UNIVERSITY OF GAZİANTEP
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EXPERIMENTAL INVESTIGATION OF OPTIMAL SPINNING PARAMETERS FOR NANOFIBERS

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BY
ÜMRAN ÖZKOÇ
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Experimental Investigation of Optimal Spinning Parameters for Nanofibers

M.Sc. Thesis
in
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University of Gaziantep

Supervisor
Prof. Dr. Ali KİREÇCİ

by

Ümran ÖZKOÇ

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science/Doctor of Philosophy.

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ABSTRACT

EXPERIMENTAL INVESTIGATION OF OPTIMAL SPINNING PARAMETERS FOR NANOFIBERS

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M.Sc.in Textile Eng.
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In this study, effects of the voltage, concentration and tip-collector distance on morphology of PAN (polyacrylonitrile), PVA (polyvinyl alcohol), PA6 (polyamide 6) electrospun nanofibers were researched to determine their optimal values. For PAN polymer the effects of temperature and humidity were also investigated. To investigate the concentration effect on PAN fiber diameter, solutions were prepared between 6-14% (2% intervals) by dissolving PAN polymer in dimethylformamide (DMF). For PA6 the concentration values were chosen between 8-14% (2% intervals) by dissolving PA6 in formic acid. For PVA the concentration values were chosen as 5-15% (2.5% intervals) by dissolving PVA in distilled water. As the concentration increases the fiber diameter increases for all polymers. Bead formation reduces as the concentration increases. To examine the effect of voltage, the values were changed between 5-40 kV (5 kV intervals) for all polymers. Generally, nanofibers diameter reduce as voltage increases. However, diameter of PAN nanofiber reduces at the beginning up to a value but later diameter increases again. Usually, the optimum results were obtained between 30-35 kV. To investigate distance effect on nanofibers values the distance were chosen as 5-25 cm for all polymers. For PVA and PA6, effect of voltage was same that diameters of these fibers decrease as the distance increases. However, PAN nanofibers behave differently that the nanofiber diameter reduces up to 15 cm distance but it increases for further distance. Commonly, better results were obtained between 10-15 cm for all polymers.

Key words: electrospinning, nanofiber, polyacrylonitrile, polyamide, polyvinyl alcohol, voltage, concentration, distance

ÖZET

NANOLIF IMALATI IÇIN OPTIMUM ÜRETIM PARAMETRELERININ DENEYSEL ARAŞTIRILMASI

ÖZKOÇ, Ümran
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Bu çalışmada voltaj, konsantrasyon ve mesafe gibi parametrelerin PAN (poliakrilonitril), PA6 (polyamid 6) ve PVA (polivinil alkol) polimerlerinden üretilen nanolif morfolojisi üzerinde etkileri araştırılmış ve en uygun değerler belirlenmeye çalışılmıştır. Ayrıca, PAN (poliakrilonitril) polimeri için sıcaklığın ve nemin etkileri de araştırılmıştır. PAN polimeri Dimetilformamidde çözülmüş ve konsantrasyonun nanolif çapına olan etkisini incelemek için değerleri 6-14% (2% aralıkla) arasında değişen çözeltiler hazırlanmıştır. Benzer şekilde PA6 polimeri formik asitte çözülmüş ve konsantrasyonun nanolif çapına olan etkisini ölçmek için değeri 8-14% (2% aralıkla) arasında değişen çözeltiler hazırlanmıştır. PVA polimeri ise 5-15% (2.5 % aralıkla) arasında hazırlanmıştır. Bunun için PVA polimeri saf suda çözülmüştür. Tüm polimerlerde konsantrasyon arttıkça lif çapında artış görülmüştür. Ancak, boncuk oluşumun konsantrasyon arttıkça azaldığı gözlemlenmiştir. Voltajın etkisini incelemek için voltaj değerleri tüm polimer çözeltileri için 5-40 kV (5 kV aralıkla) arasında değiştirilmiştir. Elde edilen deney sonuçları genelde voltajın artmasıyla lif çapında azalma meydana geldiğini göstermiştir. Fakat PAN nanolifinin çapı belli bir değere kadar azalma gösterdikten sonra tekrar artış göstermiştir. En iyi değerler genelde 30-35 kV arasında elde edilmiştir. Benzer olarak mesafenin nanolif oluşumuna etkisini incelemek için mesafe tüm polimer tiplerinde 5-25 cm arasında (5 cm aralıkla) değiştirilmiştir. Mesafenin etkisi PVA ve PA6 polimerleri için aynı olup PAN polimeri için farklılık göstermiştir. PAN nanolif çapı 15 cm ye kadar azalma gösterirken 15 cm den sonra nanolif çapında artış görülmüştür. Genel olarak tüm polimer tiplerinde en iyi sonuçlar 10-15 cm arasında elde edilmiştir.

Anahtar kelimeler: electrospinning, nanolif, poliakrilonitril, polyamid 6, polivinil alkol, voltaj, konsantrasyon, mesafe,

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CHAPTER 1

INTRODUCTION

1.1. Introduction

In this chapter an attempt is made to classify nanofibers into one or more sub-category of nanotechnology. As far as "nanostructures" are concerned, one can view this as objects or structures whereby at least one of its dimensions is within nano-scale. A "nanoparticle" can be considered as a zero-dimensional nano-element, which is the simplest form of nanostructure. It follows that a "nanotube" or a nanorod" is a one-dimensional nano-element from which slightly more complex nanostructure can be constructed of. Following this train of thought, a "nanodisk" is a two-dimensional element which, along with its one-dimensional counterpart, is useful in the construction of nanodevices. The difference between a nanostructure and a nanodevice can be viewed upon as the analogy between a building and a machine (whether mechanical, electrical or both). It goes without saying that as far as nanoscale is concerned, one should not pigeon-hole these nano-elements – for an element that is considered a structure can at times be used as a significant part of a device [1].

With regard to fibers ‘’nano’’ refers to the diameter of the fiber. Generally speaking, nanofibers have diameters less than one micron and cannot be seen without visual amplification. Nanofibers are able to form a highly porous mesh and their large surface-to-volume ratio improves performance for many applications. A variety of nanofibers can be made for applications in energy storage, healthcare, biotechnology, environmental engineering and defense and security [2].

1.2. Various Ways to Make Nanofibers

Polymeric nanofibers can be processed by a number of techniques such as drawing, template synthesis, phase Separation, self-assembly and electrospinning.

1.2.1. Drawing

The drawing process can be considered as dry spinning at a molecular level (Figure 1.1). The process can only be applied to viscoelastic materials that can undergo strong deformations while remaining cohesive enough to support the stresses developed during pulling. A typical drawing process requires a SiO2 surface; a micropipette and a micromanipulator to produce nanofibers. However, this is a laboratory-scale process in which the nanofibers have to be produced one by one preventing it from being scaled up to industrial level [3].

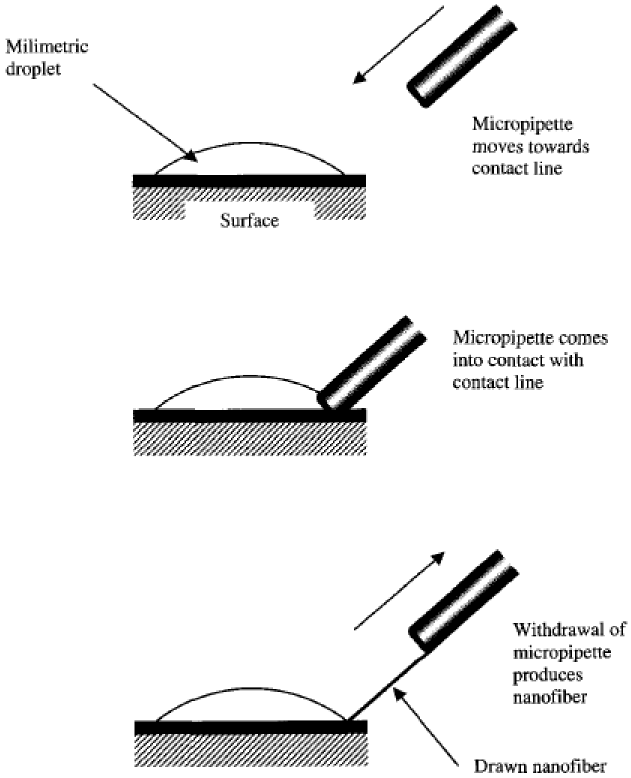


Figure 1.1 Obtaining nanofibers by drawing [1]

1.2.2. Template Synthesis

In template synthesis nanofibers are formed from specific materials within the pores of nanoporous membranes. The membranes contain cylindrical pores with uniform diameters that run through the complete thickness of the membranes, which is typically on the order of 5-50mm. Each pore can be considered as a beaker in which a nanostructure of desired material is electrochemically or chemically synthesized by a myriad of methods and oxidative polymerization. Because these pores are cylindrical, a nano cylinder of the desired material is obtained in each pore. Depending on the material and the chemistry of the pore wall, the nanocylinders may be fibrils or tubules. The template synthesis method has been used to prepare nanofibrils of polymers, metals, semiconductors and carbons (Figure 1.2). The process is simple and requires standard laboratory equipment. Nanofibers of different diameters can be produced with different templates. However, it is a laboratory scale process limited to the conversion of specific polymers directly into nanofibers structures [3].

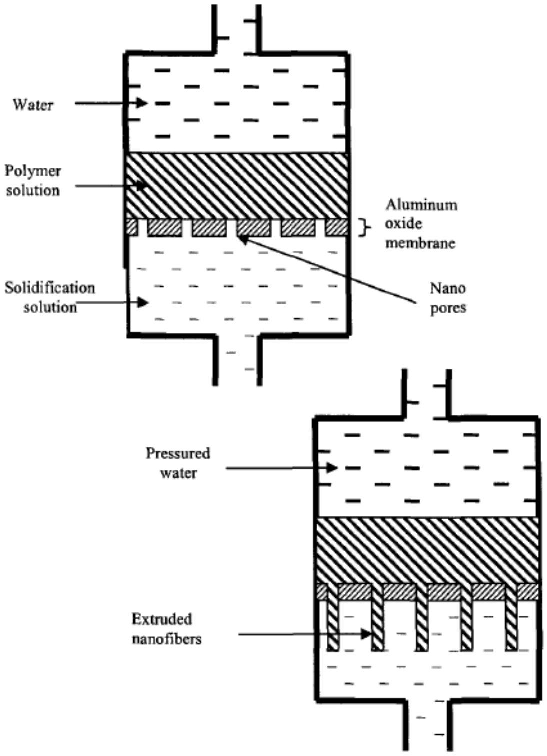


Figure 1.2 Obtaining nanofibers by template synthesis [1]

1.2.3. Phase Separation

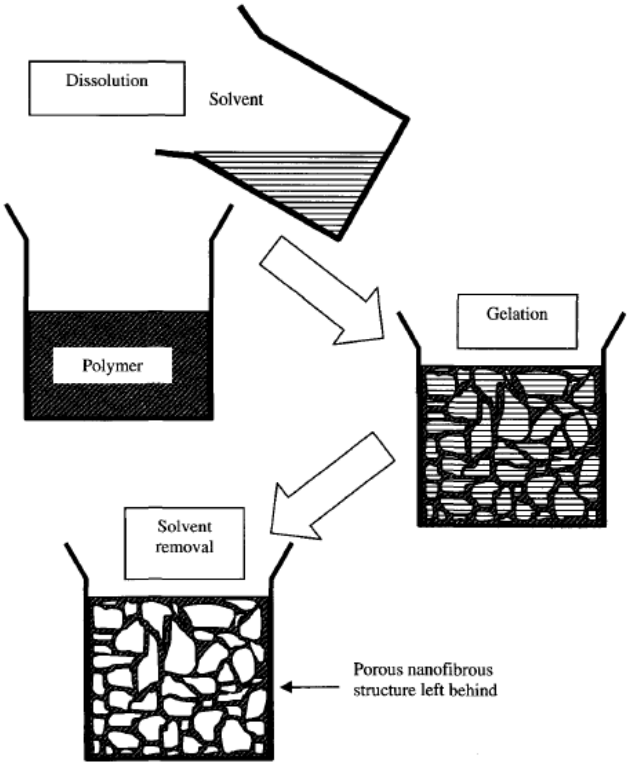


Figure 1.3 Generic schematics of phase separation for obtaining nanofibrous structure [1]

The phase separation technique is based on thermodynamic demixing of a homogenous polymer solvent solution into a polymer-rich phase and a polymer-poor phase, usually either by exposure of the solution to another immiscible solvent or by cooling of the solution below a bimodal solubility curve (Figure 1.3). Thermally induced phase separation uses thermal energy as a latent solvent to induce phase separation. The polymer solution quenched below the freezing point of the solvent is freeze-dried to produce a porous structure. Various porous structures including porous nanofiber matrices can easily be obtained with this technique by adjustment of the thermodynamic and kinetic parameters [3].

1.2.4. Self-Assembly

Self assembly is the autonomous organization of components into patterns or structures without human intervention. Self assembly processes are common throughout nature and technology and they involve components from the molecular (crystals) to the planetary (weather systems) scale and many different kinds of interactions.

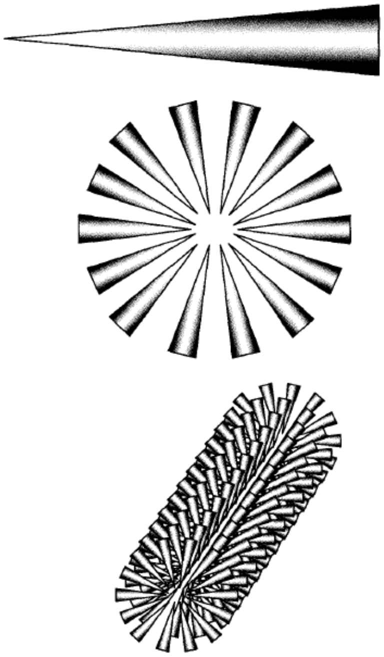


Figure 1.4 An example of self-assembly for obtaining nanofibers [1]

The concept of self assembly is used increasingly in many disciplines with a different flavor and emphasis in each field. The process requires standard laboratory equipment (Figure 1.4). However, it is laboratory scale process limited to the conversion of specific polymers directly into nanofibers [3].

1.2.5. Electrospinning

Electrospinning is an economical and simple method used in the preparation of polymer fibers. The fibers prepared via this method typically have diameters much smaller than is possible to attain using standard mechanical fiber-spinning technologies. Electrospinning has gain much attention in the last few years as a cheap and straightforward method to produce nanofibers. Electrospinning differs from the traditional wet/dry fiber spinning in a number of ways, of which the most striking differences are the origin of the pulling force and the final fiber diameters. The mechanical pulling forces in the traditional industrial fiber spinning processes lead to fibers in the micrometer range and are contrasted in electrospinning by electrical pulling forces that enable the production of nanofibers (Figure 1.5).

Depending on the solution properties, the throughput of single-jet electrospinning systems ranges around 1 ml/min. This low fluid throughput may limit the industrial use of electrospinning [4].

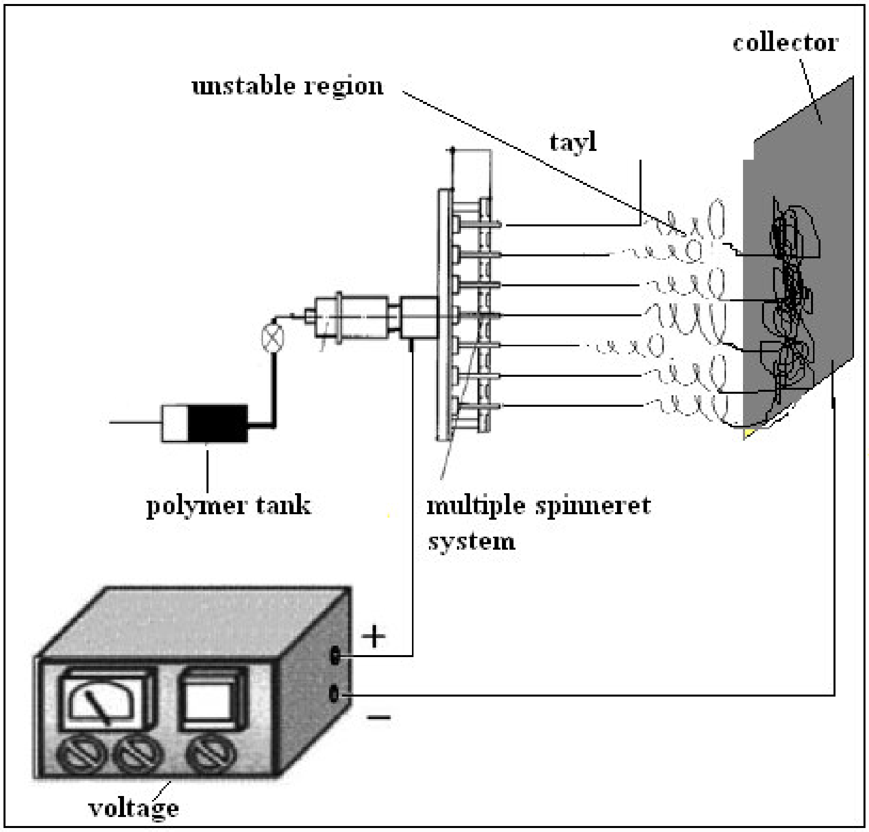


Figure 1.5 Schematic of electrospinning set up

A stable cone-jet mode followed by the onset of the characteristic bending instability, which eventually leads to great reduction in the jet diameter, necessitate the low flow rate. When the diameters of cellulose fiber materials are shrunk from micrometers (e.g. 10–100 mm) to submicrons or nanometers, there appear several amazing characteristics such as very large surface area to volume ratio (this ratio for a nanofiber can be as large as 100 times of that of a microfiber), flexibility in surface functionalities, and superior mechanical performance (e.g. stiffness and tensile strength) compared with any other known form of the material [4].

1.3. Effect of Systematic Parameters on Electrospun Nanofibers and Experimental Observation

It has been found that morphology such as fiber diameter and its uniformity of the electrospun nanofibers are dependent on many processing parameters. These parameters can be divided into three main groups:

a) System Parameters
b) Process Parameters
c) Ambient Parameters

a) System Parameters:

- Solution concentration and viscosity
- Net charge density (conductivity)
- Surface tension of the polymer fluid.
- Molecular weight
- Conductivity

b) Process Parameters:

- Voltage
- Flow rate of the polymer solution
- Distance between the capillary-end and target/collection screen
- Motion of target screen

c) Ambient Parameters**:**

- Temperature
- Relative humidity
- Pressure (environment)
- Atmosphere type
- Air velocity in the chamfer

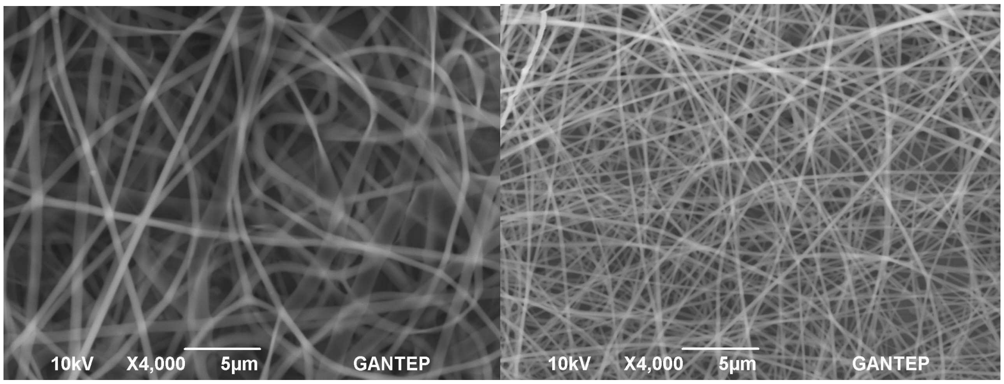
Each of the parameters has been found to affect the morphology of the electrospun fibers [5].

1.4. System Parameters

1.4.1. Solution Concentration and Viscosity

The apparent trend is with an increased viscosity the fiber diameters increased as well. General assumptions can lead to the idea that with a higher polymer concentration, there will be a higher viscosity. This assumption lends to the idea with an increased polymer concentration, the fibers produced will likewise be larger in diameter [6].

In electrospinning process, for fiber formation to occur, a minimum solution concentration is required. It should be noted that the fiber diameter increases with increasing solution concentration (Figure 1.6). Nevertheless, at higher concentration, viscoelastic force which usually resists rapid changes in fiber shape may result in uniform fiber formation. However, it is impossible to electrospin if the solution concentration or the corresponding viscosity become too high due to the difficulty in liquid jet formation.



a)15% concentration; b)10% concentration;

Figure 1.6 (a-b) PVA polymers (distance 10cm; voltage 20 kV)

As the solution concentration decreases mixture of beads and fibers is obtained. The shape of the beads changes from spherical to spindle-like when the solution concentration varies from low to high level (Figure 1.7) [7].

It has been shown in the electrospray literature that solution concentration has a significant effect on the final size and distribution of particles. Solution surface tension and viscosity also play important roles in determining the range of concentrations from which continuous fibers can be obtained in electrospinning. At low viscosities, surface tension is the dominant influence on fiber morphology and below a certain concentration drops will form instead of fibers. At high concentrations, processing will be prohibited by an inability to control and maintain the flow of a polymer solution to the tip of the needle and by the cohesive nature of the high viscosity solutions [8]. The higher viscosity solutions proved extremely difficult to force through the syringe needle of the apparatus used in these experiments, making the control of the solution flow rate to the tip unstable.

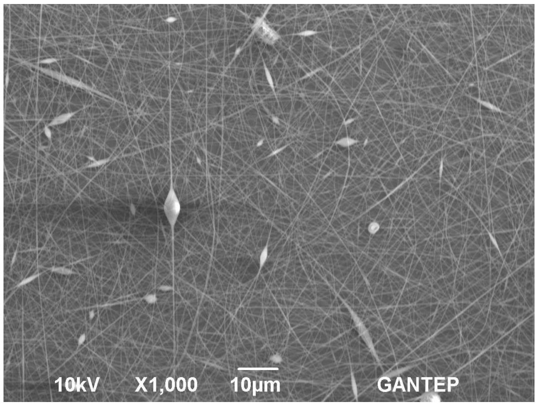


Figure 1.7 Bead formations at lower concentrations

Varying solution concentration alters the morphology of the nanofibers formed. At the low concentrations, the fibers have an irregular, undulating morphology with large variations in diameter along a single fiber. There are numerous junctions and bundles of fibers. At high concentrations, the nanofibers have a regular, cylindrical morphology and on average have a larger and more uniform diameter. At higher concentrations, the fibers exhibit a straight, cylindrical morphology with relatively few fiber bundles and junctions indicating that the fibers are mostly dry when they reach the collection screen. The apparent change in morphology may be reflective of the lower surface tension and solvent content in the high concentration solutions [8].

1.4.2. Charge Density

Some studies show that the effect of the charge density on the fiber diameter distribution is very clear and the distribution increases as charge density (E/H in kV/cm) increases. That can be explained from the effect of the charge density on the size of the hanged droplet. When E/H reach 1 KV/cm the electric field is sufficient to overcomes the surface tension of the hanged polymer solution droplet and forming a Taylor cone related to the size of the droplet. Eventually the size of the droplet is smaller than the size of the pipette diameter. As the charge density increases from 1 to 1.5 KV/cm for same height the hanged droplet disappeared and the Taylor cone formed at the tip of the pipette which is larger in diameter than that one formed from the hanged droplet, for more prove see reference, so the formed fibers in this case are larger in diameter than the previous one, further more if the charge density increases to 2 KV/cm the jet comes out also from the orifice of the pipette not only that but splitting into many jets which is the parameter reduced the fiber diameter from case two to three [9].

1.4.3. Surface Tension

Surface tension is a measure of the cohesive forces between molecules in a liquid. Atoms on the surface of a solution prefer to be at the lowest energy state possible, so they configure themselves to minimize surface area, thereby lowering the number of available bonding sites on the surface. Molecules on the surface experience an attractive force towards the interior molecules, this is called surface tension. In electrospinning, this tension holds the solution droplet at the tip until the electric field provides enough force to overcome the surface tension. A larger surface tension value signifies an increased difficulty in extending the surface of a liquid from the interior molecules. The surface tension is thought to be the force acting against the stretching of the charged jet; therefore higher surface tension leads to larger diameters. In considering the three phases of electrospinning, higher surface tension is thought to act against the whipping instability. Higher surface tension values favor a more stable jet flow, thereby creating fibers with larger diameters [10].

1.4.4. Molecular Weight

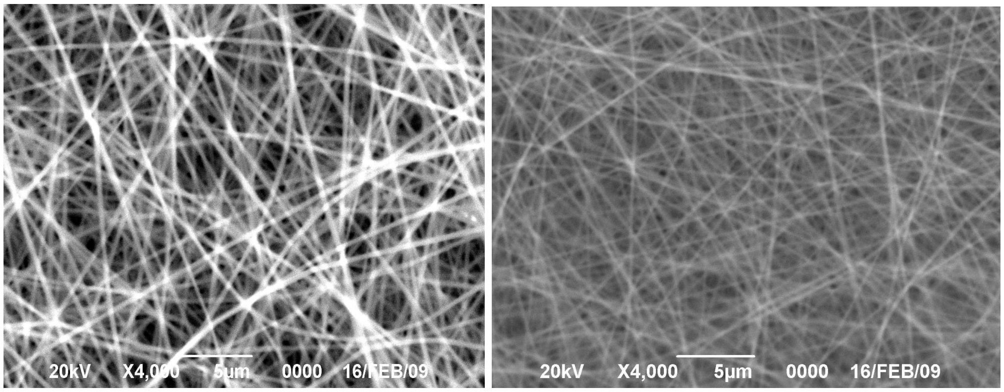
Molecular weight has a significant effect on the rheological and electrical properties such as viscosity, surface tension, conductivity and dielectric strength. Low molecular weight solution tends to form beads rather than fibers and high molecular weight nanofiber solution gives fibers with larger average diameter. The diameters of fibers electrospun from mixed solvents increase with increasing solution concentration or molecular weight. Solution viscosity is a good predictor of fiber diameter within the range of concentrations and molecular weights studied. Surface tension did not vary significantly in this range [11].

Joon Seok Lee et al. studied about molecular weight effect on PVA polymer. Through a series of characterization experiments, it was identified that the molecular weight of a-PVA had a marked influence on the structure and properties of nanofabrics produced. That is, the higher the molecular weight of PVA, the superior the physical properties of PVA nanofabric Lower optimum polymer concentration was obtained at a higher molecular weight [12].

1.5. Process Parameters

1.5.1. Voltage

The voltage is an important process parameter which influences the fiber morphology. When a high voltage is applied, the pendent drop of polymer solution at the nozzle of the spinneret will become highly electrified and the induced charges are evenly distributed over the surface. Consequently the drop will experience two major types of electrostatic forces: electrostatic repulsion between the surface charges and Coulombic force exerted by the external electric field.



a) voltage 25 kV

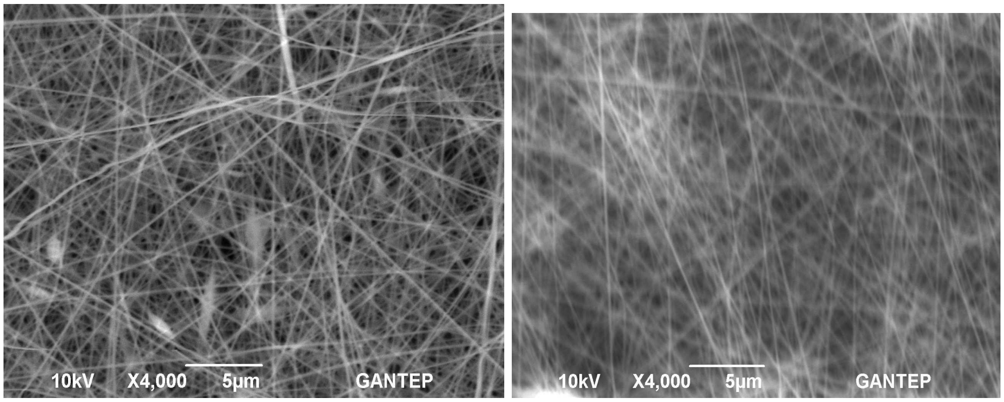
b) voltage 35 kV

Figure 1.8 (a-b) Effect of voltage on PAN polymer 10% conc., 10 cm distance

Under the action of these electrostatic interactions, the liquid drop will be distorted into a conical object commonly known as the Taylor cone. When the strength of the electric field has surpassed a threshold value, the electrostatic forces can overcome the surface tension of the polymer solution and thus force the ejection of a liquid jet from the nozzle [13].

1.5.2. Temperature

Electrospinning is a process that generates nanofibers. Temperature affects this process. Two major parameters are dependent of temperature and have their influence on the average fiber diameter. The first parameter is the solvent evaporation rate that increases with increasing temperature. The second parameter is the viscosity of the polymer solution that decreases with increasing temperature. The trend in variation of the average nanofiber diameter as a function of humidity is different for each polymer [14]. When PAN is electrospun at a higher temperature, the fibers produced have more uniform diameter (Figure 1.9). This may be due to the lower viscosity of the solution and greater solubility of the polymer in the solvent which allows more even stretching of the solution with a lower viscosity; the Columbic forces are able to exert a greater stretching force on the solution thus resulting in fibers of smaller diameter.



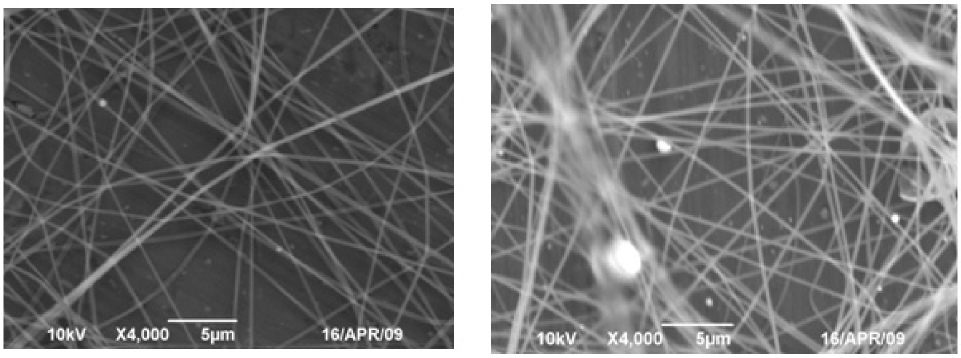
a) temperature 15°C b) temperature 25°C

Figure 1.9 (a-b) Effect of temperature on PAN nanofiber morphology voltage: 35 kV, concentration: 10%, distance: 10 cm;

Increased polymer molecules mobility due to increased temperature also allows the Columbic force to stretch the solution further. However, in cases where biological substances such as enzymes and proteins are added to the solution for electrospinning, the use of high temperature may cause the substance to lose its functionality. This parameter is related to ambient conditions [1].

1.5.3. Relative Humidity (RH)

The trend in variation of the average nanofiber diameter as a function of humidity is different for each polymer, which can be explained by variations in chemical and molecular interaction and its influence on the solvent evaporation rate. Temperature and RH are two ambient parameters that strongly affect electrospinning. RH makes the nanofibers thicker or thinner, depending on the chemical nature of the polymer. Evaporation rate of the solvent and viscosity of the solution are two opposing mechanism that have an effect on the mean fiber diameter [14]. The humidity makes PAN morphology irregular. The formation is not uniform (see Figure 1.10-b). But at lower humidity values it is observed that the formation is more regular (Figure 1.10-a).



a) humidity 25% b) humidity 50%

Figure 1.10 (a-b) Effect of humidity on PAN nanofiber (35 kV, 10%, 10 cm)

1.5.4. Flow Rate

For a given flow rate, the first mode observed by most authors is the dripping mode. This is the case when gravity is the dominant force acting on the initial drop. The initial drop diameter before it detaches from the capillary tip is characteristically larger than the diameter of the capillary. As voltage is applied and increased, the frequency of the drops increases while the diameter of the individual drops decreases. This is because the electrostatic force on the drop decreases the “apparent” surface tension of the liquid in the drop. It has also been observed that for a given flow rate in this mode, reduction of the capillary diameter results in an increase in drop frequency and a decrease in drop size. Chen and Prui have observed that the current carried to ground by the drops also increases with increasing voltage in this electrospray mode. Therefore, an increase in the electrospinning current reflects an increase in the mass flow rate away from the tip when all other variables (conductivity, dielectric constant, and flow rate of solution to the tip) are held constant [7].

1.5.5. Surface Area

Diameters of fibers currently being produced in textile industry normally ranges from 10 µm or above while the diameters of electrospun fibers ranges from few hundred nanometer to submicron depending on the spinning condition. One of the most noticeable properties of the fine fiber is the increased surface area at given volume comparing to larger fiber area. These electrospun fiber mats possesses properties like high porosity, micro-scaled pore size and highly interconnected internal structure by the nature of thin continuous fibers. The surface area was estimated by assuming the square packing of fibers in cubic centimeter. The expected surface area exponentially increases as fiber diameter decreases. Typical high performance industrial textile fibers such as carbon fibers and Kevlar are ranging 5~10 µm or bigger and electrospun fibers are ranging submicron down to a few nanometer. This decrease in fiber diameter, for example, from 10 µm to 100 nm can increase the surface area approximately 1000 times in 1 cm3 while packing with 100 times longer fibers in 1 cm^3. This increment of surface does not only contribute to increasing reactive surface area but also greatly enhances sensitivity of fibers to external environment even in case of simple diffusion. These characteristics make finer fibers more attractive in sensors, optical and electrical applications [15].

1.6. Literature Survey

1.6.1. Literature Survey about Polyacrylonitrile (PAN)

Shivalingappa Lingaiah et al. studied on Polyacrylonitrile (PAN) and polybenzimidazole (PBI) nanofibers. Polyacrylonitrile (PAN), and polybenzimidazole (PBI) nanofibers were produced using electrospinning by dissolving PAN in N,N-dimethylformamide (DMF) and PBI in N,Ndimethylacetamide (DMAc) solutions. The electrospinning was carried out for 10, 15 & 20% (by weight) concentrations at different process conditions. The diameters of the nanofibers range from 50 to 200nm for PAN nanofibers. The electrospinning process parameters are given as: voltage: 10-30 kV; flow rate: 0.5-5 ml/hr; distance between target and nozzle: 15-30 cm. They found that as the concentration of the solution increases, the diameter of the fiber also increases. At 10% concentration, the diameter of fibers is around 300 nm and increased to 500 nm at 15% and 1µ at 20% PAN concentration [16].

Ashraf Abd El Fattah Ali studied about the PAN polymer. The concentration is changed between (6, 9 & 12), charge density E/H in KV/cm is changed between (1, 1.5 &2). They found that a 100 nm PAN fiber diameter can be produced under the following conditions: 6% (Wt) concentration in DMF solvent, 1.5 to 2 KV/cm charge density, 10X10 cm target size, 15 to 20 cm height, and 0.9 mm pipette diameter and in 25°C environmental temperature. Also the phenomenon of continuous nanofiber yarn during the electro-spinning of PAN polymer solution has been discovered. As the height, the concentration and the solvent boiling point are reduced within the prescribed range the produced diameter and its distribution can be reduced. As the environmental temperature increased the fiber diameter and its distribution decreased [9].

Ji-Huan He et al. established about an algometrical scaling relationship between the diameter of electrospun nanofiber and solution concentration. The scaling exponent differs greatly between different polymers and the same polymer with different molecules or the same molecules with different properties. The diameter of electrospun polyacrylonitrile (PAN) nanofibers increases approximately linearly with solution concentration. A high voltage power supply is used for electrospinning; the voltages range from 0 to 50 kV, the voltage used in the experiment is about 20 kV. Polyacrylonitrile (PAN) solution (9 wt% to 20 wt% as concentration) was poured in a syringe attached with a capillary tip of 7 mm diameter. The original flow rate was 2.8 ml/h, and the distance between the capillary tip and collector is constant, 8 cm. They found that as the concentration increases the diameter of fiber increases [17].

Rouhollah et al. used to prepare uniaxially aligned PAN nanofibers with a collector consisting of two pieces of electrically conductive substrates separated by a gap. Solution of 15 wt % of PAN/DMF was used tentatively for electrospinning. The effects of width of the gap and applied voltage on degree of alignment were investigated using image-processing technique by Fourier power spectrum method. The electrospinning conditions that gave the best alignment of nanofibers for 10–15 wt % solution concentrations were experimentally obtained. Bundles like multifilament yarns of uniaxially aligned nanofibers were prepared using a new simple method. After-treatments of these bundles were carried out in boiling water under tension. A comparison was made between the crystallinity and mechanical behavior of post treated and untreated bundles. [18].

Wang-xi Zhang et al. obtained ultrafine polyacrylonitrile (PAN) fibers, as a precursor of carbon nanofibers, with diameters in the range of 220–760 nm by electrospinning of PAN solution using N, N-dimethylformamide (DMF) as solvent. Morphology of the nanofibers for varying concentration and applied voltage was investigated by field emission scanning electron microscopy (FESEM). The thermal properties and structural changes during the oxidative stabilization process were primarily investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Fourier transform infrared (FT-IR) and Raman spectroscopy. The nanofiber diameters increase as the applied voltage is increased and they also increase with an increase in the concentration of the polymer solution [19].

Demetrius S. Gomes et al. performed an extensive characterization of an electrospinning process to evaluate how the process parameters and precursor solution characteristics affect the fibers morphology. The work was conducted using precursor solutions with different concentrations of polyacrylonitrile (PAN) diluted in a fixed amount of N,N dimethylformamide (DMF). Fibers obtained with this process can find important applications in the field of nanosensors. The characteristics of the electrospun fibers were analyzed as a function of the solution viscosity, applied voltage and distance between the needle tip (positive electrode) and the collector plate (grounded electrode). The electrical current was monitored during the deposition process and its behavior was correlated with the characteristics of the fibers obtained. The results demonstrate that the diameter of the fibers increases with increasing viscosity and applied voltage. The number of deposited fibers also increases with the applied voltage. Also, viscosity and applied voltage strongly affect the shape, length and morphology of the fibers. They also demonstrated that it is possible to control the fibers morphology and bead concentration [20].

Rouhollah Jalili et al. prepared nanofibers by electrospinning of PAN/DMF solution of 15% wt concentration. The effects of operating parameters including applied voltage, feeding rate and tip-target distance on the morphology of electrospun PAN nanofibers were systematically evaluated. Their experiments showed that diameters of nanofibers decreased with increasing applied voltage from 10 to 20 kV, but broader distribution in diameters of nanofibers were obtained at 15 kV and above. Morphology of nanofibers was changed by the instability of the liquid surface from which the jet originates to beaded nanofibers. The morphological structure can be changed by changing the feeding rate of solution and tip-target distance. At lower and higher feeding rates, nanofibers with beads were observed. At 7.5 cm tip-target distance and below, the structures of nanofibers appeared not to be stabilized completely, indicating that the spun nanofibers were mostly wet when they reached the collecting target [21].

Juan Zhang et al. studied the effect of surface charge for Polyacrylonitrile (PAN) on electrospinning by adding LiCl. They have employed PAN/DMF solutions to verify the scaling laws; LiCl was used to control surface charge. The experiments show that the radius of jet depends upon the content of salt involved, a completely theoretical analysis was provided. When no salt was added in PAN, no fiber can be produced by electrospinning with a voltage of 5 kV. Assuming that the value of a linearly depends upon the salt concentration when salt concentration is less than 4 wt% LiCl. They found that the addition of small amount of salt is observed to dramatically increase fiber diameter and decrease the jet length [22].

Chatree Saiyasombat and Santi Maensiri reported the fabrication, morphology and structure of carbon nanofibers prepared by electrospinning a precursor of polyacrylonitrile (PAN)/dimethylformamide (DMF), followed by carbonization of the electrospun nanofibers. Effects of PAN concentration (4-12 wt %) and applied voltage (5-15 kV) on the morphology and distribution of the spun nanofibers diameter were investigated. Fibers with diameter ranging from 100 nm to 1600 nm were obtained depending on the electrospinning condition. The diameters of the as-spun nanofibers increased with increasing the solution concentration. On the other hand, the diameters of the fibers decreased with increasing applied voltage. The optimal parameters for obtaining the PAN-nanofibers with narrow size distribution of 481 ± 101 nm and without beads formation along the fibers were revealed [23].

Tong Wang and Satish Kumar studied about PAN nanofiber. Polyacrylonitrile (PAN) was electrospun as a function of electric field, solution flow rate, and polymer concentration (C). The fiber diameter increased with C and ranged from 30 nm to 3.0 µm. The fiber diameter increased with the flow rate and decreased when the electric field was increased by a change in the working distance. However, it did not change significantly when the electric field was varied by a change in the voltage at a given working distance. The fibers below about 350 nm diameter contained beads, whereas above this diameter, bead-free fibers were obtained [24].

Juthawan Sutasinpromprae et al. reported the fabrication and characterization of ultrafine polyacrylonitrile (PAN) fibers by electrospinning and further development of the as-spun PAN fibers into ultrafine carbon fibers. The effects of solution conditions and process parameters on morphological appearance and average diameter of the as-spun PAN fibers were investigated by optical scanning (OS) and scanning electron microscopy (SEM). The concentration, and hence the viscosity of the spinning solutions significantly affected the morphology and diameters of the as-spun PAN fibers. The applied electrostatic field strength and nozzle diameter slightly affected the diameters of the as-spun fibers, while the emitting electrode polarity did not show any influence over the morphology and size of the as-spun fibers [25].

S.Y. Gu et al. produced PAN nanofibers. Polyacrylonitrile (PAN) nanofibers as a precursor of carbon nanofibers with diameters in the range of 130–280 nm were obtained by electrospinning PAN/DMF solution. A flat metal plate with aluminum foil placed below served as a grounded counter electrode. The voltage between the electrode and the counter electrode could be controlled by the high voltage power supply. The applied voltages between the tip and collector were set at 20 kV with a tip-to-collector distance of 10 cm. The fibers dried in flight and collected on the aluminum foil in the form of non-woven fabric. For alignment of the fibers, two grounded stripes of aluminum foil were used as collectors. Molecular chains were oriented within the electrospun fibers during the electrospinning process. [26].

1.6.2. Literature Survey about Poly(vinyl alcohol) (PVA)

Pitt Supaphol et al. investigated the effects of solution concentration, applied electrical potential and collection distance on morphological appearance and diameters of the as-spun fiber mats. The effect of the distance from the center of the as-spun fiber mat on morphological appearance and diameters of the as-spun fibers was also investigated. At all concentrations and applied electrical potentials investigated, the average diameters of the as-spun PVA fibers ranged between 85 and 647 nm. The use lower viscosity of the solution decreases in the average diameters of the fibers [27].

Chunxue et al. prepared submicron poly(vinyl alcohol) (PVA) fiber mats by electrospinning of aqueous PVA solutions in 6– 8% concentration. Fiber morphology was observed under a scanning electron microscope and effects of instrument parameters including electric voltage, tip–target distance, flow rate and solution parameters such as concentration on the morphology of electrospun PVA fibers were evaluated. Results showed that, when PVA with higher degree of hydrolysis (DH) of 98% was used, tip–target distance exhibited no significant effect on the fiber morphology; however the morphological structure can be slightly changed by changing the solution flow rate. At high voltages above 10kV, electrospun PVA fibers exhibited a broad diameter distribution. With increasing solution concentration, the morphology was changed from beaded fiber to uniform fiber and the average fiber diameter could be increased from 87 ± 14nm to 246 ± 50nm [28].

Erika Adomavičiūtė and Rimvydas Milašius investigated the influence of applied voltage on Poly(vinyl alcohol) (PVA) nanofibre diameter. Nanofibers were manufactured using the electrospinning method for a 12% concentration solution of poly(vinyl alcohol) (PVA) water solution. Two sets of experiments were performed in order to evaluate the influence of the voltage applied on the PVA nanofiber diameters. In the first case nanofibers were collected on a PES substratum, in the second – on a PP substratum. Next, the average nanofiber diameter was calculated from all derivatives of the nanofibers and only from the thinnest nanofibers. Applied voltage does not have a significant influence on the diameter of PVA nanofibers formed directly from a rotating drum. It only influences the structure of nanofiber mat, i.e., an increase in the applied voltage causes an increase in the amount of nanofibers. After the elimination of stick nanofibers on the PES substratum, it was indicated that voltage applied does not have a significant influence on the nanofiber formation process. The same was stated when analyzing the diameter of nanofibers collected on the PP substratum; in this case all nanofibers were measured, because any stick nanofibers were visible on the substratum. Thus the elimination of stick nanofibers is a proper method for analyzing the nanofiber formation process [29].

Surawut Chuangchote and Pitt Supaphol reported a new technique, i.e., dual vertical wire technique, for fabrication of uniaxially-aligned fibers. This technique utilized two stainless steel wires that were vertically set in a parallel manner between a charged needle and a grounded collector plate. This technique allowed simultaneous collection of aligned fibers (between the parallel vertical wires) and a randomly-aligned fiber mat (on the collector plate). Application of the technique on poly (vinyl alcohol) (PVA) to prepare uniaxially-aligned fibers was found to be successful at short collection times. Unexpected formation of a large fiber tow consisting of individual as-spun nanofibers that were bound into a bundle was observed at long collection times. Morphological appearance and size of the fiber tow was affected by the change in the distance between the two vertical wire electrodes, while the average diameter of the individual fibers was not (i.e., about 340 to 350 nm) [30].

Jing Tao and Satya Shivkumar studied the cumulative effects of molecular weight and concentration on the structural transitions in the electrospun polymer. Experiments have been conducted with water as the solvent for molecular weights of polyvinyl alcohol (PVA) ranging from 9500 g/mol to 155,000 g/mol. The structural regimes for beads, beaded fibers, complete fibers and flat ribbons have been mapped. The development of a stable fiber structure generally corresponds to the onset of significant molecular entanglements. The molecular weight of the polymer has a significant role in establishing the structure in the electrospun polymer. The molecular weight dependent concentration regimes for beads, beaded fibers and fibers have been mapped. At a constant concentration, the structure changes from beads, to beaded fibers, to complete fibers and to flat ribbons as the molecular weight is increased [31].

Xiao-hong Qin et al. studied the effect of LiCl on PVA nanofibers on the variation of jet diameter with axial coordinate after the onset of whipping instability during electrospinning. Jet diameters at different points were measured by optical microscope. The results indicated that the addition of LiCl significantly accelerated jet thinning and solidification. It was found that average diameter of smooth jets decreased with increasing LiCl concentration. When LiCl concentration was equal or larger than 0.8 wt. %, surface charge became saturated and full charge on jet surface was obtained [32].

Tong Lin et.al used chitosan as a thickener for electrospinning dilute PVA solutions to improve fiber uniformity. Chitosan was added to PVA aqueous solutions as a thickener to improve the electrospinning process. The presence of a small amount of chitosan considerably improved the uniformity of as-spun nanofibers. This improvement is attributed to its significant effect on the solution viscosity and conductivity, with only a slight impact on the surface tension. The concentration of the PVA required to produce bead-free and uniform nanofibers was reduced with the increase in chitosan concentration. The chitosan thickener suppressed the jet break-up and facilitated the jet stretching so that fine and uniform fibers could be electrospun even from a dilute PVA solution. This study has shown that using the cationic polyelectrolyte chitosan as a thickener for electrospinning aqueous PVA solution can effectively improve the fiber uniformity and reduce the fiber diameter. Non-beaded and uniform fibers can be electrospun from a PVA solution of a low concentration that usually produces beaded fibers in the absence of a suitable thickener. At high solution viscosity, the jet break-up is effectively suppressed and the increased solution charge density enhances the fiber stretching. As a result, uniform nanofibers can be electrospun even if the solution concentration is close to its ‘overlap concentration’. It is expected that this concept will be suitable for electrospinning other polymer systems [33].

A. Koski et al. studied the effect of polymer weight average molecular weight (MW) on the fiber structure of electrospun polyvinyl alcohol (PVA). PVA with a degree of hydrolysis of 98–99% and with molecular weights ranging from 9000 to 186,000 g/mol was dissolved in water. The concentration of the polymer in the solution was varied depending on the molecular weight. The solution was electrospun at 30 kV and the sample obtained on the collector was examined by scanning electron microscopy. It was observed that for each molecular weight, a fibrous structure was stabilized above a minimum concentration. The fiber diameter increases with MW and concentration. At low MW (molecular weight) and/or concentrations, the fibers exhibit a circular cross-section. Flat fibers were observed at high MW and concentrations. The molecular weight of PVA and the solution concentration have a significant effect on the structure of the electrospun polymer. At each MW, there is a minimum concentration needed to stabilize the fibrous structure and maximum concentration where the solution cannot be electrospun. As the solution concentration increases, the fiber diameter and interfiber spacing increase and there is gradual shift from circular to flat fibers. In low molecular weight samples, this shift from circular to flat fibers occurs at a higher value of concentration than in polymers with high MW [34].

Mohammad Ziabari et al. studied simulated image of electrospun nonwoven web of PVA and corresponding nanofiber diameter distribution. Electrospun fiber diameter was measured by direct tracking. In order to examine the accuracy of the method, samples with known characteristics were produced. The method was also applied to measure fiber diameter of a real web produced from electrospinning of PVA. However, it could be used for measuring fiber diameter of any other electrospun webs; the choice of PVA was quite arbitrary and mostly due to ease of web formation of PVA. SEM micrograph of the web was converted to black and white by using local thresholding. Otsu's method was used to automatically determine the appropriate threshold. Mean and standard deviation of fiber diameter obtained from Direct Tracking for the real web were acceptably close to the manual method. The results indicate that the attempt to develop a high speed, computer automated algorithm for measuring electrospun nanofiber diameter has been successful [35].

Mi Nae Kim et al. prepared bicomponent polymer solutions from two immiscible polymers, poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN), and then used to prepare films and electrospun fibers. The surface morphology of the bicomponent polymer systems was determined. There was a strong relationship between the diameter of the electrospun fibers and the blend ratio used. By applying selective dissolution, using solvents such as hot water, acetic acid, or N,N-dimethylformamide, to the films and fibers, one polymer component was removed selectively without affecting the other component. This resulted in a decrease in the diameter of the electrospun fibers and the formation of grooves, pores, and craters on the fiber surface. The width of the grooves decreased as the bicomponent polymer content increased. PVA/PAN bicomponent fibers were successfully prepared using electrospinning. The PVA/ PAN had better spinnability than the homo PVA solution. To remove the PVA selectively, the fibers were immersed in hot water or acetic acid. Most of the PVA was removed by these treatments. Treatment resulted in a decrease in the diameter of the electrospun fibers and the appearance of grooves on the fiber surfaces along the fiber axis. The width of the Groove decreased as the PAN content increased. PAN was successfully removed by DMF treatment, and the resulting surface had grooves similar to those observed after PVA removal [36].

