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ABSTRACT: Electrospinning is a simple method of producing nanofibers by introducing electric field into the polymer solutions. We report an experimental investigation on the influence of processing parameters and solution properties on the structural morphology and average fiber diameter of electrospun poly ethylene oxide (PEO) polymer solution. Experimental trials have been conducted to investigate the effect of solution parameters, such as concentration, molecular weight, addition of polyelectrolyte in PEO solution, solvent effect as well as governing parameter, such as applied voltage. The concentration of the aqueous PEO solution has shown noteworthy influence on the fiber diameter and structural morphology of electrospun nanofibers. At lower concentrations of PEO polymer solution, the fibers showed irregular morphology with large variations in fiber diameter, while at higher concentrations, the nanofibers with regular morphology and on average uniform fiber diameter were obtained. We find that the addition of polyelectrolytes, such as sodium salt of Poly acrylic acid (PAA) and Poly allylamine hydrochloride (PAH), increases the conductivity of PEO solutions and thereby decreases the bead formation in electrospun nanofibers. The increase in applied voltage has been found to affect the structural morphology of nanofiber while the addition of ethanol in PEO solution diminishes the bead defects.

Keywords: Polyelectrolyte; Solution Properties; Structure; Electrospinning; Nanofibers

INTRODUCTION

The history of electrospinning dates back to 1934 when Formhals disclosed an apparatus for producing cellulose acetate filaments utilizing electrostatic repulsions between surface charges.[1,2] Formhals' invention posed some technical difficulties which encouraged many researchers, including Formhals himself, to take initiatives in addressing those challenges facing electrospinning process. Indeed, subsequent years have seen an increase in publications on electrospinning that relates to various processing parameters, system parameters, characteristics and others.[3-5] Investigations of these parameters by many researchers led to improvements in structural morphologies of electrospun nanofibers, diameters that are controllable and consistent as well as fiber surfaces that are free of defects (e.g., beads).[6] Previous studies [7-25] indicate that the development of useful applications of the electrospun nanofibers requires a thorough understanding of the electrospinning parameters as the structural morphology and diameter of the electrospun nanofiber will have an influence on the final product.

To fully explore the potential of electrospinning, it is critical and essential to exercise control on the formation of electrospun nanofibers. In the current study, the effect of processing parameters and solution properties on the morphology and diameter of electrospun nanofibers using poly ethylene oxide (PEO) solution were investigated. The effect of bead formation as a result of concentration of polymer solution was determined. Also the effect of adding polyelectrolytes or ethanol in polymer solutions to improve the structural morphology and diameter of electrospun nanofibers was examined. The parameters studied include concentration, molecular weight and conductivity of the electrospun polymeric solutions, the effect of polyelectrolyte and the applied voltage.

EXPERIMENTAL

The solutions used in the electrospinning experiments were prepared using PEO (molecular weight $M_w = 3 \times 10^5$ g/mol, 9×10^5 g/mol); poly (acrylic acid, sodium salt), 35wt% solution in water, PAA, $M_w = 15 \times 10^3$ g/mol; poly (allylamine hydrochloride) PAH, $M_w = 15 \times 10^3$ g/mol. All laboratory grade chemicals and solvents were used without further purification, while all electrospinning experiments were carried out under ambient conditions. Unless otherwise stated from here onwards the expression of PEO concentration is in w/v, while PAH concentration and ethanol concentration are in wt % by weight of PEO.

Various concentrations of PEO solution in the range of 3–7 % were prepared in distilled water with and without adding polyelectrolyte, as well as the combination of distilled water and ethanol. The electrospinning setup utilized in this study consists of a Pasteur pipette with 1mm diameter, an electrically grounded, detachable, flat metal screen that is adjustable to a desired height and direction. A high voltage power supply was used to produce voltages ranging from 0 - 30kV and a distance of 10 to 20cm was maintained between the nozzle and the collector screen.

The fiber diameter and structural morphology of electrospun PEO fibers were determined using FEI Quanta 200 Scanning Electron Microscope (SEM). The surface morphology of the polymeric nanofibers was measured by using Atomic Force Microscopy (AFM) Veeco dimension V. The conductivity of the polymer solutions was attained by HACH Conductivity Meter.

