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Morphological characteristics of electrospun PCL meshes – the influence of solvent type and concentration

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Abstract

Fibrous scaffolds, with fiber dimensions on the nanometer scale, are ideal for tissue engineering applications as they can mimic the physical structure of natural extracellular matrix. This paper investigates the effect of the solvent type and the solvent concentration on the morphological and hydrophobic characteristics of Polycaprolactone (PCL) meshes. Acetone and acetic acid with triethylamine (TEA) were used as solvents with different concentrations of PCL. Results show that its use allows the formation of meshes with high surface roughness, less surface friction and less hydrophobicity.

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Keywords: Electrospinning; Nanofibers; Polycaprolacone; Tissue Engineering.

1. Introduction

Biodegradable constructs for medical applications can be used in the form of meshes, films or three-dimensional porous scaffolds. These structures can be produced in a wide range of synthetic and natural materials trough the use of a large number of techniques [1-3].

Electrospinning is one of the most important electro-chemical processes to produce micro to nanoscale fiber meshes for medical applications [1, 4-6]. The basic requirements of an electrospinning system comprise a capillary tube with a needle, a high power voltage supply, a collector and electrical wires connecting the power voltage supply with both the capillary tube and the collector (Fig. 1). Two strategies can be considered [1,4-6]: solution electrospinning and melt electrospinning. Melt electrospinning requires the polymeric melt to be cooled, while the solution electrospinning relies on the fast evaporation of the solvent to produce the meshes [1].

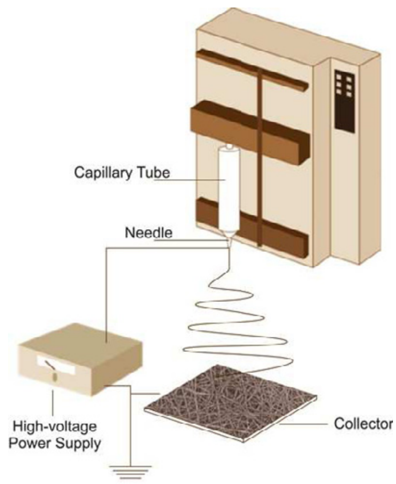

Fig. 1. Components of an electrospinning apparatus

The electrospinning process requires the control of a large number of parameters. Non-optimised processes produce non-homogeneous meshes with a significant number of material aggregates (beads) (Fig. 2) or

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spraying mechanisms without producing fibres (Fig. 3).

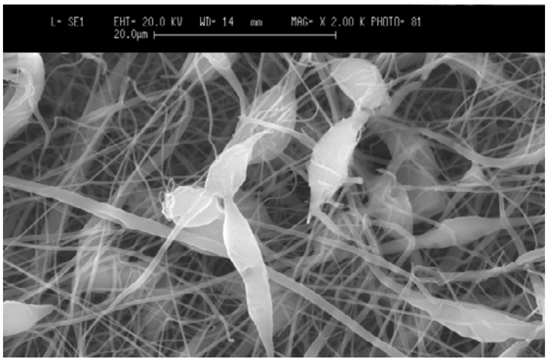

Fig 2. Non-homogeneous electrospun mesh.

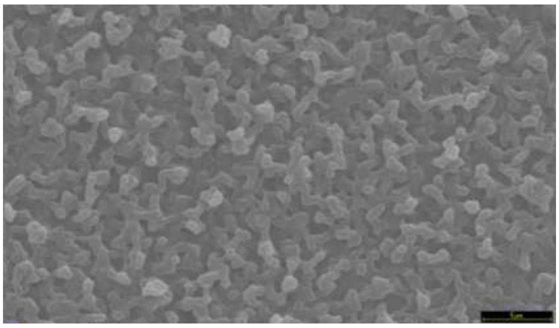

Fig 3. Electrosprayed surface.

Electrospun meshes close mimic the extracellular matrix of native tissues, providing a network structure with high surface area for cell attachment, proliferation and differentiation.

