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# A Novel Study of Electrospun Nanofibers Morphology as a Function of Polymer Solution Properties

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Electrospinning is a process of production fibers with diameters ranging from the submicron down to the nanometer size by applying a high voltage to a polymer solution. The important parameters in the morphology of electrospun polymer fibers are polymer structure, polymer solution properties, processing conditions, and ambient parameters. In the present work electrospinning of polyacrylonitrile (PAN) has been attempted to generate uniform nanofibers without beads. Electrospinning was performed at various concentrations ranging from 4 to 18 *w/v*%. The effects of polymer solution properties on electrospinnability of the PAN/DMF solutions have investigated. Fiber morphology was observed under a scanning electron microscopy (SEM). For the polymer electrospun from low concentration (Be<2), polymer droplets have formed. For the polymer electrospun from semi-dilute solution concentration (2<*Be*<3.5), the formation of nanofiber with beads. Uniform fiber formation was observed at *Be*>4. The relationship between solution viscosity and its concentration is in the form: $\eta = 0.0205C^{4.16}$ and relation between the diameter of electrospun the PAN nanofiber and solution concentration is in the form: $d = 0.0326C^{3.45}$.

**Keywords:** Electrospinning, Polyacrylonitrile, Viscosity, Berry number, Morphology

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## 1. INTRODUCTION

The term *"nanofiber"* to form two words, the term *"nano"* is a prefix that came from the Greek language. The words *nanos* and *nanas* means *"little old man"* and *"uncle"*, respectively. In international unit, nano refers to $10^{-9}$m. The other part of the term is *"fiber"*, which has many different definitions according to usage [1]. However, fibers with diameters in the range of 1-100 *nm* are referred to as nanofibers in scientific literature related to fiber science [2].

When the diameters of polymeric fibers are shrunk from micrometers to submicrons there appear several amazing characteristics such as very large surface area to volume ratio, and superior flexibility, compared with any other known form of the material [2]. These outstanding properties make the polymer nanofibers to be optimal candidates for many important applications (i.e. filter media, tissue engineering, drug delivery, sensor, hydrogen storage, protective clothing and etc). Several methods have been developed to produce nanofibers, such as Drawing, Template Synthesis, Phase Separation, Self-Assembly, and electrospinning [3]. Electrostatic spinning or electrospinning is recognized as a simple and inexpensive process for making continuous sub-micron to nano-size fibers, when compared with other methods.

Currently, electrospinning is the most promising technique for making polymeric and ceramic nanofibers within a broad range of diameters, from submicron to nanometers according to the selection of the processing parameters. Electrospinning is a process to produce nonwoven fabrics of nanofibers from a polymer solution or a melt by applying a high voltage between a tip of the needle and a collector [3]. The parameters affecting electrospinning and the fibers may be broadly classified into polymer properties, polymer solution parameters, processing conditions, and ambient parameters [4]. These parameters listed in Table 1.

The properties of the polymer solution (i.e. concentration, viscosity) have the most significant influence in the electrospinning process and the resultant fiber morphology. Several experimental and theoretical analyses, were shown fiber diameter has a power relation with solution viscosity (eq. (1)) and polymer concentration (eq. (2)) [1]:

$$d \approx \eta^{\alpha} \quad (1)$$

$$d \approx C^{\beta} \quad (2)$$

Where $d$ is the diameter of the electrospun nanofiber, η is solution viscosity, C is solution concentration, and $\alpha$, $\beta$ the scaling exponent. Combining the scaling relationships (1) and (2) we obtain a new power law between the solution viscosity and the solution concentration (eq. (3)):

$$\eta \approx C^{\delta} \quad (3)$$

Where δ is the scaling exponent. Experimental evidence has shown that the diameter of the nanofiber produced by electrospinning is influenced not only by the concentration of the polymer and solution viscosity but also by its molecular conformation. A dimensionless parameter called the Berry number (*Be*) [14-17] was used by various groups of researchers as a processing index for controlling the diameter of electrospun fibers. *Be* number is defined as [4]:

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$$Be = [\eta].C \quad (4)$$

Where [η] is the intrinsic viscosity of the polymer. In addition, the intrinsic viscosity, can also be related to the viscosity average molecular weight ($M_v$) of a polymer by the Mark–Houwink–Sakurada equation [4].

$$[\eta] = k.\bar{M}_v^{a} \quad (5)$$

Where the constants $k$ and $a$ depend on the polymer, solvent and temperature.

