SEPTEMBER 2019

M.Sc. Thesis in Textile Engineering

ŞİRİN CEYLAN

REPUBLIC OF TURKEY

GAZİANTEP UNIVERSITY

GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

PRODUCTION OF ALIGNED NANOFIBERS USING PARALLEL ELECTRODE COLLECTORS IN ELECTROSPINNING METHOD

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IN

TEXTILE ENGINEERING

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Supervisor

Prof. Dr. Mehmet TOPALBEKİROĞLU

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

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Şirin CEYLAN

ABSTRACT

PRODUCTION OF ALIGNED NANOFIBERS USING PARALLEL ELECTRODE COLLECTORS IN ELECTROSPINNING METHOD

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M.Sc. in Textile Engineering
Supervisor: Prof. Dr. Mehmet TOPALBEKİROĞLU
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Nanofibers that produce with the electrospinning method are conventionally collected in randomly arranged nonwoven format. In this study, it is emphasized to collect the aligned nanofibers as parallel to each other by using parallel electrode collectors. In this context, the effect of the width of collectors, gap distance, TCD and charge density parameters on the orientation of the nanofibers and their average diameter was studied for the PAN and PVA polymers. All nanofiber samples were imaged by scanning electron microscopy. The nanofiber array angles and average diameters are determined and the results were interpreted visually and statically. Optimal plate widths for alignment were observed as 15 mm and 20 mm for PAN and PVA. Optimal gap distances were observed 1 cm and 2 cm for PAN and 3 cm and 4 cm for PVA. It was resulted that these two parameters had no significant effect on the average nanofiber diameter. In addition, as the charge density and TCD increase, the alignment for both polymers is getting worse. 1 kV charge density and 9 cm TCD values are the best alignment values for both polymers.

Key Words: Electrospinning, Nanofiber Alignment, PAN, Parallel Electrodes, Process Parameters, PVA

ÖZET

ELEKTROÇEKİM YÖNTEMİNDE, PARALEL ELEKTROD TOPLAYICILAR KULLANARAK HİZALANMIŞ NANOLİFLERİN ÜRETİMİ

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Elektro çekim yönteminde üretilen nanolifler konvansiyonel olarak rastgele dizilmiş dokusuz yüzey formatında toplanmaktadır. Bu çalışmada elektro çekim yönteminde paralel elektrot toplayıcılar kullanılarak nanoliflerin birbirlerine paralel olarak hizalanmış olarak toplanması üzerinde durulmuştur. Bu kapsamda, PAN ve PVA polimerleri için toplayıcı elektrot genişliği, toplayıcı elektrotlar arası mesafe, TCD ve uygulanan voltaj parametrelerinin, üretilen nanoliflerin paralelliği ve ayrıca ortalama nanolif çapına etkisi araştırılmıştır. Üretilen tüm numunelerin görüntüleri alan emisyonlu taramalı elektron mikroskobuyla alınmıştır. Paralellik açısından en ideal elektrot genişlikleri PAN ve PVA için 15 mm ve 20 mm olarak tespit edilmiştir. En ideal elektrotlar arası mesafeler ise PAN için 1 cm ve 2 cm, PVA için ise 3 cm ve 4 cm olarak tespit edilmiştir. Bu iki parametrenin ortalama nanolif çapı üzerinde ciddi bir etkisi olmadığı görülmüştür. Ayrıca uygulanan voltaj ve TCD arttıkça, her iki polimer için de paralellik bozulmaktadır. 1 kV uygulanan voltaj ve 9 cm TCD değerleri her iki polimer için de en iyi paralelliğin sağlandığı değerlerdir.

Anahtar Kelimeler: Elektrospinning, Nano Lif Hizalanması, PAN, Paralel Elektrotlar, Proses Parametreleri, PVA

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Finally, I wish to express my love and gratitude to my family, especially to my husband, mother and brother for all their patience and support. Their encouragement caused me to complete my thesis after 9 years as a mother of Asel and Nevzat.

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LIST OF SYMBOLS

µ	Micron
°	Degree

LIST OF ABBREVIATIONS

AC	Alternative Current
CD	Charge Density
DC	Direct Current
DMF	Dimethylformamide
MPEM	Modified Parallel Collector Method
MW	Molecular Weight
PAN	Polyacrylonitrile
PBI	Polybenzidimazole
PCL	Polycaprolactone
PEO	Polyethylene Oxide
PTT	Polytrimethylene Terephthalate
PVA	Polyvinyl Alcohol
PVDF	Polyvinylidene Flouride
TCD	Tip-to-collector Distance
UV	Ultraviolet
WT	Weight

CHAPTER I

INTRODUCTION

1.1 Introduction

Nanofibers are generally considered by the textile industry as the diameter of fibers that shorter than one micron. Nanofibers is describes as fibers that smaller than 100 nanometer (nm) is according to National Science Foundation (NSF). The name originates from the nanometer, which represents a billionth of a meter of science measurement unit, or three to four atoms wide. Owing to their notable technical characteristics like barrier, filtration, agricultural, wipes, medical, composite, personal care, clothing, power storage and insulation, nanofibers have acquired a lot of interest and are settled in every region of our life. They are lightweight with tiny diameters, controllable porous form and an elevated surface-to volume ratio compared to standard fiber structure of nanofibers. Nanofibers have special characteristics that make them advantageous for a wide range of applications from consumer to medical products and industrial that has technological applications for transistors, aerospace, drug delivery systems, condensers, power storage, information technology, battery separators, and fuel cells [1].

Nanofiber production methods include electrospinning, drawing, melting, wet spinning (10 micron - 400 nm), island in the ocean, phase separation, temple synthesis, self-assembly, bi-component extrusion and force spinning [2]. But the method of electrospining is still most popular and widely used in the production of nanofibers due to a versatile and simple process that can produce a wide range of nanofiber diameters from micrometers to nanometers (20 nm - 1 micron), low cost and high strength [3-4].

In a classic electrospinning process, electrostatic forces draw fibers from polymer solution or melt them from a needle. The most frequently gathered electrospun nanofibers are parallel or randomly aligned webs. When a simple static collection surface is used, randomly focused fiber webs lead and multiple techniques have been

used to collect parallel-aligned mats. The most frequently a rotating mandrel is used as a collecting device to collect parallel aligned fiber webs.

Nanofibers can additionally be gathered in a linear direction at a space between two parallel conductive plates. The electrical field generated between two parallel plates allows fibers to align and extend perpendicular to the plates. Because this technique can collect individual nanofibers, it extends the prospective electrospinning applications.

Once these fibers have been obtained, structures appropriate for particular applications can be further processed. It is important to have ideas about the length of polymer fibers as maximum that can be achieved by the parallel collector method when detect the collector structures types that could be investigated [5].

Li et al. fabricated poly (vinal pyrrolidone) nanofibers between a pair of collector that was made from silicone strips have sizes longer than a few centimeters [6]. Ramakrishna and Teo produced PCL nanofibers with lengths of up to 10 cm across two thin steel blades [7].

Equally essential in determining the ultimate diameter of the fibers during the electrospinning method is the gap between the collector and needle. The charge density is applied during the method of electrospinning plays a major part in determining the fibers shape and diameter. During electrospinning, the formation of beaded fibers relies on the charge density along with other parameters like flow rate and solution viscosity.

1.2 Objectives of Thesis

There are many different collector types to produce alignment nanofibers via parallel collector electrospinning method. The producing of electrospun nanofibers between two parallel plates is an advantageous method for fabricating nanofiber structures. It enables to collect aligned nanofiber arrays as linearly and these arrays can be easily transmitted to other surfaces. One of the another reason to make this method favorable is to be versatile, cheap, high strength and simple process that can allow to produce a wide range of nanofiber diameters from micrometers to nanometers range between 20 nm and 1 micron [8].

One of the advantages of high aligned nanofibers is to allow producing high featured nanofiber yarn and provides wider application areas. In addition, alignment feature of nanofibers enable to produce strong yarns and use them at industrial areas.

In this thesis, we aim to produce aligned electrospun nanofibers via parallel electrode collectors and determine the optimum values of gap distance between electrodes, width of the collector plates, tip to collector distance (TCD) and charge density for polyvinyl alcohol (PVA) and polyacrylonitrile (PAN) polymers.

1.3 Nanofiber and Nanotechnology

Nanofibers are defined as constructions with minimum one dimension less than 100 nanometers (nm) according to the National Science Foundation (NSF) and literature associated to fiber science, but they are usually regarded to have a diameter of less than one micron. The name is coming from the word nanometer, a unit of science measurement symbolized one billionth of a meter or wide of three to four atoms [9].

Because of their exceptionally elevated volume-to-surface ratio compared to standard fibers, nanofibers display unique characteristics like low specific mass, low density, and elevated pore volume, making nanofibers useful for a broad spectrum of applications such as filtration and energy storage [10].

Besides combining nanoparticles with standard textiles to improve their characteristics, textiles that are produced completely from nanoscale fibers can now be produced. Researchers have been able to go much further with the use of these nanofibers in the development of fabrics with distinctive and useful characteristics [11].

Nanotechnology can be described as understanding, controlling and manipulating, matter in textiles, so that the chemical, biological, and physical characteristics of the atoms, molecules and also bulk matter can be processed, combined and modified to investigate the new generation of improved materials, constructions, apparatus and systems. Nanotechnology is usage to produce necessary textile properties such as smooth hand, high tensile strength, durability, specific surface structure water repellency, antimicrobial characteristics and fire repellent [12]. Figure 1.1 describes size of nanoscale as three visual examples, shows how small things have nanoscale. Figure 1.2 shows application of nanotechnology in textile areas.

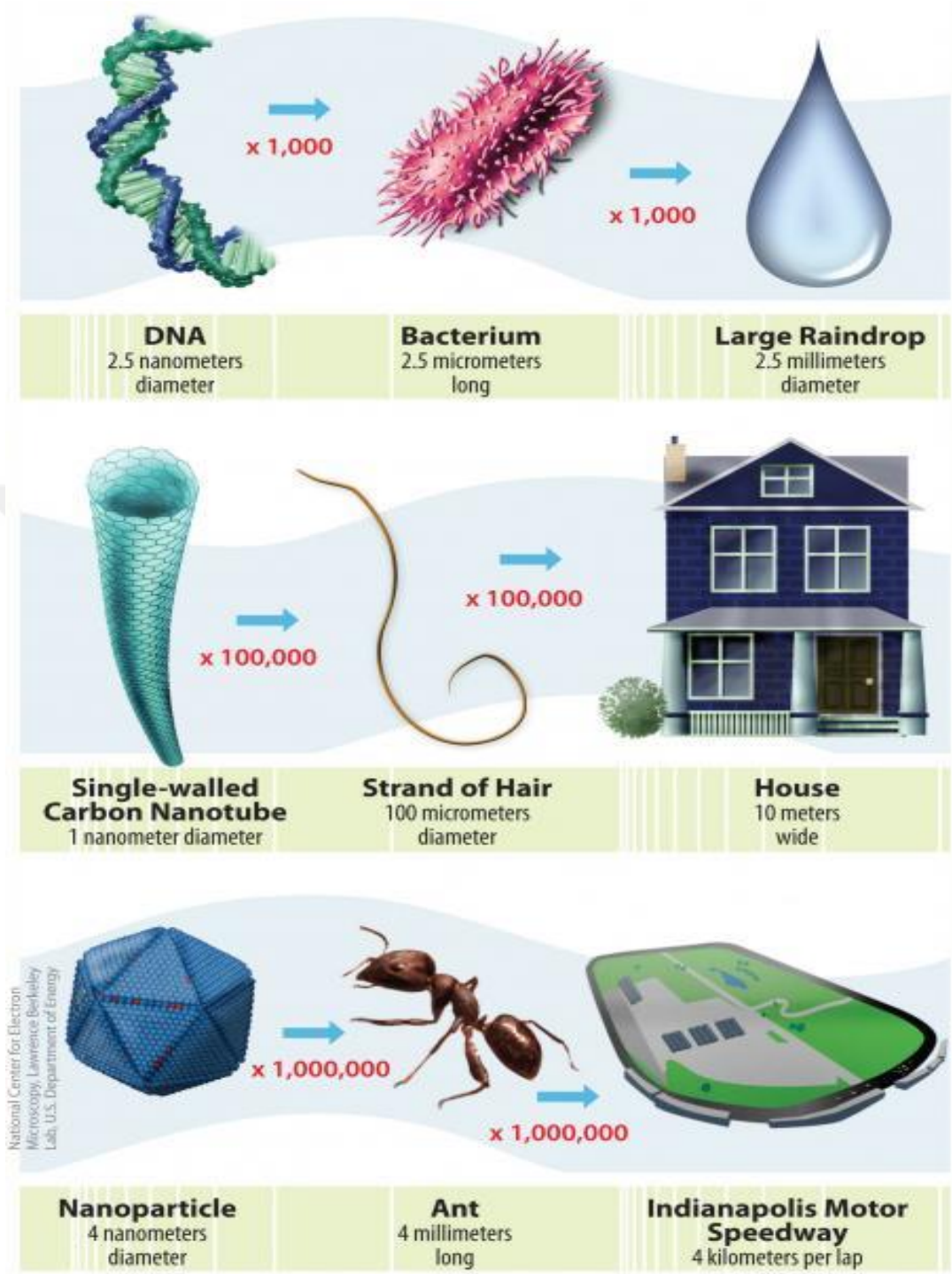


Figure 1.1 Nanotechnology size [13]

Figure 1.2 Nanotechnology applications in textiles [14].

1.3.1 Use of Nanotechnology in Textile

Because of its distinctive and useful characteristics, the use of nanotechnology in the fabric sector has risen quickly. There is significant potential in the cotton and other textile sectors for lucrative applications of nanotechnology. Its application can extend fabric processing and products characteristics and values economically. Using nanotechnology, textiles can become multifunctional and generate unique functional fabrics that contain anti-odor, antibacterial, easy-clean, UV, water-and stain-repellent properties [12].

Water Repellence: Water repellence property is one of the main topic for science of textile and fiber and produces for many centuries. Water repellence of textile defines as repulse water from the fabric surface and resistant of fabric against penetration, adsorption and absorption of water. The substrate surface energy is described by the angle of contact measurement for liquid on the material. It is also mean of wettability measurement the angle of contact for the liquid. The water repellence of textile materials can be also improved with nanotechnology support. When the nano

particles added to fabric, it has been shown some different benefits as functional performances. One of the common materials that provide water repellency characteristic to fabric is known as wax. But there is also some disadvantages of wax. Wax cover on the fabric causes to prevent air permeability and this will cause breaking on the surface [11].

UV-protection: In last centuries, the quantity of UV blocker application for textile is dramatically getting increase such as cover sheets, hats, curtains and awnings. It can be improved the UV blocker characteristic of fabrics when some parameters of fabric is changed like types of fiber, the thickness, colors and fabric opening. Inorganic UV-blockers is generally known as semiconductor oxides such as ZnO, TiO2, Al2O3 and SiO2. Nanosized zinc oxide and titanium dioxide have more powerful impact to repulse the UV radiation so they are better protector the fabric from UV radiation. The reason of this effect is greater surface area of nano particles for unit mass [11].

Antimicrobial: Although many antimicrobials are used in textiles, organic silicons, phenols, quaternary ammonium salts and organic metallic are basic antimicrobial classes in textiles. A wide spectrum of antimicrobial action exhibits bis-phenolic compound, Zinc oxide, titanium dioxide, nano-sized silver, chitosan and triclosan are used for the transmission of the antibacterial characteristics [11].

Antistatic: There are many studies to improve the anti-static characteristics of textile materials by use nanotechnology because of synthetic fibers have bad anti-static characteristic. It was calculated that nano particles size such as zinc oxide, titanium dioxide, whiskers, silanenanosol and anoantimony-doped tin oxide (ATO) can give antistatic properties. These materials help to distribution of static load on the material efficiently. On the other hand, antistatic characteristics are increased with silanenanosol [11].

Wrinkle Resistance: Resin is widely used in standard techniques to impart fabric resistance to wrinkles. Resin application constraints, however, include a reduction in fiber tensile strength, water absorption, dyeability and abrasion resistance and also breathability. Some scientists used nano-silica and nano-titanium dioxide to enhance the wrinkle strength of silk and cotton respectively to overcome the constraints of resin use [11].

Fire-proofing: One method of fire proofing is to coat with fire resistant material as a thin layer for reducing of flammability without adding flame retardant chemical additives. This method protects material's composition and properties since there is no additive introduced. There are two basic ways which a material may function as a flame retardant. First is to prevent ignition by increasing the heat capacity of the material. However, when that fails, the next step is to prevent spreading of the fire [57].

1.3.2 Nanomaterials Used in Textiles

One of the advantageous fields of nanotechnology is textile industry that has a lot of application. The nanotechnology applications in the textile field have greatly developed the robustness of textile materials, improving their comfort, hygienic property and also reduced their price of manufacturing. Nanotechnology also provides many benefits in field of economy, saving of energy, eco-friendliness, packaging, substance release control, microscopic separation and storage of products for subsequent use and release under control. Textile materials provide the highest appropriate substrates for a specified weight or quantity of fabric that has a big surface area. Nanoparticles can affect the fabric that elevated durability for treated textiles as they have big surface area and elevated surface power ensuring better affinity for textiles and resulting in increased durability of the required fabric feature. The size of particles is also necessary to determine their fiber adhesion. Some fields of nanotechnology is known sports sector, skin care, clothing, space technology, as well as technology for improved safety in huge settings. Using nanotechnology, textiles can become multifunctional and generate special-purpose fabric that include anti-odor, antibacterial, easy-clean , UV-protection, stain and water repellent [11].

For the textile industry, nanotechnology has also a true trade opportunity. This is primarily owing to the reality that standard techniques used to impart distinct characteristics to fabrics often do not result in continuous impacts, and after laundering or wearing they will lose their features. Nanotechnology adds advantages to the fabrics as high durability. Because of big surface/volume ratio and also high surface energy of nano particles shows results in higher interest for fabrics and resulting in increased function durability. Moreover, when a fabric is coated with

nano-particles it will not influence their capacity to breathe or feel their hand [12]. There are some instances in the Table 1.1.

Table 1.1 Properties of nanomaterials used in textiles [16]

Nanomaterial	Properties
Carbon black nanoparticles or nanofibers	Abrasion resistance
	Higher tensile strength
	Good chemical resistance
	Electrical conducting
Carbon nanotubes	Exceptionally strong
	Lightweight
	Electrically conducting
	Thermal conducting
Metal oxide nanoparticles	Photocatalytic
	Electrically conductive
	UV production
	Antimicrobial
Metal nanoparticles	Antimicrobial
	Solar cells
	Aesthetic properties
Clay nanoparticles	Electrically resistance
	Chemical resistance
	Fire retardant
	UV shielding

1.3.3 Application Areas of Nanofibers

The primary reasons for using them in many apps are the elevated volume to weight ratio, high strength and smooth handling in the structures produced by nanofibers and to form barriers to microorganisms and tiny particles etc. These benefits of nanofibers maske them very attractive in many industry sections for very wide range of prospective applications. Applications for nanofiber are shown in Figure 1.3.

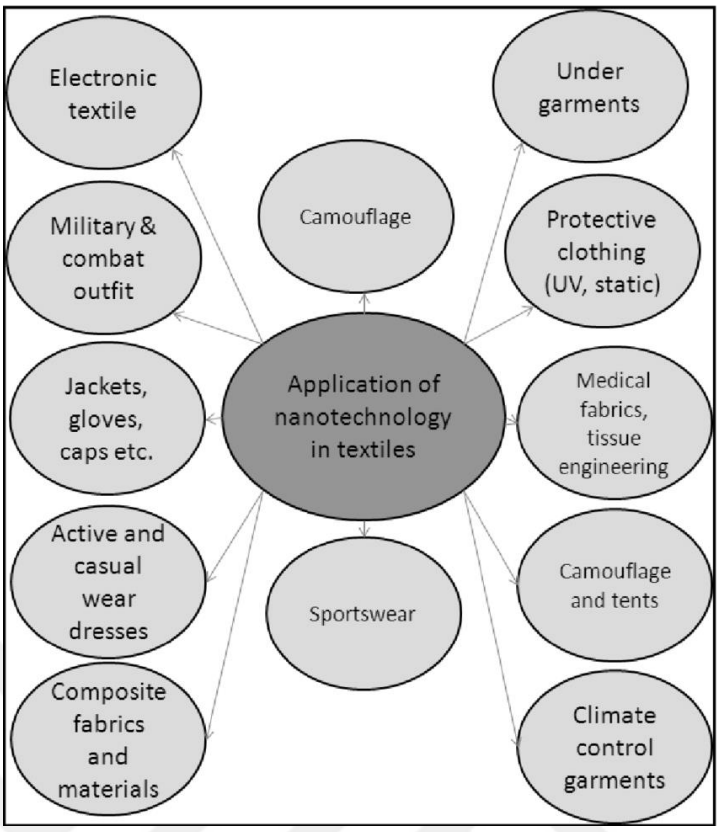


Figure 1.3 Nanofibers application areas [11]

Filtration applications: When the larger fiber is compared with small fibers at the submicron range, it will enable higher filter efficiency in the inertial interaction and interception regimens at the same pressure drop. Nanofibers have begun to be used by the filtration industry and in some cases have produced products that are commercially available. The pore size of the mat can be regulated to a relatively elevated degree with different fiber diameters. Nano-fibrous mats can therefore be intended to block particular size molecules. Nanofibers provide drastic rises in filtration effectiveness while reductions in permeability are comparatively low (and sometimes un-measurable). Nanofiber filter media has allowed fresh filtration efficiency rates with a wide spectrum of settings and contaminants in several different applications.

Composite applications: The composites sector is particularly interested in nanofiber technology because it possibly enables products to be created that are much lower and lighter in weight, yet capable of performing at the same or improved mechanical norms compared to traditional composites. Fibers such as carbon, aramid, and glass

are used in the strengthening of composites, especially in the engineering areas. The composites of reinforcement have significant characteristics like elevated modulus and weight-to-weight ratio.

Biomedical applications: Nearly all human organs and tissues are placed in a structure as nanofibrous from a biological point of view. Dentin, bone, cartilage, skin and collagen are examples. All of these examples are described with good-organized hierarchical fibrous nanometer scale realignment constructions. As such, one of their main applications in bioengineering has been concentrated on present studies in electrospun polymer nanofibers. Medical prostheses, cosmetic skin masks, intelligent clothing, wound dressings, drug delivery carriers and tissue scaffolds are biomedical applications of nanofibers.

Military and defense applications: Protecting garments in military applications is anticipated to maintain the chance of survival, allow protection for long-term, stand severe weather conditions, withstand nuclear, biological and chemical impacts, and boost effectiveness. Heavy fabrics have been produced to protect clothes that are now being used. The light and highly poriferous fabrics that absorb vapor and air of water can respond readily with chemical gasses that decompose the fabric. Due to the greater surface area and the nanofibers ' small pore size, fabrics generated by the nanofibers are appropriate for clothing protection. These fabrics can also provide neutralization. It also enables breathing of the clothes. Nanofibers with high pores with tiny pore sizes enable good resistance against chemicals diffusion to the fabrics. Nano sensors are used for discovering trace in military applications, nano electronics for multiple checks, nano composites for platforms that need to be light.

Agricultural applications: Plants are coated by a web generated by nanofibers from electrospun. Protection against damaging insects and chemicals is one of the tasks of this internet. A cover can be used for the greenhouse. In addition, fertilizers that were previously injected into the web can be given using the nanofiber web.

Space applications: In many applications of space cars and equipment such as space shuttles, particularly carbon-based nanofibers that have light weight and elevated strength, such as being hundred times stronger than steel, are used. Nanofibers can also be used in space in sun and light platforms.

Electrical and optical applications: Many benefits are created by the production of nanofibers capable of transmitting electricity. The nanofibers are basically used in the manufacture of small electronic instruments and the certain machines production. Membranes of electrospun nanofiber are appropriately used to produce improved high-performance batteries because of the electrode surface area is proportional to the velocity of the chemical reaction.

Other applications: The other potential applications of nanofibers for enzyme carriers and information technology are cables, capacitors, transistors and diodes [14].

1.4 Production Methods of Nanofibers

Drawing: The method of drawing offers easy and cost-effective production of photonic wire. But the drawing zone requires a steady temperature distribution and the wires lengths that were manufactured are delimitated to tens of millimeters. The drawing method can produce PTT nanofibers that have diameter less than 60 nm and coarser than 500 mm (see Figure 1.4). The PTT is withdrawn at speed of 0.1−1 m / s. The stretched PTT wire is quickly refrigerated and the amorphous PTT nano fibers are finally produced. The fibers manufactured with this method provide low optical performance and high flexibility [2].

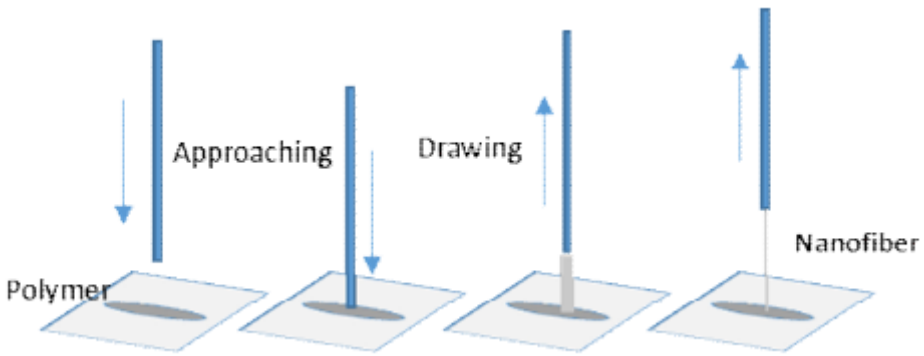


Figure 1.4 Drawing process [2]

Phase Separation: Before undergoing gelation, a polymer is first blended with a solvent in phase separation. The primary mechanism in this process is phase separation because of physical incompatibility. The main stage is the polymer is

dissolved with a solvent and created a gelation form. In the finale stage, solvent is removed and nanofiber form is created. There are many words that describe this method, as: quenching, polymer dissolution, gel solvent extraction, liquid-liquid phase separation and polymer gelation [2].

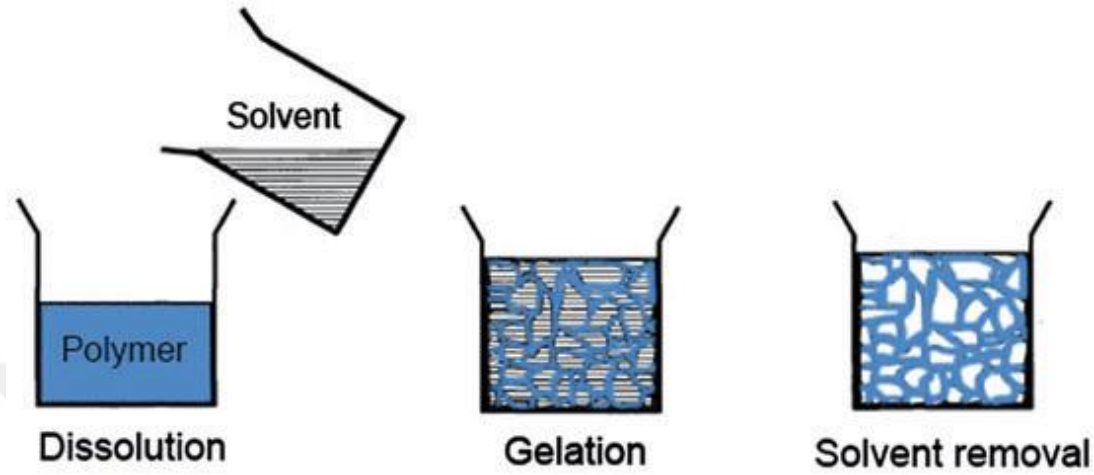


Figure 1. 5 Generic schematics of phase separation for obtaining nanofibrous structure [21]

Self-assembly: Intermolecular forces bringing the smaller units together are the primary mechanism for generic self-assembling. The shape of the lower molecular units determines the macromolecular nanofiber general shape (lower than 100 nm to a few nm). Molecular self-assembly offers an innovative way for multi-level (nano–micro–macro) design and production of novel products. Self-assembly process is the independent set up without human interference of parts in the patterns or constructions. Self-assembly procedures are prevalent throughout nature and technology, involving elements from the scale of molecular (crystals) to planetary (weather systems) and many distinct types of interactions. In many fields with a distinct flavor and emphasis in each sector, the notion of self-assembly is increasingly being used. Standard laboratory equipment is required for the method (see Figure 1.6). However, the method of transformation of particular polymers into nanofibers is restricted to the laboratory scale [17].

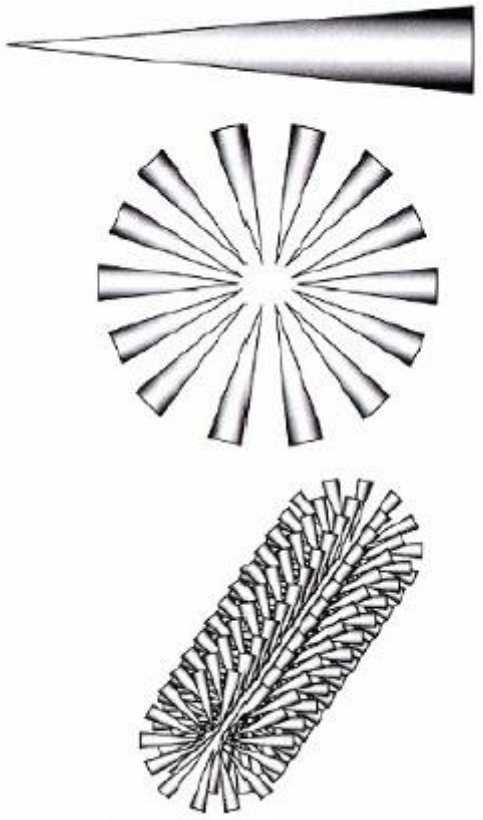


Figure 1.6 A self-assembly instance to obtain nanofibers [18]

Templete Synthesis: The template method is an efficient way to control the creation of nano-materials with various morphologies. The DNA replication and casting technique can be regarded like a synthesis based on templates. Metallic, polymeric, ceramics or semiconductors nanofibers can be fabricated by nonporous membrane including many cylindrical pores have a diameter between 5 nm and 50 mm using electrochemical oxidative polymerization or chemical. The model contains a membrane as metal oxide with nano-scale diameter holes for the case of nanofiber manufacturing. Restraining from the poriferous membrane causes the polymer extrusion that comes in contact into a solidifying solution causes production of nanofibers. The pores size determines the diameters of fibers under adding of water pressure [17].

