significantly increased to $4675 \text{ nm} \pm 135$ nm and the pore diameter was measured to be 80 ± 16 nm as depicted in Fig.1 (G-I). In contrast, it is found that the prepared 20wt% of PCL concentration was unable to draw fibres due to the high viscosity of fluid, which caused the clogging effect during the spinning process. The FESEM results indicate that the polymer concentration had significant influence on both of the fibre morphology and fibre diameter. A similar finding has been reported [16] which suggests that the increment of polymer concentration enlarged the fibre's diameter due to the increase of viscosity and surface tension of the spinning solution.

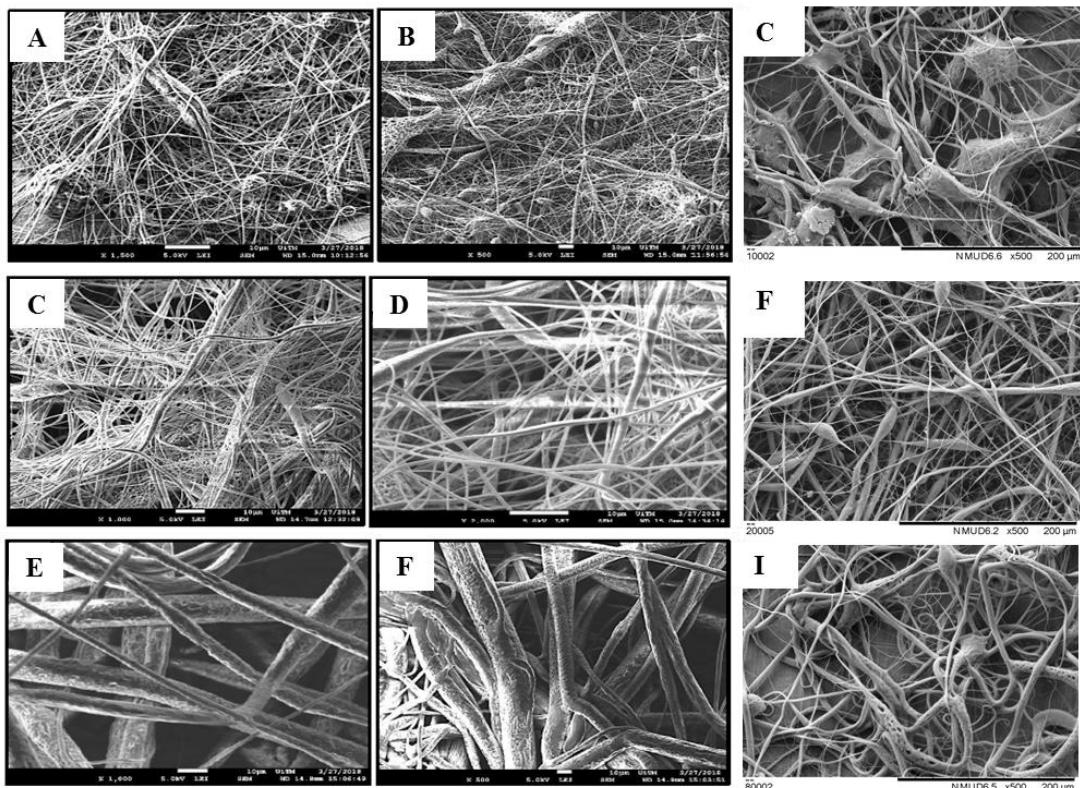


Fig. 1. FESEM micrograph of electrospun PCL fibres at the concentration of (A-C) 5wt%, (D-F) 10wt%, (G-I) 15wt%.

3.2. Effect of viscosity on fibre morphology

The effect of solution viscosity on the morphological structures of electrospun fibre was investigated by having different blend composition between PCL and DCM. Generally, the increase of PCL concentration results in an increase in viscosity (Fig.2). Representative micrographs of fibres spun at low, intermediate, and high viscosity in Fig 2 (B-D) reveal bead-on-string fibres formation at low viscosity (13.33 cPs), beaded free fibres formation at an intermediate viscosity (1004.51 cPs), and larger-diameter fibres formation at high viscosity (4511.72 cPs). The lower PCL concentration was found to have an insufficient viscosity to resist fibre deformation without defect at the applied electric field. One scenario of bead formation in electrospun fibres occurs due to the high surface tension of spinning fluid [17]. This is opposed by viscoelastic forces in the jet that resist changes to the fibre shape. Therefore, it was hypothesised that the low concentration studied here generated jets with insufficient viscoelastic forces to fully suppress droplet breakup due to the Rayleigh instability. Increasing both the polymer concentration and molecular weight results in greater polymer chain entanglements. This is necessary to maintain the continuity of the incoming jet during electrospinning. In contrast, the gradually increased viscosity of the higher concentration solutions created higher viscoelastic forces that resisted the axial stretching during whipping, resulting in larger fibre diameter. However, at 20wt% PCL concentration, the solution was unable to be spun as the solution tends to solidify quickly and gets hardened, causing needle blockage before initiation of jet. The viscosity of the 20wt% PCL solution has been drastically increased up to 20044.33 cPs.

