PREPARATION AND CHARACTERISATION OF POLYACRYLONITRILE BASED NANOFIBERS BY ELECTROSPINNING

POLİAKRİLONİTRİL BAZLI NANOELYAFLARIN ELEKTROEĞİRME YÖNTEMİ İLE ÜRETİMİ VE KARAKTERİZASYONU

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Yavuz Selim ŞAHİNTÜRK

ABSTRACT

Electrospinning, while historically first applied in 1934, is a technique that has been rarely used until the 21st century but re-invented again during the last decade which can be used to produce nanofibers by using a variety of polymers. Poly(acrylonitrile) (PAN) is one of the most widely investigated and used polymers due to its versatile applications. To investigate the effect of different solvents and solution concentrations on the nanofiber diameter, PAN was used as the polymer and Dimethylformamide (DMF), Dimethylacetamide (DMAc) and Dimethylsulphoxide (DMSO) were used as solvents in this work. For all three solvents, 8 solutions were prepared with different concentrations changing from 5% to 22.5 % (w/v). Each solution was electrospun under constant voltage, collector distance and feed ratio with a single needle system to specifically investigate the effects of solvent and concentration on the diameter of the nanofibers. Collector distance was set to 20 cm, voltage was 20kV and feed rate was 3mL/h.

The characterization of the obtained nanofibers was performed by Scanning Electron Microscopy (SEM). The effect of solution concentration and viscosity on the nanofiber diameters were investigated for all three solvents. The results showed that with low concentrations and viscosities, nanofibers with smaller diameters could be obtained, while the diameters increase with increasing concentration and viscosity. Considering the effect of the solvents, it has been seen that the smaller diameters were observed when DMF was used as solvent and DMSO was found to be the least appropriate solvent for electrospinning due to the disorder in web formation and the high diameter of the PAN nanofibers.

Bead formation on the nanofiber web was investigated and it was observed that the formation of beads was due to low viscosity. Bead formation was observed at 5% concentrations for all three solvents, disappeared for DMAc and DMSO for higher concentrations but has been observed for 7.5 % for DMF solutions. The

viscosities of DMF solutions in these two concentrations were lower than the other two solvents.

The surface tension of the solutions were measured with the platinum ring method and seen that the surface tensions of the solutions do not differ significantly for the different solvents at low concentrations. In this work, a constant voltage which was enough to start a jet for all solutions was used, so an effect of surface tension on the nanofiber diameters cannot be observed for these parameters.

Differential Scanning Calorimetry measurements showed that glass transition temperature and the peak of the exotherm decreased for about 10 ^{0}C. This decrease can be the result of the increased surface area in nanofiber form. While the surface area was higher in nanofiber form, the amount of chains exposed from the surface would be higher compared to the bulk state. Additionally, the increase in the surface area facilitates the heat transfer.

To support the SEM results, Atomic Force Microscopy (AFM) was used. The results were in harmony with SEM pictures regarding the nanofiber diameters.

Keywords: PAN, Electrospinnig, Nanofiber Diameter, Solution Properties, SEM

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Yavuz Selim ŞAHİNTÜRK

ÖZ

Elektroeğirme, tarihçesi 1934'lü yıllara dayansa da 21. Yüzyılda yeniden keşfedilmiş ve aradaki süreçte neredeyse hiç çalışılmamış, farklı polimerlerden nano boyutta elyaf üretmeyi sağlayan bir tekniktir. Poliakrilonitril, çok yönlü uygulamalara açık olması sebebi ile, üzerinde en sıkça araştırma yapılan ve çalışılan polimerlerden biridir. Çözücü cinsinin ve çözelti konsantrasyonlarının nanoelyaf çaplarındaki değişime olan etkilerini gözlemlemek için bu çalışmada polimer olarak Poliakrilonitril (PAN), çözücü olarak ise Dimetilformamid (DMF), Dimetilasetamid (DMAc) ve Dimetilsülfoxid (DMSO) kullanılmıştır. Üç farklı çözücü içinde %5 ile %22.5 (v/w) arasında değişen konsantrasyonlarda 8 farklı çözelti hazırlanmış, her bir çözelti, sadece çözücü ve konsantrasyonun etkilerini görebilmek için sabit elektrik akımı, sabit toplayıcı uzaklığı ve sabit çözelti besleme oranında tek iğneli elektroeğirme düzeneği ile çekilmiştir. Toplayıcı mesafesi 20cm, voltaj 20 kV ve debi 3mL/saat olarak ayarlanmıştır.

Elde edilen nanoelyafların karakterizasyonu Taramalı Elektron Mikroskobu ile yapılmıştır. Çözelti konsantrasyonunun ve viskozitenin değişiminin elyaf çaplarına olan etkisi incelenmiş farklı çözücüler için çalışmalar tekrar edilmiştir. Düşük konsantrasyon ve düşük viskozitede daha düşük elyaf çaplarına ulaşılabileceği, konsantrasyon, dolayısı ile viskozite yükseldikçe elyaf çaplarının da arttığı gözlemlenmiştir. Çözücülerin etkisi incelendiğinde, aynı konsantrasyonlarda daha düşük elyaf çaplarına DMF'in çözücü olarak kullanıldığında ulaşıldığı görülmüş, bu şartlarda PAN'ın elektroeğirmesi için kullanılan 3 çözücü içinde elyaf çaplarına ve oluşan ağın formasyonuna bakarak PAN'ın elektroeğirmesi için en kötü çözücünün de DMSO olduğu bulunmuştur

Nanoelyaf ağ tabakasındaki boncuk oluşumu incelenmiş, düşük çaplı elyafa sahip ağlarda boncuk oluşumunun daha olası olduğu görülmüştür. Her üç çözücü için de % 5 (w/v) konsantrasyonlarda boncuklanma oluşumu görülmüş, DMAc ve DMSO çözücülerinde daha üst konsantrasyonlarda boncuklanma görülmemiş fakat DMF

için %7,5 (w/v) konsantrasyonda da boncuklanma gözlenmiştir. Düşük viskozitenin boncuklanmaya sebep olduğu görülmüştür.

Çözeltilerin yüzey gerilimleri halka koparma yöntemi ile ölçülmüş, yüzey gerilimlerinin düşük konsantrasyonlarda çok fazla değişmediği görülmüştür. Bu çalışmada bütün çözelti ve konsantrasyonlarda elektroeğirmeyi başlatabilecek, dolayısı ile çözeltinin yüzey geriliminden daha güçlü bir voltaj uygulanması sebebi ile yüzey geriliminin elyaf çapları üzerine bir etkisi olduğu hakkında yorum yapılamamıştır.

DSC çalışmaları nanoelyaf formuna çekilen polimerin camsı geçiş sıcaklığı ve bozunma egzoterm pikinde toz polimer haline göre her ikisi için de yaklaşık 10 ^{0}C lik bir düşüş olduğunu göstermiştir. Bu düşüş nanoelyaf haline geçen polimerin yüzey alanının artması ve yüzeydeki polimer zinciri kısımların bulk haline göre daha fazla olması dolayısı ile ısınmanın daha çabuk olması ve hareketlenmenin daha hızlı olması ile açıklanabilir.

Taramalı Elektron Mikroskobu sonuçlarına destek olmak için Atomik Kuvvet Mikroskobu çalışmaları yapılmıştır. AFM çalışmaları elyaf çapları açısından SEM ile uyumlu sonuçlar vermiştir.

Anahtar Sözcükler: PAN, Elektroeğirme , Elyaf Çapı , Çözelti parametreleri, SEM.

Danışman: Prof. Dr. Olgun GÜVEN, Hacettepe Üniversitesi, Kimya Bölümü

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SU... So Much is So Less...

TABLE OF CONTENTS

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

SYMBOLS AND ABBREVIATIONS

PAN	Poly Acrylonitrile
DMSO	Dimethyl Sulphoxide
DMF	Dimethyl Formamide
DMAc	Dimethyl Acetamide
Tg	Glass Transition Temperature
DSC	Differential Scanning Calorimetry
TGA	Thermo gravimetric Analysis
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
MWCNT	Multi- Wall Carbon Nanotube

1. INTRODUCTION

Fiber is a general term for a filament of material that has a length at least 100 times its diameter. Fibers can be separated into two groups according to their origin: Natural fibers and Synthetic (Man-Made) Fibers.

Natural fibers are fibers which are produced by the nature. These raw materials can be subdivided as follows:

- Vegetable fibers: cotton, linen, hemp, ramie, jute, cocnut, sisal
- Animal fibers: wool hairs, silk.
- Mineral fibers: asbestos

Synthetic fibers is the generic name given for all fibers produced by means of technical chemical processes from synthetic polymers. In general, synthetic fibers are created by forcing, usually through extrusion, fiber forming materials through holes (called spinnerets) into the air, forming a thread.

In this section a summary of nanofibers is presented including definition, application and some production methods. Most extensively used production method, electrospining process is detailed.

1.1. Synthetic Fibers

There are 2 types of synthetic fiber products, the semisynthetics, or cellulosics (viscose rayon and cellulose acetate), and the true synthetics, or noncellulosics (polyester, nylon, acrylic and modacrylic, and polyolefin).

Semisynthetics are formed from natural polymeric materials such as cellulose. True synthetics are products of the polymerization of smaller chemical units into long-chain molecular polymers.

Fibers are formed by forcing a viscous fluid or solution of the polymer through the small orifices of a spinnerette and immediately solidifying or precipitating the resulting filaments. This prepared polymer may also be used in the manufacture of other nonfiber products such as the enormous number of extruded plastic and synthetic rubber products.

Synthetic fibers (both semi synthetic and true synthetic) are produced typically by two easily distinguishable methods, melt spinning and solvent spinning. Melt spinning processes use heat to melt the polymer to a viscosity suitable for extrusion through the spinneret. Solvent spinning processes use large amounts of organic solvents, which usually are recovered for economic reasons, to dissolve the polymer into a polymer solution suitable for extrusion through a spinneret.

The major solvent spinning operations are dry spinning and wet spinning. A third method, reaction spinning, is also used, but to a much lesser extent. Reaction spinning processes involve the formation of filaments from prepolymers and monomers that are further polymerized and cross-linked after the filament is formed (AP 42, 1993).

The spinning process used for a particular polymer is determined by the polymer's melting point, melt stability, and solubility in organic and/or inorganic (salt) solvents. The preparation of the polymer is typically carried out at the same facility that produces the fiber. After the fiber is spun, it may undergo one or more different processing treatments to meet the required physical or handling properties. Such processing treatments include drawing, lubrication, crimping, heat setting, cutting, and twisting. The finished fiber product may be classified as tow, staple or continuous filament yarn (AP 42, 1993).

Manufactured fabrics are usually made of filaments extruded as liquid and formed into various fibers. Because the fiber starts as a liquid, many of the fibers are colored before they become filament, thus they are difficult to dye after the fiber is woven into a fabric.

Cellulose acetate is not a strong fiber but can be extruded into fibers of different diameter and woven into fabrics that have the luxurious look of silk but do not wear like silk. Cellulose acetate does not absorb moisture readily but dries fast and resists shrinking. This is a resilient fabric that resists wrinkling in addition to being pliable and soft with a good drape. Cellulose triacetate is an improved acetate fabric which doesn't melt as easily.

Acrylic fiber is a fine soft and luxurious fabric with similar physical properties of wool such as touch. Light weight and springy, this fabric is non-allergenic, dries

quickly, draws moisture away from the body and is washable. Acrylic does not take even a moderate amount of heat. Modacrylics are used in pile fabrics like fake fur and are more flame resistant (Fourne, 1999).

Lastex is an elastic fiber made from nylon Latex. It is most often used with other fibers to create fabrics such as Spandex and foundation garments. Lastex will deteriorate after repeated washing and drying, losing its elasticity.

Nylon became a household word in 1940 when it was knitted into hosiery. In 1942 it was called into service for the armed forces use in parachutes, flak vests, combat uniforms, tires and many other vital military uses. Until the war was over, nylon was not available to the public. Nylon became one of the most versatile fibers of the man-made fabrics. In addition to hosiery, nylon is used in tricot, netting for bridal veils, and in carpeting.

Nylon is stronger yet weighs less than any other commonly used fiber. It is elastic and resilient and responsive to heat setting. Nylon fibers are smooth, non-absorbent and dry quickly. Dirt doesn't cling to this smooth fiber nor is it weakened by chemicals and perspiration. Extensive washing and drying in an automatic dryer can eventually cause piling.

Polyester is a strong fiber that is resistant to crease and thus keeps its shape. Polyester melts at medium to high temperatures. Although many people dislike polyester, perhaps due to the double knit fad of the 1970s, polyester remains a versatile and important man-made fabric. Blends of polyester give cotton a permanent press property and extend the wear of these blended garments. Polyester is manufactured in many weights including fiber-fill used in pillows and upholstery. Threads spun from polyester fibers are strong, wear exceptionally well, and are used extensively in home sewing and manufactured sewing.

Rayon, from cellulose, has many of the qualities of cotton, a natural cellulose fiber. Rayon is strong; extremely absorbent, comes in a variety of qualities and weights, and can be made to resemble natural fabrics. Rayon does not melt but burns at high temperatures. Rayon drapes well, has a soft, silky hand, and has a smooth, napped, or bulky surface. Rayon will wrinkle easily and may stretch when wet and shrink when washed. Technological advancements to the rayon process have

produced high wet modulus (HWM) rayon such as lyocell and modal which makes fabric less prone to stretch when damp or wet. Washable rayon will state the care on the fabric label. Like silk, if you pre-wash rayon fabric prior to construction of the garment, you have a washable garment (Koslowski, 2010).

Spandex is an elastic type fiber that can be stretched many times its length and then spring back to the original length. Spandex is more resistant to washing, perspiration, and heat than latex. Spandex is used in foundation garments and hosiery.

1.2. Nanofibers

Nanofibers, especially organic nanofibers, constitute a particularly interesting and versatile class of one-dimensional (1-D) nanomaterial. The more exotic of the conventional textile fiber technologies include “microdenier fibers” per filament, produced using multistep fabrication techniques such as melt spinning using “islands at sea” type extrusion dies. Further refinement of these textile industry techniques to obtain nanoscale fibers (that are several orders of magnitude smaller in diameter) is not practical, cost-effective, or scalable. Several techniques unrelated to electrospinning were reported in early literature for the laboratory preparation of nanofibers. Self-assembly of polymers under certain conditions and drawing of polymer melts can produce small samples of polymer nanofibers (Andrady, 2008).

Although definition of nanofibers changes across application fields, it can generally be defined as materials that have an elongated structure. It can be called that materials which have a diameter of 100 nm or less at least in one dimension, but in the industry 500 nm materials could be considered as nanofibers whereas some scientists use the term ‘sub-micron’ in the academic world. Nanofibers have several superior characteristics. They present a high surface area to volume ratio, better mechanical properties, e.g. good directional strength, and flexibility so they can be utilized for a wide variety of materials and applications considering their mechanical, biomedical, optical, electronical, and chemical properties (Schönenberger, 1997).

The study on the nanofiber mechanical properties as a result of manufacturing techniques, constituent materials, processing parameters and other factors would fall into the category of nanomechanics. Indeed, while the primary classification of nanofibers is that of nanostructure or nanomaterial, other aspects of nanofibers such as its characteristics, modeling, application and processing would enable nanofibers to penetrate into many subfields of nanotechnology (Ramakrishna, 2005).

Nanofiber-related publications and patents appear to have grown in number rapidly over recent years. An analysis of patent activity in particular allows an overall summary of the commercial potential of electrospun nanofibers and affords the identification of application areas where the technology might play a key role. A large majority of the patents issued on the technology, about two-thirds are related to biological or medical application of nanofibers. The second largest group deals with application of nanofibers in filtration, followed by other applications such as sensors, composites, and catalysis.

Numerous examples of other possible applications such as magnetoresponsive fiber materials (Li et al., 2003; Wang et al., 2004; Tan et al., 2005; Zhu et al., 2006a), electrical applications such as carbon nanofiber-based supercapacitors (Kim and Yang 2003; Kim et al. 2004a, 2004b, 2004c; Kim., 2005), nanofiber photovoltaic devices (Drew et al., 2002; Tomer et al., 2005; Onozuka et al., 2006), catalysis applications (He and Gong 2003; Demir et al., 2004; Wang et al., 2006), and superhydrophobic surfaces (Acatay et al. 2004; Jiang et al. 2004; Ma et al. 2005a, 2005b; Singh et al. 2005; Zhu et al. 2006b) have been reported in the literature (Andrady, 2008).

1.2.1. Production methods

There are several processing methods for producing polymeric micro and nanofibers. These are drawing, template synthesis, phase separation, self-assembly, and electrospinning. Electrospinning is the most efficient way to fabricate continuous fibers and it has unique a chance to be used in industrial applications.

A comparison of the various issues relating to these processing can be found in Table 1.1 (Ramakrishna, 2005).

Table 1.1 Comparison of processing techniques for obtaining nanofibers.