RESULTS AND DISCUSSION

Effect of Concentration

When the concentrations of the PEO solution were varied, noteworthy changes were observed in the structural morphology and diameter of electrospun fibers. These changes were noted when the concentrations of the solutions were increased which led to an increase in fiber diameter. Various diameter values namely min, max, mean and % change in diameter with respect 3% PEO aqueous solution increases with the increase in concentration. Table I shows that, with the increase in concentration, the minimum fiber diameters of the as spun fibers ranges from 34.37nm at lower concentration (3% PEO aqueous solution) to 83.96nm at higher concentration (7% PEO aqueous solution) while the maximum fiber diameters ranging from 89.98nm at lower concentration (3% PEO aqueous solution) to 445.95nm at higher concentration (7% PEO aqueous solution). This was attributed to the higher viscosity of the solution as a consequence of increasing concentration that was stronger enough to discourage the bending instability of the jet to set in for a longer distance as it was emerging from the spinneret.

Also, the increase in % change in diameter with respect to the lower polymer concentration (3%) indicates that the fiber diameter is increasing as the concentration increases. When the concentration of the solution is increased, the viscosity increases, thus, resulting in higher entanglements of the polymer chain in the solution which yields fibers with larger diameters. This is possibly due to greater resistance of the polymer solution when being stretched by the electrical charges on the electrospinning jet.

The results above correspond with the distribution of the electrospun nanofibers (Figure 1) which indicates quite narrow but near normal distribution for

3% and 4% PEO solutions. With further increase in PEO concentrations to 5%, 6% and 7% PEO, the fiber diameter distributions exhibit gradually widening but right-skewed non-normal distribution with characteristics "tailing effect" as evident in Figure 1. . This is attributed to the electrospinning conditions set for the process, such as distance and applied voltage (kept constant) that are not strong enough to allow for stretching of the polymer solution at higher concentrations. In other words, the concentration of PEO aqueous solution has proven to be one of the most effective parameters to control the structural morphology of the electrospun nanofibers.

Effect of Molecular Weight

The length of the polymer chain is determined by the molecular weight of the polymer, which in turn have an effect on the concentration. However, one of the required conditions for electrospinning to take place in order to form fibers is that the solution must contain a polymer of adequate molecular weight and sufficient viscosity.[18]

Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than the same polymer of lower molecular weight. This, however, is due to greater entanglement of polymer chain within the solution which is essential to form continuous jet during electrospinning. These polymer chain entanglements determine the stability of the jet and prevent formation of droplets thereby controlling morphology of resultant nanofibers, i.e., formation of beads or smooth fibers.[18] Figure 2 illustrates how the structural morphology of electrospun nanofibers improves with an increase in molecular weight of the polymer.

The examination using SEM, revealed the two distinctive scenarios in the structural morphology of the nanofiber web as a function of molecular weight.

Fibers from 5% aqueous solution of PEO (M_w= 3 x 10^5 g/mol) indicates fibers with almost spherical beads (Fig 2a) while those fibers obtained from higher molecular weight PEO (M_w= 9 x 10^5 g/mol) but of the same concentration shows fibers with less beads but spindle-like beads (Fig. 2b) thus indicating stretching of polymer solution.

Also, more uniform fibers were obtained from 6% solution of higher molecular weight PEO (M_w= 9 x 10^5 g/mol) as shown in Fig, 2d, whereas still some fibers with beads were attained from 6% solution of lower molecular weight PEO (M_w= 3 x 10^5 g/mol) as shown in Fig 2c. The results indicate that low molecular weight solution tends to form beads rather than fibers and high molecular weight solution provides bead-less fibers with larger average diameters (Figure 3).

During electrospinning process, the polymer solution would be drawn from the nozzle of the spinneret and the electrical properties of the solution, namely, viscosity and surface tension will determine the extent of stretching of the solution under electrostatic forces.[14, 21] Thus, Figure 3 illustrates a higher average fiber diameter for a polymer of higher molecular weight.

Effect of Polyelectrolyte

Structural Morphology

Since polymeric nanofibers are widely used in many industries such as textiles, composites, filtration, wound dressing, tissue engineering and electronics, the surface properties of these fibers are of utmost importance. The surface properties of such fibers can be modified utilizing various techniques or treatments to suit particular applications.[6]

In the present work, small amounts of PAA and PAH ranging from 0.1- 4 wt% by weight of PEO were added to the aqueous solution of PEO. SEM images of PEO nanofibers electrospun from 5% and 6% PEO aqueous solutions with and without 2% PAA and PAH are displayed in Figure 4. Although 5% PEO nanofibers with and without 2% PAA and PAH indicates beaded nanofibers, the images for 6% PEO solutions indicates reduction in fiber beads, as a result smooth and uniform fibers are formed from a polymer solution with 2% PAH.