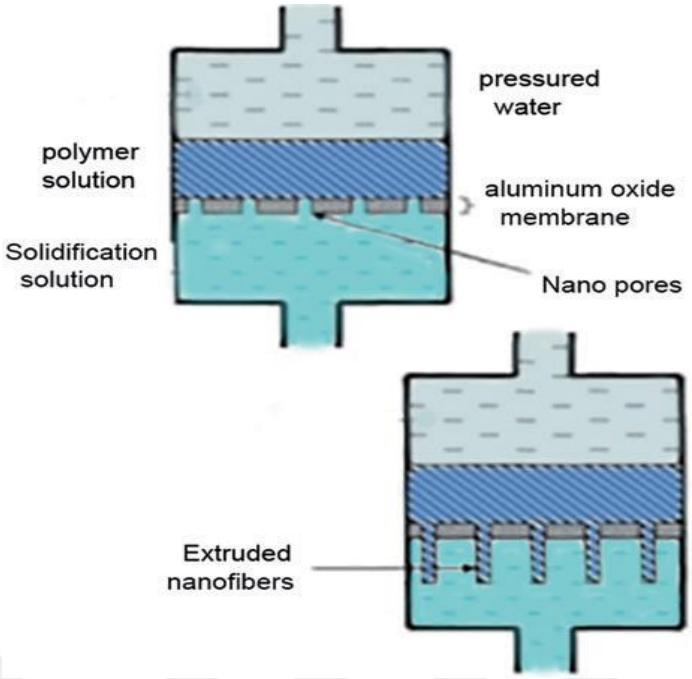


Figure 1.7 Obtaining nanofibers by template synthesis [17]

Meltblowing: The meltblown technology includes the production, at a single step, of fibers by a molten polymer that are extruded by a die body and drawn down by hot air, usually at a temperature similar to that of the molten polymer. The air usually draws the drag strength, which is then collected as a nonwoven mat. In a relatively financial method, this method offers the use of thermoplastic polymers (see Figure 1.8) [19].

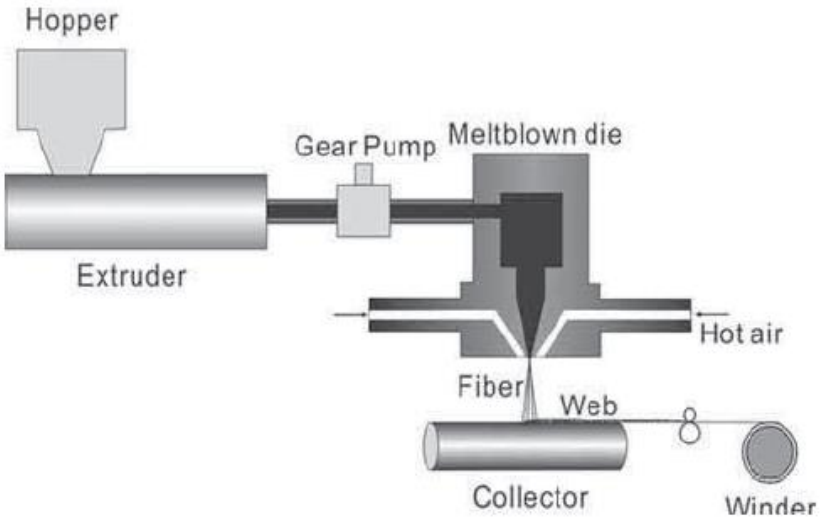


Figure 1.8 Detailed schematic of meltblowing process [19]

Force Spinning: Centrifugal (force) spinning is comparable to the spinning technique of cotton-candy. In a candy cotton machine sugars are heated and extruded into centrifugal tubes, which result in the random distribution of sucrose fibers in the free space of the spinneret. The sucrose fibers manufactured were recently used in the forming of porous polymers.

Although electrospinning method is preferred spinning type, there are some disadvantages such as high electric field requirements, low rate of production, high cost and safety problem. Force spinning is lately growing up spinning method because of fabrication rate as 500 times faster than basic electrospining method. It involves putting a polymer solution or polymer melts on a typical spinning coater with a very quick spinneret. In addition, the spinning process provides numerous technologically significant possibilities such as the delivery of hollow polymer percolations and the use of distinct polymer kinds. The parameters that affect the force spinning can definition as spinneret angular velocity, polymer viscoelasticity, orifice radius, solvent evaporation rate, solution surface tension, temperature and the tip to collector distance [19].

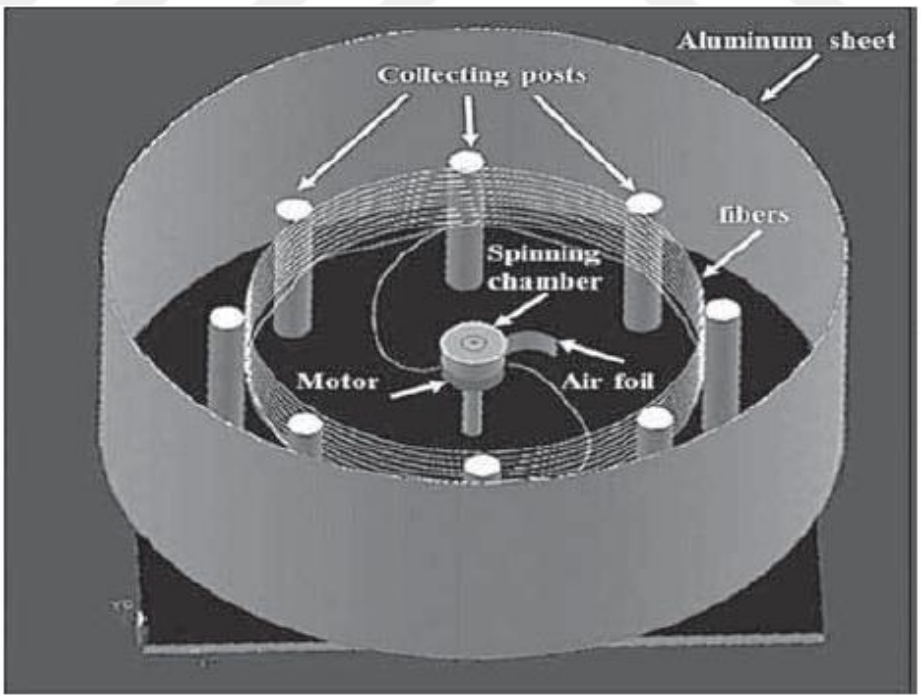


Figure 1.9 Force spinning system schematic drawing [19]

Electrospinning: Electrospinning technique is a well-established polymer fiber production method. The device comprises of a capillary needle syringe. In this method, a polymer jet is injected from a tip of needle with an electrostatic force action. The nanofibers are fabricated as a nonwoven web form. Figure 1.10 shows the set-up of electrospinning method. Although the method is advantageous and well understood, production is very slow and low fiber quality is shown. As they can make it commercially feasible, novel apps for nanofibers have renewed interest in this method [19].

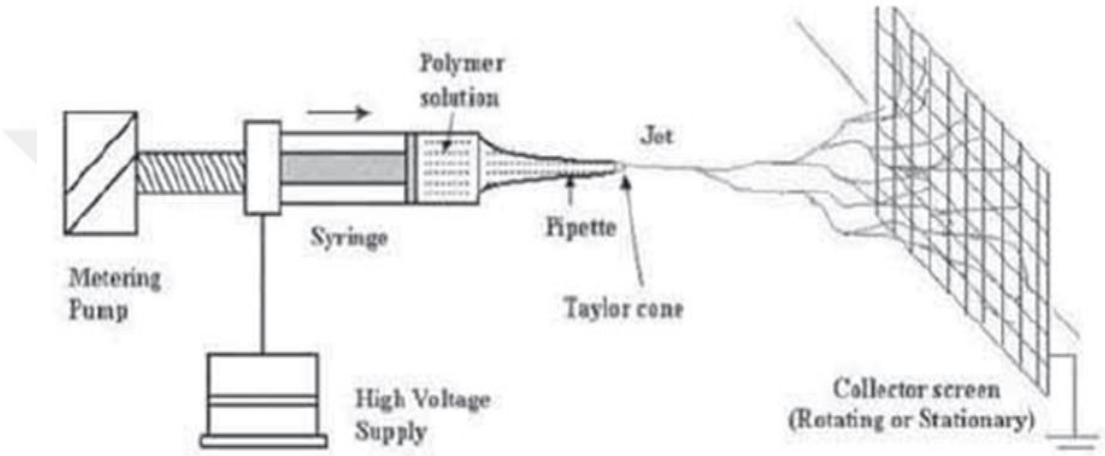


Figure 1.10 Schematic of Electrospinning Set-up [19]

Table 1.2 Comparison of advantages and disadvantages of nanofiber production methods

Method	**Advantages**	**Disadvantages**	**Scope for industry**
Drawing	1.Minimum equipment requirement 2.Produce very long single nanofibers	1.Discontinuous process 2.Diffucult to obtain fiber diameter less than 100nm 3. compatible for industry	no
Phase Separation	1.3-Dimensional pore arrangement 2.Minimum equipment requirement 3.Batch-to-batch consistency	1.Lack of the control of the fiber arrangement 2.Complex procedure 3. Limited to specific polymers. 4.Matrix directly fabricated 5.Low yield	no
Self-assembly	1.Lowest scale for nanofiber diameter (5-8 nm)	1.Complex process 2.Only short fibers 3.Low fiber collection 4.Matrix directly fabricated 5.Limited polymers as a few type 6.High cost	no
Templete synthesis	1.Enormous material selection 2.Control of fiber diameter and length 3.Continuous process	1.Limitation of fiber dimensions and arrangement	no
Melt blowing	1.High production rate	1.high cost 2.complex set up	yes
Force spinning	1.Simple process 2.High production rate 3.process safety	1.High temperature needed	yes
Electrospinning	1.Low cost 2.Simple instrument 3.Continuous process 4.Control over fiber diameter 5.Production of aligned nanofibers 6. Vast material selection 7.Tailorable mechanical properties and shape	1. Toxic solvents 2. Poor cell infiltration into the core of the scaffold 3.Jet instability 4.No control over 3D pore structure 5.Large diameter scale from nanometer to micron	no

1.5 Electrospinning Process

An ancient method is known as electrospinning since the start of this century. When it comes to manageability, it can manufacture continuous nanofibers from distinct material kinds. In addition, electrospinning is a cheaper technique than other methods. Today, nanofibers can be fabricated in varying diameter from 20 nm to 1 micron, high strength, low cost, high value.

As an all-duty manufacturing techniques for one dimensional structured, inorganic and hybrid nanomaterials with controlled dimensions, nanofiber techniques attract enormous interest. Nanofibers are produced as haphazard or oriented ongoing nanofibers with opportunities for ordered inner morphologies such as porous or hollow fiber, core-sheath or multi-channel micro tubes. Different manufacturing methods can obtain these varying types of materials. These methods can be listed as bubble electrospinning, melt electrospinning, magneto electrospinning, co-axial electrospinning, gas-jacket electrospinning, conjugate electrospinning, needless electrospinning, centrifugal electrospinning and basic electrospinning.

There is no doubt that electrospinning is the most suitable and controllable technique that used to make thin fibers from a wide range of products including polymers, composites and ceramics. Extremely high volume-to-volume surface and small diameters (nm) and aspect ratios found in electrospun fibers cannot be accomplished through standard spinning [20].

1.5.1 History of Electrospinning

Electrospinning is a straightforward technology known since the 1930s for ongoing fiber manufacturing (minimum diameter as 5 nm) from a multitude of materials containing polymers, ceramics and composites. The electrospun fibers have characteristics that are not found in standard fibers such as having high aspect ratio, a high volume-to-volume ratio, regulated pore size and perfect mechanical efficiency. The incredible mechanical properties of spun fibers let to produce a wide diameter scale of nanofibers because it is not possible to achieve these properties with conventional spinning processes.

Formhals patented the electro spinning method for the first time in 1934 [3]. Even before Formhals, the method of spinning artificial threads was experimented with,

but due to technical problems such as fiber drying and collection, it did not get much attention. The method of Formhals consisted of a mobile device for collecting threads in a stretched situation. It was still an issue to dry the fiber though. In 1940, Formhals re-patented his job to overcome this disadvantage. The gap between the feeding nozzle and the screen was changed in the refined process to give the electrospun fibers more drying time [21].

In the 1960s, Taylor introduced research on the method of jet formation. Taylor has researched in detail the form of the polymer droplet generated on the needle tip when an electrical field is applied and has shown that it is a cone and the bubbles are expelled from the cone vertices. This cone shape is known in the literature as the "Taylor cone." The jet's conical shape describes the beginning of the expansion in the process of fiber forming [22].

The electro magnification of acrylic micro-fiber has a diameter between 500 and 1100 nm was revealed by Baumgarten in 1971 [4]. He concentrated on how the fibers diameter changed as the electric field changed. Larrondo and Mandley manufactured melting polyethylene and polypropylene fibers bigger in diameter than the spun solvent fibers [23].

In 1987, Hayati et al.'s research concentrated on the impacts of electrical field, experimental circumstances, and variables influencing the features of fiber. They showed that extremely conductive liquids with increased voltage generated extremely volatile streams that whipped in various directions [24].

For water soluble poly (ethylene oxide) fibers with 0.05 to 5 μm diameter Doshi and Reneker used electro-spinning. They described the process of electric spinning, the processing conditions, and the morphology of fibers and possible use of electrospun fibres. A chain microscopy (AFM) in electrospun polyethylene oxide (PEO) by Jaeger et al. observed chain packing. They found that the electrospun PEO particles have an ordered surface layer at the molecular level. That ordered surface layer might be the consequence or the residue of the creation of the droplet [25].

The transport characteristics of electrospun fiber mats were researched by Gibson and Rivin. The electromagnetic layers have shown minimal impedance to the diffusion moisture vapor transport needed for evaporative cooling [26].

Nanofibers with a fiber diameter of around 300 nm have been electro-spun with a heterocyclic nuclear polybenzimidazole (PBI). Through sulfuric acid and heat treatments, the mechanical strength of these fibers was improved. Deitzel et al. systematically examined the impact spinning voltage and on the morphology of electrospun fibers [27-28].

1.5.2 Basic Electrospinning Set-up

An ordinary electrospinning set up includes 3 basic components: a syringe pump, a voltage supplier and a grounded collector. A polymer melt or solution is supplied by a small needle or nozzle. Typically high voltage is applied concurrently as an electrode by the nozzle. Generally, in typical set-up, distance from electrode to collector is known as TCD. The current varies during the electrospinning process from nanoamper to microampere. Electric field occurs between the collector plate and needle when a high voltage is added to electrodes. Electrostatic force excesses the surface tension after the critical voltage value and the loaded polymer solution is enforced to leave the end of the needle. The effect of electrostatic force between collectors and needle causes polymer solution jet stretched from needle to collectors, this stretching effect makes the jet very thin and long form. In same time, the solvent evaporates and fiber form of polymer start to solidify, fiber web is created on the surface of collectors [21].

Polymer solution is pumped with a constant flow-rate and voltage is applied for creation of electric field between the collector and needle tip. Liquid surface is accumulated with a charge. When the electrostatic pushing is bigger than the surface tension, the liquid starts to deform into a conically form structure. This conically shape is known as the Taylor cone.

Taylor cone form occurs then charged liquid jet starts to be ejected towards the collector. There are many types of collectors like that stationary flat plates, rotating drums, mandrels, and disks. Solid fibers would be created when the solvent evaporates depending on viscosity of solution. The whipping motion occurs pending flight time of nanofibers between Taylor cones and the collector. Finally a nonwoven nanofiber mat is collected on the collector or between the collectors [23].

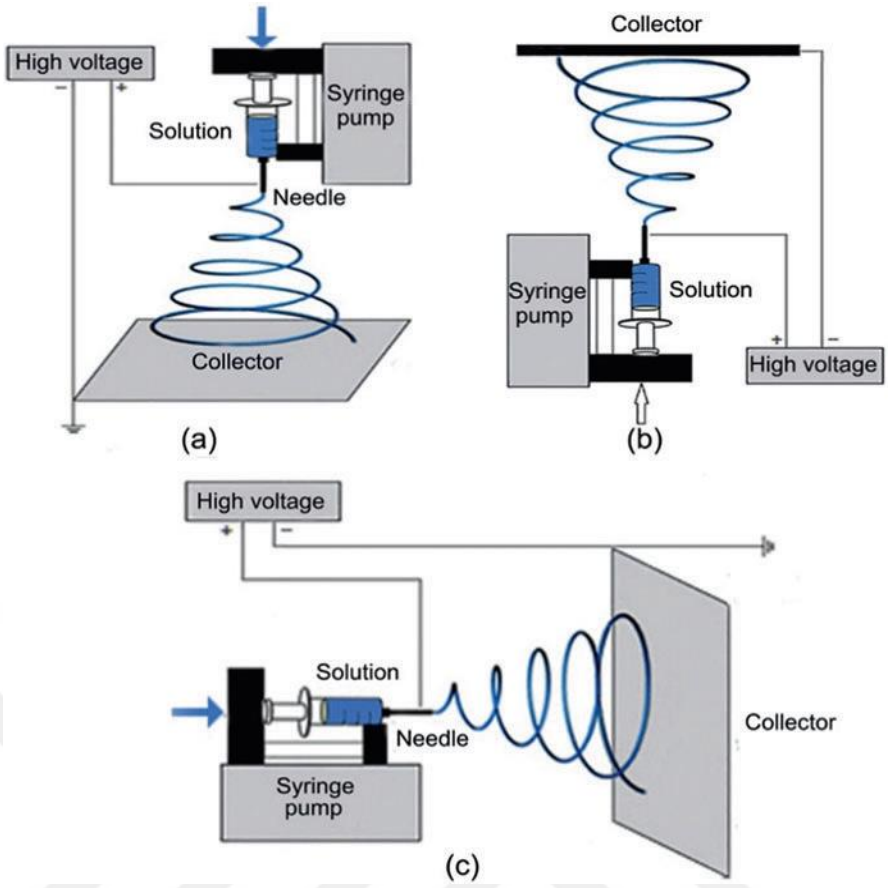


Figure 1.11 Basic electrospinning set-up [21]

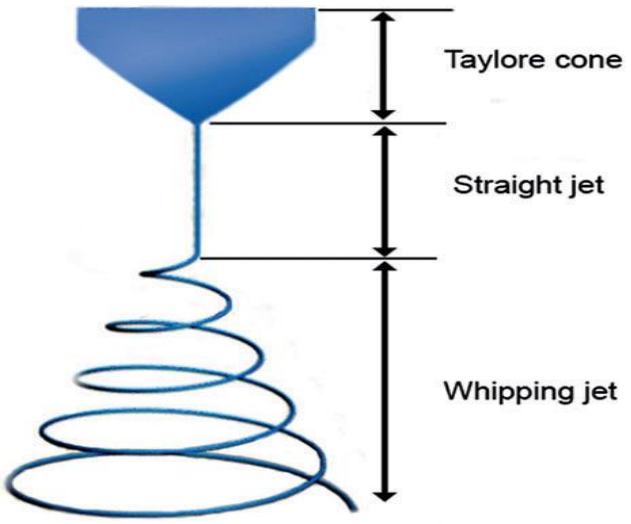


Figure 1.12 A Taylor Cone [21]

1.5.3 Electrospinning Parameters

The uniformity and morphology of nanofibers are calculated by regarding some of features that are described under three main title for electrospinning process: (a) polymer parameters, process parameters (set-up parameters), and ambient parameters. (a) Polymer solution parameters contains solution viscosity and concentration, molecular weight, dielectric constant, surface tension, and solution conductivity, (b) process parameters contains temperature, the applied voltage, diameter of the needle, tip-to-collector distance and flow rate of solution. In addition, (c) the ambient parameters include pressure, relative humidity, air velocity in the chamber and type of atmosphere. Various nanofibers with different structures, morphologies and arrangement can be fabricated by controlling these parameters and varying them [29].

1.5.3.1 Polymer Parameters

Solution concentration and viscosity: Viscosity is an important solution property that effects the fiber diameter. The strength of electrical charges is not enough to stretch the polymer solution as fiber form at high viscosity. Viscosity of the solution is calculated by the chain entanglements between the molecules of polymer. Higher solution concentration or higher molecular weight of polymer will cause increasing of viscosity and thicker fiber diameter [15].

Surface tension of the polymer fluid: The cohesive forces that occur between liquid molecules are a kind of measure that known as surface tension. Beginning of electrospinning actualized when the charges on the polymer solution exceed the surface tension of solution. When the jet of solution moves through the collector the surface tension causes to beads on the jet surface. Surface tension will cause to get little surface area per unit mass. There is a tendency to collect globally structure because of the surface tension with a big concentration between free solvent molecules. A big interaction occurs between the solvent and polymer molecules when the solution is stressed by charge at a high viscosity. Solvent molecules act to diffusion on active polymer molecules. Solvent molecules tend to be collected by the influence of surface tension [15].

Molecular weight: Effect of molecular weight is an important influence on electrical properties like surface tension, conductivity, dielectric strength and viscosity. The solution that has lower molecular weight creates beads form instead of fibers. Higher molecular weight gives a result with higher average of fiber diameter. The diameters of electrospun fibers that produced from mixed solvents get thicker with increasing of molecular weight of solution concentration. Viscosity of solution is a good sign of fiber diameter within the range of molecular weights and concentrations.

Conductivity: The solvent that is chosen to dissolve a polymer, it is necessary to have conductivity property. As an alternative, organic or inorganic salt can be used to make conductive the solution. This method has an advantage to reduce the critical voltage that required starting the electrospinning process. Another helpful method to produce highly conductive solution is to mix it with a solvent. Increasing of solution conductivity causes to improve the fiber quality and increase the electrospinning jet numbers that sprayed from the nozzle. When solution conductivity increases the Taylor cone formation increases and the diameter of the nanofibers decreases [18].

1.5.3.2 Process Parameters

Voltage: The basic parameter in electrospinning process is applied voltage to the solution. The high applied voltage will transfer the necessary charges to the solution with the external electric field. Electrospinning process starts after exceeding of surface tension of the solution in the electrostatic field. Generally more than 6kV positive or negative voltage may cause to degrade of the drop of solution as Taylor cone. Stabilization of Taylor cone hang on the solution feed rate needs high voltage. Columbic thrust forces in the jet will stretch viscoelastic solution. Increasing of applied voltage will cause to higher charge will accelerate the solution jet and more drawing polymer solution from the needle tip. Because of higher applied voltage, stabilization of Taylor cone will start to degrade. If the withdrawal solution is more than the feed solution from the needle, Taylor cone can be move on into the needle collector [25]. There are many resources about the influence of charged density on fiber alignment and morphology. Lee and Buchko reported higher applied voltage causes to more elongation of the polymer solution and more elongation will improve to produce thinner fibers [26]. Low viscosity solution with high voltage will also

create double jets during electrospinning and so this will give a result to get smaller fiber diameter. When the applied voltage decreases to critical voltage, they reported that the flight time increased and causes longer stretching time of the solution [Zhao et al., 2004]. Wu et al., 2012 studied about the fiber diameters decrease with increasing voltage to a minimum before the trend reverses with further increase in voltage. Conversely, there are some studies that observed that diameter of fiber will first increase with higher applied voltage but then up to a certain critical voltage, it starts to decrease according to Mazoochi et al. [15].

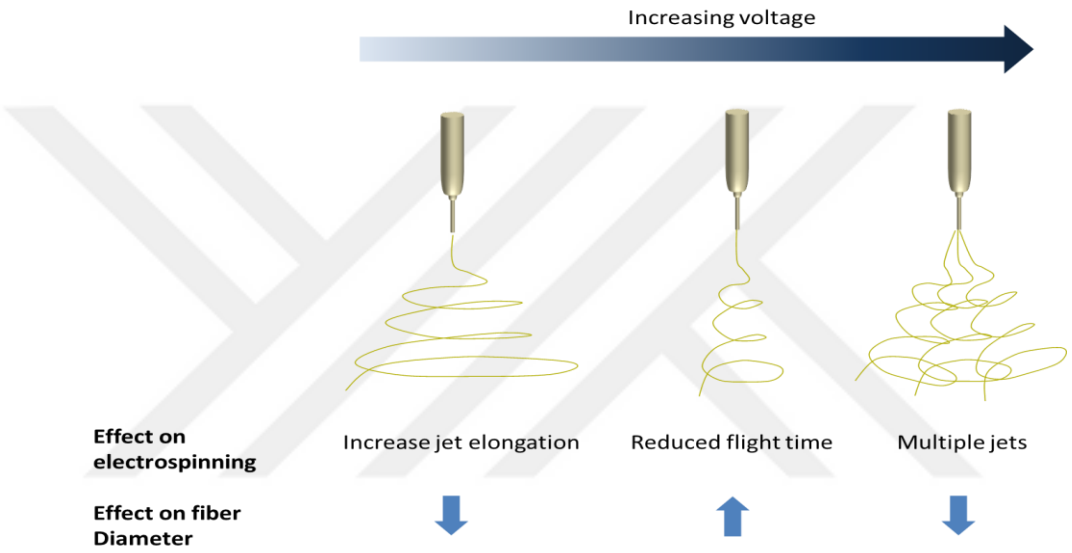


Figure 1.13 General effect of increasing voltage on electrospinning process and fiber diameter [15]

Flow rate of the polymer solution: The amount of solution that uses in electrospinning process is calculated by the feed rate. The appropriate feed rate is enabled if a stable Taylor cone continues at a certain voltage value. When the feed rate increases the quantity of solution that is drawn from the nozzle will increase. Zhong et al. observed increasing of feed rate will causes to increase the fiber diameter and also beads. The increase in fiber diameter due to feed rate is limited according to Andrady. If the feed rate is same with the solution quantity transferred with the electrospinning jet, it is observed increasing of charge density when the feed rate increase appropriately [28].

Distance of the electrode from the collector: The distance between the collecting plate and the nozzle is another important variable factor affecting the fiber morphology with deposition time, whipping interval and evaporation rate. Fiber formation occurs at this distance, the solvent is removed and the fiber solidifies. All fibers are collected at this time. Increasing this distance will cause to increase the fineness of the fiber and the fibers are accumulated in a dry form. When the wet fibers collected from the electrospinning process with the concentration parameter omitted, it is shown beaded structure on the fibers if the distance is low. At the same time low distance in Buckho's study, the transformation from round section to flat section was also observed [28].

1.5.3.3 Ambient Parameters

Temperature: Temperature of solution has an effect to reduce of viscosity same as increasing range of evaporation. The polymers that electrospin at higher temperature have more uniform structure. The reason can be low viscosity of solution and better dissolving of polymer that causes higher tension stress of solution. Low viscosity can create more stress and so thinner fibers can be manufactured. The moving of molecules increases because of increasing of temperature and it is led to columbic power for further stressing of the solution [30].

Relative humidity: Ambient moisture can affect the polymer solution during the electrospinning process. When the electrospinning process proceeds under normal atmospheric conditions high humidity can concentrate on the fiber. If the polymer is dissolved in a volatile solvent, it will be affected the morphology of fiber.

Atmosphere type: The ingredient of the air in the environment is significant on the electrospinning process. Various behaviors are observed under strong electrostatic force for different gases. For instance, deterioration helium gas occurs under strong electrostatic force and thus electrospinning process does not occur. But when a gas with a high decomposition voltage is added, it is twice as large as the fiber diameter obtained under other equal conditions [31].

1.5.4 Alignment of Nanofibers

The collector structure has an important influence on the electrospun nanofibers characteristics. There are several collector types to fabricate high aligned nanofibers as plate, grid, conveyor belt, cylinder, rotor, parallel electrode, disc etc. (see Table 1.18). Structure of collector provides alignment of nanofibers, homogeneous distribution of fibers, productions of nanofibers by various diameters and increasing of strength. By the way , only two collectors type have been realized highly ordered structures and well aligned; cylinder collectors and parallel electrodes [32].

1.5.4.1 Parallel Electrode Collectors

Gap method is known as most popular technique can produce aligned nanofibers via separated and static conductor electrodes. When two parallel collectors are put with a gap distance, the lines of electric field adjoining to the electrodes divide into each edge of the electrodes. So, jets of polymer are stretched, elongated and arranged between the collectors via the electrostatic field effect. Residual charge that occurs because of repulsive force helps this stretching and elongation of nanofibers [33].