Process	Technological advances	Can the process be scaled?	Repeatability	Convenient to process?	Control on fiber dimensions
Drawing	Laboratory	X	√	√	X
Template Synthesis	Laboratory	X	√	√	√
Phase Separation	Laboratory	X	√	√	X
Self-Assembly	Laboratory	X	√	X	X
Electro-spinning	Laboratory (with potential for industrial processing	√	√	√	√

1.2.1.1. Drawing

This method can produce long and single nanofibers. Ondarcuhu and Joachim (1998) obtained nanofibers from sodium citrate solution in chloroauric acid by using a micropipette with this method. Harfenist et al., (2004) drew PMMA fibers from 50 nm to 2 Kmin length. In that study, they used a sharp tip and they dipped the tip into the polymer solution several times in order to get a consistency in the droplet. Finally, a fiber appears between the tip and the polymer drop . Then the fiber is pulled from its tip end into another liquid solution droplet. With this direct drawing method patterned, micro and nanofiber production is possible. But with this technique, only long single nanofibers can be fabricated with viscoelastic polymers. Minimum utilization of equipment may seem an advantage but on the other hand discontinuous nature of this process makes this method inefficient.

1.2.1.2. Template synthesis

Template synthesis is a way of producing micro- and nanostructures by using nano-scaled diameter membranes. It is thought to be an alternative method to conventional lithography. Desired nanomaterials can be fabricated by adjusting

pore diameter of the template. Membranes have cylindrical pores or channels and each of them have diameters uniformly distributed throughout the membrane.

In this technique, nanomaterials (nanofibers, nanowires, nanometer-sized fibrils, rods etc.) are prepared by using polymers, conductive polymers, metals, semiconductors, carbons, and other substances. Track-etched and anodic aluminium oxide membranes have been used as templates. However, other nanoporous materials (natural, or man made) and nanostructures can be considered as templates also. There are fundamentally five techniques for template synthesis. These are electrochemical deposition, chemical deposition, chemical polymerization, sol-gel deposition, and chemical vapor deposition (CVD). The template synthesis method has a number of interesting and useful applications. These nanostructures can have potential use areas from biomedical sciences to separation technology (Martin et al., 1995, 1996; Huczko,2000; Feng et al., 2002).

For example, Feng and his coworkers used template synthesis methodology in their study of superhydrophobic surfaces with polyacrylonitrile fibers (Feng et al., 2002). They fabricated aligned PAN nanofibers with the average interfiber distance of 513.8 nm and a length of 10.7 Km. They used an anodic aluminium oxide membrane as their template. Schönenberger obtained nanowires of Ni, Co, Cu, Au, and polypyrrole in polycarbonate track-etched membrane (Schönenberger et al., 1997). They used electrochemical template synthesis technique with a membrane having nominal pore diameters between 10 and 200 nm.

1.2.1.3. Phase separation

Nanofibers, nano fibrous matrices, porous 3-D scaffolds, and highly porous foams can be fabricated by phase separation technique. Generally, a polymer is dissolved in its solvent. After dissolution, the mixture is gelated. This procedure is separated into five steps (Ma et al., 1999).

These are dissolution of polymer, gelation, extraction of solvent, freezing, and freeze-drying under vacuum. They studied the preparation of nano fibrous matrices of some biodegradable polymers (PLLA, PDLLA, and PLGA) and

investigated the effects of polymer concentration, thermal treatment, solvent exchange and freezing temperature.

Highly porous foams can be produced by liquid-liquid or solid-liquid phase separation (Lo et al., 1996; Zhang et al., 1999). Thermally induced phase separation has also been in use for the formation of scaffolds for tissue engineering applications. This method includes two phases namely polymer-rich and polymer-lean. The formation of two phases occurs by cooling or quenching of the polymer solution. In the final step, solvent is sublimed in vacuum or taken away by extraction. Zhang´s study (1999) can be given as a sample preparation of foam. In their strategy, they first dissolved 10 ml of PLLA/HAP/dioxane in a beaker at 50°C. The mixture was immediately put into a fridge in order to solidify the solvent. After 2 hours, liquid nitrogen was used for deep freezing. For dry-freezing, the vessel was kept at -5 °C and -10 °C by using an ice/salt bath. The pressure in the vessel was 0.5 mmHg and after 4 days of treatment solvent was removed fully. At the end, he obtained highly porous polymeric foam. Phase separation is a complex and time consuming process. Type of polymer, type of solvent, polymer concentration, phase separation temperature, thermal treatment, and solvent exchange are the variables of phase separation method. Control on the fiber diameter is difficult and unfortunately, phase separation is limited only to some specific polymers.

1.2.1.4. Self-assembly

In self-assembly technique, nanofibers can be derived from single smaller molecules which already exist. These individual molecules organize themselves into desired nano-scale structures. It means that they act as basic building blocks. The idea behind the self-assembly method is that intermolecular forces between those tiny molecules give the overall shape of the resulting nanofibers (Ramakrishna, 2005). Hatgerink and his research team used pH-induced self assembly. They self-assembled peptide-amphiphile (PA) nanoscale fibrous scaffold which is similar to extracellular matrix (Hartgerink et al.,2001).

Niece and his coworkers introduced a new approach to self-assembly of PA (Niece et al., 2003). Their study is in contrast with the previous studies which require low pH for self-assembly. There are also other studies carried on this

subject. Zhang et al. (2005), worked on self assembling peptide nanofiber scaffolds for tissue cells. De Moel et al. (2001), prepared nanofibers from self organized supermolecules.

Up to now, four nanofiber production methods have been reported briefly. The fifth one is electrospinning. The comparison between them was given in Table 1.1. Among all, electrospinning is the best candidate for further development with a wide range of opportunities to be utilized in all types of polymers (both synthetic and natural), and ceramics. Also, in this thesis study, electrospinning was used for the fabrication of non-woven nanofibers. Therefore, electrospinning process was given in the next section in detail.

1.3. Electrospinning

Electrospinning is a term used to describe a class of fiber forming processes by which electrostatic forces are employed to control the production of fibers. It is closely related to the more established technology of electrospraying, which generally refers to processes in which electrostatic forces are used to control the formation of droplets. “Spinning” in this context is a textile term that derives from the early use of spinning wheels to form yarns from natural fiber staples like cotton and is commonly used to identify fiber-forming processes for synthetic fibers as well. In both electrospinning and electrospraying, the role of the electrostatic forces is to supplement or replace the conventional mechanical forces (e.g. hydrostatic, pneumatic) used to form the jet and to reduce the size of the fibers or droplets (Rutledge et al., 2007).

1.3.1. History of electrospinning

The first documented accounts of electrostatic spinning of a polymer solution into nanofibers were described in 1902 by J. F. Cooley and by W. J. Morton. The spun fibers were collected as “a cob-web like mass” on the negatively charged electrode. The process was described as being the result of “electrical disruption of the fluid.” A closely related patent issued a year later in 1903 to Cooley also addressed electrospinning. The claims in the latter patent included the introduction of the viscous polymer solution near the terminus of a charged electrode, but not necessarily in contact with it, to yield electrospun fibers. These early patents

emphasize the need for the polymer solution to be of adequate viscosity and used, as a specific example, the electrospinning of nitrocellulose. Interestingly, the fundamental features of the process, as described in these century-old patents, have changed little with time (Andrady., 2008).

Electrospinning process was patented by Formhals at 1934, wherein an experimental setup was outlined for the production of polymer filaments using electrostatic force. When used to spin fibers this way, the process is termed as electrospinning. In other words, electrospinning is a process that creates nanofibers through an electrically charged jet of polymer solution or polymer melt. Following this, investigations of the process have been carried out by a number of researchers (Ramakrishna, 2005).

1.3.2. Principle of electrospinning

The principle behind electrospinning is relatively simple: a solution of a polymer flows out of the tip of a capillary, where a droplet forms under the influence of the surface tension of the solution. A sufficiently large electric charge (5–50 kV DC) is applied to the solution, which causes repulsive electrostatic forces between polymer and solvent molecules to overcome the surface tension, and a jet of polymer shoots away from the capillary towards a grounded collector. In the space between the capillary tip and the collector, the jet becomes unstable and a rapid whipping of the jet follows. This leads to evaporation of the solvent, leaving a polymer fiber, which undergoes stretching and thinning as a result of the whipping, and finally collects on the grounded collector as a randomly oriented web of micro or nanofibers.

The random orientation of the electrospun fibers in the typically obtained non-woven webs is acceptable in some applications such as filters, wound dressings and tissue scaffolds. However, nanofibers need to be obtained as continuous single nanofibers or uniaxial fiber bundles to make their commercialization in the fiber and textile industry viable (Huang et al., 2003).

The principle variables that govern nanofiber quality (or determine if electrospinning will occur at all) are the average molecular weight of the polymer,

the nature of the solvent, and the magnitude of the electric field used to induce electrospinning.

Bead formation is the most common type of defect encountered in electrospun nanofibers and occurs primarily as a result of the instability of the jet under different process conditions. Qualitatively, beads may be expected at times during electrospinning whenever the surface tension forces tend to overcome the forces (such as charge repulsion and viscoelastic forces) that favor the elongation of a continuous jet. This occurs intermittently, as fiber formation still remains the dominant process and consequently leads to the typical “beads on a string” morphology described for a variety of different polymer/solvent systems. (Entov and Shmarayan 1997; Fong et al. 1999; Lee et al. 2003; Wannatong et al. 2004; Gupta et al. 2005; Tomczak et al. 2005) Figure 2.1 shows an example of beaded nanofibers of PAN electrospun from 10 wt% solutions in DMF

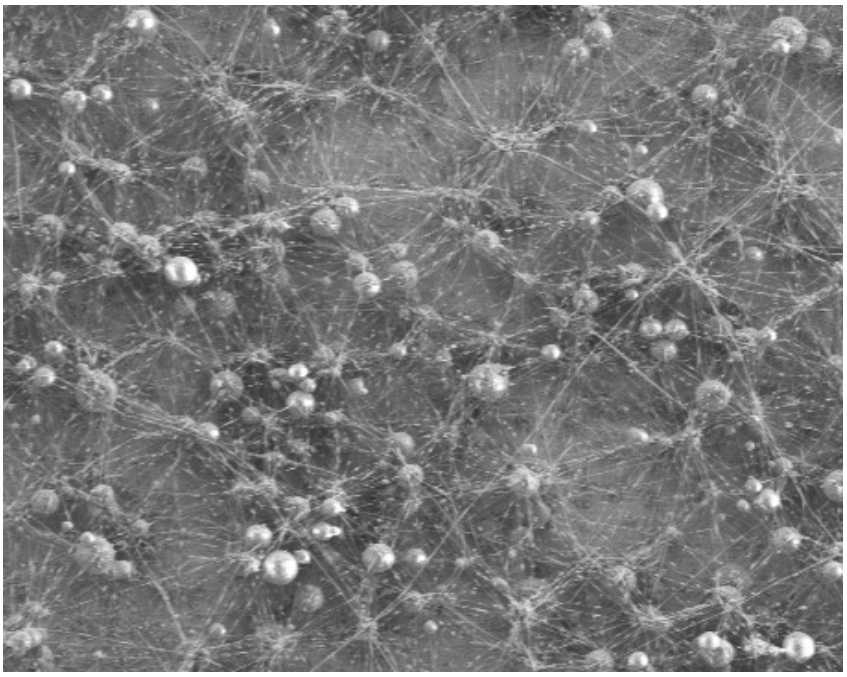


Figure 1.1 Polyacrylonitrile (PAN) electrospun from DMF (5 % w/v) showing beads. Feed rate 3 mL/h; applied voltage of 20 kV; gap distance of 20 cm.

1.3.3. Electrospinning setup

The electrospinning process, in its simplest form, consisted of a pipette to hold the polymer solution, two electrodes and a DC voltage supply in the kV range. The polymer drop from the tip of the pipette was drawn into a fiber due to the high

voltage. The jet was electrically charged and the charge caused the fibers to bend in such a way that every time the polymer fiber looped, its diameter was reduced. The fiber was collected as a web of fibers on the surface of a grounded target (Ramakrishna, 2005).

Figure 1.2 is a schematic representation of the equipment generally used in laboratory electrospinning of polymer solutions and figure 1.3 is a picture showing taylor cone and jet in electrospinning process.

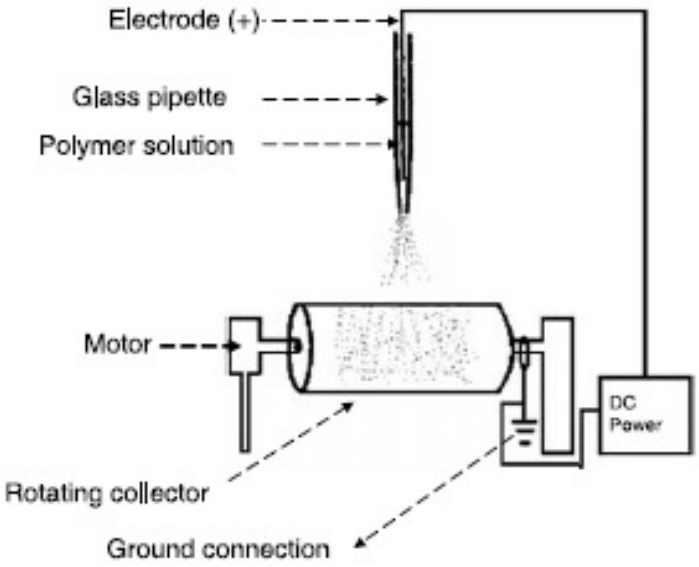


Figure 1.2 Schematic representation of electrospinning equipment (Andrady, 2008)

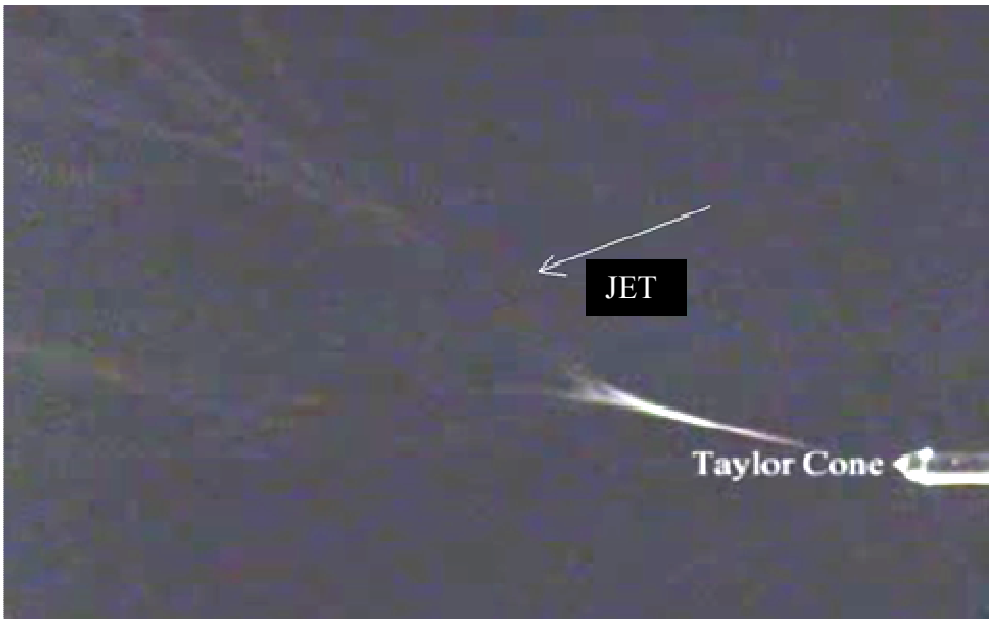


Figure 1.3 Picture showing the taylor cone and jet during electrospinning

Experimentally, an electrospinning apparatus consists of three basic components:

• A polymer of adequate average molecular weight dissolved at a high enough concentration in a good solvent having suitable conductivity, surface tension, and vapor pressure.

• A device for electrically charging the polymer solution to obtain a stable jet.

• A gap between the capillary tip (or the charged droplet) and a grounded collecting surface that is set at a suitable distance from the tip carrying the polymer solution (Andrady, 2008).

Important features of electrospinning are:

• Suitable solvent should be available for dissolving the polymer.

• The vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.

• The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the pipette.

• The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the pipette.

• The gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form (Ramakrishna, 2005).

1.3.4. Parameters effecting electrospinning

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. 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.

1.3.4.1. Polymer solution parameters

The properties of the polymer solution have the most significant influence in the electrospinning process and the resultant fiber morphology. The surface tension has a part to play in the formation of beads along the fiber length. The viscosity of the solution and its electrical properties will determine the extent of elongation of the solution. This will in turn have an effect on the diameter of the resultant electrospun fibers.

Conductivity

The electrospinning process fundamentally requires the transfer of electric charge from the electrode to the spinning droplet at the terminus of the tip. A minimal electrical conductivity in the solution is therefore essential for electrospinning; solutions of zero conductivity cannot be electrospun. Solvents commonly used in electrospinning have conductivities that are much lower than that of even distilled water; dichloromethane has a value of only 0.03 mS/m. On dissolving a polymer in the solvent, however, the solution conductivity generally increases due to the availability of conducting ionic species (mostly from impurities or additives) from the polymer. With increasing polymer concentration in solution, however, its electrical conductivity may decrease. Where the polymer itself has ionic functionalities as with polyelectrolytes, however, the solution conductivity will be much higher (relative to those of uncharged polymers) and markedly concentration dependent (Jun et al. 2003).