Surawut Chuangchote and Pitt Supaphol have demonstrated a new technique, i.e., a dual vertical wire technique, for fabricating uniaxially-aligned fibers. This technique used two stainless steel wires that were vertically set in a parallel manner between a charged needle and a grounded aluminum foil. At a right setup, simultaneous collection of aligned fibers (between the parallel vertical wires) and a randomly-aligned fiber mat (on the aluminum foil) could be achieved. When the technique was applied to PVA, aligned fibers were observed between the two vertical wires at short collection times. Further increase in the collection time resulted in some of these aligned fibers binding together to form a large nanofibrous fiber tow. While other system parameters were fixed, variation of the distance between the two wires only affected the appearance and size of the fiber tow, but did not affect those of the individual fibers. Young’s modulus, tensile stress at yield, and the maximum tensile stress were found to increase with decreasing diameter of the fiber tows. Thermal analysis revealed that the thermal behavior of the fiber tow was essentially similar to that of the as cast PVA film. This type of nanofibrous fiber tow may be of some uses to applications that require a material with a high surface to mass or volume ratio, a high porosity, and a high degree of orientation of the individual as-spun fibers within a tow [37].

1.6.3. Literature survey about Polyamide 6 (PA6)

Mohamed B. Bazbouz and George K. Stylios examined nonwoven electrospun nylon 6 nanofibers produced with formic acid under different concentrations. The effects of the solution properties, electric field, and spinneret-to-collection distance on the fiber uniformity, morphology, and average diameter have been established. Various polymer solution concentrations ranging from 15 to 25 wt % were prepared by the dissolution of the polymer in formic acid. Typical operating regimes were flow rates of 0.2 ml/h, applied voltages between 12 and 18 kV, and a working distance of 5–11 cm. The optimum polymer solution concentration (20 wt %), applied voltage (15 kV), and spinning distance (8 cm) have been found to make uniform nylon 6 fibers [38].

Yan Li et al. prepared ultrafine nylon fibers by electrospinning of nylon-6 solution in trifluoroethanol (TFE). The morphology, crystallinity and mechanical properties of the electrospun nylon-6 fibers were investigated by scanning electron microscope (SEM), differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD) and tensile test. The effects of electrospun process parameters such as solution concentration, voltage and tip to-collector distance on the morphology and the average size of the electrospun fibers were also studied. The results show that the spinnable concentration of nylon-6/TFE solution is in the range of 6–14 wt%, and higher solution concentration favors the formation of uniform fibers without beads. The diameters of the electrospun fibers increase with increasing the solution concentration and decrease slightly with increasing the voltage and needle tip-to-collector distance. But no obvious morphology changes were found with the increase of the voltage and collection distance. The electrospun nylon-6 membrane obtained from the 14 wt% concentration exhibits the largest tensile strength and elongation at break [39].

Chidchanok Mit-uppatham et al. produced ultrafine polyamide-6 (PA-6) fiber. The effects of solution conditions on the morphological appearance and the average diameter of as-spun fibers were investigated by optical scanning (OS) and scanning electron microscopy (SEM) techniques. It was shown that the solution properties (i.e. viscosity, surface tension and conductivity) were important factors characterizing the morphology of the fibers obtained. Among these three properties, solution viscosity was found to have the greatest effect. Solutions with high enough viscosities were necessary to produce fibers without beads. At a given concentration, fibers obtained from PA-6 of higher molecular weights appeared to be larger in diameter, but it was observed that the average diameters of the fibers from PA-6 of different molecular weights had a common relationship with the solution viscosities which could be approximated by an exponential growth equation. Raising the temperature of the solution during spinning resulted in the reduction of the fiber diameters with higher deposition rate, while mixing m-cresol with formic acid to serve as a mixed solvent for PA-6 caused the solutions to have higher viscosities which resulted in larger fiber diameters. Lastly, the addition of some inorganic salts resulted in an increase in the solution conductivity, which caused the fiber diameters to increase due to the large increase in the mass flow [40].

Gil Tae Kim et al. tested the filtration characteristics of a Nylon 6 nanofilter made by electrospun nanofibers as a function of the fiber diameter. Nanofilter media with diameters in the range of 100-730 nm can be produced in optimized conditions. The pressure drop of a Nylon 6 nanofilter linearly increases with the increasing face velocity. An electrospun Nylon 6 filter (mean fiber diameter: 100 nm) shows a much lower pressure drop performance relative to the commercial HEPA filter media when the filtration efficiency of the Nylon 6 nanofilter and the HEPA filter are over 99.98% with test particles of 0.02-1.0 mm in diameter. The pressure drop at 5 cm/s of the face velocity is measured as 27 mm Ag for the Nylon 6 nanofilter media, and 37.1 mm Ag for the HEPA filter media. The particle size with minimum efficiency decreases with the decreasing fiber diameter. And the minimum efficiency becomes greater as the fiber diameter is decreased [41].

C.J. Thompson et al. determined the effects of 13 material and operating parameters on electrospun fiber diameters by varying the parameter values in an electrospinning theoretical model. The complexity of the electrospinning process makes empirical determination of the effects of parameters very difficult. The results show that the five parameters (volumetric charge density, distance from nozzle to collector, initial jet/orifice radius, relaxation time, and viscosity) have the most significant effect on the jet radius. The other parameters (initial polymer concentration, solution density, electric potential, perturbation frequency, and solvent vapor pressure) have moderate effects on the jet radius. Parameters relative humidity, surface tension, and vapor diffusivity have minor effects on the jet radius. Knowing the relative effects of parameters on jet radius should be useful for process control and prediction of electrospun fiber production [42].

Pirjo Heikkila et al. demonstrated electrospinning of several polyamides, PA6, PA66, PA612, PA614, PA1012, and PA1014, with different chain structure. The fiber formation of PA66 depended predictably on polymer solution concentration, and they found that nanofibers can be formed in a wide range of the solution concentrations. Fibers were obtained with a solution concentration of 10% regardless of the used PA grade. Electrospinning of higher polyamides having longer diacid and diamine segments was, though, more difficult than electrospinning of PA66 and PA6. Viscosities of solutions at room temperature predicted slightly the diameter of the forming fibers, but also other parameters affect it. Fiber diameters of PA66 and PA612 were smaller and fiber production rates higher than of other polyamides. The largest fiber diameters were observed with those polyamides that were electrospun from heated solutions. Electrospun PA6 was found to be c-form as expected, but ageing of the electrospun sample revealed that the crystalline c-structure of PA6 is not stable and it seemed to be changing to a more stable a-form during time [43].

Chidchanok Mit-uppatham et al. produced ultra-fine polyamide-6 fibers. The effects of some of the influencing solution and process parameters (i.e. solution concentration, emitting electrode polarity, solvent type, and salt addition) on morphological appearance of the obtained fibers were visually observed from a series of scanning electron micrographs. It was found that solutions with high enough viscosity values were necessary to result in electrospun polyamide-6 fibers having uniform diameters. Mixing m-cresol with formic acid to be used as the mixed solvent for dissolving polyamide-6 affected the morphological appearance a great deal. It was found that diameters of the fibers obtained increased with increasing amount of m-cresol and, at m-cresol content of greater than 40 percent by weight, fused fibers were formed, attributable to the higher boiling of m-cresol. It was found that flat fibers were obtained with use of the negative polarity of the emitting electrode. Lastly, increased conductivity of the solutions by increasing amount of NaCl salt addition resulted in fibers of larger sizes [44].

Chaobo Huang et al. prepared nylon-4,6 nanofibres with diameters ranging from about 1 μm down to 10 nm by electrospinning. The fiber diameter was varied by adjusting the concentration of the polymer solution. Electrospinning of a concentrated solution of as high as 20% nylon-4,6 by weight in formic acid produced a ribbon-like electrospun fiber with a ribbon width of about 850 nm. A semi-dilute concentration of 2% nylon-4,6 by weight produced the thinnest nylon-4,6 nanofibers with diameters of 1.6 nm or less. A small amount of pyridine was added to the electrospinning solution to avoid the formation of beaded nanofibers in the course of electrospinning at low concentrations. Scanning and transmission electron microscopy were used to characterize the size of the nanofibers. An ultra-thin nylon-4,6 nanofiber of 1.2 nm diameter might contain six or seven nylon-4,6 molecules in a typical cross-section of the fiber [45].

Kuitian Tan et al. used to electrospinning technique fabricate nanofibrous nylon 6 membranes. To achieve antimicrobial properties, three structurally different N-halamines were introduced into the electrospinning dopes of nylon 6. Nanofibrous nylon 6 membranes were prepared with a range of nanofibers from above 500 nm to below 100 nm. X-ray analysis showed that N-halamines were uniformly distributed on the electrospun membrane surface. DSC and WAXD results showed that the presence of N-halamines in the nylon 6 system induced the formation of phase crystals. Structure–property relationships between N-halamines and antimicrobial properties were examined. It was found that with the same active chlorine contents, CDMH resulted in faster antimicrobial actions while CDDMH acted much slower due to both the slower reaction of chloroamide group and the attached long alkyl chain. With the increase in the N-halamine concentration for electrospun nylon 6 membranes, the active chlorine contents increased, resulting in a higher antimicrobial rate and larger microbial reduction [46].

Lei Li et al. prepared nanocomposite fibers of nylon-6 and an organically modified montmorillonite (O-MMT), Cloisite-30B. Dispersion and exfoliation of O-MMT in nylon-6 were achieved by melt-extrusion in a twin-screw extruder prior to dissolving in aqueous formic acid for electrospinning. The effects of O-MMT layers on the properties of the nylon-6 solution and electrospun nanocomposite fibers were investigated. Homogeneous, cylindrical nanocomposite fibers with diameters ranging from 70 to 140 nm could be prepared from the 15% composite solution. The O-MMT layers were well exfoliated inside the nanocomposite fibers and were oriented along the fiber direction. Both the degree of nylon-6 crystallinity and the crystallite sizes increased for the nanocomposite fibrous mats, most significantly for those composed of the smallest fibers electrospun from 15% solution. The mechanical properties of the electrospun fibrous mats and single fibers depended not only on the addition of O-MMT layers but also on the sizes of the fibers. Smaller fibers exhibited higher Young's modulus [47].

Andrea Bianco et al. reported, for the first time, the modification of wettability of PA6 electrospun nanofibers by means of a doping procedure. PA6 fibers were electrospun from formic acid solutions, and from FESEM images, it appeared that the polymer fibers have a smooth surface and homogeneous diameters. Contact angle measurements were carried out to study the wettability of PA6 before and after the doping with a perfluorinated acridine. The comparison between the contact angle values of films and fibers of pure PA6 pointed out that morphology does not play a relevant role in wettability. Small quantities of an acridine bearing a perfluorinated alkyl chain were used as dopant to reduce the wettability; even at low concentration, an appreciable increment of the contact angle took place, thus indicating that even at room temperature surface segregation of perfluorinated alkyl chains occurs during the electrospinning process. [48].

Satyajeet S. Ojha et al. used the electrospinning technique to produce nanoscale fibers of nylon-6. The core objective of this study was to fabricate nanofibers of high molecular weight of nylon-6 to understand the effect molecular weight has on morphology and mechanical properties of electrospun fibrous mats. Variation in surface tension was shown to be insignificant as a function of changes in molecular weight and concentration of the polymer. Not surprisingly however, the viscosity was strongly influenced by changes in molecular weight and concentration. Molecular weight and concentration significantly affect the morphology of the nanofibers. Changes in voltage have a strong effect on the morphology on nanofibers. With an increase in voltage, more fibers are formed with less beads and larger diameters. For high-molecular-weight nylon-6, it was possible to manufacture nanofibers at lower voltages (as compared with low and medium-molecular- weight nylon-6). With an increase in tip-to collector distance (thereby increasing the time of flight of nanofibers), a reduction in diameter size is observed (as well as the diameter distribution). The diameter of electrospun nanofibers increased with an increase in feed rate. Favorable feed rate to produce nanofibers was higher in case of low molecular weight and lower in case of high molecular weight nylon-6 [49].

1.7. Purpose of Thesis

The aim of the study is to determine most suitable values (or intervals) for solution and process parameters for electrospinning of Polyacrylonitrile (PAN), Poly (vinyl alcohol) (PVA) and Polyamide (PA6) polymers. These parameters have strong effect on the morphology of nanofibers. The basic parameters (not all of them) such as solution concentration, voltage and tip-collector distance were studied systematically to determine their optimal values. The optimal values were determined by analyzing SEM images of those samples by regarding following criteria;

1) bead formation,
2) finesses of diameter
3) uniform of diameter

The nanofibers should have the finer diameter without including beads and diameter variations to be most suitable one.

1.8. Structure of thesis

Chapter 2 is named as ‘’ Electrospinning Process’’. The main purpose of this chapter is to give detailed information about electrospinning process. This chapter includes the explanation of apparatus and parts of the experimental set-ups which were used in the experiments.

Chapter 3 is named as ‘’Polyacrylonitrile (PAN)’’. In this chapter the experimental study about PAN was given. The results of experimental study were explained in details with figures and graphics. Effects of voltage, concentration, tip-collector distance, humidity, temperature on PAN nanofiber morphology were searched out. The optimum values were determined at which the most uniform formations of nanofibers were obtained.

Chapter 4 is named as ''Poly(vinyl alcohol) (PVA) ''. In this chapter the experimental results about PVA are given. The results of experimental study are observed in details with figures and graphic. Effects of voltage, concentration, tip-collector distance on PVA nanofiber morphology were searched out. The optimum values were determined at which the most uniform formations of nanofibers were obtained.

Chapter 5 is named as ''Polyamide 6 (PA 6) ''. In this chapter the experimental results about PA6 is given in details supported by figures and graphics. The results of experimental study are observed in details with figures and graphic. Effects of voltage, concentration, tip-collector distance on PA6 nanofiber morphology were searched out. The optimum values were determined at which the most uniform formations of nanofibers were obtained.

Chapter 6 is named as '' Conclusions and Recommendations Future Works''. In this chapter there is a summary of chapter 3, 4 and 5.

CHAPTER 2

ELECTROSPINNING PROCESS

2.1. Introduction

Electrospinning is a process that produces continuous polymer fibers with diameters in the sub-micron range through the action of an external electric field imposed on a polymer solution or melt. Non-woven textiles composed of electrospun fibers have a large specific surface area and small pore size compared to commercial textiles, making them excellent candidates for use in filtration and membrane applications. While the process of electrospinning has been known for over half a century, current understanding of the process and those parameters, which influence the properties of the fibers produced from it, is very limited [8].

In electrospinning, a high voltage is applied to a polymer fluid such that charges are induced within the fluid as shown in Figure 2.1. When charges within the fluid reached a critical amount, a fluid jet will erupt from the droplet at the tip of the needle resulting in the formation of a Taylor cone. The electrospinning jet will travel towards the region of lower potential, which in most cases, is a grounded collector. There are many parameters that will influence the morphology of the resultant electrospun fibers, from beaded fibers to fibers with pores on its surface [1].

The parameters affecting electrospinning and the fibers may be broadly classified into polymer solution parameters, processing conditions which include the applied voltage, temperature and effect of collector, and ambient conditions [50].

Figure 2.1 Electrospinning process

With the understanding of these parameters, it is possible to come out with setups to yield fibrous structures of various forms and arrangements. It is also possible to create nanofiber with different morphology by varying the parameters [50].

2.2. Experimental Electrospinning System

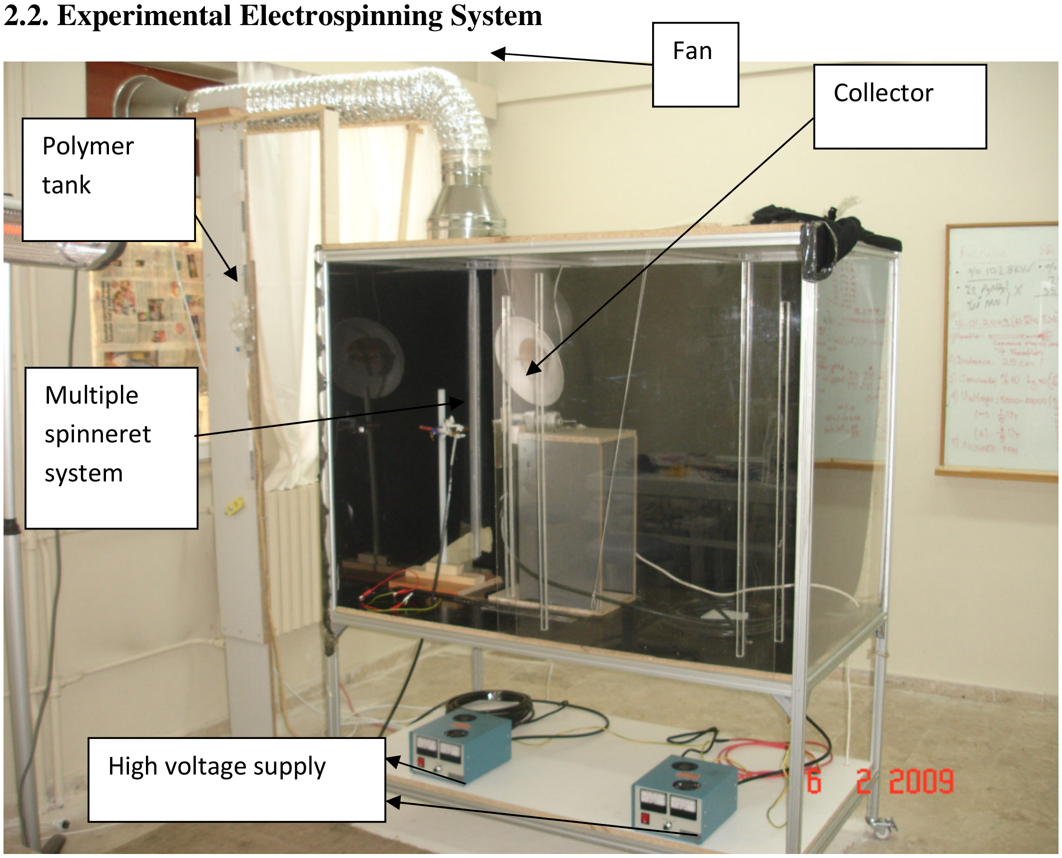


Figure 2.2 Experimental set-up

The electrospinning cabin consists of two adjustable DC high voltage sources (0-50kV), multiple spinneret system and a movable collector as shown in Figure 2.2. High voltage sources were located into the first floor of the cabinet. The needles, the needle platform and the collector (adjustable distance) were positioned in the second floor. The collector is a brass rectangular plate which is designed to move forward-backward and upward-downward while the motor is rotating in order to obtain a uniform nanofiber distribution. Also there is a fan which will send away the solvent vapor and freely flaying nanofibers from the cabinet. Negative power supply is used to direct the nanofibers on to the collector by charging the collector with negative voltage. The parts of the experimental set-up are given below.

2.3. Parts of electrospinning system

2.3.1. Multiple spinneret system

Electrospinning provides a relatively versatile method of creating a variety of ultra thin nanofibers. One of the well known problems in electrospinning is low productivity. To increase the inherently low productivity in electrospinning, an assembly of multi-needles has been widely introduced [51]. Multiple spinneret system is used in order to increase production speed and amount of nanofibers collected on rotating collector as shown in Figure 2.3.

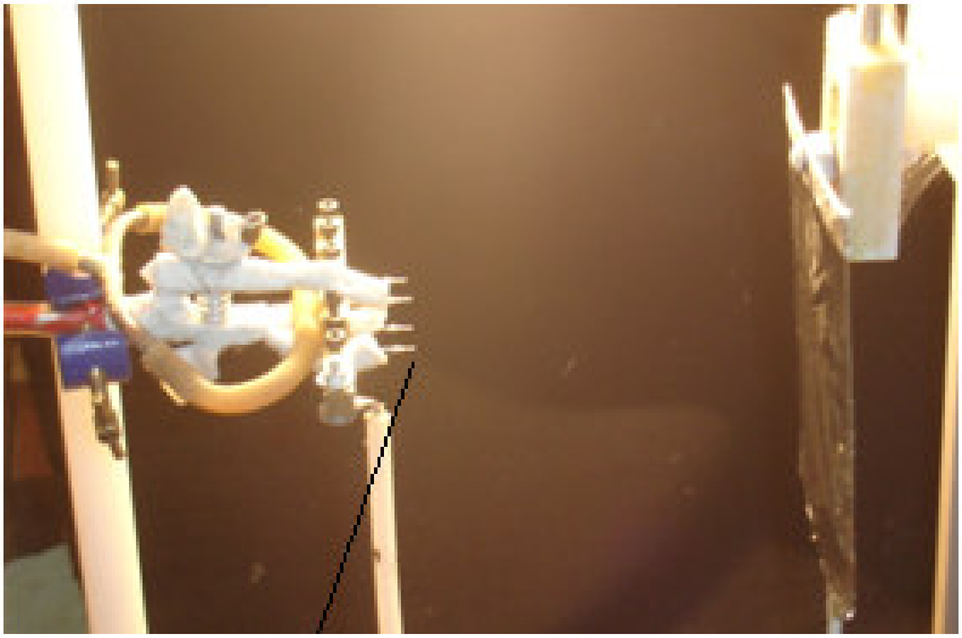


Figure 2.3 multiple spinneret system

2.3.2. Collector

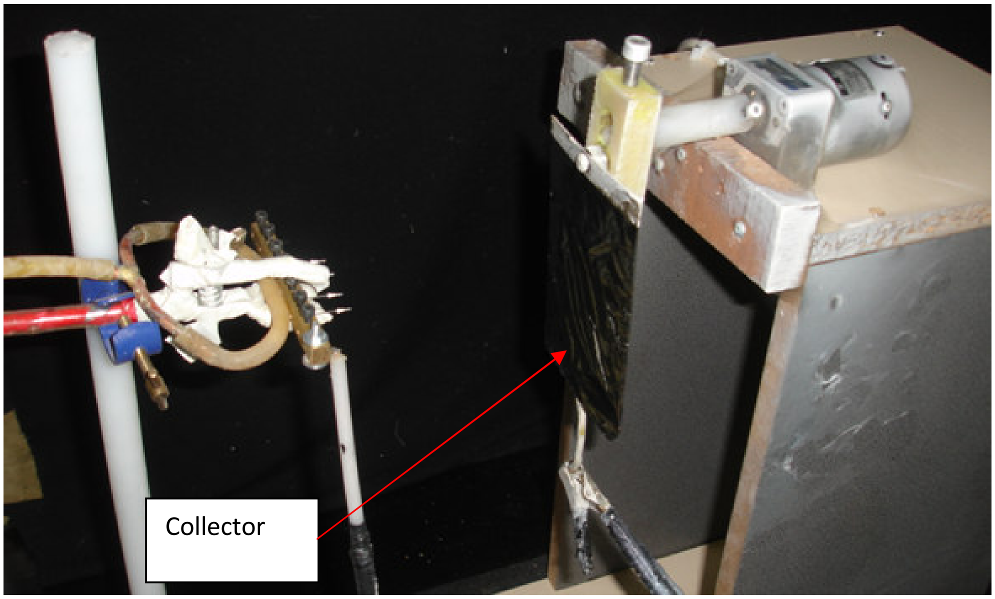


Figure 2.4 Collector

The collector is connected to a DC motor with adjustable speed (1-40 rev/min) to distribute the nanofibers uniformly on the surface of the aluminum foil as given in Figure 2.4. The distance between the collector and the needle is also adjustable to examine the effect of the tip-collector distance on the fiber morphology of nanofibers. The fibers are collected on the aluminum foil in the form of non-woven fabric.

2.3.3. Polymer reservoir

The polymer solution is driven through the needles from polymer reservoir which can be moved up and down in vertical direction to set the optimal flow rate. The optimal flow rate may be described as the flow rate that is sufficient to support the formation of drop but not high to sustain dripping.

Figure 2.5 Polymer reservoir

2.3.4. Power sources

DC power sources are at first floor of the cabin (see Figure 2.6). They are connected to the system with special cables. The positive end (+) is connected to multiple spinneret system whereas the negative end (-) is connected to collector. The negative voltage is used to direct the nanofibers on the collector rather than on to other metallic parts. Both high voltage power supply used in the experiments can provide voltages between 0 and 50 kV.

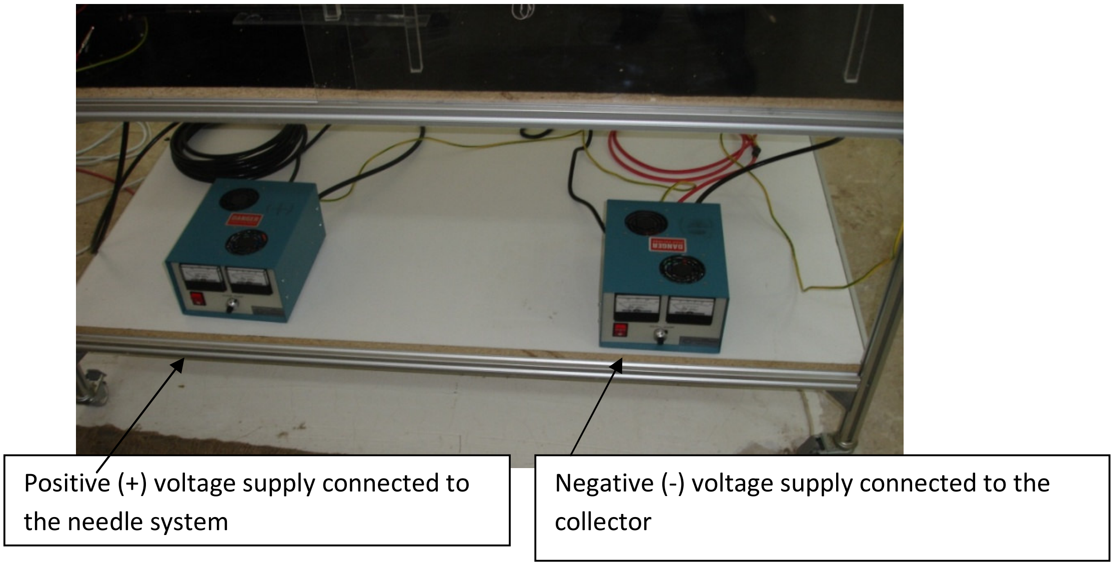


Figure 2.6 Power supply

CHAPTER 3

POLYACRYLONITRILE (PAN)

3.1. Introduction

The aim of the chapter is to search about parameters which affect the diameter of nanofiber and determine the optimal production values (thinnest, uniform and bead free) for PAN nanofibers. It has been found that morphology such as fiber diameter and its uniformity of the electrospun nanofibers are dependent on many parameters. Some of them;

- Concentration of solution
- Conductivity
- Voltage
- Distance between the tip and collector
- Flow rate
- Temperature
- Relative humidity.

3.2. Materials and preparation of spinning solutions

In the study 3 different types of fibers will be examined which are;

1-PVA (polyvinyl alcohol)

2-PA 6 (nylon 6)

3-PAN (polyacrylonitrile)

In this chapter the effects of selected parameters (concentration, voltage and tip-collector distance) on the morphology of PAN nanofibers will be examined. PAN (polyacrylonitrile) polymer [Mw 150,000] was gently supplied from AKSA Acrylic. The solvent used was dimethylformamide (DMF). To conduct the experiment a solution was prepared by dissolving PAN polymer in DMF. The solution was arranged by stirring magnetically for one hour at a temperature of 90 °C.

3.3. Electrospinning

To investigate the concentration effect on nanofiber morphology; solutions (6-16% with 2% intervals) were prepared by dissolving PAN polymer in dimethylformamide (DMF). Other parameters were kept constant (distance, voltage, flow rate, relative humidity and temperature) during the experiment to obtain the clear effect of the related parameters. To examine the effect of voltage on nanofiber diameter, the voltage was changed between 5-40 kV (5 kV intervals). Similarly, to analyze the effect of distance on nanofiber diameter, it is changed in interval 5-25 cm (5 cm interval). To examine the effect of relative humidity on electrospinning of PAN nanofibers the temperature was adjusted at 25°C and the values of relative humidity were gradually increased from 25% to 50% with 5% intervals. The other parameters such as flow rate, jet diameters were selected as 0.5ml/hour and 0.7mm respectively. The ambient temperature was adjusted at 20°C and the humidity is kept at 30 %. To analyze the effect of temperature on the electrospinning of PAN nanofibers the relative humidity was adjusted to 35% and the temperature values were increased step by step (with 5°C interval) from 15 °C to 35 °C.

3.4. Characterization

The morphological appearance of the as-spun PAN fiber mats and that of the individual fibers was investigated by a JEOL JSM-6390LV scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV.

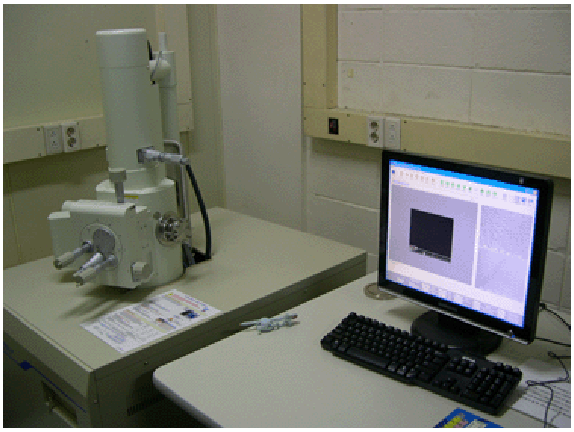


Figure 3.1 JEOL JSM-6390LV scanning electron microscope

3.5. Measurement of nanofiber diameters

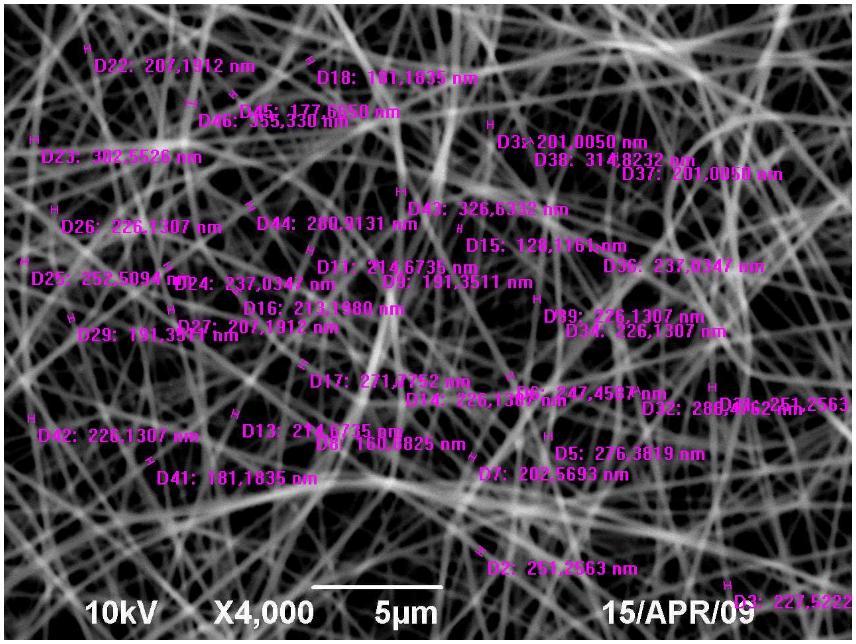


Figure 3.2 Calculation average diameters of nanofibers.

The diameters of nanofibers were measured using Image-Pro Plus 6.0. 20 measurements were performed and average diameter of the nanofibers was calculated (see Figure 3.2).

3.6. Decision parameters

After measuring the fiber diameters the morphology of nanofibers were analyzed in order to find the most favorable values. The decision parameters are fiber diameter, bead formation and diameter variation as given in Figure 3.3.

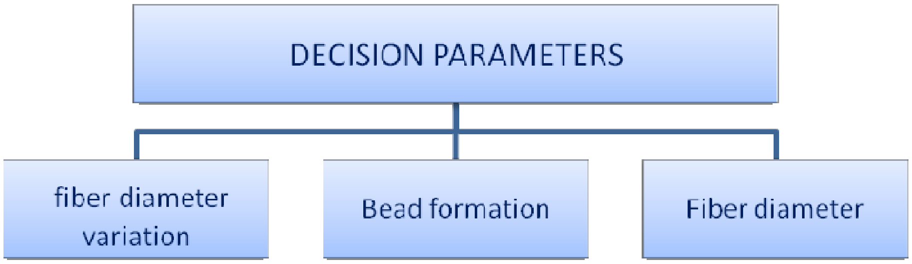
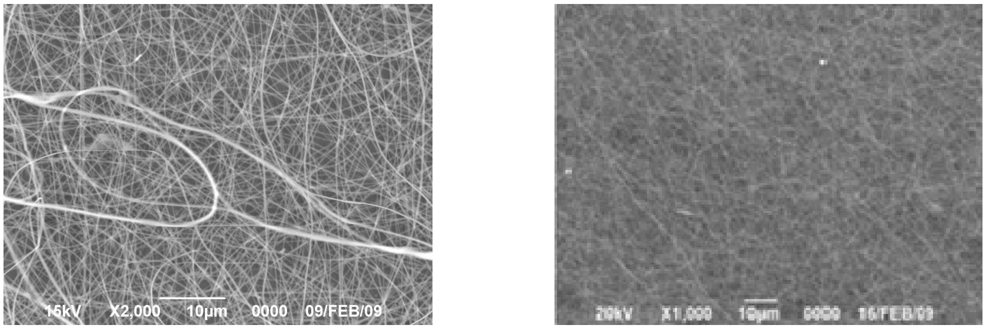


Figure 3.3 Decision parameters

3.6.1. Fiber diameter variation

The diameter of nanofibers may vary through the length of nanofiber which reduces the quality as shown in Figure 3.4. Therefore, minimum diameter variance is one of the quality criteria of good quality nanofibers as given in Figure 3.4.



a) Poor quality fiber (Diameter variations)

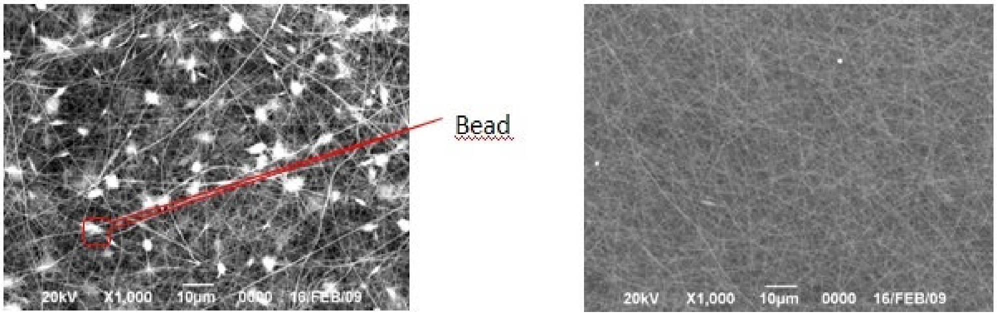
b) Good quality fiber (No diameter variation)

Figure 3.4 (a-b) Fiber diameter variations

3.6.2. Bead Formation

Electrospun fibers often have beads as ''by products''. The formation of beaded fibers has been observed widely. The electrospun beaded fibers are related to the instability of the jet of polymer solution. The breakup of water jets are depended on the electrical current. The more current the water jet carried, the less likely it was to form droplets. Nanofibers show that solution viscosity, net charge density carried by the electrospinning jet and surface tension of the solution are the main factors. Higher viscosity favors formation of fibers without beads. Higher net charge density not only favors formation of fibers without beads, but also favors the formation of thinner fibers. Surface tension drives towards the formation of beads, hence reduced surface tension favors the formation of fibers without beads [11, 18]. As the concentration increases the bead formation decreases. The other factor that supports the bead formation is the high surface tension. The contraction of the radius of the jet, which is driven by surface tension, causes the remaining solution to form beads. As the viscosity of the solution is increased, the beads become bigger, the average distance between beads longer, the fiber diameter larger, and the shape of the beads changes from spherical to spindle-like. As the net charge density increases, the beads become smaller and more spindle like, while the diameters of fibers become smaller. Decreasing the surface tension make the beads disappear gradually [18].

The minimum bead formation (no beads) is the first priority of good quality of nanofiber. Figure 3.5 show the images of nanofibers with and without beads.

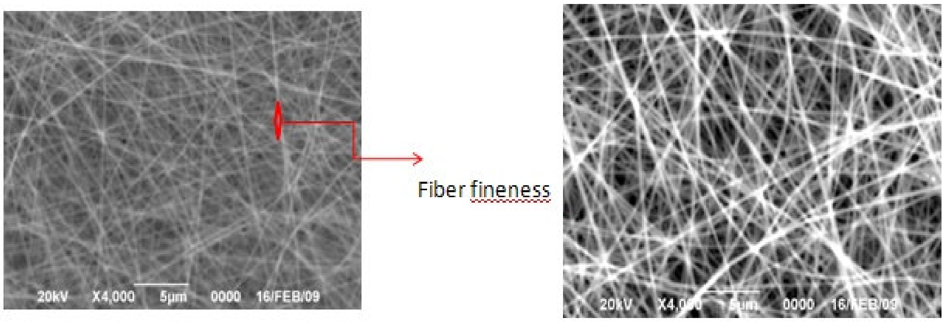


a) Poor quality fiber (with beads) b) Good quality fiber (no beads)

Figure 3.5 (a-b) Nanofibers with and without beads

3.6.3. Fiber diameter fineness

It is considered that electrospun nanofibers with high surface area can supply better efficient reinforcement and may be possible to achieve excellent mechanical performance. Because of their great surface area, nanofiber fabrics are capable of neutralization for chemical agents without impedance of the air and water vapor permeability to the clothing. It was also shown that those with smaller diameter of fibers had better filtration efficiencies. Therefore the third quality criterion is the fiber fineness and hence small in diameter means better in quality [1]. Figure 3.6 show two PAN nanofibers where Figure 3.6-a shows thin but Figure 3.6 -b shows thick nanofibers.



a)Good quality fiber (fine fibers) b)Poor quality fiber (coarse fibers)

Figure 3.6 (a-b) Fiber diameter fineness

3.7. Experimental study

At this part SEM photos of nanofibers were analyzed to examine effects of concentration, voltage, distance, temperature and humidity.

3.7.1. Effect of concentration

It is known that, in order to get uniform nanofiber diameter, the spinning solution with a proper concentration is required. When the concentration of the solution is too low, a uniform formation of nanofiber isn’t formed. Instead, low concentration causes formation of droplets. However, if the solution concentration is too high, continuous electrospinning process becomes difficult. As a result, there is a processing limit in terms of the concentration or the viscosity range within which the polymer solutions are electrospinnable. For a given applied electrical potential, the diameters of the spun fiber mats increases monotonically with increasing the solution concentration.

The concentration range is between 6-14%. In fact concentration 16% was also tried. But the production speed was so low and electrospinnability was difficult. Therefore, the regular experimental samples could be taken upto 14% concentration. In the experiments it was observed that as the concentration increases, the fiber diameter increases by representing a linear relationship as shown in Figures 3.7-3.18. At low concentrations (at 6%), the electrospinning process generated a mixture of fibers and droplets (see Figure 3.8(a)). The amount of beads was reduced considerable when the concentration was 8% as shown in Figure 3.12(b). However, beads were not observed for the values of concentration between 10% and 14%. As it is mentioned before the fineness is an important parameter and finer nanofiber diameter is demanded. As a result the most suitable concentration values were obtained between 10-12% since lower concentrations produce beads but higher concentrations produce larger fiber diameter. The average fiber diameter at this concentration was between 220-260 nm. Experimental study could not be carried out at short distance (5cm) regularly for most of solution concentrations and voltage values due to spark formation and other reasons. Therefore, their graphics and SEM images were not included. In the same way, nanofiber formation was not observed or it was quite time consuming at low voltage values, therefore they were also not included herein.

3.7.1.1. When the distance is 10 cm

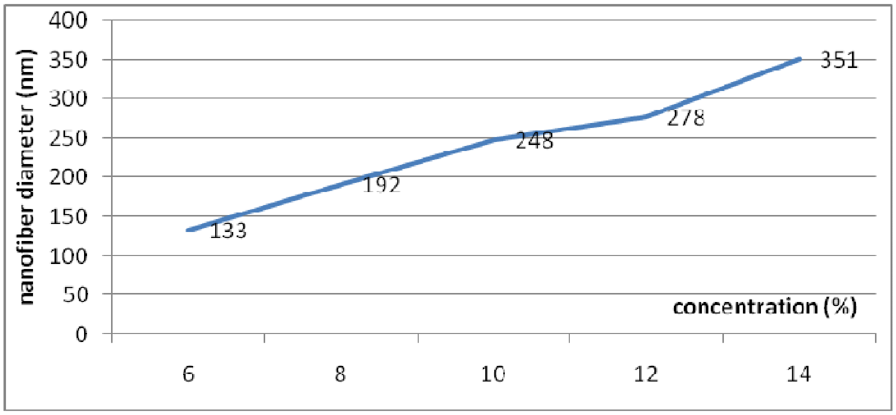
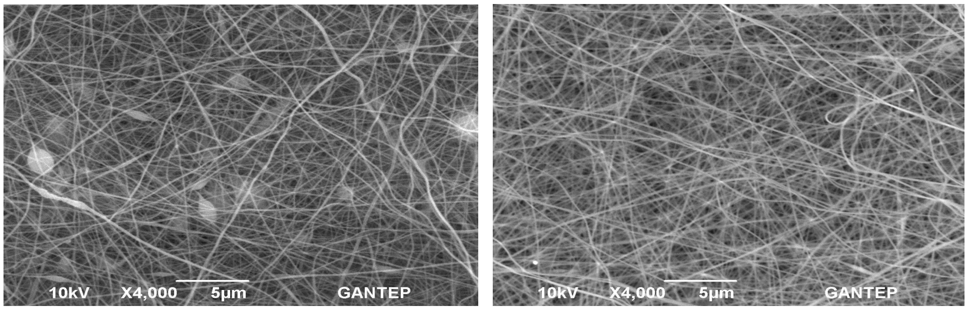
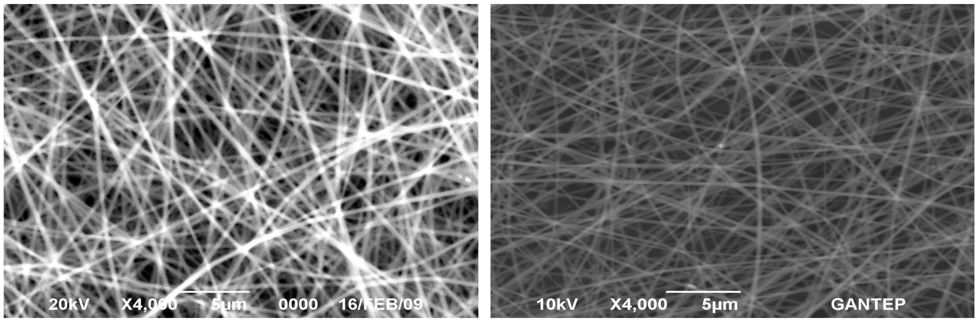


Figure 3.7 Effect of concentration on PAN fiber diameter (10 cm and 25 kV)



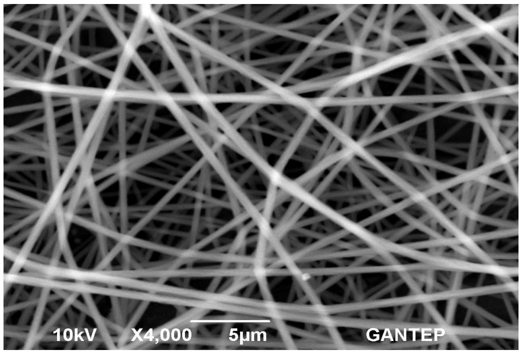
a) concentration 6%

b) concentration 8%



c) concentration 10%

d) concentration 12 %



e) concentration 14 %

Figure 3.8 (a-e) Effect of concentration on PVA fiber diameter (10 cm and 25 kV)

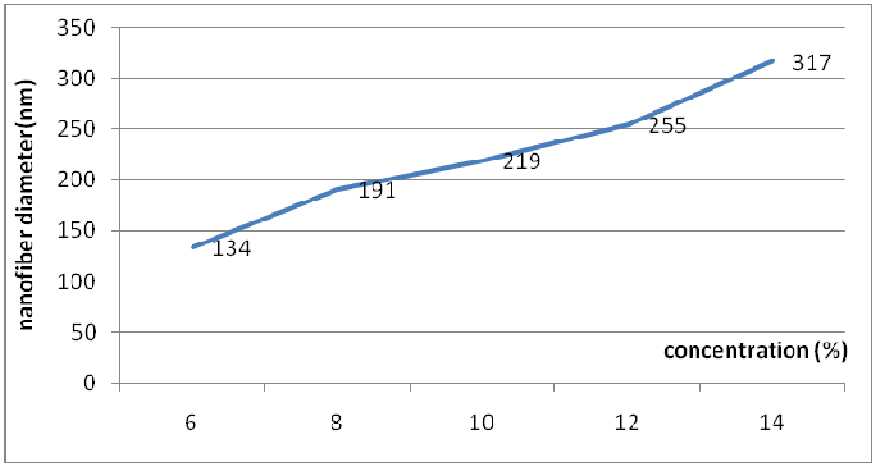
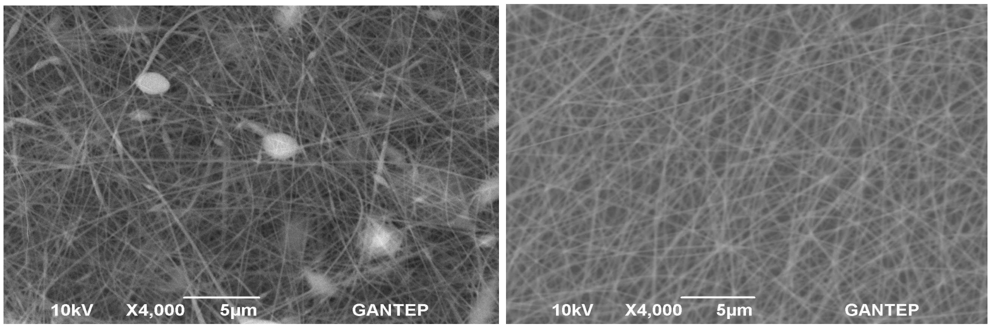
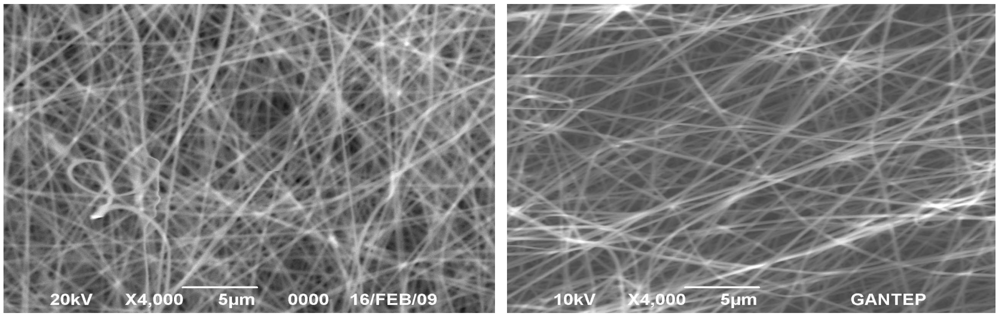


Figure 3.9 Effect of concentration on PAN fiber diameter (10 cm and 30 kV)



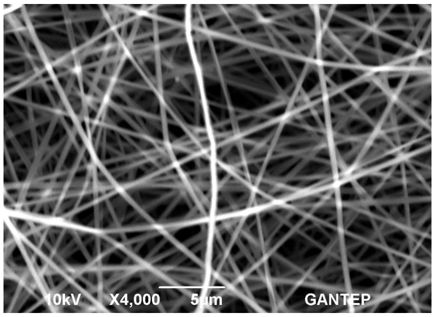
a) concentration 6%

b) concentration 8%



c) concentration 10 %

d) concentration 12 %



e) concentration 14 %

Figure 3.10 (a-e) Effect of concentration on PAN fiber diameters (10 cm and 30 kV)

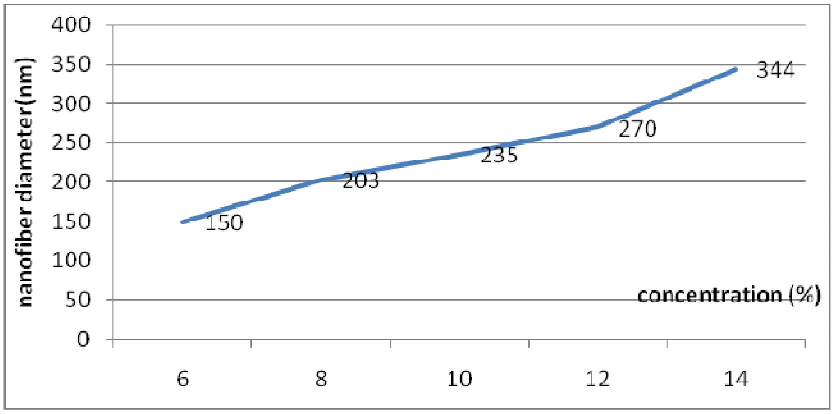
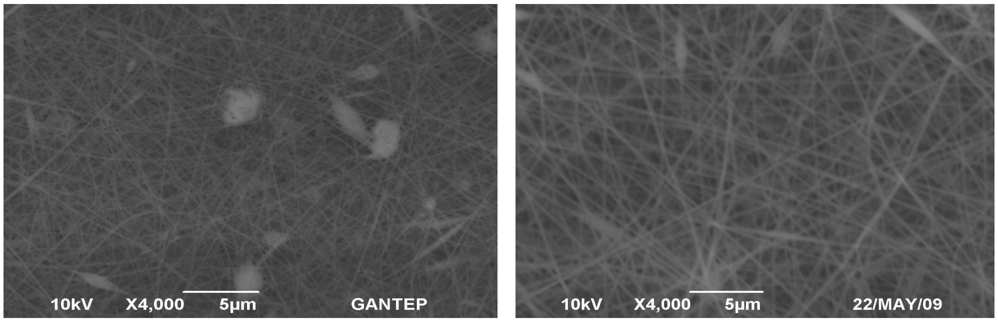
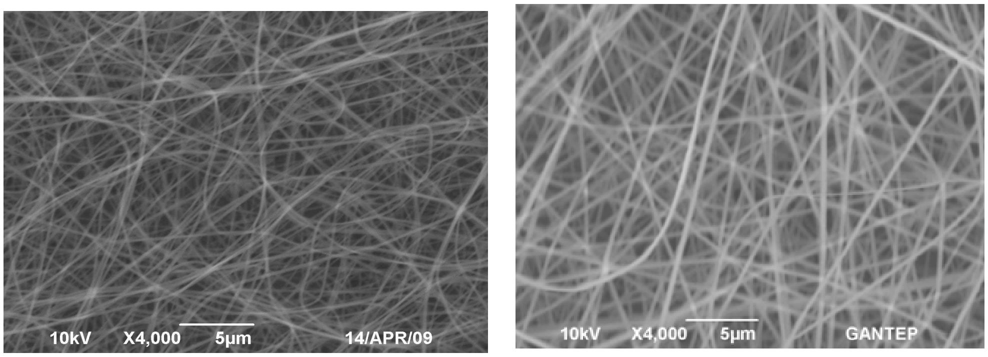