A polyelectrolyte, by definition, is a macromolecule that upon being placed in water or in any other ionizing solvent dissociates into highly charged polymeric molecule. Since the ionic charges have a direct relation with the electric conductivity of the solution, the addition of a polyelectrolyte increases the charge density on the surface of the ejected jet, leading to an increase in the electric charges carried by the jet. As a result, when the charge density increases in the jet, more stretching and elongation of the jet takes place during electrospinning, and thereby causing reduction in the bead formation.

These results were further confirmed by the AFM image (Figure 5) that the as spun PEO fibers in the presence of 2% PAH indicate uniform fiber diameters and smooth surfaces. Therefore, the inclusion of the polyelectrolyte in the PEO aqueous solution diminishes bead formation, as a result, smooth fiber were observed at 6% PEO solution with 2% PAH.

Conductivity

When polyelectrolytes of various concentrations were added to the PEO solution, the ions in the polymer solution increased the electrical conductivity of the solution, thereby increasing the charge carrying capacity of the jet (Table II). As a result, the

stretching of the solution jet was increased leading to the formation of electrospun fibers with uniformity and fewer beads.

It was observed that the addition of polyelectrolyte of the same concentration, lesser conductivities for PAA were obtained as opposed to the higher conductivities attained for PAH. However, these results agree well with the results shown in Figure 4, showing fibers with fewer beads on addition of PAH rather than PAA. It is evident that the addition of polyelectrolyte in the polymer solution increases the conductivity of the solution and encourages the formation of smooth fibers.

Effect of Solvent

Solvent characteristic is one of the major contributors in the morphology and diameter of electrospun nanofibers. When ethanol was added in 3% PEO aqueous solution, bead formation was decreased, and the shape of the beads transformed from spherical into spindle-like shape as indicated by the increase in bead length (Figure 6).

The length of the beads appeared to be smaller at lower ethanol concentration, but increases with an increase in ethanol concentration. This is attributed to the reduction in the charge density carried by the jet and the increase in viscosity and evaporation rate of the mixed solvent.[12]

Effect of Applied Voltage

Applied electric field is one of the most important parameters in the electrospinning process due to its direct influence on the dynamics of the fluid flow. In the electrospinning process, a high voltage is introduced into a polymer solution such that charges are induced within the fluid. However, the changes in the applied voltage, will be reflected on the shape of the suspending droplet at the nozzle of the spinneret,

its surface charge, dripping rate, velocity of the flowing fluid and hence on the structural morphology of electrospun fibers.

Although the applied voltage is shown to have a less significance on the morphology and diameter of electrospun nanofibers than the solution concentration, certain influences have been observed in this study.

Depending upon the feed-rate and viscosity of the polymeric solution, a higher applied voltage may be required to keep the stability of jet. As the voltage supplied has an influence on the stretching and acceleration of the jet, it will have an influence on the morphology of the fibers obtained.

In this study, applied potential voltage, in the range 5kV – 25kV was varied for electrospinning 7% PEO solutions while keeping all other parameters constant. It was observed that as the applied voltage was increased; there was an increase in "cluster" bead formation (Figure 7).

At 5kV voltage, the fiber formation was just not enough; some irregular beaded fibers were noticed. As the voltage increased (10kV-17.5kV), the beads indicated the formation of thicker fibers with higher diameter which resembled a web-like structure. This may be attributed to the instability of the jet causing an increase in bead density with increasing voltage. With further increase in applied voltage (20kV), fiber diameter decreased and the "bead-on-string" shape was visible at 25kV.

During electrospinning, it was interesting to note that the distribution of the fiber diameter was very broad at an applied voltage of 5kV, and then became quite narrow as the applied potential voltage was increased from 10 – 25kV. This, however, might be due to the charges on the jet, which are influenced by the external electric field affecting the jet path. Though not shown in Figure 7, with the additional increase in the applied voltage (above 25kV), the droplet at tip of the nozzle receded

completely and the jet was initiated directly from the tip of the spinneret. Therefore, it is evident that the processing parameters and solution traits have a significant influence on the structural morphology and diameter of electrospun PEO nanofibers.