Surface tension

Surface tension is the primary force opposing coulomb repulsion and its role in determining electrospinnability cannot be overstated. In the instability region of the jet that obtains fiber extension, electrostatic forces are countered primarily by surface tension forces. It is this balance between surface tension cohesive forces and the surface electrostatic repulsion that determine the curvature in bending of the jet during whipping instability. Also, bead formation in electrospinning can be induced by changing the surface tension of the solution (Dietzel, 2001).

The initiation of electrospinning requires the charged solution to overcome its surface tension. However, as the jet travels towards the collection plate, the

surface tension may cause the formation of beads along the jet. Surface tension has the effect of decreasing the surface area per unit mass of a fluid. In this case, when there is a high concentration of free solvent molecules, there is a greater tendency for the solvent molecules to congregate and adopt a spherical shape due to surface tension. A higher viscosity will mean that there is greater interaction between the solvent and polymer molecules thus when the solution is stretched under the influence of the charges, the solvent molecules will tend to spread over the entangled polymer molecules thus reducing the tendency for the solvent molecules to come together under the influence of surface tension as shown in Figure 1.4 (Fong, 1999).

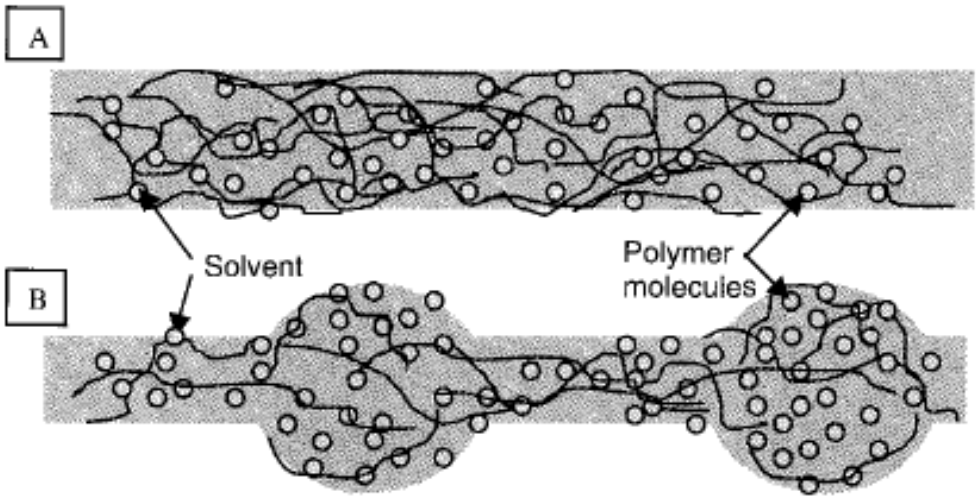


Figure 1.4 (A) At high viscosity, the solvent molecules are distributed over the entangled polymer molecules. (B) With a lower viscosity, the solvent molecules tend to congregate under the action of surface tension.

As with electrical conductivity, low concentrations of additives may be used to alter the surface tension of polymer solutions.

Solvent such as ethanol has a low surface tension thus it can be added to encourage the formation of smooth fibers. Another way to reduce the surface tension is to add surfactant to the solution. The addition of surfactant was found to yield more uniform fibers. Even when insoluble surfactant is dispersed in a solution as fine powders, the fiber morphology is also improved (Jung, 2005; Lin T. et al., 2005).

Dielectric constant

The dielectric constant of a solvent has a significant influence on electrospinning. Generally, a solution with a greater dielectric property reduces the beads formation and the diameter of the resultant electrospun fiber. Solvents such as N,N-Dimethylformamide (DMF) may be added to a solution to increase its dielectric property to improve the fiber morphology. The bending instability of the electrospinning jet also increases with higher dielectric constant. This is shown by increased deposition area of the fibers. This may also facilitate the reduction of the fiber diameter due to the increased jet path.

However, if a solvent of a higher dielectric constant is added to a solution to improve the electrospinnability of the solution, the interaction between the mixtures such as the solubility of the polymer will also have an impact on the morphology of the resultant fibers. When DMF is added to polystyrene (PS) solution, beads are formed even though electrospinnability should improve due to the higher dielectric constant of DMF. This could be the result of the retraction of PS molecule due to poor interaction between PS and the solvent molecules (Son, 2004; Wannatong, 2004).

Solution viscosity

One of the factors that affect the viscosity of the solution is the molecular weight of the polymer. Generally, when a polymer of higher molecular weight is dissolved in a solvent, its viscosity will be higher than solution of the same polymer but of a lower molecular weight. One of the conditions necessary for electrospinning to occur where fibers are formed is that the solution must consists of polymer of sufficient molecular weight and the solution must be of sufficient viscosity. As the jet leaves the needle tip during electrospinning, the polymer solution is stretched as it travels towards the collection plate. During the stretching of the polymer solution, it is the entanglement of the molecule chains that prevents the electrically driven jet from breaking up thus maintaining a continuous solution jet.

The molecular weight of the polymer represents the length of the polymer chain, which in turn have an effect on the viscosity of the solution since the polymer length will determine the amount of entanglement of the polymer chains in the

solvent. Another way to increase the viscosity of the solution is to increase the polymer concentration. Similar to increasing the molecular weight, an increase in the concentration will result in greater polymer chain entanglements within the solution which is necessary to maintain the continuity of the jet during electrospinning (Buchko et al., 1999; Shenoy et al., 2005).

Volatility

Invariably, it is the evaporation of solvent from the jet that yields a solid polymer nanofiber at the collector plate. Ideally, all traces of solvent must be removed by the time the nanofiber hits the collector. If not, the wet fibers may fuse together to form a melded or reticular mat. Sometimes a flat ribbon-like nanofibers derived from the fluid–filled, incompletely dry nanofiber due to slow subsequent evaporation of solvent and collapse of the tube, are obtained. Using volatile solvents avoids this difficulty. However, when using highly volatile solvents the solution may dry on the capillary or needle, causing blockage to flow (Hsu and Shivkumar, 2004).

The smaller fiber diameters in electrospinning result from jet extension and it is critical that a minimal elongational viscosity be maintained in the jet during this stage. Essentially, the relaxation time for the polymer chains in solution needs to be matched to the rate of extensional deformation due to instability. Very rapid drying can therefore hinder the development of smaller diameters in the nanofibers (Wannatong, 2004).

1.3.4.2. Polymer processing parameters

Another important parameter that affects the electrospinning process is the various external factors exerting on the electrospinning jet. This includes the voltage supplied, the feed rate, temperature of the solution, type of collector, diameter of needle and distance between the needle tip and collector. These parameters have a certain influence in the fiber morphology although they are less significant than the solution parameters (Ramakrishna, 2005).

Voltage

A crucial element in electrospinning is the application of a high voltage to the solution. The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution. Generally, both high negative or positive voltage of more than 6kV is able to cause the solution drop at the tip of the needle to distort into the shape of a Taylor Cone during jet initiation. Depending on the feedrate of the solution, a higher voltage may be required so that the Taylor Cone is stable. The columbic repulsive force in the jet will then stretch the viscoelastic solution. If the applied voltage is higher, the greater amount of charges will cause the jet to accelerate faster and more volume of solution will be drawn from the tip of the needle. This may result in a smaller and less stable Taylor Cone. When the drawing of the solution to the collection plate is faster than the supply from the source, the Taylor Cone may recede into the needle.

As both the voltage supplied and the resultant electric field have an influence in the stretching and the acceleration of the jet, they will have an influence on the morphology of the fibers obtained. In most cases, a higher voltage will lead to greater stretching of the solution due to the greater columbic forces in the jet as well as the stronger electric field. These have the effect of reducing the diameter of the fibers and also encourage faster solvent evaporation to yield drier fiber. When a solution of lower viscosity is used, a higher voltage may favor the formation of secondary jets during electrospinning. This has the effect of reducing the fiber diameter (Buchko et al., 1999; Megelski et al., 2002)

Another factor that may influence the diameter of the fiber is the flight time of the electrospinning jet. A longer flight time will allow more time for the fibers to stretch and elongates before it is deposited on the collection plate. Thus, at a lower voltage, the reduced acceleration of the jet and the weaker electric field may increase the flight time of the electrospinning jet which may favor the formation of thinner fibers. In this case, a voltage close to the critical voltage for electrospinning may be favorable to obtain finer fibers (Zhao et al., 2004).

The effect of high voltage is not only on the physical appearance of the fiber, it also affects the crystallinity of the polymer fiber. The electrostatic field may cause the polymer molecules to be more ordered during electrospinning thus induces a greater crystallinity in the fiber. However, above a certain voltage, the crystallinity of the fiber is reduced. With increased voltage, the acceleration of the fibers also increases. This reduces the flight time of the electrospinning jet. Since the orientation of the polymer molecules will take some time, the reduced flight time means that the fibers will be deposited before the polymer molecules have sufficient time to align itself. Thus, given sufficient flight time, the crystallinity of the fiber will improve with higher voltage.

Since electrospinning is caused by charges on the jet, these charges can be influenced by the external electric field which will in turn affect the jet path. It is thus not surprising that there are several attempts to control the electrospinning jet through changing the electric field profile between the source of the electrospinning jet and the collector. This can be achieved by using auxiliary electrodes or by changing the orientation or shape of the collector. Aligned and even patterned nanofibers can be obtained by clever manipulation of the electric field (Kessick et al., 2004)

Feedrate

The feedrate will determine the amount of solution available for electrospinning. For a given voltage, there is a corresponding feedrate if a stable Taylor cone is to be maintained. When the feedrate is increased, there is a corresponding increase in the fiber diameter or beads size. However, there is a limit to the increase in the diameter of the fiber due to higher feedrate. If the feedrate is at the same rate which the solution is carried away by the electrospinning jet, there must be a corresponding increase in charges when the feedrate is increased. Thus there is a corresponding increase in the stretching of the solution which counters the increased diameter due to increased volume (Rutledge et al., 2000; Zhong et al., 2002).

Distance

In several cases, the flight time as well as the electric field strength will affect the electrospinning process and the resultant fibers. Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength. For independent fibers to form, the electrospinning jet must be allowed enough time for most of the solvents to be evaporated. When the distance between the tip and the collector is reduced, the jet will have a shorter distance to travel before it reaches the collector plate. Moreover, the electric field strength will also increase at the same time and this will increase the acceleration of the jet to the collector. As a result, there may not have enough time for the solvents to evaporate when it hits the collector. When the distance is too short, excess solvent may cause the fibers to merge where they contact to form junctions resulting in inter and intra layer bonding.

Depending on the solution property, the effect of varying the distance may or may not have a significant effect on the fiber morphology. In some cases, changing the distance has no significant effect on the fiber diameter. Decreasing the distance has the same effect as increasing the voltage supplied and this will cause an increase in the field strength (Buchko et al., 1999; Zhong et al., 2002).

Effect of collector

The simplest and the most used collector reported in laboratory electrospinning is a stationary metal plate or a foil placed at a fixed distance from the tip. The conical spray pattern impinging on it results in a symmetric circular patch of nanofiber on the surface of the metal. As the collector is grounded, the residual charges on the as-spun fibers are rapidly removed, allowing the fibers to consolidate into a mat of high areal density. A moving collector surface allows some control in the areal density (Teo and Ramakrishna, 2006)

The porosity of the collector seems to have an effect on the deposited fibers. Experiments with porous collector such as paper and metal mesh had shown that the fiber mesh collected had a lower packing density than smooth surfaces such as metal foils. This can be attributed to the diffusion and rate of evaporation of the residual solvents on the fibers collected. In a porous target, there is faster

evaporation of residual fibers due to higher surface area while smooth surfaces may cause an accumulation of solvents around the fibers due to slow evaporation rate.

Whether or not the collector is static or moving also have an effect on the electrospinning process. While rotating collector has been used to collect aligned fibers, it was found to assist in yielding fibers that are dry. This is useful because certain solvents such as Dimethylformamide (DMF) which is good for electrospinning but have a high boiling point that may result in the fibers being wet when they are collected. A rotating collector will give the solvent more time to evaporate and also increase the rate of evaporation of the solvents on the fibers. This will improve the morphology of the fiber where distinct fibers are required (*Wannatong et al., 2004*).

Diameter of needle

The internal diameter of the needle or the pipette orifice has a certain effect on the electrospinning process. A smaller internal diameter was found to reduce the clogging as well as the amount of beads on the electrospun fibers. The reduction in the clogging could be due to less exposure of the solution to the atmosphere during electrospinning. Decrease in the internal diameter of the orifice was also found to cause a reduction in the diameter of the electrospun fibers. When the size of the droplet at the tip of the orifice is decreased, such as in the case of a smaller internal diameter of the orifice, the surface tension of the droplet increases. For the same voltage supplied, a greater columbic force is required to cause jet initiation. As a result, the acceleration of the jet decreases and this allows more time for the solution to be stretched and elongated before it is collected. However, if the diameter of the orifice is too small, it may not be possible to extrude a droplet of solution at the tip of the orifice (*Mo et al., 2004; zhao et al., 2004*).

1.3.4.3. Ambient parameters

Any interaction between the surrounding and the polymer solution may have an effect on the electrospun fiber morphology. High humidity for example was found to cause the formation of pores on the surface of the fibers. Since electrospinning

is influenced by external electric field, any changes in the electrospinning environment will also affect the electrospinning process.

Humidity

Humidity of the electrospinning environment may have an influence in the polymer solution during electrospinning. At high humidity, it is likely that water condenses on the surface of the fiber when electrospinning is carried out under normal atmosphere. As a result, this may have an influence on the fiber morphology especially when polymer was dissolved in volatile solvents.

Humidity of the environment will also determine the rate of evaporation of the solvent in the solution. At a very low humidity, a volatile solvent may dry very rapidly. The evaporation of the solvent may be faster than the removal of the solvent from the tip of the needle. As a result, the electrospinning process may only be carried out for a few minutes before the needle tip is clogged (Bognitzki et al., 2001; Megelzki et al., 2002).

Pressure

Under enclosed condition, it is possible to investigate the effect of pressure on the electrospinning jet. Generally, reduction in the pressure surrounding the electrospinning jet does not improve the electrospinning process. When the pressure is below atmospheric pressure, the polymer solution in the syringe will have a greater tendency to flow out of the needle and there causes unstable jet initiation. As the pressure decreases, rapid bubbling of the solution will occur at the needle tip. At very low pressure, electrospinning is not possible due to direct discharge of the electrical charges (Ramakrishna, 2005).

Type of atmosphere

The composition of the air in the electrospinning environment will have an effect on the electrospinning process. Different gases have different behavior under high electrostatic field. For example, helium will break down under high electrostatic field and thus electrospinning will not be possible. However, when a gas with higher breakdown voltage is used, the fibers obtained have twice the diameter of those electrospun in air given all other conditions are equal (Baumgarten, 1971).

2. ELECTROSPINNING STUDIES

In this chapter, previous studies about electrospinning of nanofibers, and electrospinning of Polyacrylonitrile (PAN) solutions were introduced briefly.

2.1. Electrospun Nanofibers

Innovative modifications of the basic spinning apparatus and methodology used in electrospinning allow a wide range of fiber and mat morphologies to be produced. Many interesting variations of the basic electrospinning process have been described in the literature over recent years. These include novel electrode arrangements, the use of AC voltage to drive the process, reactive electrospinning, unusual collector geometries, unique tip designs, vibrating tip designs and the use of different spinning environments.

Most of these are intriguing scientific phenomena that help better understand the complexities of the process but invariably remain laboratory curiosities. A few however, show promise in terms of extending the range of applications of nanofibers. These include process and material changes that result in unusual surface morphologies in nanofibers and complex mat structure. Although the full range of applications that best exploit these new developments are yet to be developed, the emerging innovative applications of nanofibers in biomedical, sensor, electronic, and other areas will likely be enabled or enhanced by these recent advances in several key techniques (Andrady, 2008).

Rutledge and Fridrikh (2007), reviewed some of the basic aspects of the electrospinning process. They determined that electrospun fibers were essentially continuous which was supported by both modeling and observations; fiber ends were rarely observed in micrographs of fibers obtained during steady state operation. They discussed the dependence of the jetting phenomenon on operating variables. They also summarized the continuum level models of the jet thinning and jet instability.

E. Smit et al. (2005), described a technique for making continuous uniaxial fiber bundle yarns from electrospun fibers. They analyzed yarns from electrospun fibers of poly(vinyl acetate), poly(vinylidene difluoride) and polyacrylonitrile. They stated that the fibers in the obtained yarns are aligned and exhibit typical electrospinning

fiber characteristics, such as concentration dependence on fiber diameter and bead formation.

Megelski et al. (2002), produced electrospun nanofibers by using a variety of solvents to investigate the influence of polymer/solvent properties on the fiber surface morphology. They made four different solutions of polystyrene electrospun from various solvents. According to this study, it was seen that ability to produce polymeric fibers or materials with a tailorable surface morphology increases their range of application significantly. They also determined that solvent diffusion in polymers plays an important role in the evaporation process as already mentioned. The diffusion coefficients of the solvents and the solubility parameters of the polymers and of the solvents as well as the interaction parameters between polymer and solvent are parameters of influence.

Bazbouz and Stylios (2008), reported a novel mechanism by Electrospinning of highly aligned and twisted composite Nylon 6 nanofibers incorporating multiwall carbon nanotubes. Results of their work were presented for the morphology of nanofibers, the dispersion of MWCNTs and their alignment inside the fiber body. They concluded that mechanical and electrical stretching of composite nanofibers align MWCNTs along the axis of the nanofiber.