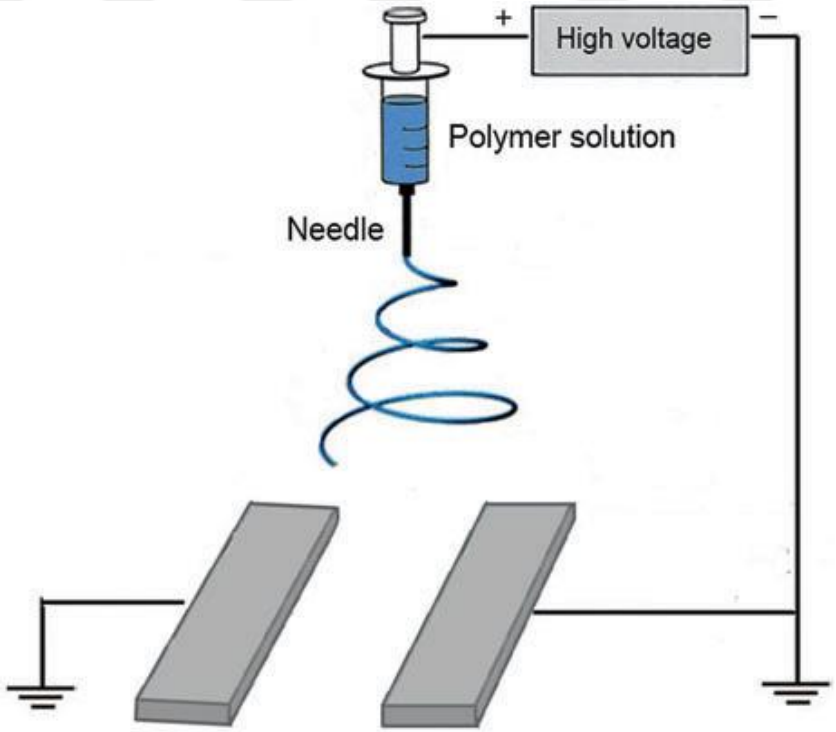


Figure 1.14 Electrospinning using parallel conducting collector [21]

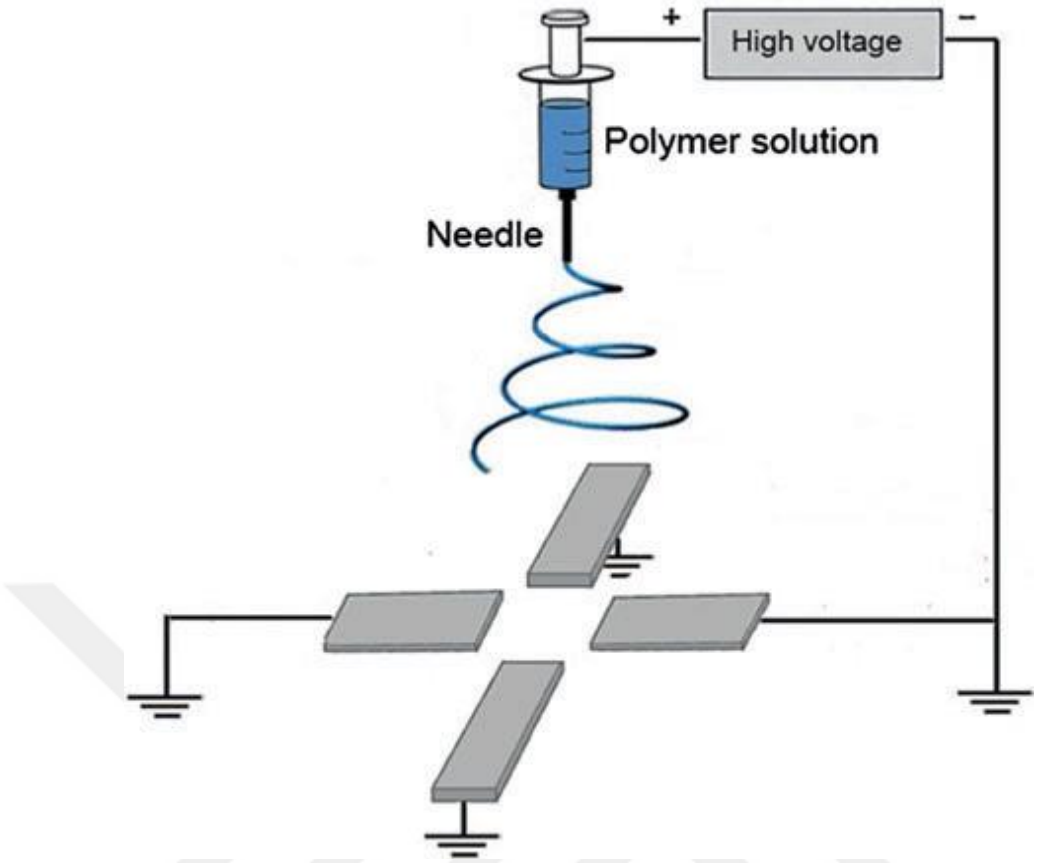


Figure 1.15 Electrospinning using patterned electrodes [21]

1.5.4.2 Rotating Drum Collectors

Rotating collector is the oldest, easiest and most straightforward method to produce aligned nanofibers. A cylindrical mandrel, a spaced wire drum, a wheel, a thin disk include a sharp edge and a cone were used as the rotating grounded collectors for this method. Best collector was reported as a thin disk with a sharp edge that provided better nanofibers alignment when it compared with the other collector. Aligned fibers are collected by inspecting of drum rotation speed that is placed as a ground platform. Alignment of fibers is improved by increasing of the drum speed. But also the disadvantage of this technique is the limitation production of parallel nanofiber due to the geometrical form of a disk collector [34].

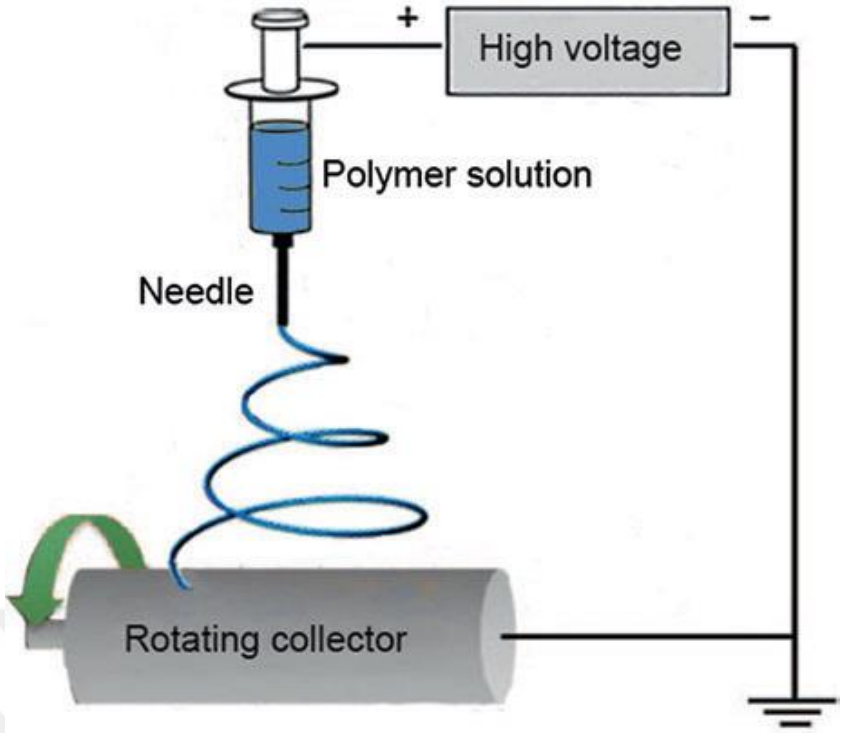


Figure 1.16 Electrospinning with rotating cylinder collector [21].

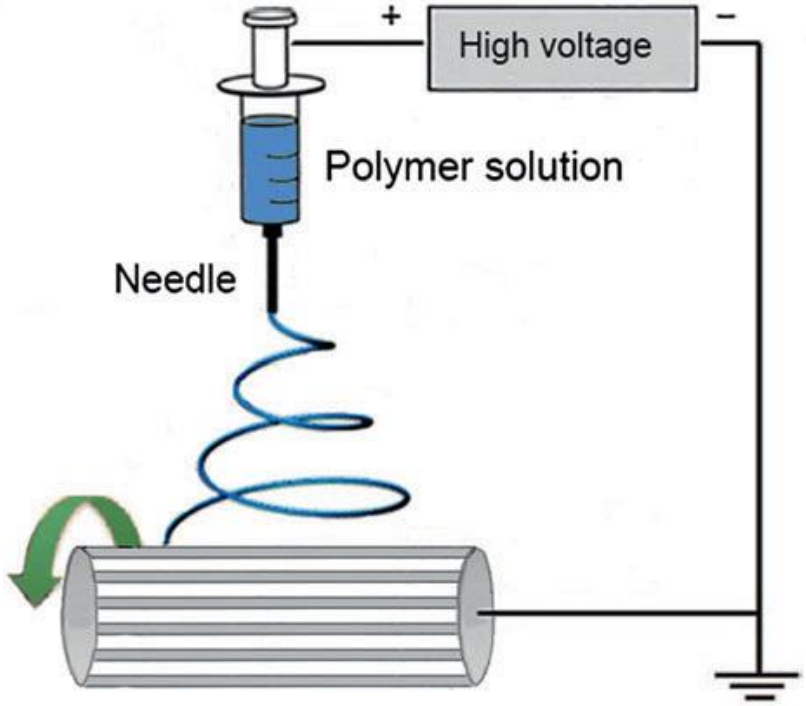


Figure 1.17 Electrospinning with rotating wire drum collector [21].

1.5.4.3 Others

Rotating Disc: Industrial applications prefer fibers without pores, beads and uniformly aligned fibers. Rotating disk creates oriented fibers without any beads. A monotonous web of fibers can be manufacture by rotating the collector as shown in Figure 1.18. The jet flows from the needle tip of the tube to the rotating disk under the effect of an electrostatic field and experiences bending instability because of the surface charges interactions. As a result, the nanofibers were collected on the rotating disk that has a constant speed. A thick continuous mat of nanofibers can be manufactured with this process [8].

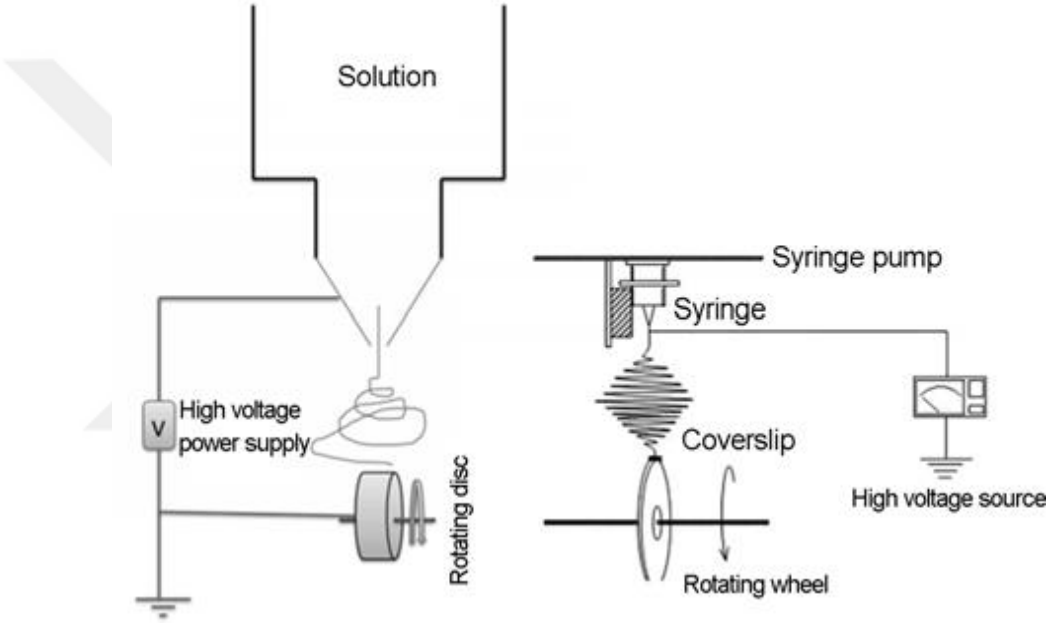


Figure 1.18 Schematic of electrospinning with rotating disk [35]

Sharp Pin with a Rotating Mandrel: In this process, a sharp pin that charged negatively is placed in the rotating drum (Figure 1.19). It helps to develop the alignment of the fabricated nanofibers by creating an electric field from the needle tip to drum and incorporates at the sharp pin into the rotating drum [21].

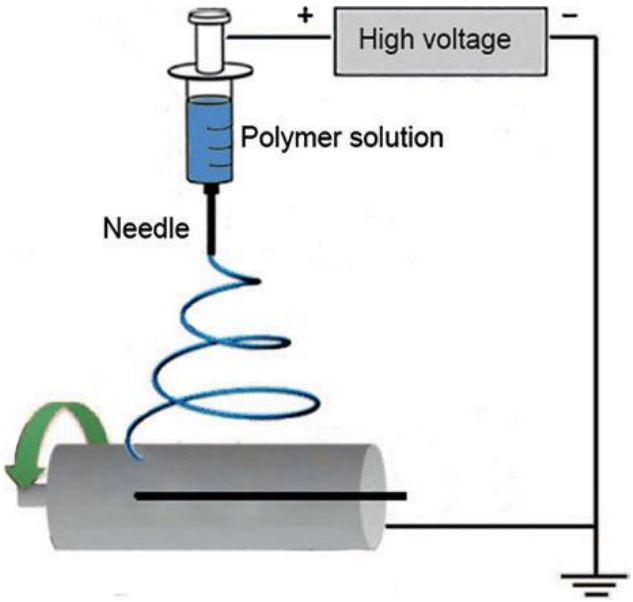


Figure 1.19 Electrospinning using a sharp pin with a rotating mandrel collector [21]

Two-Ring Collector: Nanofibrous yarns can produce with this technique. Two-ring electrodes serve as collector (Figure 1.20) and one of the electrodes rotates by the determined quantity of twists at the end of electrospinning process. This target geometry lets the fabrication of high aligned nanofibers, however the fibers that produced with this method are difficult to retouch and characterize and without harming the fiber orientation [29].

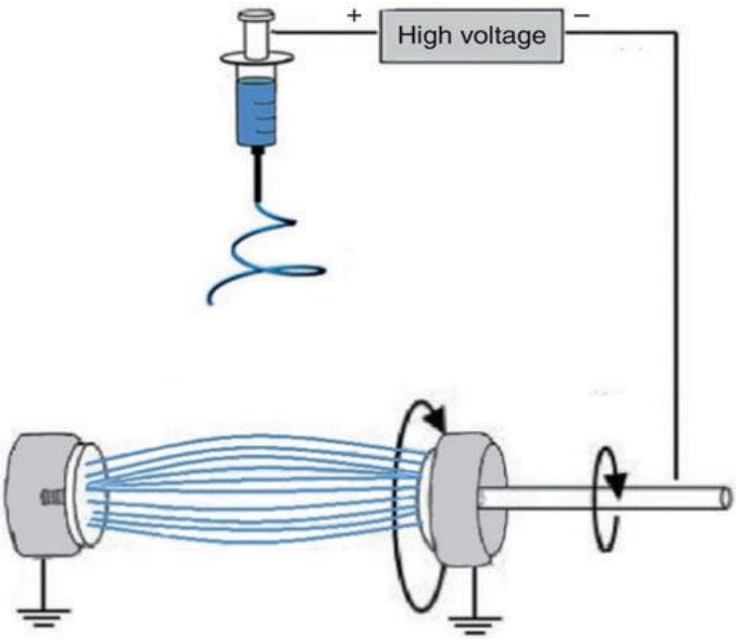


Figure 1.20 Electrospinning using two-ring collectors [29]

A Frame Collector: This technique has been investigated to create an single nanofibers for the experimental specifications aim. Fiber alignment is successfully produced by fixing a rectangular frame down the spinning jet (see Figure 1.21). When frame materials change, various fiber alignments obtain. For instance, the aluminum frame benefits higher fiber orientation when it compares with wooden frames. The effect of shape and size of its rods, frame inclined angel and the distance between them on orientation of fiber is improved by many researchers [36].

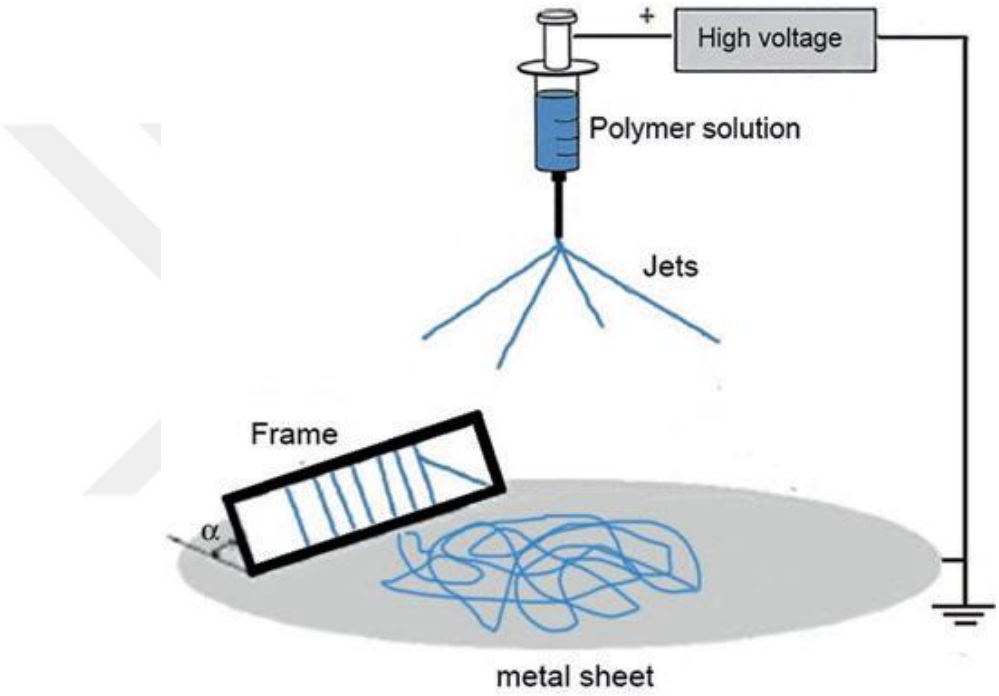


Figure 1.21 Electrospinning setup using a frame collector [29]

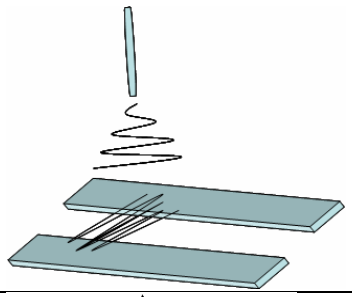
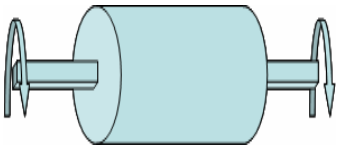
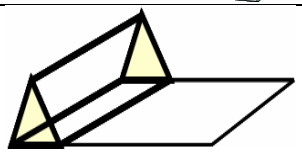
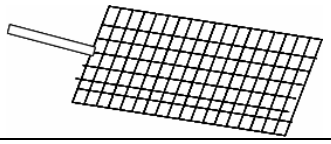
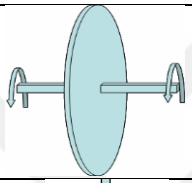
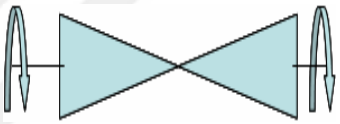
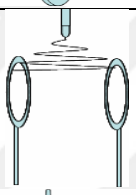
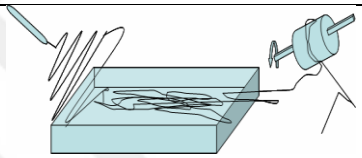
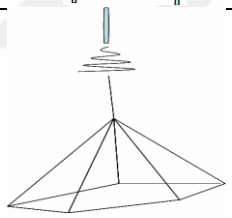
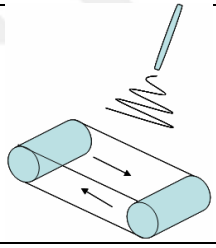
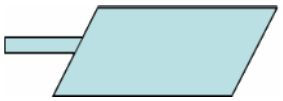
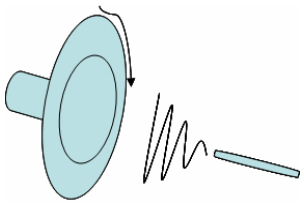
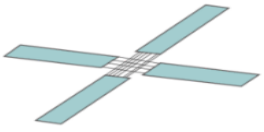
Collector Name	Collector Shape	Collector name	Collector shape
Parallel electrodes		Rotating cylinder	
Triangle Frame		grid	
Rotating Disc		Rotating cones	
Parallel Rings		Liquid bath And wrapper	
pyramid		Conveyor belt	
Plate		rotor	
Arrays of Counter electrodes			

Figure 1.22 Collector types that used at electrospinning method [37]

CHAPTER II

LITERATURE REVIEW

In this study, the effect of gap distance, charge density (CD), tip-to-collector distance (TCD) and plate width on nanofiber alignment and diameter were investigated for polyvinyl alcohol (PVA) and polyacrylonitrile (PAN). No study about effect of plate width on alignment of nanofibers was found as a result of the literature searches. One study about effect of three dimensions of plate together widths on the nanofiber was found Beachley et al. [5]. The studies about parallel electrode collectors were explained as 3 groups with separate titles (studies about effect of gap distance, studies about gap distance with other process parameters and studies about modified parallel electrode method).

Studies about effect of gap distance

Wei Liang et al. studied to find the effect of the gap distance on the fiber alignment for Polyvinyl alcohol (PVA). They fabricated the PVA 16 wt % by using parallel round metal collector. Electrospinning was carried out at 4 cm, 5 cm and 6 cm gap distances. TCD was experimented for 6 cm, 8 cm and 10 cm TCD and applied voltage has a range 12 kV, 15 kV and 18 kV. SEM images were observed and orientation angles were determined. They declared increasing the gap distance is decreased the alignment of nanofibers and reported in order of importance applied voltage, spinning distance and electrode gap, respectively. Wei Liang et al. found optimal values as 12 kV charge density, 6 cm TCD and 5 cm gap distance [38].

Yusril Yusuf et al. were investigated the effect of gap distance and solution concentration on the diameter and alignment of nanofibers [39]. They produced PVA nanofibers from 11,13,15,17 and 19 wt % solutions, applied voltage 15 kV, 9cm TCD and gap distance varied as 5 mm, 10 mm, 15 cm and 20 mm with a traditional parallel cooper collector method. Electrospining samples were analyzed by SEM and then observed by Optical Polarizing Microscope (OPM). They used ImageJ software

for diameter measurement. They pointed out to increasing the gap distance is decreased the alignment of nanofibers and fiber diameter will first decrease and reduced to minimum value as 355 nm for 15 mm of gap distance and then increase again. However they noted that when the concentration increase average diameter of nanofibers increases too, but the concentration don't affect the alignment. Best alignment was declared at 10 mm plate width for 15% PVA concentration. The parallel aligned fibers can be fabricated at 20 mm as maximum Gap distance for cooper collector.

Lihua Liu and Yuris A. Dzenis were investigated the effect of gap distance and residual charges on the fiber alignment with conventional parallel collector method [40]. Their parameters were 4.5 wt. % PEO solution, 3 cm, 5 cm, 8 cm, 12 cm, 15 cm and 18 cm for gap distance, 40 cm TCD for spinning distance, 12 kV for applied voltage. They defined that increasing of alignment with increasing of gap distance. Optimum gap distance was found as 18 cm.

Vasudha Chaurey et al. was investigated the effect of gap distance on the fiber alignment for PLAGA (15 wt. %) via pattern collector [41]. They studied for gap distance a range between 0.2 mm and 20 cm, 5 cm TCD and 10 kV applied voltage. As a result they revealed increasing of gap distance causes increasing of alignment of nanofibers.

Xiaomei Cai et al. studied to electrospin highly aligned and very long fibers. Polyvinylidene fluoride polymer was electrospun using U-shape collector [42]. Six collectors with different sizes were performed for 1cm, 6 cm, 15 cm, 30 cm, 50 cm and 60 cm. They verified a high alignment for 30 cm, 50 cm and 60 cm collector gap width, with over 90% of the nanofibers aligned in an angle range between -2.5° and 2.5°. When the collector gap width decrease they saw that the fiber alignment became poor. U-shape collectors are more effective and efficient to fabricate aligned nanofibers when it compare with other parallel conducting collectors, such as parallel strips and parallel blades-like structures. Results reveal that very good aligned fibers with over half a meter length can be fabricated and the sling fibers can be transferred without deforming to other substrates for specific uses. Optimum gap distance was reported as 50cm.

Christopher Fryer et al. examined the effect of gap distance on the modulus, alignment and diameter of individual nanofibers by the traditional parallel plate method. POE (8 wt %) polymer was spun at 20 cm TCD , 18kV charge density, and 4 cm, 6 cm, 8 cm and 10cm gap distances [43]. They mentioned that increasing of gap distance causes to improve alignment of nanofibers and optimal value reported as 10 cm gap distance. They found electrostatic alignment produces fibers with a smaller diameter than their nonaligned fibers and aligned nanofibers have average thinner diameter than nonaligned nanofibers. The average of aligned fiber modulus was found almost 1.5 to 2 times greater than nonaligned nanofibers.

Rouhollah Jalili et al. examined the effect of gap distance and charge density of PAN (15 wt %) polymer on the alignment of nanofibers [44]. Process parameters were used as 2 cm, 3 cm, 4 cm and 5 cm for gap distance, 10 kV, 11 kV, 12 kV and 13 kV applied voltages and 15-20 cm TCD. When gap distance increases the alignment of nanofibers first increase and then decrease. Best results was observed for 3 cm gap distance. Then best gap distance was examined with variable charge density. As a result , they clearly observed that increasing of applied voltage causes to fist increase and then decrease of fiber alignment.

Pokorny et al. analyzed the effect of gap distance for PVA (16 wt %) polymer on the alignment of nanofibers with patterned of collector 16 cm TCD, 1 mm, 2 mm, 5 mm, 10 mm, 20 mm, and 45 mm for gap distance, applied voltages between 20-25 kV [45]. The results show the dependence of transversal electrical strength on the gap distance between collectors including of two or more grounded electrodes. When gap distance increases, the alignment of nanofibers first increase and then decrease. Best results was observed for 10 mm gap distance.

Studies about gap distance with other process parameters

Wei Liang et al. investigated the effect of TCD and CD on the nanofiber alignment in addition to gap effect [38]. They pointed that all these parameters affect the alignment as proportional. When the TCD and charge density were decreased, the orientation angle of nanofibers decrease too same as gap effect. They thought that reason may be increasing of high charge density may cause the unstability of jet.

Increasing of spinning distance caused to increase of the orientation angle of nanofibers. They said that the reason can be decreasing of electric field strength when the other conditions especially the charge density was get fix. Some jets were out of control which caused the increase of the number of instable nanofibers. Increasing orientation angle of nanofibers can be related with the electrode gap after controlling other factors. The increase of orientation angle of nanofibers might be caused by the variation of electric field. They declared that the biggest effect on the orientation angle is charge density, then TCD and finally the electrode gap.

Rouhollah Jalili et al. examined the effect of CD and Gap distance on the alignment of nanofibers together [44]. Gap distance was 2 cm, 3 cm, 4 cm and 5 cm for gap distance and applied voltage was varied as 10 kV, 11 kV, 12 kV and 13 kV for 15-20 cm TCD. The effect of both parameter shows same results. Increasing of charge density causes first to increase than decrease of alignment. The optimal value reported as 11 kV for applied voltage.

Yanli Gou et al. viewed the effect of concentration, flow rate, TCD and CD on fiber morphology and alignment [46]. They experimented PVDF solution with varied concentration: 10 wt %, 12 wt % and 14 wt %. The voltage applied as 5 kV, 6 kV, 7 kV and 8 kV, TCD was 8 cm, 10 cm, 12 cm and 14 cm. Electric field distribution was analyzed with COSMOS multiphysics software. Increasing of concentration shows that thinner fiber and higher alignment, best result was observed for 12 wt %. Fibers diameter and alignment started getting worse up to 12 wt %. They also declared the great influence of flow rate on fiber alignment, there is a critical value for flow rate. Increasing of charge density first increase and then decrease the alignment of nanofibers. Same result was also reported for effect of TCD. Optimum values were resulted as 12 wt % of solution concentration, 100-250 μL/hr, 7kV applied voltage and 10 cm TCD.

Studies for modified parallel electrode method

Mohamed B. Bazbouz and George K. Stylios studied effect of solution characteristics, gap distance between discs, TCD distance and charge density on the diameter of nylon 6 with and also effect of gap distance and collecting time on the alignment of nanofibers via two parallel grounded discs [47]. They declared

optimum values of solution concentration 20 wt%, charge density 15 kV, spinning distance 8cm and Gap distance between discs 6cm.

Dongzhi Yang et al. studied to produce aligned nanofibers via electrospinning method that include magnetic field. PEO solution was electrospun between two ferrit magnets on a magnetic field surface with a TCD 20 cm and 7.5 kV/cm charge density. Characterization was enable with polarized Raman spectroscopy and FRIT spectroscopy. As a result, fiber alignment was shown excellent. They explain this perfect alignment of electrospun nanofibers with effect of the magnetic field produced by the separated nonconductive ferrite magnets and by the moving of the charged electrospun nanofibers [48].

Hao Yan et al. investigated to fabricate oriented electrospun nanofibers with the help of dielectric materials [49]. They used PVA polymer at 10 cm TCD, 5 cm gap distance and 15 kV applied voltage. Ansoft Maxwell 2D program was used to analysis orientation of nanofibers. Theoretical simulations present it is possible to manually adjust the electric field using dielectric materials for collectors.

