

Manufacturing and morphology of poly(ϵ -caprolactone) based microfibre webs for biomedical applications through airbrush technique

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The objective of this study is to fabricate poly(ϵ -caprolactone) (PCL)-based micro/nano fibrous structures by using different types of solvents and nozzle sizes and to investigate the morphology of fabricated airbrushed structures for future biomedical applications. It is observed from the morphology and diameter of micro/nanofibres structures based on nozzle size, concentration of PCL and solvents, that these airbrushed biocompatible and biodegradable webs offer a potential in the medical field requiring direct, rapid and conformable applications.

Keywords: Airbrush technique, Biodegradable fibre, Microfibre, Nanofibre, Poly(ϵ -caprolactone)

1 Introduction

Micro/nano fibrous structures possess unique properties such as increased surface area to volume ratio making them a good candidate for application in diverse areas, including medical, environmental, agricultural and energy sciences¹. Their applications in biomedical area such as tissue engineering, wound dressing and drug delivery have been growing for last several years². Electrospinning technique, a widely studied and cost effective, can produce long, continuous micro/nanofibres from a variety of materials such as polymers, polymer alloys, polymer composites, metals and ceramics¹ with diameters usually in the range from 40 nm to 2 μ m^{3,4}. A few other techniques to fabricate micro/nanofibres are melt spinning⁵, melt blowing⁶, spun bonding^{7,8}, self-assembly^{9,10}, nanolithography¹¹, polymerization¹², drawing^{13,14}, template synthesis¹⁵, phase separation¹⁶ and electrospinning¹⁷. Among the other nanofibres manufacturing techniques, although electrospinning is the only technique having industrialization potential, the low efficiency in fibre production *is still* the main *limitation* for scaling to commercial production¹⁸. Furthermore, airbrushing also known as solution blow spinning or solution spraying¹⁹ is used to obtain polymer-based micro/nano fibres in which compressed gas is used to blow polymer solutions to fabricate fibres onto a wide range of targets of the same size range as produced by

electrospinning²⁰. The airbrushing technique was first patented as the blowspinning device in 1936 just two years later than first patent of electrospinning¹⁷. In this technique, no high-voltage equipment is required. The fabrication can be performed using a larger array of polymer solutions at the high injection rates and low cost^{20,22}. In addition, more aligned loosely packed bundles of nanofibres with a high porosity, and lower modulus can be produced²⁰, which can expand their usage areas and commercialization potentials^{22,23}. Recently, many researchers are attracted with the performances of the micro/nano webs fabricated using this technique and their applications. A number of research papers are published in the literature using airbrushing technique based on different polymers, microtextured surfaces and applications^{20,24,25}. For example, to support osteogenic differentiation of primary human bone marrow, stromal cells were fabricated, and it was shown that airbrushed nanofibre scaffolds can support stem cell differentiation²⁰. Also, degradation and biocompatibility of direct nanofibre deposition using airbrush technique onto different targets and living organism for surgical hemostatic, a surgical sealant, or for tissue reconstruction were discussed by authors²⁴. However, a very limited work is done in this field.

In this study micro-/nanofibre structures have been fabricated using an airbrush technique to study the effect of different types of solvents, nozzle diameters, and polymer on the morphology of the fabricated structures via scanning electron microscopy (SEM). To the best of our knowledge, the effect of different solvents and

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nozzle size on airbrushed PCL Poly(ϵ -caprolactone) to study possible future usages of airbrush technique has not been reported so far.

2 Material and Methodology

2.1 Materials and Solvents

Belonging to the aliphatic polyester family, PCL is a biocompatible and biodegradable polymer²⁶. Its semi-crystalline structure and a glass transition temperature (T_g) (-60°C) characterise its limited solubility in many solvents, which are able to dissolve other amorphous polyester structures. It includes long biodegradation time, which makes it a good candidate for medical applications such as drug delivery systems²⁷. Also, being extensive in vitro and in vivo biocompatibility, a number of medical devices are composed of PCL and efficacy studies have been performed^{22-24,27-29}. It has potential for tissue engineering of bones, cartilage and scaffolds. However, limited work has been reported in the fabrication and characterization of PCL airbrushed structure for biomedical applications. In our study, with above background, PCL is selected for the fabrication of airbrushed fibrous structure.