2.2. Electrospinning of PAN Solutions

Polyacrylonitrile (PAN) is the most extensively used in electrospinning because of its excellent properties. PAN is damaged only by strong concentrated acids, not normally affected by alkalies and very resistant to ultraviolet light. Polyacrylonitrile is a versatile polymer that is widely used for making membranes, and is not only hydrophobic but is also insoluble in a wide range of solvents.

Polyacrylonitrile polymers are produced by the industry using two methods, suspension polymerization and solution polymerization. Either batch or continuous reaction modes may be employed (Koslowski, 2010).

He et al. (2008), studied the effect of concentration on electrospun nanofibers by using (PAN). They demonstrated that the diameters of electrospun nanofibers are greatly affected by solution viscosity, which is directly related to its concentration.

They concluded that the diameter of electrospun PAN nanofibers increases approximately linearly with solution concentration.

Yordem et al. (2008), investigated electrospinning process and material parameters to produce PAN fibers. They studied the interactive effects of the parameters on the resultant fiber to establish a prediction scheme for the domain/window of the parameters where targeted PAN nanofiber diameter. They stated that the response surface predictions revealed the interactions for the resultant nanofiber diameter, and showed that there is a negative correlation between the mean diameter and coefficient of variation for the fiber diameter. They suggested sub-domain of the parameter space consisting of the solution concentration, applied voltage and collector distance for the potential nano-scale fiber production.

Ra et al. (2005), studied the effect of anisotropic electrical conductivity of MWCNT/polyacrylonitrile nanofiber. They used electrospinning process to fabricate the multiwalled carbon nanotubes-embedded PAN nanofiber paper. They reported that large anisotropic electrical conductivity, i.e., the electrical conductivity of the carbonized nanofiber paper along the spinning direction was about three times larger than that normal to the spinning direction.

Qin et al. (2007), used various inorganic salts including LiCl, $NaNO_3$, NaCl, and $CaCl_2$ to investigate the effect of salts on electrospinning process. They observed that the viscosity and shearing strength of electrospinning solutions are slightly affected by the addition of salts and mainly affected by the changes in concentration of PAN electrospinning solutions. They demonstrated that the viscosity and shearing strength of electrospinning solutions all decrease slightly by the addition of salts when the concentration of electrospinning solutions is more than 4 wt %, whereas they increase slightly by the addition of salts when the concentration of electrospinning solutions is 4 wt %.

Wan et al. (2006) studied the vibrorheological effect on electrospun polyacrylonitrile nanofibers. They studied the relation of Electrospun fiber diameter with solution viscosity and the concentration. It was obtained that vibration applied in electrospinning process can dramatically decrease fiber diameter, but at the

same time, polymer molecule structures are partly changed, the crystal region is destroyed at a certain degree.

Saiyasombat and Maensiri (2007), studied the the fabrication, morphology and structure of carbonnanofibers prepared by electrospinning a precursor of polyacrylonitrile (PAN)/dimethyl formamide (DMF), followed by carbonization of the electrospun nanofibers. They investigated the effect of solution concentration on the nanofiber and carbonised nanofibers under nitrogen and argon atmosphere.

3. EXPERIMENTAL

3.1. Materials Used

AKSA Polyacrylonitrile (PAN) copolymer was used for spinning nanofibers in this thesis. All Solvents; Dimethylformamide (DMF) (Merck), Dimethyacetamide (DMAc) (AKKIM) and Dimethylsulphoxide (DMSO) (Merck) were pure and used as obtained. AKSA polymer is a copolymer containing a certain amount of vinyl acetate as second monomer, the amount of vinyl acetate in the polymer is less than 10 %. The reason for selecting PAN as polymer and these three solvents was due to industrial realization of this work.

Electrospinning setup is purchased from the company NanoFMG. It has different types of collectors as rotating drum or single plate. A range of 1 to 18 needles may be used for electrospinning. The applied voltage may be controlled between 0 to 50 kV. Collector distance can be set to a value between 5 to 40 cm. The rotating speed of the collector drum can be controlled, and the system has a syringe pump which the amount of the solution being pumped can be controlled between 0,1 to 100 mL/h. Figure 3.1 shows the photograph of the electrospinning setup used for this thesis.

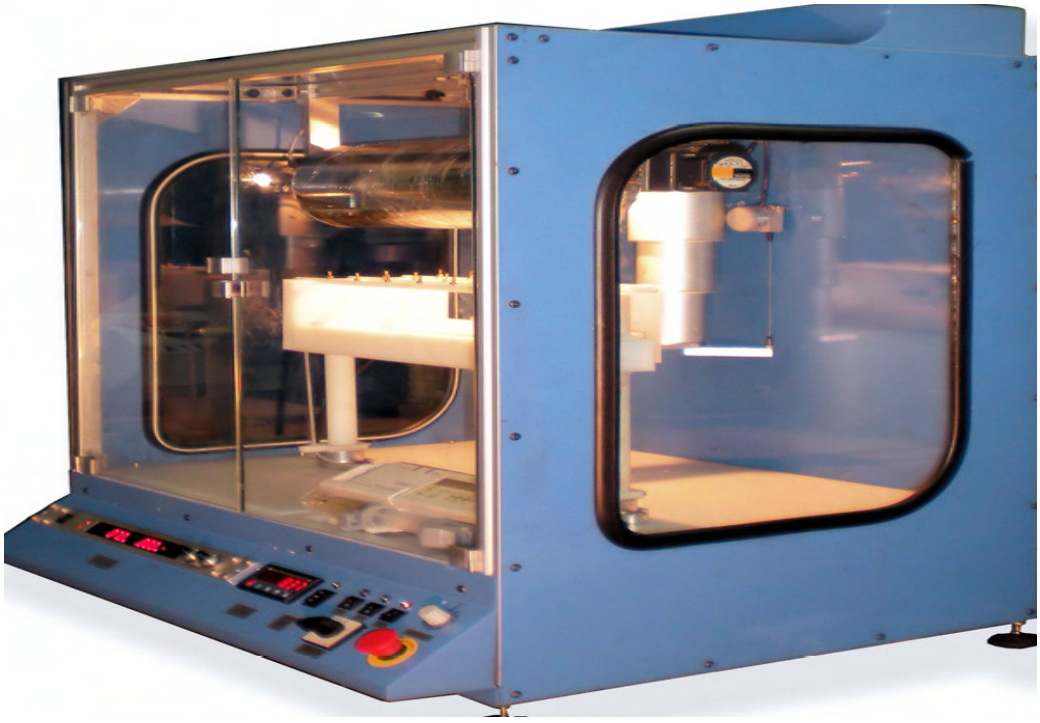
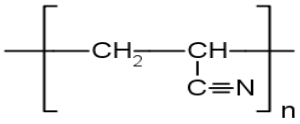
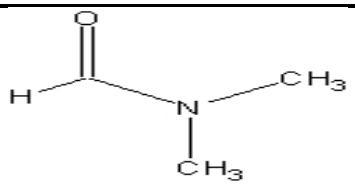
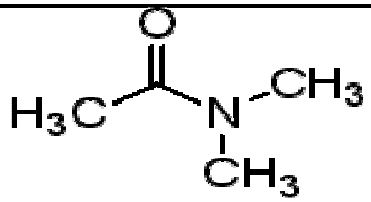
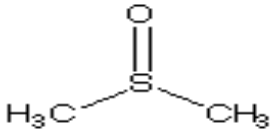


Figure 3.1 Electrospinning setup used

Materials, their chemical formulae and solvent properties are presented in Table 3.1.

Table 3.1 Materials used in experiments

Name of the compound	Formula	Boiling point (^{0}C)	Dielectric Constant	Viscosity at 25 ^{0}C (cP)
Polyacrylonitrile				
N,N-Dimethylformamide		153	38,3	0,92
N,N-Dimethylacetamide		165	37,8	1,956
Dimethylsulfoxide		189	47,2	1,996

3.2. Method

3.2.1. Preparation of PAN solutions

AKSA polymer is dried in the oven at 60 ^{0}C for 4 hours. All solutions are prepared by slowly adding polymer into the solvent while the mixture is mixed. After the entire polymer is added and a homogenous mixture is obtained, the closed container is kept in oven at 70 ^{0}C for 6 hours to obtain a clear homogenous solution. A total of 24 solutions were prepared for the same polymer but with three different solvents and eight different concentrations. Table 3.2 shows the prepared solutions.

Table 3.2 Prepared solutions and concentrations

	SOLVENT		
	DMF	DMAc	DMSO
CONCENTRATION %(v/w)	5		
	7,5		
	10		
	12,5		
	15		
	17,5		
	20		
	22,5		

Each solution is electrospun with a single needle onto an aluminum sheet for 10 minutes. The electrospinning distance, voltage and flow rate of the polymer solution were kept constant for all 24 solutions to truly investigate the effect of solvent and concentration on the nanofiber diameter. The constant values can be seen on Table 3.3.

Table 3.3 Constant operational parameters on electrospinning process

Distance (cm)	20
Voltage (kV)	20
Flow rate (mL/h)	3

Electrospun nanofiber webs were dried in the oven at 60 ^{0}C for 24 hours to evaporate the excess solvent.

3.3. Experimental Measurements

3.3.1. Measurement of solution viscosity

Bulk viscosities of the prepared solutions were measured by using Brookfield DVII type viscosimeter using a spindle # 64. Temperature was kept constant at 25 ^{0}C .

The measurements were performed with rotational speeds of 100, 50, 20, 10 and 5 rpm.

3.3.2. SEM (Scanning Electron Microscope) measurements

The most important type of measurements carried out in this work is SEM measurements. To characterize the nanofibers, their sizes and the structure of the nanofiber web, SEM pictures were mainly used. LEO supra VP-35 FE-SEM at Sabanci University was used with on operation voltage of 2.0 kV and 8 mm working distance. Secondary electron signals were collected.

3.3.3. Measurement of electrical conductivity

Electrical conductivities of the solutions were measured using a handheld conductometer, Hanna Instruments, Model HI 8633. To prevent film formation, the probe was washed with solvent each time between the measurements.

3.3.4. Measurement of surface tension

The surface tension of the solutions was measured by a digital tensiometer. Platinium ring method is used to measure the surface tension of each solution. The ring was immersed into the solutions and the force needed to pull the ring out of the solution surface was measured. The measurements were made at a constant temperature of 25 ^{0}C.

3.3.5. AFM measurements

An AFM (VEECO, Nanoscope 5A) was used to investigate the nanofibers formed. AFM measurements showed the same results with SEM measurements.

3.3.6. Thermal measurements

A DSC-TGA module (METTLER, STARE) is used to investigate the thermal properties of the nanofibers formed and to compare if any changes had occurred.

DSC measurements were performed with a heating ramp of 10 ^{0}C/min from 25 ^{0}C to 400 ^{0}C. Pre heating-cooling were performed to get rid of any water or solvent vapor within the cells.

4. RESULTS AND DISCUSSION

4.1. Solution Viscosity

It is well known that solution viscosity has an important effect on the electrospinning process. The amount of the polymer dissolved in the solution changes the solution viscosity. Viscosity may be increased or decreased by adding various additives but they are not a part of this work. A rotatory viscometer is used to measure the viscosities of the solutions. The effect of viscosities on fiber diameters and bead formation tendencies can clearly be seen on Table 4.1.

Table 4.1 Viscosities of the prepared solutions and corresponding fiber diameters.

	CONCENTRATION %(v/w)	VISCOSITY AT 25°C (cP)	AVARAGE FIBER DIAMETER (nm)	STANDART DEVIATION OF FIBER DIAMETER	BEAD FORMATION
DMF	5	36	30	3,2	*
	7,5	84	76	8,6	*
	10	336	101	7,3	
	12,5	870	221	17,4	
	15	2148	293	82,3	
	17,5	4908	573	88,7	
	20	12450	1537	156,7	
	22,5	28860	6300	207,6	
DMAC	5	30	72	4,6	*
	7,5	168	113	9,6	
	10	492	220	19,3	
	12,5	1296	301	23,5	
	15	3444	400	98,2	
	17,5	8064	600	134,7	
	20	18990	1770	200,3	
	22,5	54780	5900	254,9	
DMSO	5	96	127	13,5	*
	7,5	396	254	22,4	
	10	1170	308	98,7	
	12,5	3414	520	102,8	
	15	8208	874	187,6	
	17,5	20190	1200	200,5	
	20	44520	2582	245,6	
	22,5	95520	6200	457,5	

Table 4.2. shows the diameters of three different nanofibers obtained when three different solvents were used at a concentrations of 5 %, 10% and 15% (w/v) respectively. One can clearly see that, at same concentrations, the lowest diameter fibers were obtained when DMF was used as solvent.

Table 4.2 Diameters of the nanofibers obtained at 5%, 10% and 15%(w/v) solution concentrations respectively

	Diameter (nm)
DMF	30
DMAc	72
DMSO	127

	Diameter (nm)
DMF	101
DMAc	220
DMSO	308

	Diameter (nm)
DMF	293
DMAc	400
DMSO	874

For all solutions, nanofiber diameters increase as the viscosity and concentration of the solution increases. This can be explained with the amount of carried polymer by the jet increases as concentration increases. Since the electrospinning distance and electric voltage are kept constant in this work for all solutions, this is an expected result. One can clearly see that the smaller fiber diameters were achieved using DMF as the solvent. The reason is that DMF is a better solvent for PAN for electrospinning process. The viscosities of DMF solutions are lower than the other solvents and the increase in viscosity according to the concentration is very low for DMF as compared to the other two solvents. The viscosity of DMSO solution dramatically increases as the concentration increases, and this increase results as increasing fiber diameter, the biggest diameters were observed for solutions which DMSO is used as solvent. When DMSO was used as solvent, the quality and the morphology of the nanofibers were also observed to be poor, this can be explained with the low volatility of DMSO compared to the two other solvents which leaded the inadequate evaporating of the solvent during the electrospinning process before the jet reaches the collector plate. This was showed with pictures also in section 4.2. SEM Results.

For all three solvents, the fibers formed at the concentrations bigger than 15 % (w/v) cannot be categorized as nanofibers due to the definition “of nano”. Also at these concentrations the control of electrospinning precess is very hard and a variety of fibers with different diameters are formed. It can clearly be seen that; to form nanofibers, solution concentrations below 15% should be worked with.

Figure 4.1. shows the SEM picture of fibers obtained with 22.5% DMF solution which has a diameter of 6 microns.

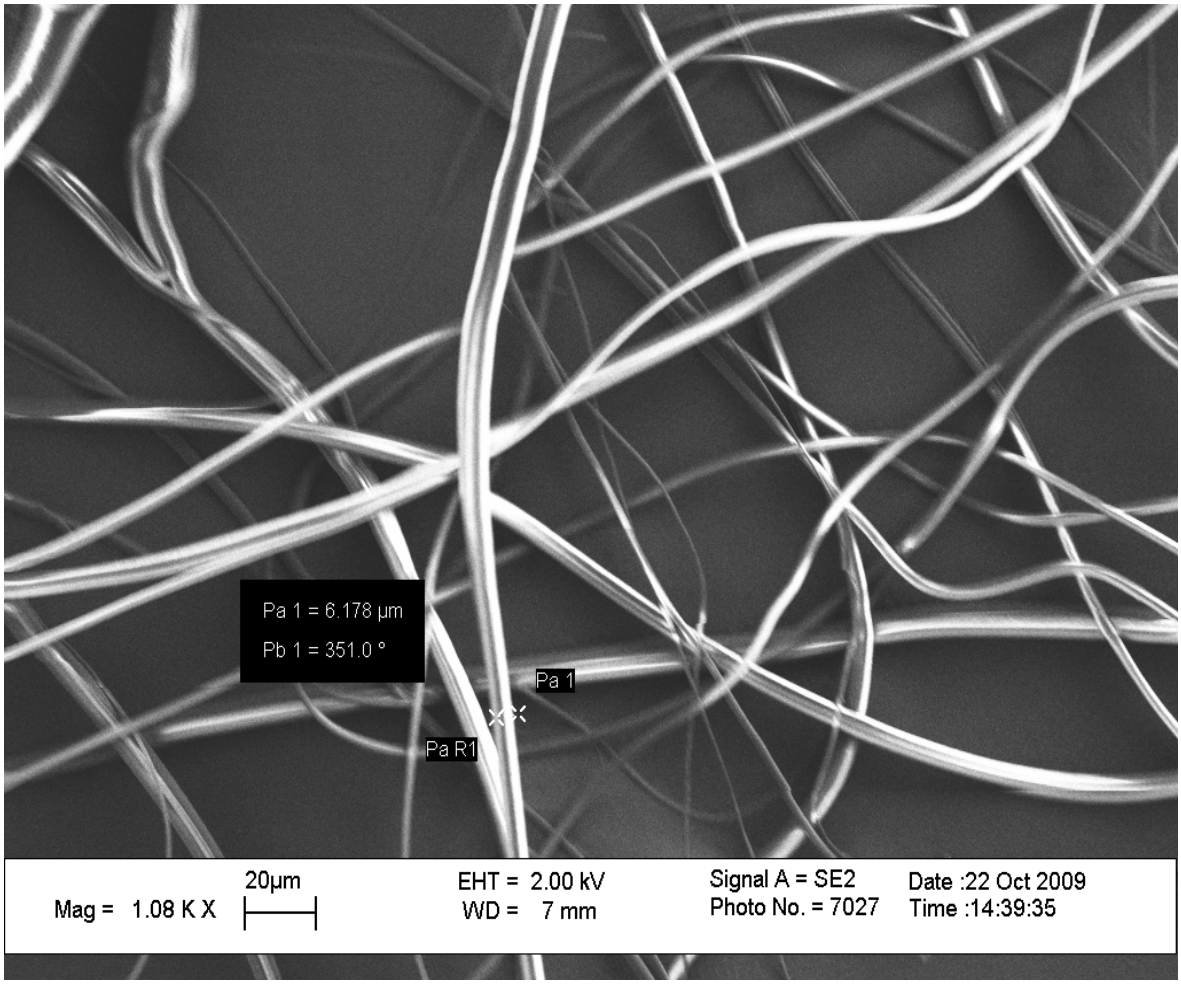


Figure 4.1 SEM picture of fibers obtained with 22.5% DMF solution

At figures 4.2-4.4, relations between viscosity, concentration and nanofiber diameters were shown with graphs for all three set of solutions with different solvents, and at figure 4.5, some selected SEM pictures were represented.