Farzad Dabirian investigated the effect of applied voltage and diameter of collector diameter on the alignment of nanofiber production by using modified parallel method with rotating jet [50]. PAN polymer with concentration 17 wt % was examined with a range between 6-22 kV and 20-50 cm collector diameter. Fibers diameter was measured by SEM instrument. Numerical values were obtained to calculate nanofibers alignment by using Fourier power spectrum (FPS) technique and digital image processing. The results show that increasing of collector cylinder diameter causes to increase diameter of nanofibers. They also verified that higher cylinder diameter needed higher charge density to obtainer greater alignment of nanofibers.

Shu Hee Park and Dong-Yol Yang examine the effect of inclined parallel collector method on alignment of nanofiber and effect of spinning time on the alignment [51]. They fabricated nanofibers from 4 different concentration: 10 wt %, 14 wt %, 18 wt % and 22 wt %. They reported that when the collectors is placed in parallel configuration, the lines of electric field separated to two fractions to make the fibers aligned between the collectors. In their study, they placed the collector in asymmetric form as one horizontal and the other vertical position. Distance from horizontal plate

to needle was varied between 80-160 mm and voltage was applied from 6 to 20 kV. They observed effect of inclined collectors too much better than parallel electrode placing because of providing sufficient time to stretch, self-aligned and regular distribution of nanofibers. They declared that longer spinning time causes lower orientation but higher density.

Zhao et al. investigated highly aligned electrospun nanofibers with a kind of modified parallel collector method [52]. The effect of applied ring voltage was examined for quality of nanofiber and optimum parameters was obtained such as the alignment and diameter. The results revealed the effect of MPEM (modified parallel collector method) is very advantageous. The diameter of nanofibers decreased and alignment is improved when the nanofibers electrosun with MPEM. Consequently, tensile strength of nanofibers was improved when degree of orientation increased. They also analyzed the effect of spinning time and applied ring voltage on the alignment of nanofibers. The result showed that increasing of spinning time caused decreasing alignment of nanofibers. When ring voltage increase, alignment first increase and then decrease. Optimal ring voltage was reported as 5 kV. Diameter of nanofibers first decrease and reach to minimum value at 4 kV applied voltage and then increase when the ring voltage increases.

Yanhua Song et al. studied to produce high oriented nanofibers via modified parallel electrode technique that include a cooper ring charged positively [53]. PAN solution (8 wt %) was used with 15 kV applied voltage to parallel collectors and 5 kV applied voltage to the ring. The distance between parallel collectors and needle was 21 cm, the distance between ring and needle was 4 cm. They declared the alignment of nanofibers was improved by modified parallel electrode method. They also reported the increasing of diameter with increasing of concentration of solution.

Lei et al. investigated to fabricate high aligned nanofibers with a modified hallow cylinder that includes many parallel electrodes [54]. PVDF polymer with 12 wt % was studied for variable cylinder diameter, gap width and TCD. Cylinder diameter was performed for 4 cm, 10 cm, 20 cm, 35 cm and 50 cm, gap width was 2 cm, 4 cm, 6 cm, 8 cm and 10 cm, TCD was determined as 5 cm, 10 cm, 12 cm and 20 cm. Increasing of cylinder diameter was first increase the alignment and reach 10 cm

optimal diameter value ant then decrease for 2 cm gap distance. And optimum value is 2 cm for gap distance for all cylinder diameters.

Sophia Chan et al. produced orthogonally oriented Polyacrylonitrile co-methylacrylate (PAN-Co-MA) fiber web via a parallel electrode method as defined the gap between the parallel copper collectors was approximately 7 cm. The perpendicular fibers were produced on a desktop set up by the collector and syringe needle horizontally parallel to each other [55]. The voltage was kept at 17 kV, with a spinning distance of 10 cm cooper plates. Even though the influence of orthogonally organized fibers is not obvious, the results declare the advantage of using CNF catalyst that supported with tailorable material characteristics.

V.Beachley and X.Wen examined the impact of electrospinning parameters, geometry and gathering device material features on the maximum length of PCL fibers with parallel collector [5]. They reported that bigger collecting device would have the effect of gathering longer fibers and electro-spinning parameters to generate maximum fiber length. These parameters were the composition of the solution, feed rate of the polymer solution, the drop height and the voltage applied. The collecting device's geometry and material features and these parameters influenced the maximum fiber length. They showed that by optimizing these parameters, the production of longer constant fibers of a required length and diameter could be generated. They presented that nanofibers with an average diameters of about 350 nm to 1 μm could be collected over relatively long continuous polycaprolactone (PCL) across parallel plates up to lengths of 35–50 cm. Experimental findings showed that even longer permanent nanofibers over 50 cm can be produced if the size of the parallel sheets has been reduced. According to their study, fiber diameter and length decreased when they increased voltage but fibers uniformity increase at big level. Plate width effect was observed in significant differences.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

3.1.1 Materials for PAN Nanofiber Study

Polyacrylonitrile polymer was supplied from AKSA acrylic (PAN, Mw = 150,000 g/mol) was dissolved in dimethylformamide (DMF) (sigma-aldrich, product of Germany) as 12 wt % concentration. PAN solution was stirred magnetically at 90°C in a glass beaker for 3 hours until they became homogeneous.

3.1.2 Materials for PVA Nanofiber Study

Polyvinyl alcohol (PVA, Mw = 80,000–100,000 g/mol) was dissolved in distilled water as 10 wt % concentration. PVA solution was stirred at 80°C in a glass beaker for 3 hours until they became homogeneous.

3.2 Method

3.2.1 Solution Characterization

3.2.1.1 Viscosity Measurement

Viscosity of PAN and PVA solutions was measured by Brookfield DV-III Ultra viscometer at 25°C (see Figure 3.1).

Figure 3.1 Rheometer instrument

3.2.1.2 Surface Tension Measurement

Surface tension of PAN and PVA solutions was measured with a surface tension meter instrument as namely Attension by KSV instruments at 25°C (See Fig.3.2).

Figure 3.2 Surface tension meter instrument

3.2.1.3 Conductivity Measurement

Conductivity of PAN and PVA solutions was measured with a conductivity meter instrument as namely Thermo Scientific Orion 4-Star at 25°C (See Fig.3.3).

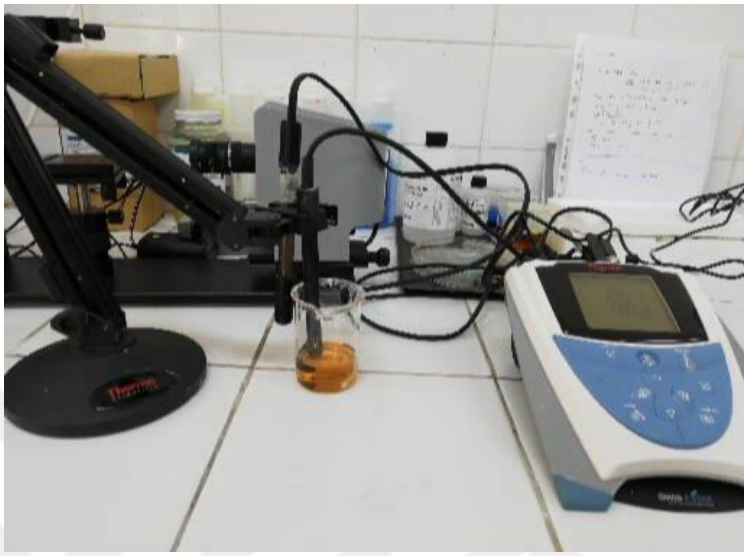


Figure 3.3 Conductivity meter instrument

3.2.2 Nanofiber Production

3.2.2.1 Electrospinning Set up and Process

The schematic of the electrospinning device was represented in Figure 3.4. The device consisted of a needle, a syringe pump, a parallel electrode collectors and two variable DC high-voltage power supplier. In order to obtain the aligned nanofibers, the traditional aluminum plate collector was replaced by two parallel metal electrodes. Both the two electrodes were connected directly to negative (-) voltage supply in electrospinning. The process was similar to traditional electrospinning process. The needle was connected to positive (+) power supply. The voltage supplied by the power generator was adjusted as the identified equal voltages for positive and negative (see Figure 3.5).

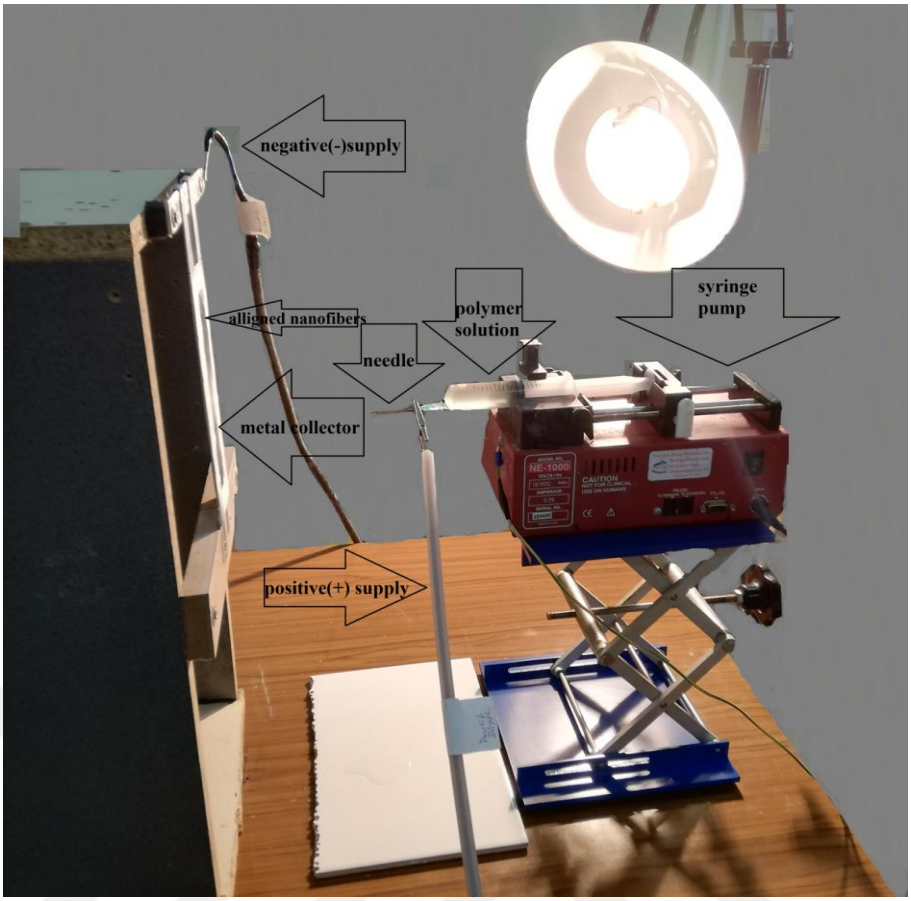


Figure 3.4 The schematic diagram of the parallel electrode electrospinning

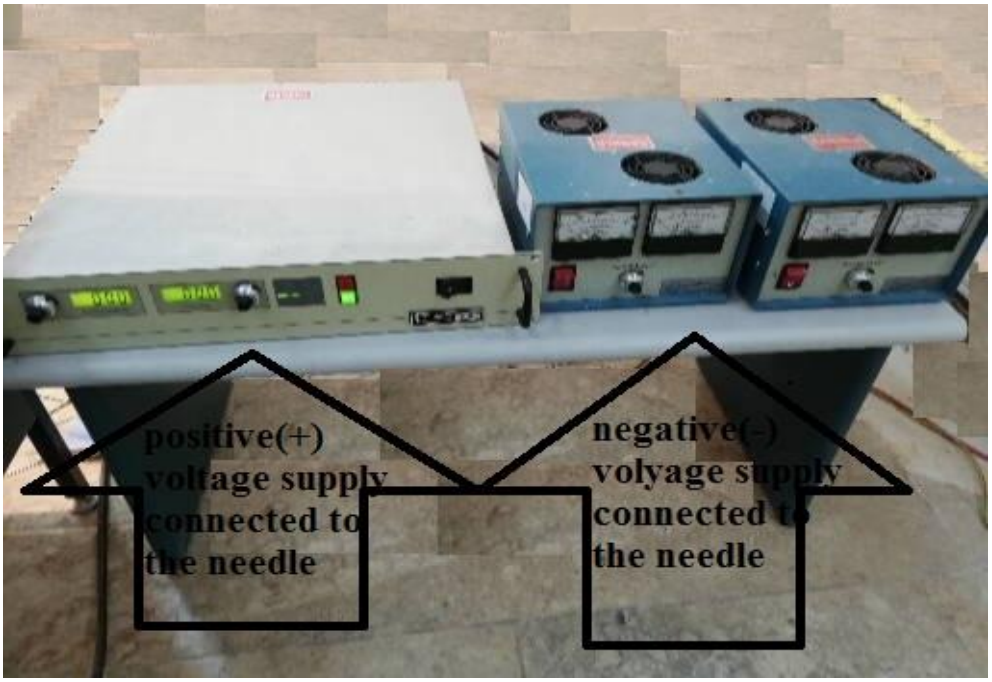


Figure 3.5 High voltage power supplier

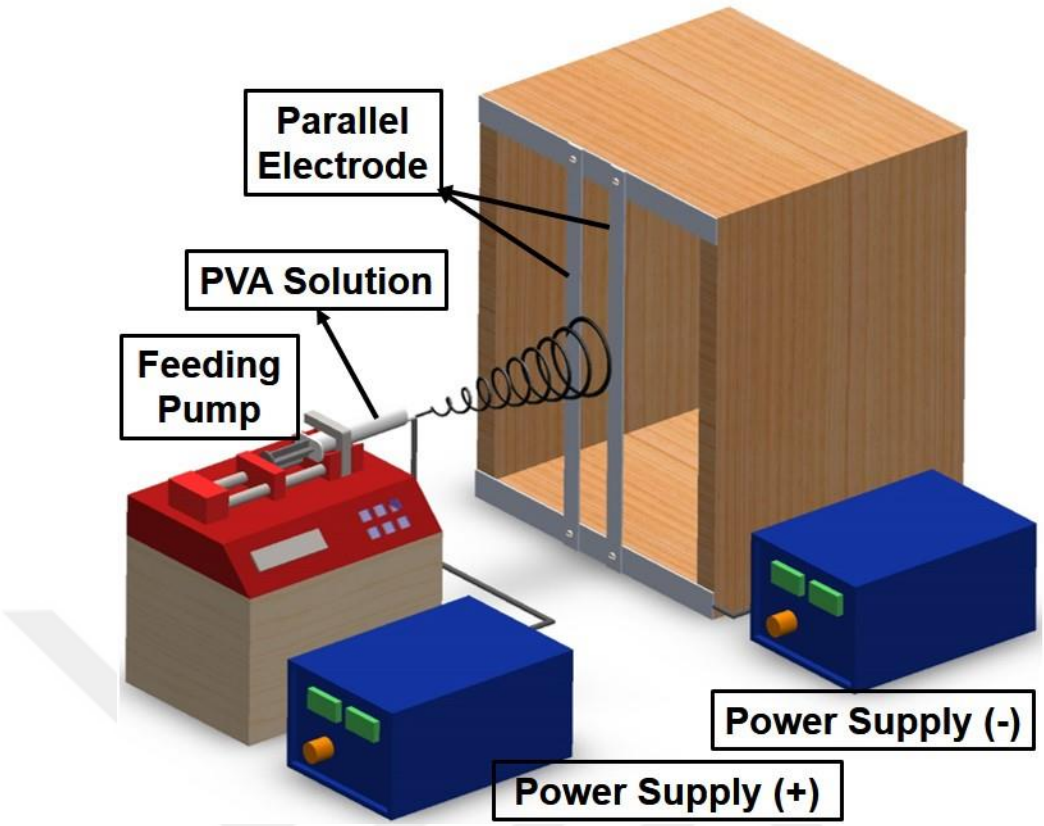


Figure 3.6 Schematic illustration of electrospinning

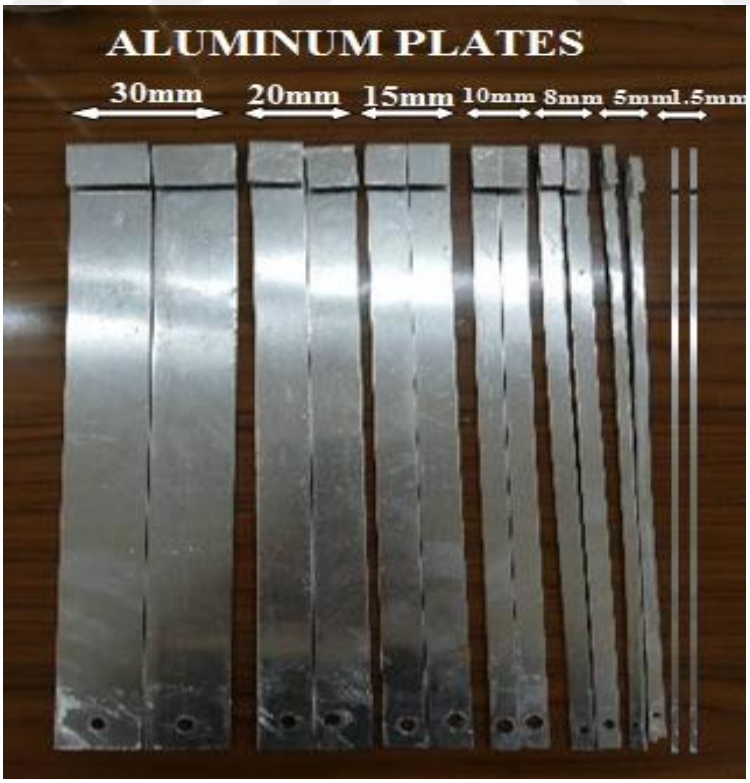


Figure 3.7 Aluminum plates that used as parallel collector.

Aluminum plates with different widths were used as parallel electrode collectors in the electrospinning set up (Figure 3.7).

3.2.2.2 PAN Nanofiber Production

The PAN/DMF (12 wt %) solution was loaded into a 20 ml syringe. The needle inner diameter and the solution flow rate were selected as 0.51 mm and 15 μl/min, respectively. Also in production of PAN nanofibers ambient temperature and relative humidity were constant as 25 °C and 40%, respectively. 3 different studies were performed. In study I, effect of electrode parameters such as gap distance and plate width on nanofiber alignment were investigated. In study II and III, charge density and TCD were examined, respectively. The investigated parameters were given in Table 3.1.

Table 3.1 Production process table for PAN polymer

Group No	Charge Density (kV/cm)	TCD (cm)	Gap Distance (cm)	Plate Width (mm)
Study-I	1.5	15	1-2-3-4-5	1.5-5-8-10-15-20-30
Study-II	1-1.5-2-2.5-3	15	1	20
			2	15
Study-III	1.5	9-12-15-18-21	1	20
			2	15

Figure 3.8 shows fabrication of PAN nanofibers with 1.5 mm plate width for 1cm, 2 cm, 3 cm, 4 cm, 5 cm GAP distances.

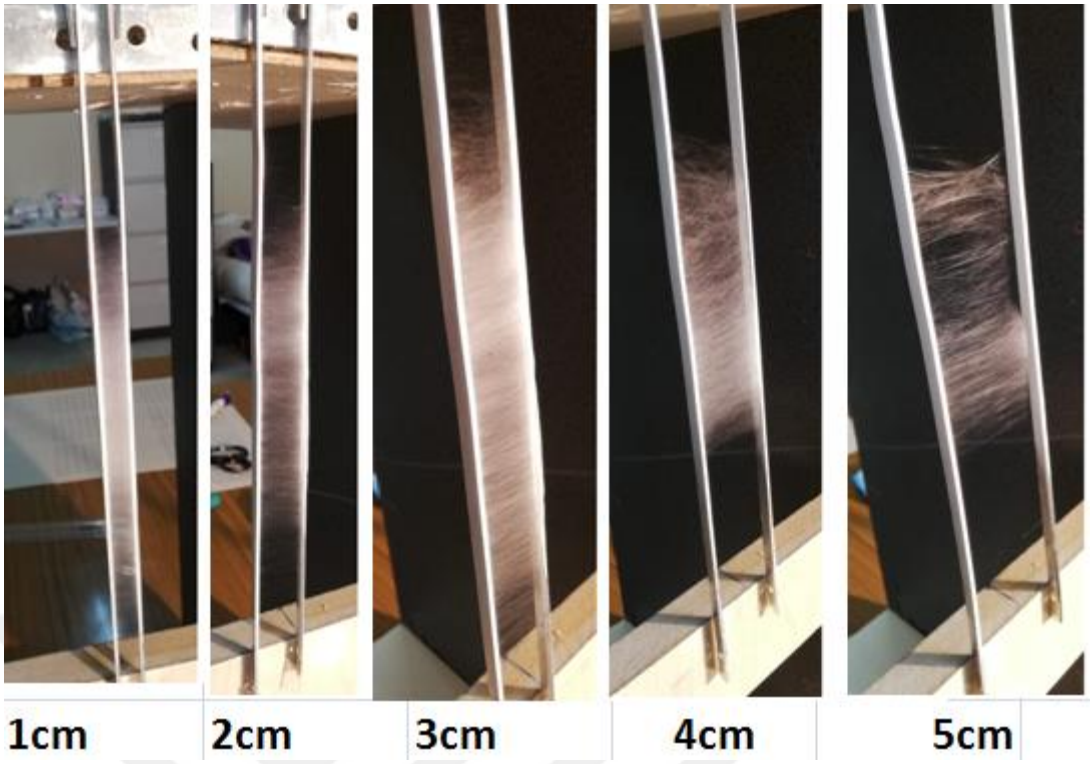


Figure 3.8 Nanofiber fabrication for 1.5 mm plate width

3.2.2.3 PVA Nanofiber Production

The PVA/distilled water (10 wt %) solution was loaded into a 20 ml syringe. The needle inner diameter and the solution flow rate were selected as 0.51 mm and 15 µl/min, respectively. Also in production of PVA nanofibers ambient temperature and relative humidity were constant as 25 °C and 40%, respectively. 3 different studies were performed. In study I, effect of electrode parameters such as gap distance and plate width on nanofiber alignment were investigated. In study II and III, charge density and TCD were examined, respectively. The investigated parameters were given in Table 3.2.

Table 3.2 Production process table for PVA polymer

Group No	Charge Density (kV/cm)	TCD (cm)	Gap Distance (cm)	Plate Width (mm)
Study-I	2	15	1-2-3-4-5	1.5-5-8-10-15-20-30
Study-II	1-1.5-2-2.5-3	15	3	20
			4	15
Study-III	2	9-12-15-18-21	3	20
			4	15

3.2.3 Nanofiber Characterization

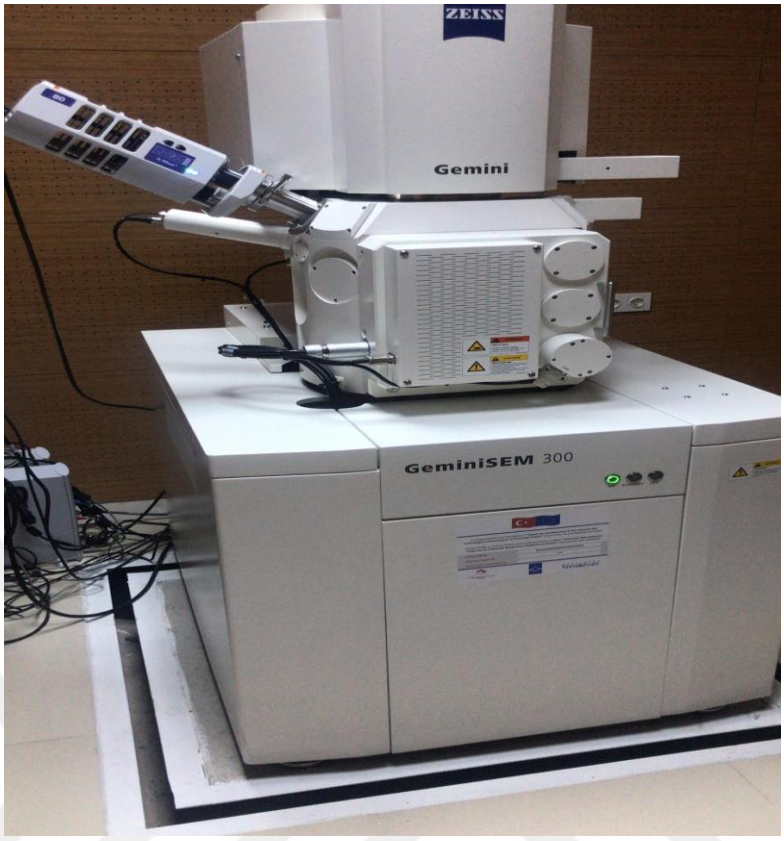


Figure 3.9 FE-SEM, GeminiSEM 300 (ZEISS, USA)

The micrographs of electrospun nanofibers were taken by using a field-emission scanning electron microscope (FE-SEM, Gemini SEM 300, ZEISS, USA). The morphologies of the PAN and PVA nanofiber mats analyzed at magnification of 10,000X for nanofiber alignment and at 20,000X for average nanofiber diameter.

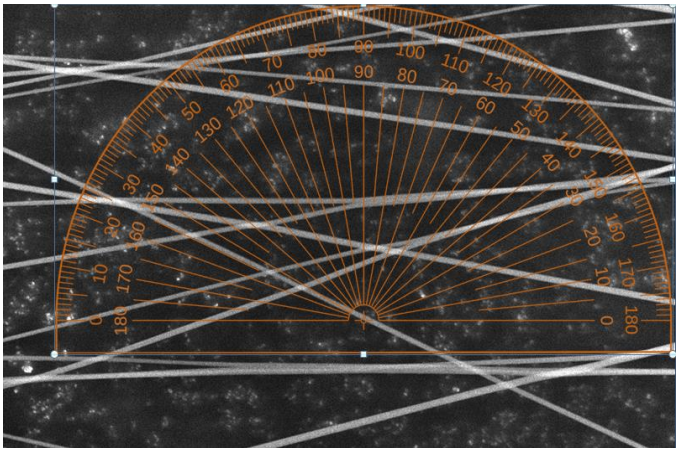


Figure 3.10 Angle measurement of nanofibers

For nanofiber alignment determination, the angle distribution of each nanofiber was measured with a protractor on the Microsoft Office Powerpoint software as given in Figure 3.10. We set a vertical axis from the center, than we recorded as positive angle at the right side fibers and negative angle at the left side fibers. An image processing program (Image J) was used for the measurement of diameters of nanofibers. The average diameters of the nanofibers were determined by taking an average of 40 measurements.

3.2.4 Statistical Analysis

The trial version of SAS JMP® 14 statistical software was used for statistical data analyses. Unequal variances was used to assess the effect of the parameters on the alignment, ANOVA was used to assess the effect of parameters on the average diameter. When the p value is greater than 0.05 it is considered not significant. Results is considered significant when $p<0.05$, very significant when $p<0.01$, highly significant when $p<0.001$ and extremely significant when $p<0.0001$.

CHAPTER IV
RESULT AND DISCUSSION

In this chapter, the effect of the electrospinning parameters on the resultant nanofiber mats alignment and diameter was reported and discussed. Distance between conducting collectors allows stretching of spinning jets and the self-alignment of nanofibers because of magnetic field line occur both edges of the conducting collectors. However, the difference of this thesis from the previous studies about gap method is comparable four parameters at the same time.

4.1 Results of Polyacrylonitrile (PAN) Nanofiber Study

4.1.1 Results of Solution Properties

Viscosity, surface tension and conductivity of PAN/DMF solution (12 wt %) were approximately 1635 cP, 34.01 mN/m and 96.3 μS/cm at 25°C, respectively.

4.1.2 The Results of Gap Distance and Plate width Study (Study-I)

Nanofibers were successfully collected between the parallel aluminum plates using the gap method for all parameter combinations except for 5 cm gap distance with 30 mm plate width. 34 different samples were electrospun for each parameter of gap distances and plate widths. We kept constant the TCD as 15 cm and voltage as 1.5 kV. All SEM micrographs were processed and compared for gap distance of 1 cm, 2 cm, 3 cm, 4 cm and 5 cm with plate widths of 1.5 mm, 5 mm, 8 mm, 10 mm, 15 mm, 20 mm and 30 mm. Figure 4.1 shows SEM micrographs of electrospun PAN nanofibers according to gap distance and plate width at 10,000X magnification (CD: 1.5 kV/cm, TCD: 15 cm) and we measured the angles from these images. Diameter of nanofibers was measured from the images at 20,000X magnification.