This paper focuses on the use of a solution electrospinning process to produce PCL meshes, investigating the effect of the solvent type and solvent content on the morphology and hydrophobicity characteristics of the produced meshes.

2. Materials and Methods

2.1. Materials

PCL (Mw 50000[g/mol]), from Perstorp (CAPA 6500), was dissolved in two different solvents:

i) acetone (Mw 58.08 [g/mol]), from Sigma-Aldrich
ii) acetic acid (Mw 60.05 [g/mol]), from Labsolve mixed with 2wt% of triethylamine (Mw 101.19 [g/mol]) supplied by Sigma-Aldrich.

Solutions with different concentrations (1.5wt%, 3wt%, 6wt%, 9wt%, 11wt % and 17wt% of PCL) were placed in a shaking incubator during 24 hours, and heated between 25ºC and 65ºC, with a heating rate of 5ºC/min.

2.2. Methods

2.2.1 Electrospinning apparatus

Electrospun meshes were produced using the homemade system shown in Fig. 4. The following processing conditions were considered: syringe volume - 2,5ml; needle diameter - 0, 6 mm; applied voltage - 10kV; distance between the needle and the collector - 10cm and flow rate - 0.72ml/h.

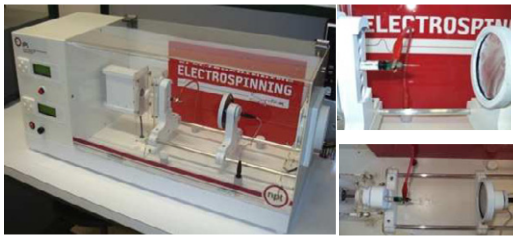

Fig 4. Electrospinning apparatus.

2.2.2 Characterisation techniques

Produced meshes were characterised using the following techniques:

- Scanning electron microscopy (SEM);
- Atomic force microscopy (AFM);
- Contact angle (CA).

SEM tests were performed to evaluate the mesh structure and the diameter of the fibres, using the FEI QUANTA 600F system (FEI Company, USA). Samples were coated with gold prior observation.

AFM uses a flexible cantilever as a type of spring, to measure the force between the tip and the sample, was used to determine surface roughness. All measurements were obtained using the NanoWizard system (maximum scan range: 100x100 µm; z-range: 15 µm; spring constant: 2N/m) with the TopViewOptics software (JPK instruments, Germany).

Water contact angle was used to measure the hydrophobicity of the produced meshes. A contact angle below 90º means a hydrophilic surface, while a contact angle above 90º corresponds to hydrophobic surfaces [7]. The contact angle was measured by delivering a droplet of water to the surface and determining its height and width (Fig. 5), according to the following equation [7]:

$$\tan\left(\frac{\theta s}{2}\right) = \frac{h}{(x)} \qquad (1)$$

where ϴs is the static contact angle, h is the water droplet height, and x corresponds to the half of the water droplet width.

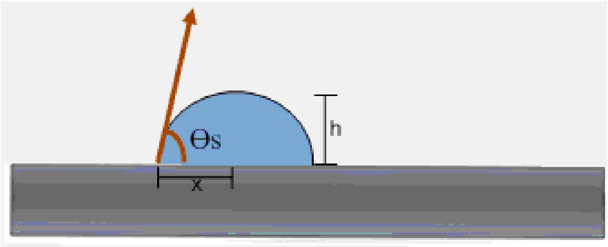

Fig 5. The water contact angle.

Contact angle measurements were performed using the Optic Tensiometer model Theta (Paralab, Portugal).

3. Results and Discussion

3.1. Scanning Electron Microcopy (SEM)

Figures 6 and 7 shows the obtained structures. Better electrospun meshes were produced with solutions containing 17wt% of PCL dissolved in acetone (Fig. 8) and 11wt% of PCL dissolved acetic acid with triethylamine (Fig. 9). In the first case, the average diameter of the fibers is 876 nm, while in the second case is 47 nm. Results show, that for low polymer concentrations no spinning is obtained.