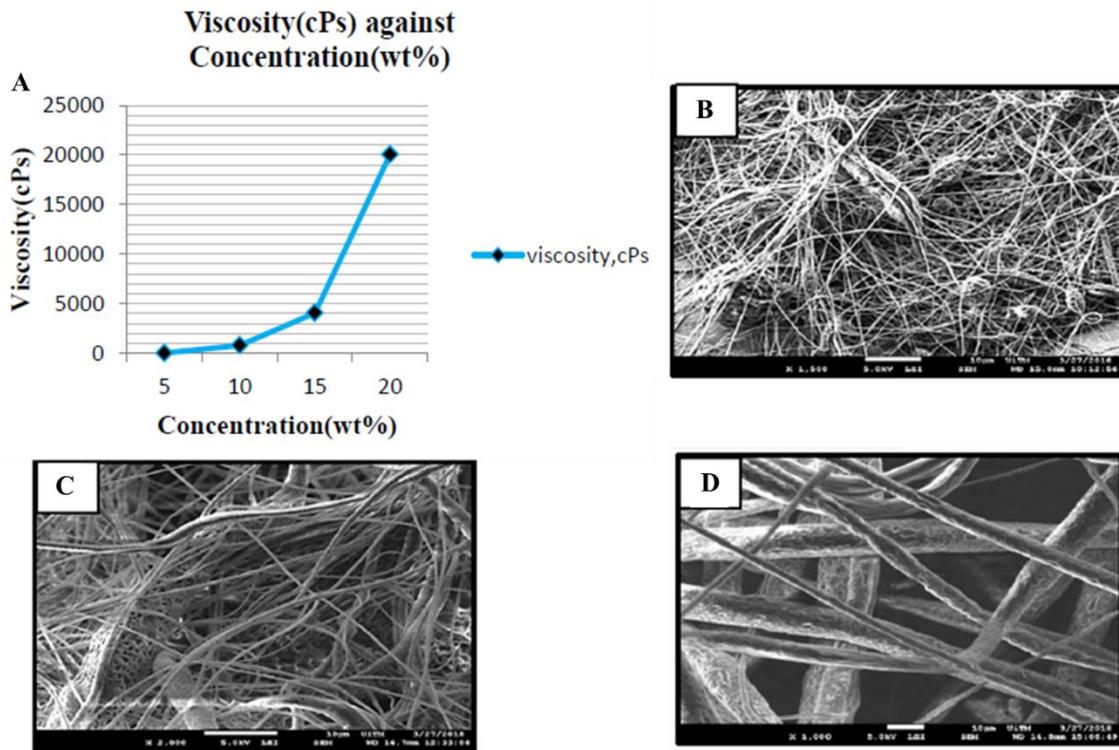


Fig. 2. (A) Solution viscosity of PCL in DCM as a function of concentration (B–D) FESEM micrographs of PCL fibres at varying PCL concentration of (B) 5wt%, (C) 10wt% and (D) 15wt%.

Fig.3 (a) depicts the graph of fibre diameter (nm) versus concentration (wt%) for the electrospun PCL fibres. Based on the experimental works, the optimal applied voltage was found to be at 15 kV, with the resultant fibre diameter size reduced. Fig.3 (b) depicts a graph of membrane deposition area (cm^2) versus applied voltage (kV) of electrospun PCL fibre. For the membrane deposition area, it was found that the resultant fibre deposition has varied depending on the voltage used. The largest and smallest deposition areas were found to be 244cm^2 and 10cm^2 , at 10wt% and 15wt% respectively.