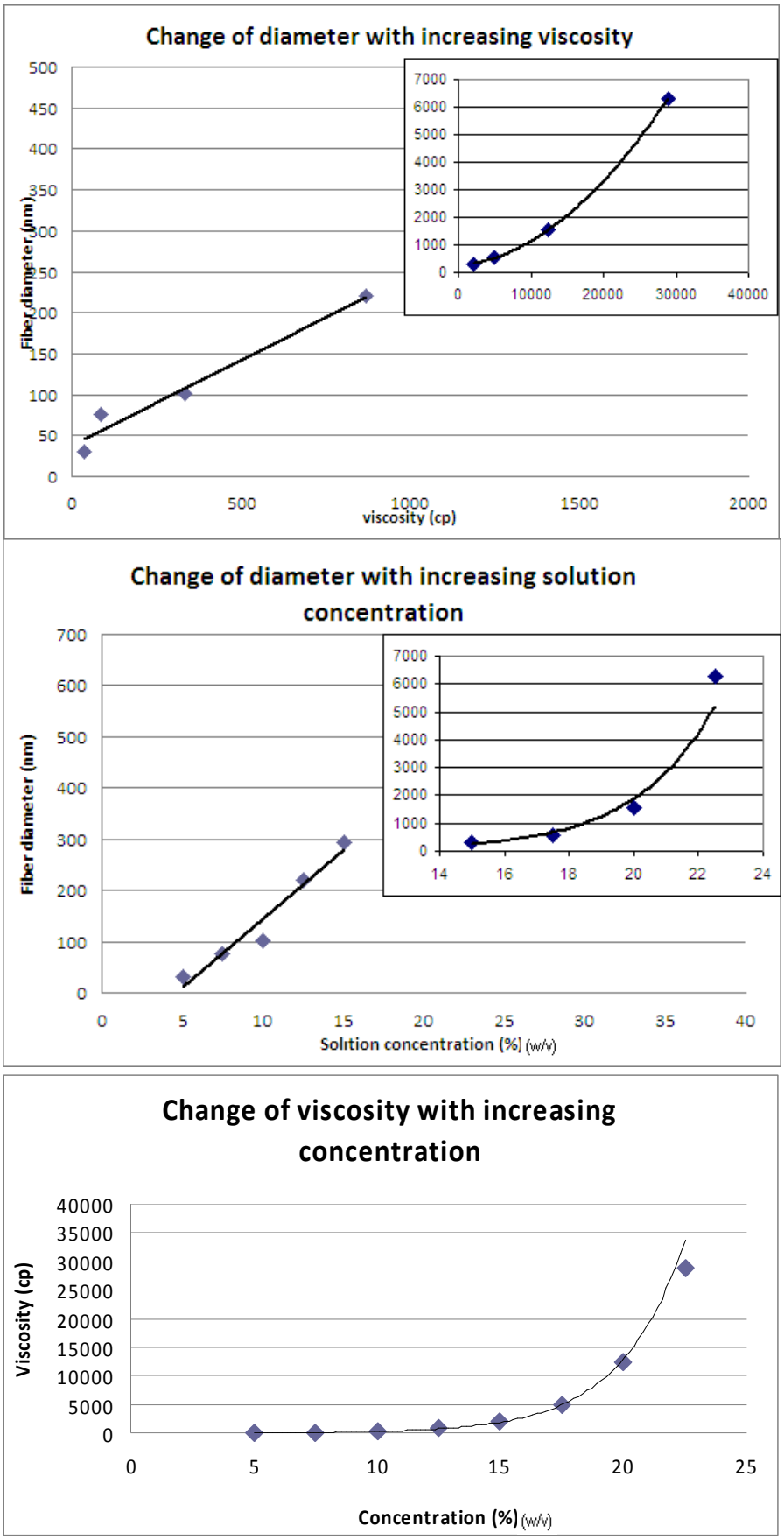


Figure 4.2 Graphs showing relations between viscosity, concentration and nanofiber diameter for DMF solutions

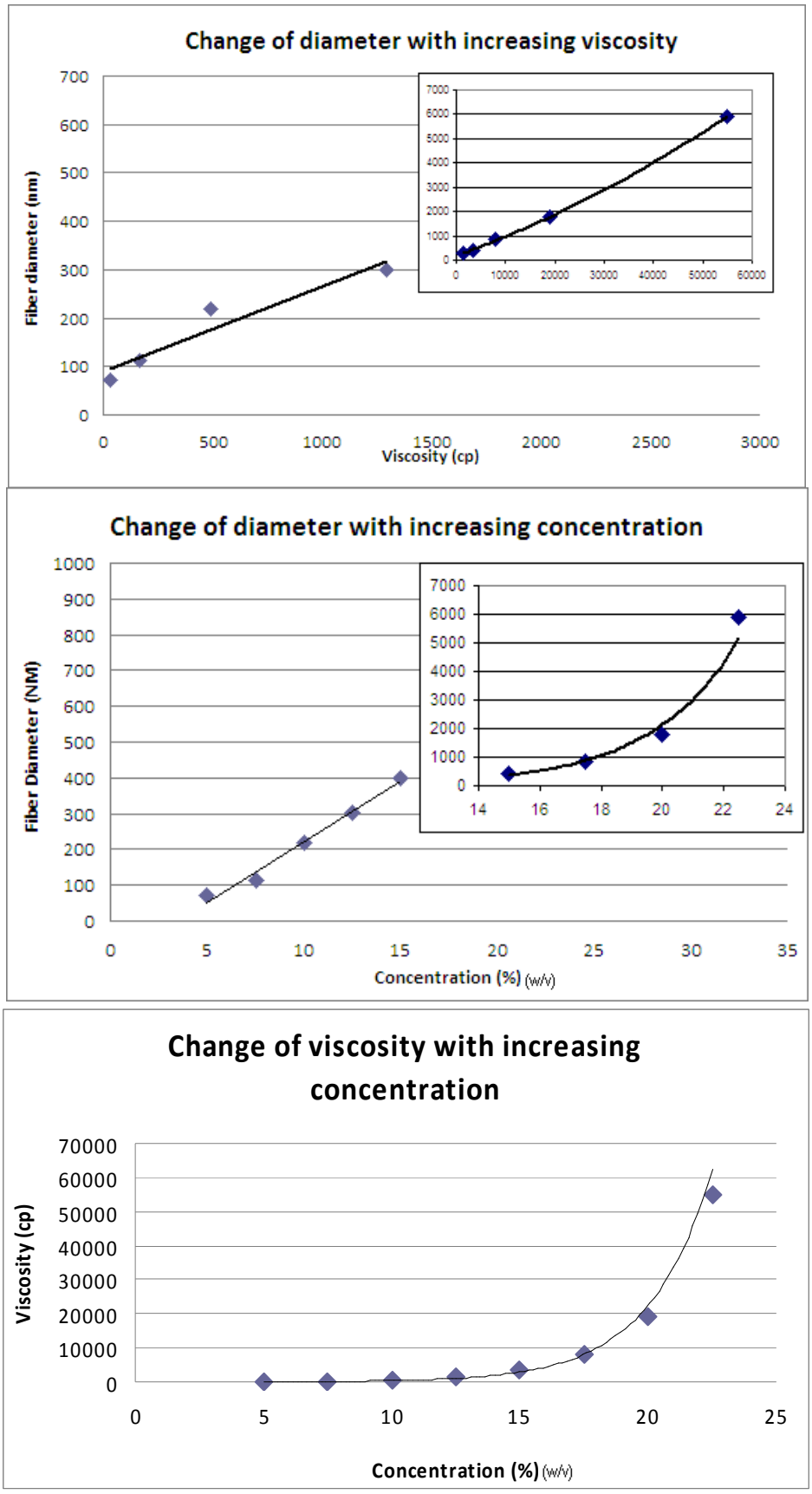


Figure 4.3 Graphs showing relations between viscosity, concentration and nanofiber diameter for DMAc solutions

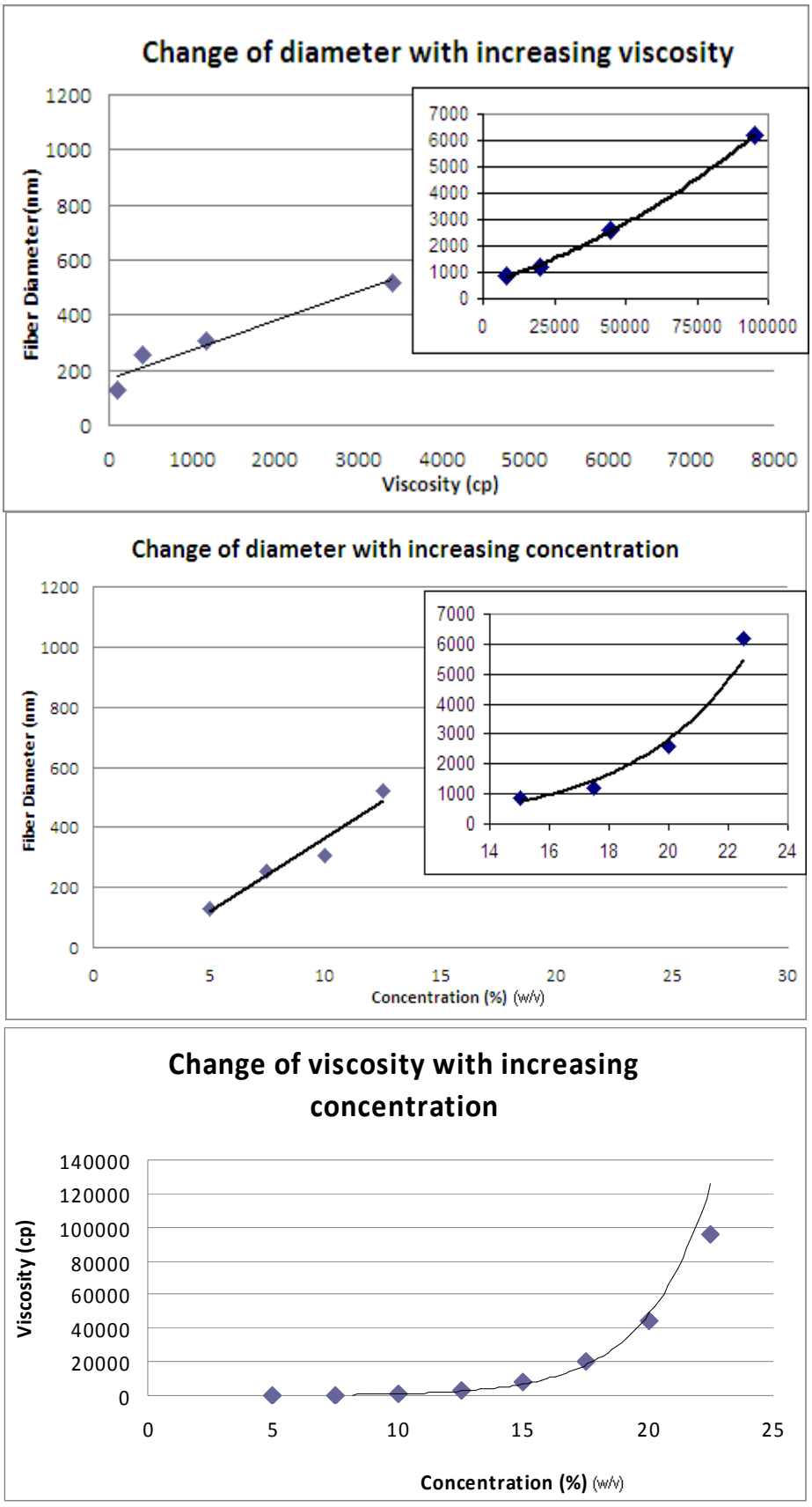
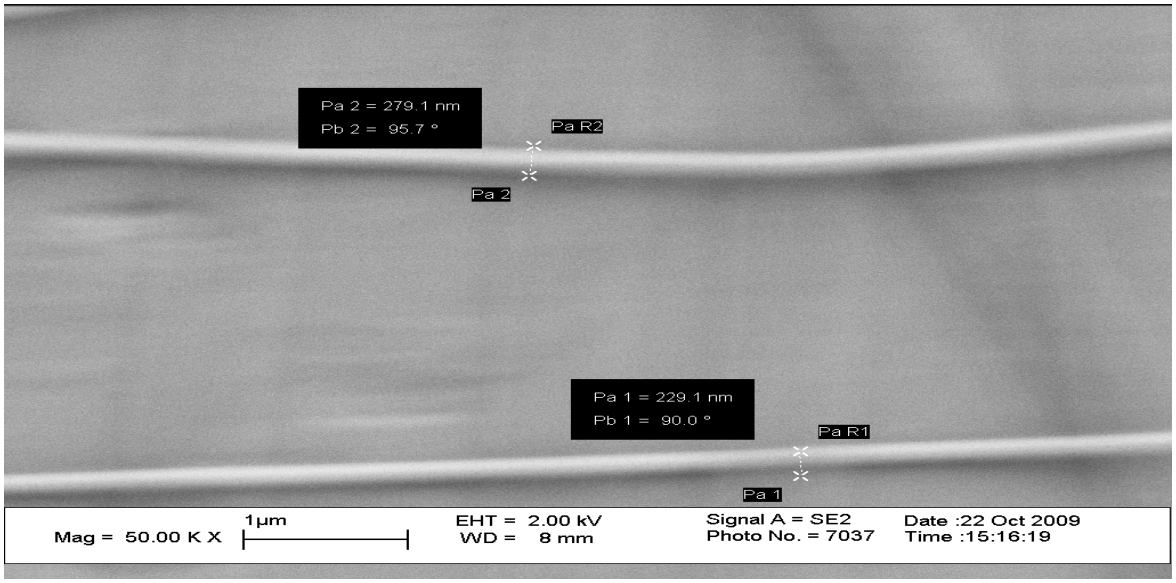
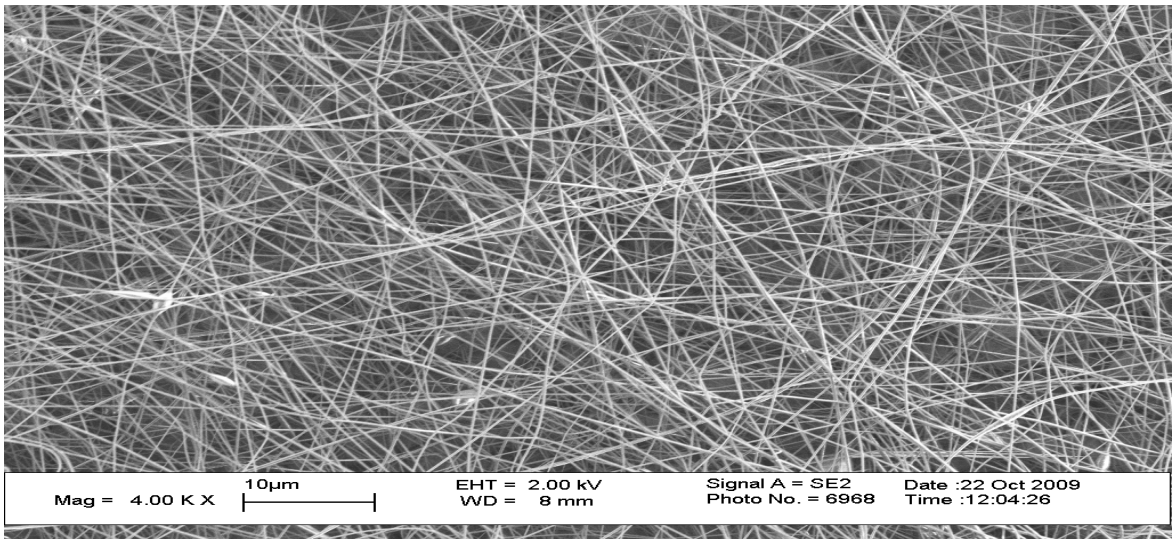


Figure 4.4 Graphs showing relations between viscosity, concentration and nanofiber diameter for DMSO solutions