**Table 1** – The effective parameters on electrospinning process

| Parameter | Description | Ref. |
|---|---|---|
| Polymer properties | Molecular weight | [5] |
| | Solubility | [6] |
| Polymer solution parameters | Concentration | [6] |
| | Viscosity | [6] |
| | Conductivity | [6] |
| | Surface tension | [6] |
| | Additive | [7] |
| | pH | [8] |
| Processing conditions | Distance | [9] |
| | Applied voltage | [9] |
| | Feed rate | [10] |
| | Polarity of the needle | [11] |
| | Needle diameter | [12] |
| Ambient parameters | Relative humidity | [13] |
| | Temperature | [10] |

In the present work, solutions of PAN in DMF were prepared in eight different concentrations (e.g. 4%, 6%, 8%, 10%, 12%, 14%, 16% and 18% ($w/v$)). These solutions were tested for some basic properties, such as solution viscosity, intrinsic viscosity, and Berry number. The effects of polymer concentration, viscosity, and Berry number on electrospinnability of the as-prepared PAN solutions and morphological appearance of the obtained PAN fibers were qualitatively observed by means of a scanning electron microscope (SEM).

## 2. EXPERIMENTAL

### 2.1 Materials

Polyacrylonitrile powder (PAN, $M_w = 10^5$ g/mol), consisting of 93.7 *wt%* acrylonitrile (AN) and 6.3 *wt%* methylacrylate (MA) was supplied with Polyacryl Co. (Isfahan, Iran) and N,N-dimethylformamide (DMF) were obtained from Merck, respectively, as polymer and solvent. The solubility parameters were 25.3 and 24.8 $(MPa)^{1/2}$ for PAN and DMF respectively, which suggested that DMF was a best solvent for PAN.

### 2.2 Preparation of PAN Nanofibers

The solutions of PAN were prepared by dissolving 4, 6, 8, 10, 12, 14, 16 and 18 $w/v$% ($g/dl$) of sample in DMF separately via magnetic stirrer (Corning Hot Plate Stirrer PC-351) at 40 °C for 24 hours. The prepared PAN solution was added to a glass syringe with a needle tip (22G, $L = 34$ mm, $D = 0.7$ mm). The feeding rate of the polymer solutions was 0.25 ml/h, electrospinning voltage (14 kV) was applied to the needle, the distance between the needle tip and collector was 15 cm and take-up speed 50 RPM was collected electrospun nanofiber. The electrospinning of PAN was performed at 22±2 ºC and constant relative humidity (40%).

### 2.3 Measurement and Characterization

The intrinsic viscosity of PAN solutions was measured for a series of concentrations made by successive dilutions by using an Ubbelohde viscometer at 22±0.1 ºC. Solution viscosities were determined by a Rheometer (DV-II+Programmable, Brookfield Co. USA) at 22±1 ºC. The morphology of the electrospun nanofibers was observed using scanning electron microscope (SEM, AIS-2100, Seron. Co., Korea) at an accelerating voltage of 25 kV and the average fiber diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 200 fibers/sample.

## 3. RESULTS AND DISCUSSION

### 3.1 PAN/DMF Solution Properties

The intrinsic viscosity of PAN in DMF at 22 ºC was determined by the extrapolation of specific viscosity ($\eta_{sp}$) to zero polymer concentration as 0.39 $dl/g$. The reasons for this non-linear relationship can be attributed to the power-low relationship between the polymer concentration and the solution viscosity. As illustrated in Fig. 1, when the polymer concentration is low, the solution viscosity increases slightly with the increase in the polymer concentration. As the polymer concentration increases, the viscosity increases gradually until the concentration reaches a specific value, after which the viscosity increases considerably. Moreover, the scaling law for the polymer concentration dependence of viscosity, was also altered from $\eta = 0.0205C^{4.16}$ (unit: $\eta$ in $cP$ and $C$ in $w/v$%) at 22 ºC.