Figure 3.11 Effect of concentration on PAN fiber diameter (10 cm and 35 kV)



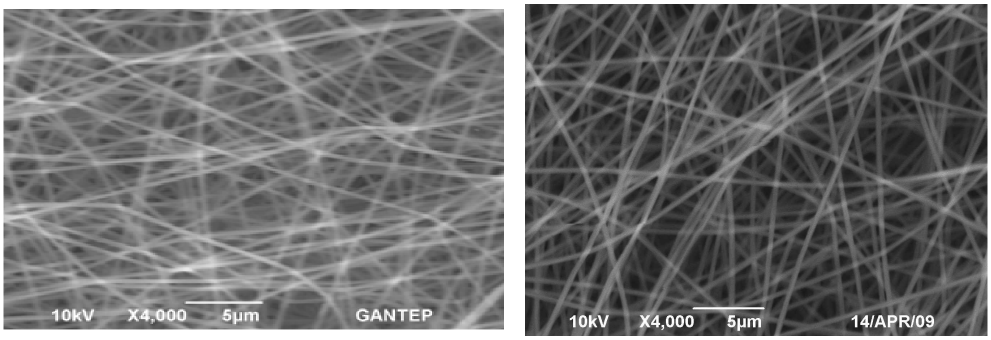
a) concentration 6%

b) concentration 8%



c) concentration 10 %

d) concentration 12 %



e) concentration 14 %

f) concentration 16 %

Figure 3.12 (a-f) Effect of concentration on PAN fiber diameters (10 cm and 35 kV)

3.7.1.2. When the distance is 15 cm

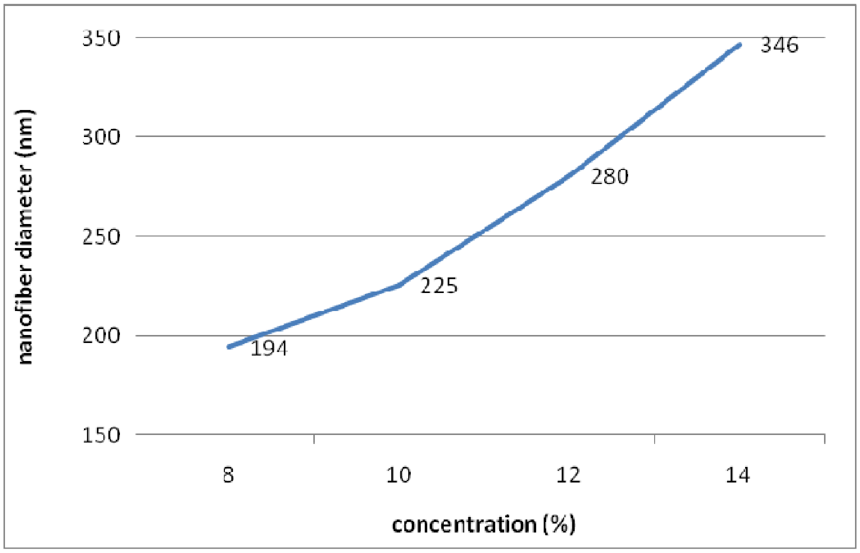
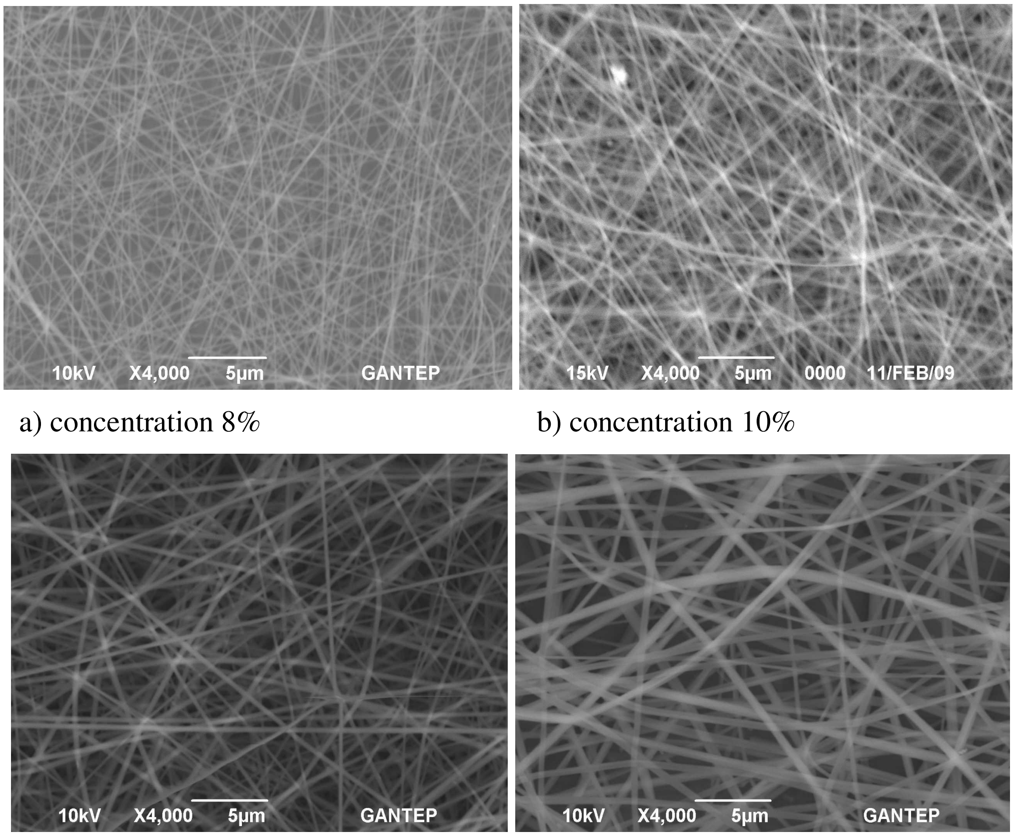


Figure 3.13 Effect of concentration on PAN nanofiber diameter (15 cm and 25 kV)



a) concentration 8%

b) concentration 10%

c) concentration 12 %

d) concentration 14%

Figure 3.14 (a-d) Effect of concentration on PAN fiber diameter (15 cm and 25 kV)

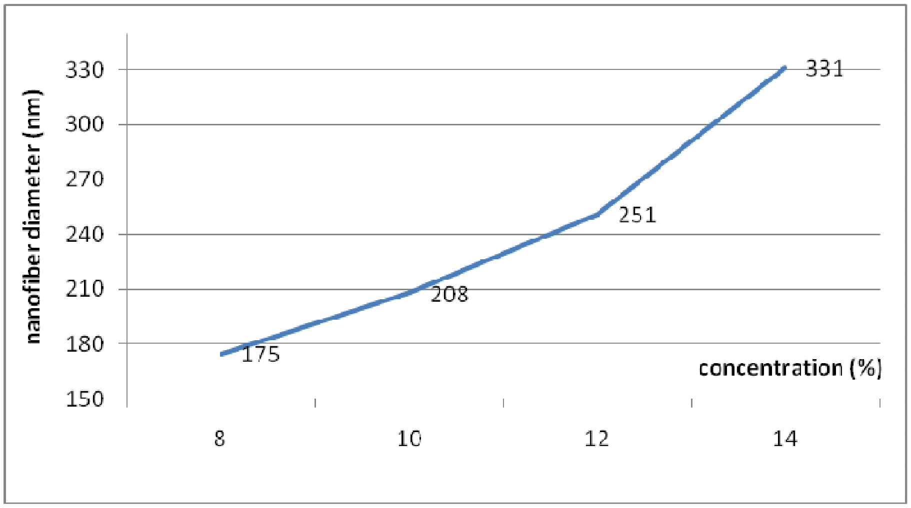
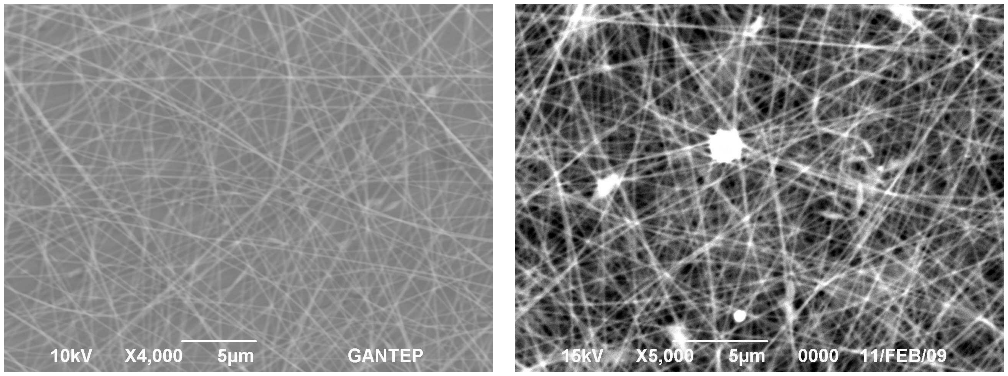
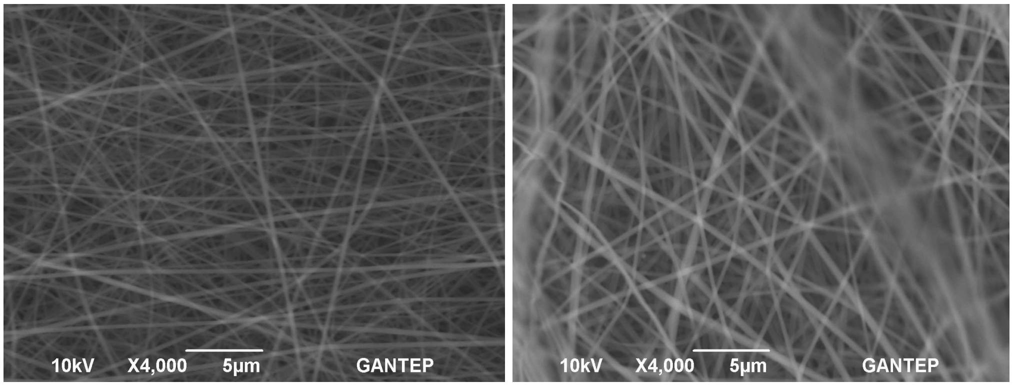


Figure 3.15 Effect of concentration on PAN nanofiber diameter (15 cm and 30 kV)



a) concentration 8%

b) concentration 10%



c) concentration 12 %

d) concentration 14%

Figure 3.16 (a-d) Effect of concentration on PAN fiber diameter (15 cm and 30 kV)

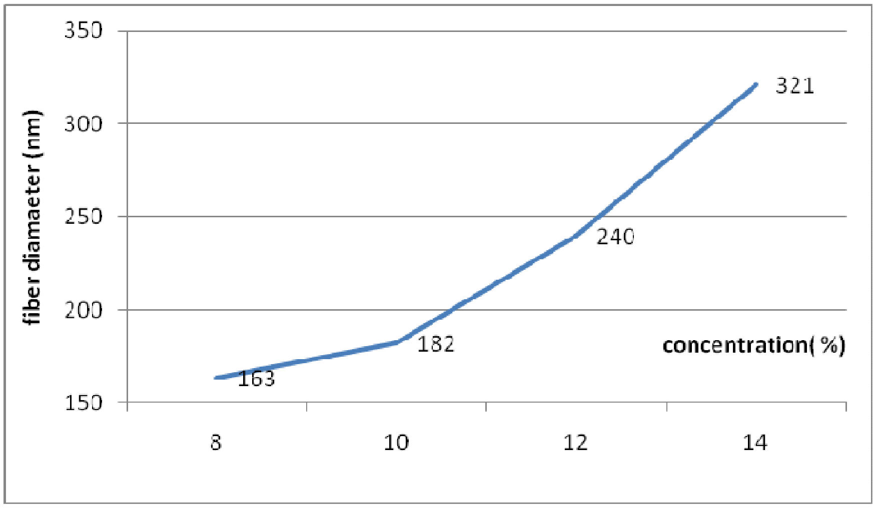
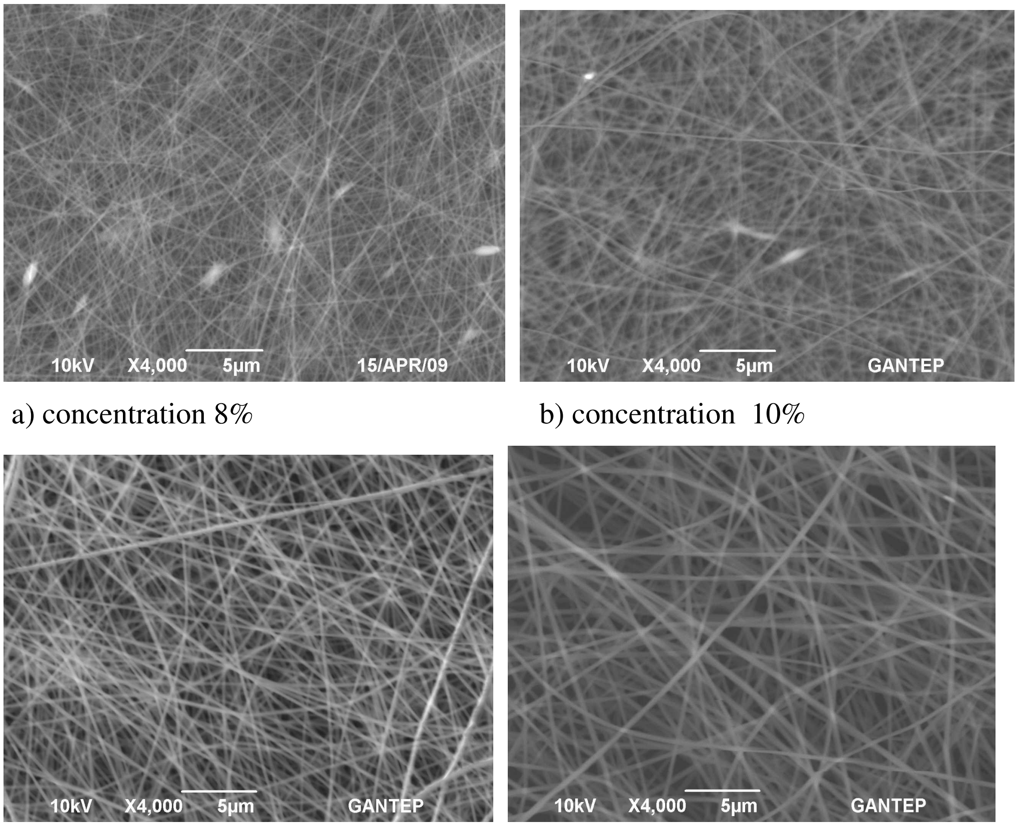


Figure 3.17 Effect of concentration on PAN fiber diameter (15 cm and 35 kV)



a) concentration 8%

b) concentration 10%

c) Concentration 12 %

d) concentration 14%

Figure 3.18 (a-d) Effect of concentration on PAN fiber diameters (15 cm and 35 kV)

3.7.2. Effect of voltage

A series of experiments were carried out using different concentrations of PAN/DMF solutions. SEM images of electrospun PAN nanofibers with different voltages were shown in Figures 3.19-3.28. The experimental results showed that as the voltage increased the fiber diameter decreased to a certain value then it increased. Also the bead formation was seen at 40 kV. The most uniform formation was seen at 30-35 kV. The average diameters of nanofibers decreased with increasing applied voltage from 10 to 30 kV. Generally at 40 kV the nanofiber distribution got worse.

In this study the production speed was also important. So high speed production values were also monitored and high speed production was obtained usually after 15 kV when the distance was 10cm. However, when the distance was 15cm and above, high production speed was observed after 25 kV. High production speed means long and continuous jets and collecting high number of nanofibers on the collector.

It was observed that variation in applied voltage significantly changes diameter of nanofibers, resulting in a change in fiber morphology. The experimental results showed that as the voltage increases the fiber diameter decreases to a certain value then it tends to increase again. The other outcome of high voltage value was that it intensifies the bead formation especially at lower concentrations as given in Figure 3.20(f) and Figure 3.22(f). Consequently, the finest formations were obtained between 30-35 kV. Furthermore, SEM images showed that PAN nanofibers synthesized at higher applied voltages exhibited higher average diameters, which can be due to increase in drawing rate of the jet from the channel. At 40 kV the nanofiber diameter was increased suddenly.

It is observed that the most uniform formation was happened when the voltage is between 25-35 kV. Also the bead formation was not common because of sufficient concentration. At higher concentrations (after 10 %), fibers were more uniform and cylindrical with average diameter of 250 nm. At higher polymer concentrations, lower solvent content dried the fibers completely before they reached the collector, resulting in lower fiber entanglement.

3.7.2.1. When distance is 10 cm

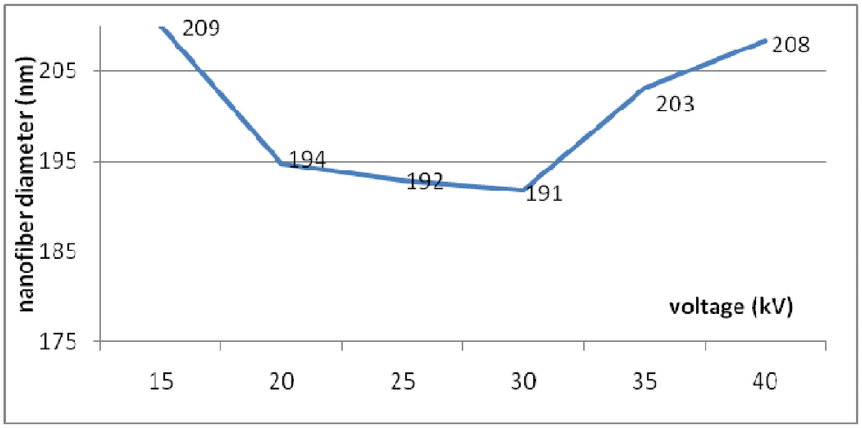
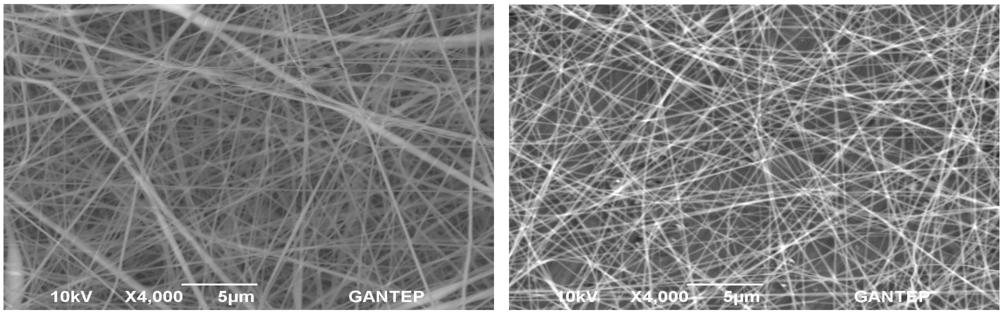
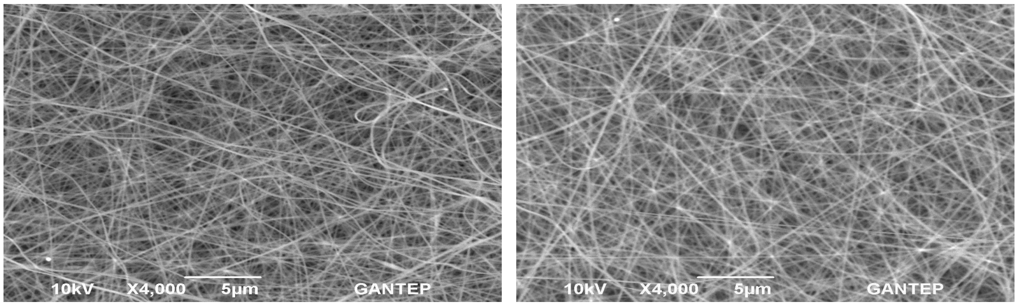


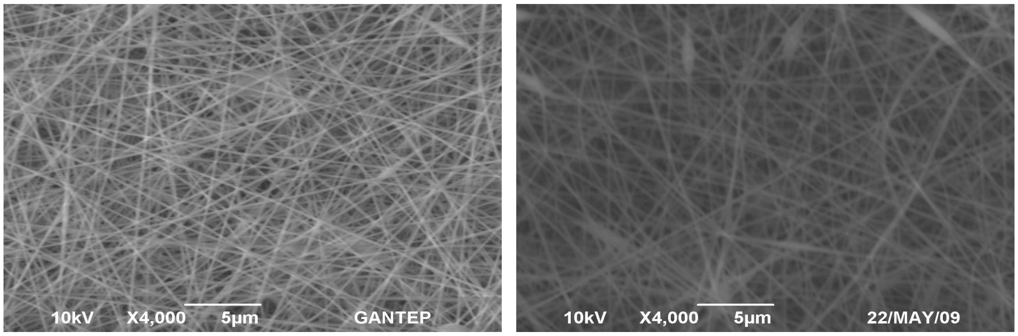
Figure 3.19 Effect of voltage on PAN fiber diameter (10cm and 8%)



a) voltage 15 kV b) voltage 20 kV



c) voltage 25 kV d) voltage 30 kV



e) voltage 35 kV f) voltage 40 kV

Figure 3.20 (a-f) Effect of voltage on PAN fiber diameter (8 % and 10 cm)

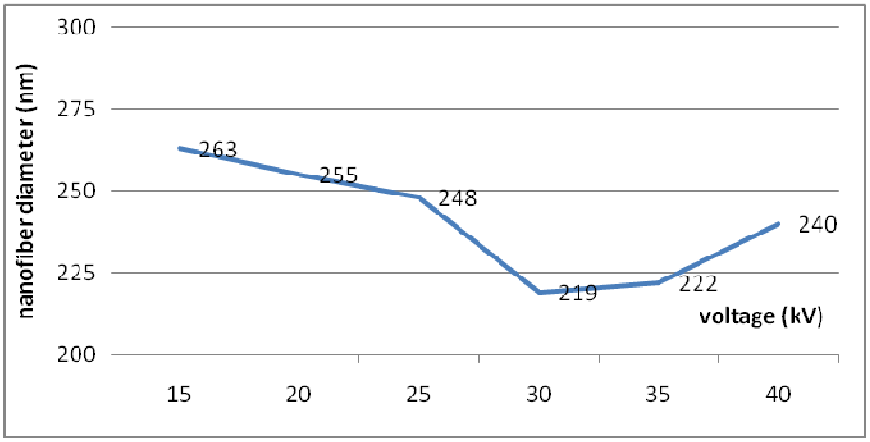
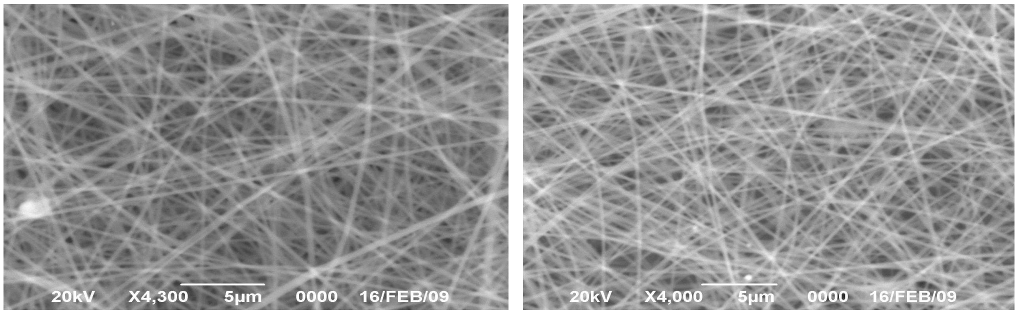
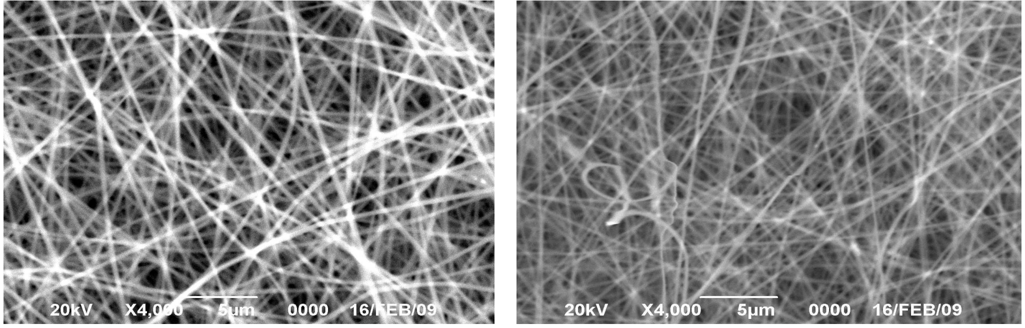


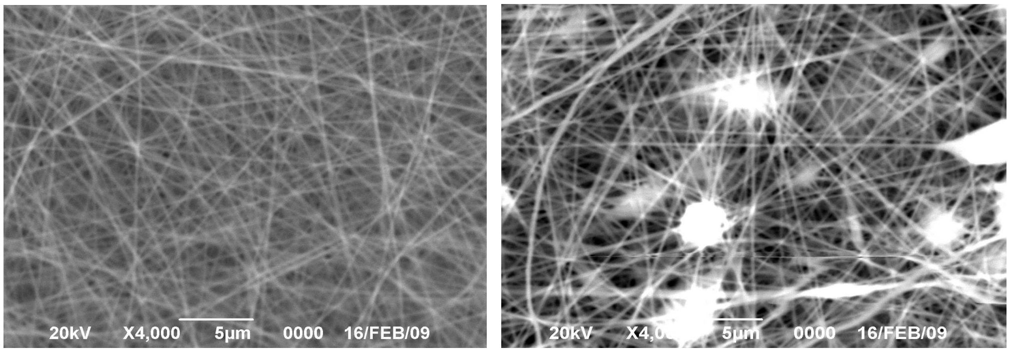
Figure 3.21 Effect of voltage on PAN fiber diameter (10cm and 10%)



a) voltage 15 kV b) voltage 20 kV



c) voltage 25 kV d) voltage 30 kV



e) voltage 35 kV f) voltage 40 kV

Figure 3.22 (a-f) Effect of voltage on PAN fiber diameter (10cm and 10%)

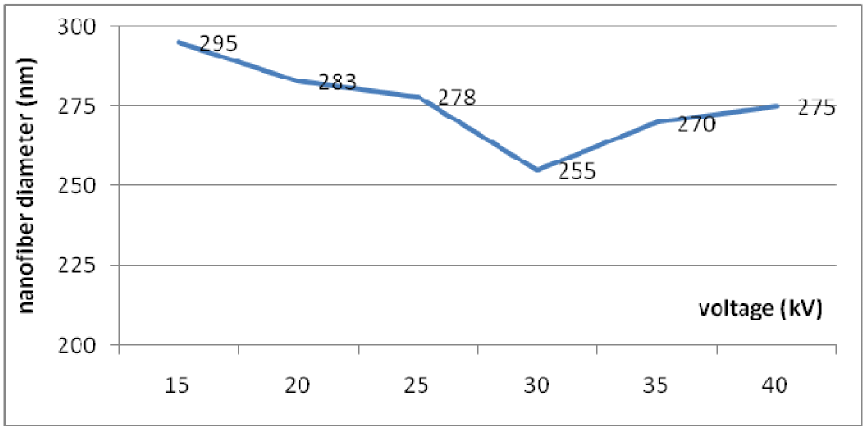
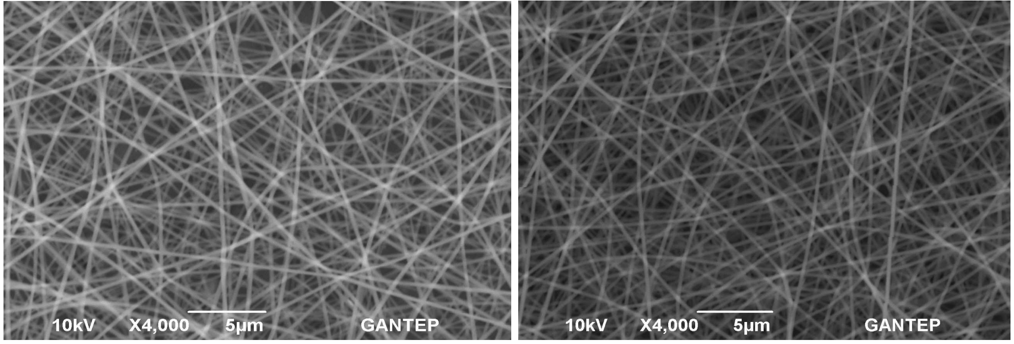
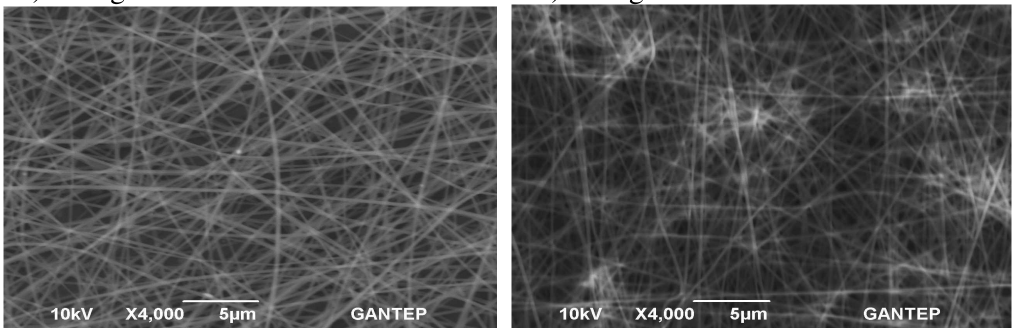


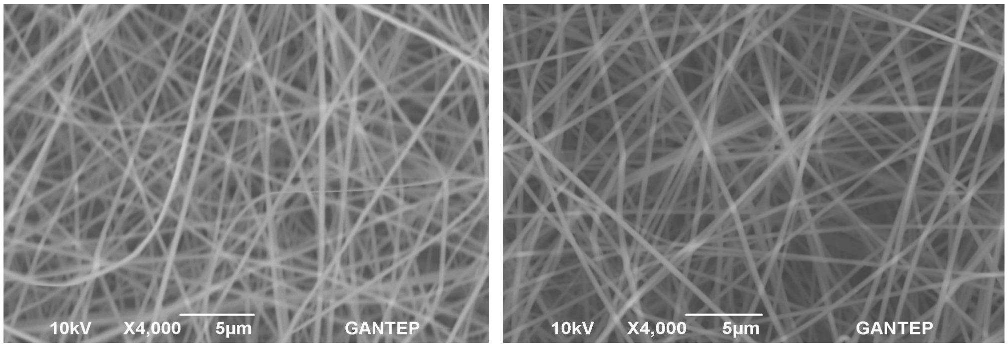
Figure 3.23 Effect of voltage on PAN fiber diameter (10cm and 12%)



a) voltage 15 kV b) voltage 20 kV



c) voltage 25 kV d) voltage 30 kV



e) voltage 35 kV f) voltage 40 kV

Figure 3.24 (a-f) Effect of voltage on PAN fiber diameter (12 % and 10 cm).

3.7.2.2. When distance is 15 cm

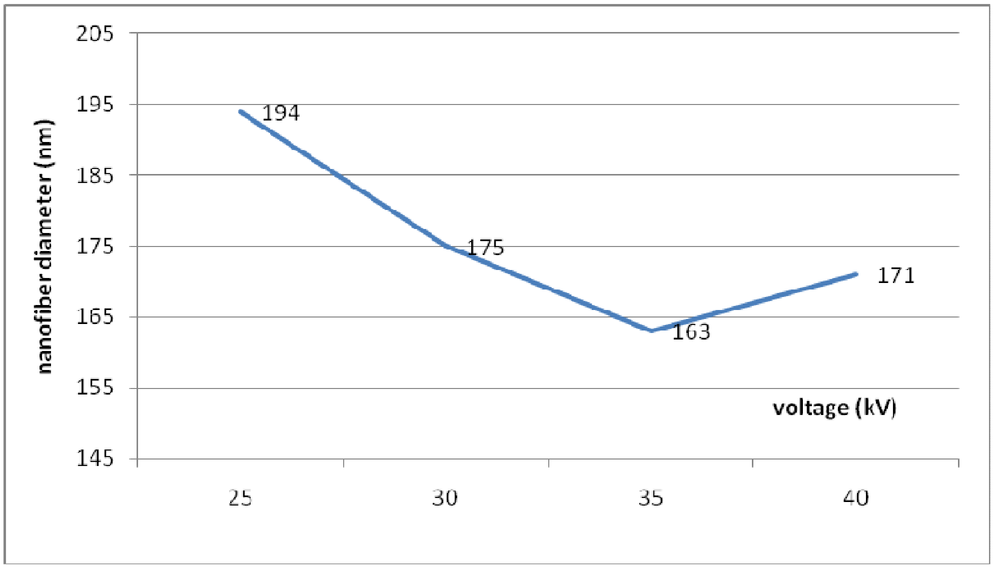
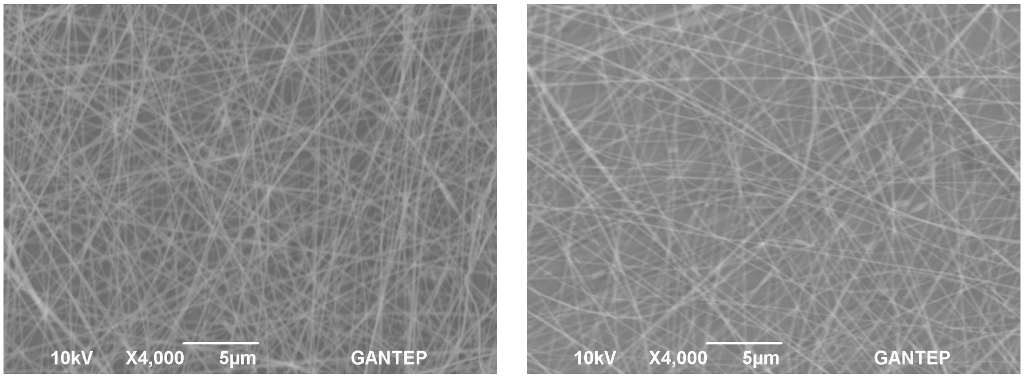
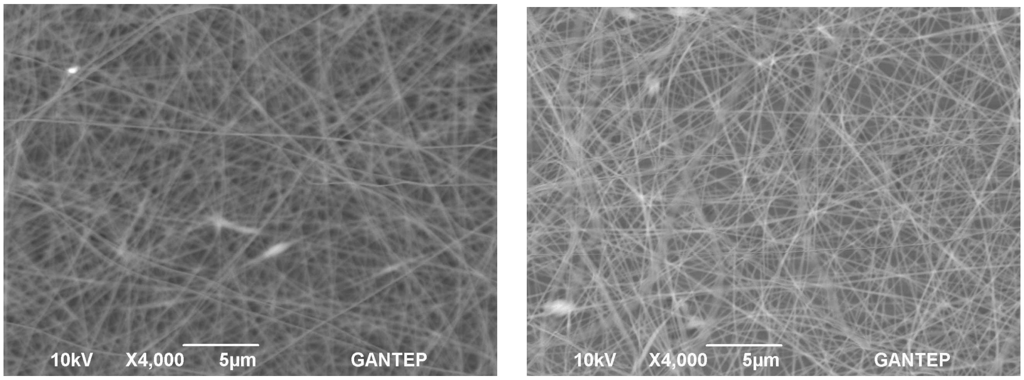


Figure 3.25 Effect of voltage on PAN fiber diameter (15cm and 8%)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 3.26 (a-d) Effect of voltage on PAN fiber diameter (8% and 15 cm).

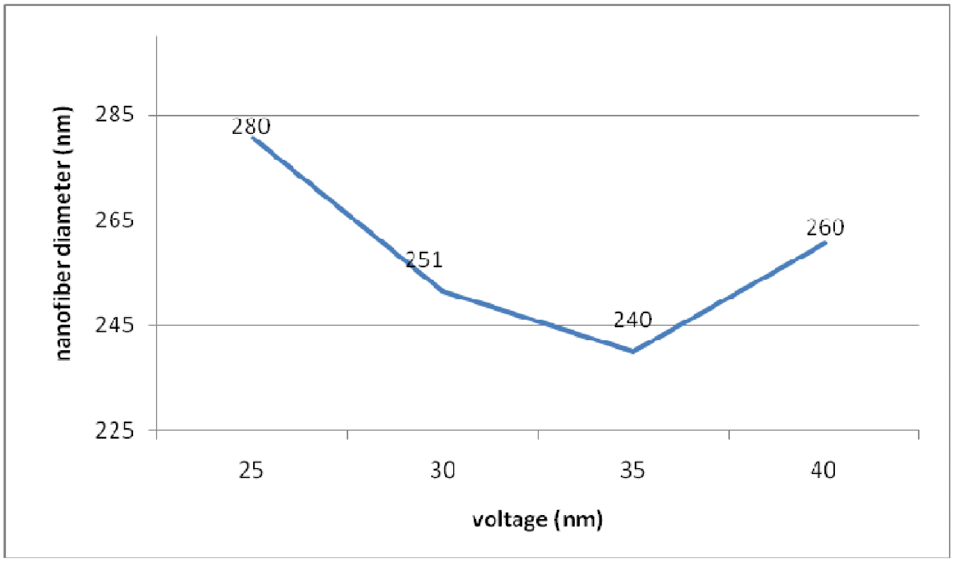
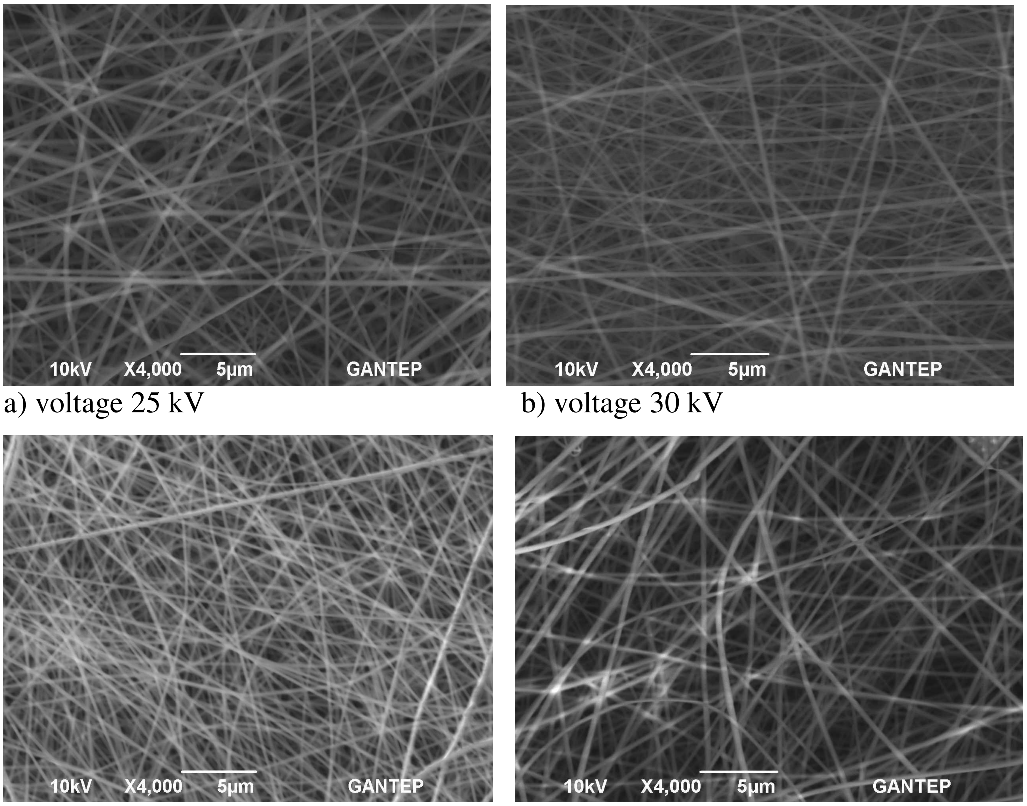


Figure 3.27 Effect of voltage on PAN fiber diameter (15cm and 12%)



a) voltage 25 kV
b) voltage 30 kV
c) voltage 35 kV
d) voltage 40 kV

Figure 3.28 (a-d) Effect of voltage on PAN fiber diameter (12 % and 15 cm).

3.7.3. Effect of distance

The figures between 3.29-3.40 were about the effect of distance on PAN nanofiber morphology. It was observed that the nanofiber diameter decreases gradually as the tip-collector distance increases up to 15 cm. But, further increasing the tip-collector distance generates a negative effect on the nanofiber diameter as shown in the figures. Therefore, the diameter was at lowest level when tip-collector distance was 15cm approximately for all voltage values. However, observations on the SEM images of the nanofiber mat samples was shown that the most uniform formation was likely to occur when tip-collector distance was 10 cm. There were some investigation in the literature which show that the fiber diameter increases at a longer distances. This was due to the decrease in the electrostatic field strength resulting in less stretching of the fibers.

Nanofiber formation was not uniform at a distance of 5 cm since solvent cannot find enough time to evaporate. So they directly pass to collector which causes beads and droplets. Moreover, it was observed that production speed was really lower at a distance of 25 cm. As a result, the best nanofibers formation was observed for 10 cm and 15 cm.

3.7.3.1. When the voltage is 25 kV

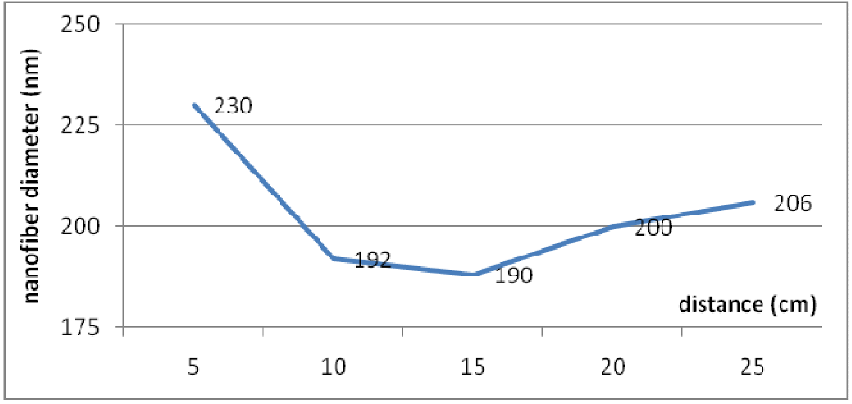
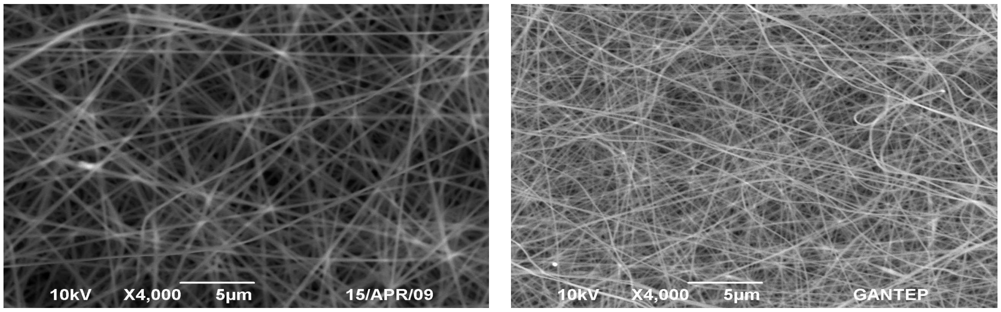
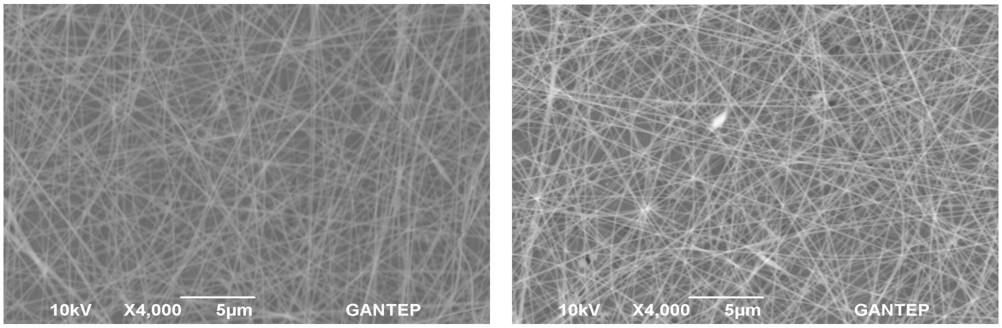


Figure 3.29 Effect of distance on PAN fiber diameter (25 kV and 8 %)



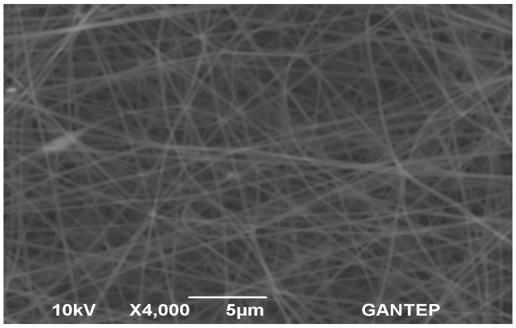
a) tip-collector distance 5 cm

b) tip-collector distance 10 cm



c) tip-collector distance 15 cm

d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.30 Effect of distance on PAN fiber diameter (25 kV and 8 %)

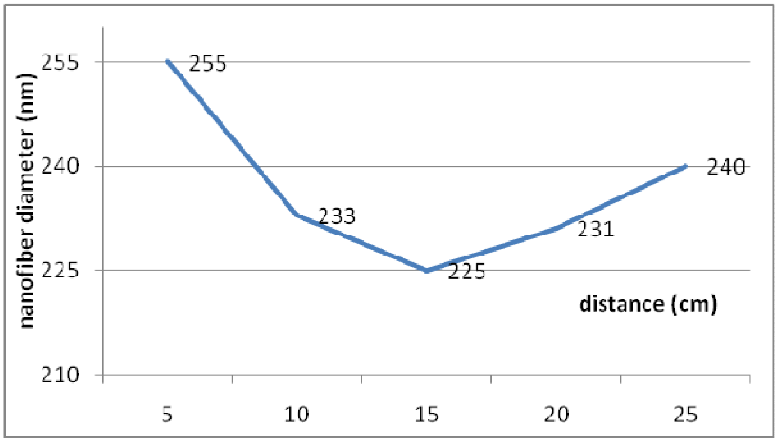
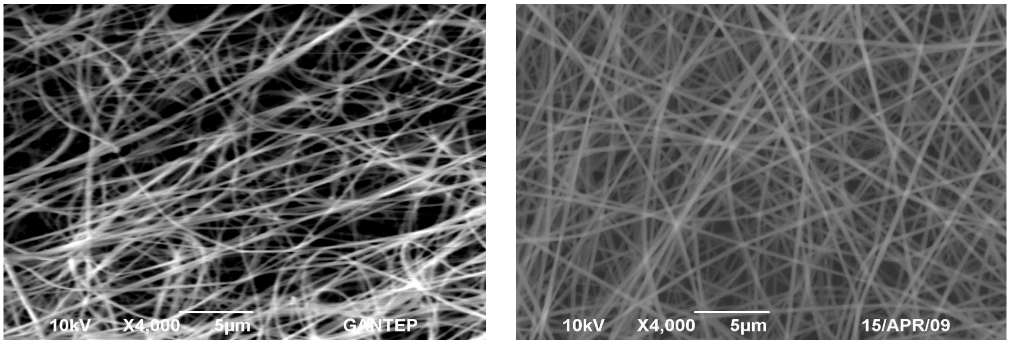
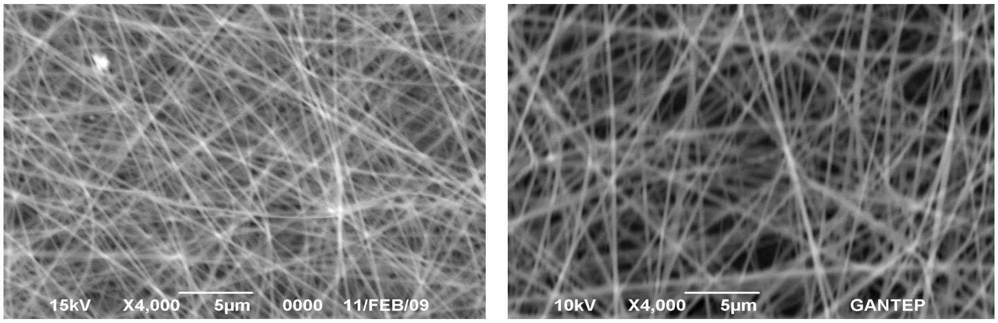


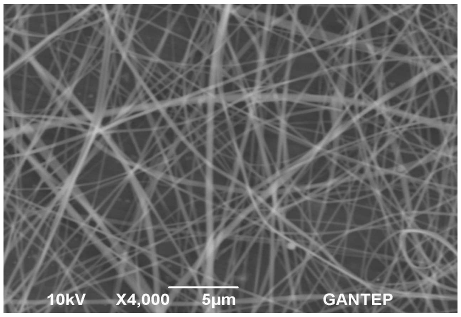
Figure 3.31 Effect of distance on PAN fiber diameter (25 kV and 10 %)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.32 Effect of distance on PAN fiber diameter (25 kV and 10%)