7.5 % DMSO



10 % DMAc



12,5 % DMF

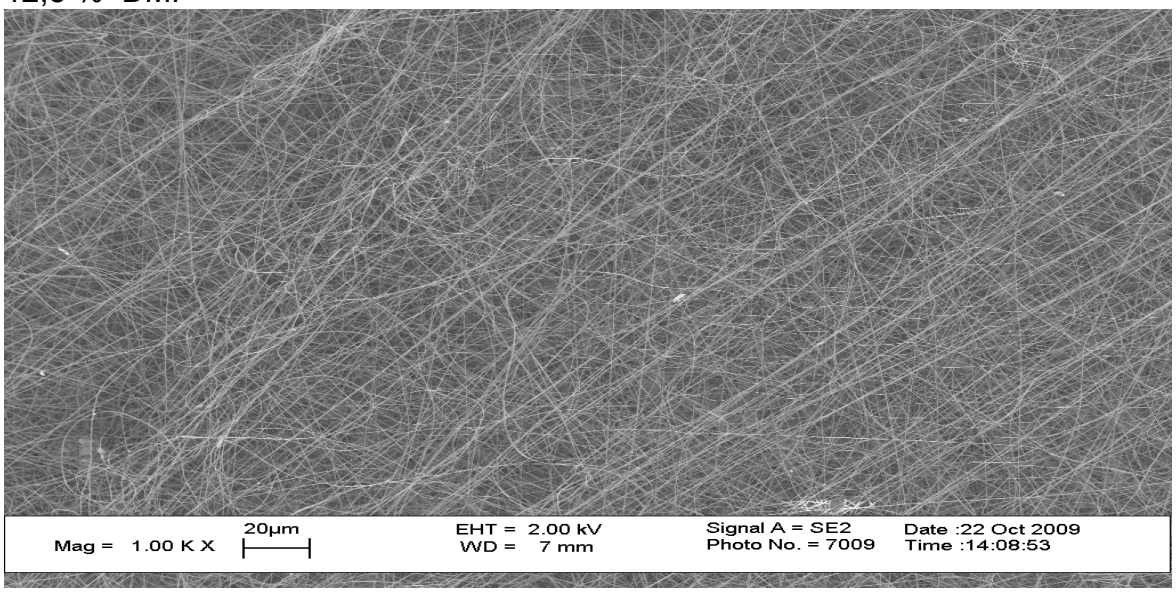


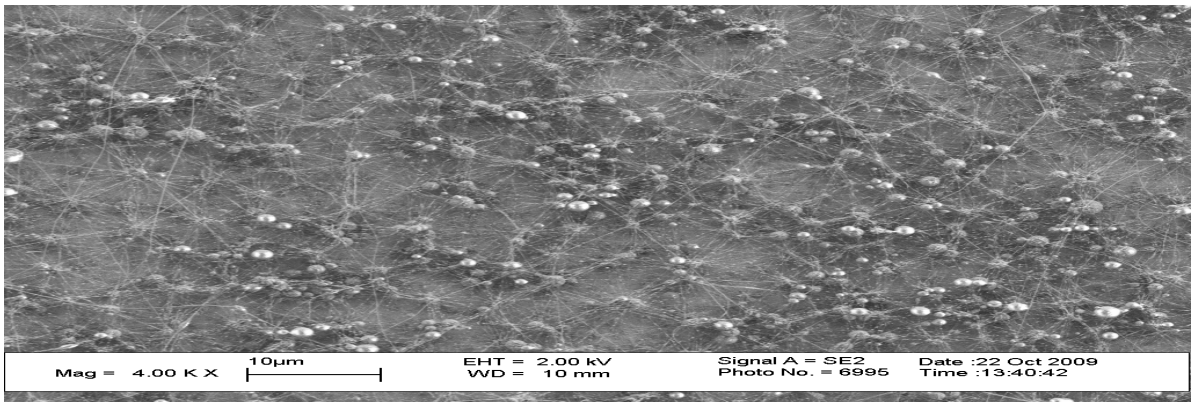
Figure 4.5 Some selected SEM pictures showing nanofibers

4.2. SEM Results

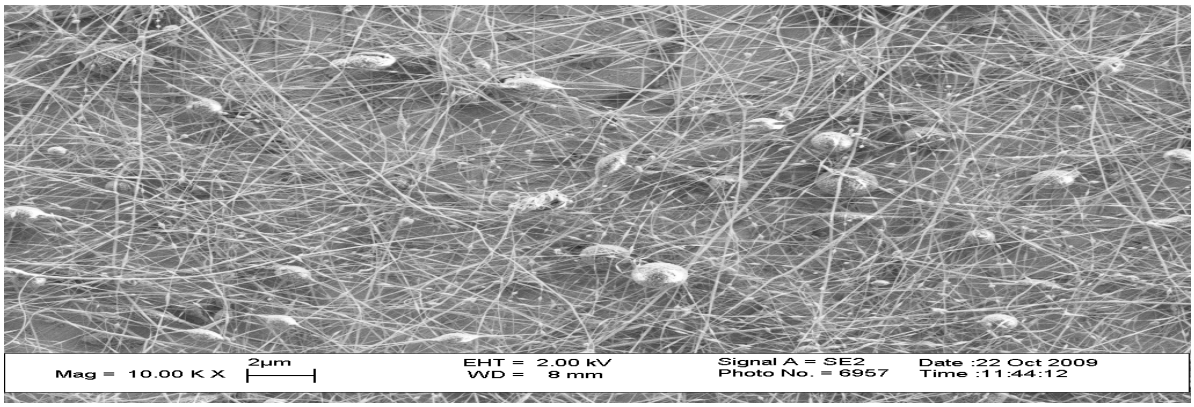
In this section, a variety of SEM pictures will be presented showing nanofibers obtained, using different solvents and different solution concentrations.

Figure 4.6 shows SEM pictures of nanofibers obtained with a solution concentration of 5% (w/v) for all three solvents. Although, the lowest diameter fibers were obtained at this concentration, an increased trend to bead formation can be observed at this concentration.

DMF



DMAc



DMSO

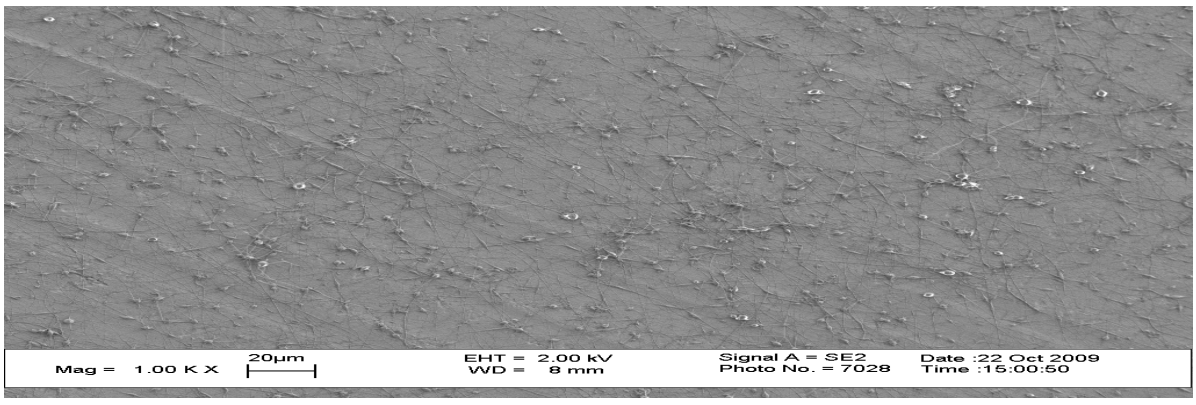
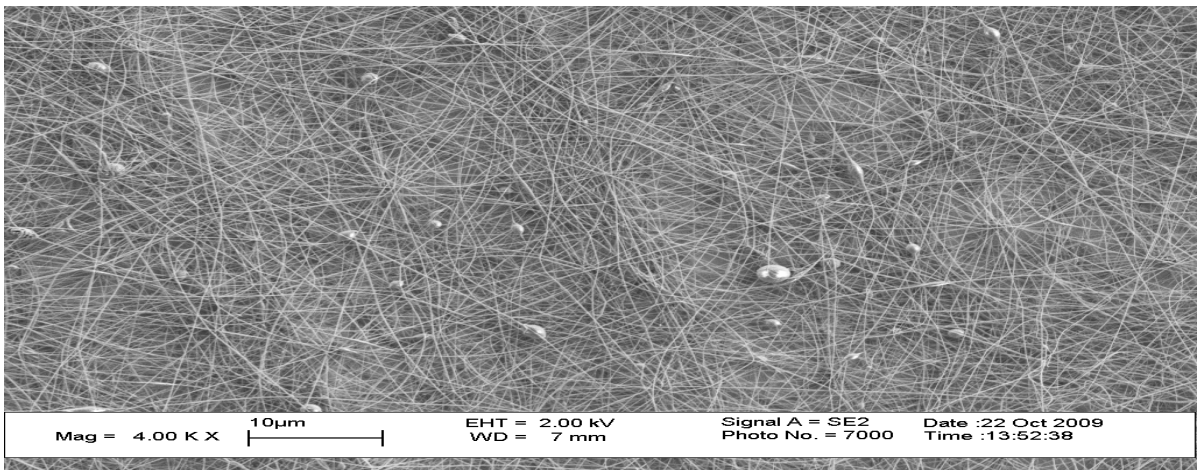


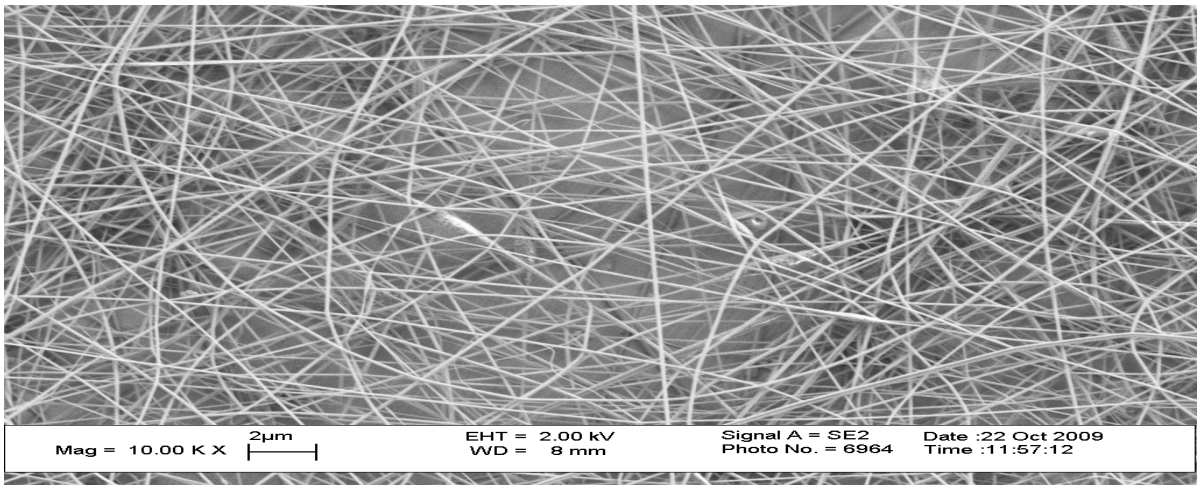
Figure 4.6 SEM pictures for 5% (w/v) solutions

Figure 4.7 shows SEM pictures of nanofibers obtained with a solution concentration of 7.5% (w/v) for all three solvents. At this concentration, the beads had disappeared except for DMF solution, the viscosity of DMF solution at this concentration is still too low so beads were formed.

DMF



DMAc



DMSO

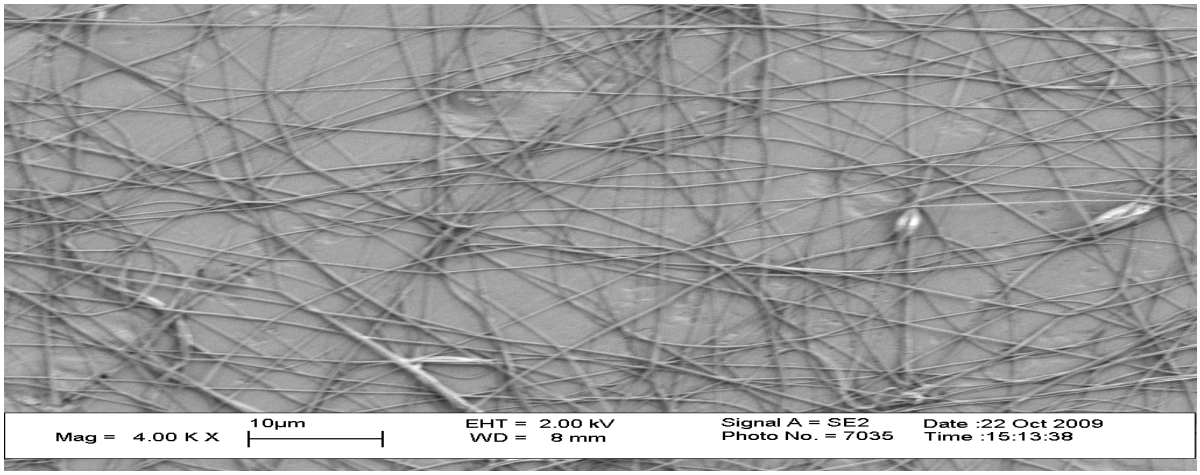
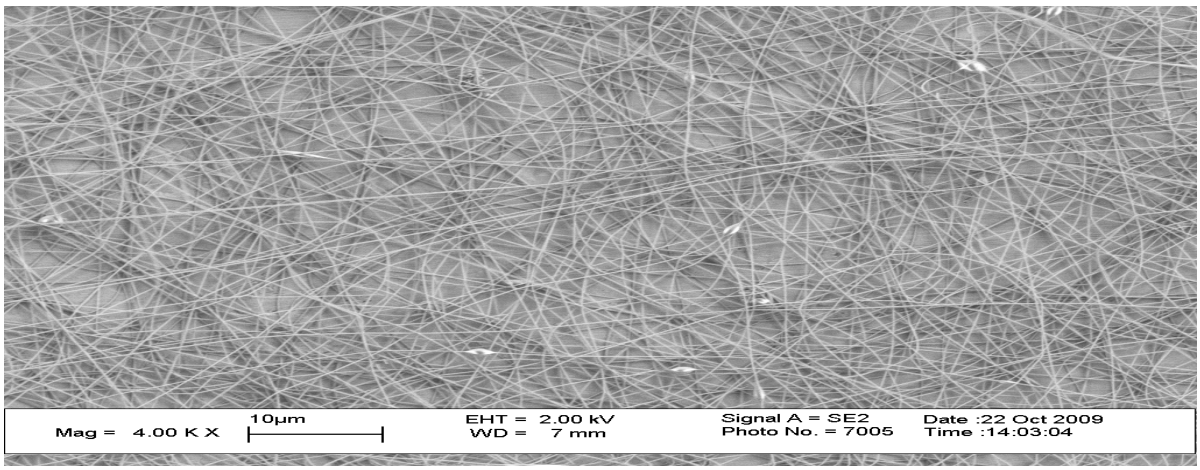


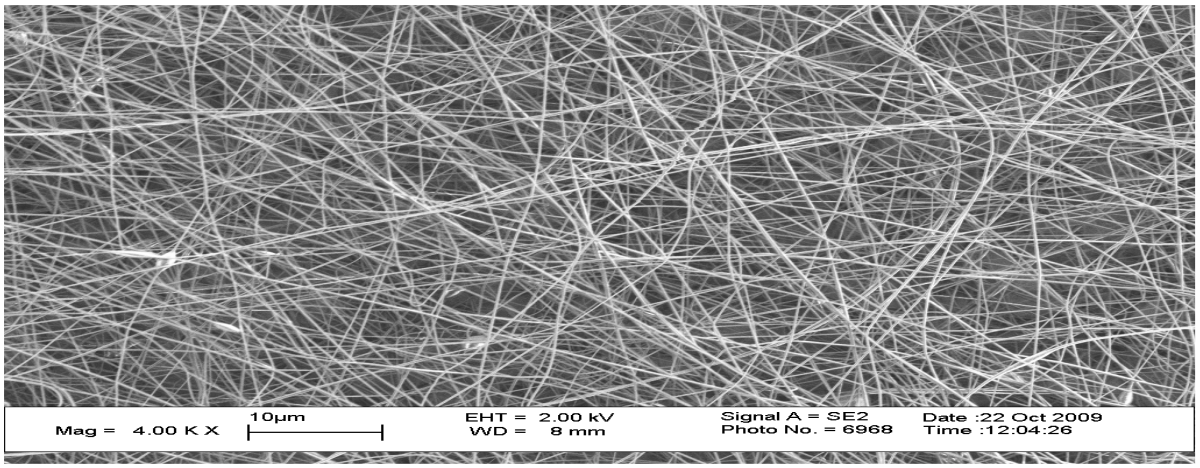
Figure 4.7 SEM pictures for 7.5% (w/v) solutions

Figure 4.8 shows SEM pictures of nanofibers obtained with a solution concentration of 10% (w/v) for all three solvents. The homogeneity of distribution of fiber diameters can clearly be seen at these pictures.