PCL being in harmony with water is semi crystallized polymer. Crystallization tends to decrease with the increase in molecular weight. Because of its good solubility in organic solvents, low melting point ($59-64^\circ\text{C}$) and good capability of mixing, it is a substance which can be used in the field of biomedical with great potentiality³⁰. PCL (Sigma Aldrich) with a molecular weight of 80 000 g/mol was dissolved in organic solvents, including chloroform (≥ 99), chloroform/methanol

(85:15) mixture, acetone (≥ 99.5) and acetic acid (≥ 99.7)/water (80%+20%) mixture to prepare solutions of 2 and 4 wt. % of PCL. Mixtures with chloroform were subsequently stirred vigorously for 3h at room temperature. Other solvents were stirred for 24 h at 40°C .

2.2 Fabrication of PCL Airbrushed Structure

A commercially available airbrush connected to an air compressor (pressure=50 psi) with the nozzle diameters of 0.35 mm and 0.5 mm was used to fabricate nanofibres mats on aluminum foil. Polymer solutions at different concentrations and solvents were sprayed through the nozzles having two different diameters onto the substrate, which was positioned 25 cm distance away from the nozzle. The airbrush was held fixed during the spraying processes. Five milliliters solution was deposited onto the substrate to fabricate nanofibres.

2.3 Characterization

Surface studies of micro and nano fibrous structures were performed using scanning electron microscope (SEM, Zeiss Evo MA10) after samples were dried at room temperature. A thin layer of gold was sputter coated onto micro/nanofibre structures and then the detailed images were taken to investigate the micro/nano fibrous structure via SEM. Diameters of fibres were also determined from SEM images.

3 Results and Discussion

3.1 Solvent Chloroform based PCL Micro/Nanofibres Structures

The SEM images of PCL micro/nanofibre structures using on chloroform, a more convent solvent for PCL due to higher surface tension, are shown in Fig. 1.

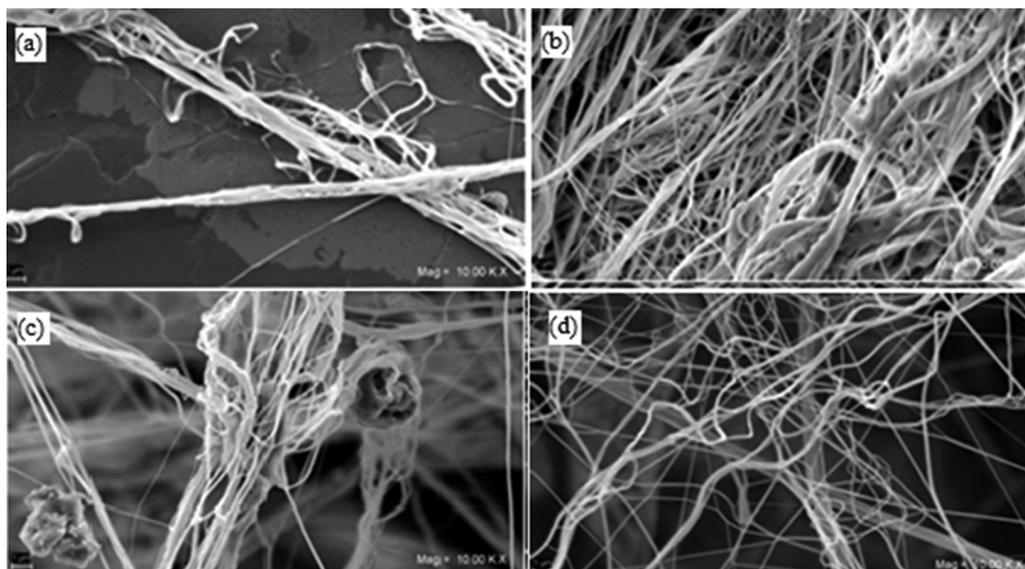


Fig. 1—SEM images of PCL nanofibres produced with chloroform ($\times 10.00\text{ K}$) [Nozzle diameter-concentration: (a) 0.35 mm-2%, (b) 0.35 mm -4%, (c) 0.50 mm -2% and (d) 0.50 mm -4%]