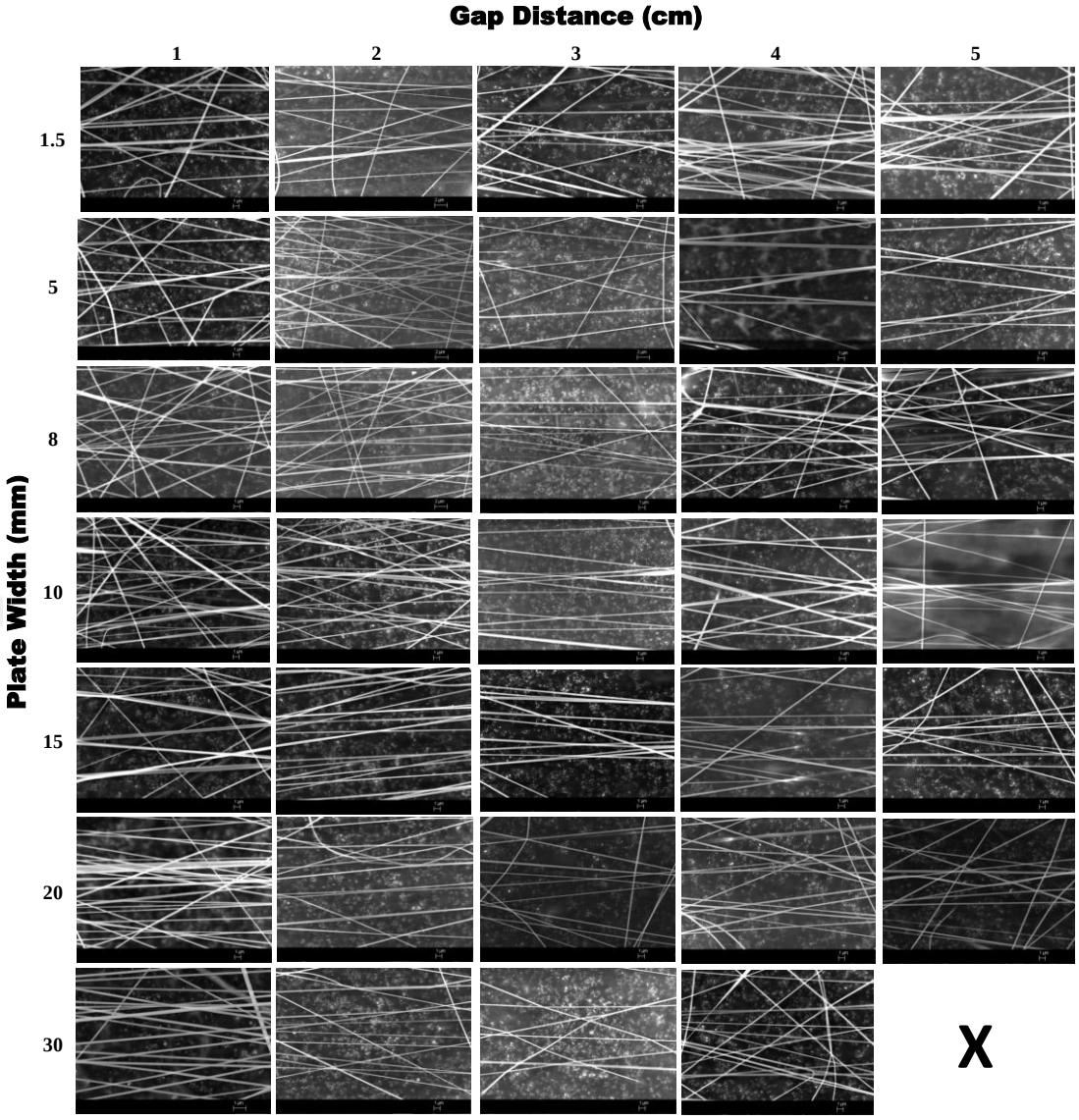


Figure 4.1 SEM micrographs of electrospun PAN nanofibers

4.1.2.1 Nanofiber Alignment Results

At least 30 measurements were taken. The lowest and the highest values were eliminated prior to calculating the average. SEM micrographs of electrospun PAN nanofibers according to gap distance and plate width are shown in Figure 4.1 for 10,000X magnification.

As seen in Figure 4.1, alignment of fibers increased with increasing of gap distance for 1.5 mm plate width (minimum plate width). However, when we started to increase plate width, we saw that the alignment started to increase at lower gap size.

The best alignment can be achieved at narrow plate width with large gap distance or wider plate width with narrow gap distance.

Effect of Gap Distance on the Fiber Alignment: To examine effect of gap distance and plate width on alignment and diameter of the nanofibers, PAN solution was electrospun at five different gap distance (1-5 cm, 1 cm interval) values and seven different plate width (1.5-5-8-10-15-20-30 mm) values. Figure 4.2 and Figure 4.3, given as an example at 15 mm and 20 mm of plate widths, show SEM micrographs and distributions of nanofiber alignment of electrospun PAN nanofibers according to gap distance.

The best alignment formation is obtained 2 cm of gap distance for 15 mm and 20 mm of plate size according to SEM micrographs and angle distribution graphs given in Figure 4.2 and Figure 4.3. It is seen that gap distance affects the alignment of nanofibers however there is no obvious relationship between gap distance and plate size for 15 mm and 20 mm of plate width. Distributions of nanofiber alignment of electrospun PAN nanofibers according to gap distance for the other plate width values are given in Figure 4.4. According to Figure 4.4, the effect of gap distance on nanofiber alignment differs at different plate width values. For example, alignment degrees of nanofibers at 1 cm gap distance values are generally lower for all of the plate size values than that of 2 cm and 3 cm of gap distance values. Best result is shown for 3 cm gap distance with 10 mm plate size. Statistical analysis results show the effect of gap distance on the alignment is statistically insignificant ($p = .1725 > .05$)

Figure 4.2 shows SEM micrographs and distributions of nanofiber alignment of electrospun PAN nanofibers according to gap distance plate width as 15 mm, charge density as 1.5 kV/cm and TCD as 15 cm. Figure 4.3 SEM micrographs and distributions of nanofiber alignment of electrospun PAN nanofibers according to gap distance (Plate width: 20 mm, CD: 1.5 kV/cm, TCD: 15 cm). Figure 4.4 shows distributions of nanofiber alignment of electrospun PAN nanofibers according to gap distance for different plate width values. A: 1.5 mm, B: 5 mm, C: 8 mm, D: 10 mm, E: 15 mm, F: 20 mm, G: 30 mm.

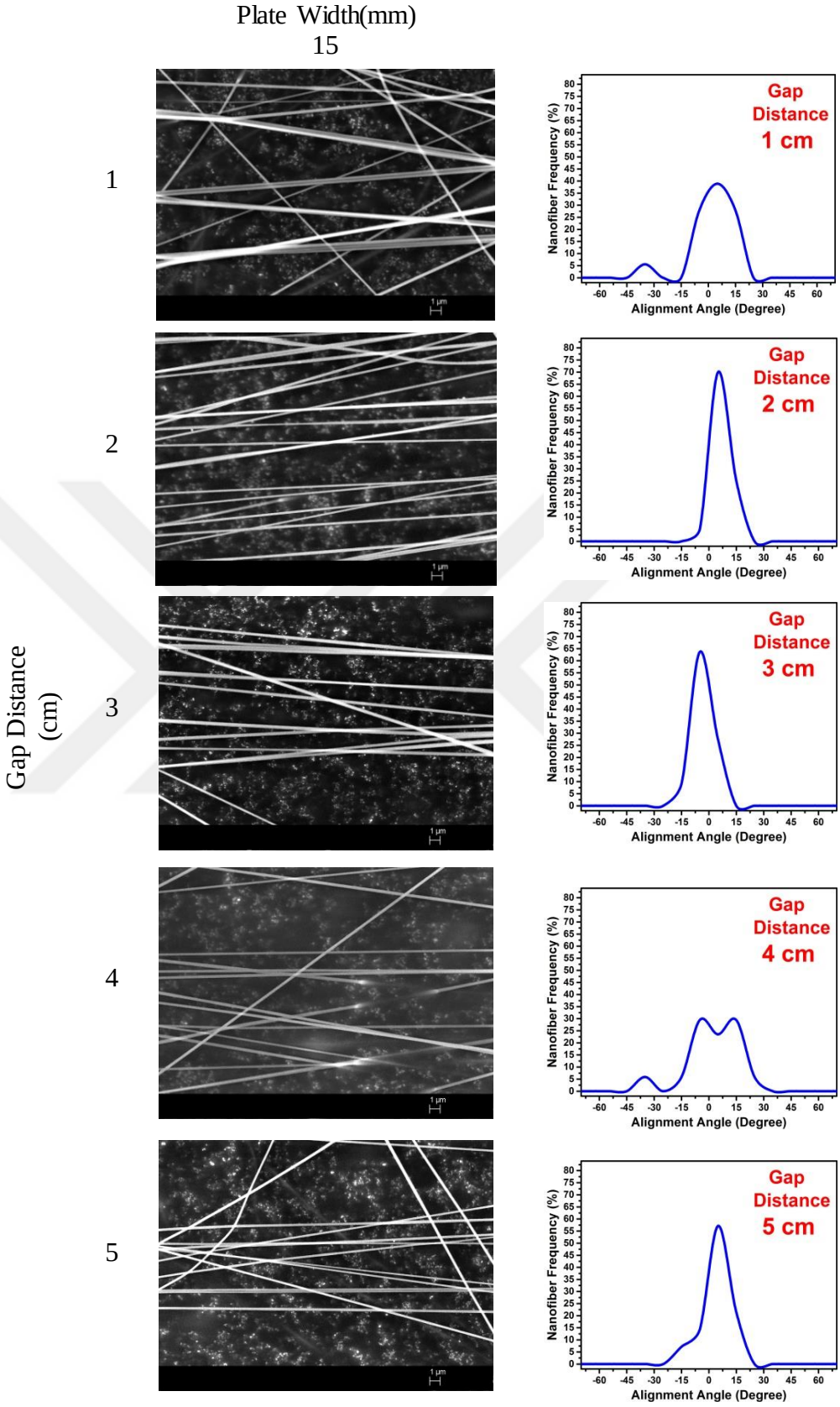


Figure 4.2 SEM micrographs and distributions of nanofiber for 15 mm plate width.

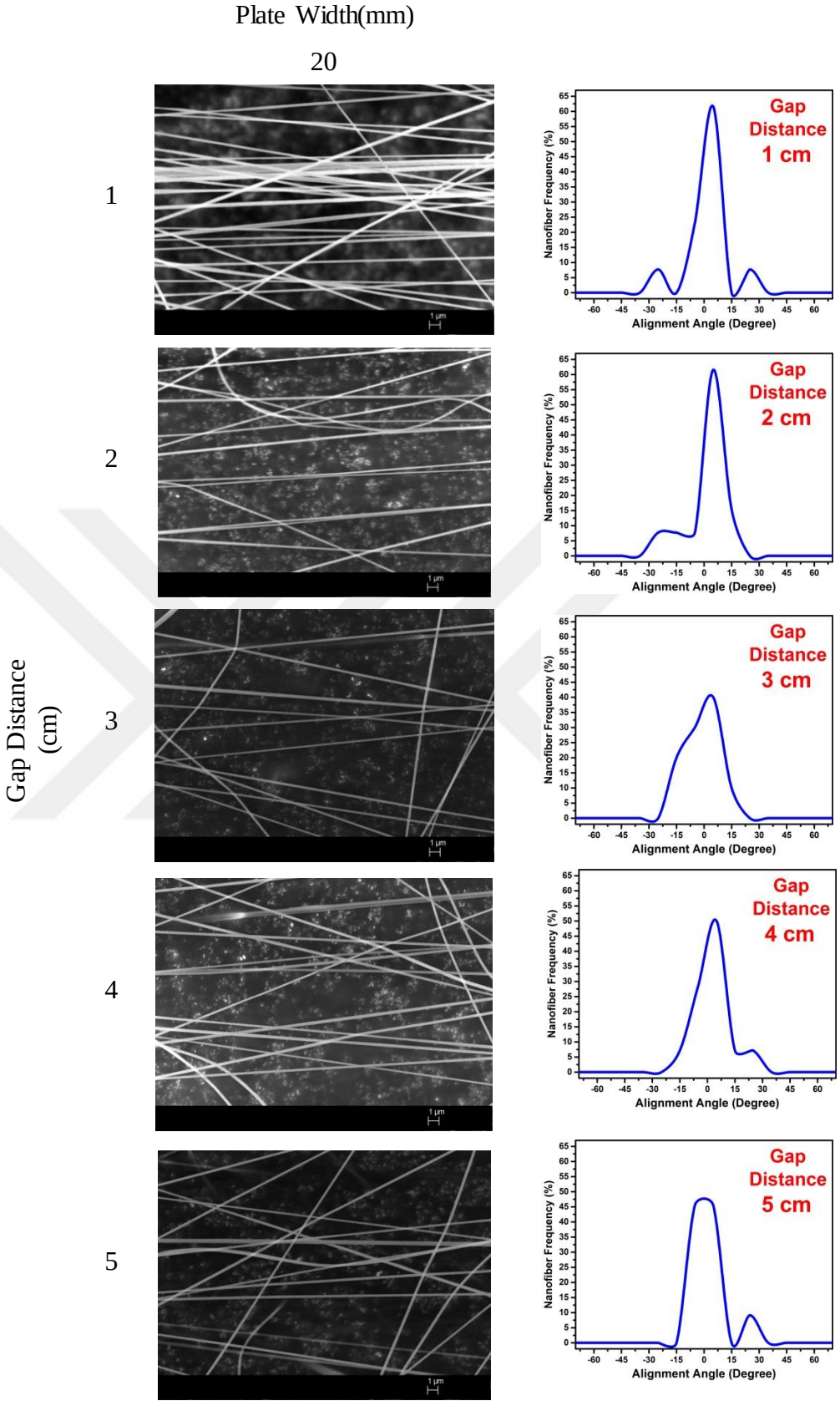


Figure 4.3 SEM micrographs and distributions of nanofiber for 20 mm plate width.

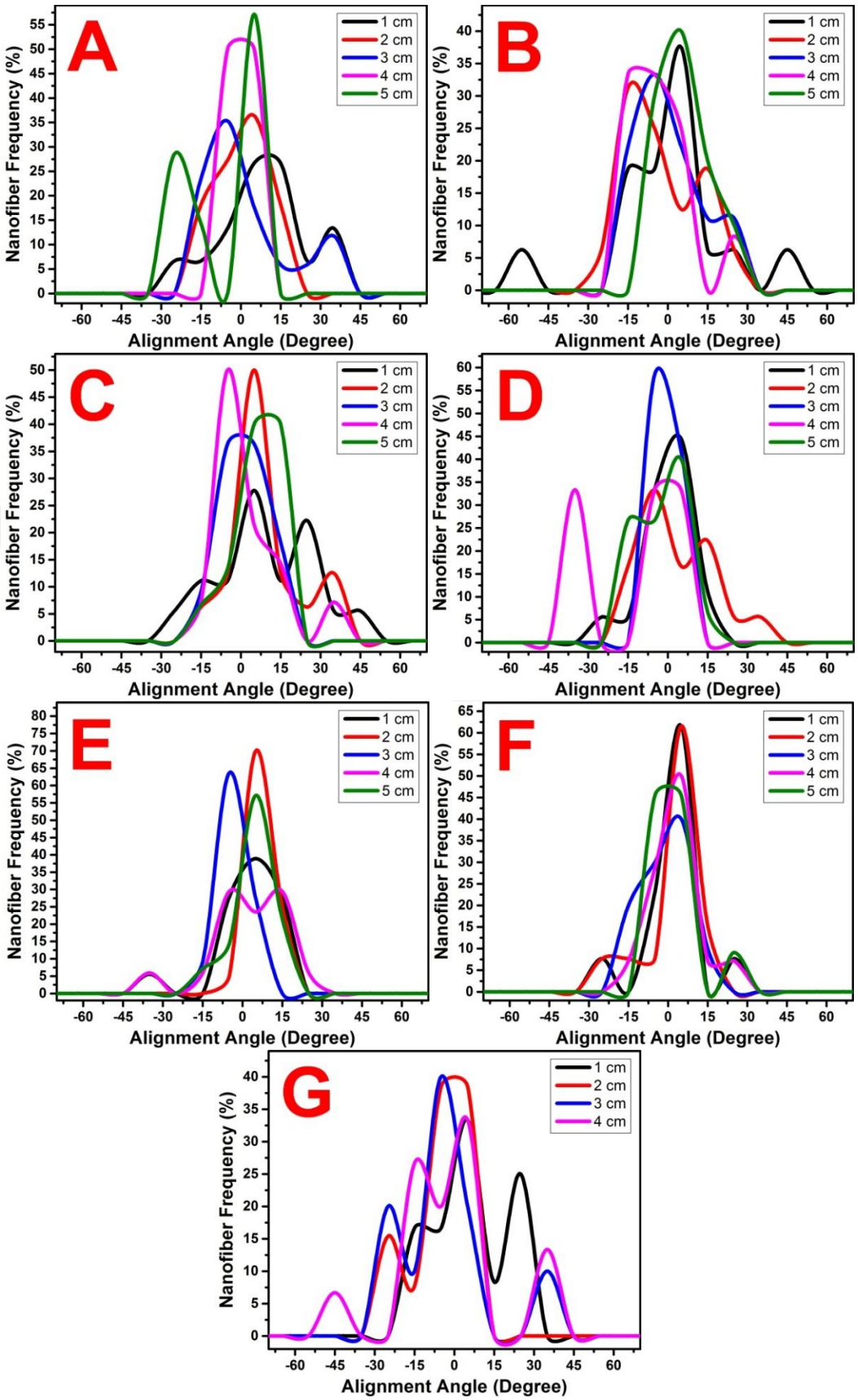


Figure 4.4 Distributions of nanofiber alignment for all plate sizes.

Effect of plate width on the fiber alignment: Interaction between plate width and alignment of PAN nanofibers was found to be statistically insignificant Statistical analysis results show the effect of plate width on the alignment is statistically insignificant ($p = .0649 > .05$) according to unequal variances results. Figure 4.4 shows the effect of gap distance on nanofiber alignment differs at different plate width values. For example, alignment degrees of nanofibers at 1.5 mm and 5 mm of plate width values are generally lower for all of the gap distance values than that of 15 mm and 20 mm of plate width values. Figure 4.5 shows SEM micrographs and distributions of nanofiber alignment of electrospun PAN nanofibers according to plate width (Gap Distance: 2 cm, CD: 1.5 kV/cm, TCD: 15 cm). Figure 4.6 show SEM micrographs and distributions of nanofiber alignment of electrospun PAN nanofibers according to plate width (Gap Distance: 4 cm, CD: 1.5 kV/cm, TCD: 15 cm).

The best alignment formations are obtained 15 mm of plate width for 2 cm of gap distance according Figure 4.5. It can be also seen that increasing of plate width generally increases of the alignment of the nanofibers for 2 cm of gap distance. The best alignment formations are obtained 1.5 mm of plate width for 4 cm of gap distance according Figure 4.6. It can be also seen that increasing of plate width generally decreases of the alignment of the nanofibers for 4 cm of gap distance.

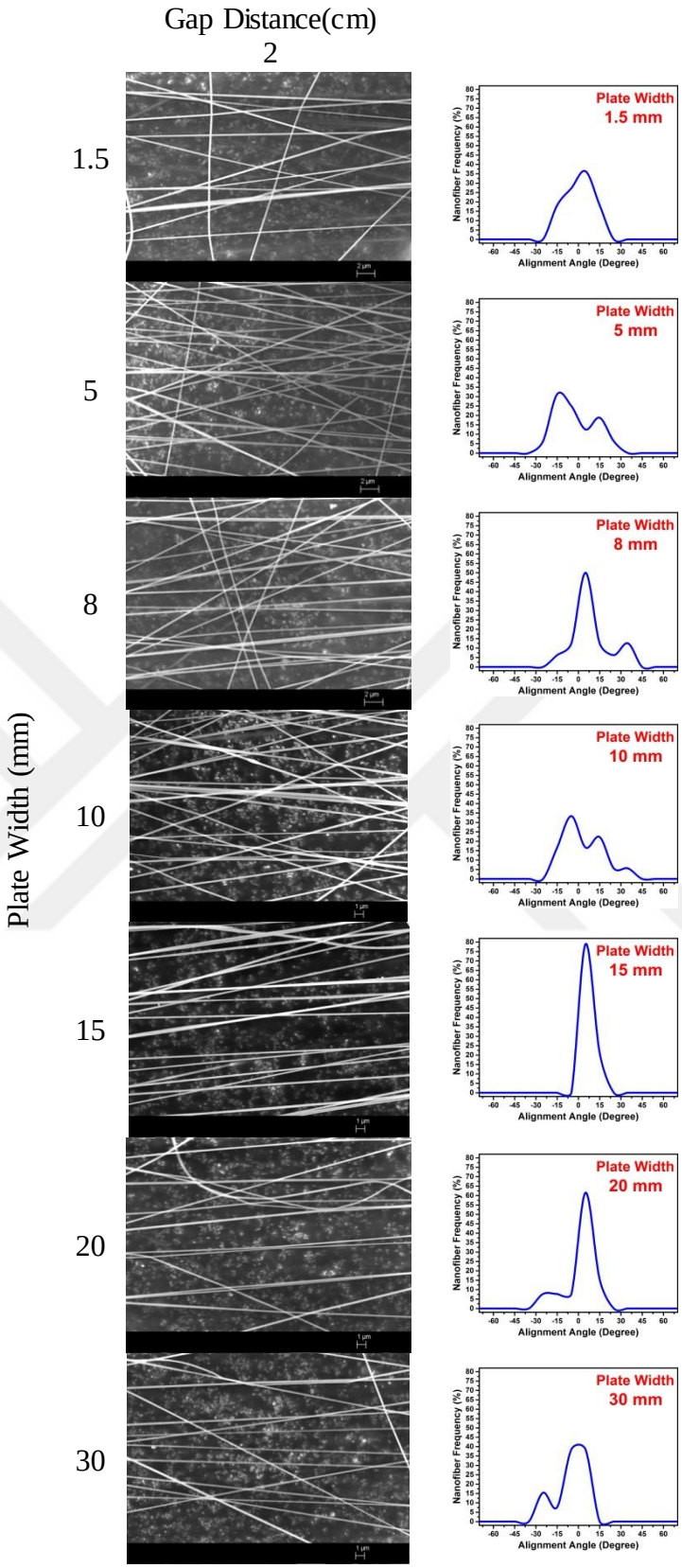


Figure 4.5 SEM micrographs and distributions of nanofibers for 2 cm gap distance.

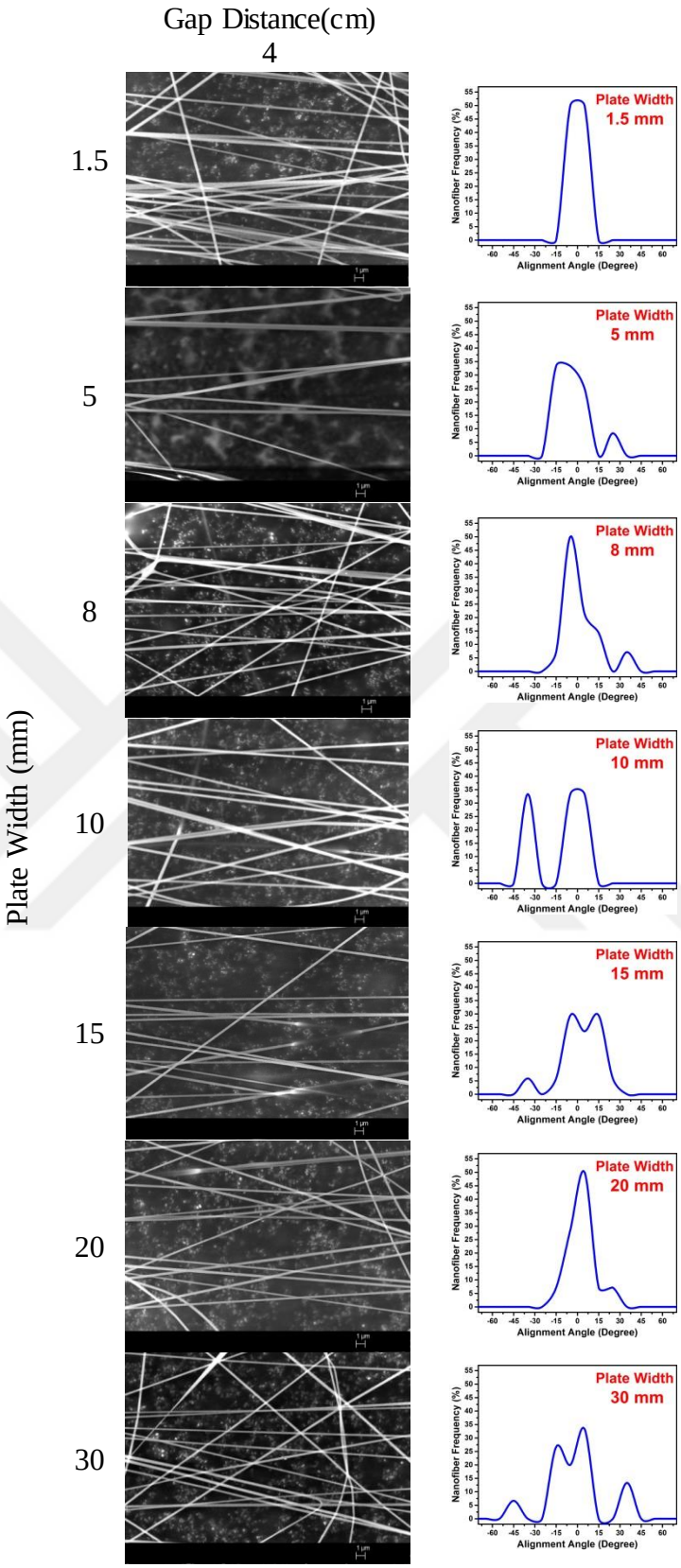


Figure 4.6 SEM micrographs and distributions of nanofibers for 4 cm gap distance.

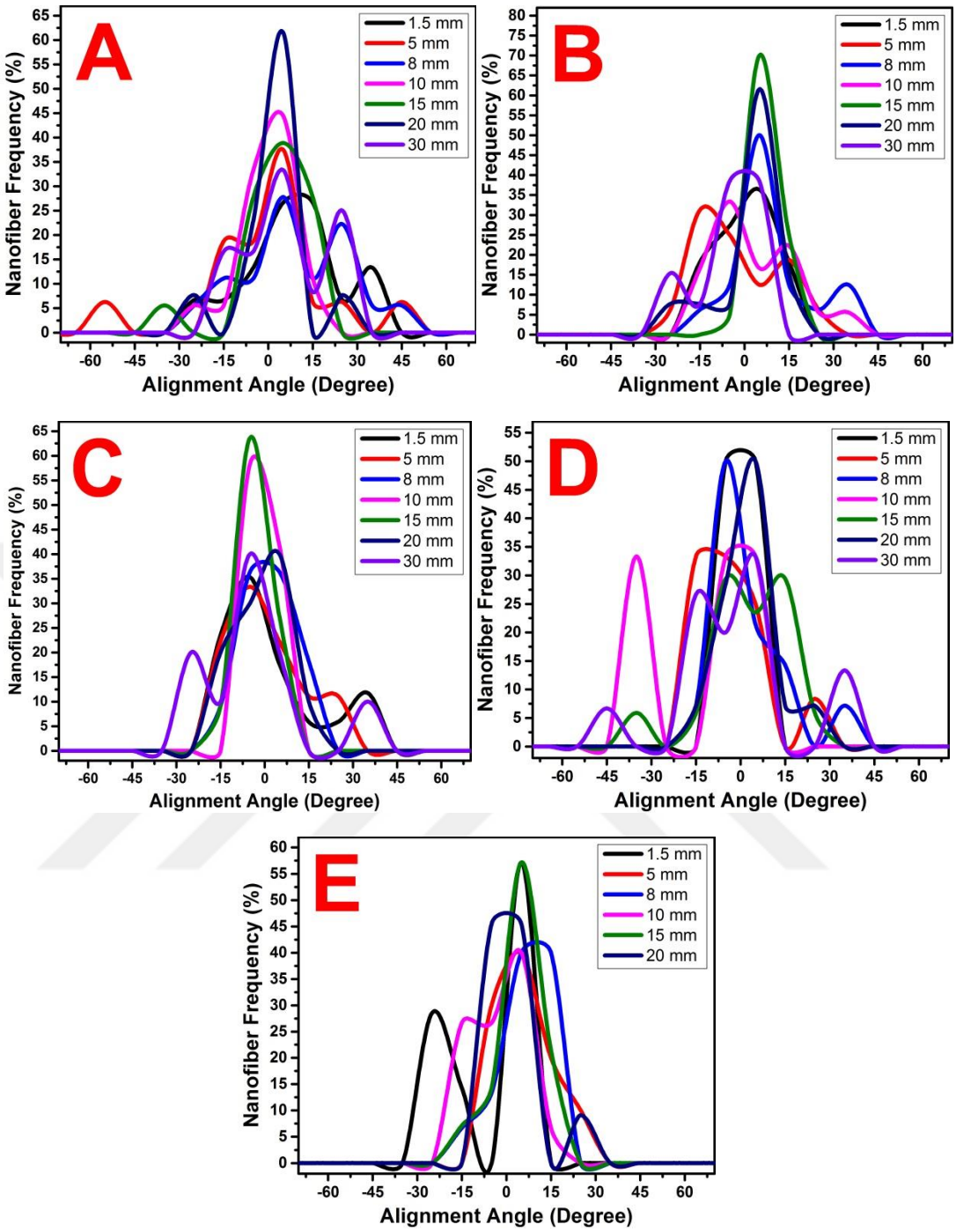


Figure 4.7 Distributions of nanofiber alignment for all gap distances.

Figure 4.7 Distributions of nanofiber alignment of electrospun PAN nanofibers according to plate width for different gap distance values. A: 1 cm, B: 2 cm, C: 3 cm, D: 4 cm, E: 5 cm. According to Figure 4.7, the effect of plate width on nanofiber alignment differs at different gap distance values. Figure 4.7 show that as the plate width increases, alignment of nanofibers increase for 1 cm Gap distance. Best result of nanofiber alignment was examined for 2 cm gap distance with 15 mm plate width.

The reason of various alignments of nanofibers was thought as electric field variation between parallel collectors.