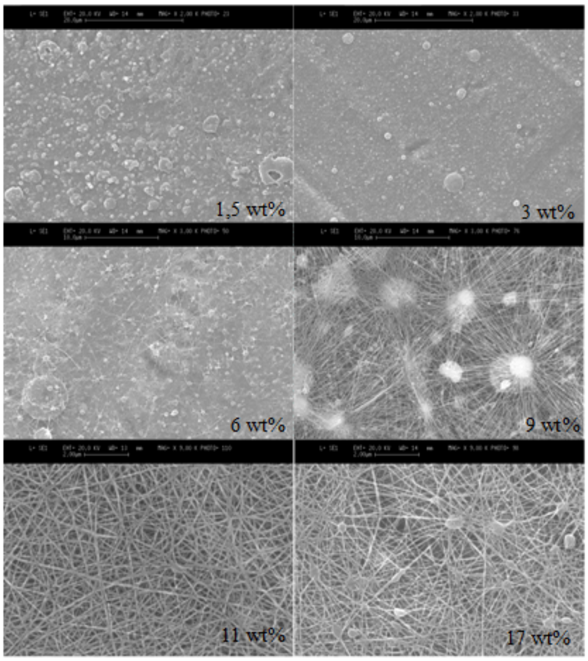

Fig 6. Morphology of the structures produced with solutions containing different concentrations of PCL dissolved in acetone.

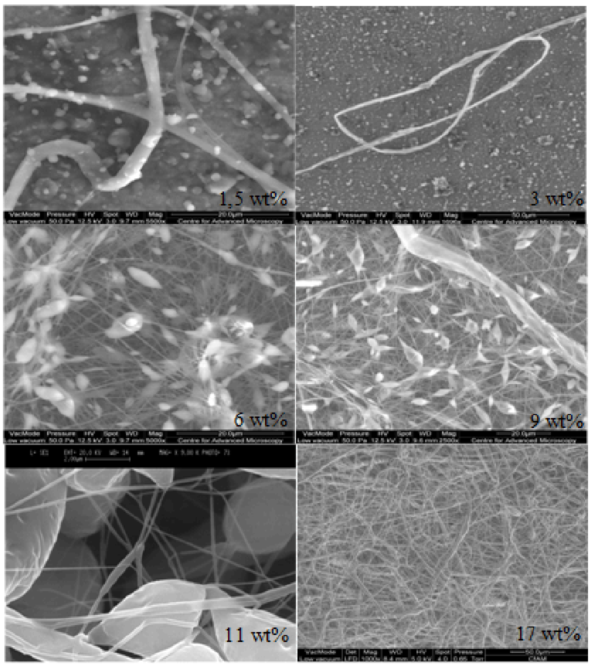

Fig 7. Morphology of the structures produced with solutions containing different concentrations of PCL dissolved in acetic acid with triethylamine.

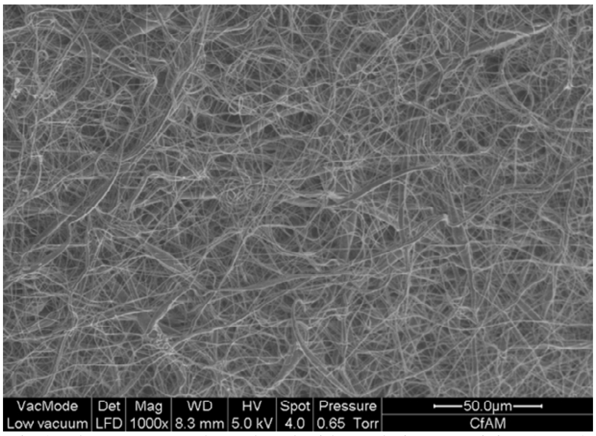

Fig 8. Electrospun mesh produced with a solution containing 17wt% of PCL dissolved in acetone.