A very thin nanofibres (~100 nm) were uniformly produced in the study. This uniformity is more when structures are fabricated with higher (4%) polymer concentrations as compared to that with lower (2%) polymer concentration. The diameters of fibres are found almost proportional to the diameter of the nozzle used in their fabrication. Furthermore, bead formation is observed more in the fibres produced with lower polymer concentrations (2%) using 0.50 mm diameter nozzle. In addition to that, lumps of solution and cellular structures are formed in the fibre mat with 2% polymer concentration and 0.50 mm diameter nozzle. On the other hand, structures with more uniform and lower rate of lumps are fabricated in the case of higher polymer concentrations (4%). Also, masses of fibres have been

seen in some parts along with the formation of microsphere-shaped beads as well, which is more in fabrication with 0.50 mm diameter nozzle compared to 0.35 mm diameter nozzle. Moreover, uniform porosity is found due to lower boiling point of solvent. The measured diameter of fibres from SEM images is given in Fig. 2. Diameters are changing between nanometer to micrometers as shown in Fig. 2. Nanofibres are formed consisting of a bundle rather than individually.

3.2 Solvent Chloroform-Methanol based PCL Micro/Nanofibre Structures

In micro/nanofibre structures produced from PCL with chloroform-methanol mixture beads, cellular, net formation and irregular thickness distribution are observed in SEM images (Fig. 3).

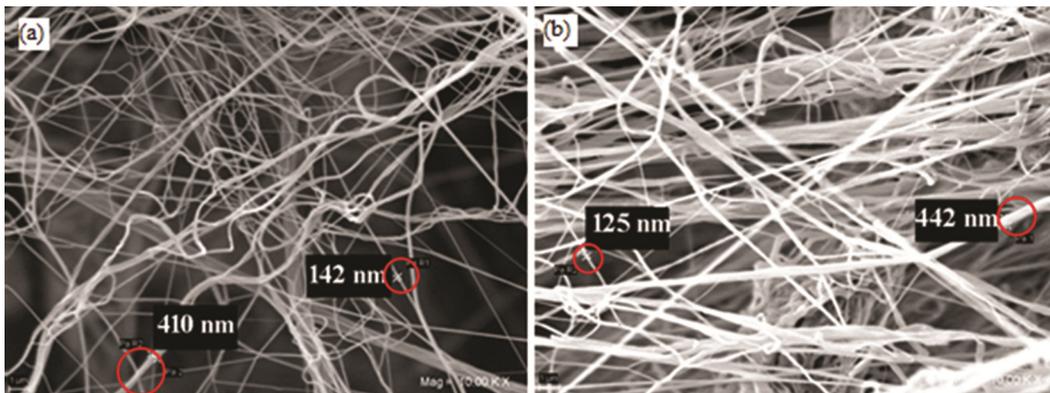


Fig. 2—SEM images of diameter measurements of PCL nanofibres with chloroform (a), and chloroform + methanol (b) ($\times 10.00$ K) [Nozzle diameter-concentration: 0.50 mm -4%]