CONCLUSIONS

This study investigates the effect of solution parameters (concentration, molecular weight, solvent and addition of polyelectrolyte) and processing parameter (applied potential voltage). The concentration of the aqueous PEO solutions has shown significant influence on the fiber diameter and structural morphology of electrospun nanofibers. At lower concentrations of PEO solutions, the fibers showed irregular morphology with large variation in fiber diameter, while at higher concentration, the nanofibers indicated regular morphology and on average had a larger but uniform fiber diameter. Higher average fiber diameter has been obtained for electrospun nanofibers of higher molecular weight and lower average fiber diameter for the same polymer but, of lower molecular weight.

The inclusion of polyelectrolyte in the polymer solution did not only improve the structural morphology of electrospun nanofibers, but, the conductivities of the polymeric solutions were also increased with the increase of polyelectrolyte in these solutions. The addition of small amounts of polyelectrolyte in higher concentrations of PEO aqueous solution results in fibers without beads. When the applied voltage was increased, beaded fibers formed cluster of beads which resulted in increased fiber diameter. As the applied potential voltage was further increased, the cluster appeared to diminish, as a result, the fiber diameter became thinner and "bead on string" morphology similar to that at lower applied voltages, was observed.

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TABLE CAPTIONS

TABLE I   Relationship between the Concentration of PEO (Mw= 9 X 10^5 g/mol) Polymer Solution and the Change in Fiber Diameter of Electrospun Nanofibers

TABLE II   The Effect of Polyelectrolyte on the Conductivity of 6% PEO (Mw= 3 X 10^5 g/mol) Aqueous Solution

TABLE I

Sample Code	Concentration of PEO (%)	Diameter (nm) Mean		% Change in diameter w.r.t 3% PEO Mean	
		Min	Max	Min	Max
NF-P3	3	34.37	89.98	-	-
NF-P4	4	48.03	102.79	40	14
NF-P5	5	59.21	155.82	72	73
NF-P6	6	69.44	280.82	102	212
NF-P7	7	83.96	445.95	144	396

TABLE II

Polyelectrolyte concentration (%)	Conductivity (mS/cm)	
	PAH	**PAA**
0	0.17^{-2}	0.22^{-2}
1	0.74^{-2}	0.28^{-2}
2	0.95^{-2}	0.31^{-2}
3	1.06^{-2}	0.48^{-2}
4	1.16^{-2}	0.61^{-2}
5	1.31^{-2}	0.62^{-2}
6	1.52^{-2}	0.67^{-2}

FIGURE CAPTIONS

Figure 1 Fiber diameter distribution of electrospun PEO nanofibers from SEM image analysis for nanofiber PEO 3% (NF-P3); 4% (NF-P3); 5% (NF-P3); 6% (NF-P3) and 7% (NF-P3) respectively.

Figure 2 SEM micrographs showing the effect of molecular weight on the microstructures of electrospun nanofibers from a) 5%, b) 6% PEO (3×10^5 g/mol) aqueous solution; c) 5%, d) 6% PEO (Mw= 9×10^5 g/mol) aqueous solution. All other parameters were kept constant.

Figure 3 Comparison between concentrations (4%-7%) and the corresponding average fiber diameter of electrospun nanofiber, PEO Mw= 3×10^5 g/mol (NF-P3), 9×10^5 g/mol (NF-P9).

Figure 4 SEM images of electrospun nanofibers from a) 5%, b) 5%*, c) 5%**, d) 6%, e) 6%*, f) 6%** PEO (Mw= 3×10^5 g/mol) aqueous solution.
*   denotes with 2% PAA
**   denotes with 2% PAH

Figure 5 AFM image showing the effect of polyelectrolyte on PEO (Mw= 3×10^5 g/mol) electrospun nanofibers with 2% PAH (scale shown in nm $\times 10^2$).