3.7.3.2. When the voltage is 30 kV

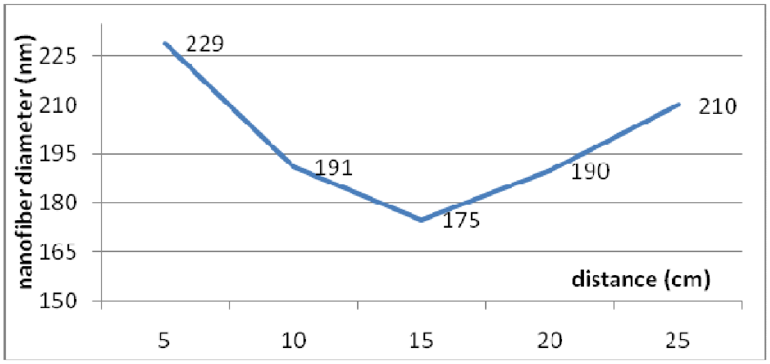
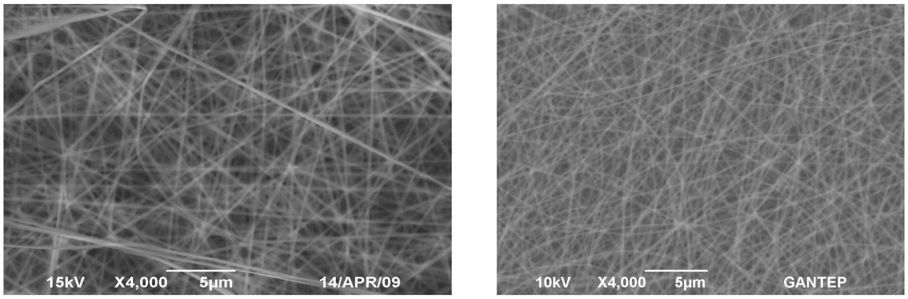
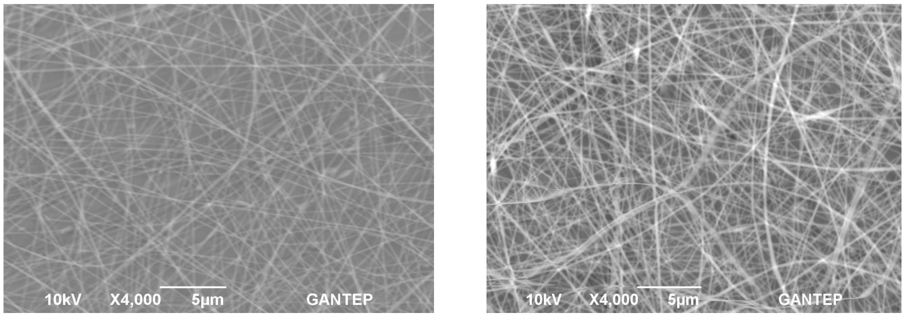


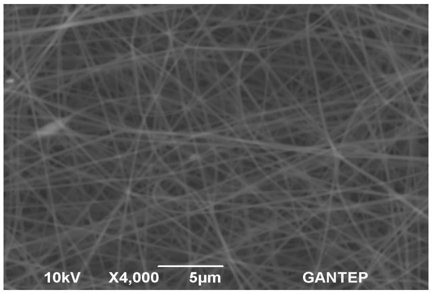
Figure 3.33 Effect of distance on PAN fiber diameter (8% and 30 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.34 Effect of distance on PAN fiber diameter (30 kV and 8%)

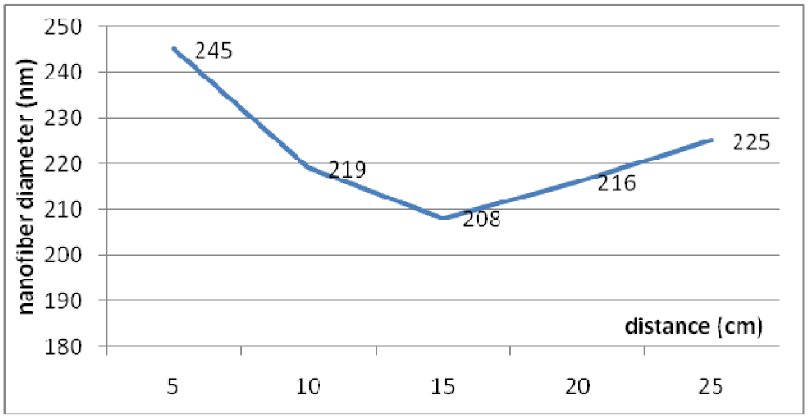
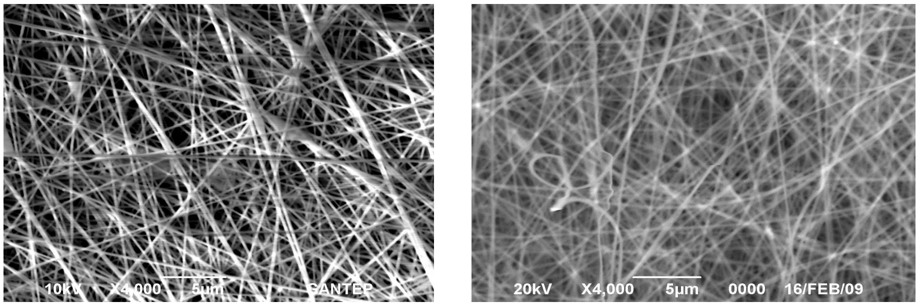
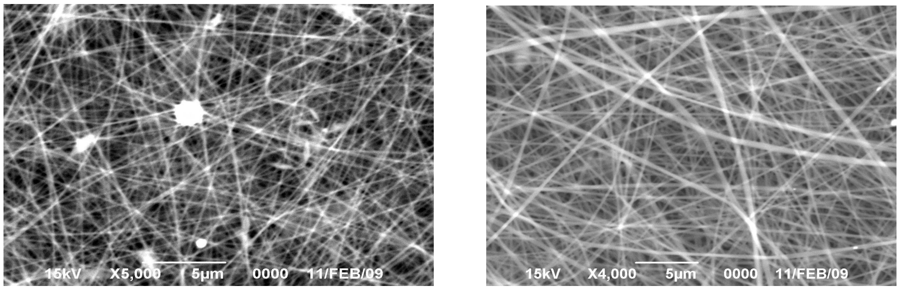


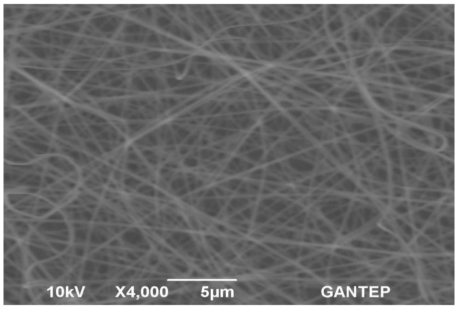
Figure 3.35 Effect of distance on PAN fiber diameter (10% and 30 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.36 Effect of distance on PAN fiber diameter (30 kV and 10%)

3.7.3.3. When the voltage is 35 kV

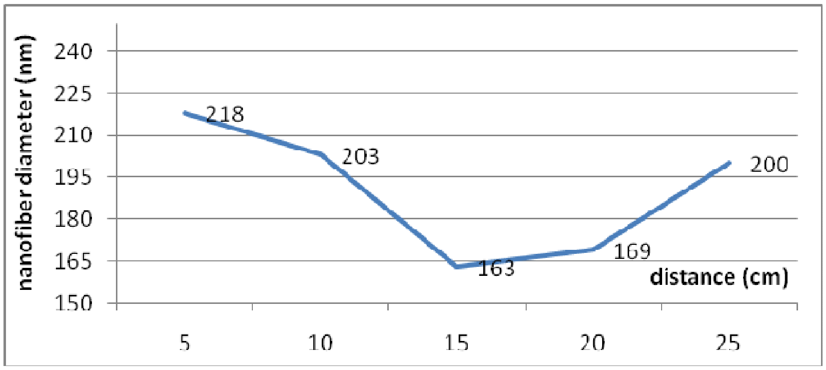
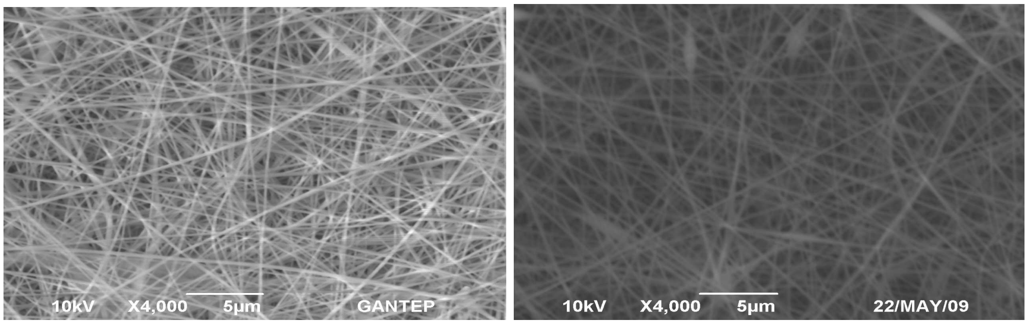
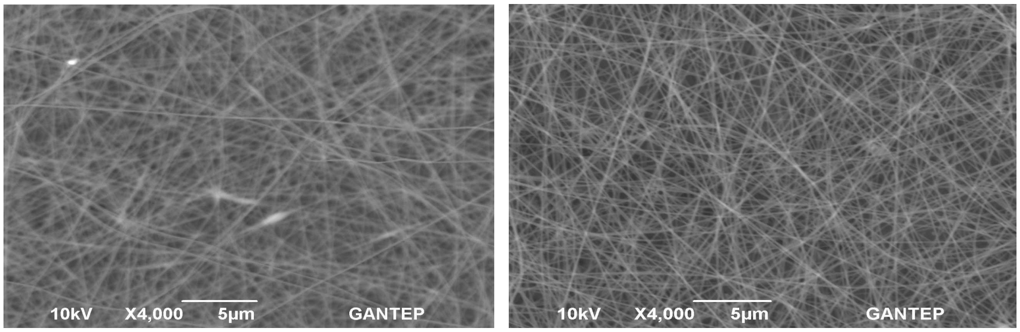


Figure 3.37 Effect of distance on PAN fiber diameter (35 kV and 8 %)



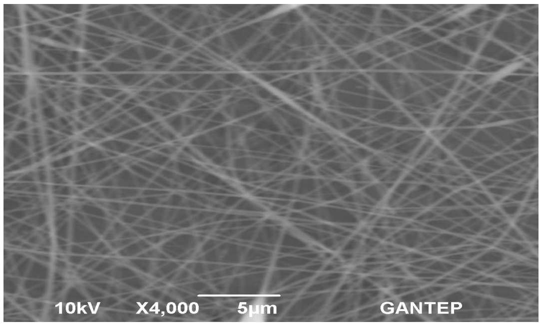
a) tip-collector distance 5 cm

b) tip-collector distance 10 cm



c) tip-collector distance 15 cm

d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.38 Effect of distance on PAN fiber diameter (35 kV and 8%)

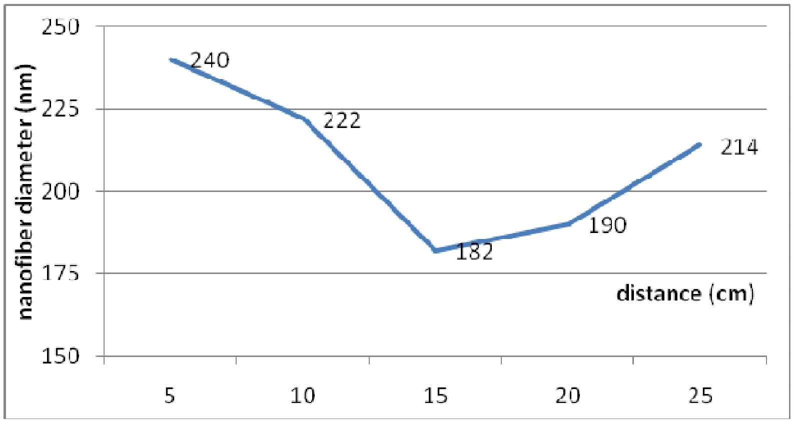
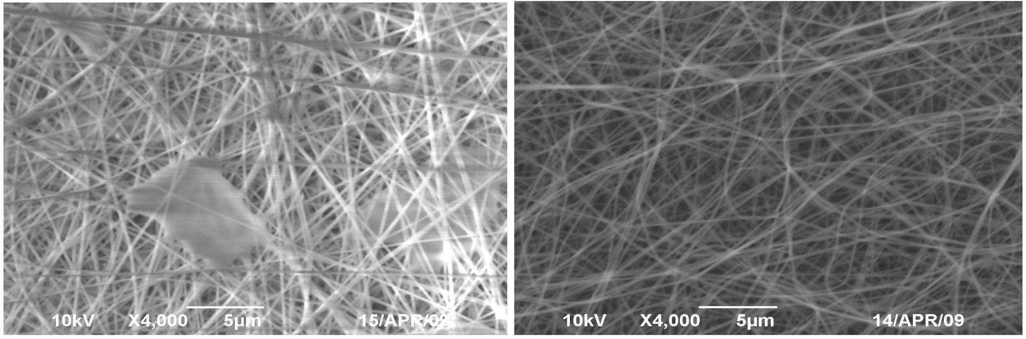
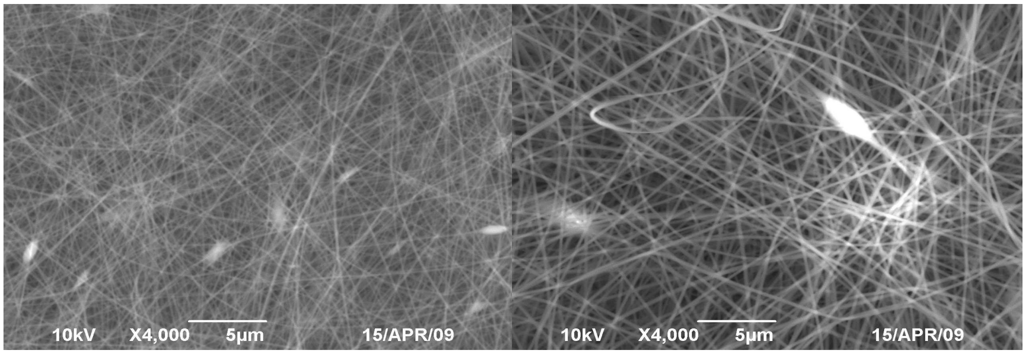


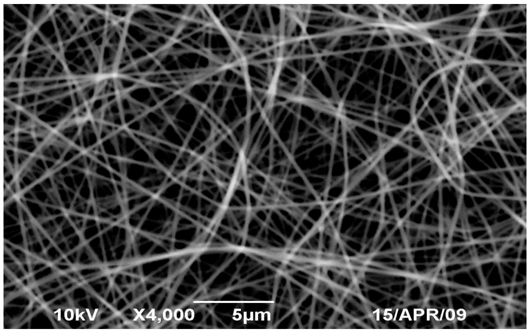
Figure 3.39 Effect of distance on PAN fiber diameter (35 kV and 10%)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 3.40 Effect of distance on PAN fiber diameter (35 kV and 10%)

3.7.4. Effect of ambient parameters

The temperature and humidity effect on fineness and morphology of Polyacrylonitrile (PAN) electrospun nanofiber were investigated.

It was found that increasing humidity had a negative effect on fiber morphology. The fiber diameter was decreased to a point after then it was increased. The optimum formation of fibers was obtained at 30%. The average fiber diameter was 205 nm.

On the other hand increasing temperature had a positive effect on fiber morphology up to a point but at higher temperatures the fiber morphology got worse. The ambient temperature was very good at a temperature of 25°C. The other parameters were chosen as 35 kV voltage, 10 cm tip to collector distance, 10% concentration (Figure 3.41-42). The effect of temperature was observed. The fiber diameter didn't change very much between 15-20 °C. But after 25 °C there was a sharp increase in nanofiber diameter. At 25 °C the optimum formation was observed. The average fiber diameter was 225 nm and the bead formation was at least level. The fiber diameter variation was not seen anymore. However, it was observed that the nanofiber formation became inferior at 35°C while the other parameters were constant (35 kV voltage, 10 cm tip- collector distance, 10% concentration and humidity 30% as shown in Figure 3.43 and Figure 3.44.

3.7.4.1. Effect of humidity on PAN nanofiber

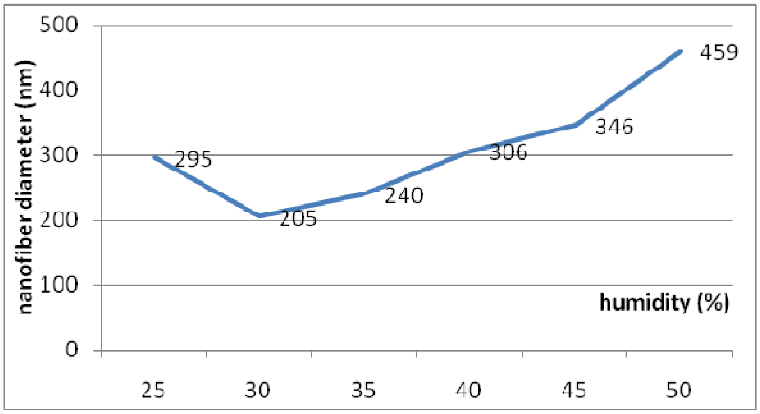
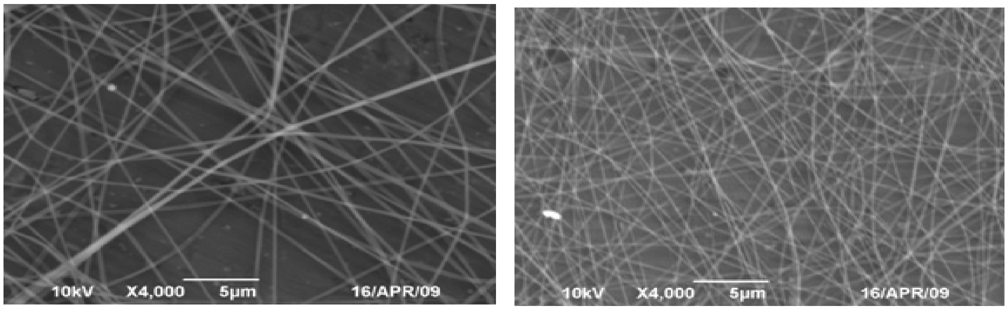
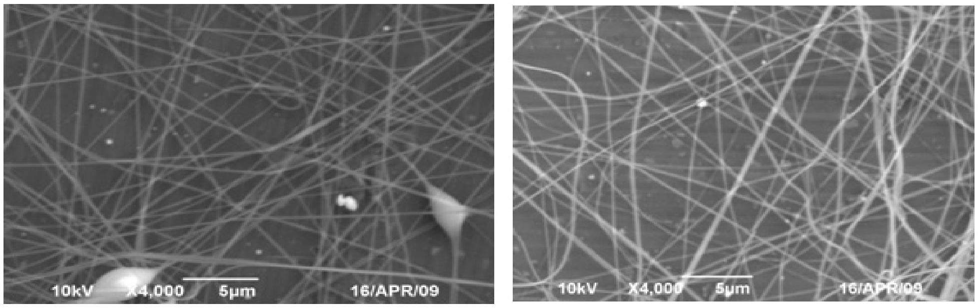


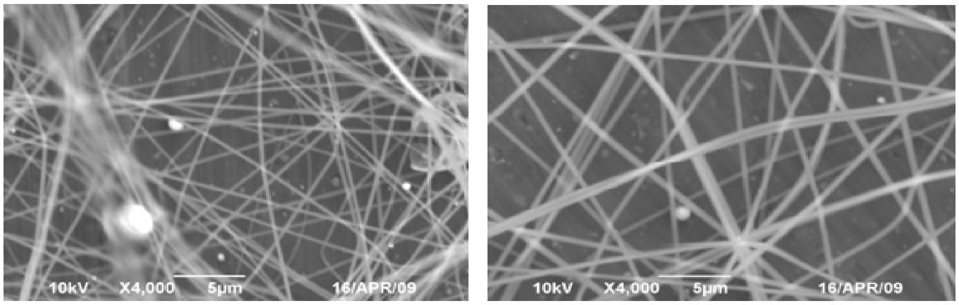
Figure 3.41 Effect of humidity on PAN fiber diameter



a) humidity 25% b) humidity 30%



c) humidity 35% d) humidity 40%



e) humidity 45 % f) humidity 50%

Figure 3.42 Effect of humidity on PAN fiber diameter (35 kV, 10%, 10 cm)

3.7.4.2. Effect of temperature on PAN nanofiber

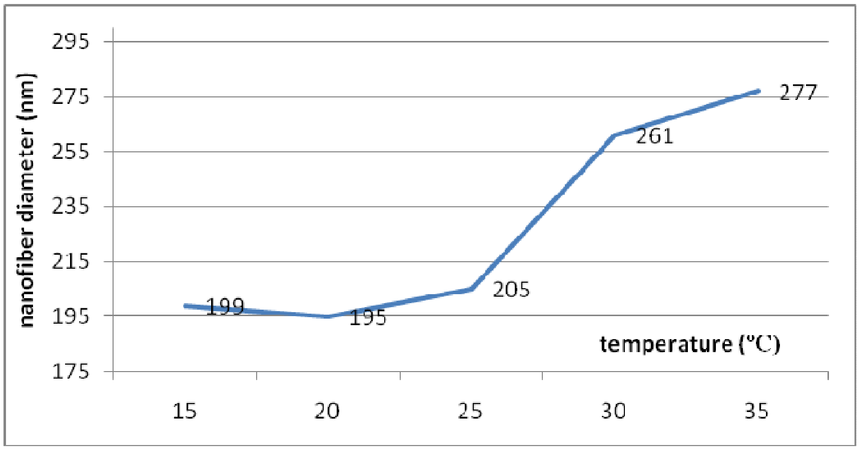
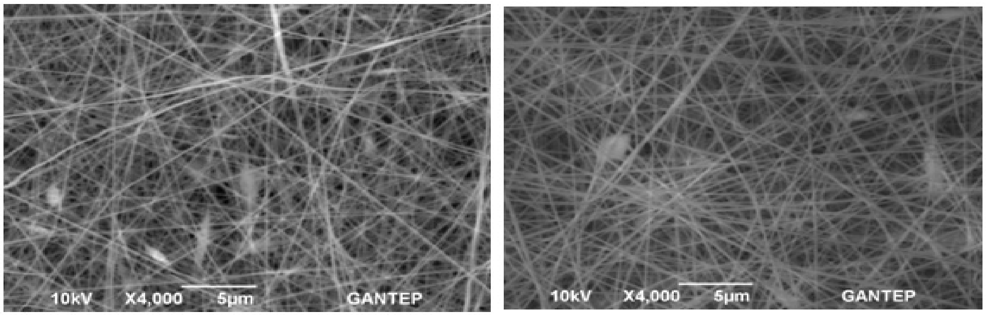
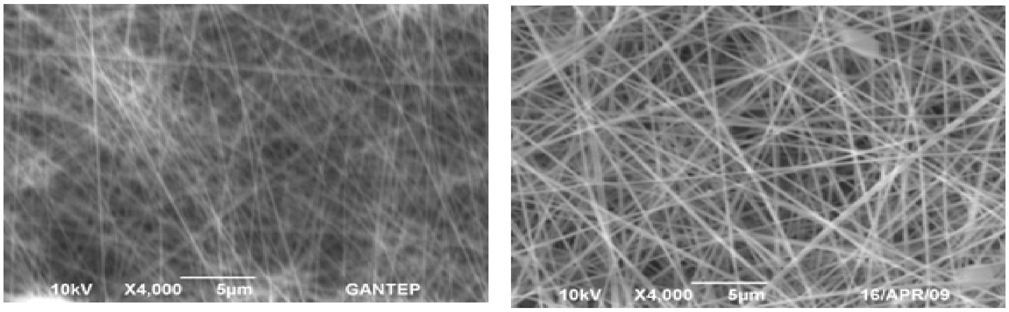


Figure 3.43 Effect of temperature on PAN fiber diameter



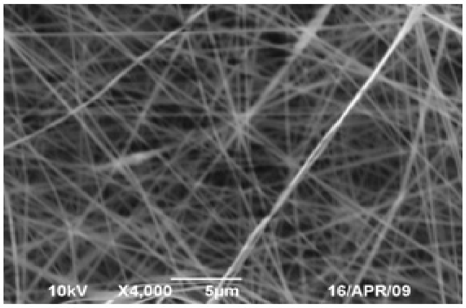
a) temperature 15°C

b) temperature 20°C



c) temperature 25°C

d) temperature 30°C



e) temperature 35°C

Figure 3.44 (a-c) Effect of temperature on PAN fiber diameters (35 kV, 10%, 10 cm)

CHAPTER 4

POLY (VINYL ALCOHOL) (PVA)

4.1. Introduction

In this part, the parameters which affect the diameter of PVA nanofiber were investigated. It was found that morphology such as fiber diameter and its uniformity of the electrospun nanofibers were dependent on many parameters. These parameters were explained in previous chapters. They are:

- Concentration of solution
- Voltage.
- Distance between the tip and collector.

In this chapter, PVA nanofibers were investigated to find out the optimum values of parameters, that means the fiber formation was uniform, thin and bead free. In order to examine systematically the effect parameters one of them was gradually increased while the other were kept constant and sample nanofibers were produced for each different value of the parameter. The images of these sample nanofibers were taken from SEM. The best possible interval or a value for those parameters was decided by examining SEM images. The key factors to determine the optimal values were fineness of the fiber and the morphology. To conduct the experiments solutions were prepared by dissolving PVA polymer in distilled water. The solution was arranged by stirring magnetically for 2 hours at a temperature of 90 °C.

4.2. Electrospinning

To investigate the concentration effect on nanofiber morphology; solutions (5-7.5% with 2.5% intervals) were prepared by dissolving PVA polymer in distilled water. To examine the effect of voltage on nanofiber diameter, the voltage was changed between 5-40 kV (5 kV intervals). Similarly, to analyze the effect of distance on nanofiber diameter, it was changed 5 to 25 cm with 5 cm interval). The other parameters such as flow rate and jet diameters were selected as 0.5ml/hour and 0.7mm respectively.

The fibers were collected on the aluminum foil in the form of non-woven fabric. The ambient temperature was adjusted at 25°C and the humidity is kept at 25 %.

4.3. Characterization

The morphological appearance of the as-spun PVA fiber mats and that of the individual fibers was investigated by a JEOL JSM-6390LV scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV.

4.4. Measurements of nanofiber diameters

The diameters of nanofibers were measured using Image-Pro Plus 6.0. 20 measurements were performed and average diameter of the nanofibers was calculated.

4.5. Experimental study

The results showed that the diameters of electrospun PVA nanofibers were greatly affected by solution concentration. The diameter of nanofibers undoubtedly increased as the concentration increased. The third parameter tip-collector distance has not a considerable effect on the PVA nanofiber diameter. At all concentrations and applied electrical potentials investigated, the average diameters of the PVA fibers ranged between 185 nm and 424 nm. Nanofiber diameter, bead formation and not-uniformity of nanofiber diameter were observed for all parameter values when make a decision about the optimal values. The most suitable values for production of PVA nanofibers were determined as follows;

- concentration: 10%,
- voltage: 25kV and
- the tip-collector distance: 15cm.

4.5.1. Effect of concentration

A wide spectrum of the effect of solution concentration (PVA/water) on the nanofiber diameter was given through Figure 4.1 to 4.20. Each of these figures matches a series of experiment where the voltage and distance were kept constant and the concentration value was increased gradually. To investigate the concentration effect on nanofiber morphology, different solution concentrations (5-15% with 2.5% intervals) were prepared by dissolving PVA polymer in distilled water. To examine the effect of voltage on nanofiber diameter, the voltage was changed between 5-40 kV (5 kV intervals). Similarly, to analyze the effect of distance on nanofiber diameter, it was changed between 5-25cm (5cm interval). Examinations show that the nanofiber diameter changes slowly at low concentrations (7,5% and 10 %) however, it increases sharply (after 10%) as the concentrations increases.

The effect of solution concentration on the nanofiber diameter and their morphology at different voltage values were seen through Figure 4.1 to 4.8. These figures show that the nanofiber diameter increases slowly (7,5% and 10 %) at low concentrations however it increases sharply after 10% as the concentration increases. On the other side, increasing the voltage value reduces the diameter of the nanofiber but, this condition also may cause to bead formation especially at low concentrations as shown in Figure 4.6(a), 4.6(b) and 4.8(a).

Some experimental studies for 5 cm tip-collector distance were not performed satisfactorily because of frequently spark formation between the tip and the collector. These sparks were caused uneven and irregular nanofiber mats. Moreover, for the same reasons experiments for high voltage values (such as 40kV) were not done especially for short distance, therefore all the set for 40kV were not included here.

When the tip-collector distance was increased to 15 cm, the relationship between nanofiber diameter versus applied voltage and the SEM images of sample nanofiber mats are seen through Figure 4.9 to 4.14. Those results demonstrate that the diameter of nanofibers increases as the voltage increases for 10 cm tip-collector distance.

SEM images of electrospun PVA nanofibers with different concentrations are shown in Figure 4.10 (a-e). Regardless of the electrospinning voltage, nanofibers and fine particles were produced on the collecting target when 5% concentration.

At 7.5% concentration, nanofibers with average fiber diameter (about 203 nm) were formed, but some beads were seen too. By increasing the concentration to 10%, the morphology of nanofibers was changed to a uniform fiber structure and the fiber diameter was increased slightly.

The relationship between nanofiber diameter versus applied voltage and the SEM images of sample nanofiber mats are seen through Figure 4.15 to 4.20 when the distance is 20 cm. Generally, fiber diameter increases as the voltage increases. These results display parallel consequences to the previous results for solution concentration at different tip-collector distance. For example, for 5% concentration nanofiber formation was not good enough since the polymer solution droplets were jumped down on to the collector due to the effect of short distance and high voltage value as expected. For 7.5, 10 and 12.5 % polymer concentration the nanofiber formation were very good.

All the experimental studies related with the concentration show that, lower concentrations may cause bead formation because of high surface tension however increasing concentrations increases viscoelastic forces that prevent rapid elongation and resulted in thicker fibers. Generally, good experimental results were obtained for 7.5% solution concentration however some beads may be observed at this concentration especially at short distance and higher voltage value. Therefore the most suitable concentration value (bead free form, fine and uniform nanofiber diameter) was determined as 10%.

4.5.1.1. When the distance is 10 cm

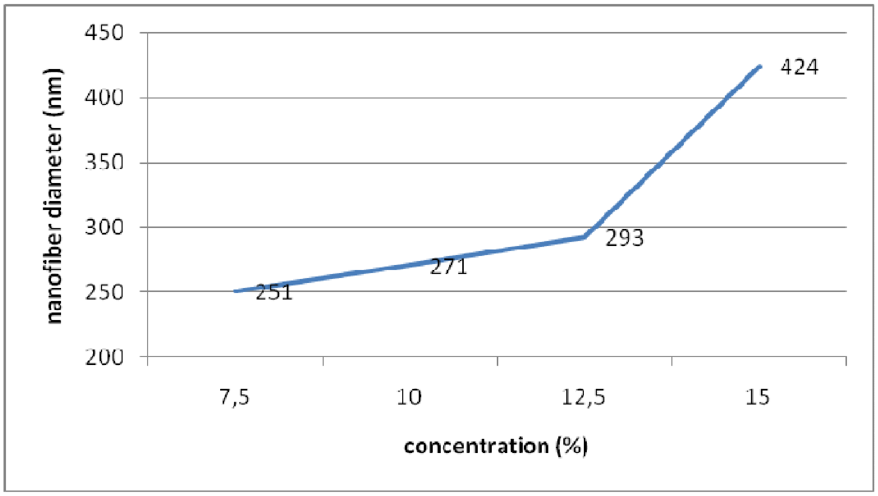
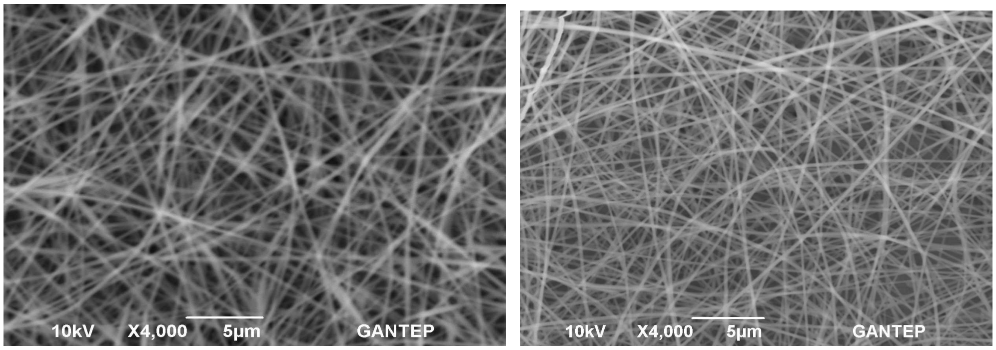
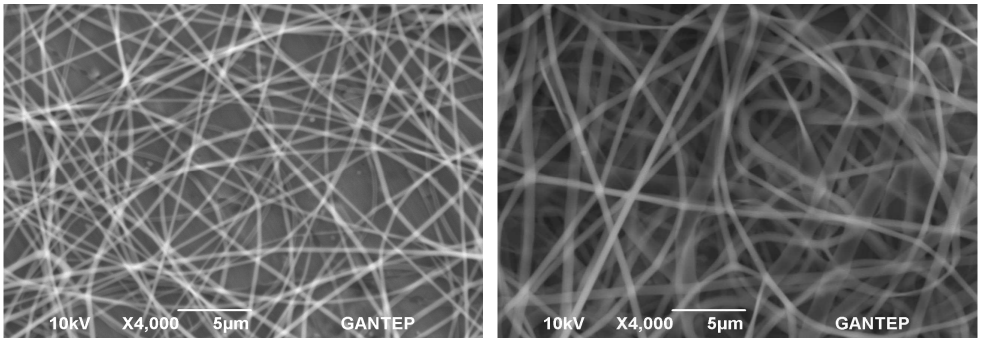


Figure 4.1 Effect of concentration on PVA fiber diameter (20 kV, 10 cm)



a) concentration 7.5%

b) concentration 10%



c) concentration 12.5%

d) concentration 15%

Figure 4.2 (a-d) Effect of concentration on PVA fiber diameter (20 kV, 10 cm)

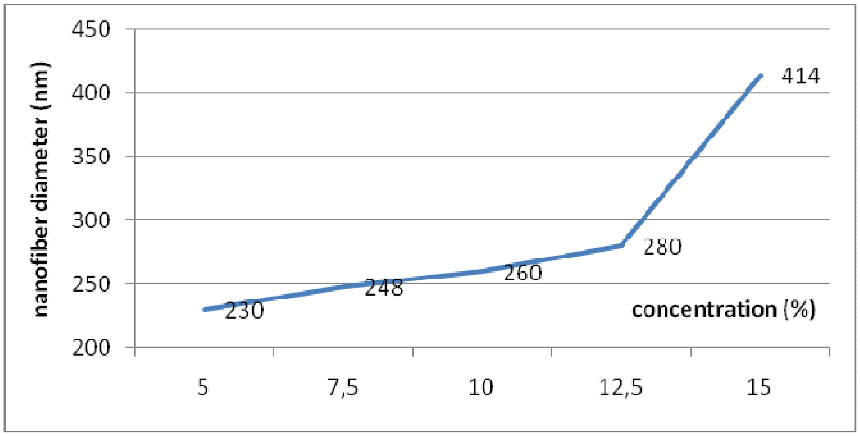
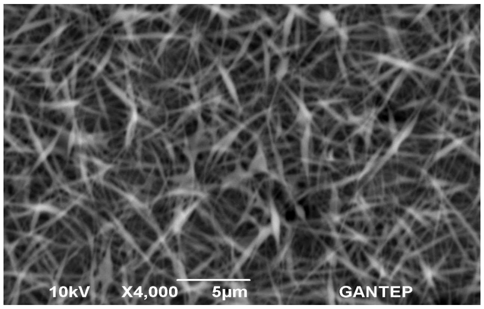
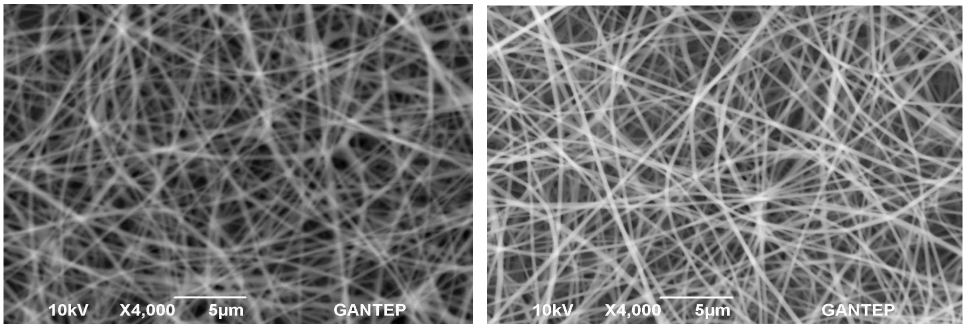


Figure 4.3 Effect of concentration on PVA fiber diameter (25 kV, 10 cm)

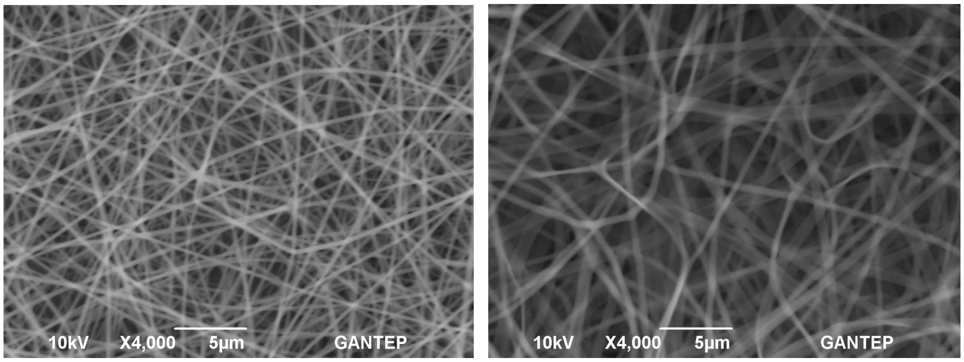


a) concentration 5%



b) concentration 7.5 %

c) concentration 10 %



d) concentration 12.5%

e) concentration 15%

Figure 4.4 (a-d) Effect of concentration on PVA fiber diameter (25 kV, 10 cm)

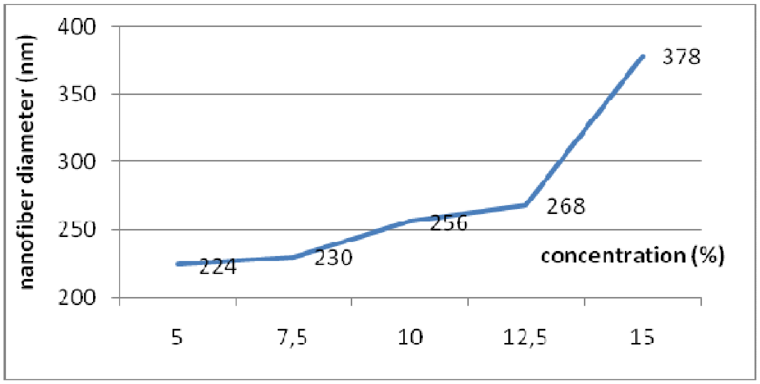
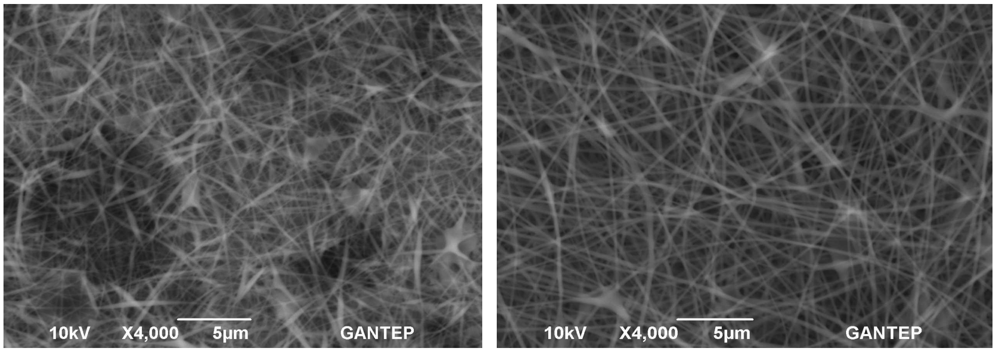
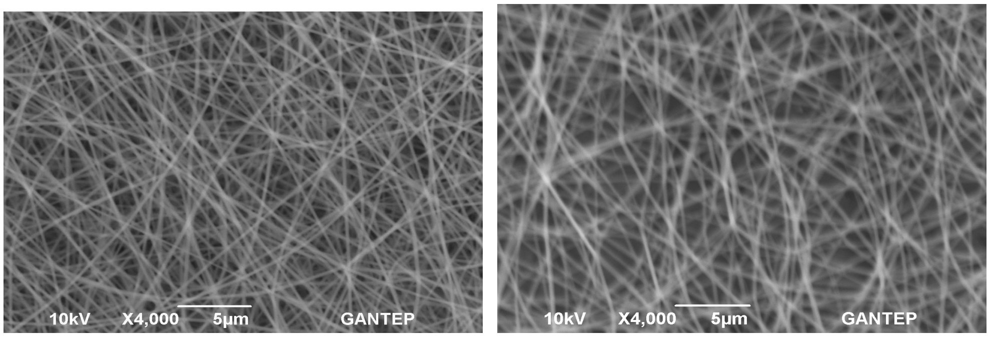


Figure 4.5 Effect of concentration on PVA fiber diameter (30 kV, 10 cm)



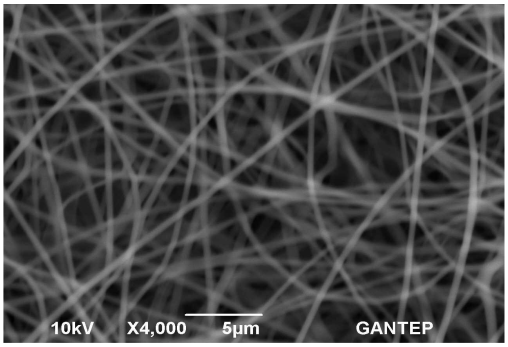
a) concentration 5 %

b) concentration 7.5 %



c) concentration 10 %

d) concentration 12.5%



e) concentration 15%

Figure 4.6 (a-e) Effect of concentration on PVA fiber diameter (30 kV, 10 cm)

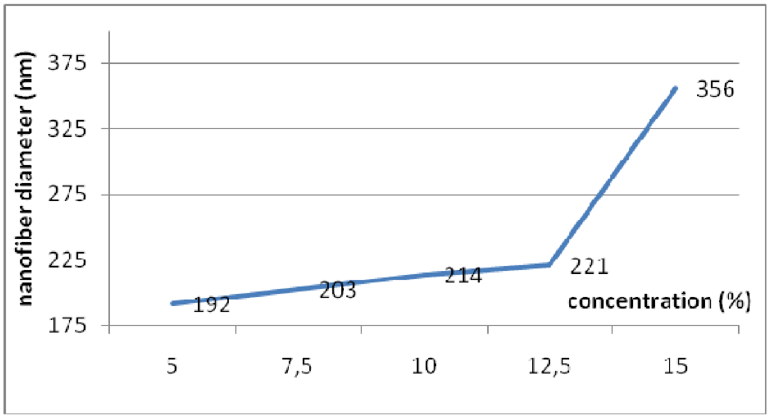
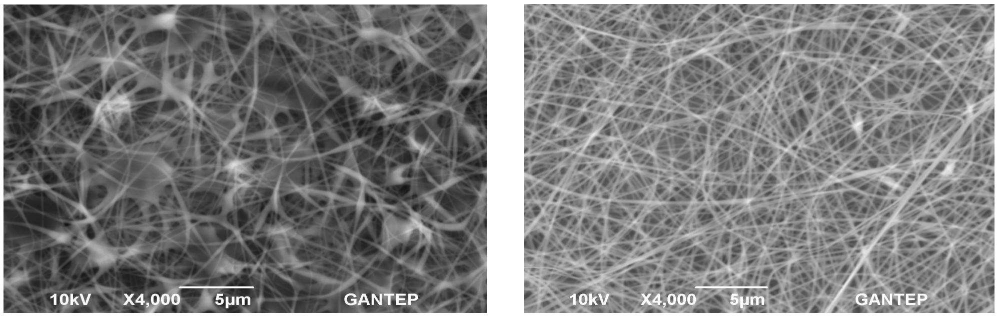
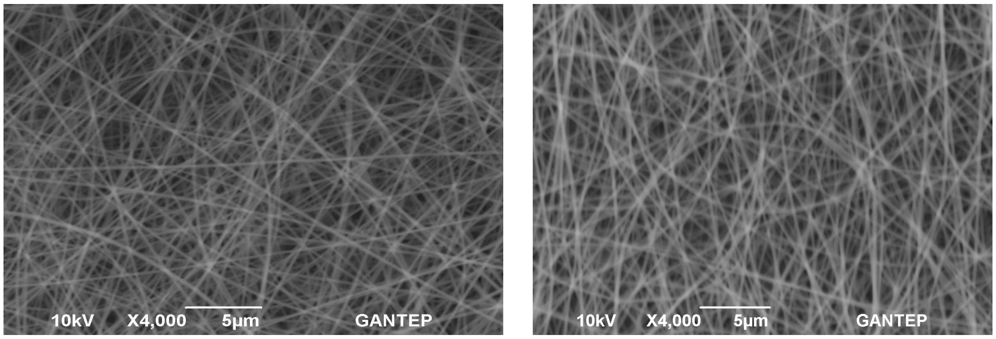


Figure 4.7 Effect of concentration on PVA fiber diameter (35 kV, 10 cm)



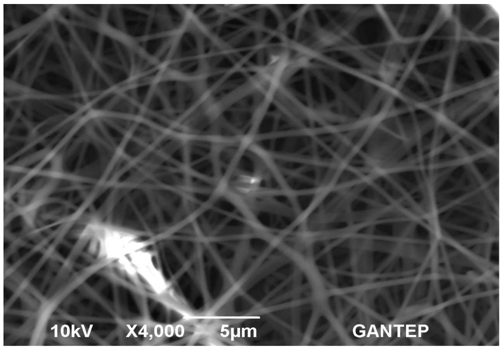
a) concentration 5 %

b) concentration 7.5 %



c) concentration 10 %

d) concentration 12.5 %



e) concentration 15 %

Figure 4.8 (a-e) Effect of concentration on PVA fiber diameter (35 kV, 10 cm)

4.5.1.2. When the distance is 15 cm

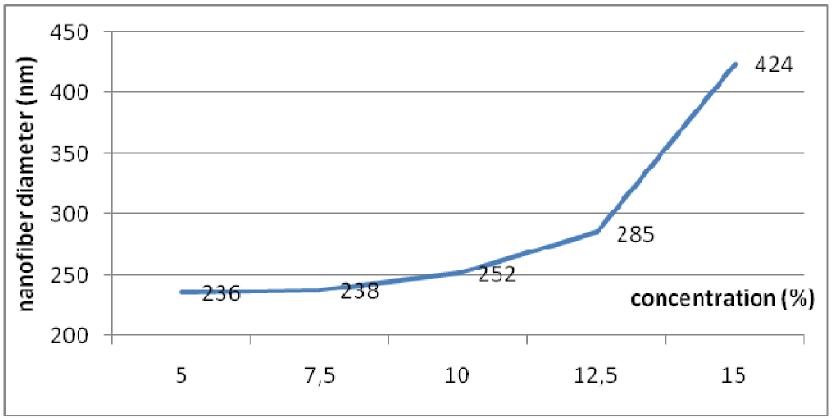
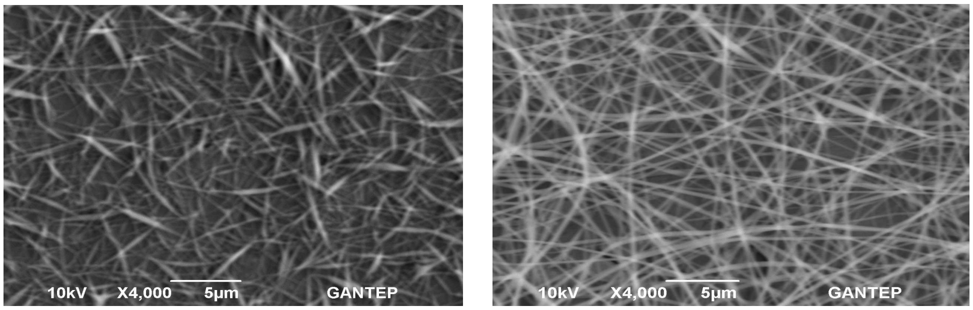
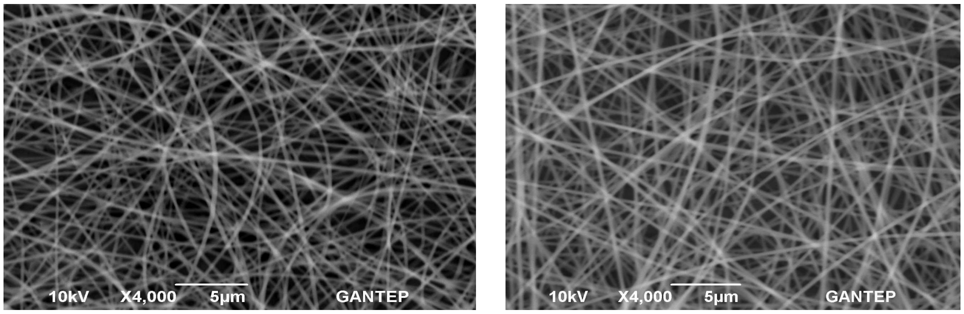