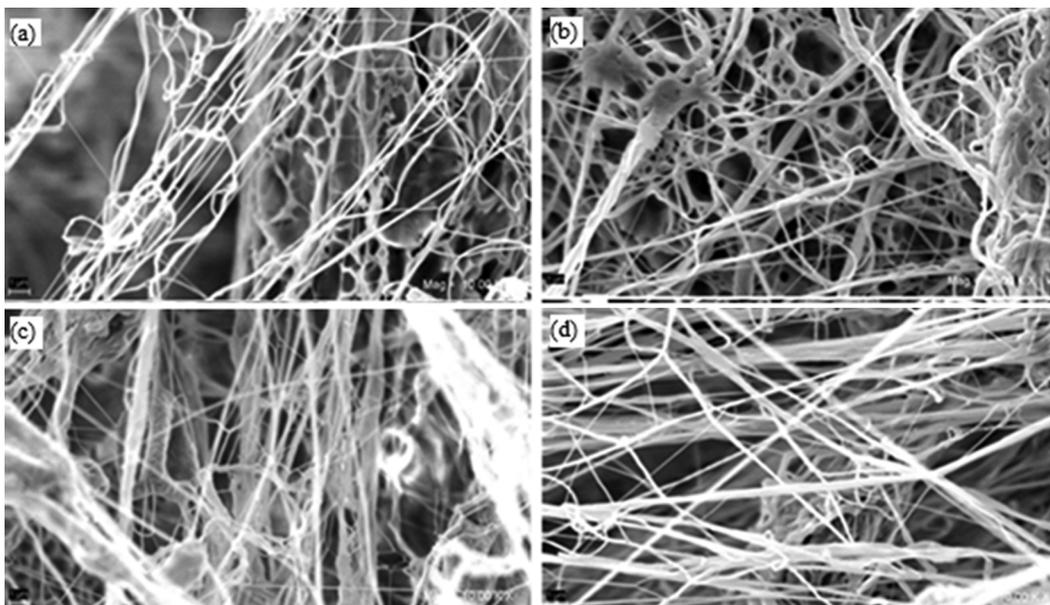


Fig. 3—SEM images of PCL micro/nanofibres produced with chloroform + methanol ($\times 10.00$ K) [Nozzle diameter-concentration: (a) 0.35 mm-2%, (b) 0.35 mm-4%, (c) 0.50 mm-2%, and (d) 0.50 mm-4%]

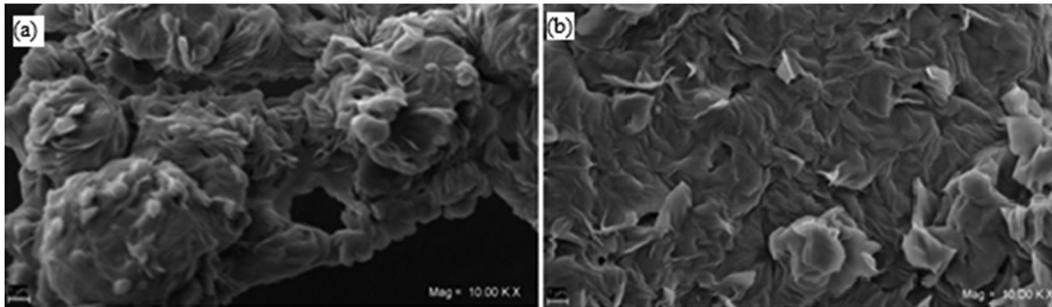


Fig. 4—SEM images of PCL structures produced with acetic acid ($\times 10.00$ K) [Nozzle diameter-concentration:(a) 0.35 mm -4%, and (b) 0.50 mm -4%]