Table 4.1 The angular standard deviations of electrospun PAN nanofibers

Standard Deviation		Plate Width (mm)						
		1.5	**5**	**8**	**10**	**15**	**20**	**30**
Gap Distance (cm)	**1**	15.81	21.72	18.27	10.46	12.51	10.99	15.79
	2	22.35	13.75	18.67	14.02	5.57	9.81	11.13
	3	17.16	12.48	8.60	4.37	6.41	11.26	16.70
	4	6.35	10.63	12.45	18.07	15.00	9.47	18.86
	5	13.98	9.94	8.93	8.91	9.16	18.79	

Table 4.1 shows the angular standard deviations (degree) as a function of the gap distance and plate width for 1.5 kV/cm charge density and 15 cm TCD. It is seen that there is no obvious relationship between the alignment of nanofibers and gap distance generally for all plate widths. Statistical analysis results show the effect of gap distance on the alignment is statistically insignificant ($p = .1725 > .05$). However, alignment of nanofibers regularly increases for 5 mm plate widths. While there is no obvious relationship between the alignment of nanofibers and plate width for 1 cm, 2 cm and 4 cm of gap distance, alignment of nanofibers generally first increases and then decrease for 3 cm and 5 cm gap distances. In the literature, no studies about the effect of plate width on nanofiber alignment were seen. Also, there were different results about the effect of gap distance on the alignment. While some researchers found that increasing of gap distance decreases nanofiber alignment [35,39], the others found the opposite relationship [40,41,42,43]. Moreover, there are some researchers who found that increasing of gap distance firstly increases then decreases nanofiber alignment [44,45]. The reason of the different results seen in those studies may be some differences about polymer type, gap distance values and other process parameters. That reason is more likely that the effect of plate width was not taken into consideration. Because the effect of gap distance on nanofiber alignment are dissimilar at different plate width values according to our results. When all of the angular deviation results are taken into consideration, it is seen that higher alignment degrees are obtained at wider gap distance and plate width values together. A tendency for the increasing orientation angle of nanofibers in relation to

the electrode gap after controlling other factors, but the numbers were not statistically significant. The increase of orientation angle of nanofibers might be caused by the variation of electric field [38]. According to statistical analysis results, while the effect of gap distance on the alignment is not statistically significant ($p > 0.05$), that of plate width on the alignment is statistically significant ($p \leq 0.05$). As the plate width increases, the collector area increases and this may improve the whipping instability of the nanofibers. Thus, the nanofibers may follow a more uniform way between the plates. Similarly, the wider plates have more nanofiber deposition than narrower plates. That may be also related to more stretching of the nanofibers collected on the gap between the parallel electrodes.

4.1.2.2 Nanofiber Diameter Results

In this study, there are 2 variables that are used as a reference to determine the average diameter of nanofibers. Minimum of 20 measurements was taken lowest and highest values were eliminated prior to calculating the average.

Table 4.2 The average PAN nanofiber diameters (nm) and standard deviations

Plate Width (mm)	Gap Distance (cm)				
	1	2	3	4	5
1,5	178 ± 26	180 ± 30	186 ± 27	195 ± 27	259 ± 17
5	218 ± 27	181 ± 26	187 ± 39	196 ± 30	264 ± 23
8	225 ± 43	183 ± 32	188 ± 32	245 ± 35	276 ± 43
10	224 ± 26	193 ± 27	191 ± 17	278 ± 25	217 ± 27
15	215 ± 11	225 ± 27	231 ± 38	225 ± 31	208 ± 35
20	225 ± 22	178 ± 30	219 ± 16	222 ± 30	224 ± 43
30	200 ± 30	169 ± 21	192 ± 16	218 ± 25	0 ± 0

The average PAN nanofiber diameters (nm) and standard deviations as a function of the gap distance and plate width (CD: 1.5 kV/cm, TCD: 15 cm) was shown in the Table 4.2. According to Table 4.2, there is no obvious relationship between the average nanofiber diameter and gap distances for all plate widths except 1.5 mm plate width. It shows an increasing diameter trend for 1.5 mm plate width. When we observed the relationship between plate width and average diameter, it is seen that

first increasing and then decreasing of average diameter for all gap distances. Some researchers declared that variations of the distance between two collectors (the width of gap) also influence the diameter of nanofibers. This is possible because of the existence of a horizontal force pulling the fiber. Increasing the distance of two copper collectors, the average diameters of nanofibers decrease [39]. Statistical analysis results show the effect of gap distance on the diameter is statistically significant ($p = .001 < .05$) when it examined alone and effect of plate size on the alignment is statistically insignificant ($p = .4846 > .05$).

4.1.3 The Results of Charge Density Study (Study-II)

It has been known that the effect of the electric field on the spun nanofiber alignment and diameter is extremely important. Figure 4.8 and Figure 4.9 shows SEM micrographs of electrospun PAN nanofibers according to charge density values for 20 mm of plate width / 1 cm of gap distance and 15 mm of plate width / 2 cm of gap distance according to CD values as 1 kV/cm, 1.5 kV/cm, 2 kV/cm, 2.5 kV/cm, 3 kV/cm at TCD: 15 cm. The best alignment formations are obtained the lowest CD for both of the selected gap distance and plate width values according to SEM micrographs given in Figure 4.8 and Figure 4.9. It is obviously seen that increasing of charge density negatively affects the orientation of the nanofibers.

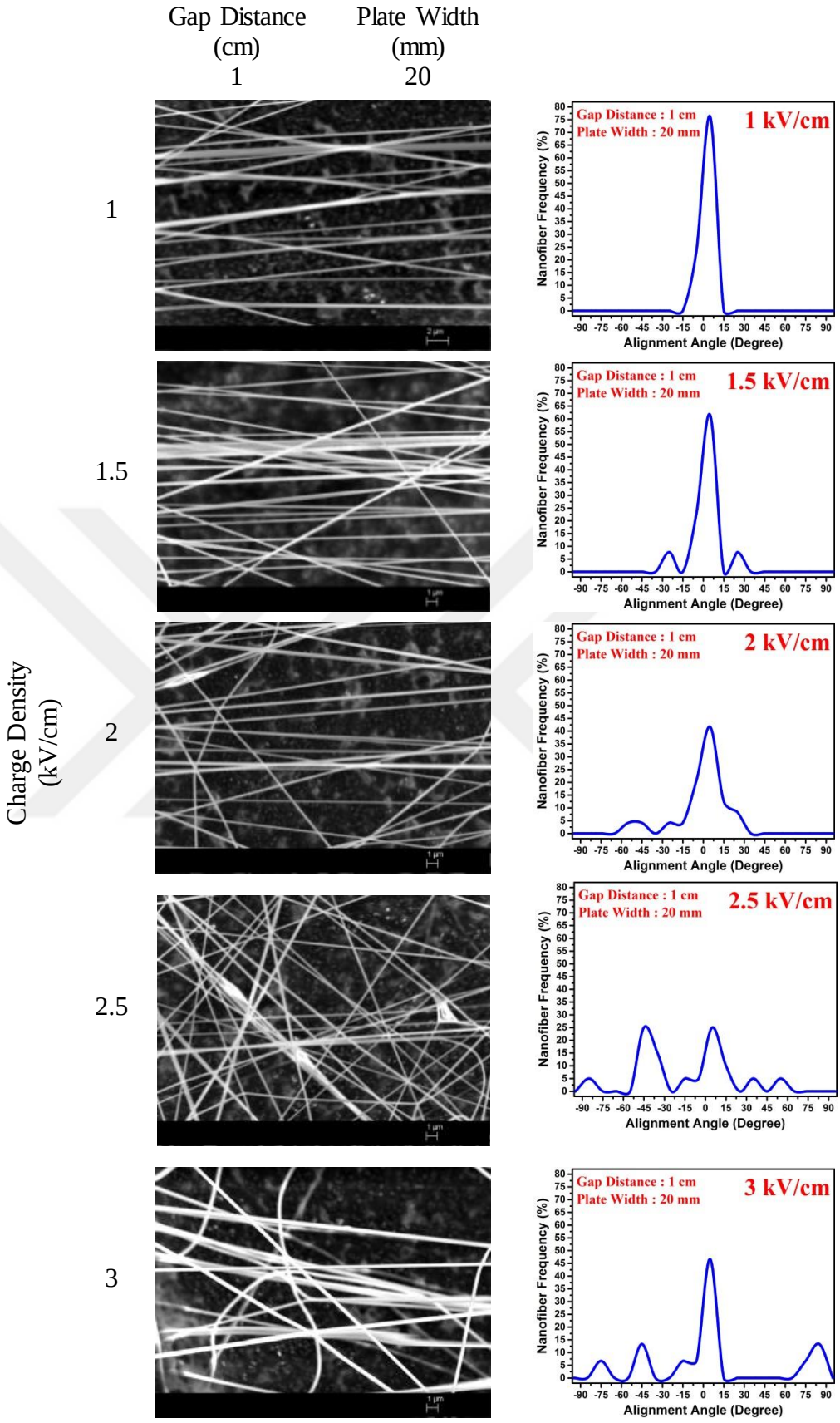


Figure 4.8 SEM micrographs and distributions of nanofibers for 20 mm of plate width / 1 cm of gap distance according to CD values.

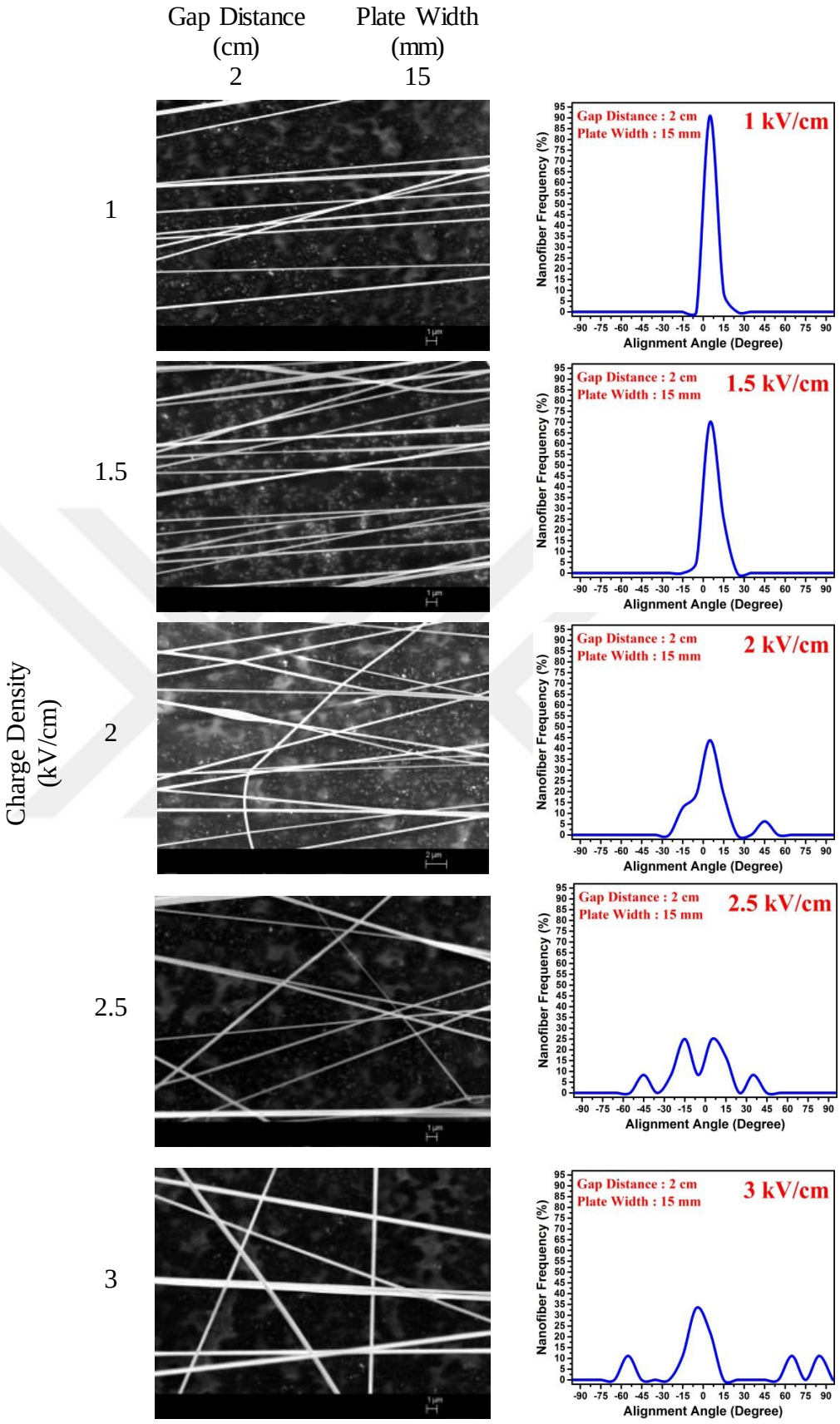


Figure 4.9 SEM micrographs and distributions of nanofibers for 15 mm of plate width / 2 cm of gap distance according to CD values.

4.1.3.1 Nanofiber Alignment Results

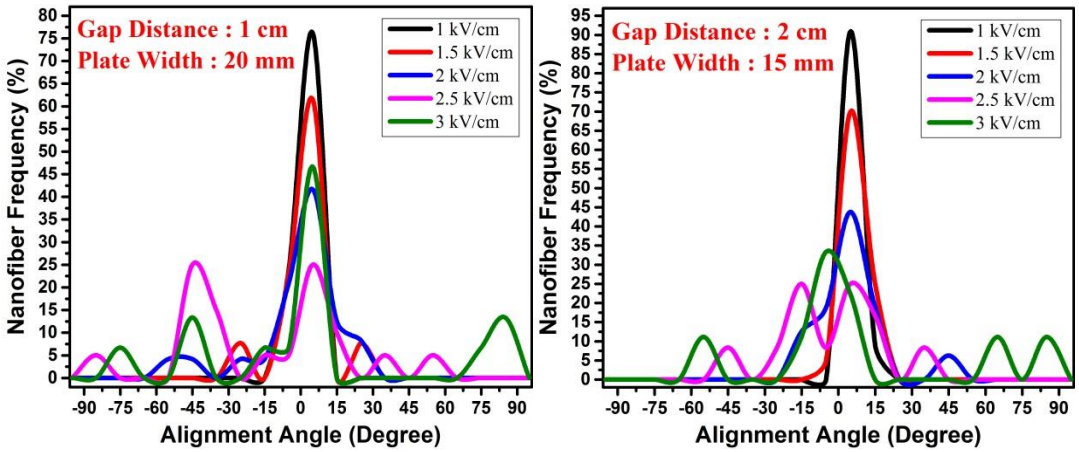


Figure 4.10 Distributions of nanofiber alignment of electrospun PAN nanofibers according to charge density (TCD: 15 cm).

While higher frequencies of nanofiber alignment are seen at lower CD values, lower frequencies of that are seen at higher CD values for both of the selected gap distance and plate width values (Figure 4.10). The angular standard deviation values are given according to CD values for better evaluation on the alignment of electrospun PAN nanofibers. Table 4.3 shows the angular standard deviations of electrospun PAN nanofibers as a function of the charge density.

Table 4.3 The angular standard deviations as a function of CD

Plate Dimension		**Charge Density (kV/cm)**				
Gap D.	**Width**	**1**	**1.5**	**2**	**2.5**	**3**
1cm	**20mm**	5.69	10.99	20.40	33.93	47.79
2cm	**15mm**	4.70	5.16	13.30	23.66	44.62

Table 4.3. shows the angular standard deviations (degree) as a function of CD at 15 cm TCD. It is seen that there is obvious relationship between the alignment of nanofibers and CD for both of the selected gap distance and plate width values. Increasing CD causes decrease in the alignment of nanofibers. According to statistical analysis results, the effect of CD on the alignment is statistically significant ($p = .0001 < .05$) The similar results are seen in the previous studies [38-44]. The applied voltage produces an electrical field between the needle tip and the collector, and that controls strongly the motion of the polymer jet. When applied voltage is

increased, stable motion of the polymer jet is decreased. That may cause to distortion of the nanofiber alignment directly.

4.1.3.2 Nanofiber Diameter Results

SEM measurements of fiber diameter revealed aligned fibers have a smaller diameter than nonaligned nanofibers for voltage variant. Increasing of voltage was decreased the alignment of nanofiber, furthermore it was increased the diameter of nanofibers.

Table 4.4 The average PAN nanofiber diameters (nm) and standard deviations as a function of CD (TCD: 15 cm).

Gap D. (cm)	Plate Width (mm)	CD (kV/cm)				
		1	1.5	2	2,5	3
1	20	220 ± 30	225 ± 22	233 ± 39	240 ± 160	257 ± 16
2	15	201 ± 14	225 ± 27	223 ± 30	314 ± 28	381 ± 101

According to Table 4.4, increasing CD causes increase in the average diameter of nanofibers for both of the selected gap distance and plate width values. Statistical analysis results show the effect of CD on the diameter is statistically significant ($p = .0001 < .05$). When applied voltage at a fixed TCD is increased, the flight time of the polymer jet is decreased [52]. Therefore, less stretching is applied and thicker nanofibers can be obtained. When the flight time is reduced, the solvent in the solution may not completely evaporate, and consequently nanofiber diameters are increased. This is possibly as a result of the stability of the jet due to increased charge density on the surface of the jet, polymer jet velocity and polymer strand elongation forces [56].

4.1.4 The Results of TCD Study (Study-III)

Figure 4.11 and Figure 4.12 shows SEM micrographs of electrospun PAN nanofibers according to tip to collector distance (TCD) values as 9 cm, 12 cm, 15 cm, 18 cm, 21 cm values for 20 mm of plate width / 1 cm of gap distance and 15 mm of plate width / 2 cm of gap distance.

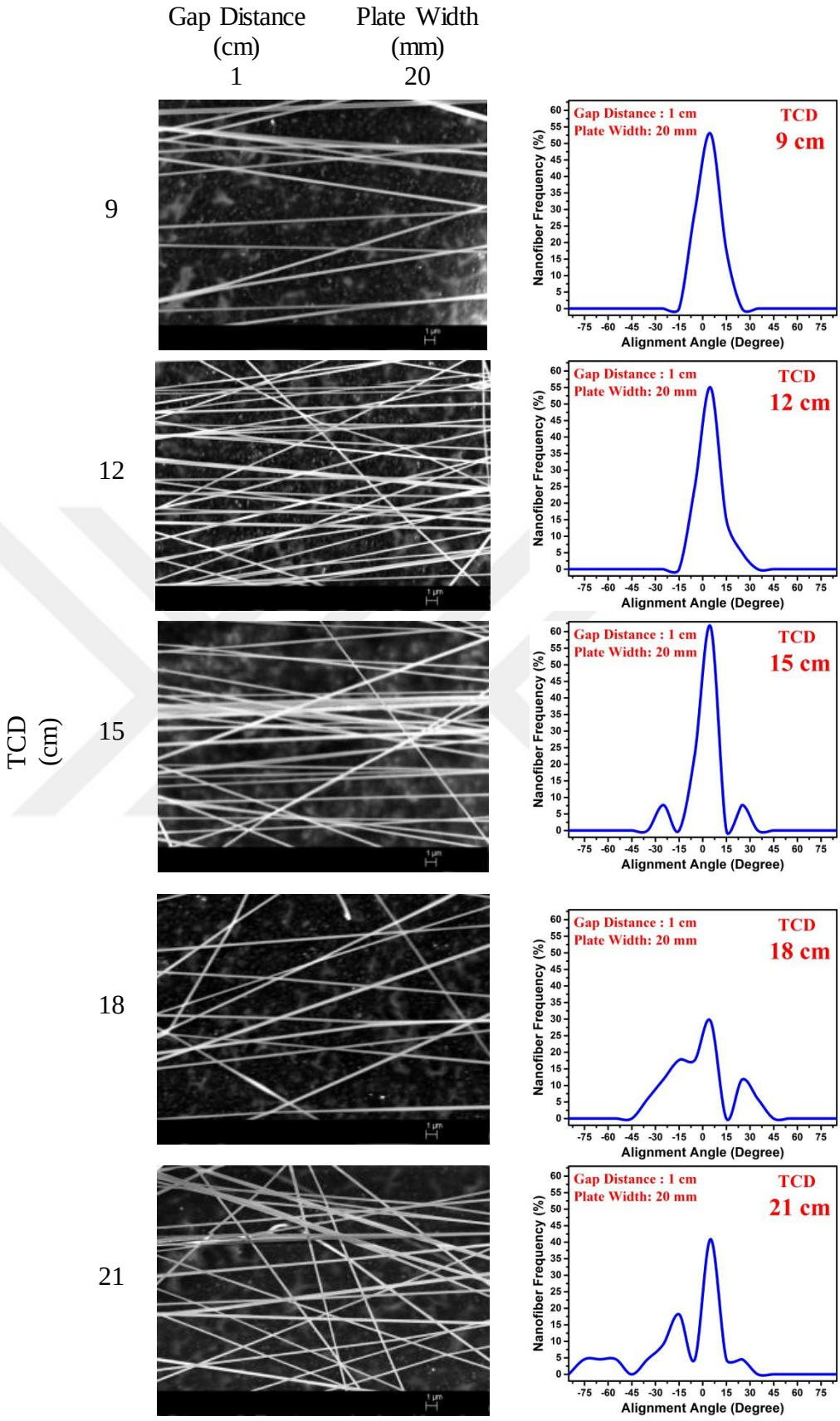


Figure 4.11 SEM micrographs and distributions for 20 mm of plate width / 1 cm of gap distance with all TCD values.

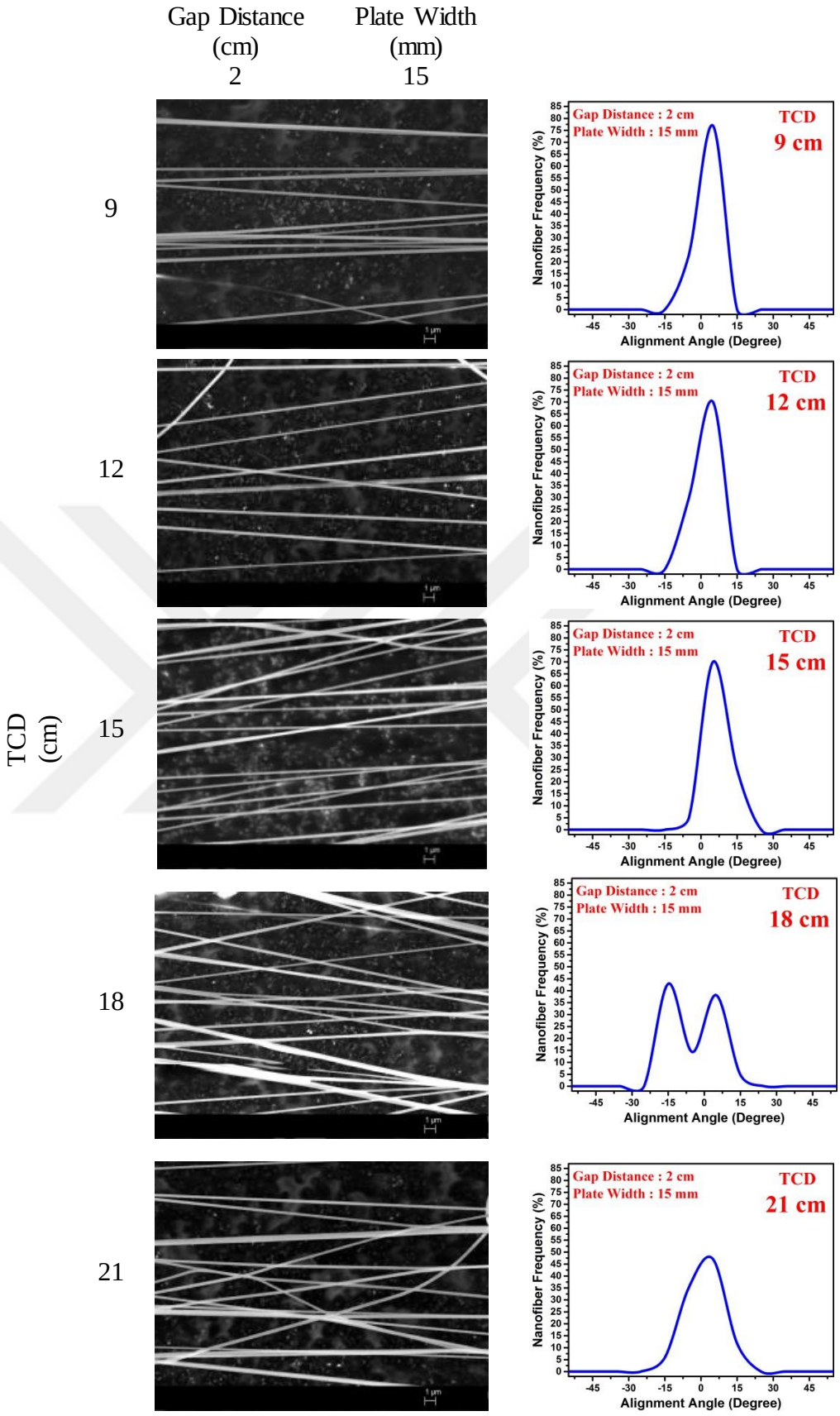


Figure 4. 12 SEM micrographs and distributions 15 mm of plate width / 2 cm of gap distance according with all TCD values.

The best alignment formations are obtained the lowest TCD for both of the selected gap distance and plate width values according to SEM micrographs given in Figure 4.11 and Figure 4.12. It is obviously seen that increasing of tip to collector distance distorts the orientation of the nanofibers.

4.1.4.1 Nanofiber Alignment Results

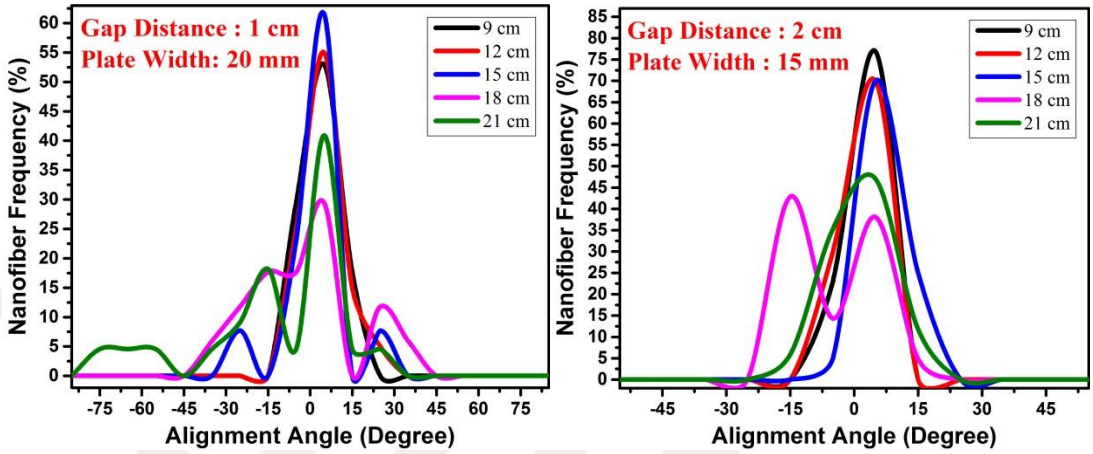


Figure 4.13 Distributions of nanofiber alignment of electrospun PAN nanofibers according to TCD (CD: 1.5 kV/cm).

While higher alignment degrees of the nanofibers are seen at lower TCD values, the lower alignment degrees are seen at higher TCD values for both of the selected gap distance and plate width values (Figure 4.13).

Table 4.5 The angular standard deviations as a function of TCD (CD: 1.5 kV/cm).

Plate Dimension		TCD (cm)				
Gap D.	**Width**	**9**	**12**	**15**	**18**	**21**
1cm	**20mm**	7.32	9.00	10.99	19.51	25.67
2cm	**15mm**	3.48	5.40	5.16	8.69	8.83

The angular standard deviation values are given according to TCD values for better evaluation on the alignment of electrospun PAN nanofibers. Table 4.5 shows the angular standard deviations of electrospun PAN nanofibers as a function of the TCD. It is seen that there is obvious relationship between the alignment of nanofibers and TCD for both of the selected gap distance and plate width values. Increasing TCD causes decrease in the alignment of nanofibers. According to statistical analysis

results, the effect of TCD on the alignment is statistically significant ($p = .0001 < .05$) the similar results are seen in the previous studies [38-46]. When TCD is increased for a fixed charge density, the polymer jet instability is increased due to the longer path of the jet. That may cause to distortion of the nanofiber alignment. This distortion is clearly seen when TCD becomes 21 cm (Table 4.5).

4.1.4.2 Nanofiber Diameter Results

Table 4.6 The average PAN nanofiber diameters (nm) and standard deviations as a function of TCD (CD: 1.5 kV/cm).

Gap Distance (cm)	Plate Width (mm)	TCD (cm)				
		9	12	15	18	21
1	20	246 ± 17	208 ± 21	225 ± 22	253 ± 28	255 ± 68
2	15	244 ± 51	259 ± 32	225 ± 27	168 ± 18	244 ± 37

Table 4.6 shows the average PAN nanofiber diameters and standard deviations as a function of TCD. According to statistical analysis results, the effect of TCD on the alignment is statistically insignificant ($p = .7362 > .05$). This may be related to fixed CD (1.5 kV/cm) applied for all TCD values. That means same electrostatic forces are applied to polymer jets during electrospinning process.

An increase in fiber diameter and a decrease in fiber diameter with increasing spinning distance were reported in the literature. There were also some cases in which spinning distance did not have a significant influence in fiber diameter [56].