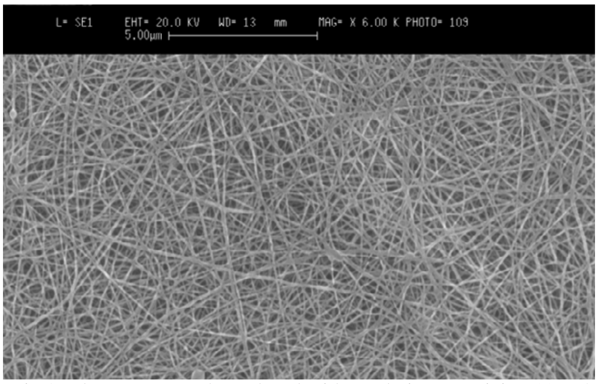

Fig 9. Electrospun mesh produced with a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine.

The addition of triethylamine to the acetic acid allows the formation of a salt that increases the dielectric constant and the volatility of the solvent, which facilitates the electrospinning process [8]. Results also show that for the PCL solution in acetic acid with triethylamine, there is a critical concentration value after which non-homogeneous meshes were produced.

3.2. Atomic Force Microscopy

AFM measurements enable to determine different mechanical and adhesive properties by determining three fundamental parameters (Fig. 10): height (represents the surface roughness), slope (represents the stiffness of the sample) and adhesion (represents surface friction).
Figures 11 and 12 show the topography of the meshes produced by solution containing 17wt% of PCL dissolved in acetone and a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine. Slope and adhesion values are indicated in Figures 13 and 14.

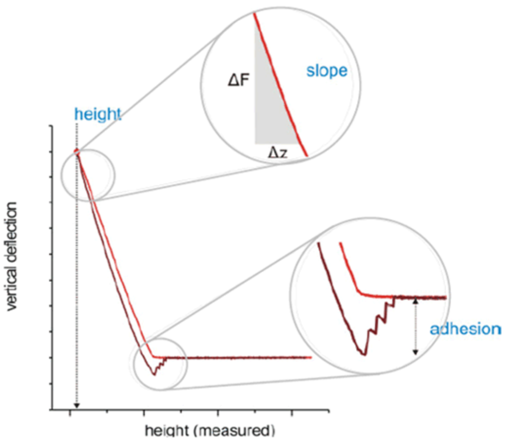

Fig 10. AFM measured parameters.

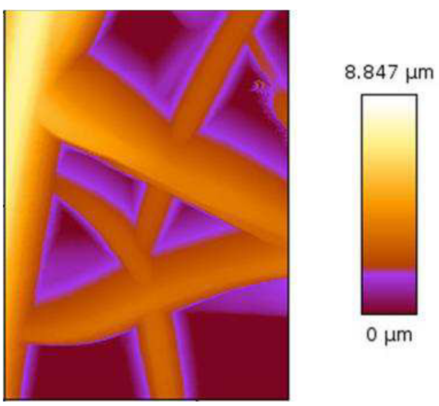

Fig. 11. Surface topography of a mesh produced using a solution containing 17wt% of PCL dissolved in acetone.

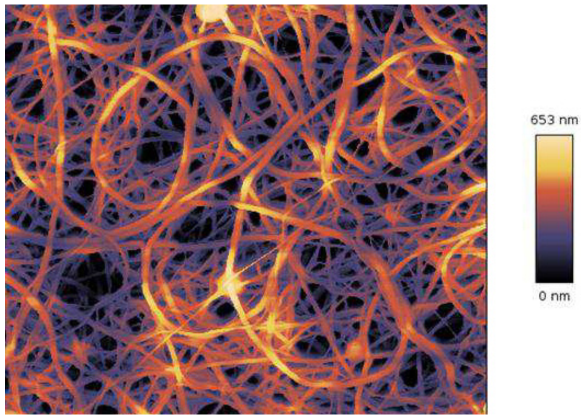

Fig. 12. Surface topography of a mesh produced using a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine.