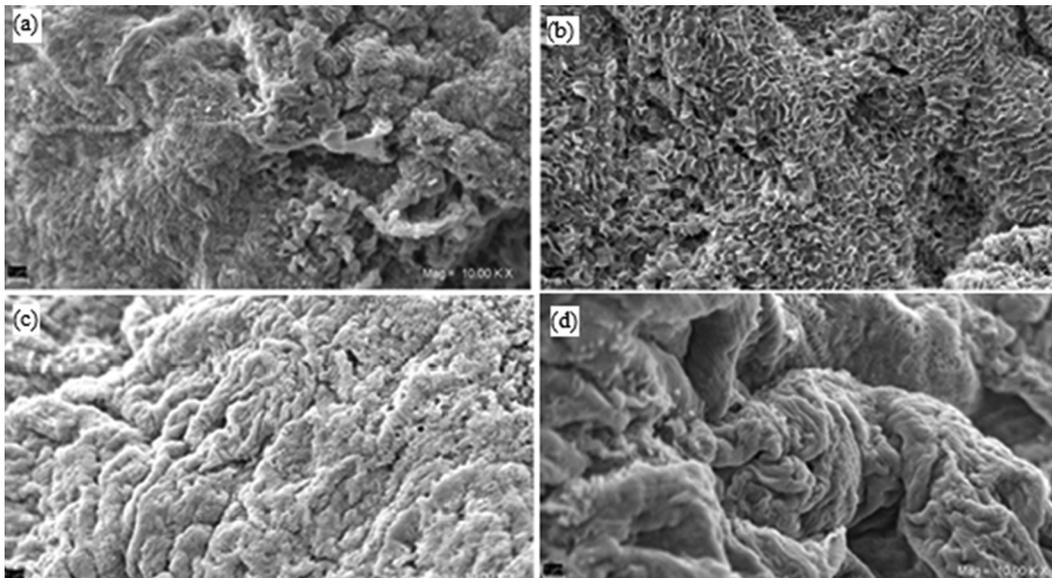


Fig. 5— SEM pictures of PCL structures produced with acetone ($\times 10.00$ K) [Nozzle diameter- concentration: (a)0.35 mm-2%, (b) 0.35 mm -4%, (c) 0.50 mm -2% and (d) 0.50 mm -4%]

The cellular structures are observed densely in case of small size (0.35mm) nozzle. Formations of microsphere-shaped beads and adhesiveness of polymer solution are found higher in this case. The most successful results for fibres are obtained when higher polymer concentration (4% PCL) is used, but nozzle blockage occurs very frequently. The measured diameter of fibres from SEM images is given in Fig. 2. Diameters are changing between nanometer and micrometers.

3.3 Solvent Acetic Acid-Water based PCL Micro/Nanofibre Structures

Micro or nanofibre formation is not obtained for acetic acid-water mixture solvent (Fig. 4). Acetic acid, miscible with water, behaves as a surfactant in the mixture and decreases the surface tension. Acetic acid is adsorbed onto the interface and changes the hydrogen bond structure of water³⁰. It is observed that PCL is completely dissolved in the solvent mixture.

However, when it is airbrushed, due to the high boiling point of this solvent (water at 100° C and acetic acid at 18.10 C), fibre formation is not obtained. Leaf-like structures and water drop-like structures occur with higher and lower PCL concentrations respectively. Besides, unfavorable working conditions due to bad smell and acidic vapor along with the stoppages due to nozzle blockages are noticed especially with smaller nozzle.

3.4 Solvent Acetone based PCL Micro/Nanofibre Structures

Acetone, a sustainable and non-toxic solvent, is used for electrospinning with biocompatible polymers especially PCL. PCL is completely soluble in acetone. However, micro or nanofibre formation is not obtained via air-brushing since adhesiveness of the polymer solution is high and stoppages happen due to nozzle blockages (Fig. 5). However, interesting textured surface on the airbrushed structures is obtained when a bigger nozzle is used (Fig.5).

Overall it is found that PCL webs produced by using 4% chloroform solution, and 0.35 mm nozzle diameter gives more homogenous and thinner fibres. These airbrushed biocompatible and biodegradable micro- and nanofibre webs could have a potential in the medical field requiring direct, rapid and conformable applications.

4 Conclusion

PCL-based micro/nanofibre based structures are obtained with an airbrush technique using different solvents chloroform, chloroform/methanol, acetic acid and acetone with different nozzle sizes. While PCL is found well soluble in chloroform and methyl alcohol, solubility of PCL structure in acetone and acetic acid is found more difficult. Moreover, compared to chloroform-methanol solvent mixture, thinner nanofibres (~100 nm) are formed on using chloroform solvent. Furthermore, using mixture of PCL with acetic acid solvent, different micro-texture such as leaf-like and water drop-like structures are observed, whereas with acetone, tissue like crimped micro-textured structures are noticed. According to morphology and diameter of micro/nanofibres structures which depend on nozzle size, concentration of PCL and solvents could promote their candidature for a variety of applications in tissue engineering.

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