Figure 6 Relationship between the amounts of Ethanol added to a 3% PEO (Mw= 9×10^5 g/mol) aqueous solution and the corresponding bead lengths of electrospun nanofibers.
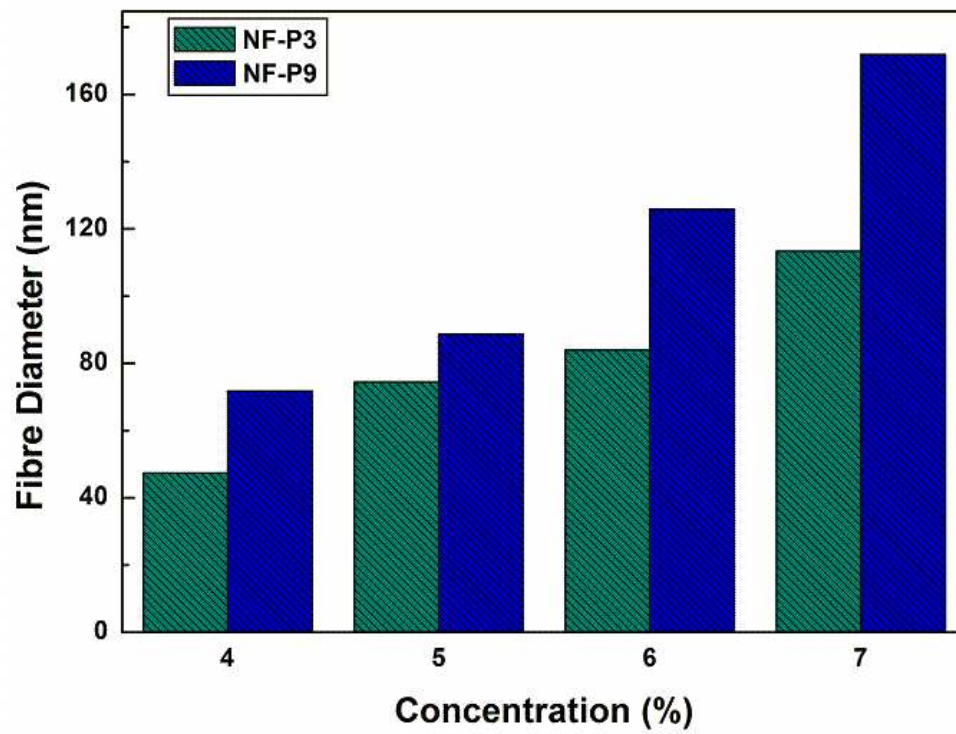