4.1.5 Statistical Analysis Results

Gap distance and alignment:

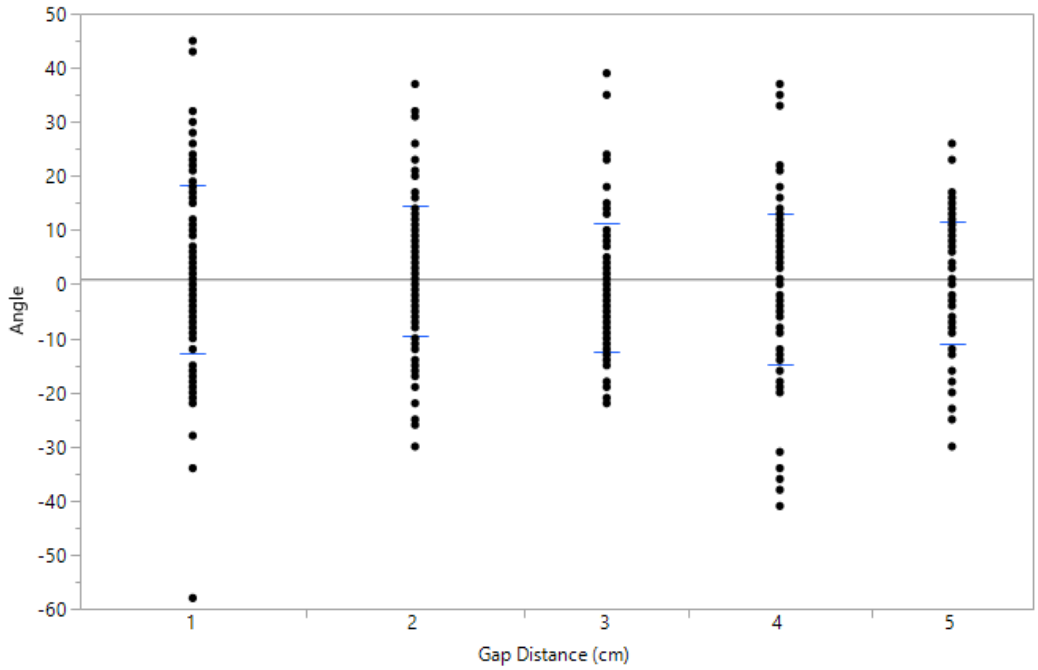


Figure 4.14 Effect of gap distance on angle distribution of PAN nanofiber

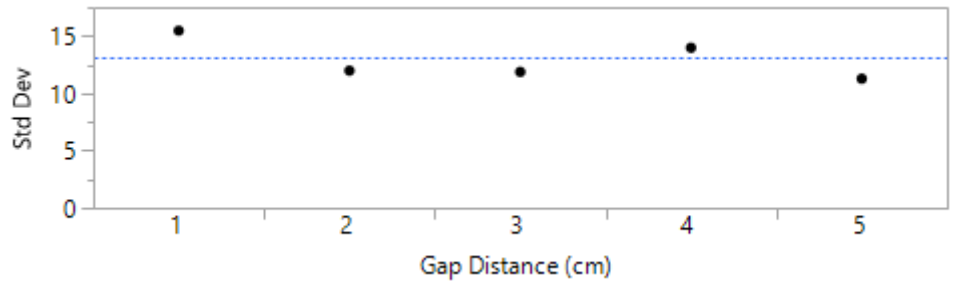


Figure 4.15 Standard deviation of nanofiber angles with variance of gap distance.

Table 4.7 Probability result of the relationship between alignment and gap distance

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1,9555	4	460	0,1003
Brown-Forsythe	1,5663	4	460	0,1822
Levene	1,6027	4	460	0,1725
Bartlett	3,4190	4	.	0,0084*

Figure 4.14 and 4.15 shows the angle distribution and standard deviation of PAN nanofibers for gap distance variance. According to Unequal variances results, interaction between gap distance and angle of nanofibers was found to be statistically insignificant on alignment of PAN nanofibers (p = .1725 > .05) (see Table 4.7).

Gap distance and diameter:

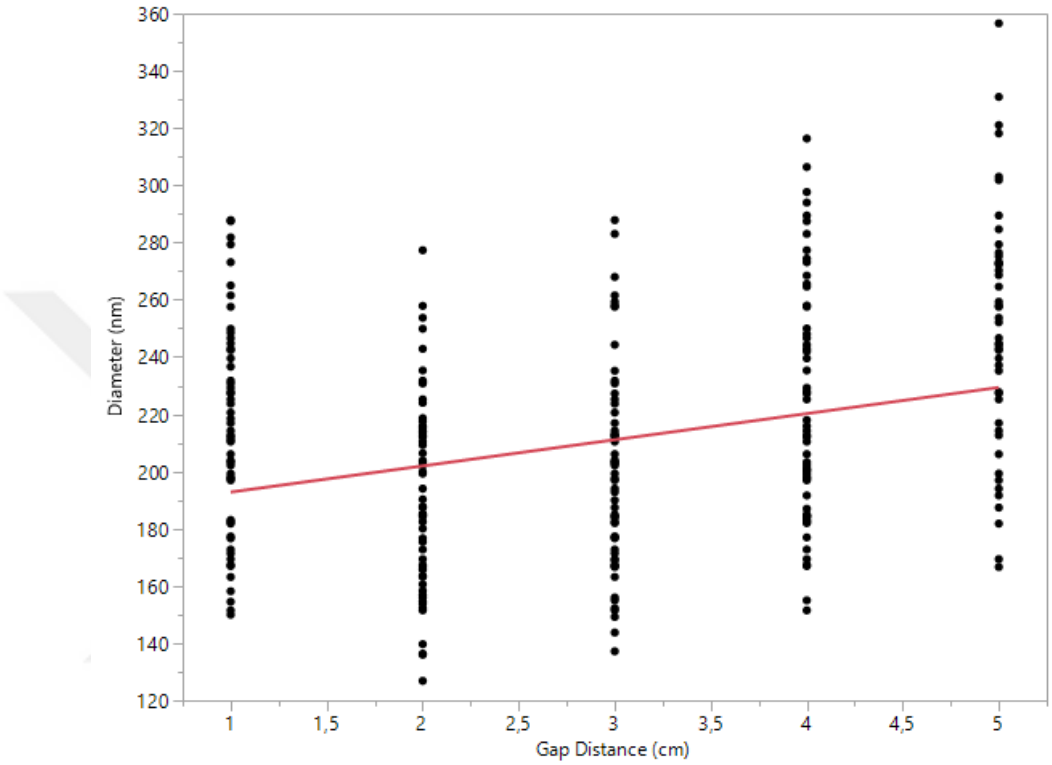


Figure 4.16 Effect of gap distance on diameter of PAN nanofiber

Table 4.8 Probability result of the relationship between diameter and gap distance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	74512,93	74512,9	54,6818
Error	485	660891,68	1362,7	**Prob > F**
C. Total	486	735404,61		<,0001*

Figure 4.16 shows the diameter distribution of PAN nanofibers for gap distance variance. According to ANOVA results, gap distance has a statistically significant effects on diameter of PAN nanofibers (p = .0001 < .05) (see Table 4.8).

Plate width and alignment:

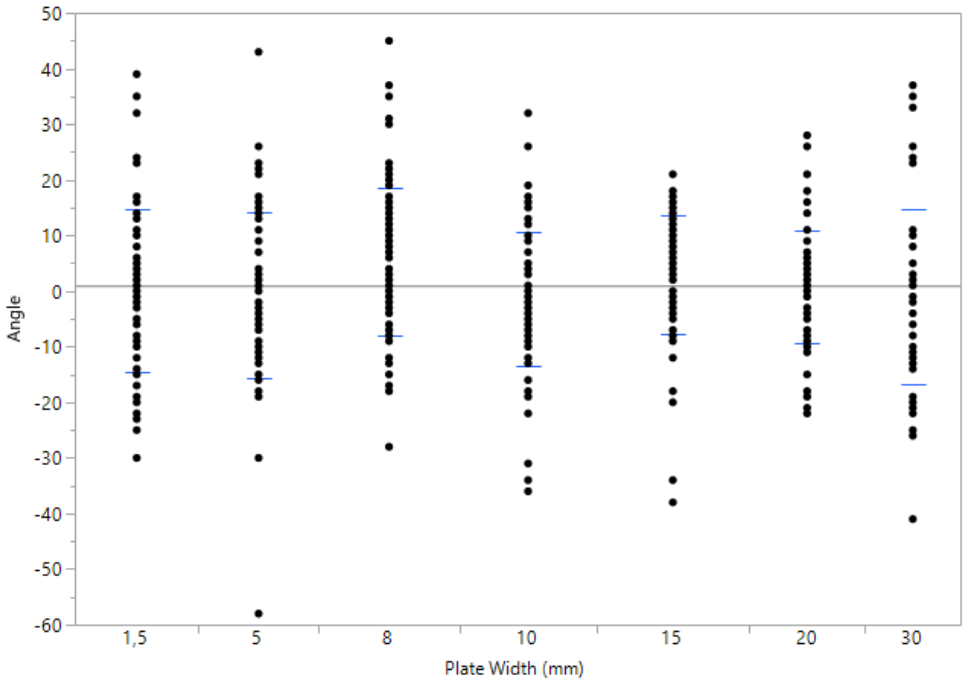


Figure 4.17 Effect of plate width on angle distribution of PAN nanofiber

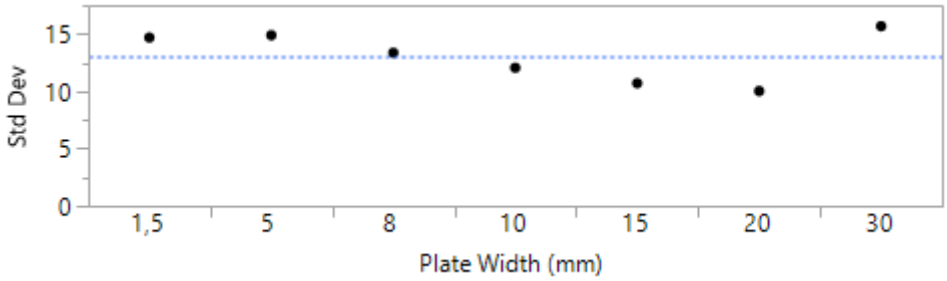


Figure 4.18 Standard deviation for effect of plate width on alignment

Table 4.9 Probability result of the relationship between alignment and plate width.

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1,8500	6	458	0,0879
Brown-Forsythe	1,9303	6	458	0,0744
Levene	1,9958	6	458	0,0649
Bartlett	3,5561	6	.	0,0016*

Figure 4.17 and 4.18 shows the angle distribution and standard deviation of PAN nanofibers for plate width variance. According to Unequal variances results, interaction between plate width and alignment of PAN nanofibers was found to be statistically insignificant (p = .0649 > .05) (see Table 4.9)

Plate width and diameter:

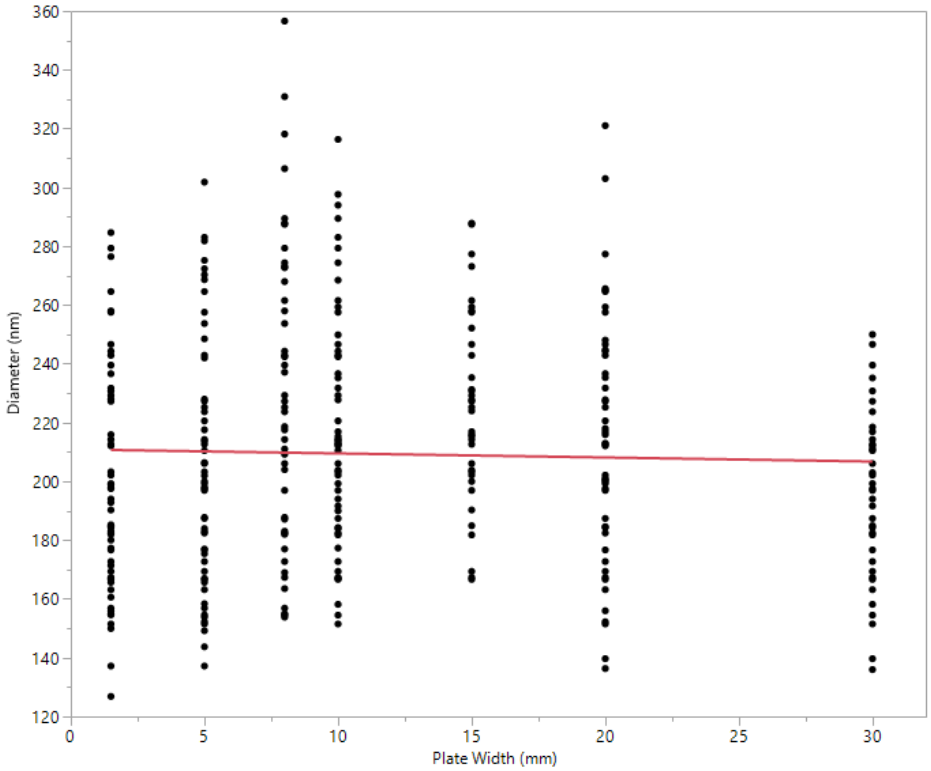


Figure 4.19 Effect of plate width on diameter of PAN nanofiber

Table 4.10 Probability result of the relationship between diameter and plate width

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	741,23	741,23	0,4893
Error	485	734663,38	1514,77	**Prob > F**
C. Total	486	735404,61		0,4846

According to ANOVA results the interaction between plate width and diameter of nanofibers was found to be statistically insignificant effects on diameter of PAN nanofibers (p = .4846 > .05) (see Table 4.10)

Charge density and alignment:

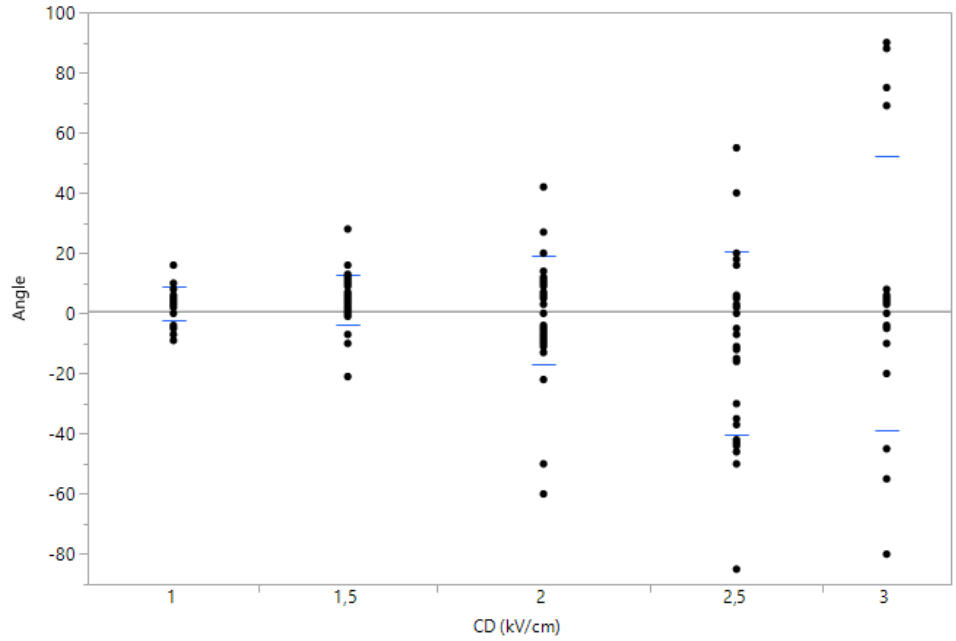


Figure 4.20 Effect of charge density on angle distribution of PAN nanofiber

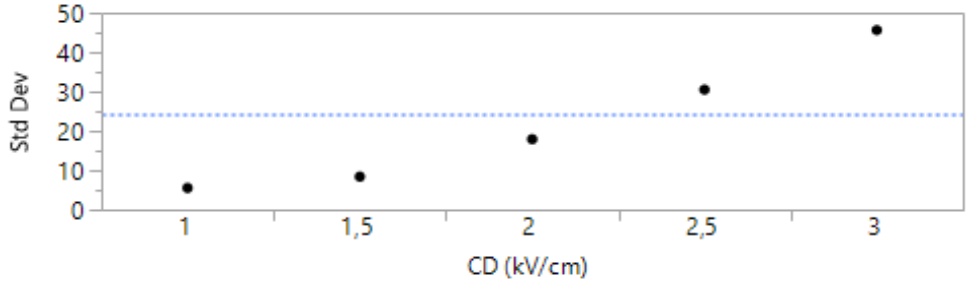


Figure 4.21 Standard deviation of nanofiber angles with variance of charge density.

Table 4.11 Probability result of the relationship between alignment and charge density.

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	11,4674	4	156	<,0001*
Brown-Forsythe	13,3502	4	156	<,0001*
Levene	15,1437	4	156	<,0001*
Bartlett	34,8036	4	.	<,0001*

Figure 4.20 and 4.21 shows the angle distribution and standard deviation of PAN nanofibers for charge density variance. According to Unequal variances results, interaction between charge density and alignment of PAN nanofibers was found to be statistically highly significant (p = .0001 < .05) (see Table 4.11)

Charge density and diameter:

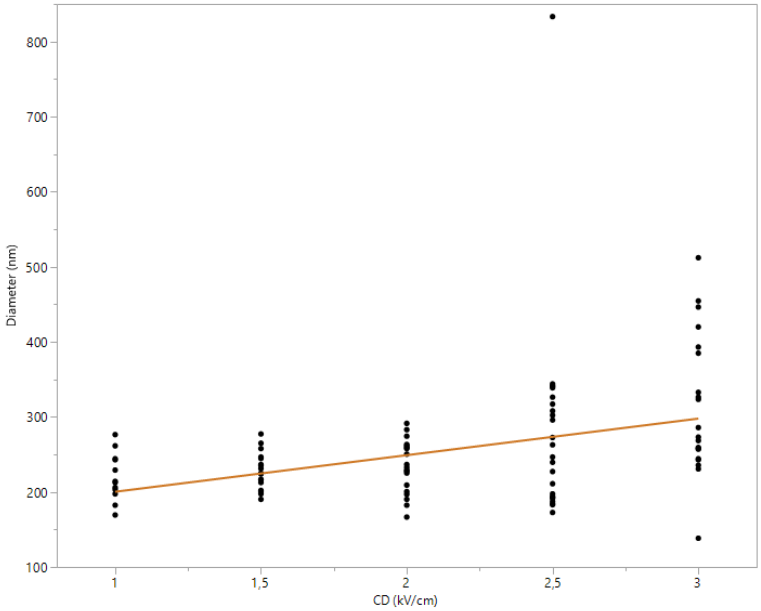


Figure 4.22 Effect of charge density on nanofiber diameter

Table 4.12 Probability result of the relationship between diameter and charge density.

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	138325,35	138325	23,4324
Error	118	696574,01	5903	**Prob > F**
C. Total	119	834899,36		<,0001*

According to ANOVA results the interaction between charge density and diameter of nanofibers was found to be statistically highly significant effects on diameter of PAN nanofibers (p = .0001< .05) (see Table 4.12)

TCD and alignment:

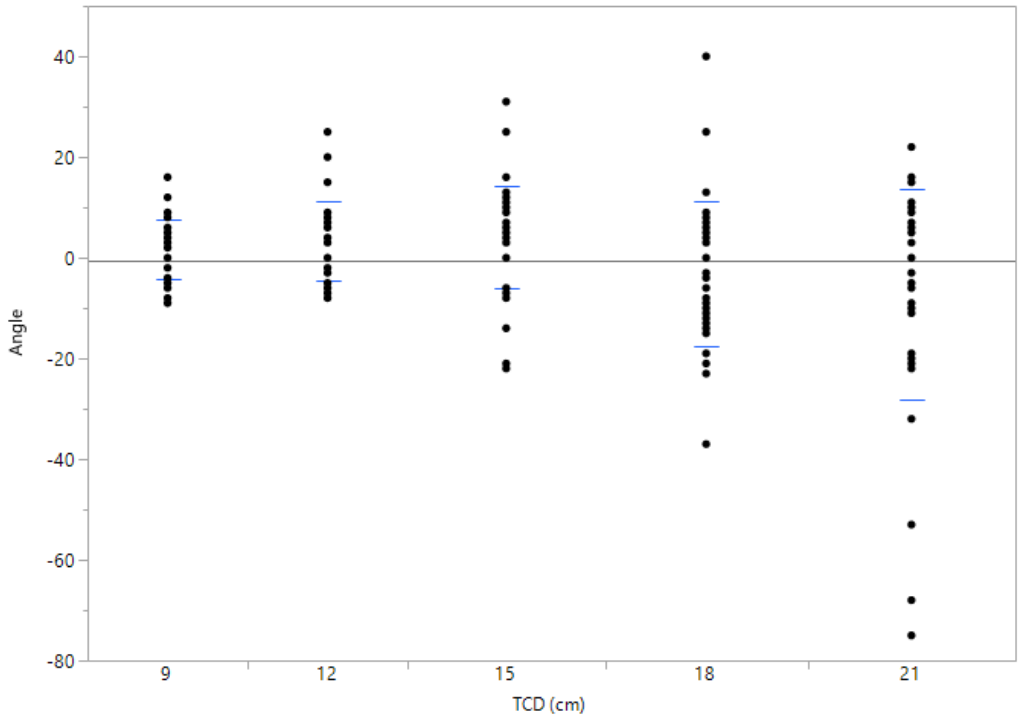


Figure 4.23 Effect of TCD on nanofiber alignment

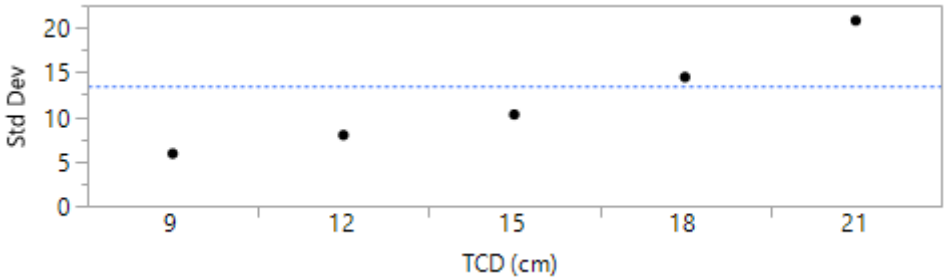


Figure 4.24 Standard deviation for effect TCD on alignment

Table 4.13 Probability result of the relationship between alignment and TCD

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	3,5757	4	169	0,0079*
Brown-Forsythe	4,8327	4	169	0,0010*
Levene	7,4152	4	169	<,0001*
Bartlett	15,0100	4	.	<,0001*

Figure 4.23 and 4.24 show the angle distribution and standard deviation of PAN nanofibers for TCD variance. According to Unequal variances results, interaction between charge density and alignment of PAN nanofibers was found to be statistically highly significant (p = .0001< .05) (see Table 4.13)

TCD and diameter:

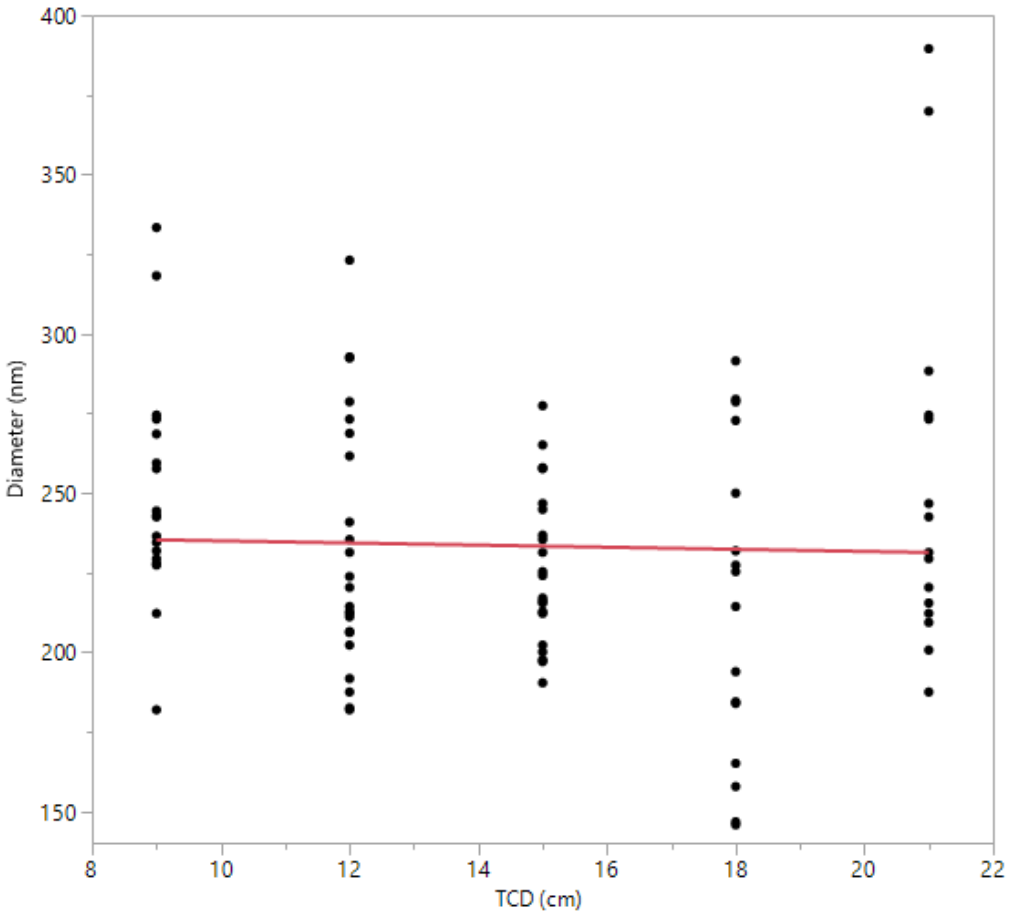


Figure 4.25 Effect of TCD on nanofiber diameter

Table 4.14 Probability result of the relationship between diameter and TCD

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	195,30	195,30	0,1140
Error	114	195271,03	1712,90	**Prob > F**
C. Total	115	195466,34		0,7362

According to ANOVA results the interaction between TCD and diameter of nanofibers was found to be statistically insignificant effects on diameter of PAN nanofibers (p = .7362> .05) (see Table 4.14).

4.2 Results of Polyvinylalcohol (PVA) Nanofiber Study

4.2.1 Result of Solution Properties

Viscosity, surface tension and conductivity of PVA/water solution (10 wt %) were approximately 305 cP, 41.37 mN/m and 858 μS/cm at 25°C, respectively.

4.2.2 The Results of Gap Distance and Plate Width Study (Study-I)

PVA (%10) nanofibers were successfully produced between the parallel aluminum plates using the gap method for all parameter combinations. 35 different samples were electrospun for each parameter of GAP distances and plate widths. We kept constant the TCD as 15 cm and voltage as 2 kV. Each image was processed and compared for collector separations (GAP distance) of 1 cm, 2 cm, 3 cm, 4 cm and 5 cm with plate widths of 1.5 mm, 5 mm, 8 mm, 10 mm, 15 mm, 20 mm and 30 mm using SEM analyzing Software. A minimum of 20 measurements was taken and lowest and highest values were eliminated prior to calculating the average. General table is shown in Figure 4.26 for 10,000X magnification and we measured the angles from these images. Diameter of nanofibers was measured from 20,000X magnification.

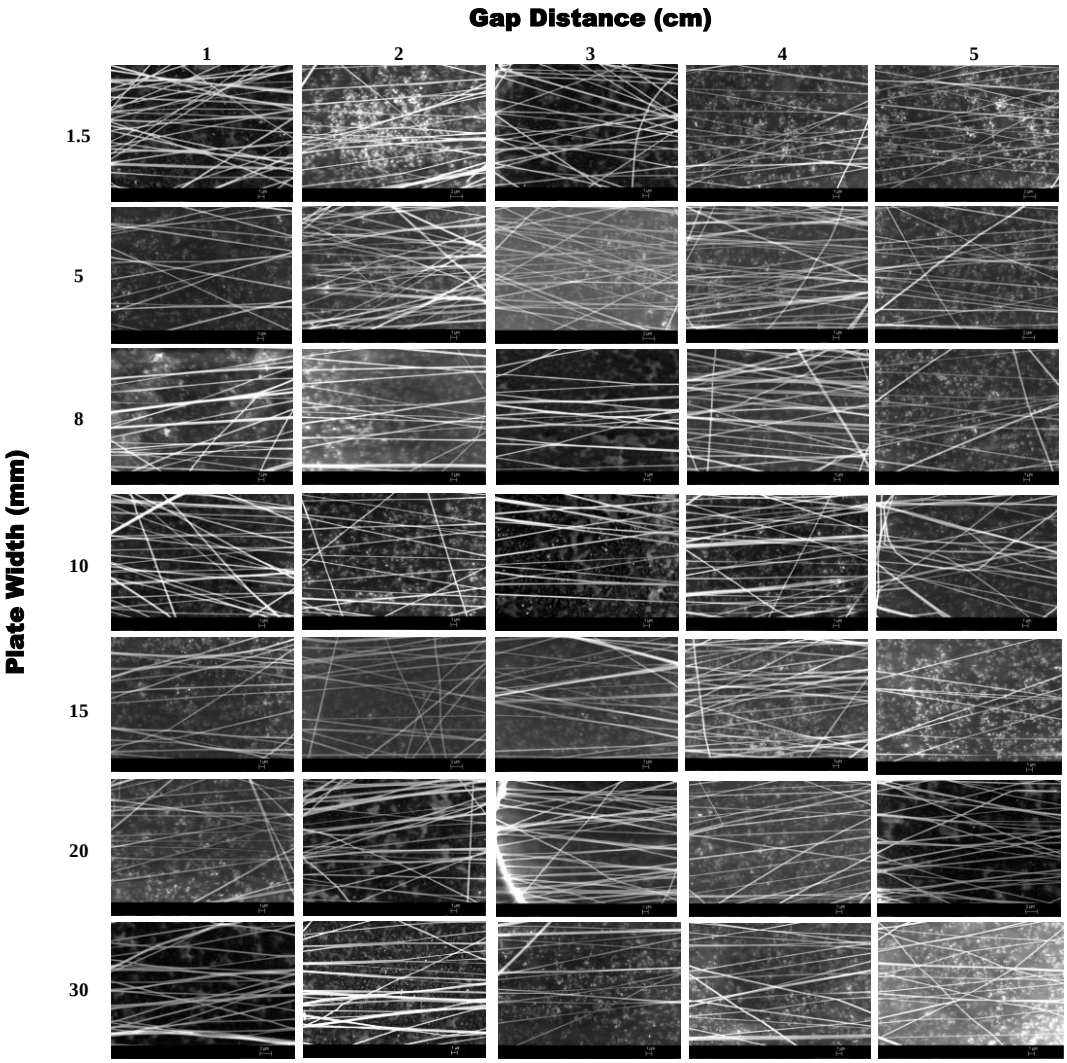


Figure 4.26 SEM micrographs of electrospun PVA nanofibers

4.2.2.1 Nanofiber Alignment Results

Effect of GAP distance on the fiber alignment: To examine effect of gap distance and plate width on alignment and diameter of the nanofibers, PVA solution was electrospun at five different gap distance (1-5 cm, 1 cm interval) values and seven different plate width (1.5-5-8-10-15-20-30 mm) values. Figure 4.27 shows SEM micrographs and distributions of nanofiber alignment of electrospun PVA nanofibers according to gap distance plate width as 10 mm, charge density as 2 kV/cm and TCD as 15 cm. Figure 4.28 shows SEM micrographs and distributions of nanofiber alignment of electrospun PVA nanofibers according to gap distance for 20 mm plate width, CD: 2 kV/cm, TCD: 15 cm.