DMF



DMAc



DMSO

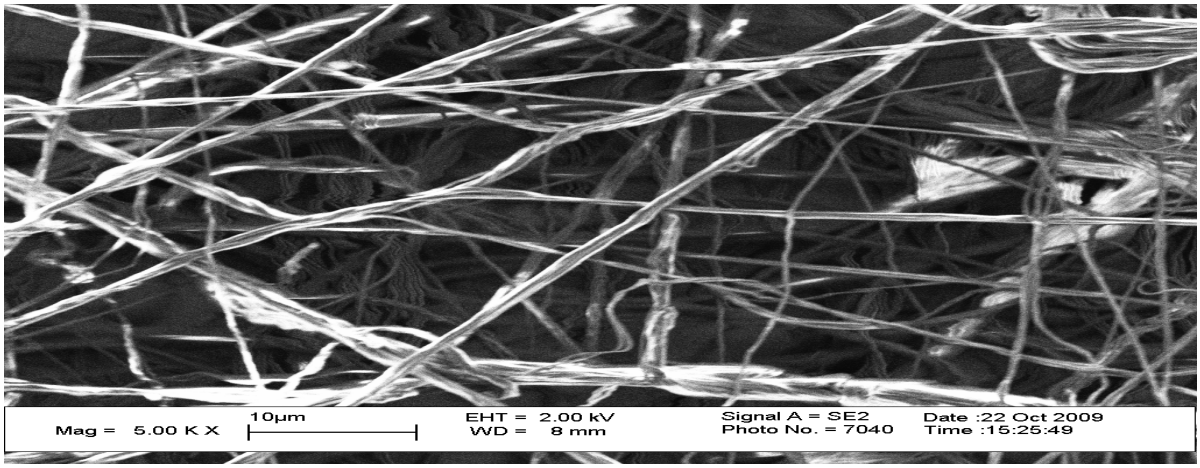
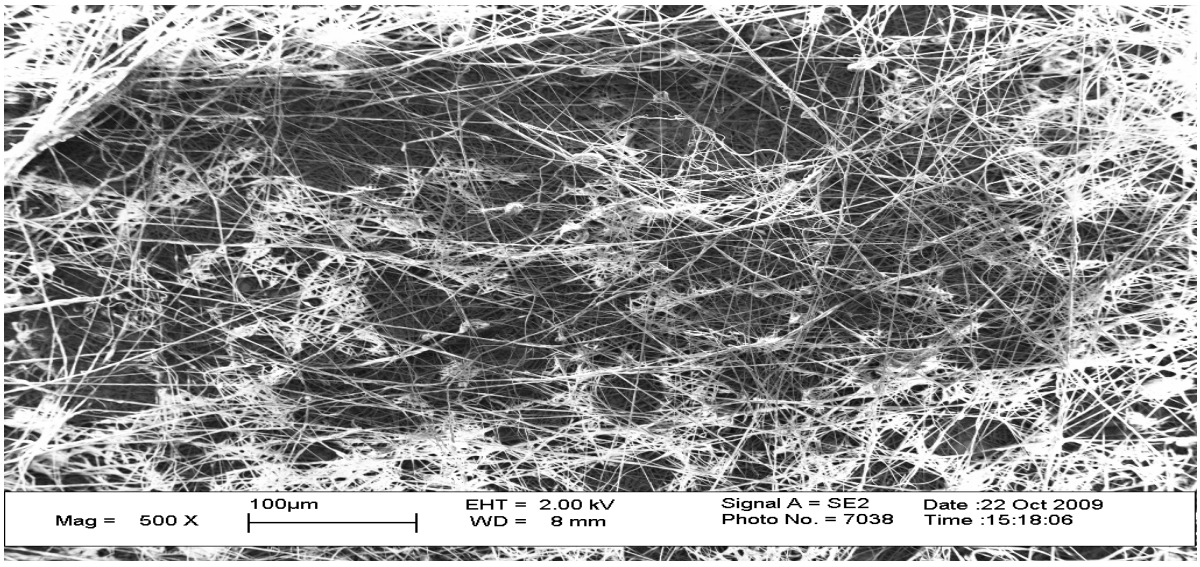


Figure 4.8 SEM pictures for 10% (w/v) solutions

One can clearly see from the pictures that the fibers obtained from the DMSO solutions were observed to be very poor in both quality and morphology. This can be explained with the low volatility of DMSO compared to the two other solvents. The excess solvent cannot evaporate during the jet stage of the electrospinning process. DMSO also reaches the collector with the polymer and dissolves the fibers partially and results a disorder on the shapes of the fibers.

Figure 4.9 shows two SEM pictures of the nanofibers obtained when DMSO is used as solvent. The disorder on the nanofiber web is seen on these pictures.

10% (w/v)



12,5% (w/v)

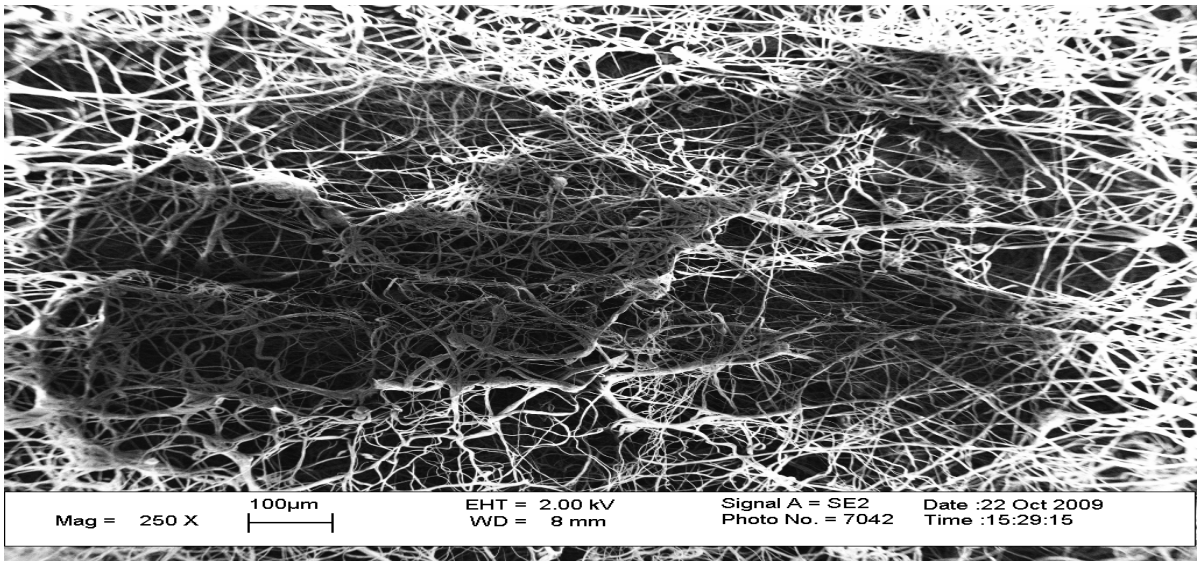
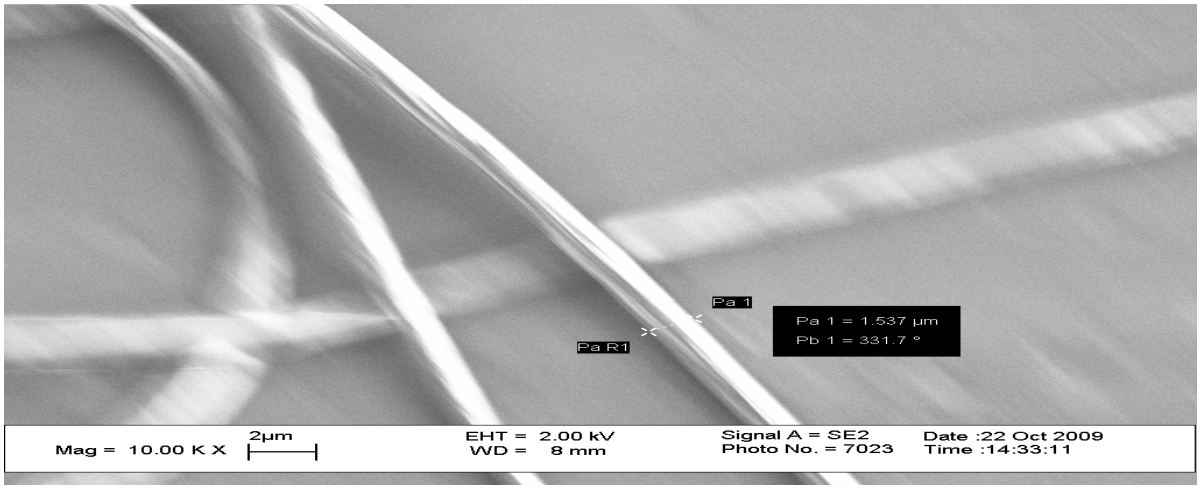


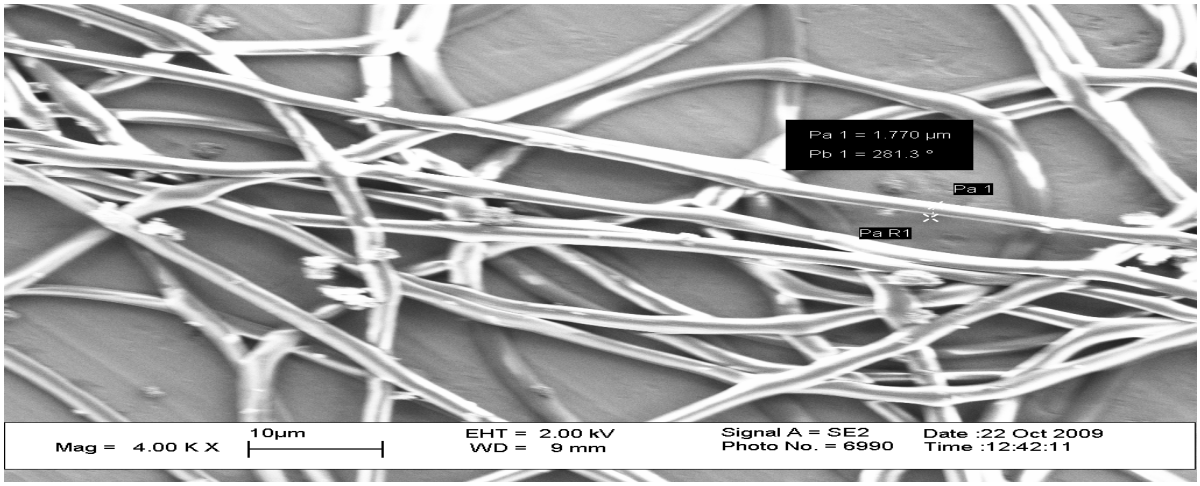
Figure 4.9 Two SEM pictures of the nanofibers obtained, when DMSO is used as solvent, showing the disorder on the nanofiber web

Figure 4.10 shows SEM pictures of fibers obtained with a solution concentration of 20% (w/v) for all three solvents. The fibers formed at these concentrations cannot be defined as nanofibers because of the high diameters.

DMF



DMAc



DMSO

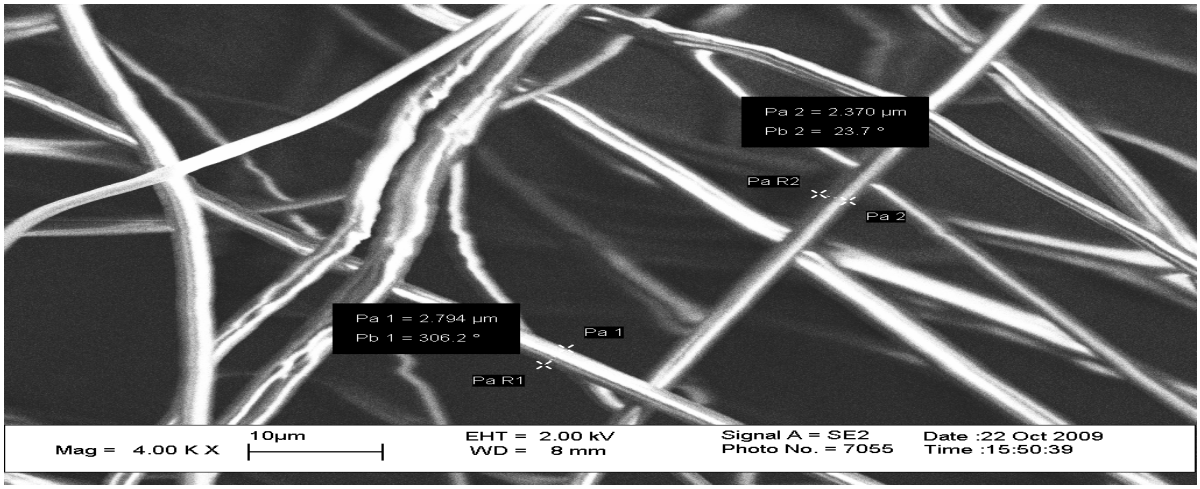


Figure 4.10 SEM pictures for 20% (w/v) solutions

4.3. Bead Formation

Bead structures were found on 5% (w/v) concentrations for all three solvents. The beads have an average diameter around 800 nm. The beads are mostly seen on the nanofibers which DMF was used as solvent in the solution. 7.5%(w/v) concentration solution with DMF as solvent also formed beads, in the two other solvents, the beads were not formed above 5% concentrations. Formation of beads can be explained with lower viscosities. Low viscosities tend to form lower diameters but also favor bead formation. This trend is also related to surface tension as explained before. Whenever the surface tension forces tend to overcome the forces that favor the elongation of a continuous jet, bead formation can easily be observed. Figure 4.11 shows the beads observed at 5% (w/v) solution concentrations for all three solvents.

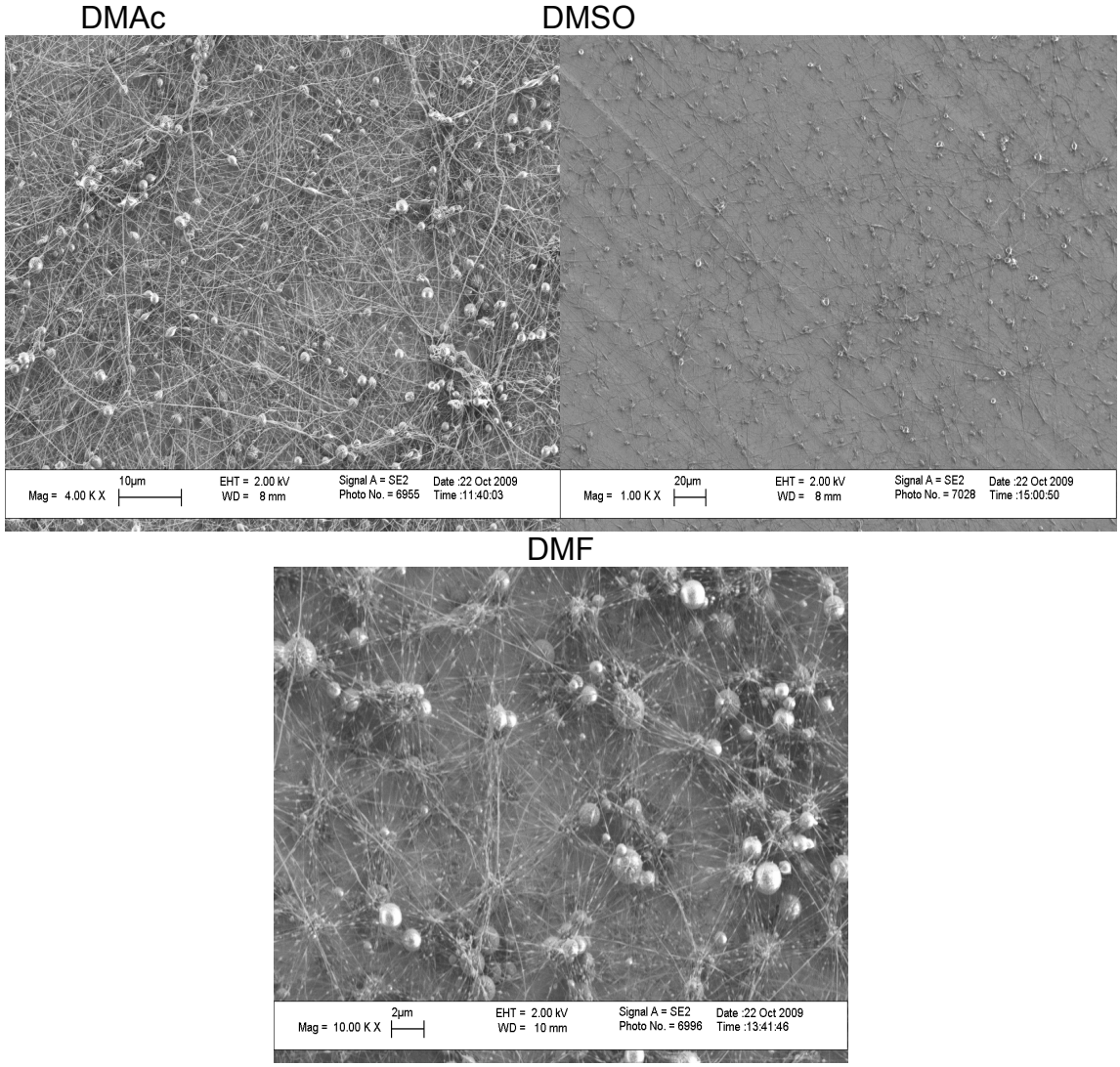


Figure 4.11 SEM pictures showing bead formation on the nanofibers

4.4. AFM Results

To observe the surface morphology of the obtained nanofibers, Atomic Force Microscopy (AFM) pictures were taken. Because of the physical properties of the collected nanofiber webs, some difficulties were faced. Due to these difficulties, only one AFM picture showing the nanofibers obtained with the 10% (w/v) solution using DMAc as solvent was represented which is shown on figure 4.12. The AFM picture taken was in harmony with SEM results concerning nanofiber diameter.