Figure 7 SEM micrographs showing the effect of an electric field on the microstructures of electrospun 7% PEO (Mw= 3×10^5 g/mol) solution at a tip-to-collector distance of 10cm and at applied potential voltage of 5kV- 25kV.
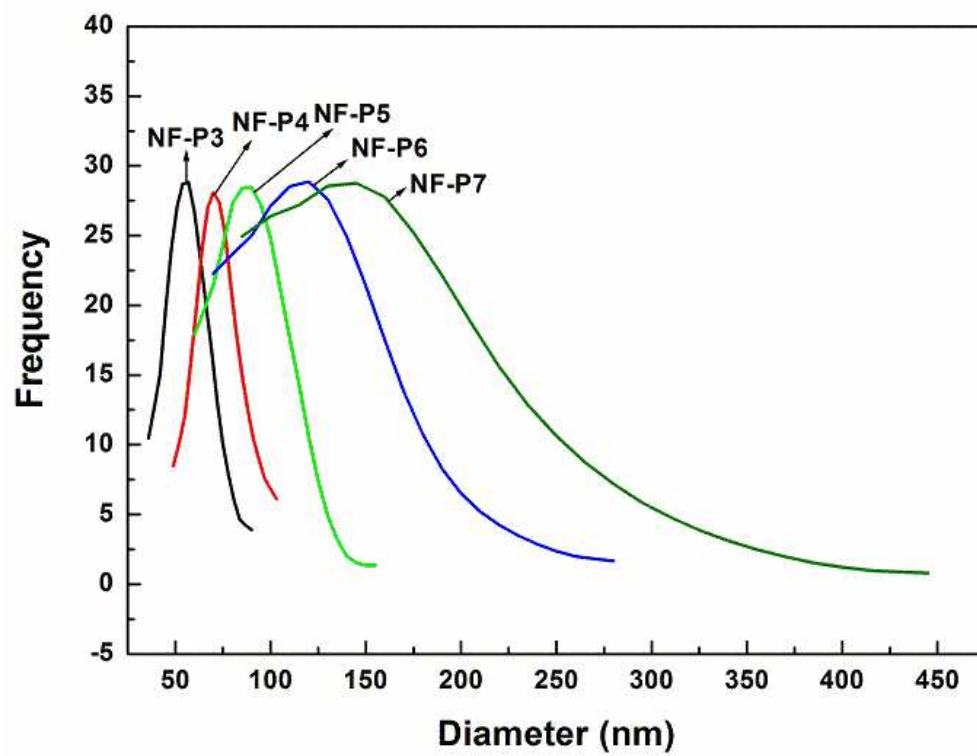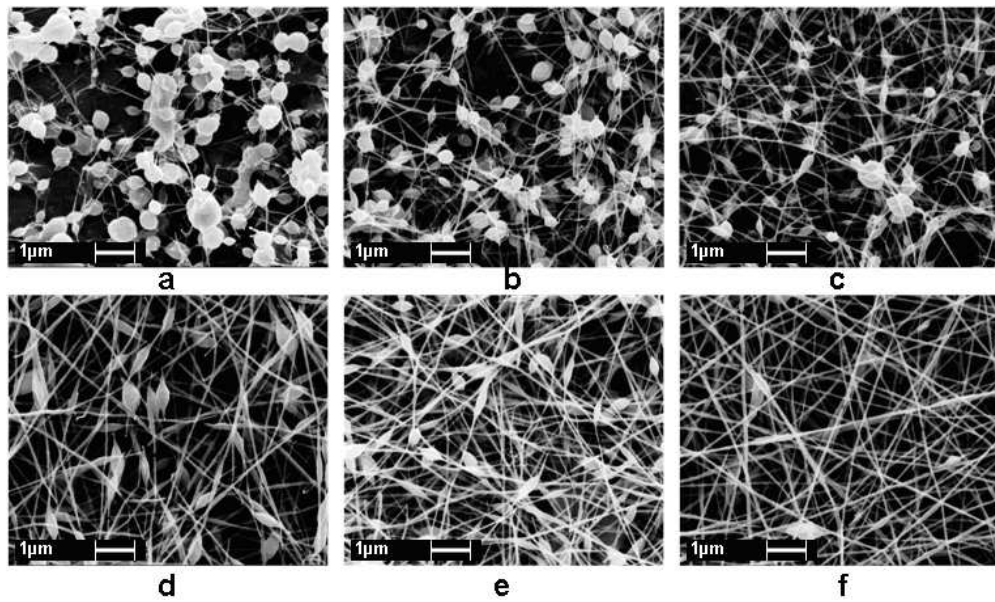
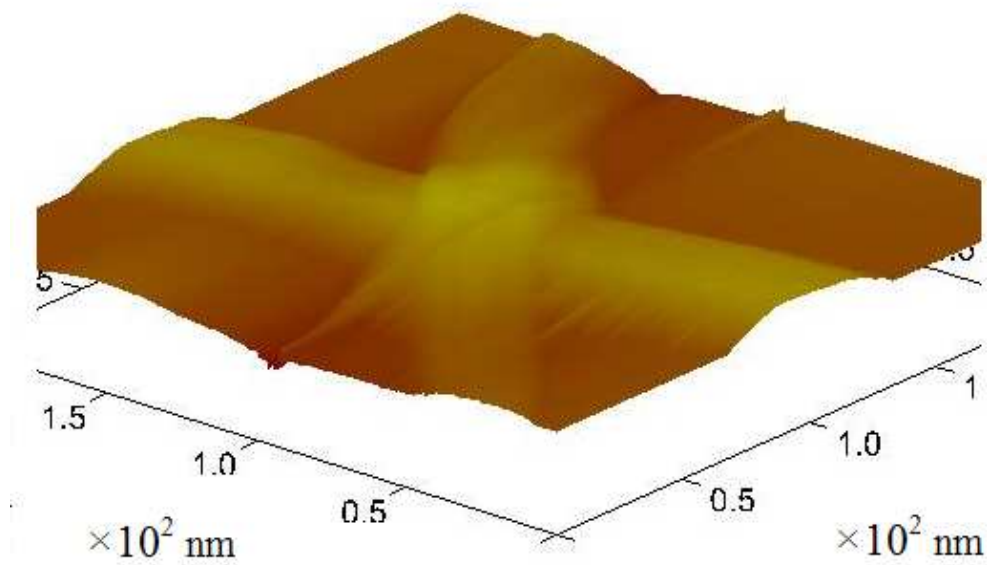182x140mm (96 x 96 DPI)
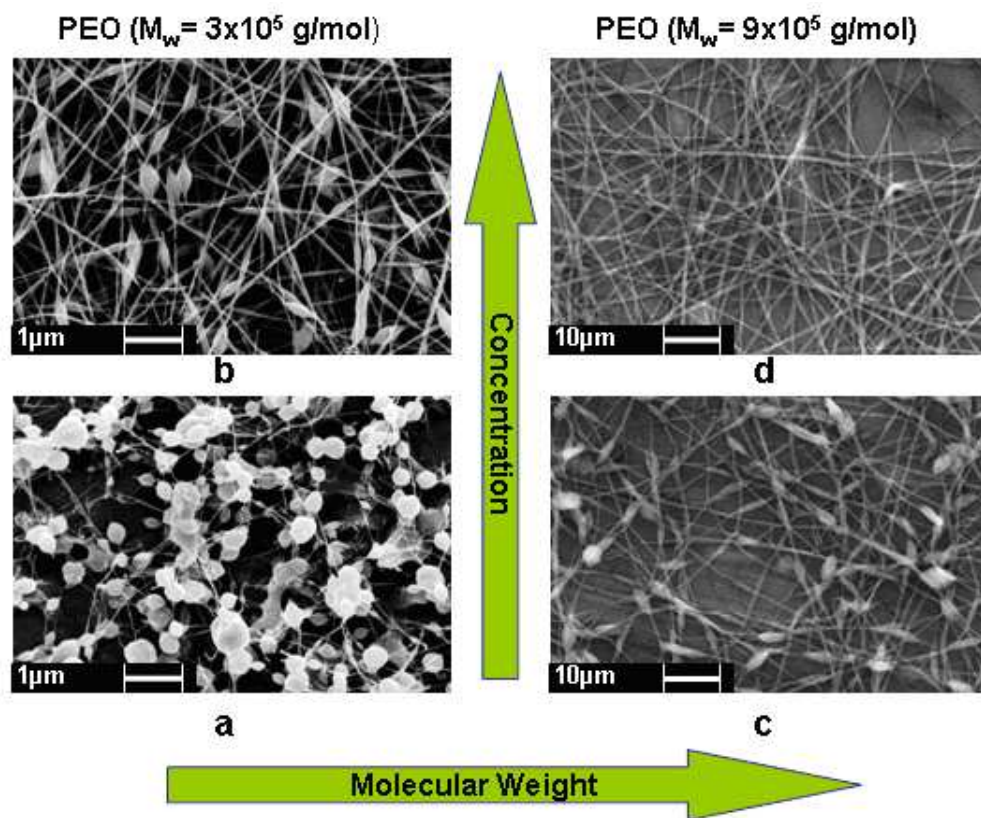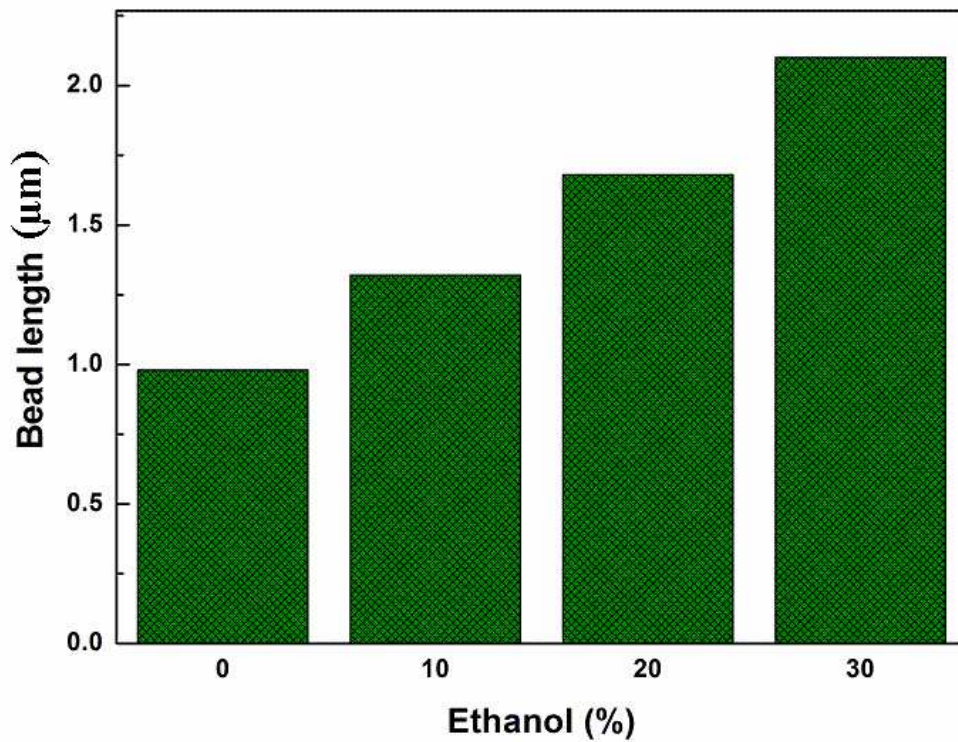
141x117mm (96 x 96 DPI)