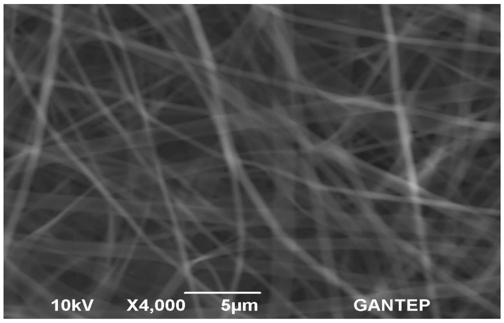
Figure 4.9 Effect of concentration on PVA fiber diameter (25 kV, 15 cm)



a) concentration 5% b) concentration 7.5%



c) concentration 10% d) concentration 12.5 %



e) concentration 15%

Figure 4.10 (a-e) Effect of concentration on PVA fiber diameter (25 kV, 15 cm)

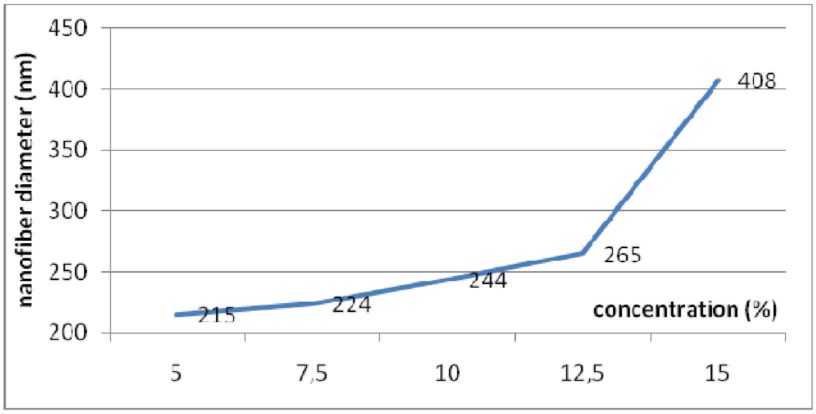
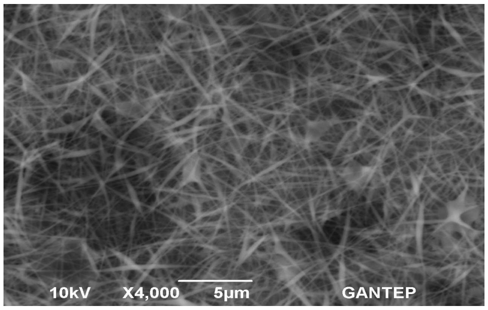
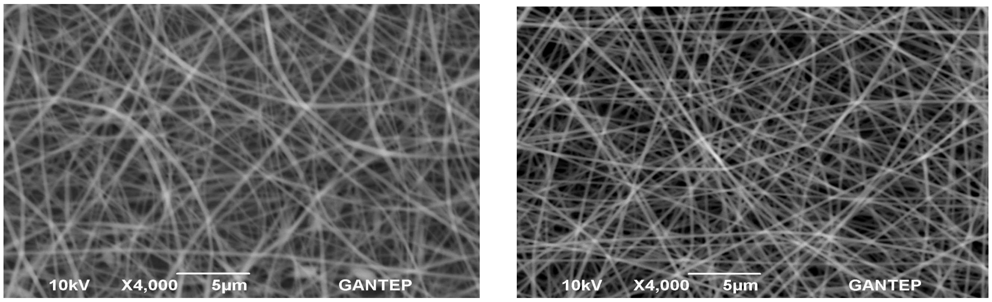


Figure 4.11 Effect of concentration on PVA fiber diameter (30 kV, 15 cm)

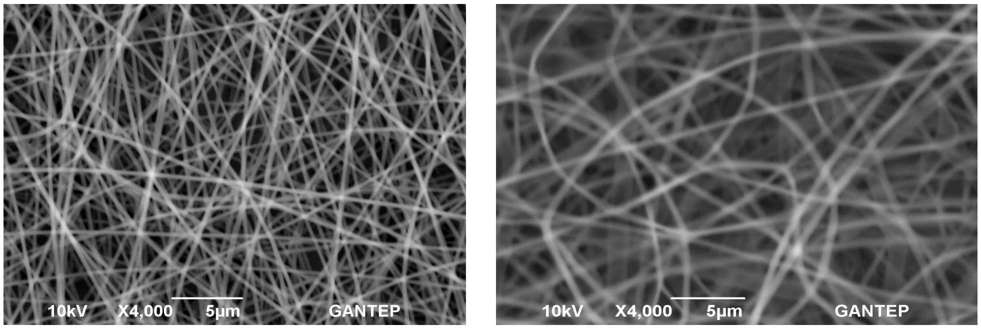


a) concentration 5 %



b) concentration 7.5%

c) concentration 10%



d) concentration 12,5 %

e) concentration 15%)

Figure 4.12 (a-e) Effect of concentration on PVA fiber diameter (30 kV, 15 cm)

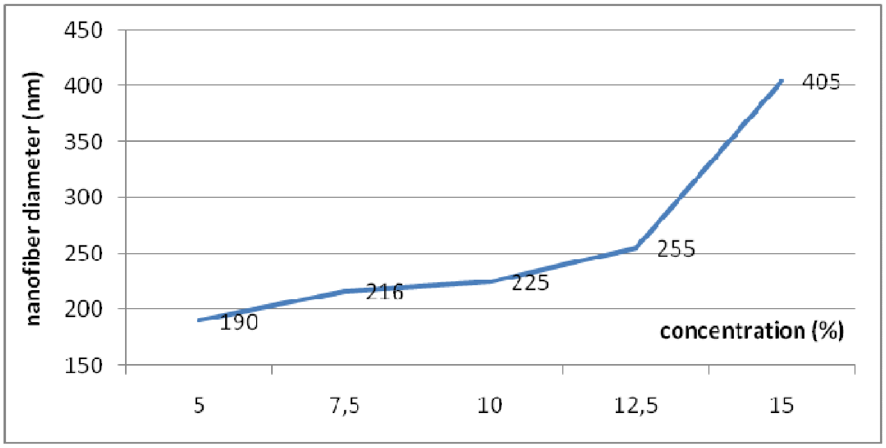
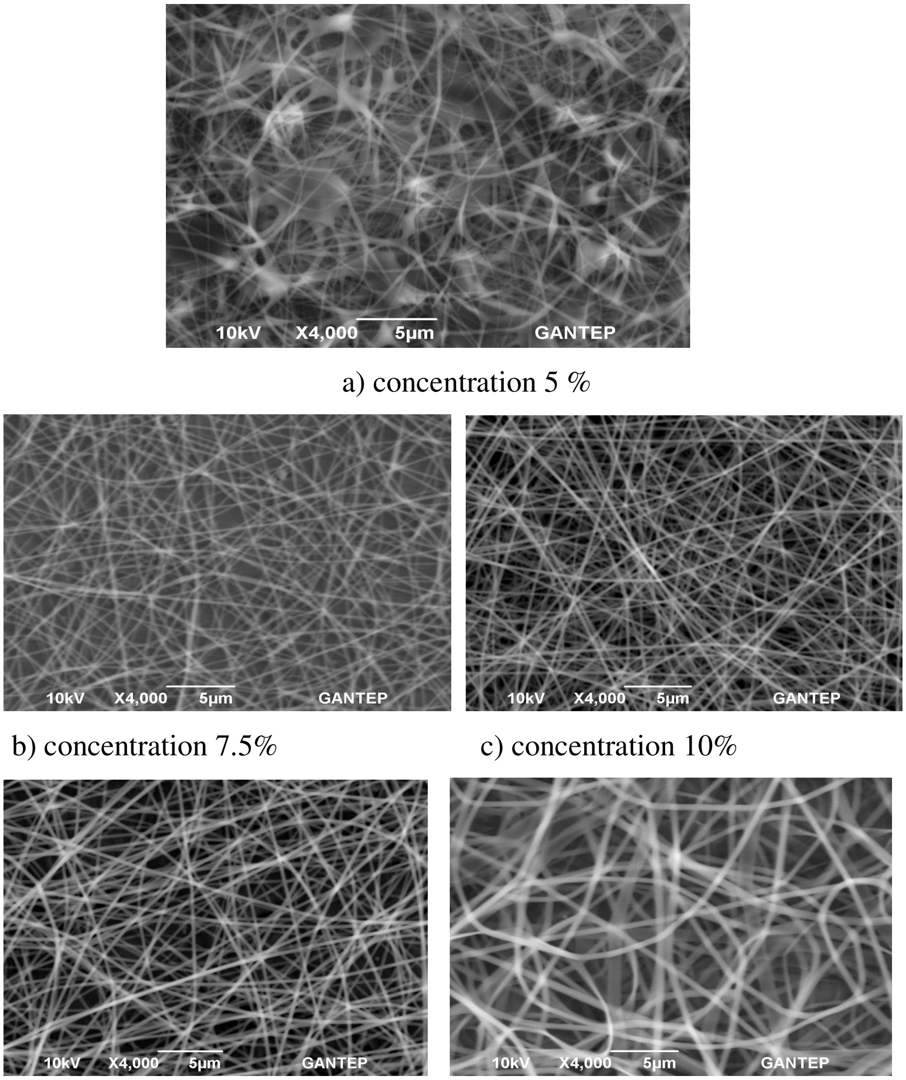


Figure 4.13 Effect of concentration on PVA fiber diameter (35 kV, 15 cm)



a) concentration 5 %

b) concentration 7.5%

c) concentration 10%

d) concentration 12.5 %

e) concentration 15%

Figure 4.14 (a-e) Effect of concentration on PVA fiber diameter (35 kV, 15 cm)

4.5.1.3. When the distance is 20 cm

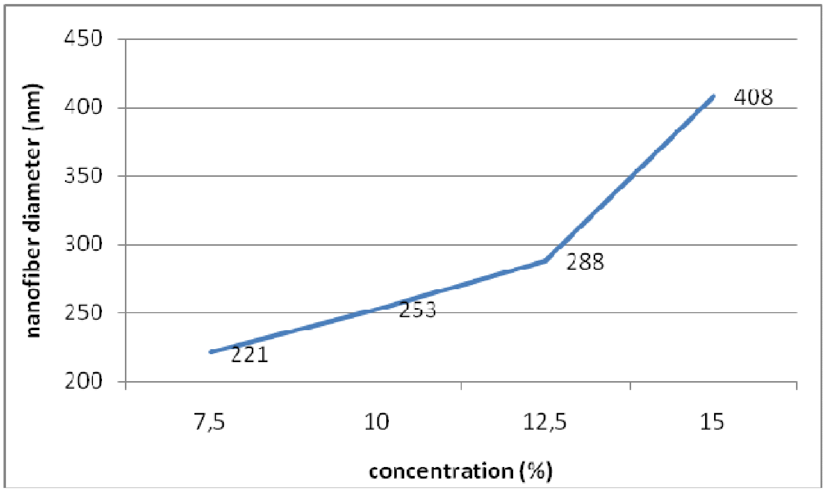
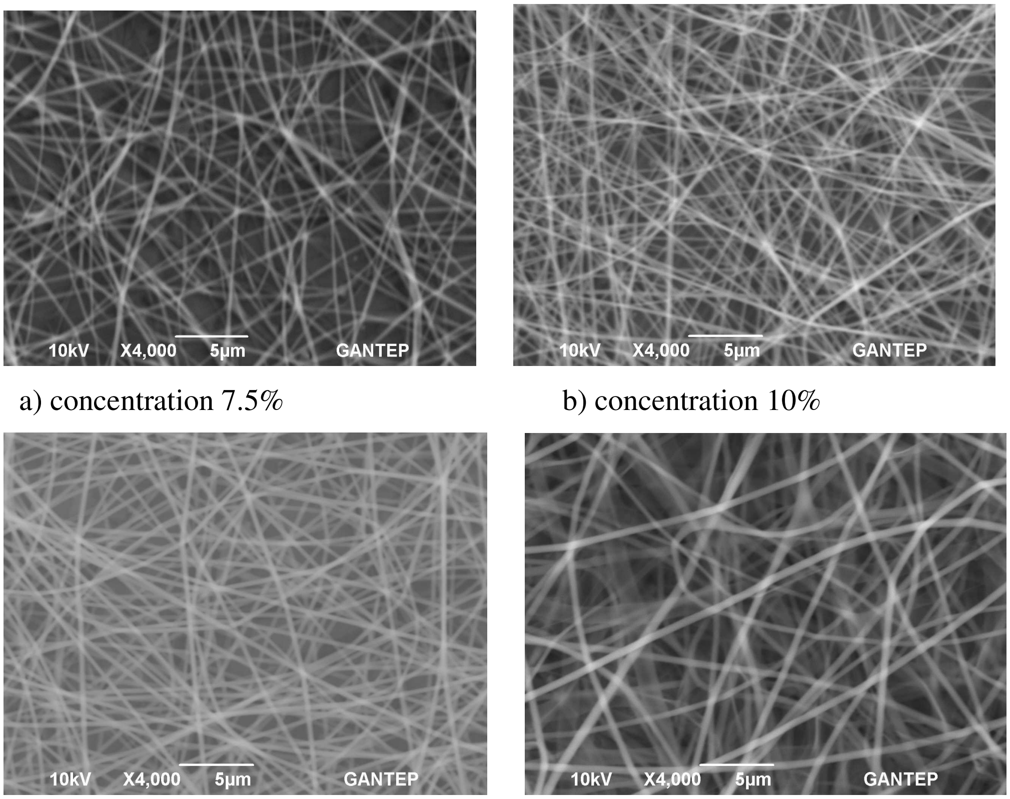


Figure 4.15.Effect of concentration on PVA fiber diameter (25 kV, 20 cm)



a) concentration 7.5%

b) concentration 10%

c) concentration 12,5 %

d) concentration 15%

Figure 4.16 (a-d) Effect of concentration on PVA fiber diameter (25 kV, 20 cm)

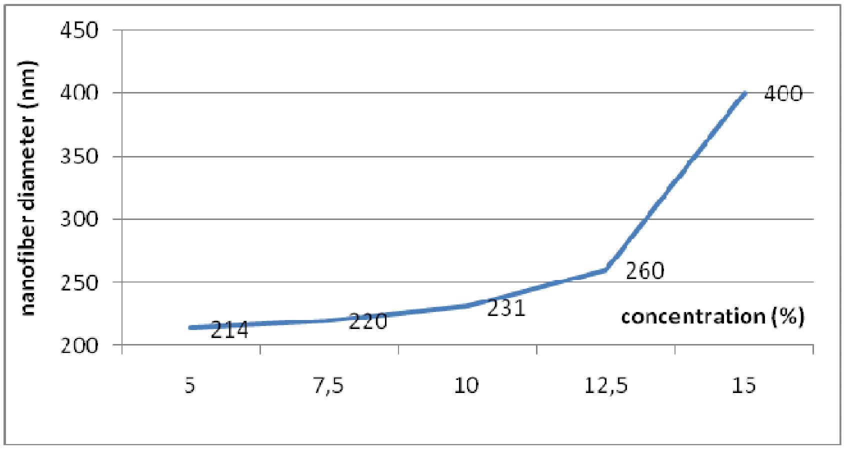
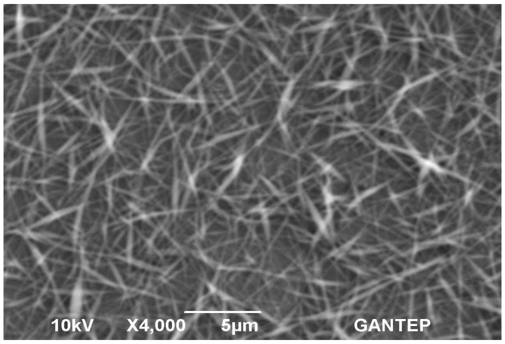
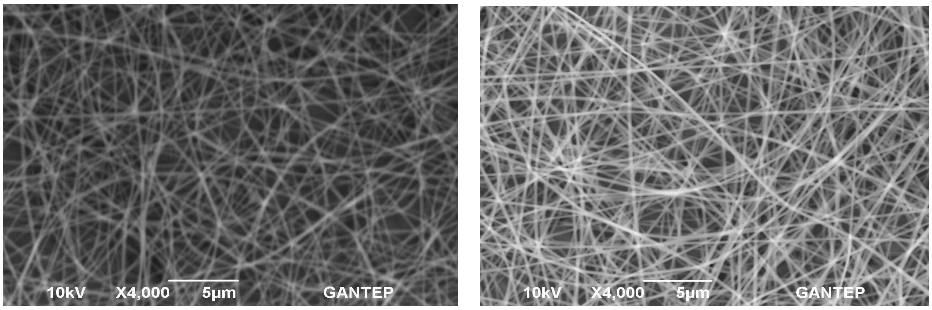


Figure 4.17 Effect of concentration on PVA fiber diameter (30 kV, 20 cm)

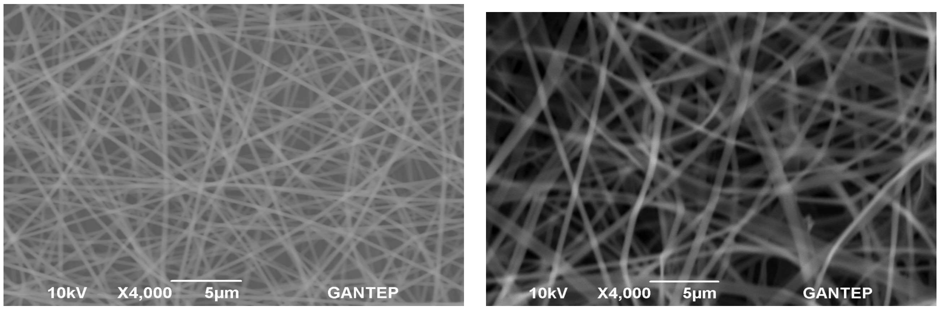


a) concentration 5 %



b) concentration 7.5%

c) concentration 10%



d) concentration 12.5 %

e) concentration 15%

Figure 4.18 (a-e) Effect of concentration on PVA fiber diameter (30 kV, 20 cm)

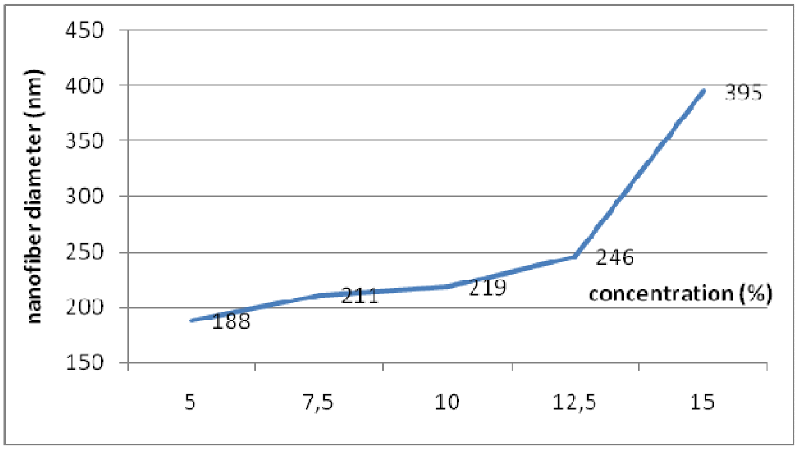
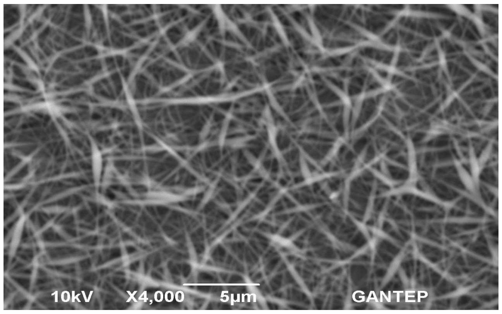
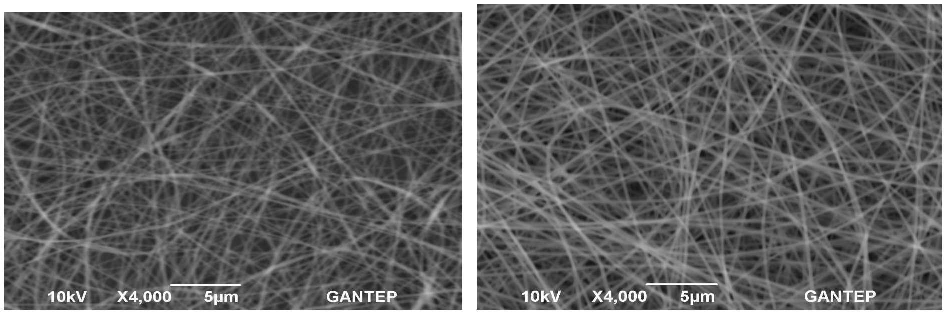


Figure 4.19 Effect of concentration on PVA fiber diameter (35 kV, 20 cm)

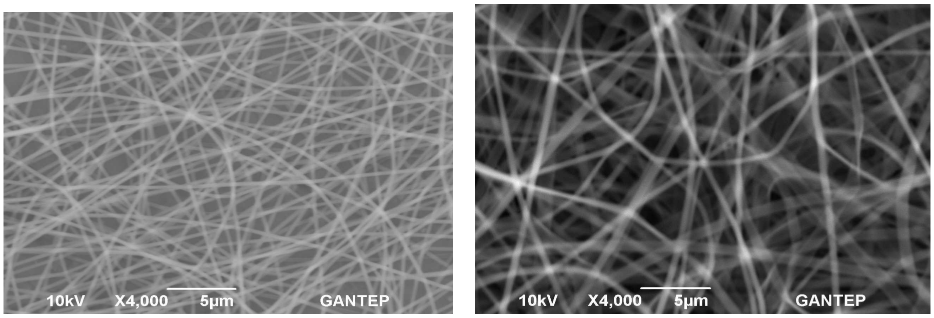


a) concentration 5%



b) concentration 7,5%

c) concentration 10%



d) concentration 12,5 %

e) concentration 15%

Figure 4.20 (a-e) Effect of concentration on PVA fiber diameter (35 kV, 20 cm)

4.5.2. Effect of voltage

The effect of applied voltage (PVA/water) on the nanofiber diameter was given through Figure 4.21 to 4.36. Each of these figures matches a series of experiment where the concentration and distance were kept constant and the voltage value was increased gradually. To investigate the voltage effect on nanofiber morphology, different voltages (5kV-40kV with 5kV intervals) were applied. These figures showed that the nanofiber diameter reduces steadily as the voltage increases. The effect of voltage on the nanofiber diameter and their morphology at different tip collector distance for low concentration were seen through Figure 4.22(e) to 4.22(f). The fiber morphology shows that the bead formation could increase as the voltage increases. Bead formations were especially obvious at low concentrations however, it reduces as the concentration increases (see Figure 4.23(f)). As a conclusion bead formation is more dependent on concentration than other parameters.

Another situation was observed in the experiments that the production rate of nanofiber formation was much higher at shorter distance and higher voltage values but it reduces as the distance increases or voltage reduces. Therefore, some sample nanofiber mats were not obtained. For example, the nanofiber mats were produced after 20 kV when the distance was 15 cm. Therefore, the some SEM images of samples were not included in the study. Generally, no diameter variation was observed in the samples after 15 cm distance and the fiber formation in all voltage values was very uniform.

In section 4.5.2 the best solution concentration for PVA/water was determined as 10%. Because, lower concentrations may cause bead formations and higher concentrations may cause larger nanofiber diameter. The diameter of nanofibers reduced as the voltage increased but the tendency of bead formation increased as well at higher voltage values. Therefore the most suitable interval for voltage was determined as 30-35 kV at 10% concentration. At this point the average nanofiber diameter was calculated as 240 nm.

4.5.2.1. When the concentration is 7,5%

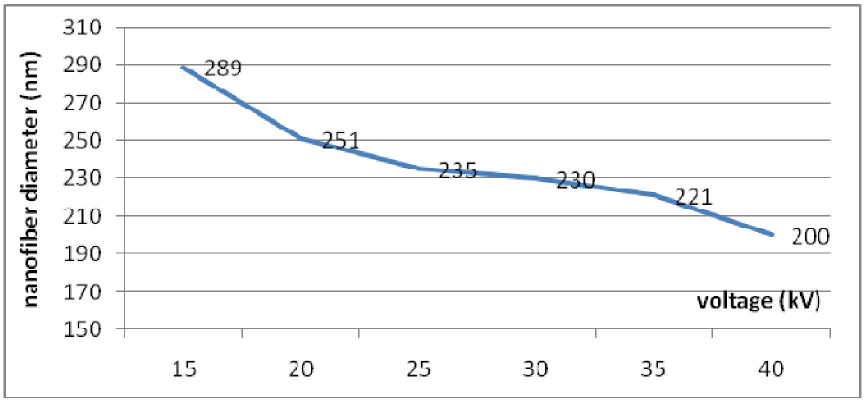
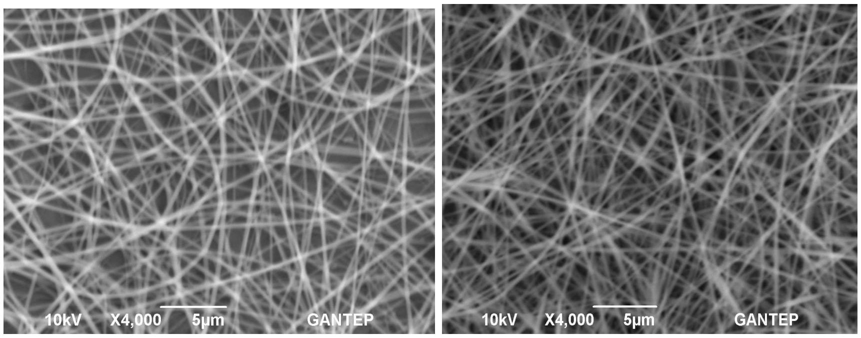
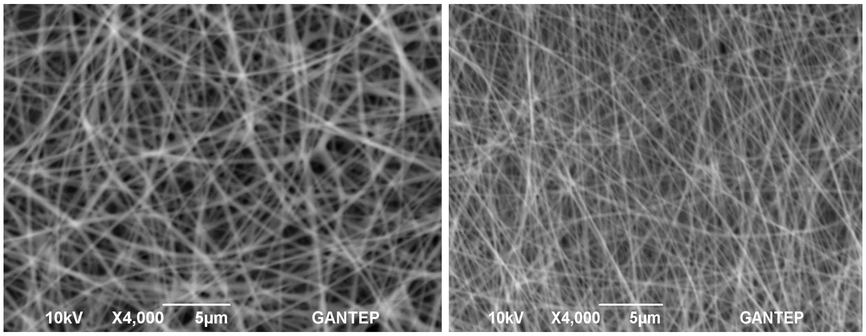


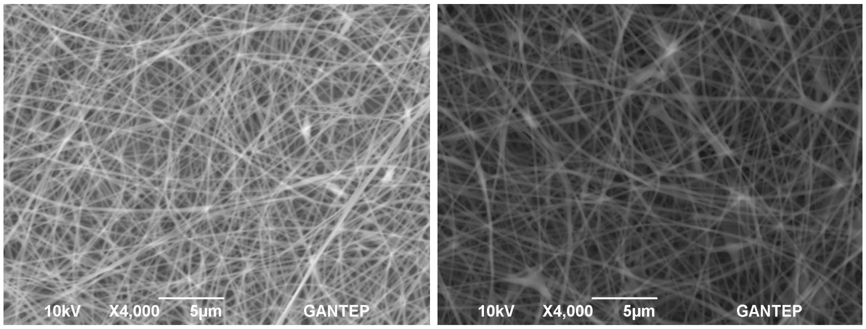
Figure 4.21 Effect of voltage on PVA fiber diameter (7,5% , 10cm)



a) voltage 15 kV b) voltage 20 kV



c) voltage 25 kV d) voltage 30 kV



e) voltage 35 kV f) voltage 40 kV

Figure 4.22 (a-f) Effect of voltage on PVA fiber diameter (7,5 % , 10cm)

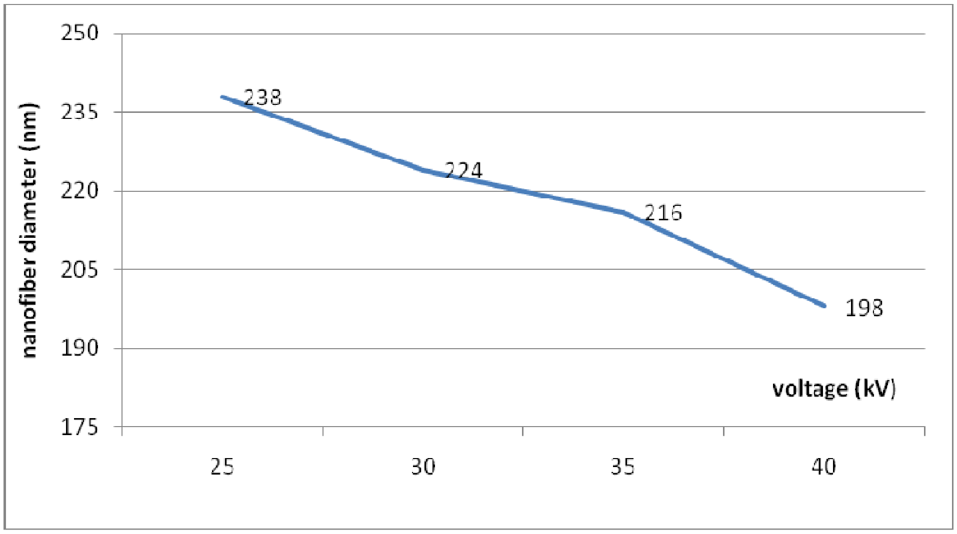
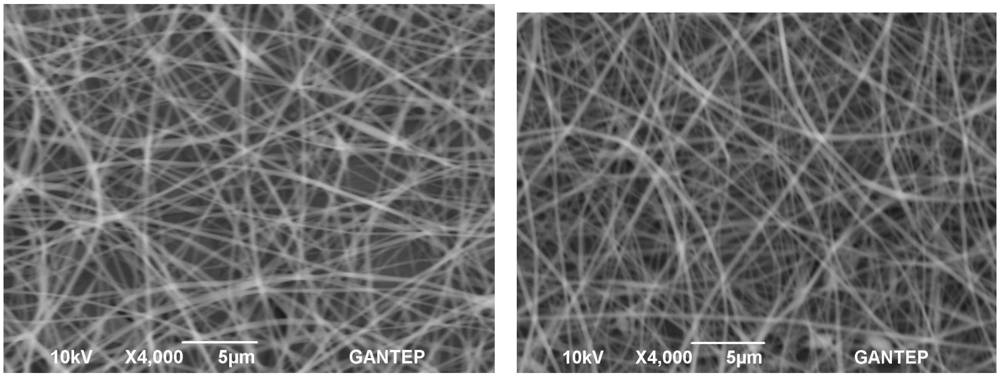
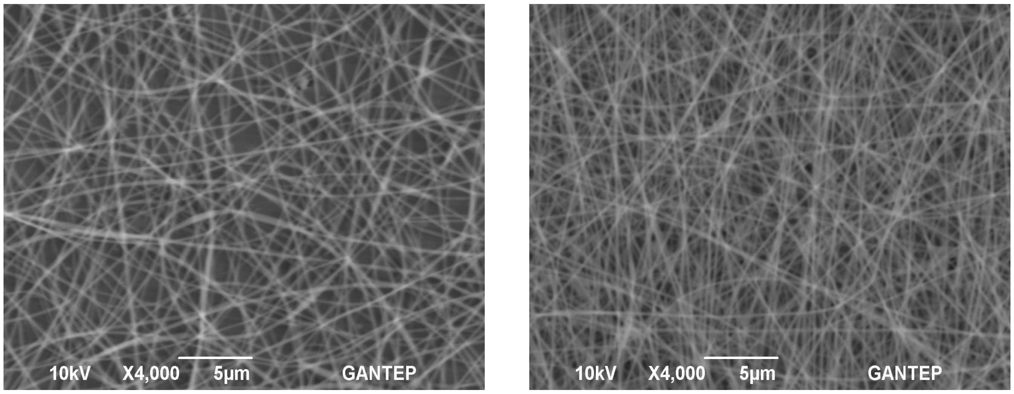


Figure 4.23 Effect of voltage on PVA fiber diameter (7,5 % ,15cm)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 4.24 (a-d) Effect of voltage on PVA fiber diameter (7,5 % and 15cm)

4.5.2.2. When the concentration is 10 %

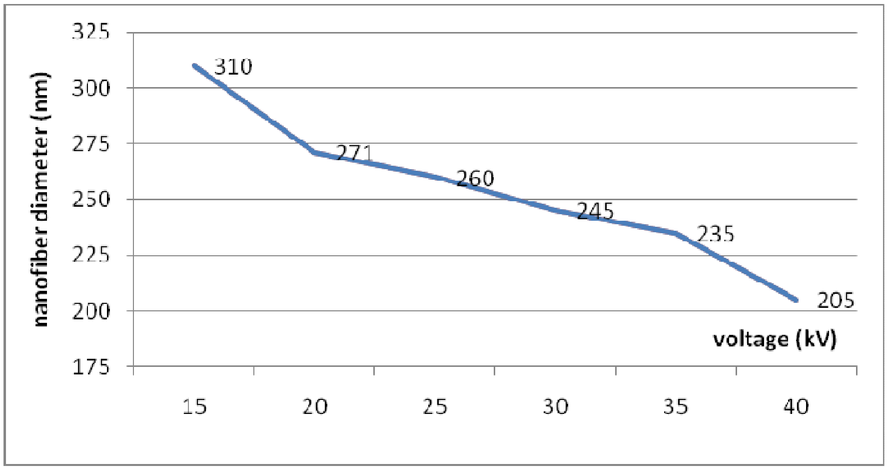
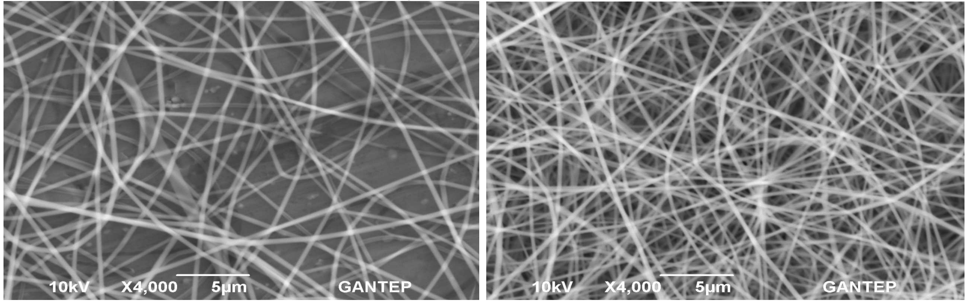
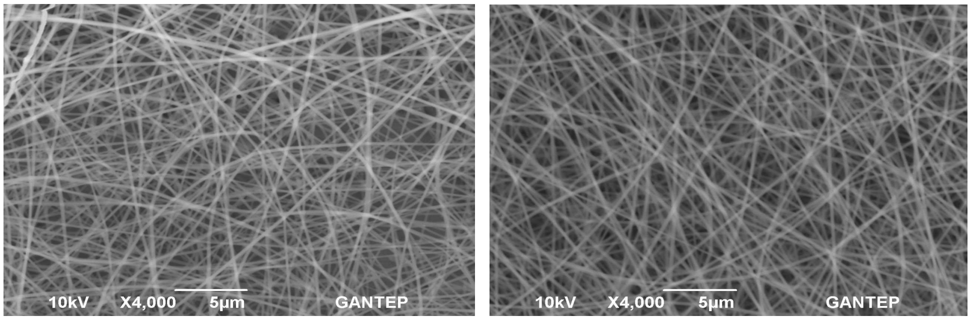


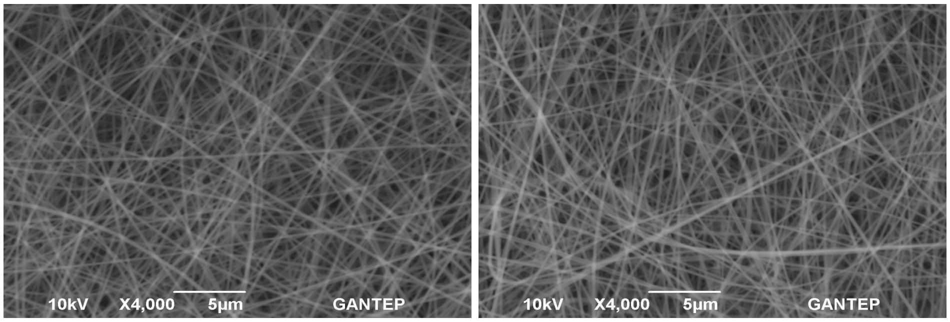
Figure 4.25 Effect of voltage on PVA fiber diameter (10 %, 10cm)



a) voltage 15 kV b) voltage 20 kV



c) voltage 25 kV d) voltage 30 kV



e) voltage 35 kV f) voltage 40 kV

Figure 4.26 (a-f) Effect of voltage on PVA fiber diameter (10 % , 10cm)

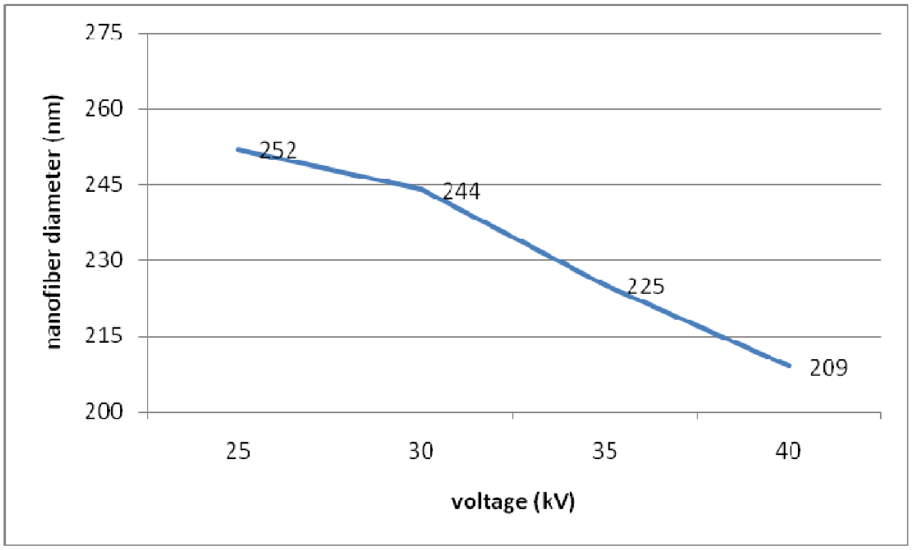
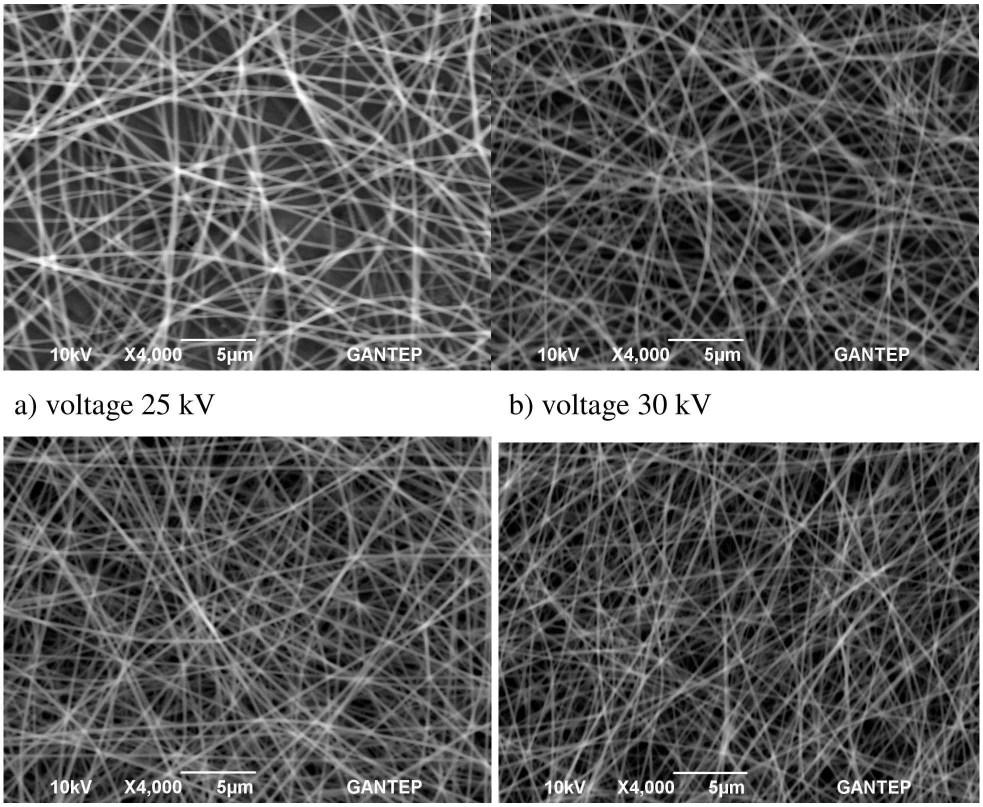


Figure 4.27 Effect of voltage on PVA fiber diameter (10 %, 15cm)



a) voltage 25 kV

b) voltage 30 kV

c) voltage 35 kV

d) voltage 40 kV

Figure 4.28 (a-d) Effect of voltage on PVA fiber diameter (10 %, 15cm)

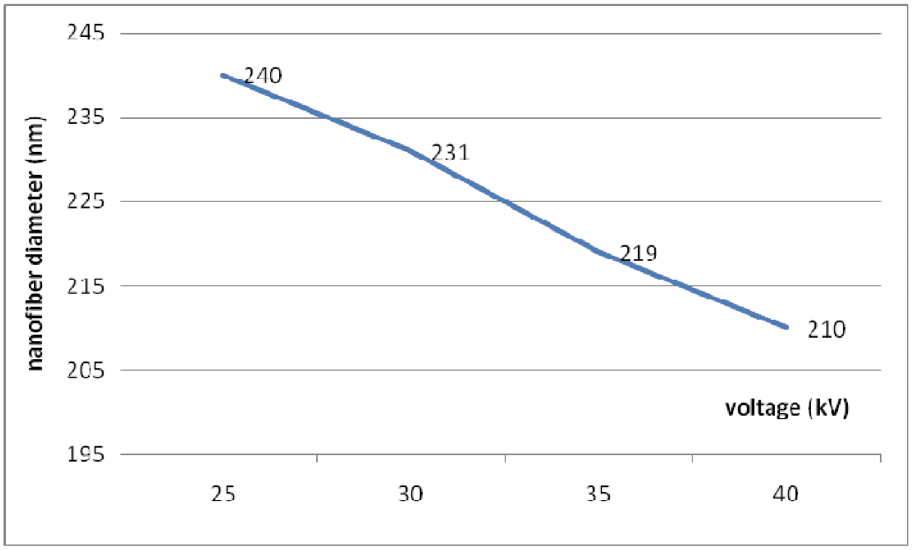
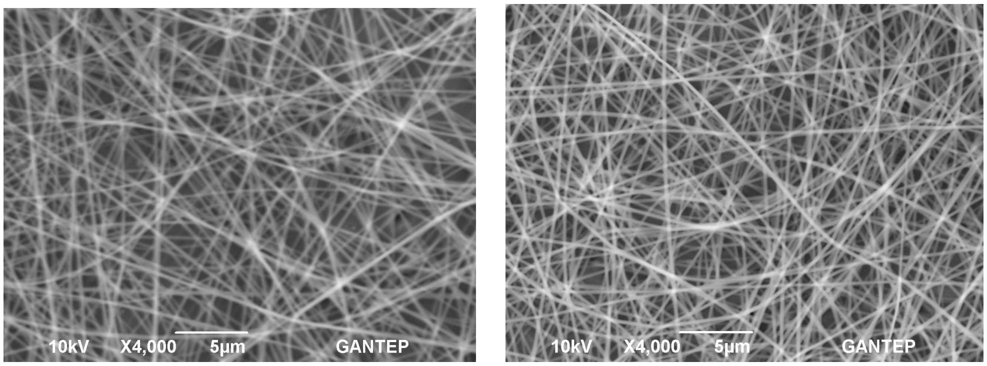
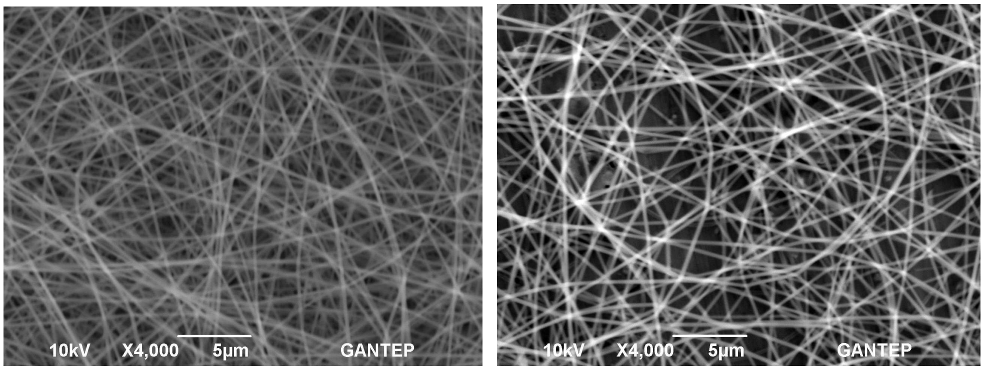


Figure 4.29 Effect of voltage on PVA fiber diameter (10 %, 20cm)



a) voltage 25 kV
b) voltage 30 kV



c) voltage 35 kV
d) voltage 40 kV

Figure 4.30 (a-d) Effect of voltage on PVA fiber diameter (10 % and 20cm)

4.5.2.3. When the concentration is 12,5 %

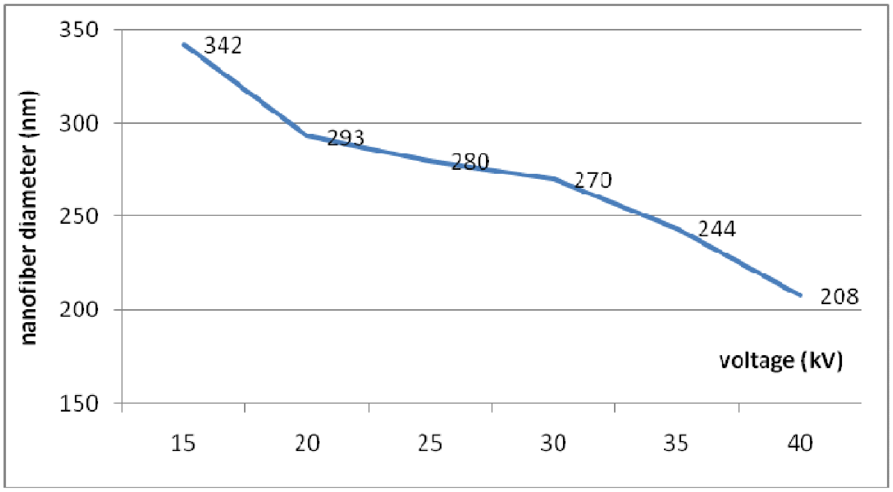
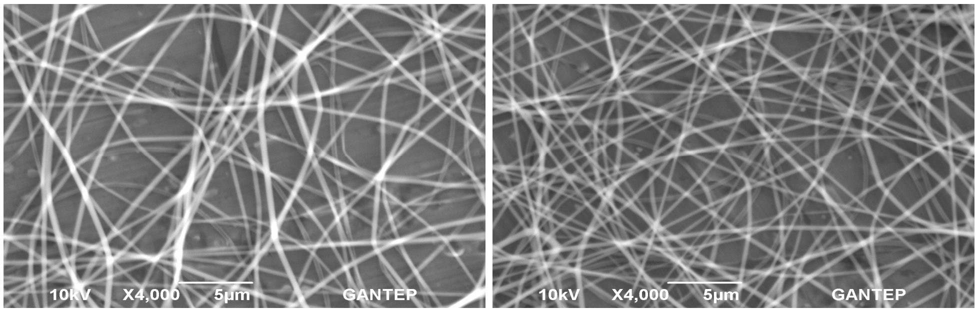
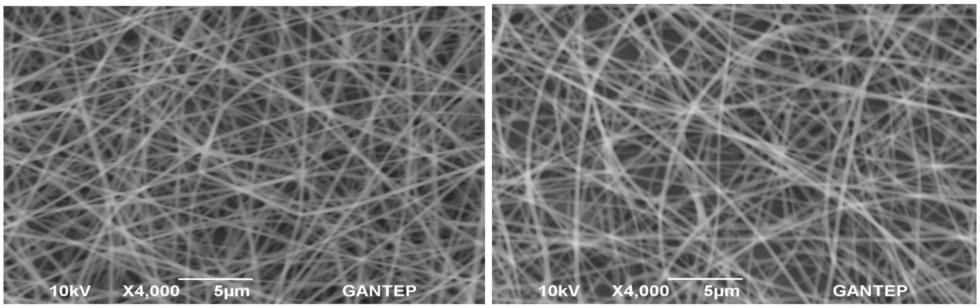


Figure 4.31 Effect of voltage on PVA fiber diameter (12,5 % , 10cm)



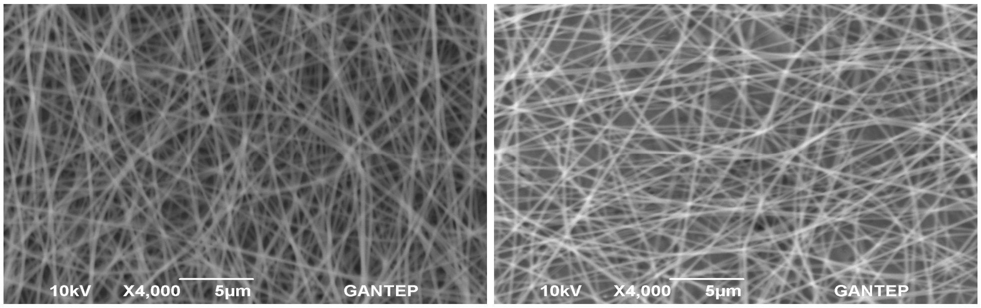
a) voltage 15 kV

b) voltage 20 kV



c) voltage 25 kV

d) voltage 30 kV



e) voltage 35 kV

f) voltage 40 kV

Figure 4.32 (a-f) Effect of voltage on PVA fiber diameter (12.5 %, 10cm)