4. Discussions

4.1. Relation polymer-solvents in electrospinning

Although all sets of fibres have porous structures, their porosity and surface morphologies are varied, as the morphology of PCL fibres is mainly governed by the relation between polymer-solvent blends. Solvent induced phase separation is another solvent-based technique which is applicable to evaluate the mechanism of porosity formation. This study found that the phase separation technique was affected by the difference in the PCL concentration, where a small change of in the polymer-solvent region may lead to significant morphology alteration of the resultant fibre. This finding indicates that the solvent-rich region at low PCL concentration undergoes both polymerization and solvent-induced phase separation during fluid solidification. Polymerization induced phase separation occurs within a homogenous polymer solution in reactive solvent mixture during electrospinning. Whereas, the increase of the spinning fluid viscosity increased the polymer-rich region in the blend composition [15]. Thus, the high viscous solution hindered the process of solvent evaporation, creating a groovy fibre surface. Fig. 4 illustrates the likely formation mechanism for porosity on the surface of ejected fibres during electrospinning process.

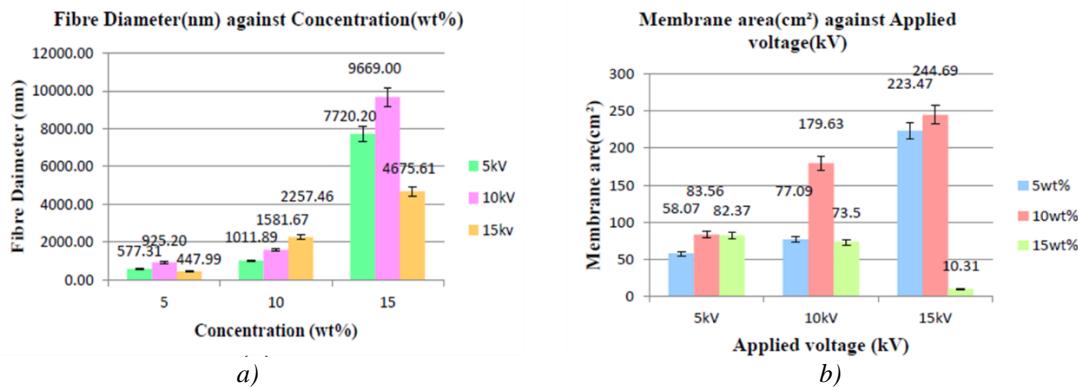


Fig. 3. (a) Graph of fibre diameter (nm) versus concentration (wt%) of electrospun PCL fibre (b) Graph of membrane area (cm²) versus applied voltage (kV) of electrospun PCL fibre.

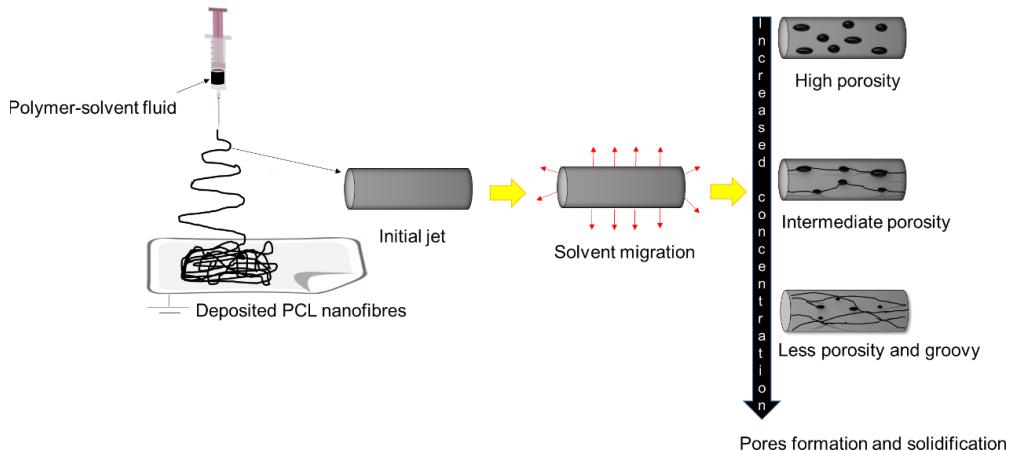


Fig. 4. Illustration of porosity formation in electrospinning.

5. Conclusions

A simple technique that can generate surfaces with desired roughness onto electrospun PCL fibres has been highlighted in this work. The results demonstrate that the usage of different PCL concentration has contributed to the fast phase separation process between solvents-polymer regions while pore size distribution was found to depend on the viscosity of the blend composition of spinning solutions.

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