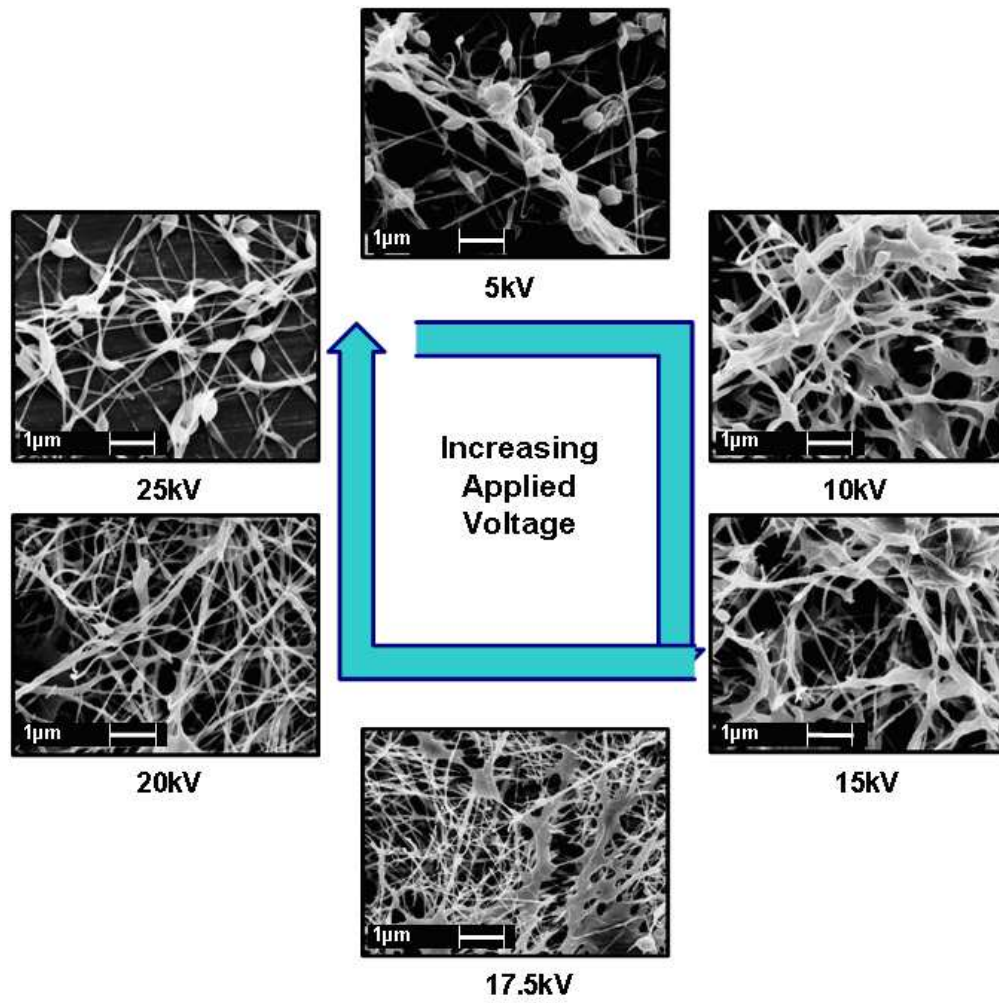184x139mm (96 x 96 DPI)

202x120mm (96 x 96 DPI)

138x86mm (96 x 96 DPI)

186x146mm (96 x 96 DPI)

178x178mm (96 x 96 DPI)