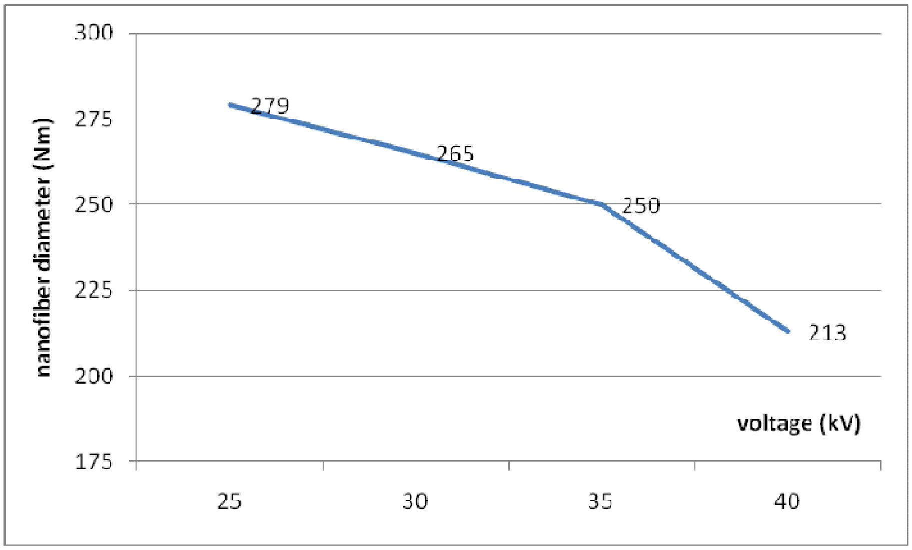
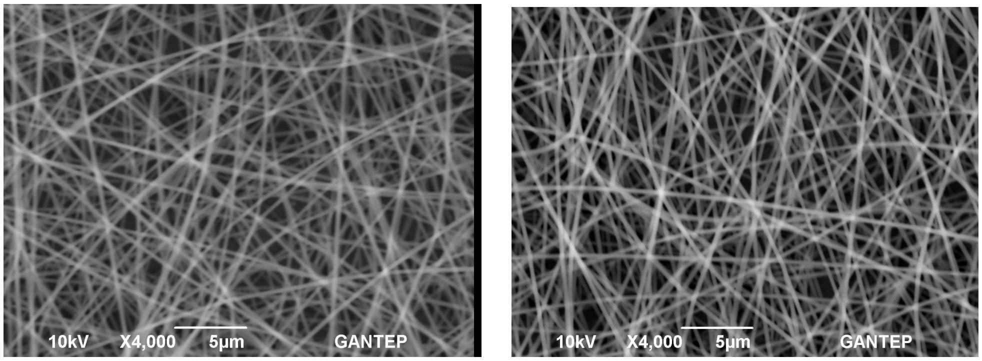
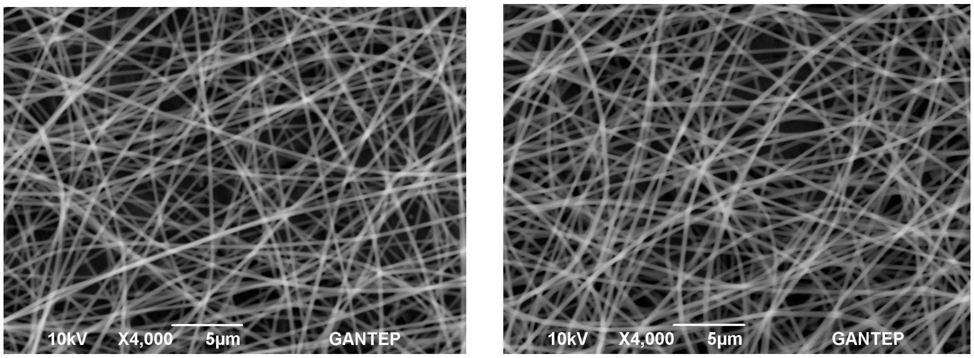


Figure 4.33 Effect of voltage on PVA fiber diameter (12.5 %, 15cm)



a) voltage 25 kV b) voltage 30 kV



c) voltage 35 kV d) voltage 40 kV

Figure 4.34 (a-d) Effect of voltage on PVA fiber diameter (12.5%, 15cm)

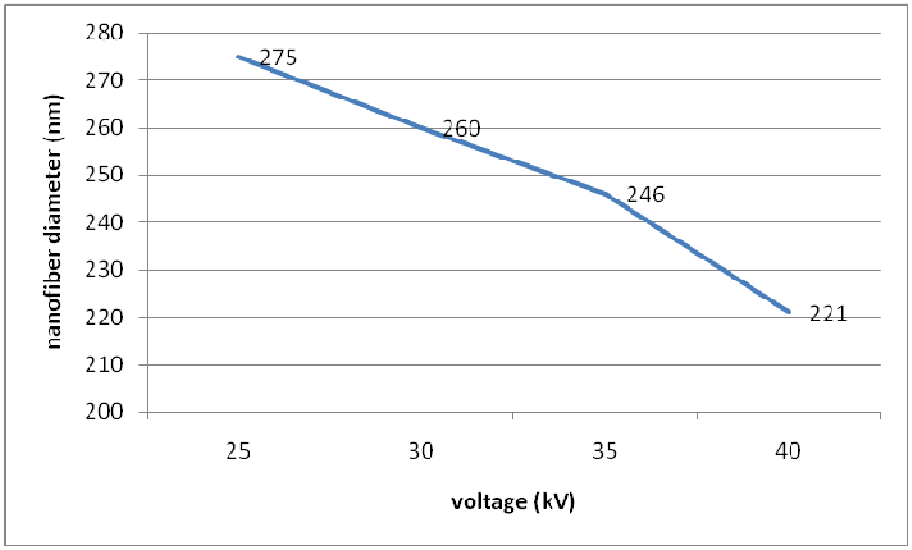
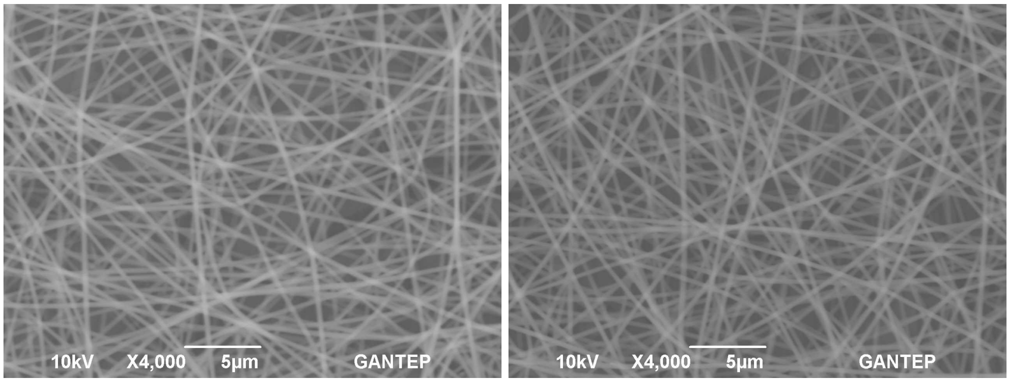
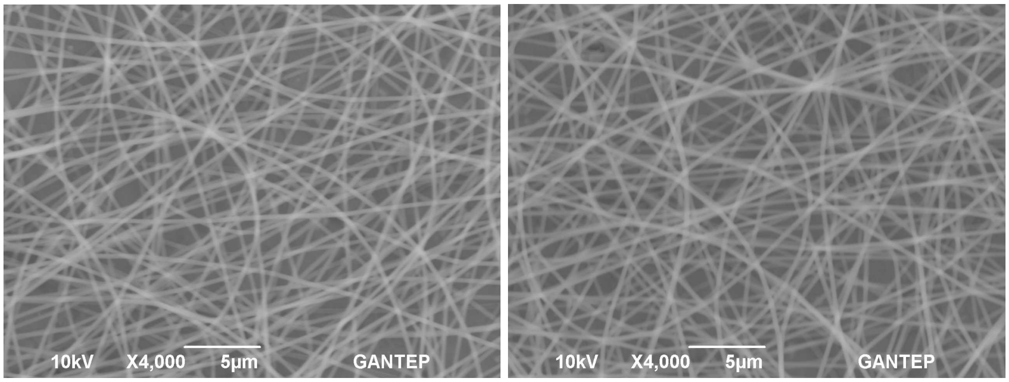


Figure 4.35 Effect of voltage on PVA fiber diameter (12.5 %, 20cm)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 4.36 (a-d) Effect of voltage on PVA fiber diameter (12,5%, 20cm)

4.5.3 Effect of tip-collector distance

The effect of tip-collector distance on the nanofiber diameter was given through Figure 4.37 to 4.50. Each of these figures matches a series of experiment where the concentration and voltage were kept constant and the distance value was increased gradually. To examine the effect of the distance on nanofiber diameter, the tip-collector distance was changed between 5–25 cm (5cm intervals). Examinations show that the nanofiber diameter reduces slowly as the tip-collector distance increases.

Another drawback of short tip-collector distance is that the tendency of bead formation increases at shorter distance at low concentration values, however, this tendency diminishes as distance increases as shown in Figure 4.40(a-d). Examination of the SEM images shows that the effect of distance on the nanofiber diameter variation is very limited. Average diameter variation (between maximum and minimum diameter) was observed about 23nm.

Some experimental studies and SEM images were not included in the study because of the difficulties. For example, 5 cm tip-collector distance was not performed satisfactorily because of frequently spark formation between the tip and the collector. These sparks were caused uneven and irregular nanofiber mats. Moreover, for the same reasons experiments for high voltage values (such as 40kV) were not done especially for short distance, therefore all the set for 40kV were not included here.

In previous sections the most suitable concentration and the voltage values were determined 10% and 30-35 kV respectively. The tip collector distance examinations show that as the distance increases the fiber diameter reduces and also the possibility of bead formation reduces; however fiber production rate decreases at longer distances. Therefore, the most proper tip-collector distance was determined 15cm (by regarding the most favorable concentration and voltage values). At this point the average nanofiber diameter was calculated as 235 nm. At this point the average nanofiber diameter was calculated as 234 nm.

4.5.3.1. When the concentration is 7,5%

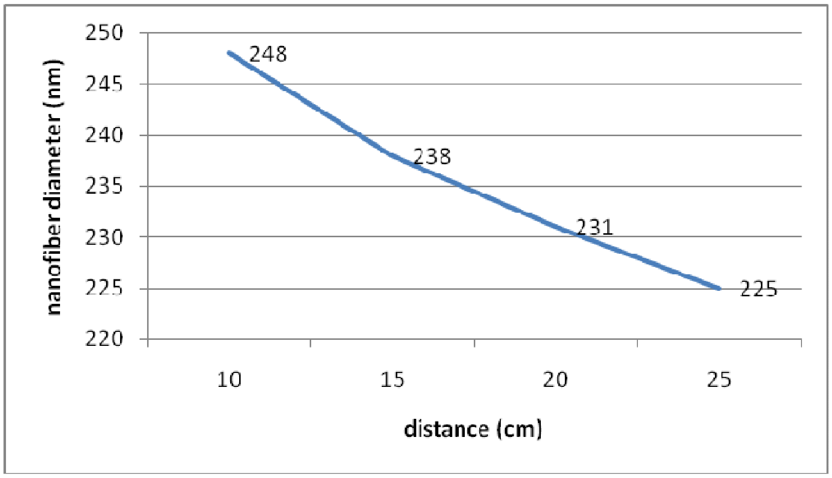
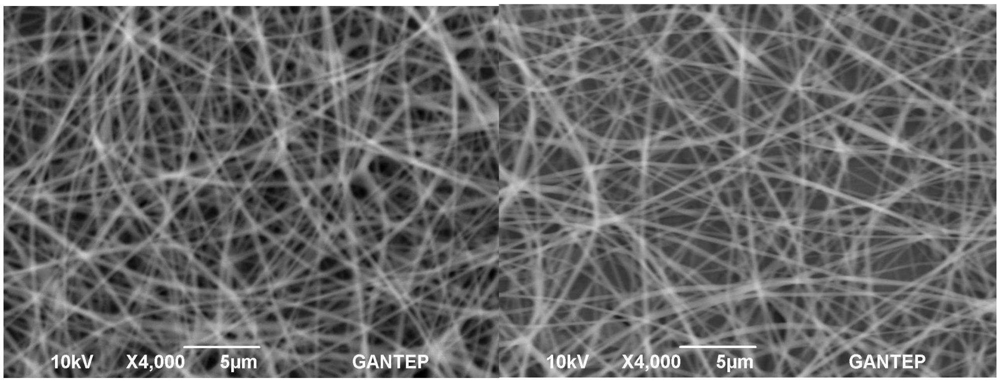
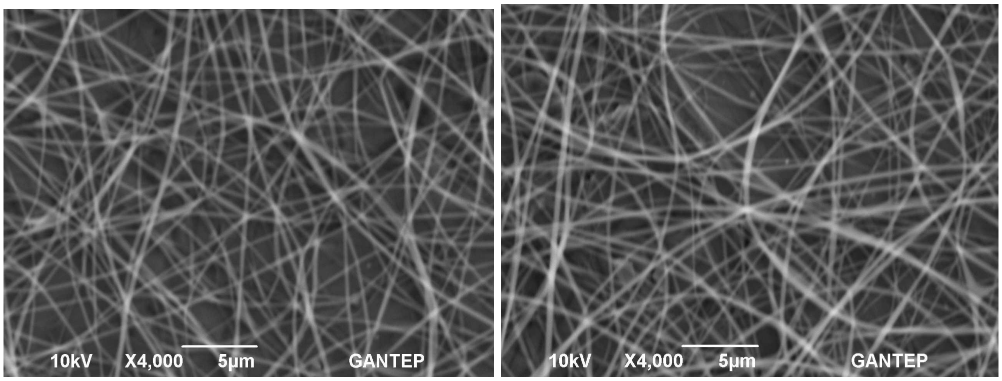


Figure 4.37 Effect of distance on PVA fiber diameter (7,5% , 25 kV)



a) tip-collector distance 10 cm b) tip-collector distance 15 cm



c) tip-collector distance 20 cm d) tip-collector distance 25 cm

Figure 4.38 (a-d) Effect of distance on PVA fiber diameter (7,5% , 25 kV)

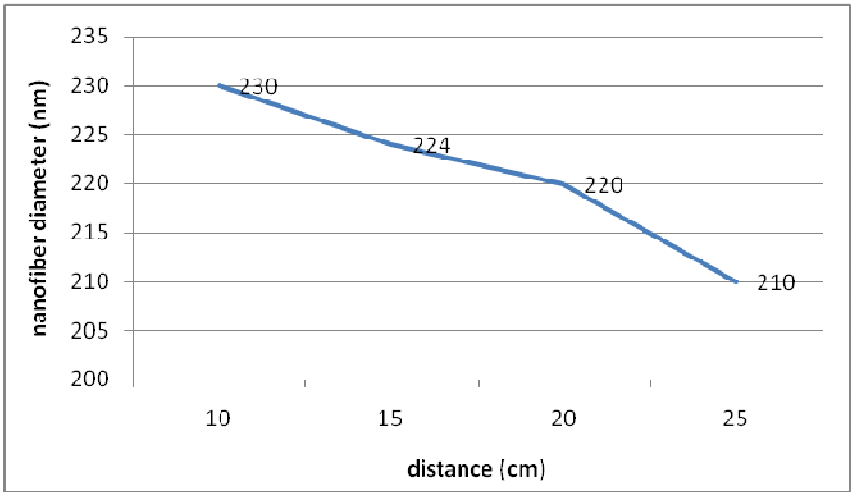
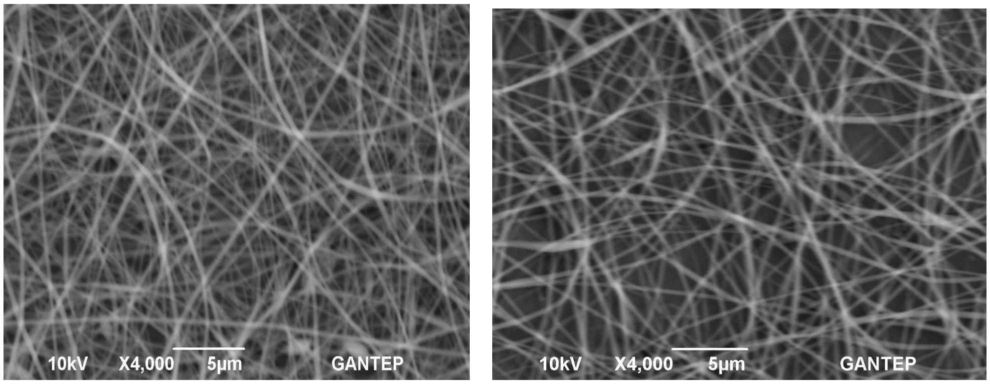
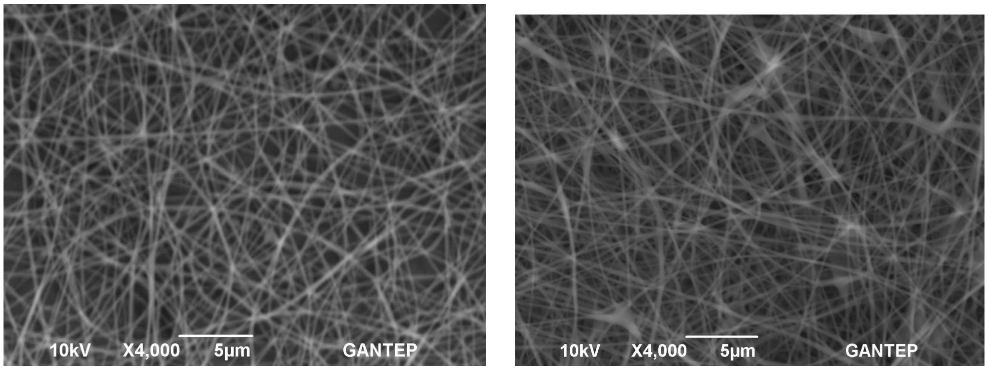


Figure 4.39 Effect of distance on PVA fiber diameter (7.5%, 30 kV)



a) tip-collector distance 10 cm

b) tip-collector distance 15 cm



c) tip-collector distance 20 cm

d) tip-collector distance 25 cm

Figure 4.40 (a-d) Effect of distance on PVA fiber diameter (7,5% , 30 kV)

4.5.3.2. When the concentration is %10

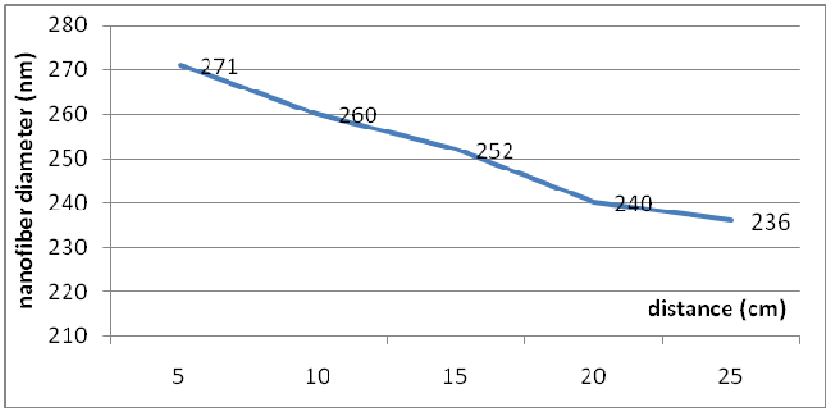
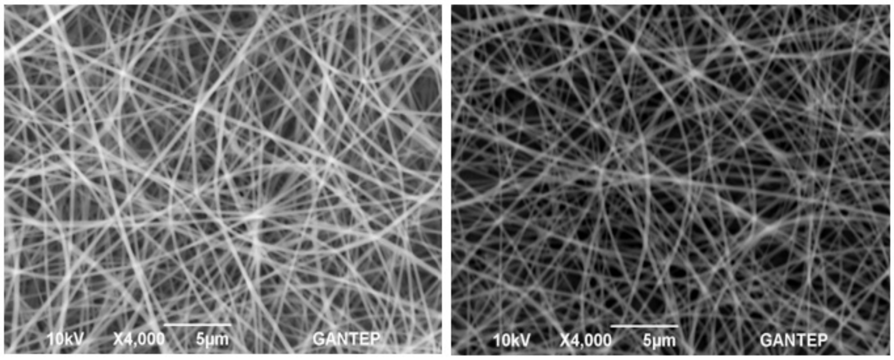
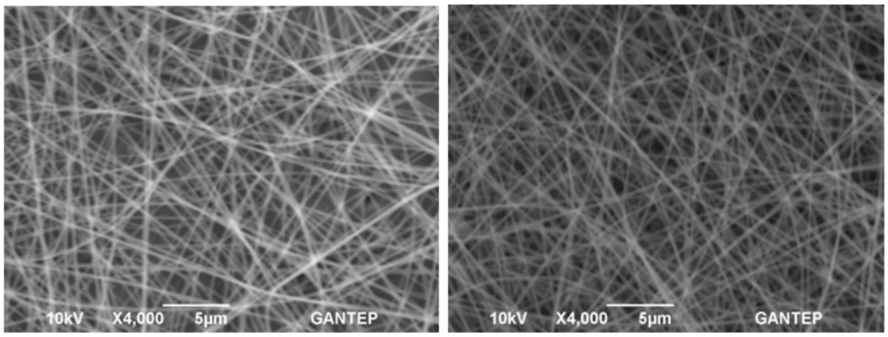


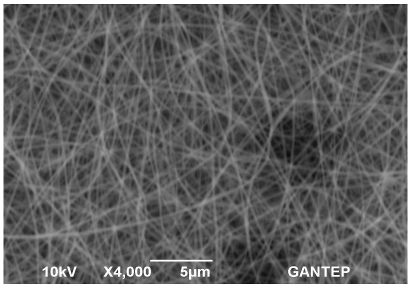
Figure 4.41 Effect of distance on PVA fiber diameter (10%, 25 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 4.42 (a-d) Effect of distance on PVA diameter (10%, 25 kV)

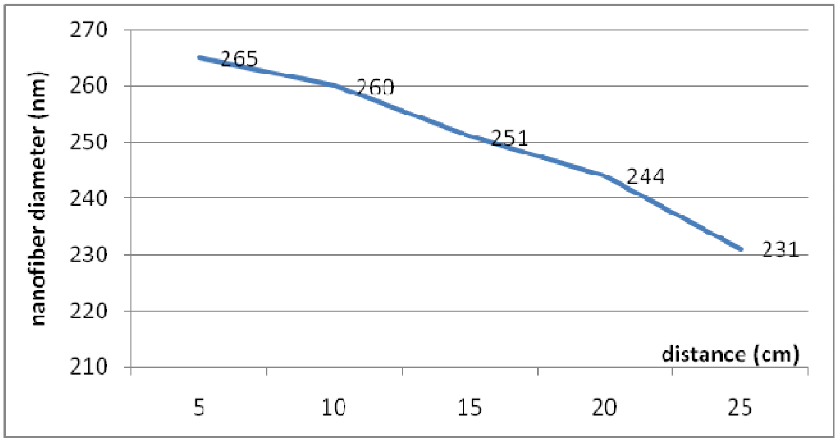
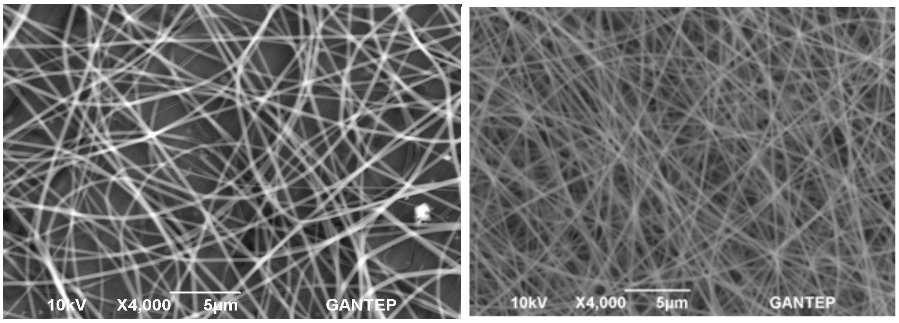
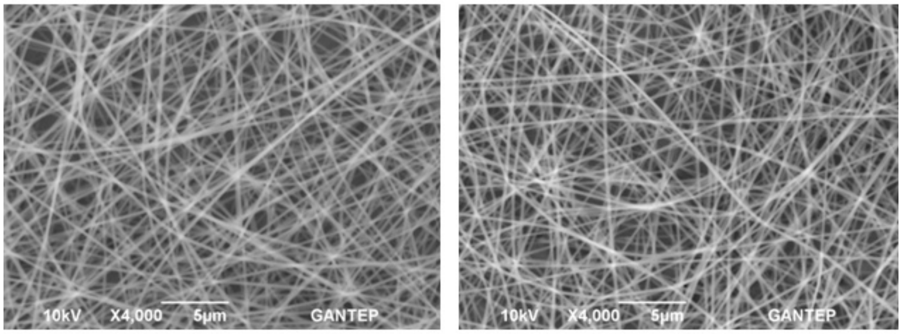


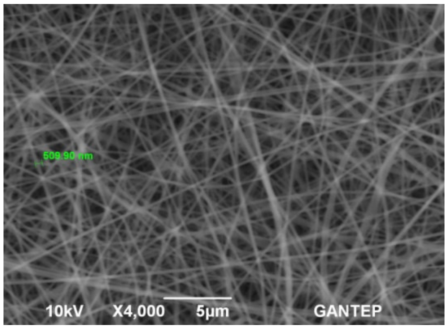
Figure 4.43 Effect of distance on PVA fiber diameter (10%, 30 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 4.44 (a-d) Effect of distance on PVA fiber diameter (10%, 30 kV)

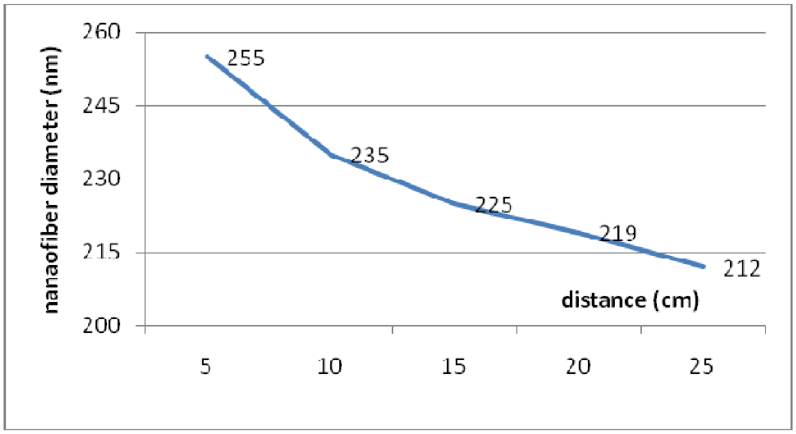
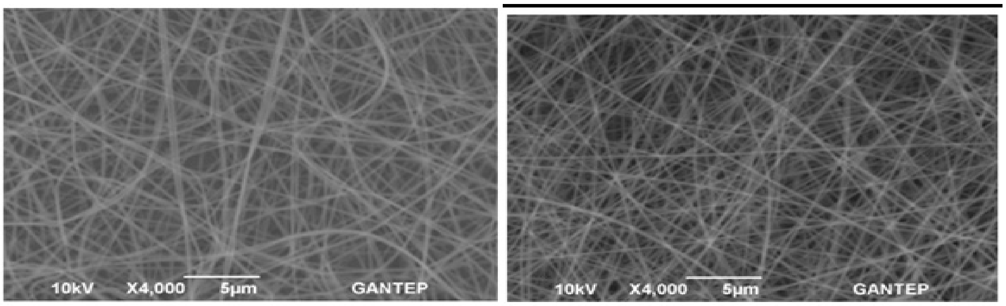
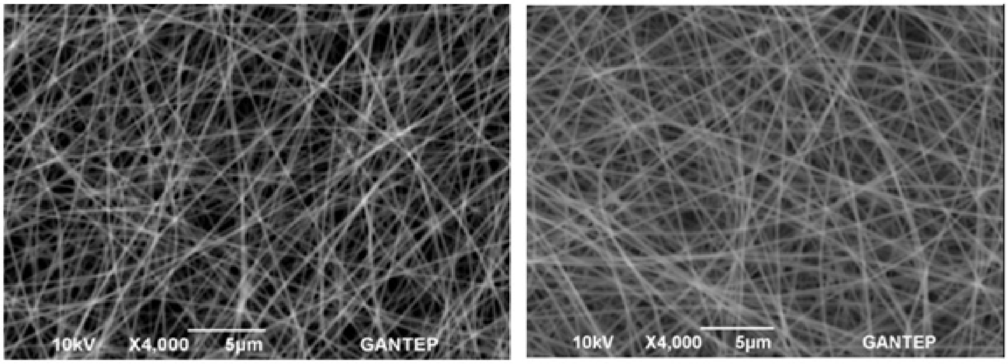


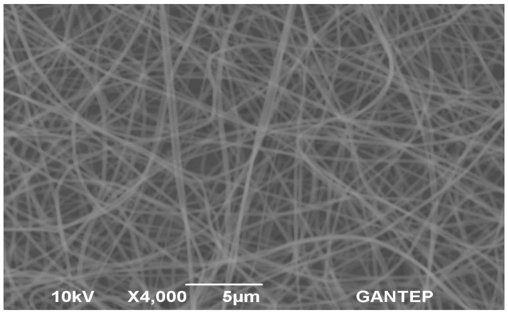
Figure 4.45 Effect of distance on PVA fiber diameter (10%, 35 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 4.46 (a-e) Effect of distance on PVA fiber diameter (10%, 35 kV)

4.5.3.3. When the concentration is % 12.5

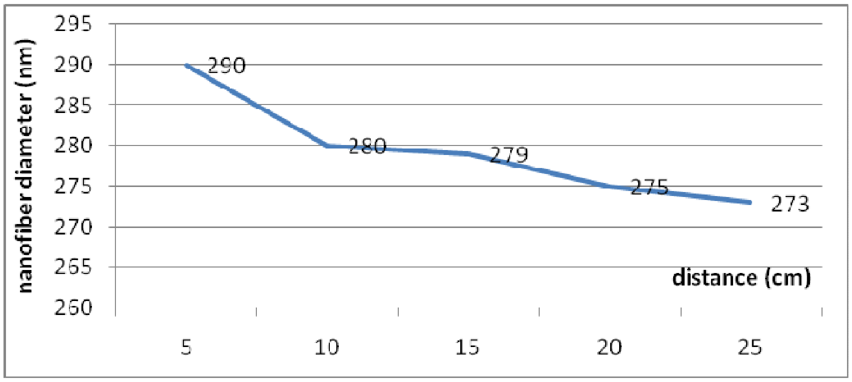
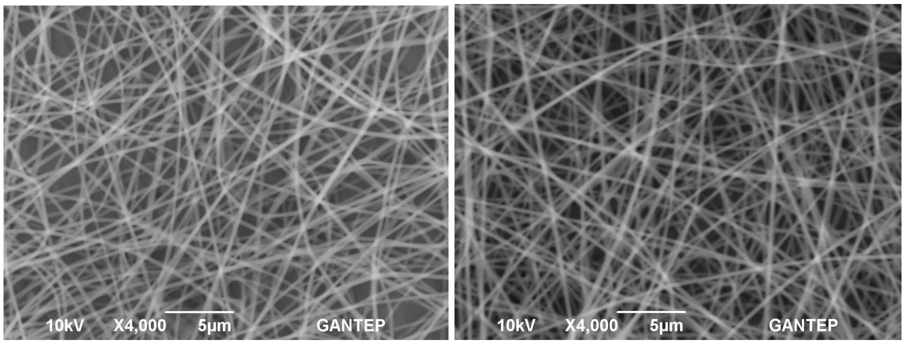
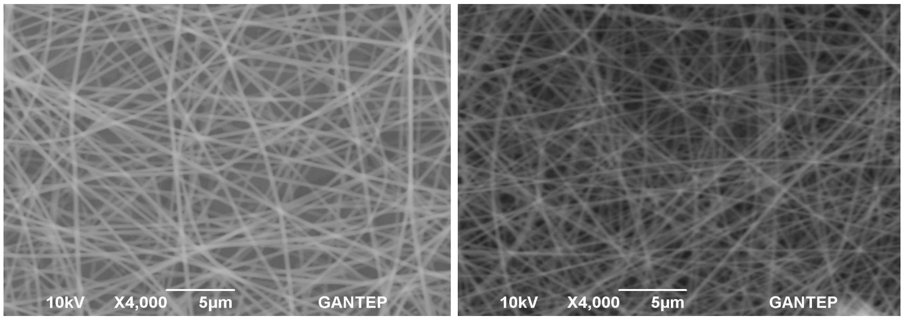


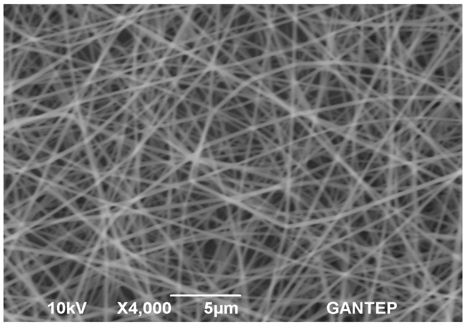
Figure 4.47 Effect of distance on PVA fiber diameter (12.5%, 25 kV)



a) tip-collector distance 5 cm b) tip-collector distance 10 cm



c) tip-collector distance 15 cm d) tip-collector distance 20 cm



e) tip-collector distance 20 cm

Figure 4.48 (a-d) Effect of distance on PVA fiber diameter (12,5%, 25kV)

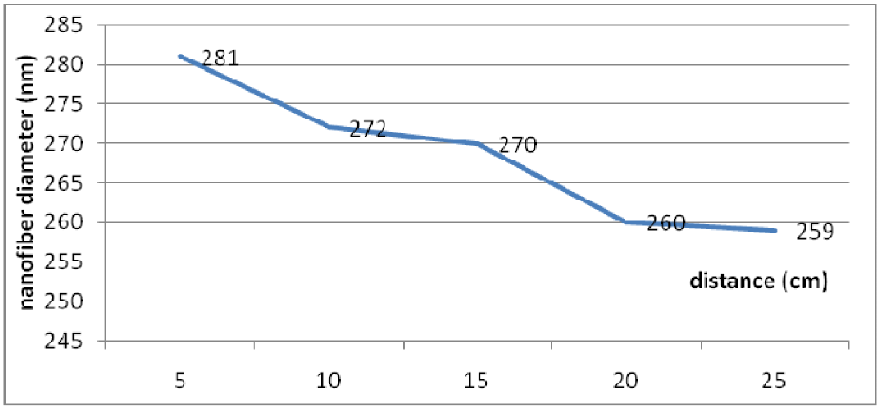
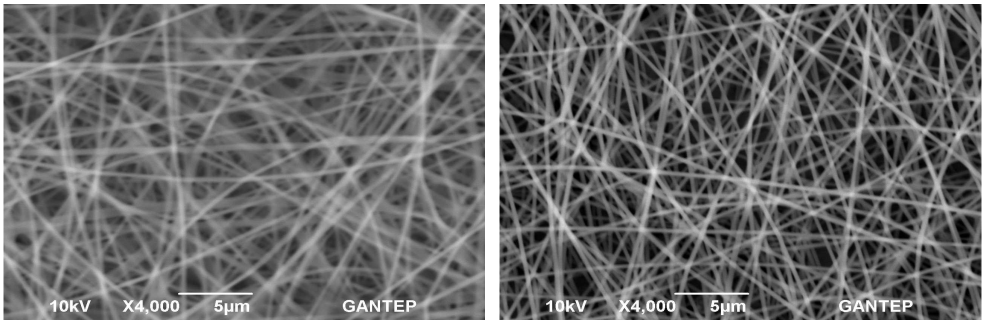
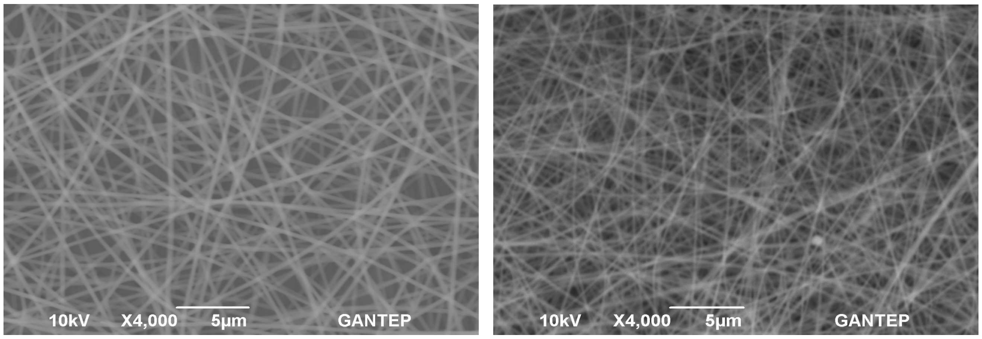


Figure 4.49 Effect of distance on PVA fiber diameter (12.5%, 30 kV)



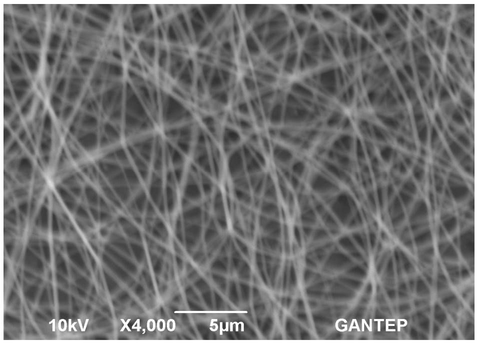
a) tip-collector distance 5 cm

b) tip-collector distance 10 cm



c) tip-collector distance 15 cm

d) tip-collector distance 20 cm



e) tip-collector distance 25 cm

Figure 4.50 (a-e) Effect of distance on PVA fiber diameter (12.5%, 30kV)

CHAPTER 5

POLYAMIDE 6

5.1. Introduction

In this chapter, the parameters which affect the morphology of PA6 nanofiber were tried to determine and the best possible solution concentration and process parameters for electrospinning searched out. The images of these sample nanofibers were taken from SEM and the best possible interval or a value for those parameters was decided by examining these SEM images as done in the previous chapters. To conduct the experiment a solution was prepared by dissolving PA6 polymer in formic acid. The solution was arranged by stirring magnetically for one hour at a room temperature.

5.2. Electrospinning

To investigate the concentration effect on nanofiber morphology; solutions (6-14% with 2% intervals) were prepared by dissolving PA6 polymer in formic acid. To examine the effect of voltage on nanofiber diameter, the voltage was changed between 5-40 kV (5 kV intervals). Similarly, to analyze the effect of distance on nanofiber diameter, it was changed between 5-25 cm (5 cm interval). The ambient temperature was adjusted at 25°C and the humidity is kept at 25 %.

5.3. Characterization

The morphological appearance of the as-spun PA6 fiber mats and that of the individual fibers was investigated by a JEOL JSM-6390LV scanning electron microscope (SEM), operating at an acceleration voltage of 10 kV.

5.4. Measurements of nanofiber diameters

The diameters of nanofibers were measured using Image-Pro Plus 6.0. Twenty measurements were performed to calculate the average diameter of the nanofibers.

5.5. Experimental Study

The results showed that the diameters of electrospun PA6 nanofibers were greatly affected by solution concentration. As the concentration increases the fiber diameter increases as well. Generally, beads were seen for concentration less than 10% however, between 10-12% concentrations uniform nanofiber formation was observed. The inspections show that the bead formation was mostly affected by concentration. An increase in the electric field was resulted in the decrease of the average diameter of the electrospun fibers. Continuous and smooth fibers were formed in the electrospinning voltage ranging from 25 to 35 kV. On the contrary to concentration bead formation was less likely to be effected from the potential difference. On the other hand, high voltage was caused non-uniformity on the fiber diameter. The distance effect on PA6 nanofiber was observed that as the distance increases the fiber diameter decreases. The optimum formations were observed between 10-15 cm. The nanofiber diameter was between 250 and 170 (average diameter 210 nm).

5.5.1. Effect of concentration

Figures 5.1 to 5.18 show the concentration effect on PA6 nanofiber. It was observed that as the concentration increases the fiber diameter increases and the diameter was very fine with respect to other polymers (PVA and PAN). Continuous PA6 fibers were successfully electrospun from the PA6/formic acid solutions in the concentration ranging between 8-14%. For the low concentration (8%) no continuous fibers but a mixture of beads and nanofibers were obtained. Most uniform nanofibers were achieved between 10-12% concentrations. For the higher concentration electrospinning process was difficult and the diameter of nanofibers were increased sharply at 14% concentration. On the other hand, the PA6 was not dissolved easily in formic acid to form higher concentrated solution. Also, electrospinning was not happened no matter how high an electric voltage was applied. So, the spinnable concentration of PA6/formic acid solution in electrospinning was 8-14 wt%.

5.5.1.1. When the distance is 10 cm

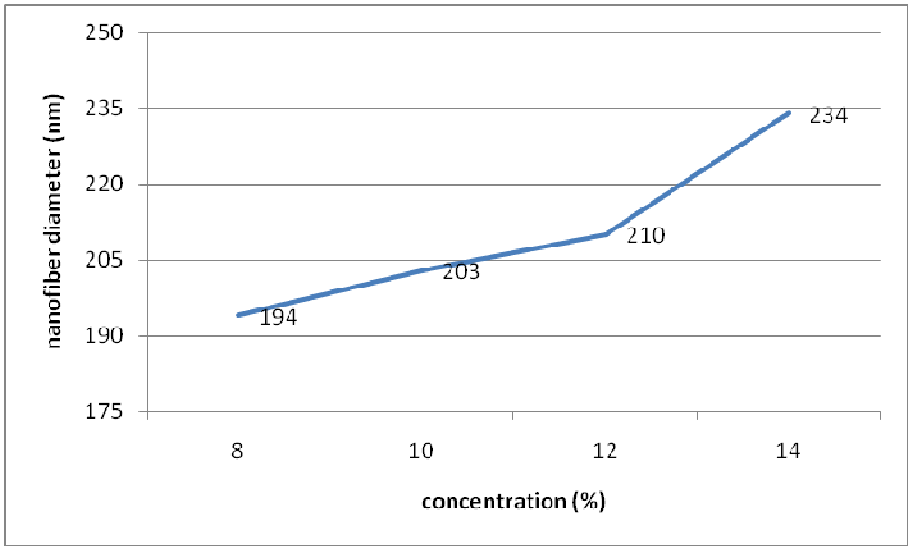
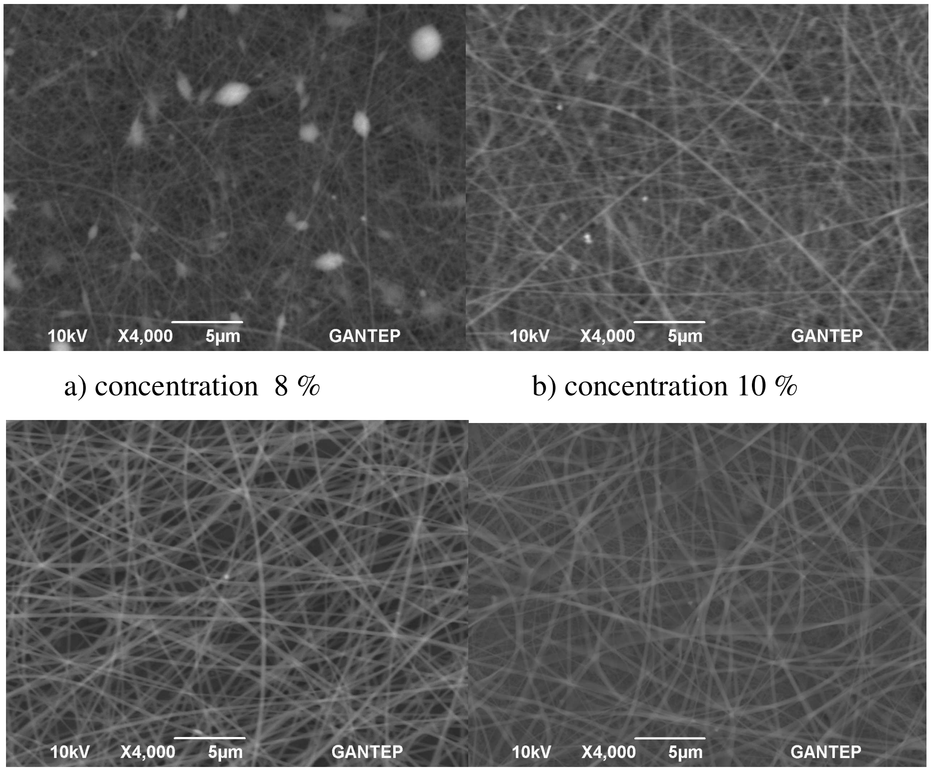


Figure 5.1 Effect of concentration on PA6 fiber diameter (10 cm, 25 kV)



a) concentration 8 %

b) concentration 10 %

c) concentration 12%

d) concentration 14 %

Figure 5.2 (a-d) Effect of concentration on PA6 fiber diameter (10 cm, 25 kV)

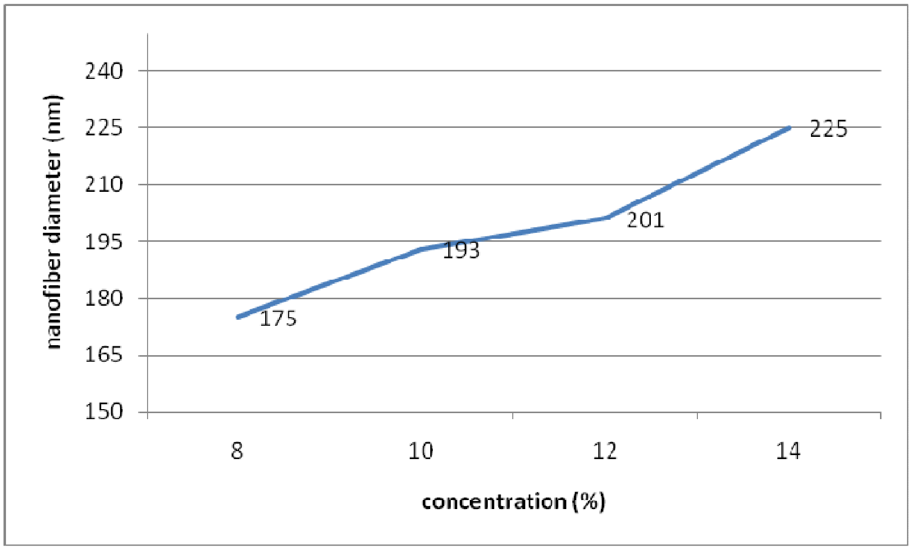
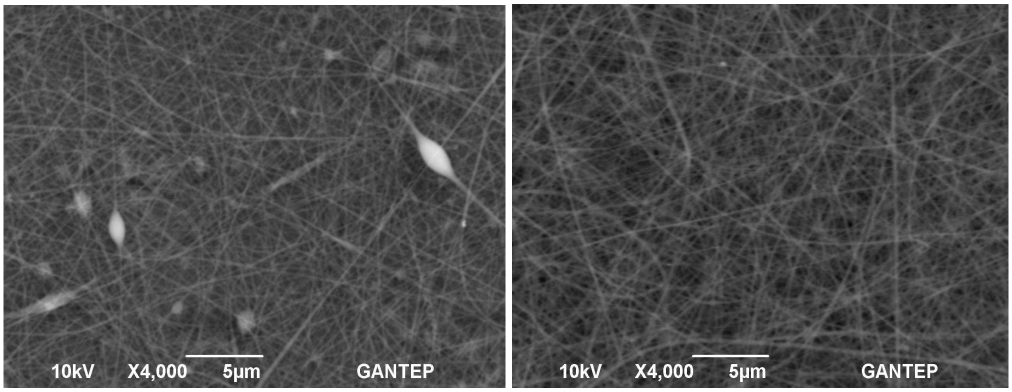
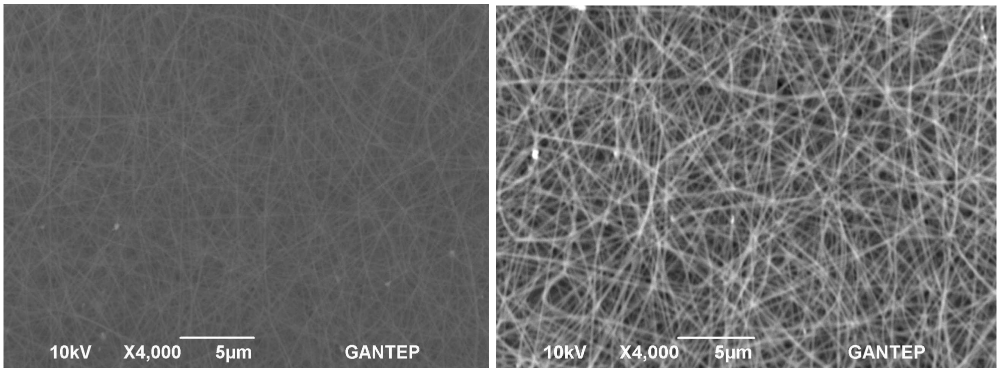


Figure 5.3 Effect of concentration on PA6 fiber diameter (10 cm, 30 kV)



a) concentration 8 %

b) concentration 10 %



c) concentration 12%

d) concentration 14 %

Figure 5.4 (a-d) Effect of concentration on PA6 fiber diameter (10 cm, 30 kV)

