Study the effect of flow rate on some physical properties of different polymeric solutions

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Abstract: In this study, three different polymers were used to produce electrospun scaffolds, polyvinyl alcohol (PVA) in a concentration of 8% w/v, nylon 6 in a concentration of 25% w/v, and poly (vinylpyrrolidone) (PVP) in a concentration of 4% w/v. These three polymer solutions were electrospun at different flow rates, to compare the effect of flow rate on the porosity, fiber diameter, and pore size of the scaffolds prepared from these polymer solutions. The flow rate range for PVA electrospinning started with (0.5, 1, 1.2, 1.5, and 2) ml/hr. While for nylon 6, the flow rate range started with (0.1, 0.5, 1, 1.5, and 2) ml/hr.; and for PVP, it started with (0.5, 0.7, 1, 1.2, and 1.5) ml/hr. It was observed that increasing the flow rate resulted in decreasing the porosity % and pore size due to increasing fiber diameter.

Keywords: Electrospinning, PVA, scaffold, flow rate, porosity, nanofiber, pore size.

1. Introduction
Porosity and pore size has been shown to be a key determinant of the success of tissue engineered scaffolds. A high degree of open porosity and an appropriate pore size are necessary for cell spreading and penetration inside the scaffold as well as to offer proper exchange of nutrients and waste between the scaffold and the surrounding tissues. Electrospinning technique offers an attractive method for mimicking the natural extracellular matrix (ECM) for tissue engineering applications. However, a major problem in electrospinning is the accumulation of fibers, resulting in poor porosity and small pore size. The porosity and pore sizes in the electrospun scaffolds are highly dependent on the fiber diameter which is mainly affected by the flow rate during electrospinning process [1]. The basic mechanism of electrospinning involves ejection of a solution containing a dissolved polymer in the proper solvent through a metallic nozzle by electrostatic attraction to generate ultrafine fibers, which are deposited onto a grounded metal collector. The resultant structure is a randomly oriented micro- or nanofiber network mesh with a highly open porous structure [2]. Figure 1 illustrates the basic schematic of electrospinning technique [3]. In order to get uniform nanofiber, many investigations on the effective parameters such as surface tension, viscosity, capillary-collector distance, flow rate, applied voltage, and solution temperature have been studied [3]. Flow rate is considered one of the process parameters affecting electrospinning technique. Increasing the flow rate tends to increase fiber diameter and bead diameter [4]. The high flow rate also results in residual solvent in the deposited fibers because it doesn’t take the necessary time to evaporate which may cause the fibers to fuse together [5].

Controlling the fiber diameter in electrospinning is possible by adjusting the electrospinning parameters like solution concentration, applied voltage, flow rate, capillary- collector distance and all the other solution and process parameters. Unlike fiber diameter, controlling the pore size and porosity% is more difficult and is
highly related with the fiber diameter [6]. Choosing the scaffold material is related to the application. PVA is one of the semi-crystalline hydrophilic polymers, dissolve in water and it’s the largest volume synthetic resin produced in the world. The excellent physical properties, chemical resistance, biocompatibility and biodegradability of PVA have led to the development of various commercial products based on this polymer. PVA is characterized by being a biodegradable polymer and the degradation products are water and carbon dioxide. Therefore, it is used in many biomedical and pharmaceutical applications, due to its characteristics such as: nontoxic, noncarcinogenic, and bioadhesive properties with the ease of processing [7].

Electrospun nanofibers from nylon 6 already found a number of applications. Nylon 6 has a superior fiber forming ability. It is a biodegradable and biocompatible synthetic polymer with good mechanical properties, which are further enhanced by hydrogen bonds. Unlike other polymers, such as polyethylene oxide and PVA, nylon 6 is resistant to both humidity and water [8]. Poly (vinyl pyrrolidone) (PVP) is known as an important amorphous polymer, with excellent biocompatibility, low chemical toxicity, high solubility in most organic solvents, good spinnability, and ability to interact with a wide range of hydrophilic materials [9]. The aim of this study is to compare the effect of increasing flow rate on some important physical properties of electrospun scaffold which are porosity %, pore size and fiber diameter; using three different polymers which are PVA, nylon 6, and PVP which are used widely in tissue engineering due to their biocompatibility and biodegradability.