The relationship between the solution viscosity and the polymer concentration is highly dependent on the nature of the polymer (i.e. structure, conformation, polydispersity, and molecular weight) and the intermolecular interactions within the polymer solution and temperature of solution. For example, it was calculated experimentally the dependence of the viscosity on solution concentration in a power law relationship for electrospun poly(methyl methacrylate) (PMMA) nanofibers: $\eta \sim C^4$ [15].

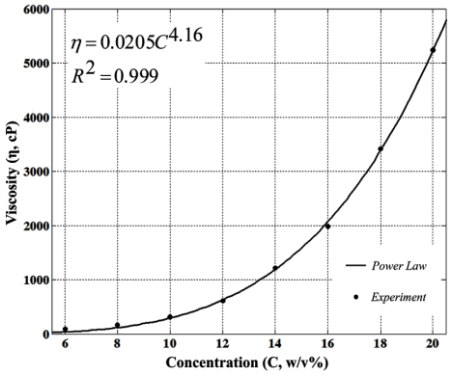


**Fig. 1** – Relationship between polymer concentration and solution viscosity

### 3.2 PAN Nanofibers Morphology Properties

The SEM photograph of electrospinning PAN from low concentration solution (4 *w/v%*, *Be*=1.56) is shown in Fig. 2. At low concentrations, 4 *w/v%*, the solutions were not spinnable due to low solution viscosity. For the polymer electrospun from low concentration (*Be*<2), polymer droplets have formed.

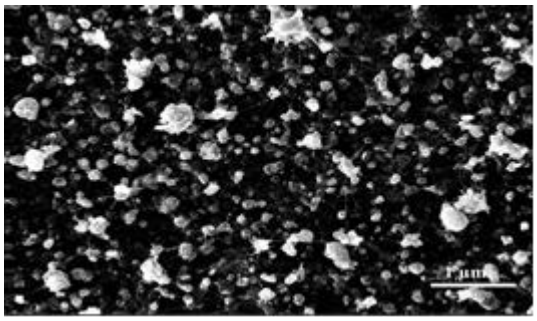

**Fig. 2** – SEM photograph of 4 *w/v%* PAN electrospun product.

As the solution concentration was increased 6 *w/v%*, in addition to polymer droplets, some limited fiber formation occurred in the form of thin fibers that were connected by polymer droplets was observed (Fig. 3(a)). With more increase in polymer concentration to 8 *w/v%*, the amount of beads decreased (Fig. 3(b)). For the polymer electrospun from semi-dilute solution concentration (2<*Be*<3.5), the formation of nanofiber with beads. Uniform PAN nanofibers (*d*<500nm) without beads were obtained from electrospinning of 10, 12, 14 and 16 *w/v%* PAN solutions in DMF was observed in Fig. 3(c), (d), (e), and (f), respectively. Ultrafine fiber formation (*d*>500nm) was obtained from electrospinning of 18 *w/v%* (*Be*=7.02) PAN solution in DMF was observed in Fig. 3(g).

Fig. 4 shows the relationship between the Berry number and the diameter of electrospun PAN nanofibers. In diluted solutions, when *Be*<2, the molecules of the polymer are sparsely distributed in the solution. A physical representation of the semi-dilute concentration (unentangled regime), where the concentration is large enough to have some chain overlap (2<*Be*<3.5) but it is not enough to cause any significant degree of entanglement. As the concentration is further increased (entangled regime, 3.5<*Be*<7.5), the topological constraints induced by the larger occupied fraction of the available hydrodynamic volume in the solution, introduce chain entanglements. Meanwhile, at the Be>7.5, fibers was not achieved due to higher viscosity.