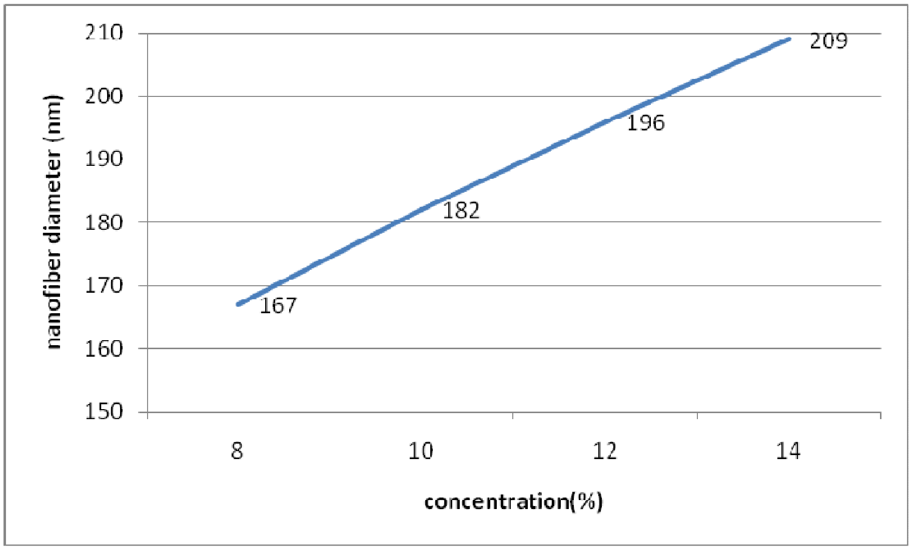
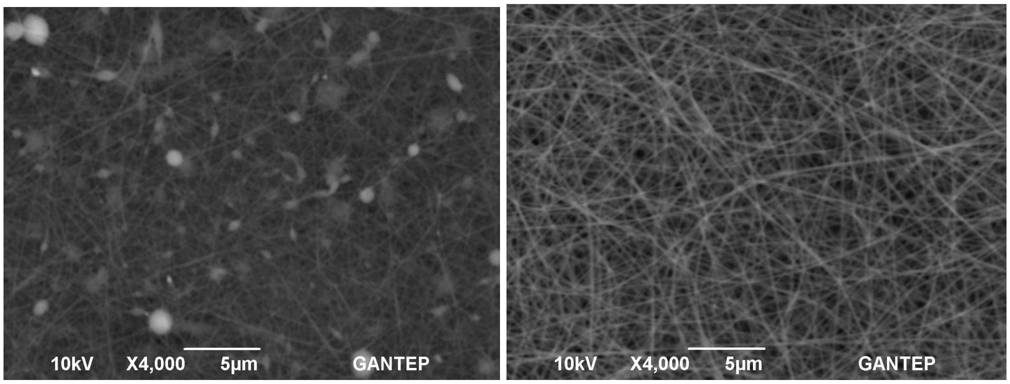
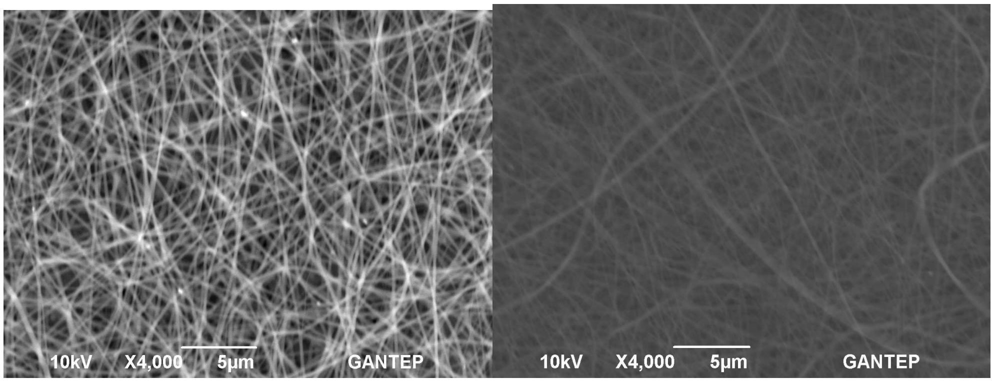


Figure 5.5 Effect of concentration on PA6 fiber diameter (10 cm, 35 kV)



a) concentration 8 %

b) concentration 10%



c) concentration 12%

d) concentration 14%

Figure 5.6 (a-d) Effect of concentration on PA6 fiber diameter (10 cm, 35 kV)

5.5.1.2. When the distance is 15 cm

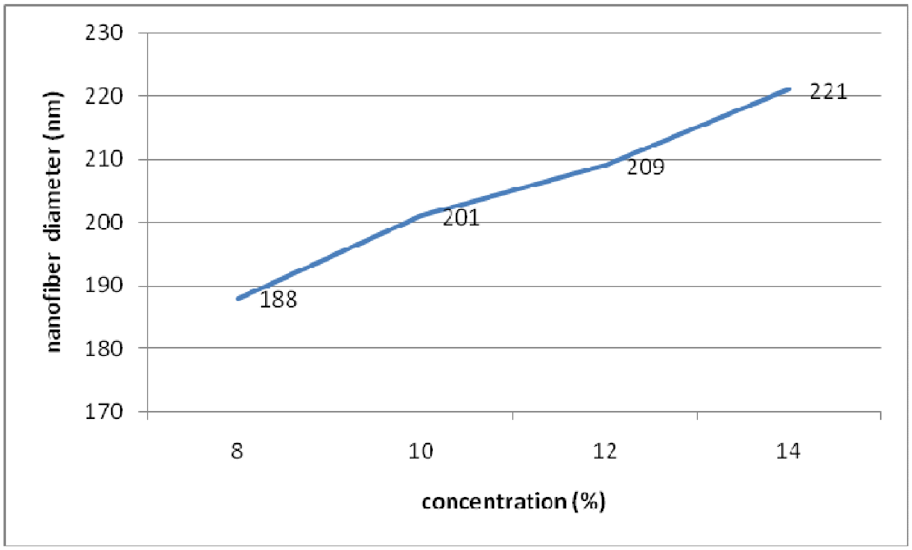
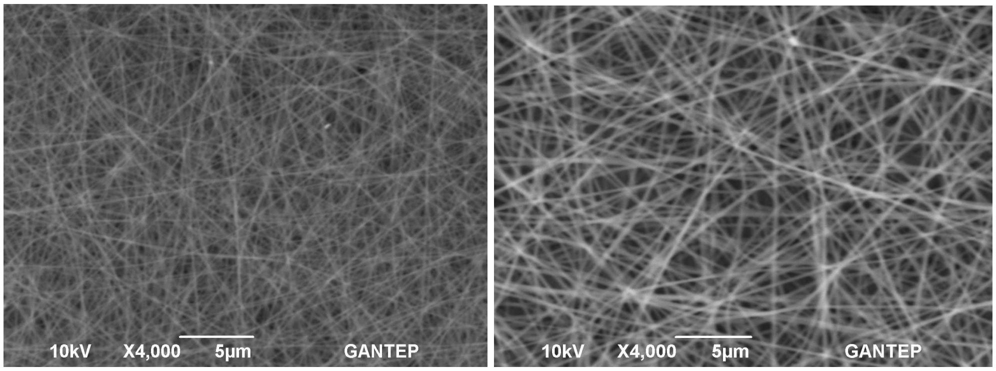
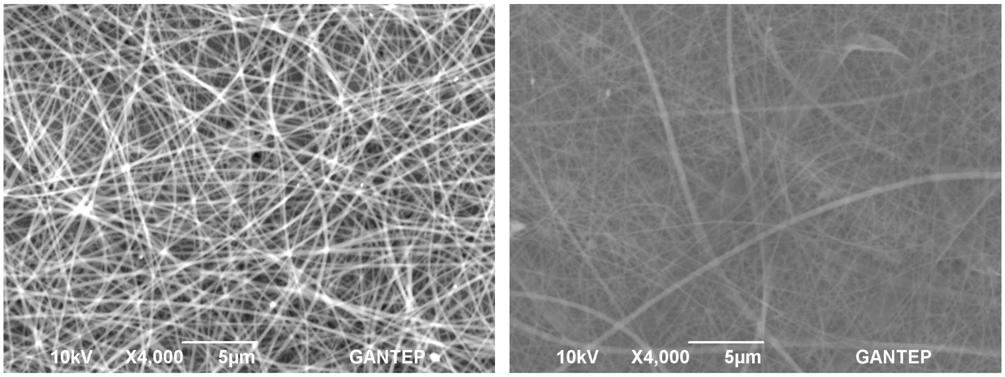


Figure 5.7 Effect of concentration on PA6 fiber diameter (15 cm, 25 kV)



a) concentration 8 % b) concentration 10%



c) concentration 12% d) concentration 14%

Figure 5.8 (a-d) Effect of concentration on PA6 fiber diameter (15 cm, 25 kV)

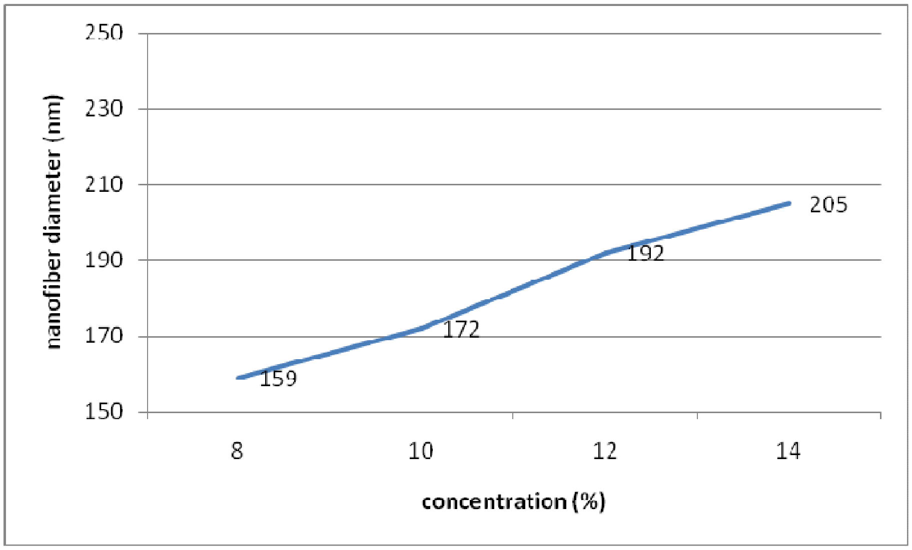
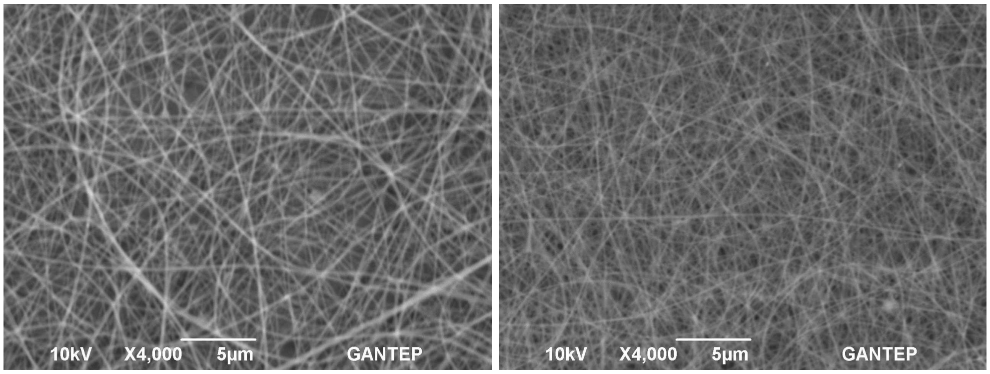
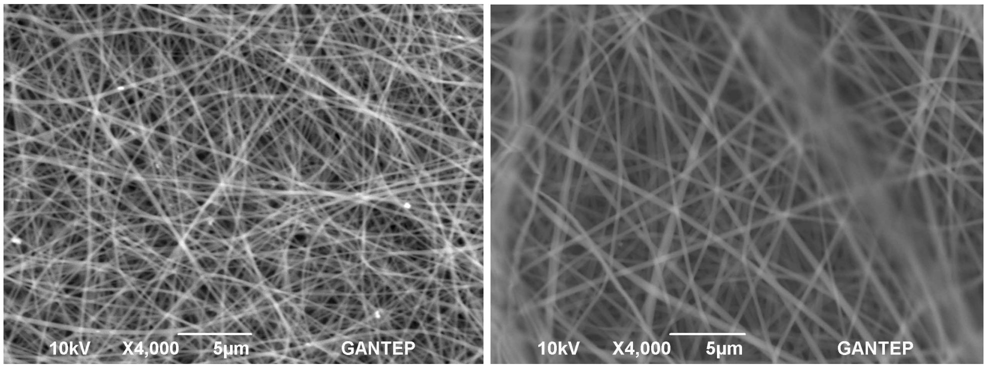


Figure 5.9 Effect of concentration on PA6 fiber diameter (15 cm, 30 kV)



a) concentration 8 %

b) concentration 10%



c) concentration 12%

d) concentration 14%

Figure 5.10 (a-d) Effect of concentration on PA6 fiber diameter (15 cm, 30 kV)

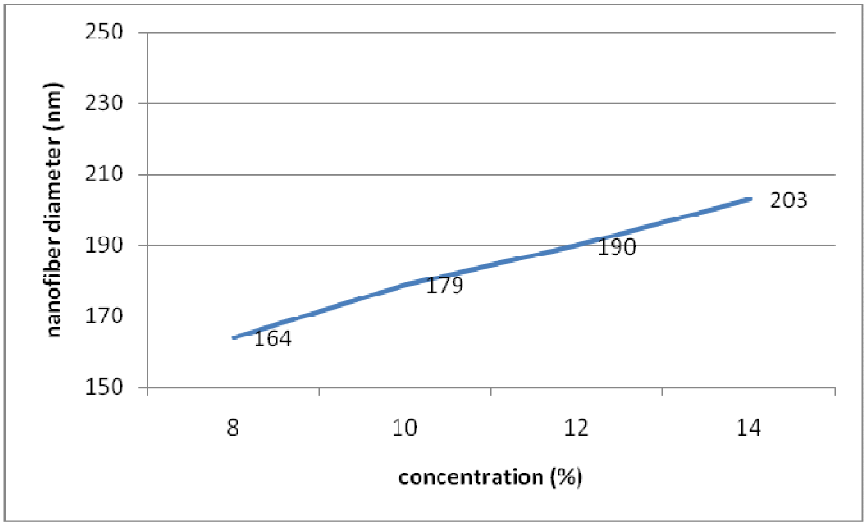
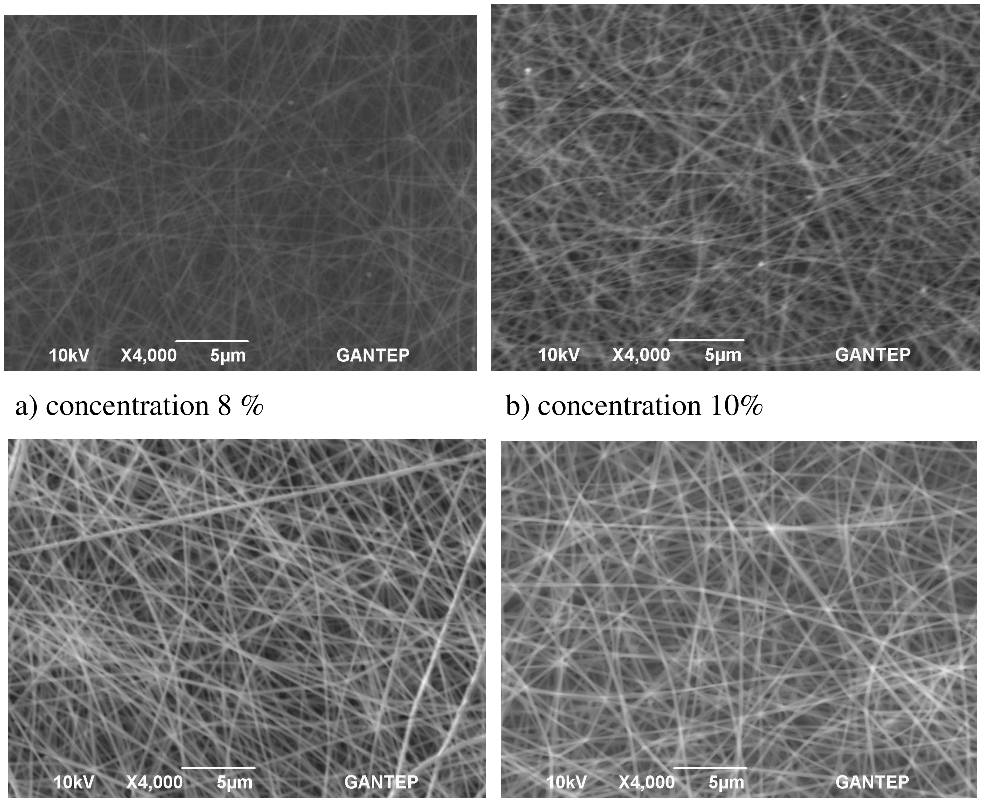


Figure 5.11 Effect of concentration on PA6 fiber diameter (15 cm, 35 kV)



a) concentration 8 %

b) concentration 10%

c) concentration 12%

d) concentration 14%

Figure 5.12 (a-d) Effect of concentration on PA6 fiber diameter (15 cm, 35 kV)

5.5.1.3 When the distance is 20 cm

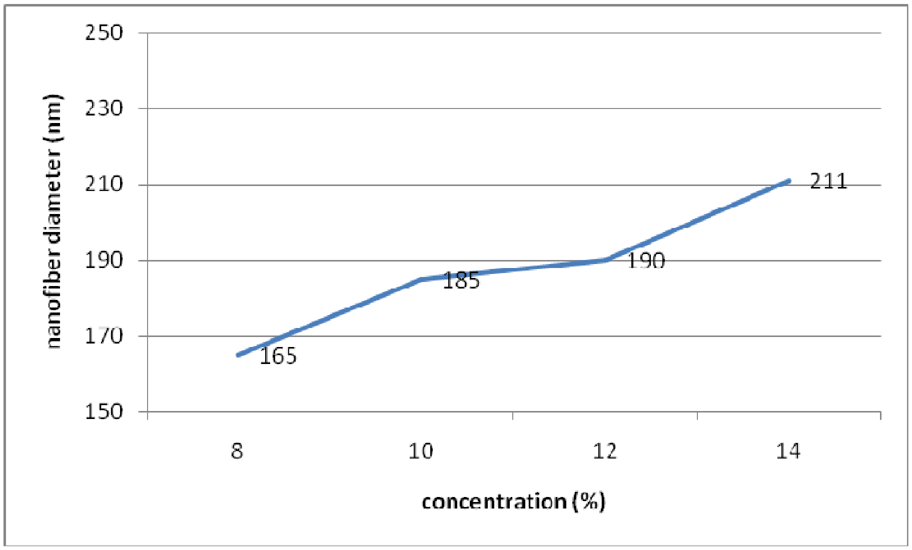
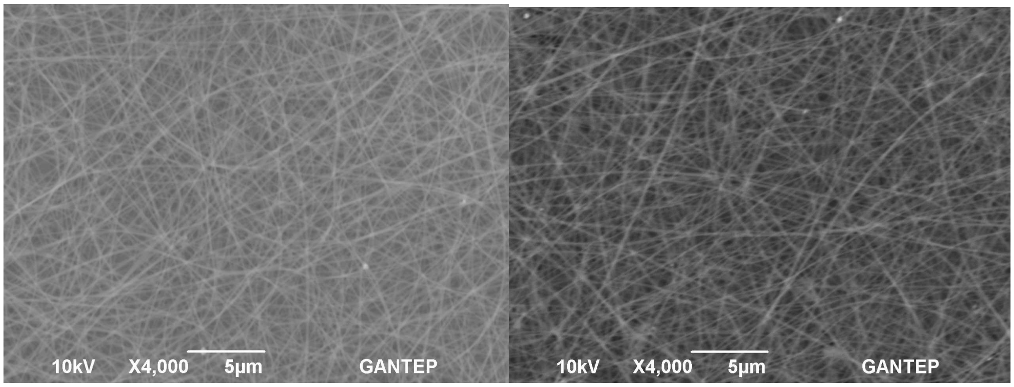
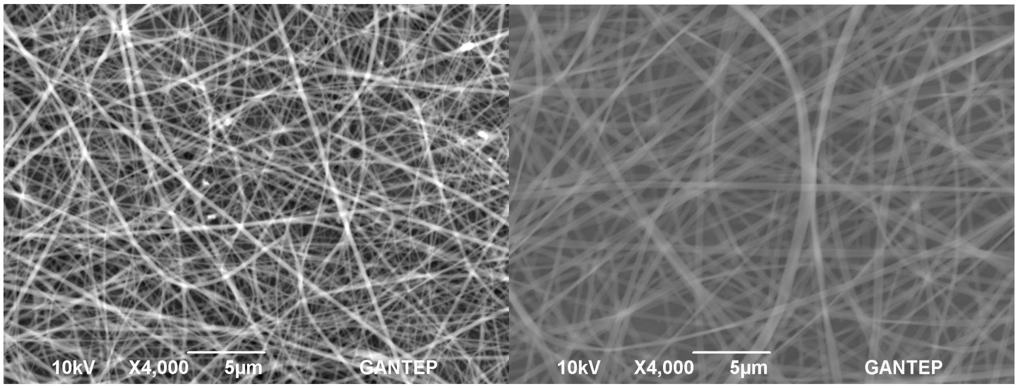


Figure 5.13 Effect of concentration on PA6 fiber diameter (20 cm, 25 kV)



a) concentration 8 %

b) concentration 10%



c) concentration 12%

d) concentration 14%

Figure 5.14 (a-d) Effect of concentration on PA6 fiber diameter (20 cm, 25 kV)

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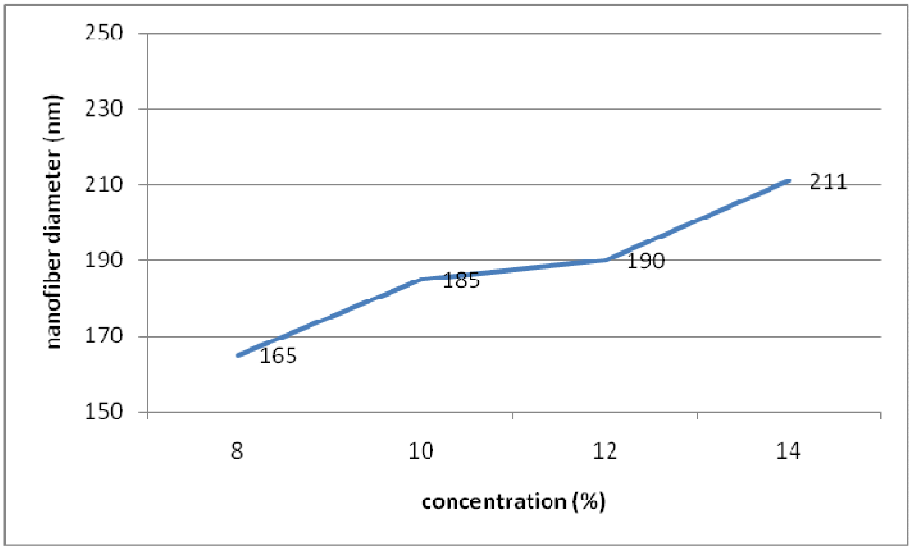
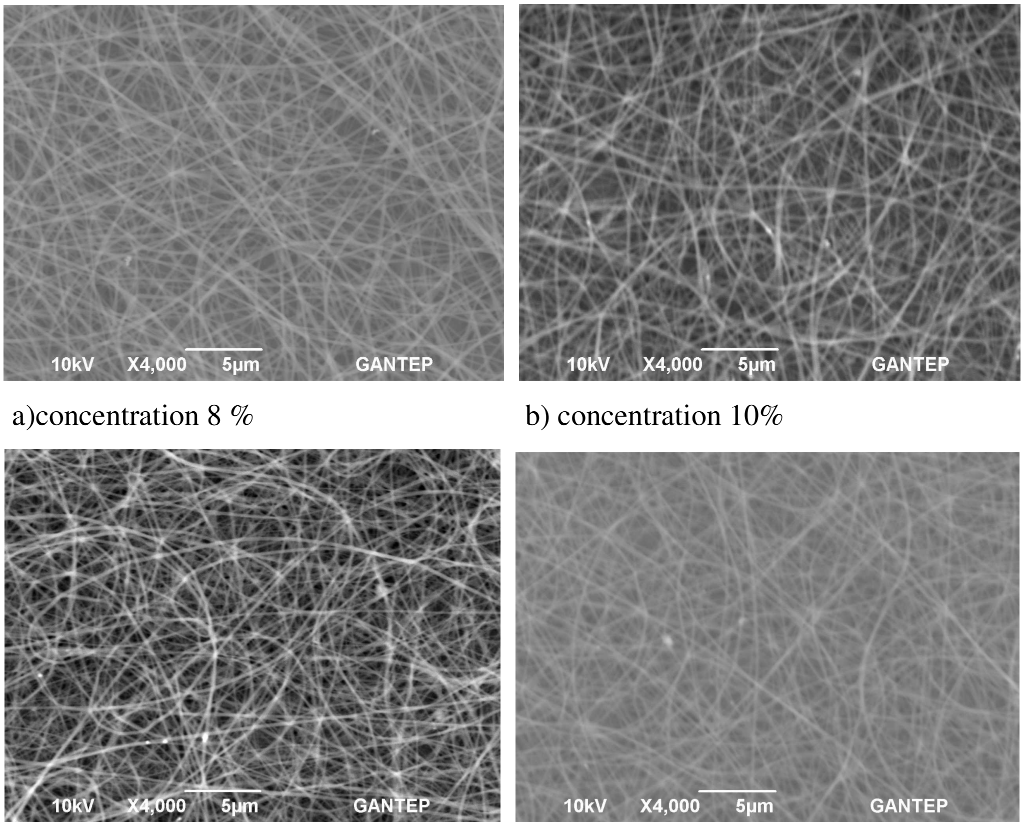


Figure 5.15 Effect of concentration on PA6 fiber diameter (20 cm, 30 kV)



a)concentration 8 %

b) concentration 10%

c) concentration 12%

d) concentration 14%

Figure 5.16 (a-d) Effect of concentration on PA6 fiber diameter (20 cm, 30 kV)

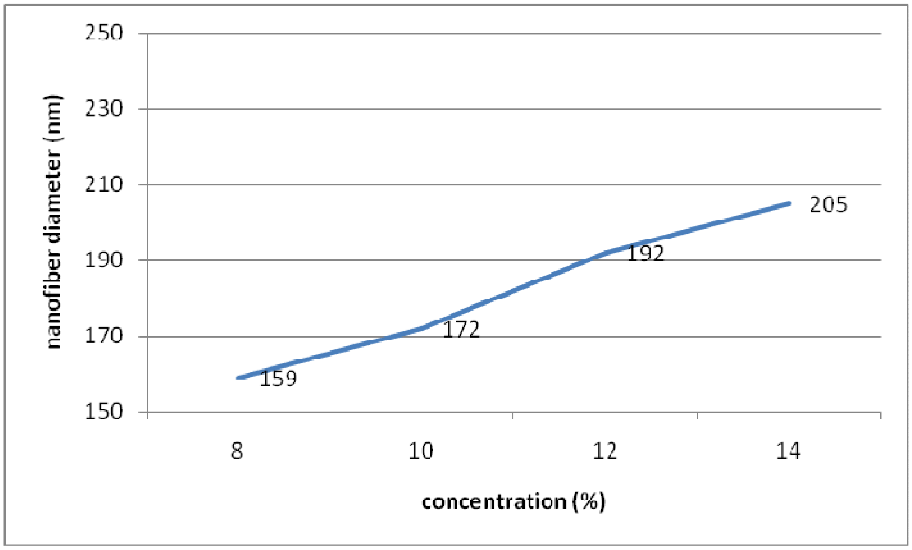
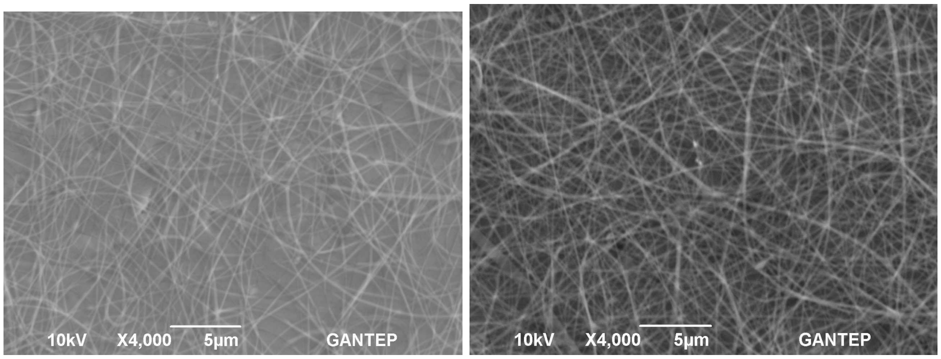
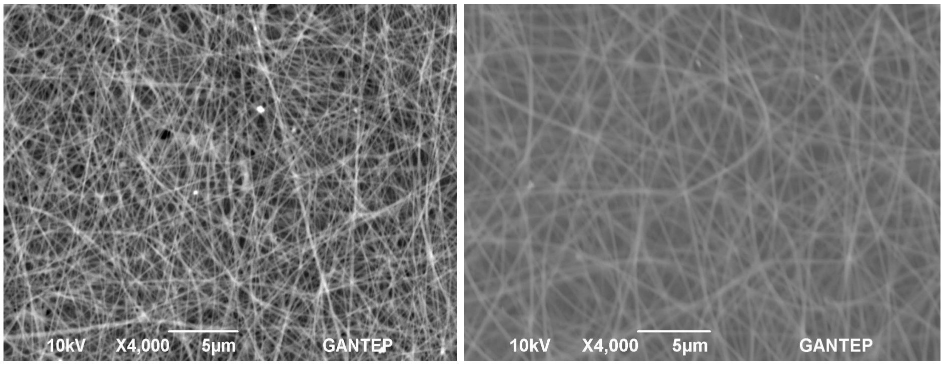


Figure 5.17 Effect of concentration on PA6 fiber diameter (20 cm, 35 kV)



a) concentration 8 %

b) concentration 10%



c) concentration 12%

d) concentration 14%

Figure 5.18 (a-d) Effect of concentration on PA6 fiber diameter (20 cm, 35kV)

5.5.2. Voltage effect

The voltage effect on PA6 nanofiber was observed. The figure between 5.19 and 5.42 show the effect of voltage on PA6 nanofiber morphology. These figures obviously show that as the voltage increases, the fiber diameter decreases too. The best results were obtained between 30-35 kV. The experimental study includes the effect of voltage ranging from 5kV to 40kV however at low voltage values no fiber formation (or very limited) was obtained. Therefore those values were not taken into consideration. The images show that the nanofiber mats includes very much of beads at 8% solution concentration for all the values of voltages as given in Figure 5.20. The best morphology was obtained for voltage value of 30 kV. The diameter of nanofibers changes between 150-220 nm and the average diameters of nanofibers were measured as 200 nm. It is possible to say that PA6 has the lowest diameter value with respect to PAN and PVA. Sometimes high voltage could cause fiber diameter variations (see Figure 5.24-e).

5.5.2.1. When the concentration is 8 %

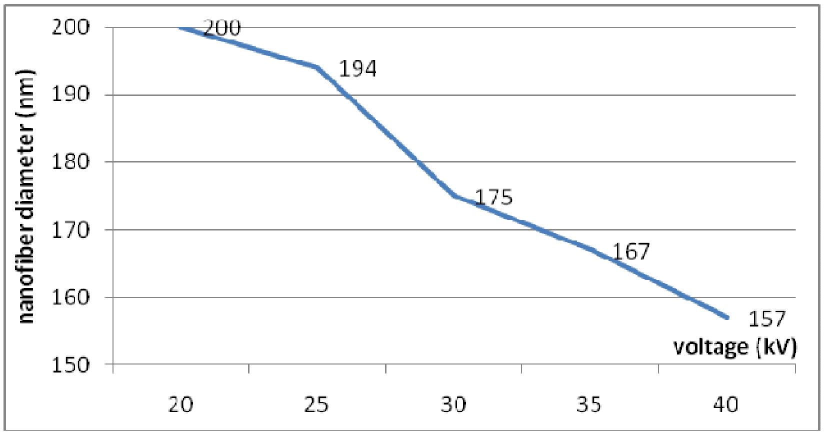
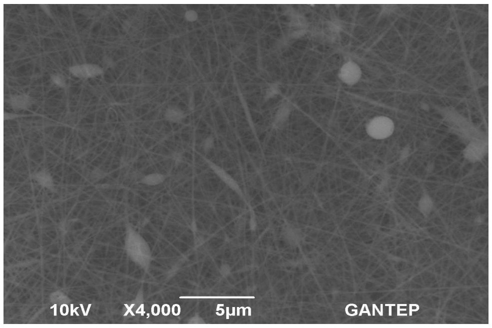
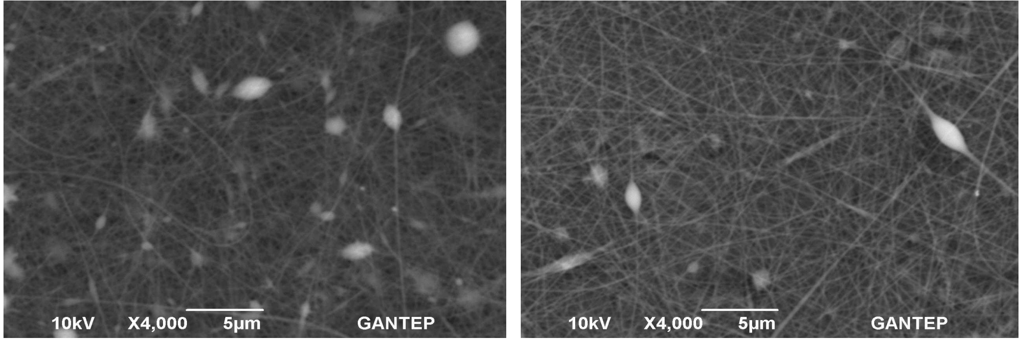


Figure 5.19 Effect of voltage on PA6 fiber diameter (10 cm, 8%)

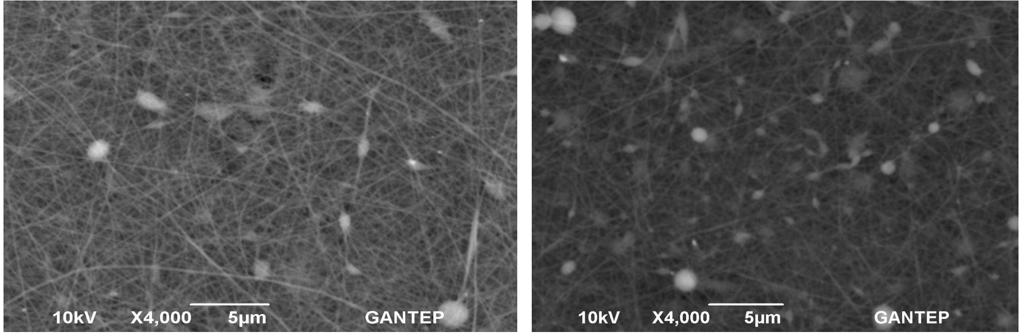


a) voltage 20 kV



b) voltage 25 kV

c) voltage 30 kV



d) voltage 35 kV

e) voltage 40 kV

Figure 5.20 (a-e) Effect of voltage on PA6 fiber diameter (10 cm, 8%)

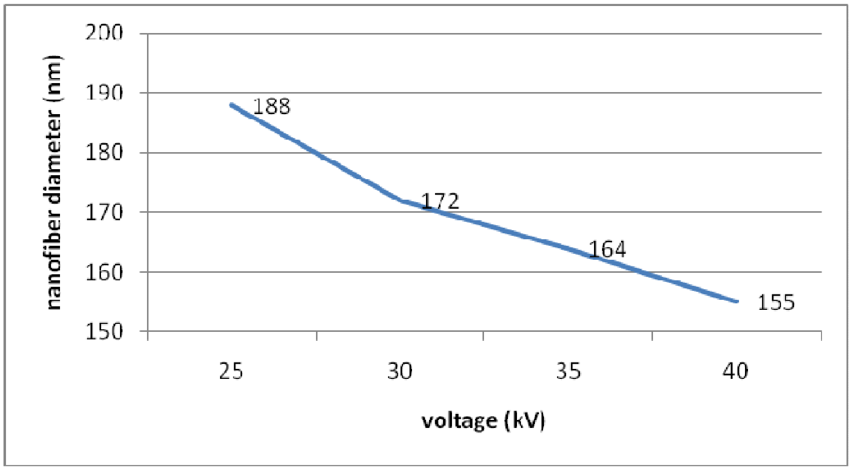
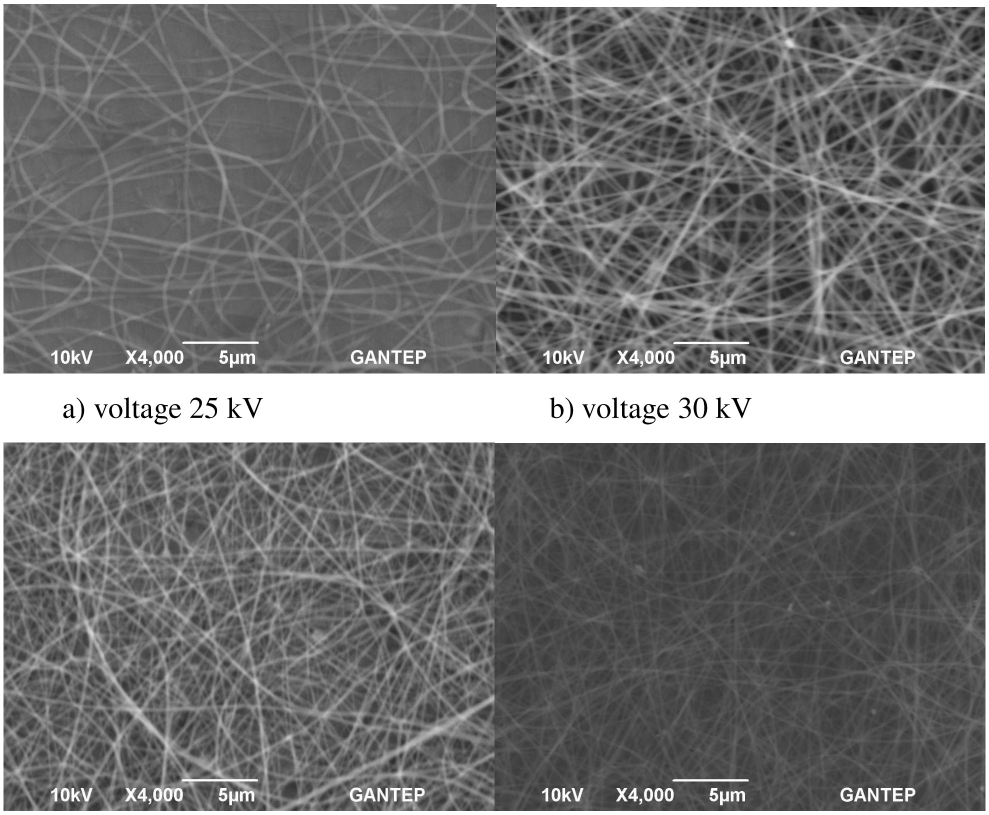


Figure 5.21 Effect of voltage on PA6 fiber diameter (15 cm, 8%)



a) voltage 25 kV

b) voltage 30 kV

c) voltage 35 kV

d) voltage 40 kV

Figure 5.22 (a-d) Effect of voltage on PA6 fiber diameter (15 cm, 8%)

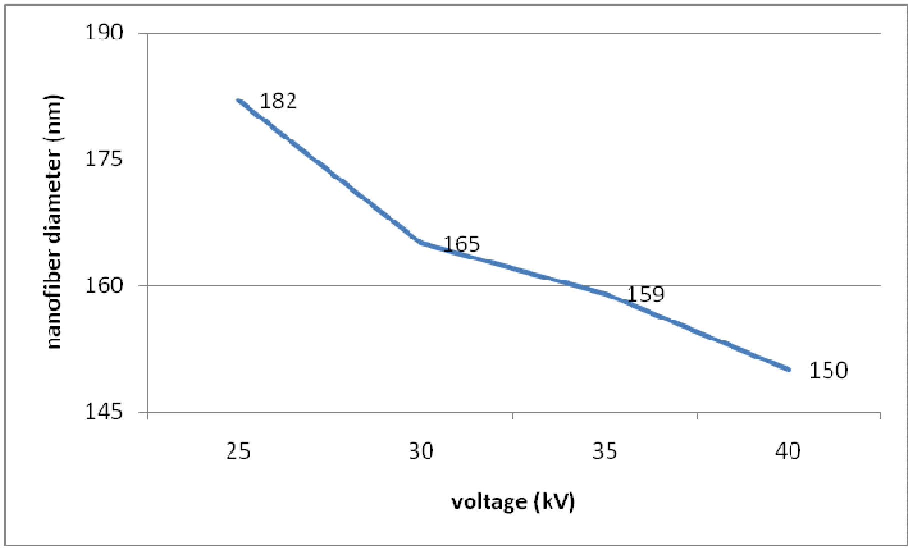
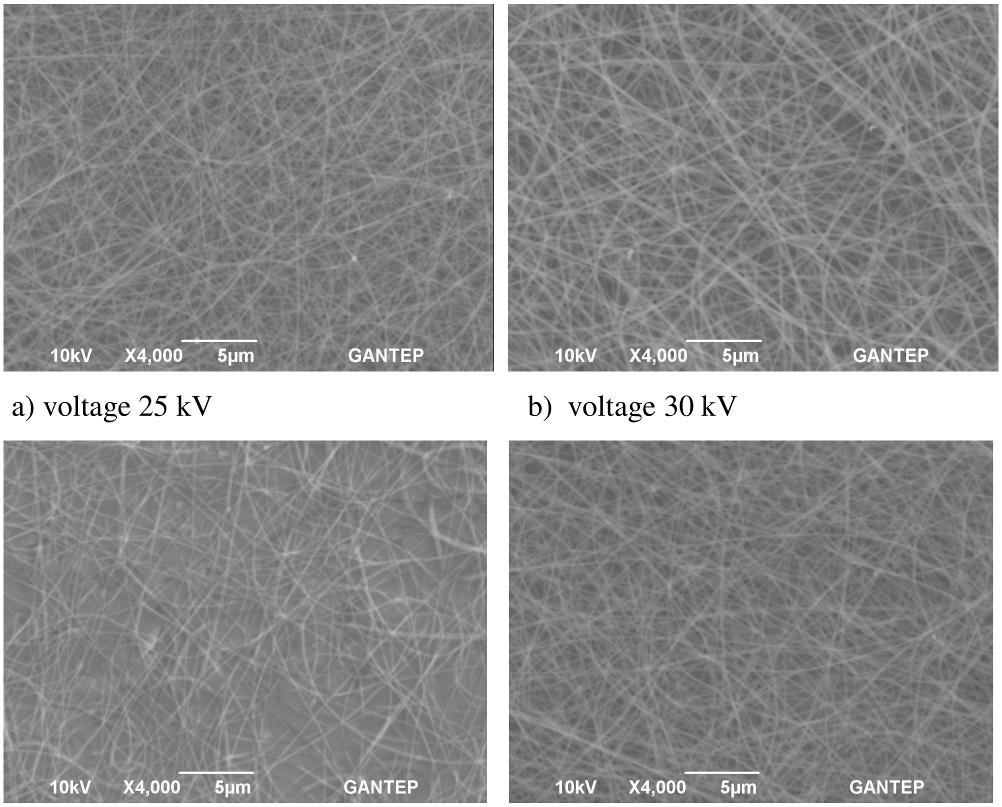


Figure 5.23 Effect of voltage on PA6 fiber diameter (20 cm, 8%)



a) voltage 25 kV

b) voltage 30 kV

c) voltage 35 kV

d) voltage 40 kV

Figure 5.24 (a-d) Effect of voltage on PA6 nanofiber diameter (20 cm, 8%)

5.5.2.2. When the concentration is 10 %

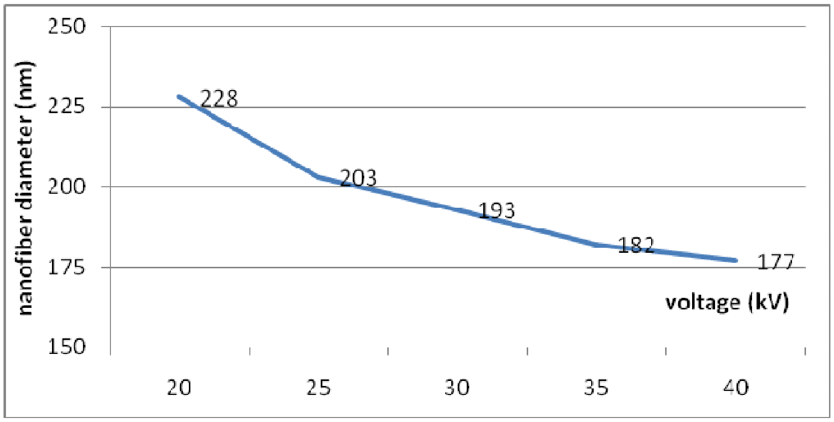
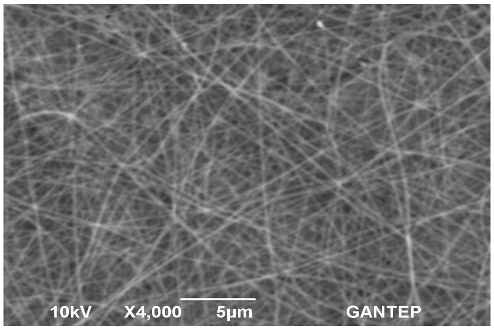
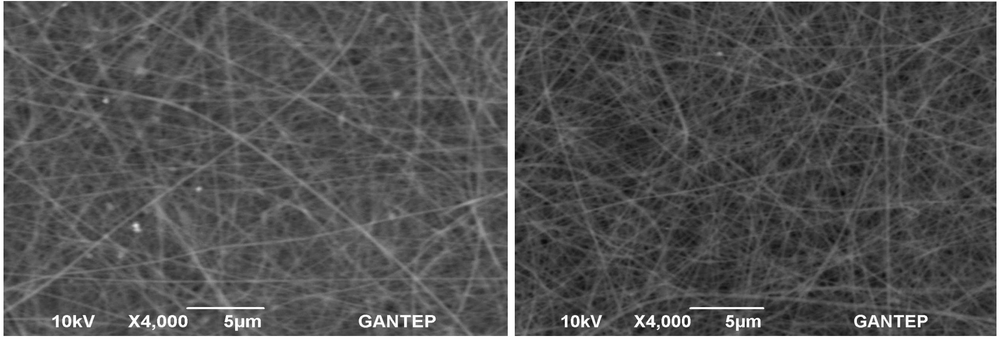


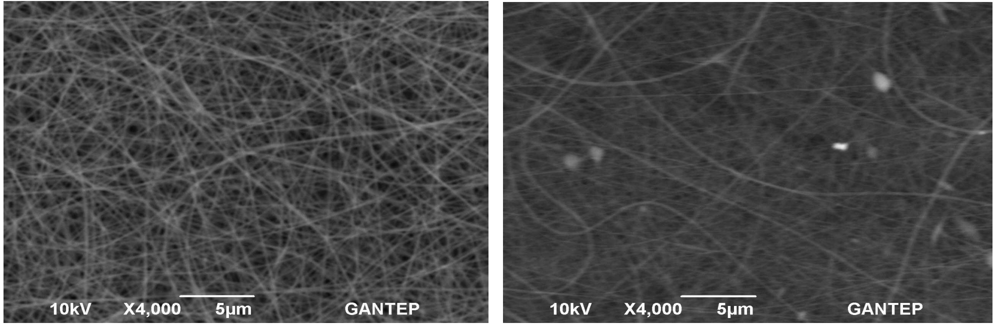
Figure 5.25 Effect of voltage on PA6 fiber diameter (10 cm, 10%)



a) voltage 20 kV



b) voltage 25 kV c) voltage 30 kV



d) voltage 35 kV e) voltage 40 kV

Figure 5.26 (a-e) Effect of voltage on PA6 fiber diameter (10 cm, 10%)

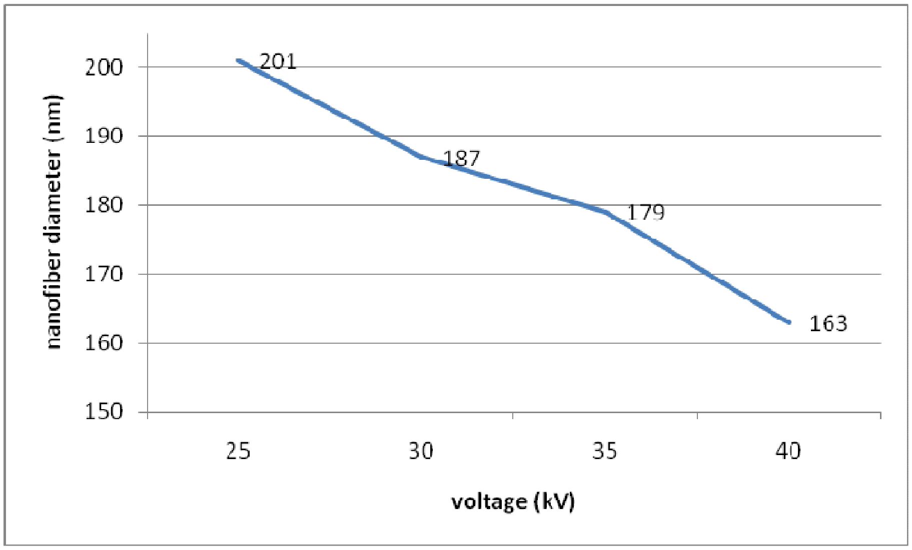
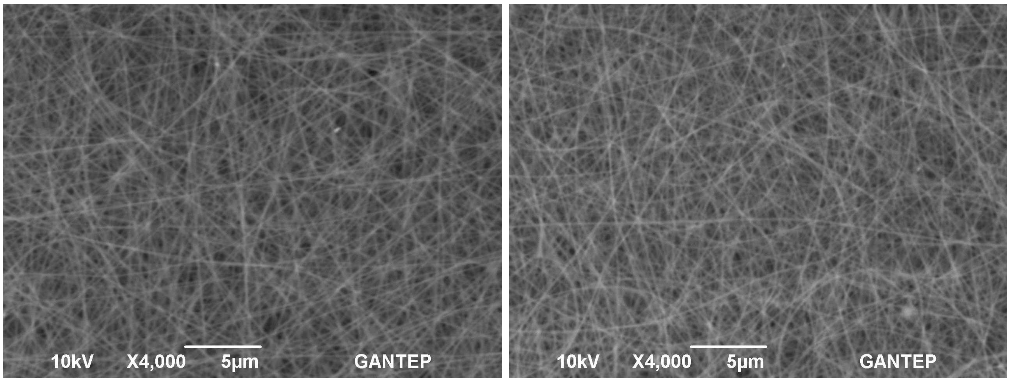
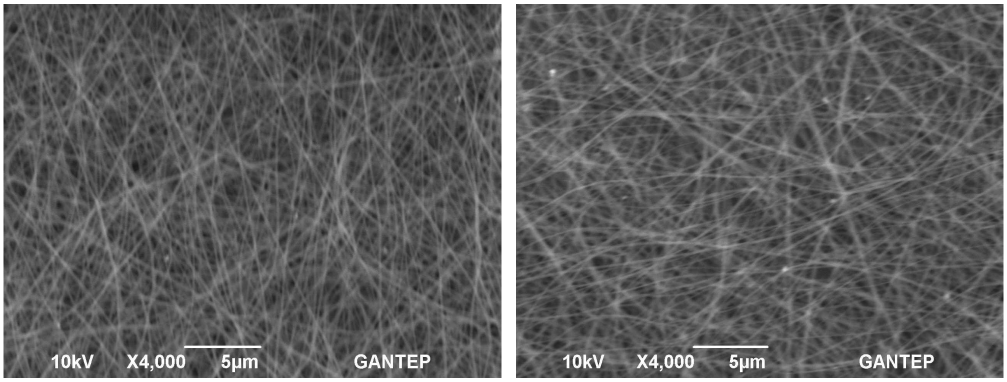