2. Materials and Methods

2.1. Preparation of solutions
(PVA, molecular weight 124000) was purchased from (Gerhard Buchmann KG Tuttlingen / Germany). Distilled water was used as a solvent to prepare the solution with a concentration of 8% w/v. using magnetic stirrer at 70°C.
Nylon 6 was purchased from SIGMA-ALDRICH CHEMINE GmbH, USA; the molecular weight for the repeated unit is equal to 113.16 g/mol., the relative density for Nylon 6 at 25°C is equal to 1084 g/ml, and the melting point is equal to 220°C. Nylon 6 solution was prepared in a concentration of 25% w/v, with formic acid as a solvent by using magnetic stirrer at room temperature.
The used Poly (vinylpyrrolidone) (PVP), with molecular weight equal to 1,300,000 g/mol., was dissolved using ethanol in a concentration of 4% w/v with magnetic stirring at room temperature.
2.2. Fabrication of nanofiber scaffold

Electrospinning process is performed by (NaBondElectrospinning from NaBondTecchnologies Co.). The polymer solution has been kept in a plastic syringe with 10 ml capacity. A metal capillary needle with inside diameter equal to 0.6 mm has been attached to the plastic syringe; this metallic needle is connected to positive side of high voltage. The syringe is then fixed on a syringe pump obtained from (NaBond Technologies Co). An aluminum square plate (14.5*14.5 cm) has been used as a collector for nanofibers. The end of the capillary has been always positioned in such a way aligned with the center of the plate collector. The set-up is illustrated in Figure 2 and Table 1 shows the electrospinning conditions used in this research.

![Electrospinning apparatus](image)

**Figure 2.** Electrospinning apparatus, (a) Chamber of electrospinning; (b) plate collector; (c) metallic needle.

**Table 1.** Electrospinning parameters used in preparing scaffolds.

| Electrospinning parameters | PVA  | Nylon 6 | PVP  |
|----------------------------|------|---------|------|
| High voltage applied       | 20 KV| 20 KV   | 15 KV|
| Capillary- collector distance | 15 cm| 15 cm   | 10 cm|
| Concentration%             | 8%   | 25%     | 4%   |

2.3. Porosity% test

The porosity% of the prepared specimens was determined by using Archimedes principle. Ethanol was selected as the displacement liquid since it penetrates inside the specimen without swelling or shrinking the matrix [10]. The specimens were individually immersed in a cylinder containing a determined volume of ethanol (V1). Each sample was immersed for 5 min. with inducing pore filling by physically press air from the scaffold. The total volume of ethanol and ethanol filled scaffold became (V2). Finally, the scaffold filled with ethanol was removed from the cylinder, and the residual ethanol volume was recorded as (V3) [11]. The Porosity percentage of each scaffold was calculated by the equation (1) [11].

\[ P\% = \left( \frac{V1 - V3}{V2 - V3} \right) \times 100\% \] (1)
2.4. Statistical analysis
The statistical analysis for fiber diameter and pore size was accomplished using scanning electron microscope (SEM) images and AutoCAD 2010 software, as shown in Figure 3. The number of the selected data of fibers and pores in each image was 100. The average fiber diameter and average pore size with the standard deviation were calculated using Excel.

![SEM images](image)

Figure 3. SEM images in AutoCAD 2010 software for measuring the dimensions of 100 fibers and pores, (a) Fibers; (b) pores.