Gupta et al. [14], electrospinning PMMA in DMF at 4<*Be*<10, obtained continuous fibers from samples of PMMA of different average molecular weights (range of $M_w$ = 12,470–365,700 g/mol).
Casper et al. [15] observed that *Be*>13 is required to form stabilized fibrous structures in electrospinning of polystyrene (PS) in tetrahydrofuran (THF).

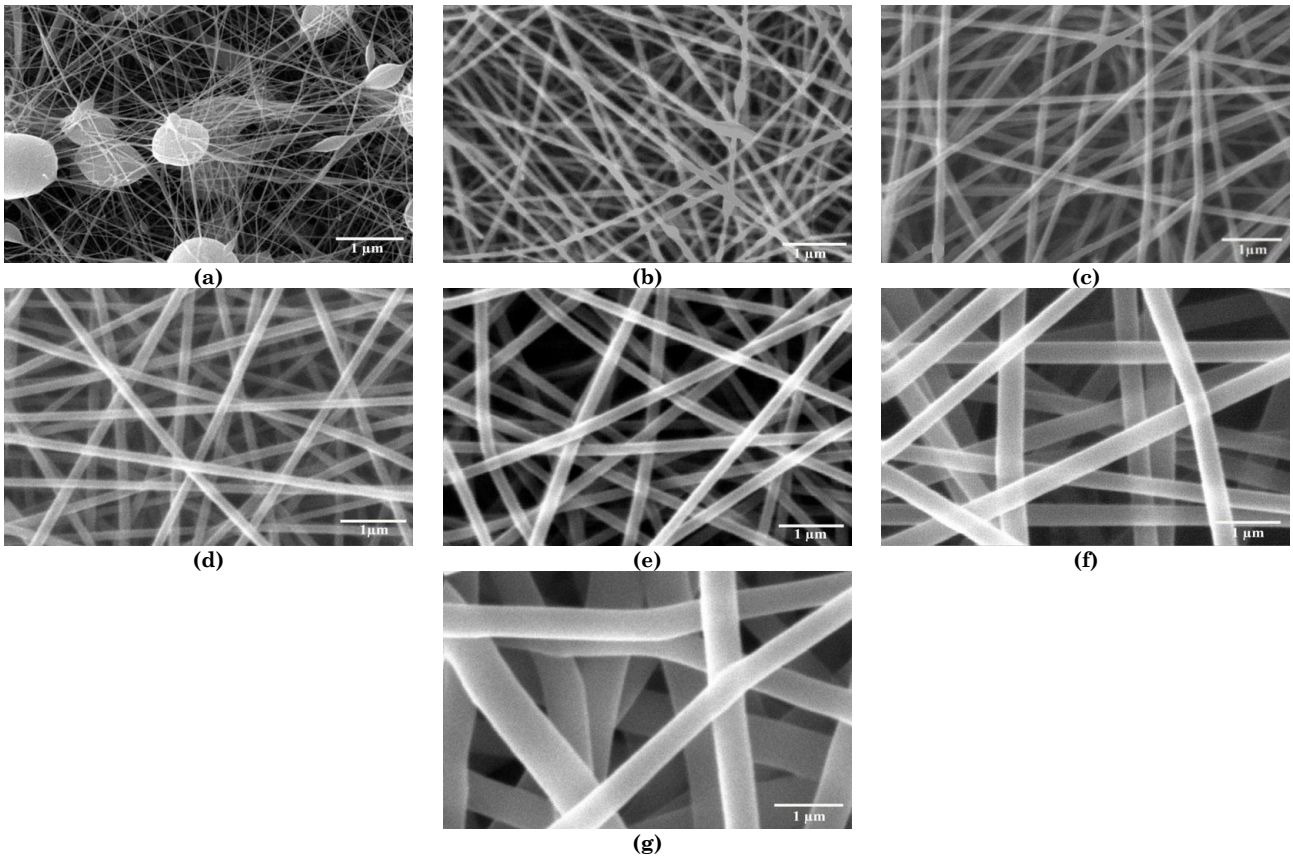


**Fig. 3** – SEM photograph (left) and fiber diameter distribution (right) of electrospun PAN fibers in DMF at various concentration: (a) 6 *w/v%* (*Be* = 2.34), (b) 8 *w/v%* (*Be* = 3.12), (c) 10 *w/v%* (*Be* = 3.90), (d) 12 *w/v%* (*Be* = 4.68), (e) 14 *w/v%* (*Be* = 5.46), (f) 16 *w/v%* (*Be* = 6.24), and (g) 18 *w/v%* (*Be* = 7.02)