Figure 4.12 AFM picture showing nanofibers obtained with 10% (w/v) solution of DMAc

4.5. Effect of Electrical Conductivity

In this work, no salts or polyelectrolytes were introduced to the solutions thus the electrical conductivities of the additive free solutions were measured. As seen on the results the electrical conductivity of DMF solutions have higher conductivities which promotes the electrospinning process.

Table 4.3 Conductivities of the solutions

	Conductivity (μS/cm)	Standart Deviation
5 % DMSO	63.0	0.75
7.5 % DMSO	47.3	0.32
10 % DMSO	44.4	0.11
12.5 % DMSO	70.3	0.06
15 % DMSO	52.7	0.25
17.5 % DMSO	48.9	0.15
5 % DMF	67.2	0.29
7.5 % DMF	77.4	0.40
10 % DMF	85.1	0.56
12.5 % DMF	90.9	0.12
5 % DMAc	36.1	0.12
7.5 % DMAc	45.9	0.06
10 % DMAc	48.3	0.75
12.5 % DMAc	47.4	0.01
15 % DMAc	57.9	0.15

4.6. Effect of Surface Tension

Surface tension is an important parameter for electrospinning. The electrical force should break the surface tension of the solution to start a jet. The electrical force has been kept constant in this work for all solutions above a threshold value which at least a jet is initiated. Thus under the same electrical force for all solutions which can start a jet, the effect of surface tension occurs in the jet distance and diameter. The less the surface tension is, the bigger the jet diameter occurs and this tends to form nanofibers with smaller diameters. The linear increase in the first

four concentrations was also observed for surface tension of the solutions. The surface tension of the solutions can be seen in Table 4.3.

Table 4.4 Surface tensions of the solutions

Solution concentration (%)	Surface Tension (mN/m)		
	DMF	DMSO	DMAc
0	42	49	42
5	42	49	42
7, 5	42,5	50	42
10	43	51	42
12,5	43,5	51	42
15	45	52	42,5
17,5	50	53	45
20	52	57	48
22,5	62	59	62,5

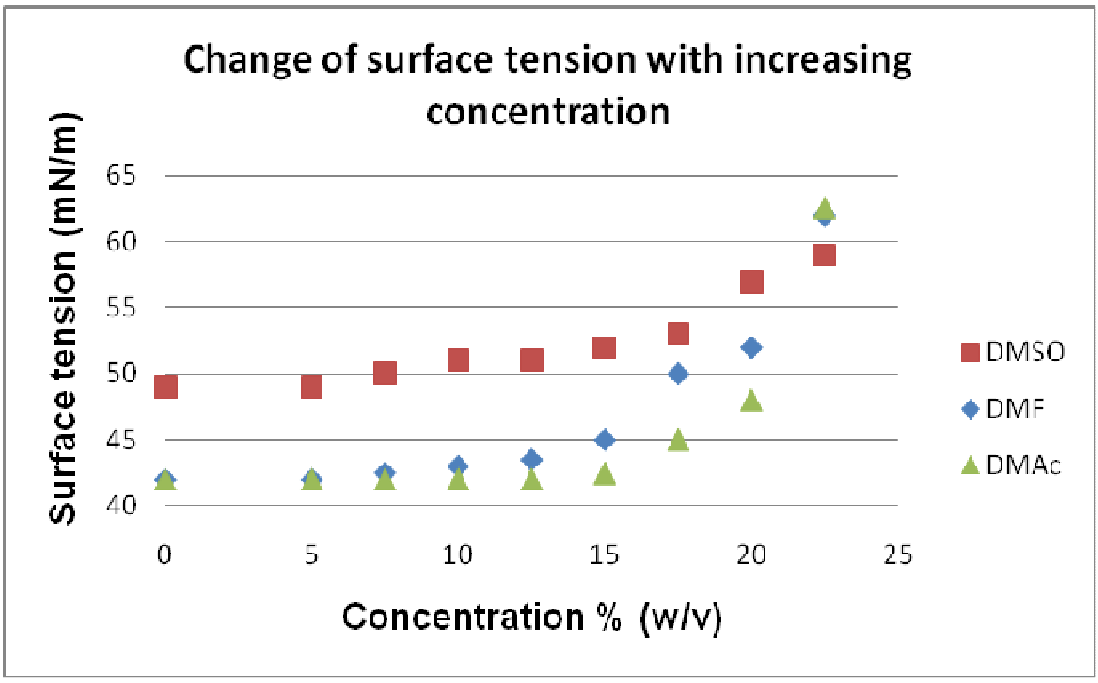


Figure 4.13 Graph showing the increase in the surface tension with increasing solution concentration

4.7. DSC Measurements

DSC measurement was performed to investigate the changes in the thermal properties of the nanofibers. Glass transition temperature and the peak of the cyclization exotherm were investigated on the DSC thermogram. Both of the above mentioned properties showed a 10 ^{0}C decrease, the Tg of the polymer which is 111 ^{0}C decreased to 100 ^{0}C and the peak point of the exotherm decreased from 325 to 315 ^{0}C. This shows the increase in the surface energy due to the enormous increase in the surface of nanofibers for a given mass. This trend can also be seen on the width of the exotherm.

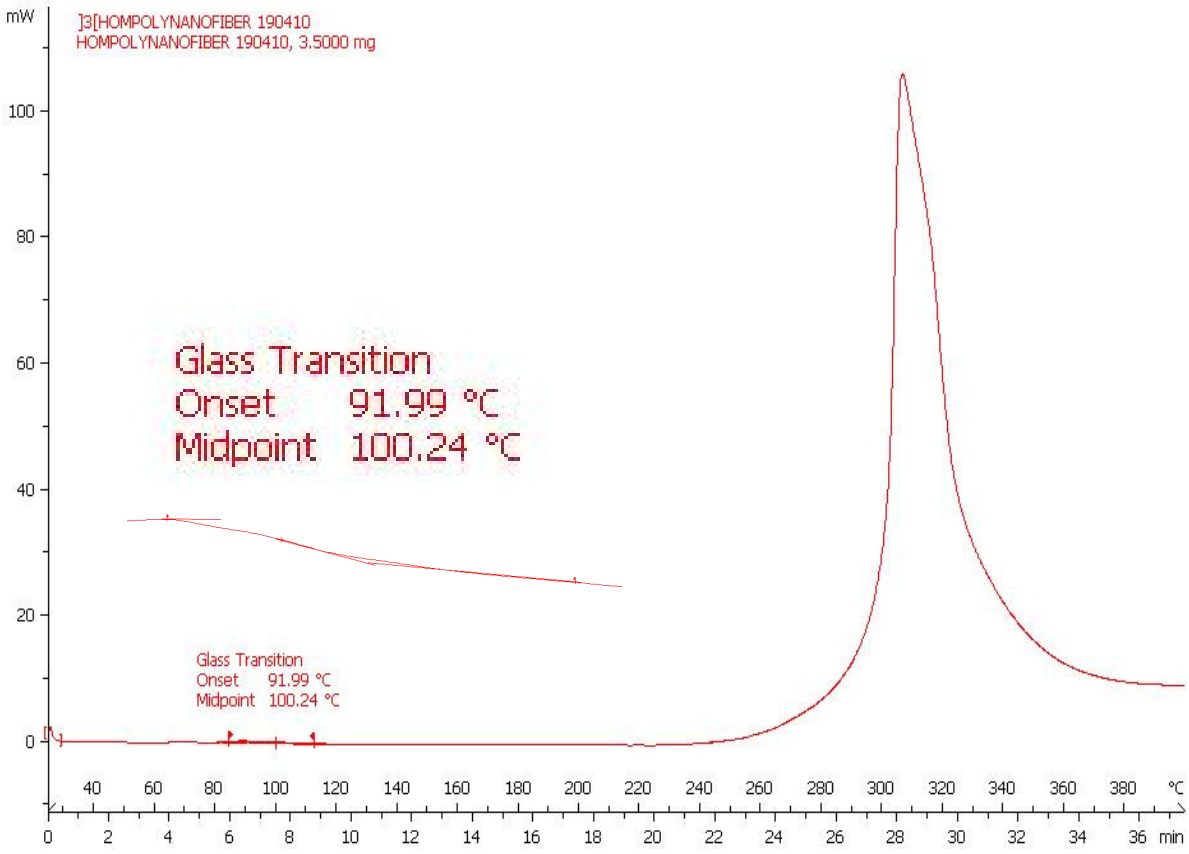


Figure 4.14 DSC thermogram for PAN nanofiber

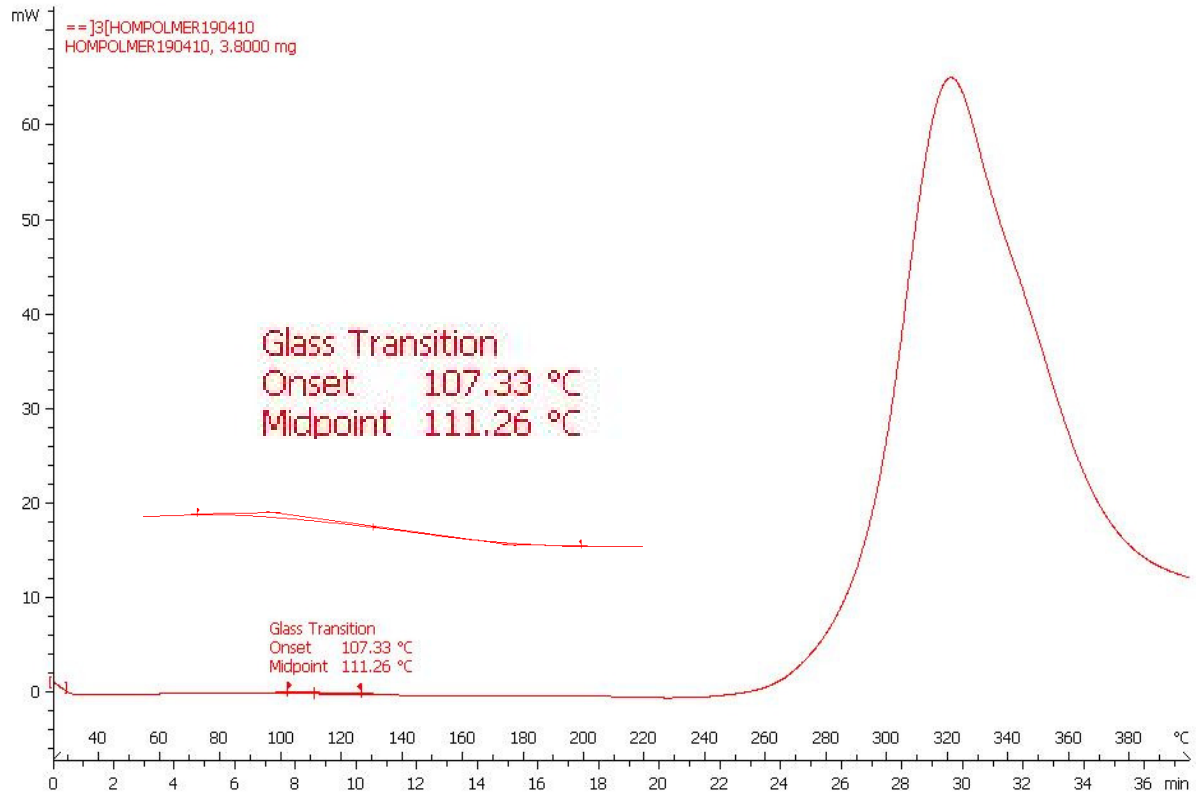


Figure 4.15 DSC thermogram for bulk PAN Polymer

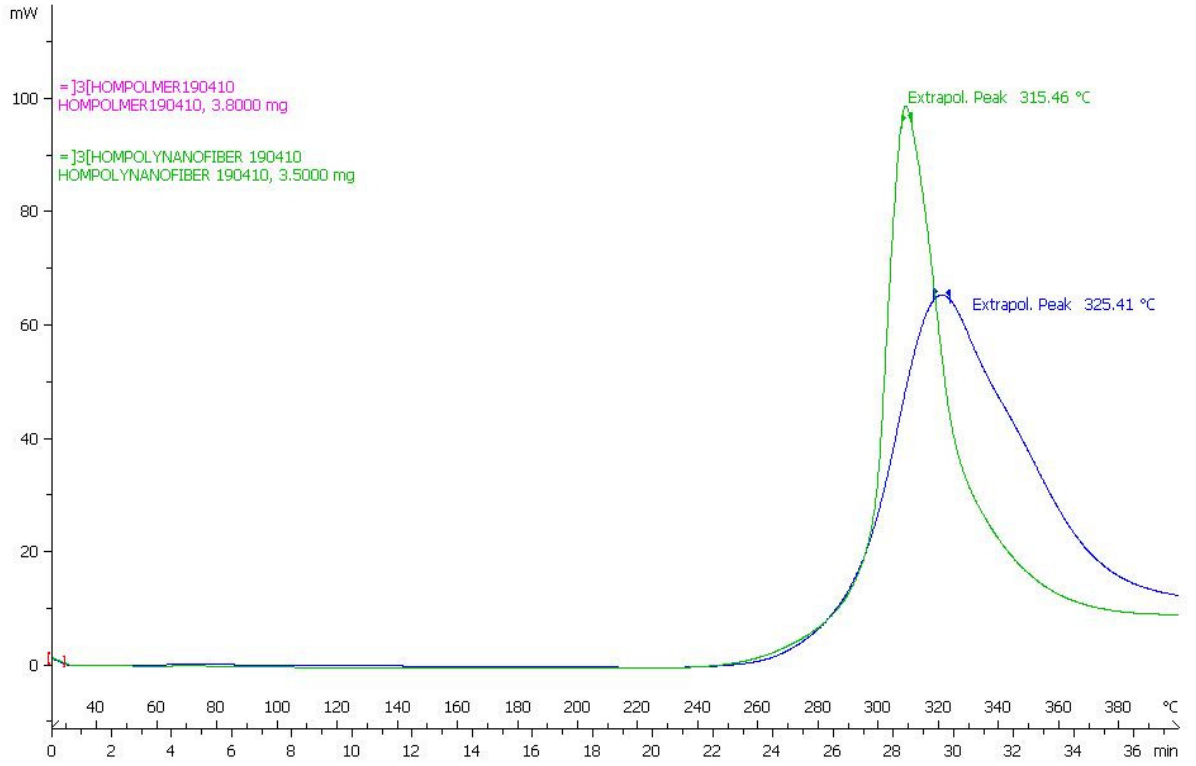


Figure 4.16 DSC thermogram showing the change of peak temperature values for both bulk polymer and nanofiber

5. CONCLUSIONS

In this work, Polyacrylonitrile (PAN) based nanofibers were produced by using electrospinning technique. 24 solutions were prepared with 3 different solvents and 8 concentrations to investigate their effects on nanofiber formation.

Dimethylformamide (DMF), Dimethylacetamide (DMAc) and Dimethylsulphoxide (DMSO) were used as solvents in the solutions. For each solvent, 8 different solutions were prepared having different concentrations from 5% to 22.5 %.

The nanofibers were mainly characterized by using Scanning Electron Microscopy (SEM).The diameters of the nanofibers were investigated with SEM and Atomic Force Microscopy (AFM) Measurements.

Nanofibers with diameters of 50 nm to 900 nm were produced. It has been observed that an increase in the diameters was observed with increasing solution concentrations as well as solution viscosities.

Bead formation was observed in 5% (w/v) concentrations of solutions for all solvents. This is also the concentration where the smallest diameters of nanofibers were observed. Beads occur as a result of the instability of jets as the jet diameter and the amount of polymer carried within the jet decreases.

Surface tension measurements showed that at low surface tension values, nanofibers with smaller diameters were formed. The increase of surface tension with increasing concentration is in harmony with the increase of nanofiber diameter with increasing concentration. The effect of surface tension on bead formation was also observed.

Solution conductivities were measured. As no additives which may change the conductivity of the solutions were added, the conductivities of the additive free solutions showed that the DMF solutions which had higher conductivity compared to the other two solvents had a positive effect on the electrospinning process.

DMF is found to be the best solvent for electrospinning of PAN among the solvents tested. The most homogeneous and well distributed nanofiber webs were formed with solutions which DMF was used as solvent. Also, regarding the nanofiber

diameters, the smallest diameters were observed with DMF solutions. This trend can be explained as better solutions form with DMF at lower concentrations. Also the deposition of DMF during the jet is easier because of the high volatility compared to the other two solvents. DMSO solutions showed the worst properties regarding both diameters and uniformity

DSC Measurements were performed to investigate the thermal properties of the nanofibers. A decrease of 10 ^{0}C was observed for both the glass transition temperature and the peak of the exotherm. This is explained with the increase in the surface area of the polymer in nanofiber form.

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