Figure 5.27 Effect of voltage on PA6 fiber diameter (15 cm, 10%)



a) voltage 25kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 5.28 (a-d) Effect of voltage on PA6 fiber diameter (15 cm, 10%)

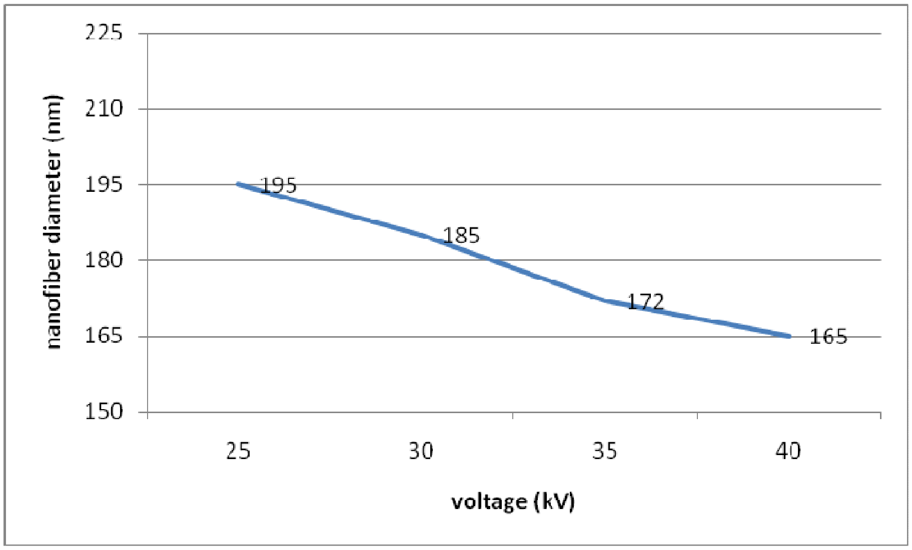
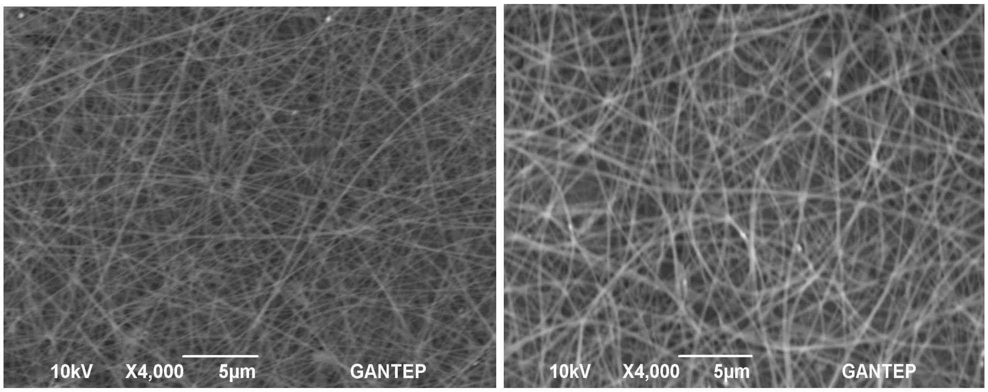
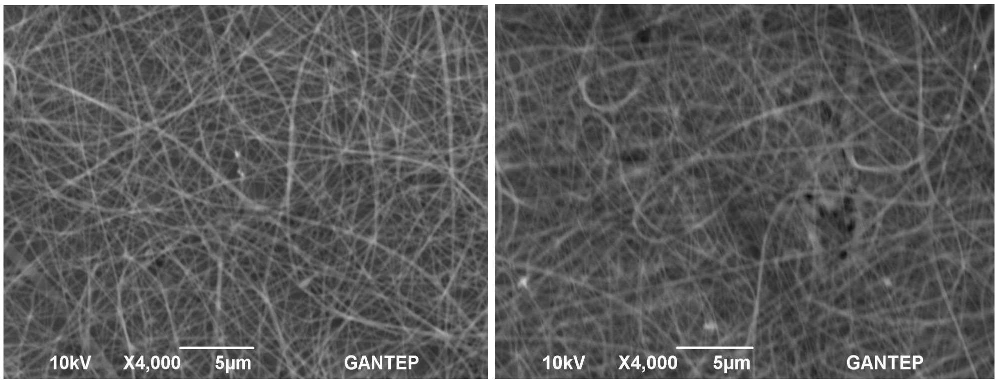


Figure 5.29 Effect of voltage on PA6 fiber diameter (20 cm, 10%)



a) voltage 25 kV b) voltage 30 kV



c) voltage 35 kV d) voltage 40 kV

Figure 5.30 (a-d) Effect of voltage on PA6 fiber diameter (20 cm, 10%)

5.5.2.3. When the concentration is 12 %

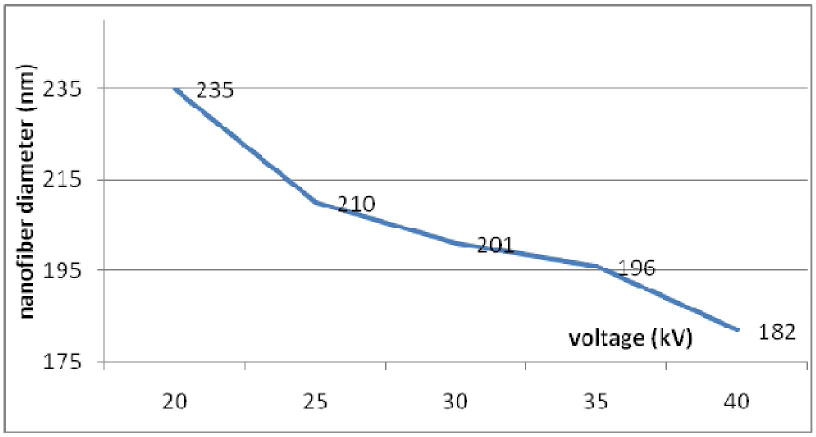
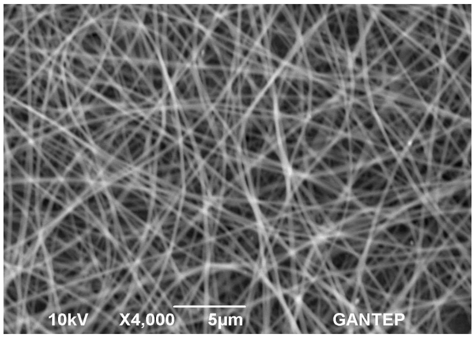
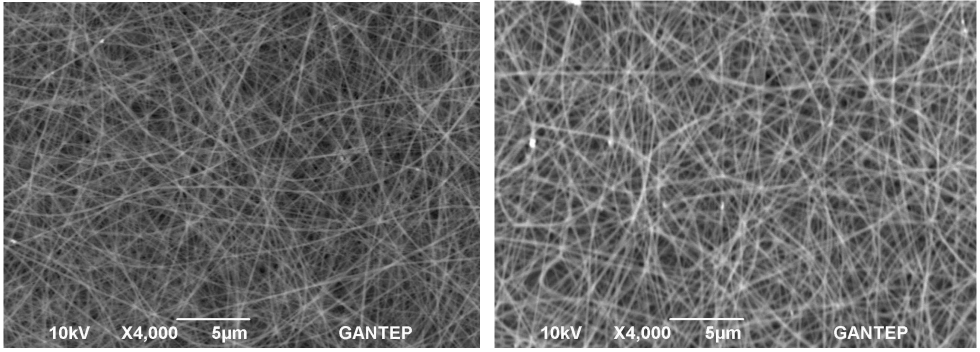


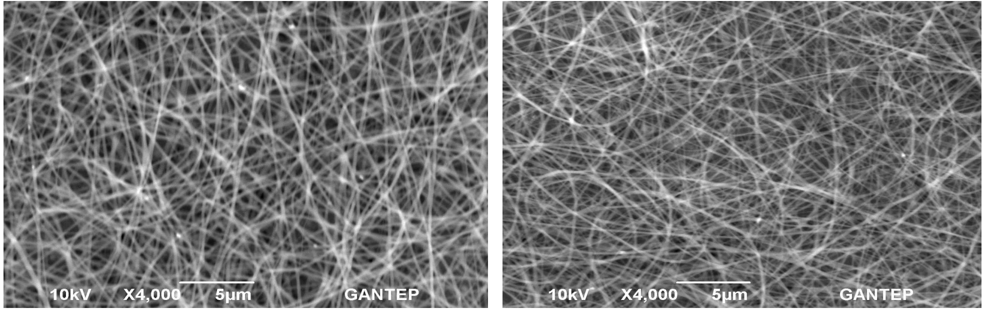
Figure 5.31 Effect of voltage on PA6 fiber diameter (10 cm, 12%)



a) voltage 20 kV



b) voltage 25 kV c) voltage 30 kV



d) voltage 35 kV e) voltage 40 kV

Figure 5.32 (a-e) Effect of voltage on PA6 fiber diameter (10 cm, 12%)

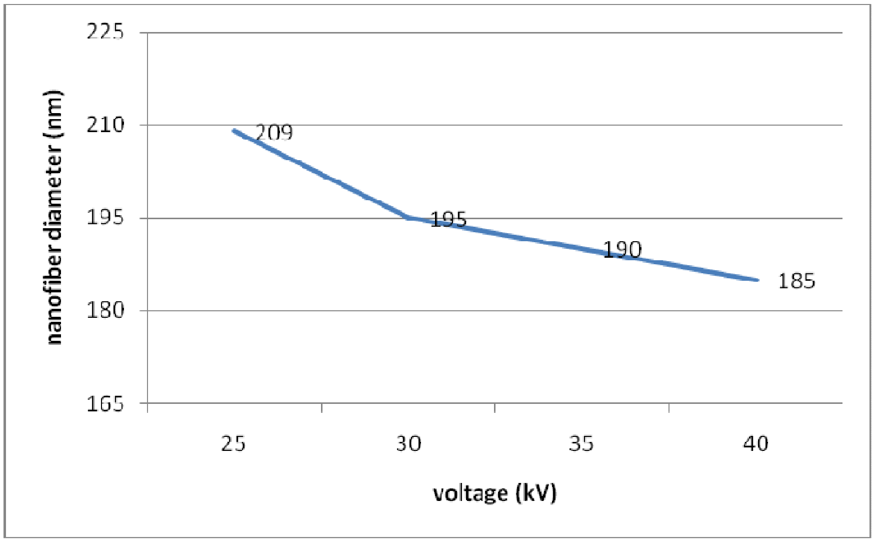
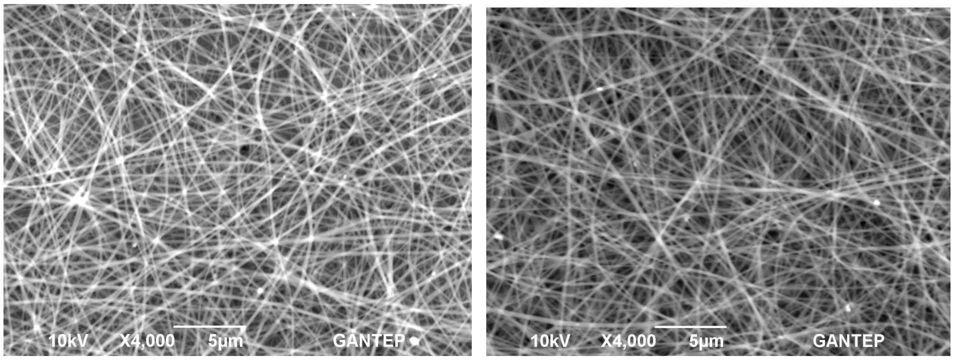
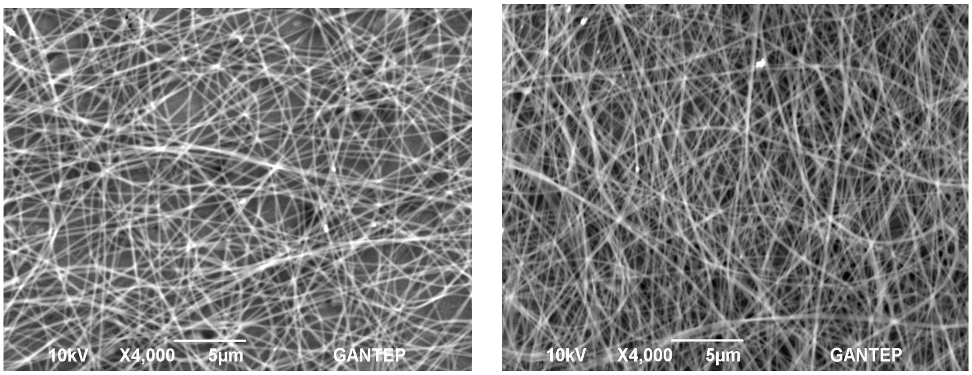


Figure 5.33 Effect of voltage on PA6 fiber diameter (15 cm, 12%)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 5.34 (a-d) Effect of voltage on PA6 fiber diameter (15 cm, 12%)

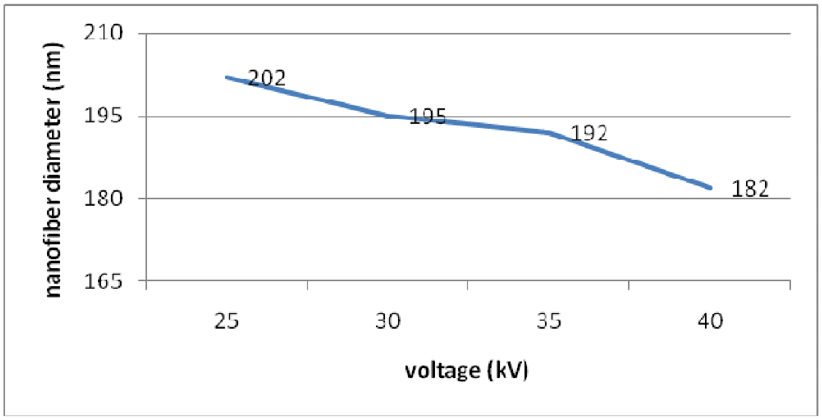
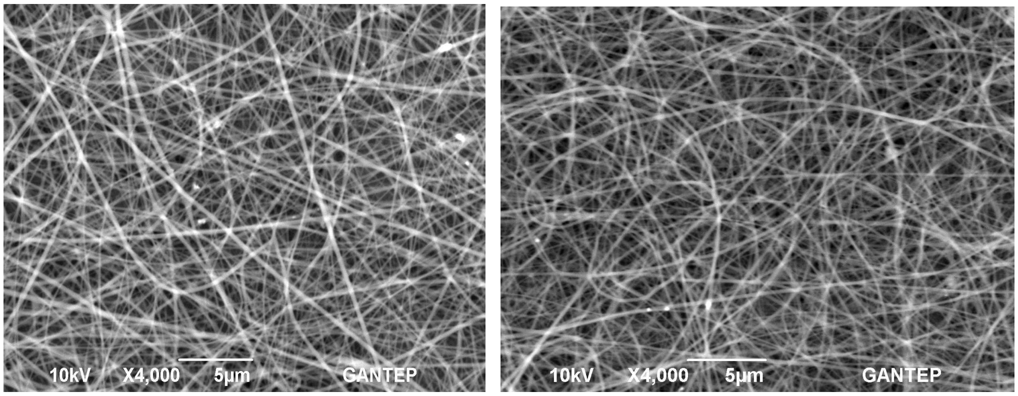
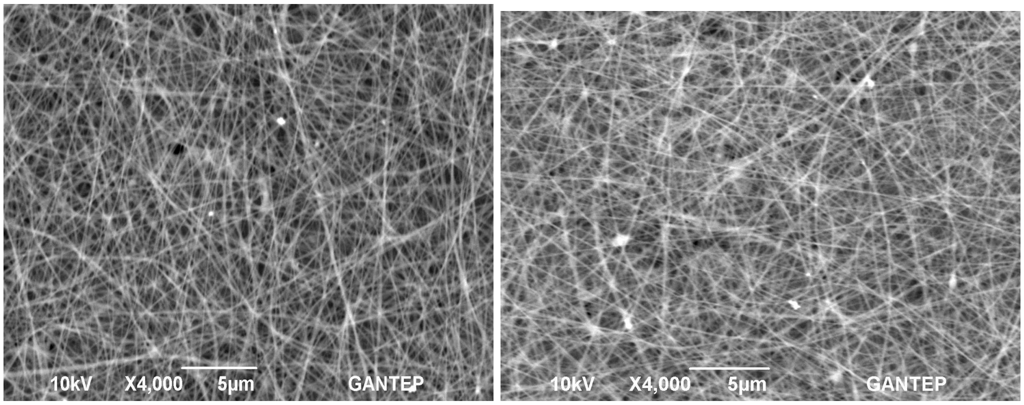


Figure 5.35 Effect of voltage on PA6 fiber diameter (20 cm, 12%)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 5.36 (a-d) Effect of voltage on PA6 fiber diameter (20 cm, 12%)

5.5.2.4. When the concentration is 14%

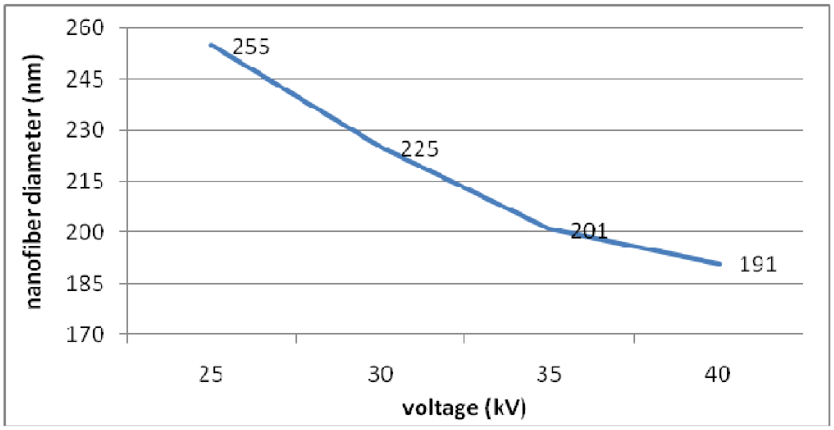
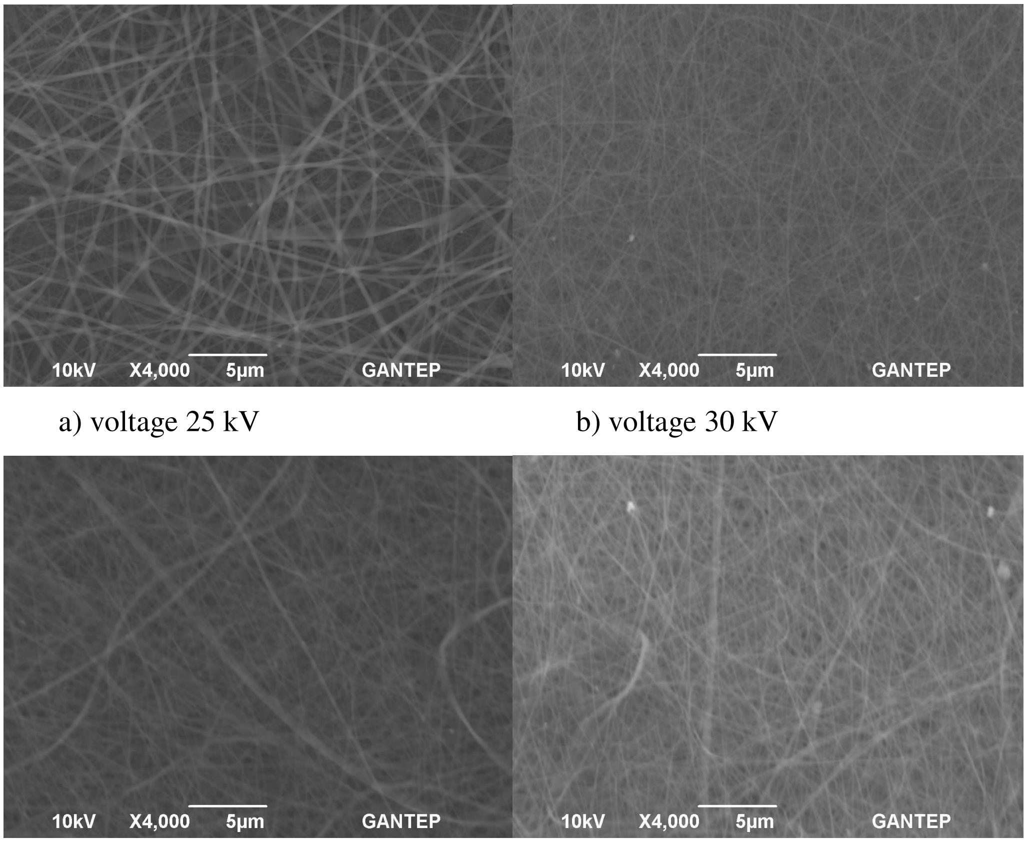


Figure 5.37 Effect of voltage on PA6 fiber diameter (10cm, 14%)



a) voltage 25 kV

b) voltage 30 kV

c) voltage 35 kV

d) voltage 40 kV

Figure 5.38 (a-d) Effect of voltage on PA6 fiber diameter (10 cm, 14%)

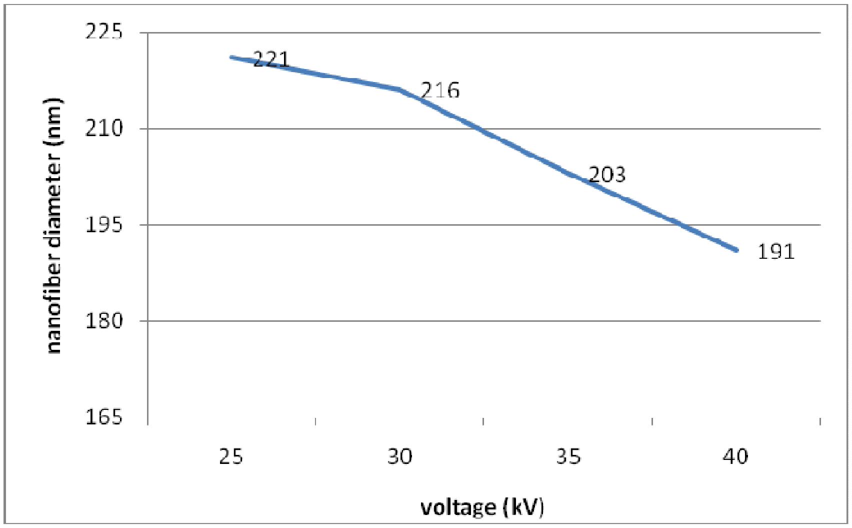
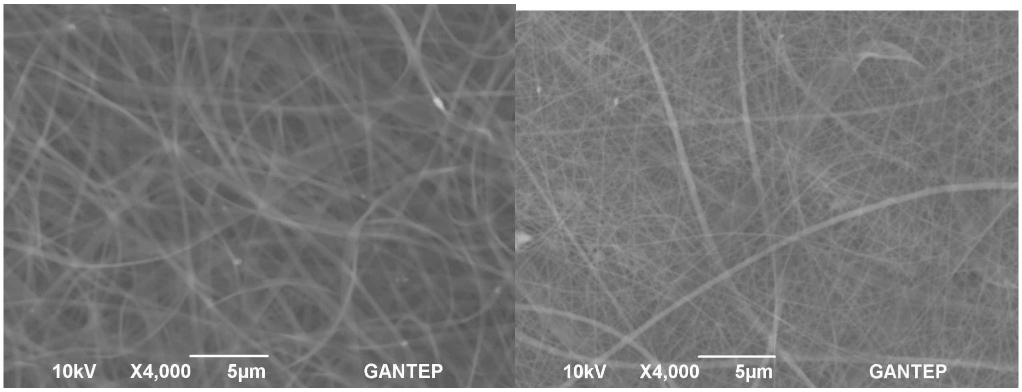
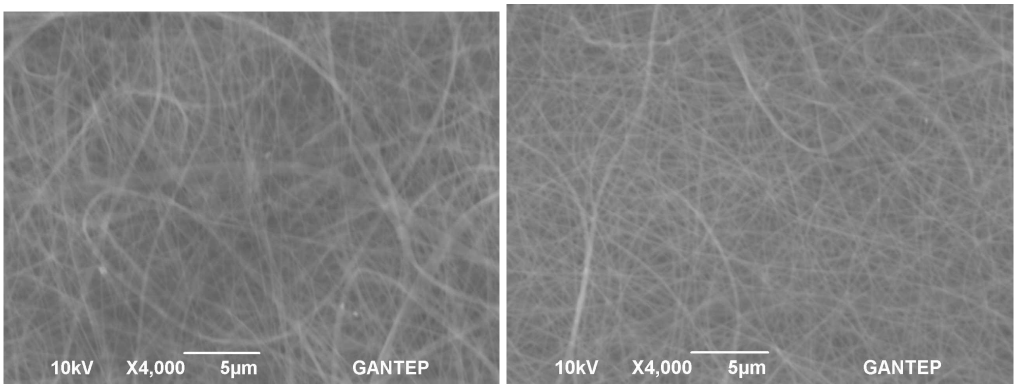


Figure 5.39 Effect of voltage on PA6 fiber diameter (15 cm, 14%)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 5.40 (a-d) Effect of voltage on PA6 fiber diameter (15 cm, 14%)

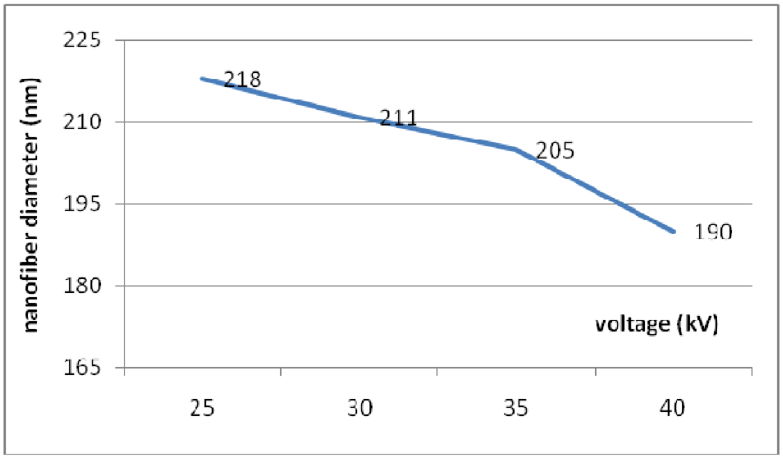
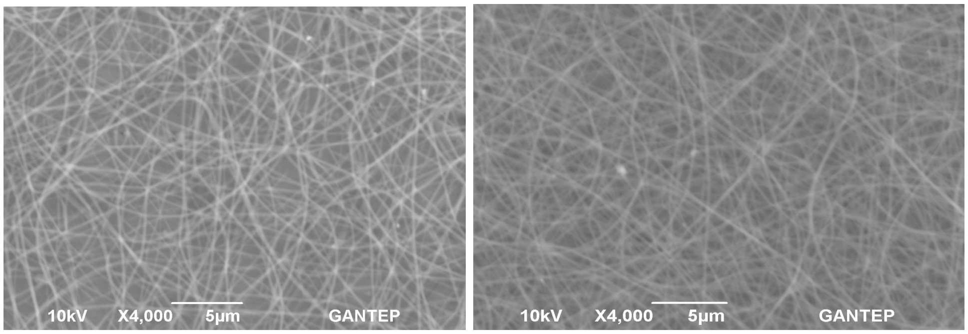
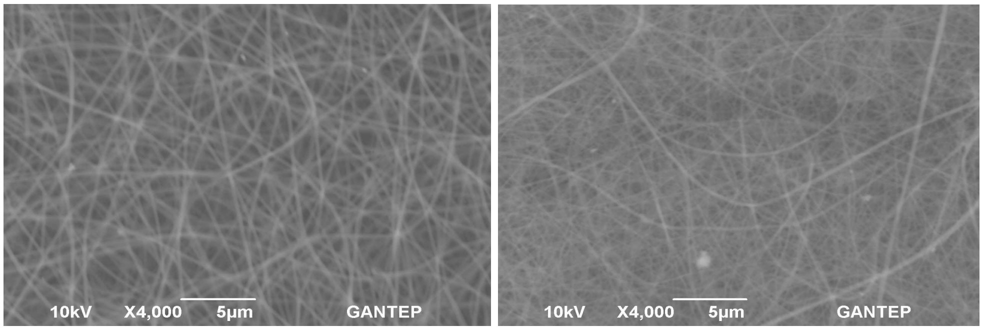


Figure 5.41 Effect of voltage on PA6 fiber diameter (20 cm, 14%)



a) voltage 25 kV

b) voltage 30 kV



c) voltage 35 kV

d) voltage 40 kV

Figure 5.42 (a-d) Effect of voltage on PA6 fiber diameter (15 cm, 14%)

5.5.3. Distance effect

It was found that the fibers morphology changed and the fiber size decreased slightly with increasing the tip-collector distance as shown in Figure 5.43 to 5.50. In fact the nanofiber formations were regular and the diameters very fine. The electropinning process became difficult after 14% concentration. The optimum values were obtained between 10-15 cm. It was clearly seen that the fiber formation was regular without beads.

In order to perform the experimental study an experimental set-up in a controlled environment was prepared. The ambient temperature was held constant at 25°C and 25 % humidity during all experiments.

5.5.3.1. When the concentration is 10%

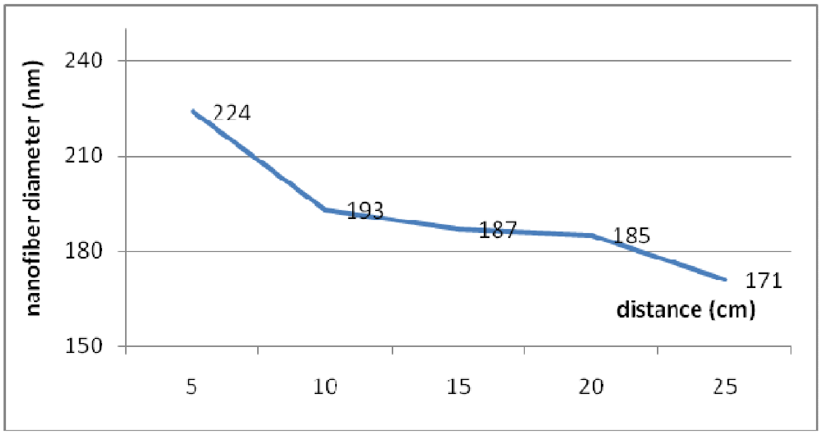
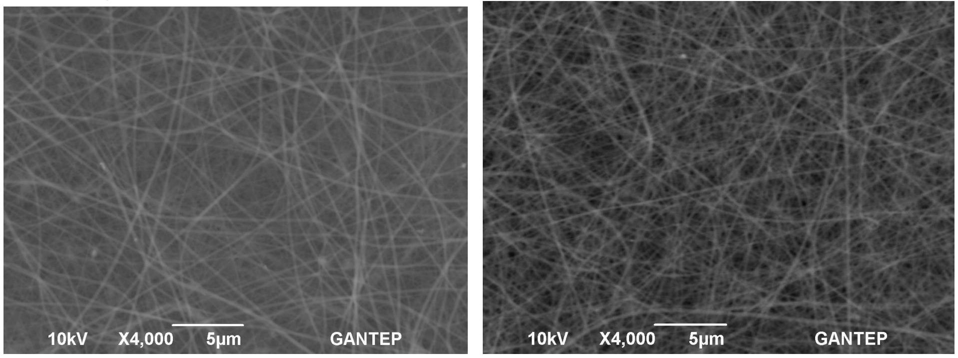
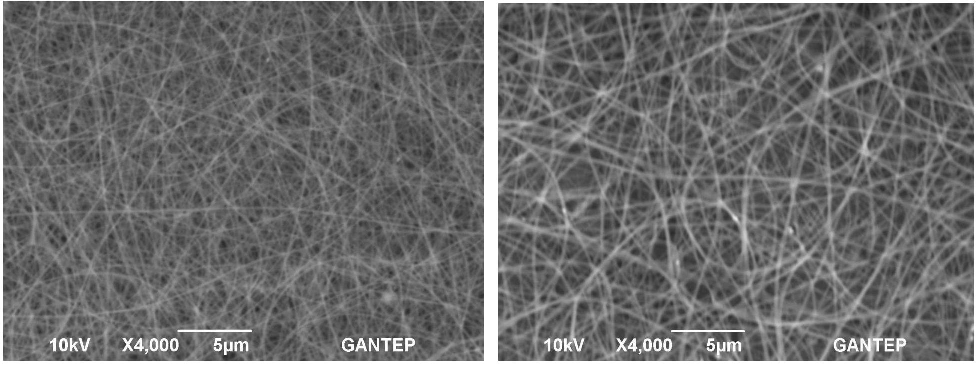


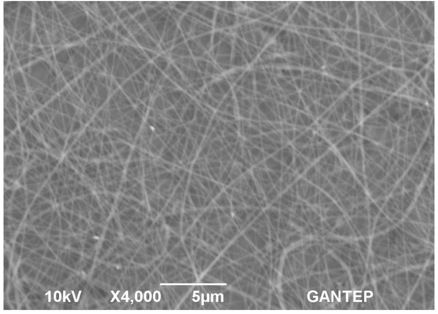
Figure 5.43 Effect of distance on PA6 fiber diameter (30 kV, 10%)



a) tip-collector distance 5 cm b) tip-collector distance10cm



c) tip-collector distance 15cm d) tip-collector distance 20cm



e) tip-collector distance 25 cm

Figure 5.44 (a-e) Effect of distance on PA6 fiber diameter (30 kV, 10%)

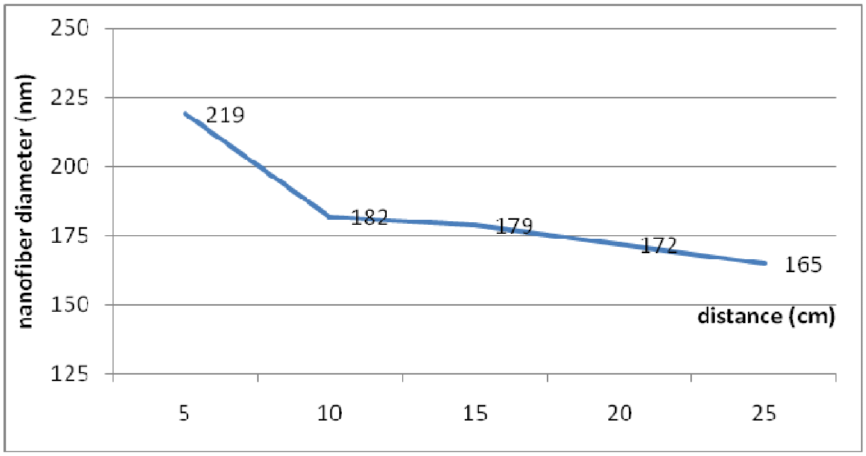
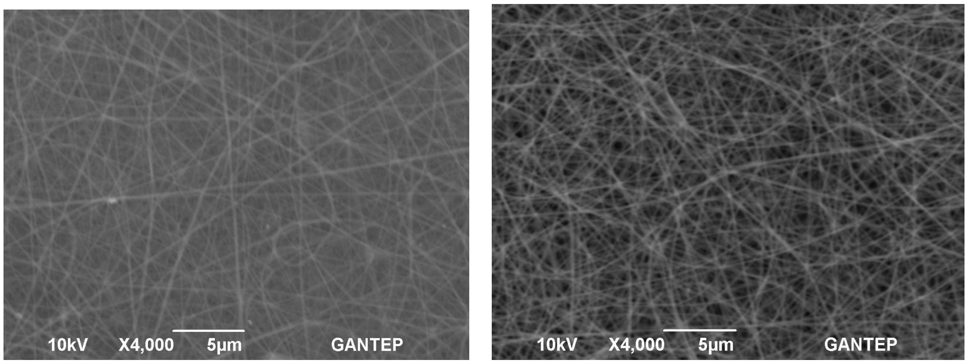
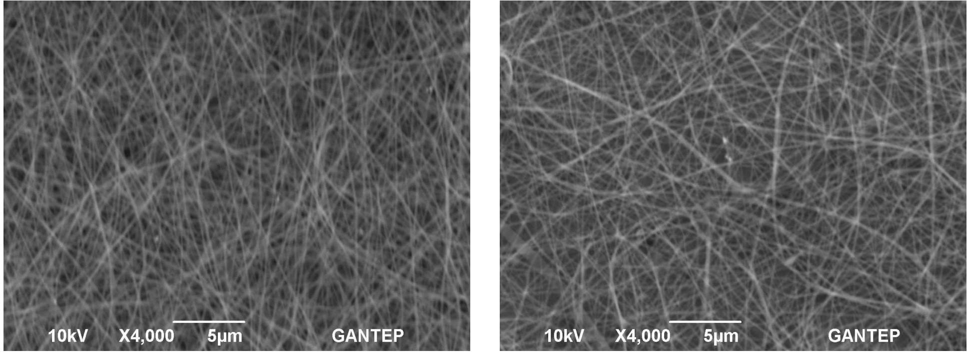


Figure 5.45 Effect of distance on PA6 fiber diameter (35 kV, 10%)



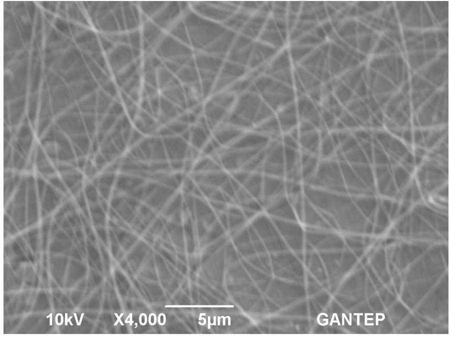
a) tip-collector distance 5 cm

b) tip-collector distance 10 cm



c)tip-collector distance 15cm

d) tip-collector distance20cm



e) distance 25 cm

Figure 5.46 (a-e) Effect of distance on PA6 fiber diameter (35 kV, 10%)

5.5.3.2. When the concentration is 12%

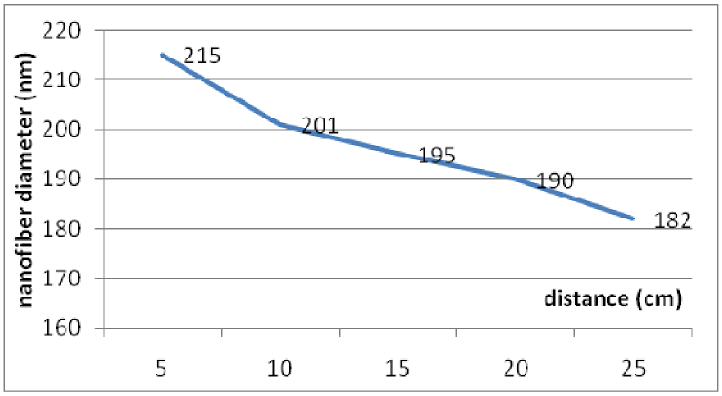
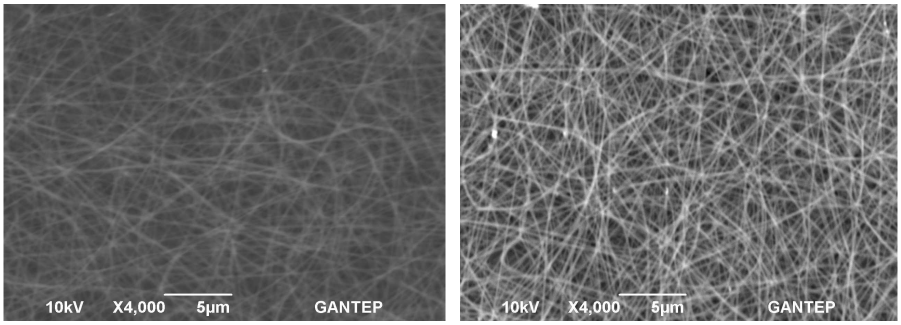
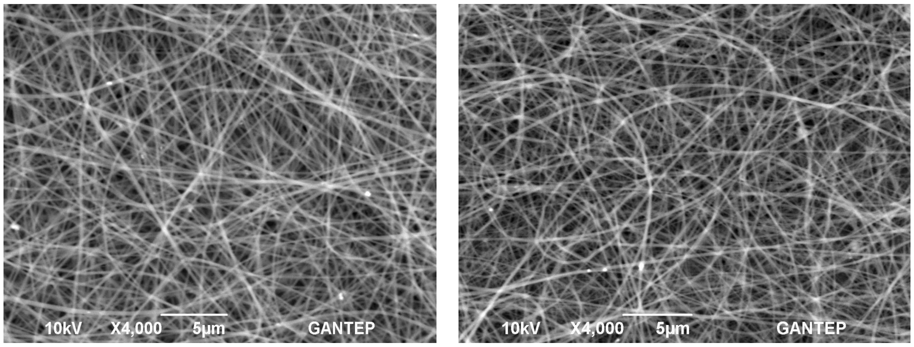


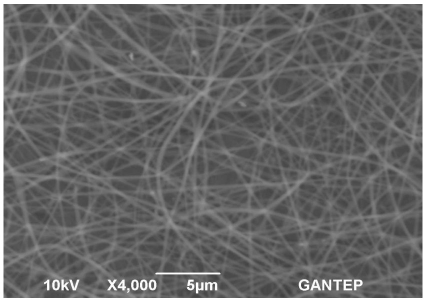
Figure 5.47 Effect of distance on PA6 fiber diameter (30 kV, 12%)



a) tip-collector distance 5 cm b) tip-collector distance 10cm



c) tip-collector distance 15cm d) tip-collector distance 20cm



e) tip-collector distance 25 cm

Figure 5.48 (a-e) Effect of distance on PA6 fiber diameter (30 kV, 12%)

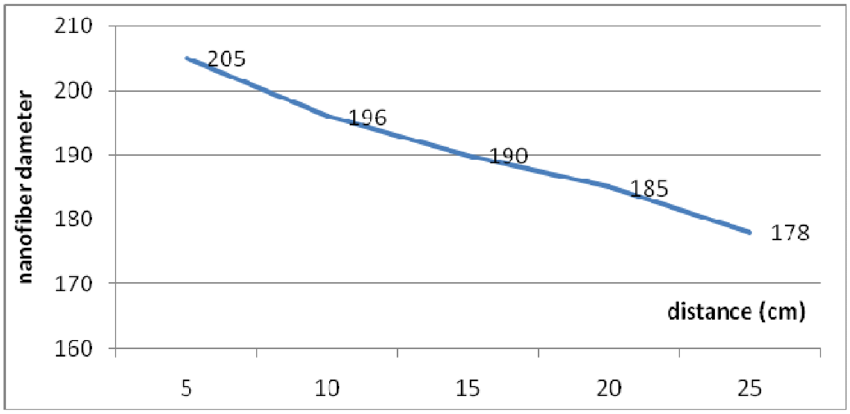
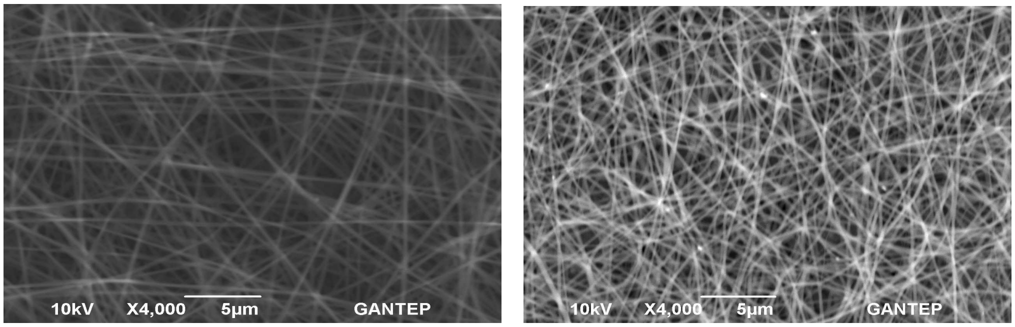
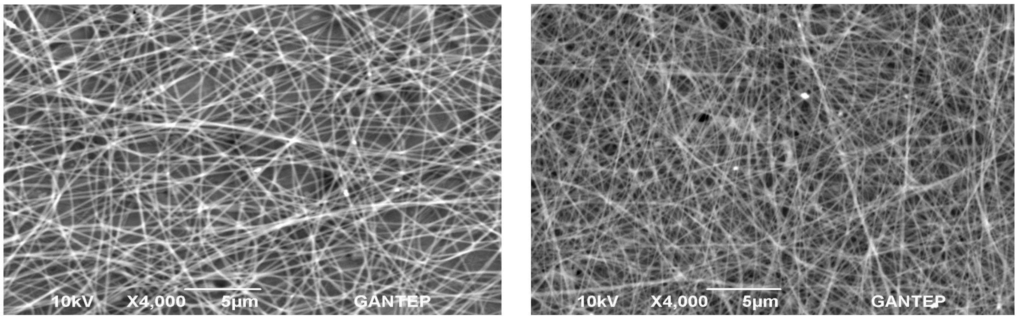


Figure 5.49 Effect of distance on PA6 fiber diameter (35 kV, 12%)



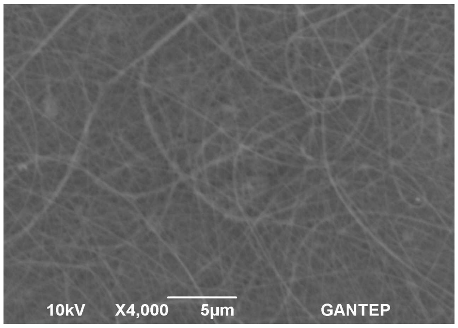
a) tip-collector distance 5 cm

b) tip-collector distance 10cm



c) tip-collector distance 15cm

d) tip-collector distance 20cm



e) tip-collector distance 25 cm

Figure 5.50 Effect of distance on PA6 fiber diameter (35 kV, 12%)

CHAPTER 6

CONCLUSIONS AND RECCOMENDATIONS FUTURE WORKS

Basic solution and process parameters of three polymers (PVA, PA6 and PAN) were examined to determine the most suitable electrospin conditions. In order to investigate the effects of concentration, voltage and tip-collector distance on fiber morphology nanofiber mat samples were produced by changing the value of each parameter systematically while keeping all the other parameters constant. The SEM images of these samples were examined to determine the most suitable production conditions. Bead formation, fiber fineness and the fiber uniformity were the basic criteria to decide the optimal production conditions. For PAN polymer, the temperature and humidity effects are also investigated.

For PAN polymer, the electrospinning process generated a mixture of fibers and droplets at low concentrations. However, it was observed that as the concentration increases the bead formation decreases at the same time the fiber diameter increases as well. Examinations were shown that beads tends to diminish when the solutions concentrations approaches to 10%wt for most of situations (such as different voltage and tip-collector distance values). Therefore, the optimal values for solution concentration were decided between 10-12%. The SEM images disclose that PAN nanofibers synthesized at higher applied voltages were exhibited relatively lower average diameters. The most uniform formation was seen at 30-35 kV. On the other side, experimental study showed that the nanofiber diameter decreases slightly when tip-collector distance were increased (not more than 7%). However, larger distance reduces the electrospinning rate of nanofibers considerable. Therefore, the most suitable tip-collector distance was determined as 10 cm. At optimal conditions, the average nanofiber diameter was calculated as 250 nm in the study. Those optimal solution and process parameter approximately matches with the studies of other researchers.

The study was started at 5% solution concentration for PVA polymer. Large amount of beads and irregular fiber formation were observed at this concentration especially at high voltage values and at short distances. However, SEM images were shown that beads reduced considerably 7.5% concentration. As a result the most suitable value was established between 7.5 and 10%. Increasing, solution concentration to 15% may provide better fiber structure but the fiber diameter also gradually increases. Increasing voltage value effects the fiber diameter positively (diameter reduces) but the possibility of bead formation also increases at higher voltage values. Therefore, the most appropriate voltage values were obtained between 30-40kV. The analysis of SEM images were also shown that as the distance increases the fiber diameter decreases but increasing the distance reduce the charge density, therefore the production speed of nanofibers reduce considerably. For that reason, the optimal tip-collector distance determined as 15 cm. At this point the average nanofiber diameter was calculated as 235 nm. It was observed that the worse situation happens at low concentration (less that 5%) high voltage values (higher than 35kV) and shorter tip-collector distance (less that 5 cm).

For PA6 nanofiber mats show more bead formations with respect to the other polymers (PAN and PV6) at the same concentration. Beads were quite obvious up to 8% solution concentration. However, bead formation was reduced by increasing the solution concentration but this situation also increase the nanofiber diameter. Therefore, 12% concentration was determined as the most favorable value. At this point, there were no bead formation, no fiber diameter variation, and the nanofibers were fine enough. Continuous and smooth fibers were obtained for voltage values ranging from 25 to 35 kV, keeping the polymer concentration at 12 wt%. In the same manner, the effect of distance was explored and the most suitable distance was obtained between 10-15 cm.

This work may be considered a basic study for future works about selected polymers (PAN, PVA and PA6), since most of the previous studies examine just one parameter usually omitting the effects values of some parameters such as temperature, humidity, nozzle diameter and molecular weight. In this study those parameters were kept constant all the experiments, therefore the effect of the parameters on the nanofiber morphology more clearly observed.

The other restrictive point of the previous studies is that the lower and upper limits of parameters were hold very narrow. For example, voltage values were usually selected between 6kV to 20 kV and tip-collector distance again limited by 5 to 15 cm. However, in the study the limit of those parameters were much wider than the usual values.

The effect of ambient parameters such as temperature, humidity, pressure and type of atmosphere still need to be investigated. The continuation of the study may be to research the effects of those parameters.

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