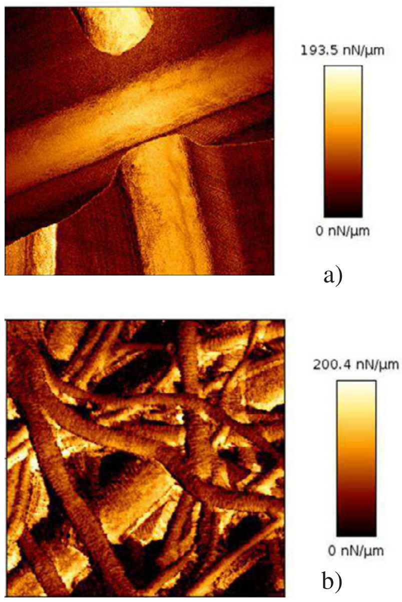

Fig. 13. Slope variation of a) mesh produced using a solution containing 17wt% of PCL dissolved in acetone; b) mesh produced using a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine.

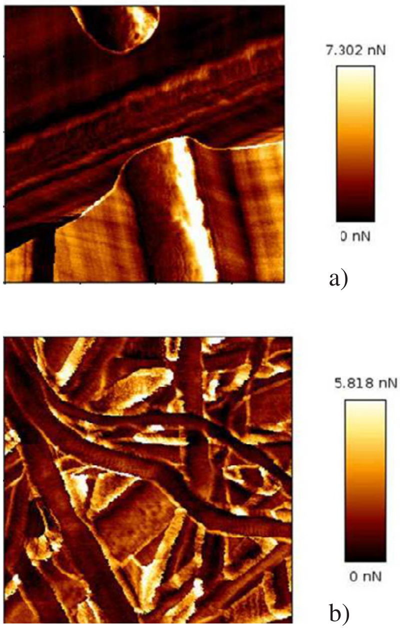

Fig. 14. Adhesion variation of a) mesh produced using a solution containing 17wt% of PCL dissolved in acetone; b) mesh produced using a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine.

Results show that the meshes produced, using a solution containing 17wt% of PCL dissolved in acetone, present a smooth structure. This mesh is also a stiffer and higher friction structure compared to the meshes produced using a solution containing 11wt% of PCL, dissolved in acetic acid with triethylamine.

3.3 Contact Angle

The contact angle photographs (Fig. 15 and Fig. 16) show that the produced meshes are hydrophobic, as expected. However, the use of acetic acid with triethylamine enables the fabrication of less hydrophobic meshes, as indicated in Table 1.

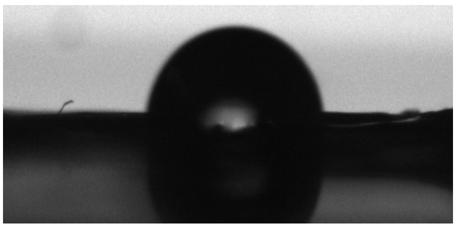

Fig. 15. Contact angle on the mesh produced with a solution containing 17wt% of PCL dissolved in acetone.

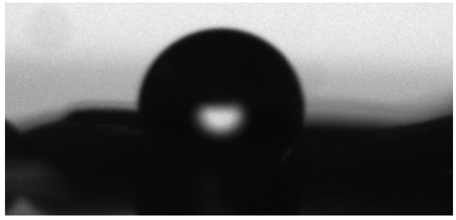

Fig. 16. Contact angle on the mesh produced with a solution containing 11wt% of PCL dissolved in acetic acid with triethylamine.

Table 1. Contact angle values.

Sample	Contact Angle (°)	95% Confidence interval mean
17wt% PCL dissolved in acetone	101,1 ±0,94	[83,35; 93,92]
11wt% PCL dissolved in acetic acid with triethylamine	83,64±2,72	[100,94; 101,18]

4. Conclusions

Results show that the type and concentration of the solvent strongly determine the characteristics of the produced meshes. The use of a solvent with high dielectric constant (acetic acid with triethylamine) allows the formation of electrospinning meshes with low PCL concentration. These meshes are also characterised by high surface roughness, less surface friction and less hydrophobicity.

Acknowledgments

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