Koski et al. [16], electrospinning poly(vinyl alcohol) (PVA) in aqueous solution at 5<*Be*<9, obtained continuous fibers from samples of PVA of different average molecular weights (range of $M_w$ = 9,000–186,000 g/mol). Hsu and Shivkumar. [17], observed that *Be* > 4.5 is required to form stabilized fibrous structures in electrospinning of poly(ε-caprolactone) (PCL) in chloroform ($CHCl_3$).

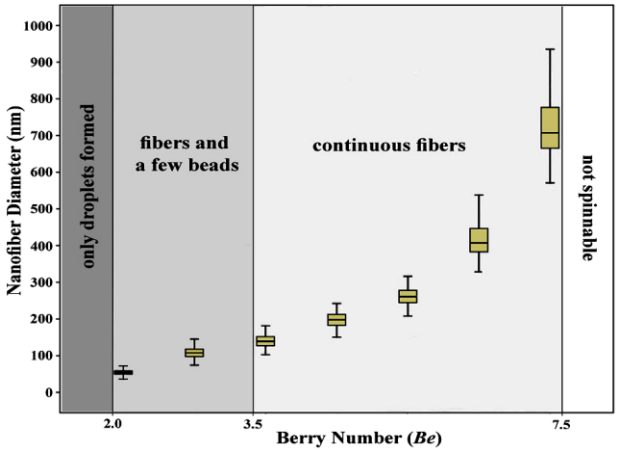


**Fig. 4** – Berry number-fiber diameter relationship.

### 3.3 Scaling of Nanofiber Diameter on Concentration

The dependence of the average electrospun fiber diameter on solution concentration is shown in Fig. 5, which leads to a power low relationship of, $d = 0.032C^{3.45}$ (unit: *d* in *nm* and *C* in *w/v%*), indicating that solution concentration plays a very important role in determining the nanofiber diameter.

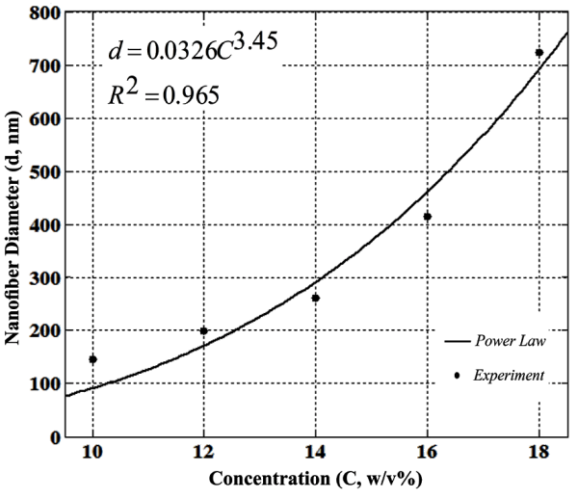


**Fig. 5** – Relationship between polymer concentration and average nanofiber diameter of electrospun PAN fibers.

## 4. CONCLUSION

In this paper, PAN in DMF is used to study the effect of polymer concentration and viscosity on electrospun nanofibers. Our analysis shows that the diameters of nanofibers are greatly affected by polymer concentration. Electrospinning of low concentration solutions (*Be* < 2) resulted in the formation of polymer droplets due to insufficient chain overlap between the chains. As the concentration was increased (2 < *Be* < 3.5), polymer beaded fibers were observed. Uniform and nanofiber formation was observed at 3.5 < *Be* < 7.5 (10 *w/v%* < *C* < 18 *w/v%*). The relationship between diameter of electrospun PAN nanofiber and solution concentration is in the form: $d = 0.0326C^{3.45}$ ($R^2 = 0.965$).

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