3. Results and Discussion
The average fiber diameter and average pore size for the prepared scaffolds were determined depending on one flow rate (0.5 ml/hr.), using the scanning electron microscope (SEM) images shown in Figure 4. The results showed that using the same flow rate for different prepared polymer solutions resulted in different average fiber diameter and pore size. The highest fiber diameter resulted in the scaffold prepared from 8% w/v PVA, while the smallest average fiber diameter resulted in the scaffold prepared from 25% w/v nylon6. Although increasing the polymer concentration resulted in increasing fiber diameter [12], but with different polymers and different molecular weight this may not become true, because decreasing the molecular weight resulted in decreasing the fiber diameter. The largest average pore size resulted in 4% PVP scaffold, while the smallest average pore size resulted in the scaffold prepared from 25% w/v nylon6. The small fiber diameter resulted also in small pore size and this may be attributed to the high entanglement between the fibers which reduced the pore size or may be resulted from the beads formation. The beads formation was obvious in the scaffold prepared from 25% w/v nylon6 as shown in Fig. 4b. For scaffold application the high pore size is necessary for cell penetration and spread inside the scaffold to mimic the scaffold structure and form a three dimensional tissue after scaffold degradation [13]. Table 2 shows the results of the average fiber diameter and average pore size for the prepared scaffolds with flow rate equal to 0.5 ml/hr. with the calculated standard deviation in fiber diameter and pore size.

![Table 2](table)

| Scaffold type          | Average fiber diameter (nm) | Standard Deviation ± nm in fiber diameter | Average pore size (nm) | Standard Deviation ± nm in pore size |
|------------------------|-----------------------------|------------------------------------------|------------------------|--------------------------------------|
| 8% PVA, flow rate 0.5  | 504.24                      | 133.38                                   | 2031.8                 | 755.61                               |
| 25% nylon6, flow rate 0.5 | 123.07                      | 30.214                                   | 1381.15                | 835.8                                |

Table 2. The results of the average fiber diameter and average pore size with the calculated standard deviation using Excel.
The porosity % test results based on Archimedes principle showed a decrease in the porosity % with increasing the flow rate as shown in Figure 5 (a,b and c). This may be attributed to the increase in the fiber diameter with increasing the flow rate due to the increase in the amount of the delivered polymer through the metallic needle [14, 15]. The increase in flow rate leads sometimes to beads formation especially when the polymer concentration or the molecular weight of the polymer were low leading to lower viscosity levels, high solvent to polymer ratio and beads formation [16,17]. This occurred in nylon6 scaffold as shown from the SEM image Figure 4.b, the lower molecular weight levels leads to beads formation and this in turn caused low average pore size and decreased porosity %. For the tissue engineering applications; where the porosity% and big pore size are important, the lower flow rate is predominant, because lower polymer amount will be delivered leading to lower fiber diameter and lower porosity%. From the three used polymers in this research both PVA and PVP started with approximately the same porosity %, and a decrease was noticed with increasing the flow rate. For nylon6 scaffold the porosity% at 0.1 ml/hr. was much lower than that for PVA and PVP scaffolds at 0.5 ml/hr. flow rate, and also decreased with increasing the flow rate. Therefore lower flow rate is required for nylon 6 to achieve good porosity levels for tissue engineering applications; or increasing the molecular weight of the used polymer in order to increase the viscosity and reduce the beads formation that decrease the porosity%.

| 4% PVP, flow rate 0.5 | 383.38 | 94.78 | 3900.75 | 1318.25 |

**Figure 4.** (a) SEM image and statistical analysis of 8% PVA with 0.5 ml/hr. flow rate, the magnification is equal to 9994 X; (b) SEM image and statistical analysis of 25% nylon 6 with 0.5 ml/hr. flow rate, the magnification is equal to 23648 X; (c) SEM image and statistical analysis of 4% PVP with 0.5 ml/hr. flow rate, the magnification is equal to 9323X.
Figure 5. The effect of increasing flow rate on the porosity %. (a) PVA scaffold, (b) Nylon6 scaffold, and (c) PVP scaffold.

4. Conclusion
Increasing the flow rate, the porosity% will be decreased due to increasing the fiber diameter. Besides, using polymers with lower molecular weight resulted in beads formation which may leads to decreasing the pore size and porosity%.

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