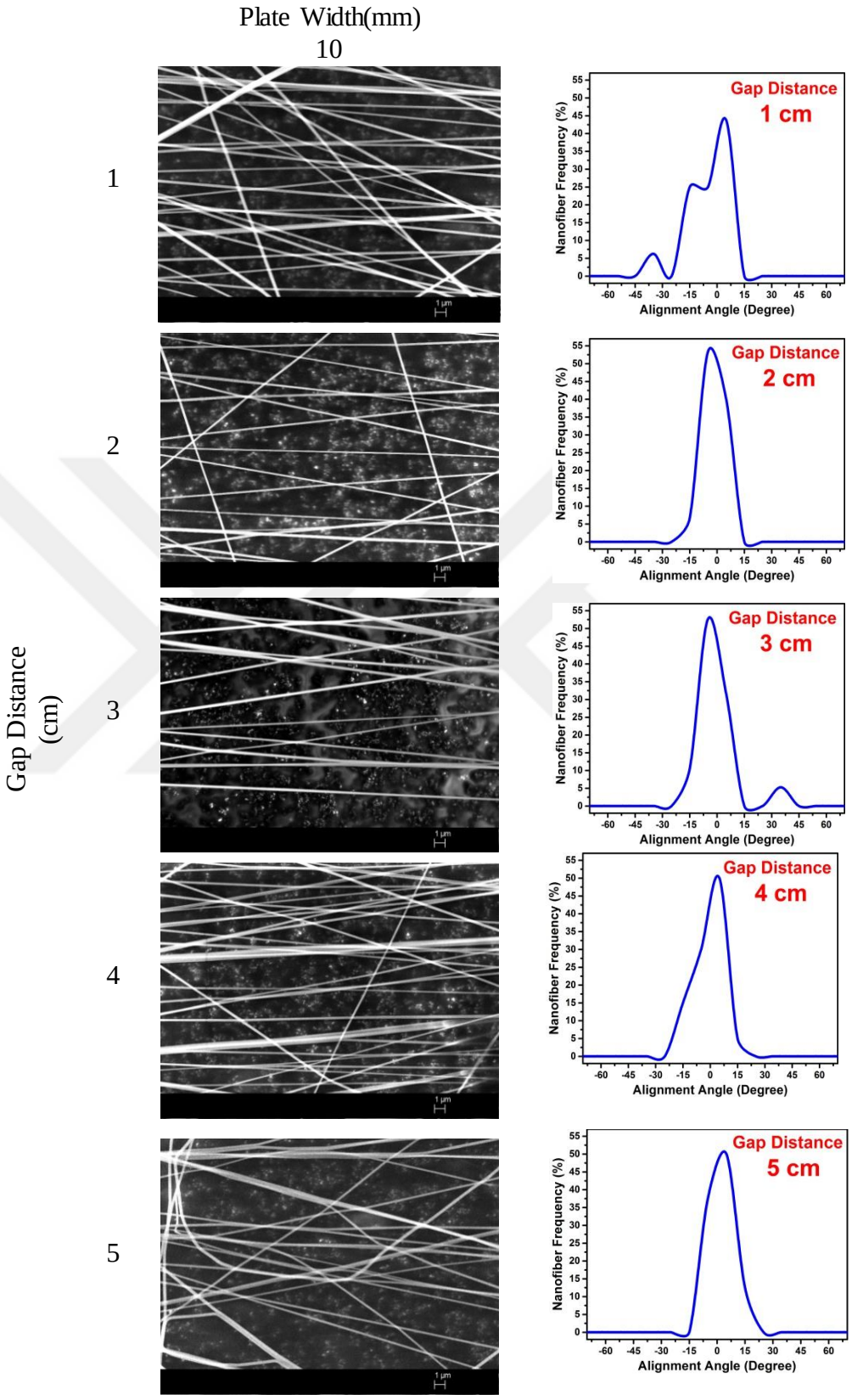


Figure 4.27 SEM micrographs and distributions of nanofiber for 10 mm plate width.

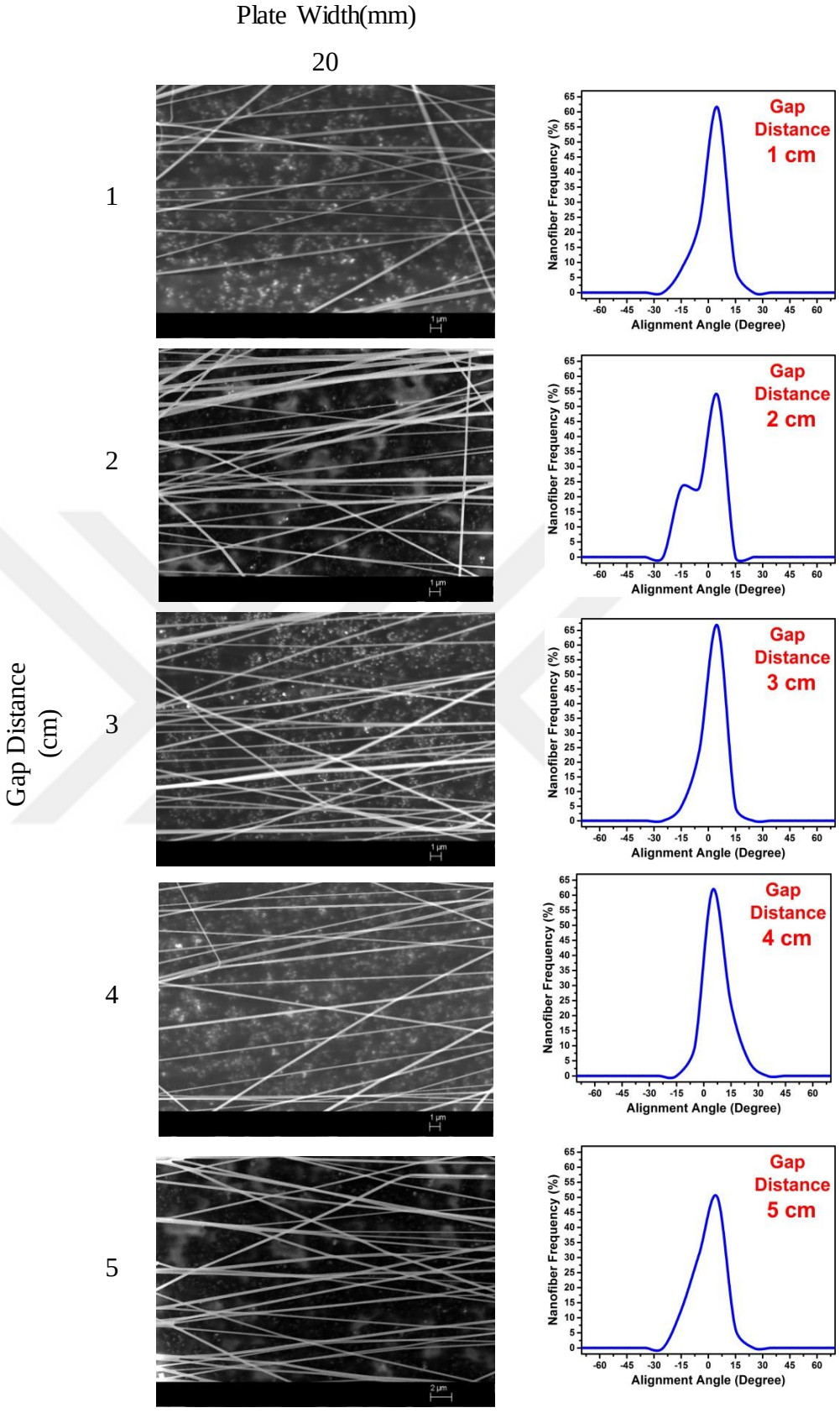


Figure 4.28 SEM micrographs and distributions of nanofiber for 20 mm plate width

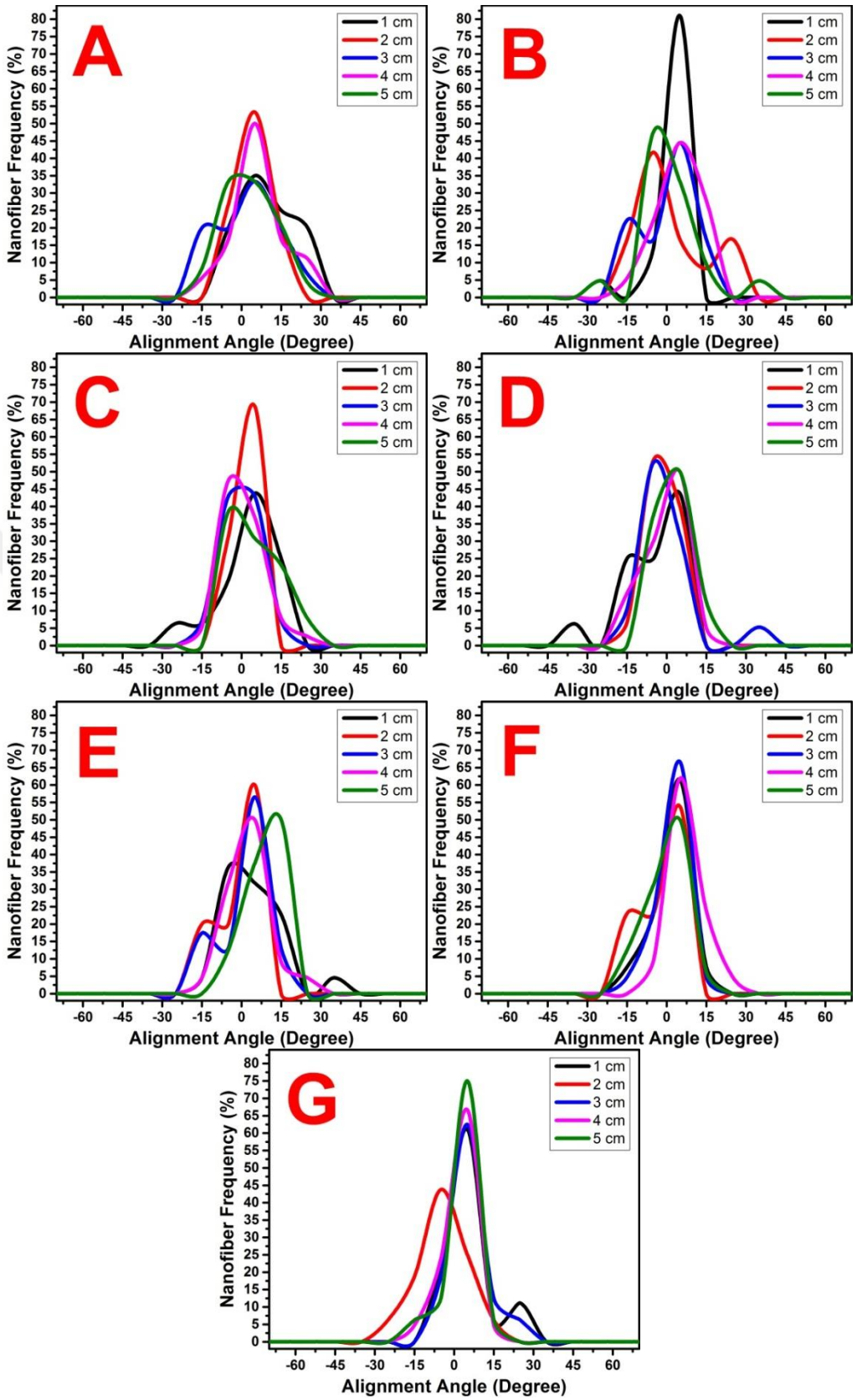


Figure 4.29 Distributions of nanofiber alignment for all plate sizes.

Figure 4.29 shows distributions of nanofiber alignment of electrospun PVA nanofibers according to gap distance for different plate width values. A: 1.5 mm, B: 5 mm, C: 8 mm, D: 10 mm, E: 15 mm, F: 20 mm, G: 30 mm. The best alignment formation is obtained 2 cm of gap distance for 10 mm of plate size according to SEM micrographs and angle distribution graphs given in Figure 4.27 and 3 cm of gap distance for 20 mm of plate size given in Figure 4.28. It is seen that gap distance affects the alignment of nanofibers however there is no obvious relationship at 10 mm and 20 mm of plate width. Distributions of nanofiber alignment of electrospun PVA nanofibers according to gap distance for the other plate width values are given in Figure 4.29. According to Figure 4.29, the effect of gap distance on nanofiber alignment differs at different plate width values. For example, alignment degrees of nanofibers at 5 mm and 15 mm of plate width values are generally lower for all of the gap distance values than that of 20 mm and 30 mm of plate width values.

Effect of plate width on the fiber alignment: Figure 4.30 is given as an example for SEM micrographs and distributions of nanofiber alignment of electrospun PVA nanofibers according to plate width (Gap distance: 3 cm, CD: 2 kV/cm, TCD: 15 cm). Figure 4.31 is given as an example SEM micrographs and distributions of nanofiber alignment of electrospun PVA nanofibers according to plate width (Gap Distance: 4 cm, CD: 2 kV/cm, TCD: 15 cm). The best alignment formations are obtained 20 mm and 30 mm of plate width for 3 cm and 4 cm of gap distance according Figure 4.30 and Figure 4.31. It can be also seen that increasing of plate width generally increases of the alignment of the nanofibers for 3 cm and 4 cm of gap distance.

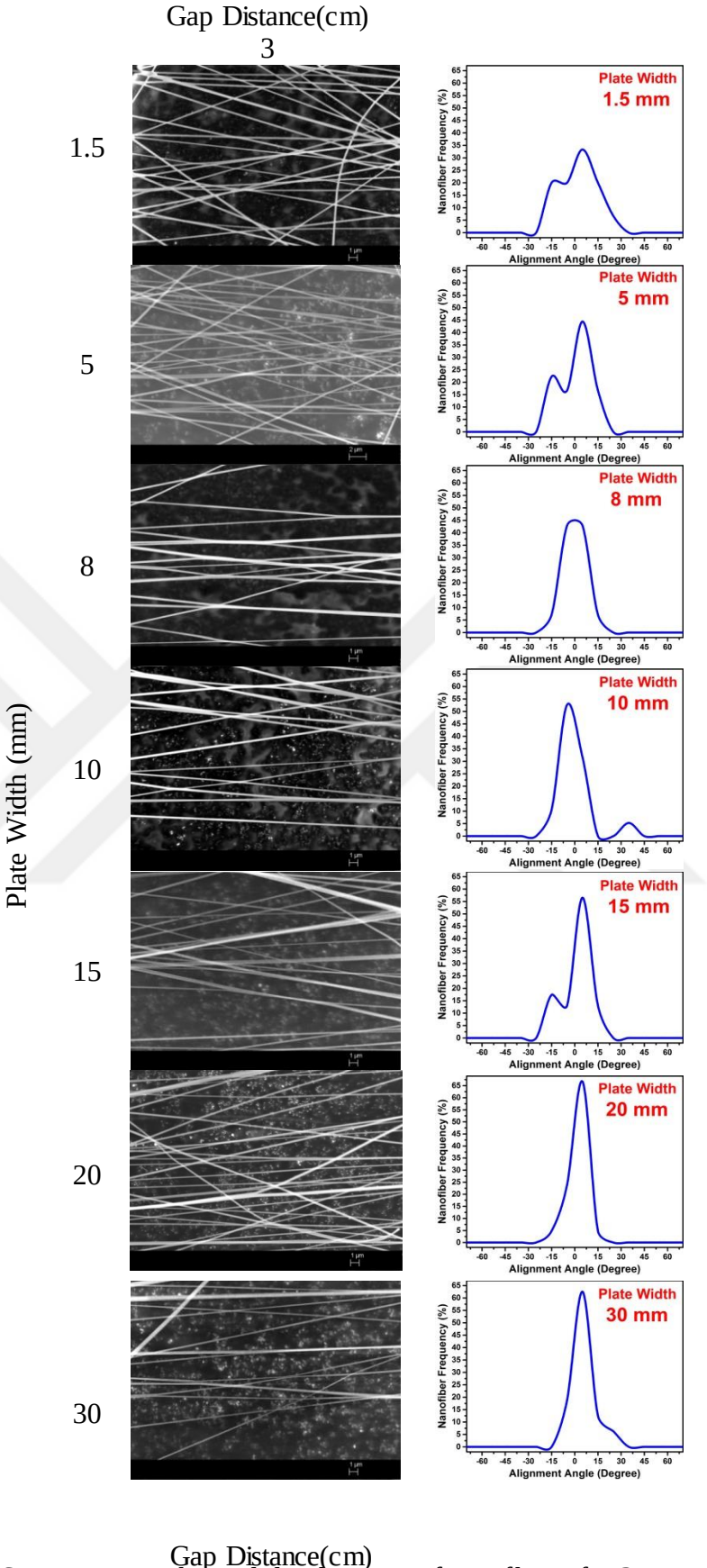


Figure 4.30 SEM micrographs and distributions of nanofibers for 3 cm gap distance.

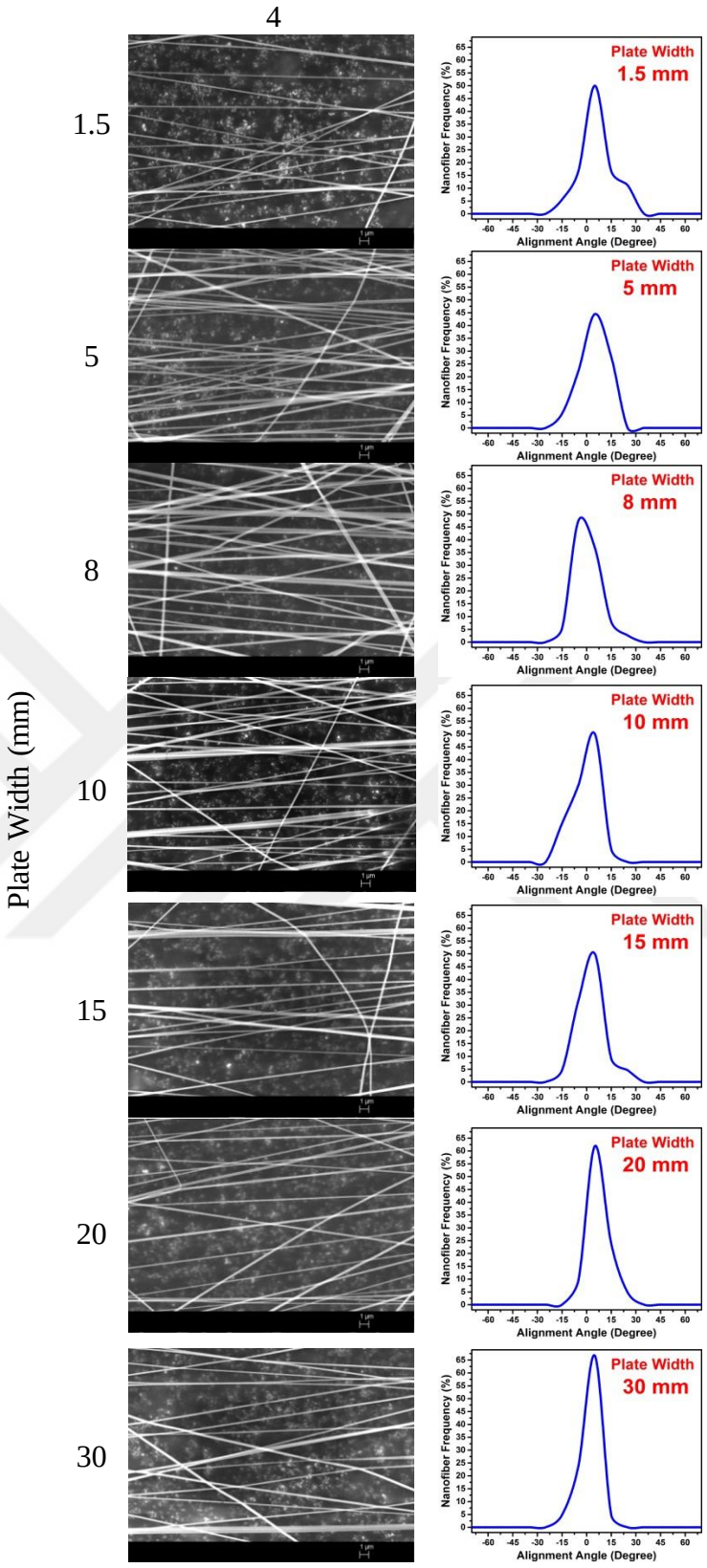


Figure 4.31 SEM micrographs and distributions of nanofibers for 4 cm gap distance.

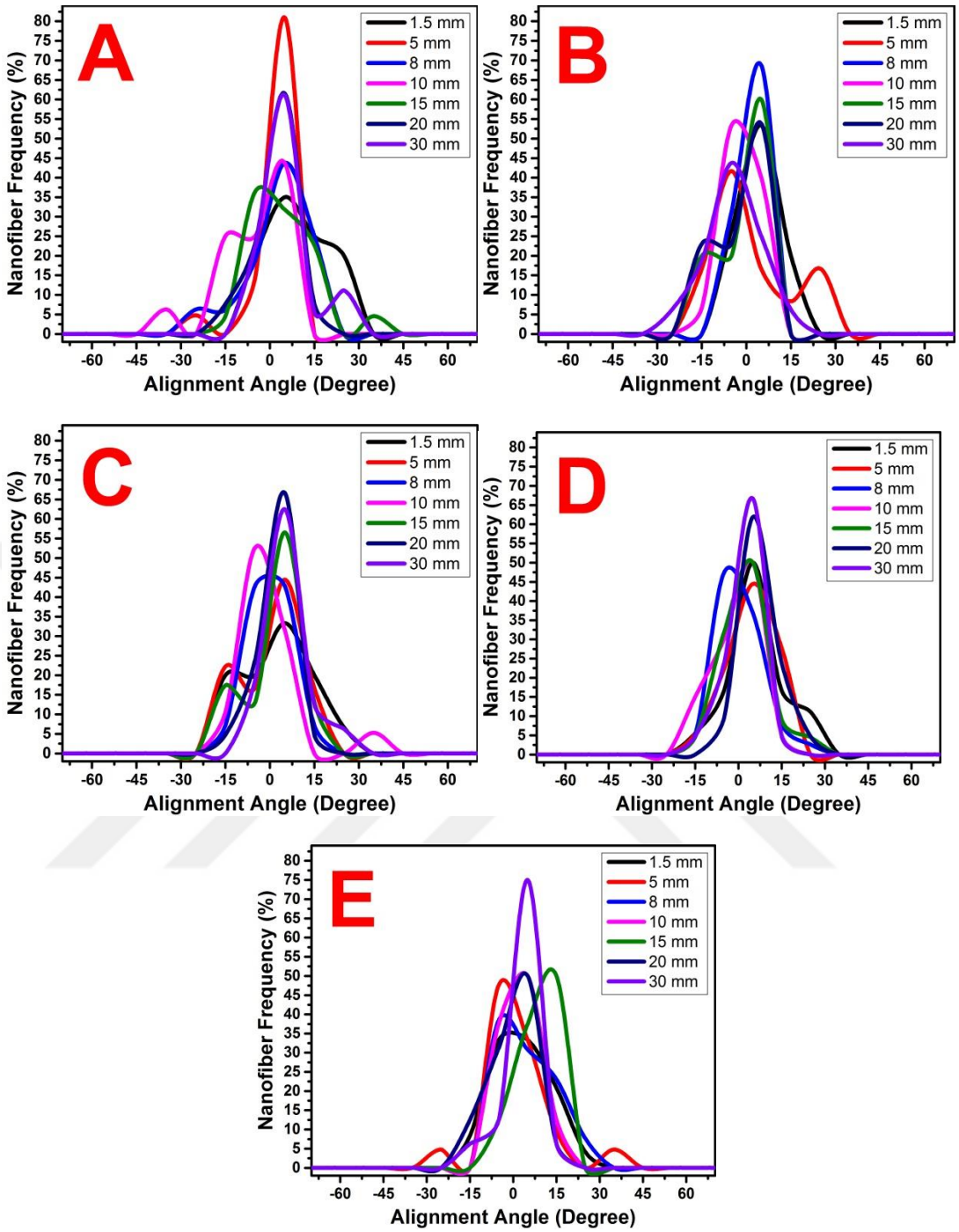


Figure 4.32 Distributions of nanofiber alignment for all gap distances.

Figure 4.32 shows distributions of nanofiber alignment of electrospun PVA nanofibers according to plate width for different gap distance values. A: 1 cm, B: 2 cm, C: 3 cm, D: 4 cm, E: 5 cm. According to Figure 4.32, the effect of plate width on nanofiber alignment differs at different gap distance values. While alignment degrees of nanofibers at 4 cm of gap distance are generally similar for all plate width values,

those at 1 cm and 5 cm of gap distance are different to each other for all plate width values. The angular standard deviation values are calculated for all investigated parameters for better evaluation on the alignment of electrospun PVA nanofibers [41]. Table 4.15 shows the angular standard deviations of electrospun PVA nanofibers (degree) as a function of the gap distance and plate width (CD: 2 kV/cm, TCD: 15 cm).

Table 4.15 The angular standard deviations of electrospun PVA nanofibers.

Standard Deviation		Plate Width (mm)						
		1.5	**5**	**8**	**10**	**15**	**20**	**30**
Gap Distance (cm)	**1**	10.90	7.76	12.28	12.32	10.64	7.90	9.08
	2	6.87	14.04	5.51	5.91	8.15	8.38	9.66
	3	14.10	9.74	9.44	9.50	8.19	6.71	6.98
	4	10.78	7.90	8.75	8.67	8.85	7.74	6.65
	5	10.00	11.50	9.39	8.51	5.68	6.28	5.19

It is seen that there is no obvious relationship between the alignment of nanofibers and gap distance for narrower plate widths. However, alignment of nanofibers generally increases for wider plate widths (15-20-30 mm). Similar trend is seen for the effect of plate width on nanofiber alignment. While there is no obvious relationship between the alignment of nanofibers and plate width for 1 cm and 2 cm of gap distance, alignment of nanofibers generally increases for wider gap distances (3-4-5 cm). In the literature, no studies about the effect of plate width on nanofiber alignment were seen. Also, there were different results about the effect of gap distance on the alignment. While some researchers found that increasing of gap distance decreases nanofiber alignment [38,39], the others found the opposite relationship [40,41,42,43]. Moreover, there are some researchers who found that increasing of gap distance firstly increases then decreases nanofiber alignment [44,45]. The reason of the different results seen in those studies may be some differences about polymer type, gap distance values and other process parameters. That reason is more likely that the effect of plate width was not taken into consideration. Because the effect of gap distance on nanofiber alignment are dissimilar at different plate width values according to our results. When all of the

angular deviation results are taken into consideration, it is seen that higher alignment degrees are obtained at wider gap distance and plate width values together. According to statistical analysis results, while the effect of gap distance on the alignment is not statistically significant ($p > 0.05$), that of plate width on the alignment is statistically significant ($p \leq 0.05$). Statistical analysis results show the effect of gap distance on the alignment is statistically insignificant ($p = .3678 < .05$) when it examined alone and effect of plate size on the alignment is statistically significant ($p = .0196 < .05$).

As the plate width increases, the collector area increases and this may improve the whipping instability of the nanofibers. Thus, the nanofibers may follow a more uniform way between the plates. Similarly, the wider plates have more nanofiber deposition than narrower plates. That may be also related to more stretching of the nanofibers collected on the gap between the parallel electrodes.

4.2.2.2 Nanofiber Diameter Results

Table 4.16 shows the average PVA nanofiber diameters (nm) and standard deviations as a function of the gap distance and plate width (CD: 2 kV/cm, TCD: 15 cm). According to Table 4.16, there is no obvious relationship between the average nanofiber diameter and gap distance for all plate width values. Similarly, it is seen that the plate width does not affect the average diameters. According to statistical analysis results, while the effect of gap distance on the average diameter is statistically significant ($p \leq 0.01$), that of plate width on the average diameter is not statistically significant ($p > 0.05$). When the gap distance increases, the average diameter generally decreases. However that effect is different if the plate width values are taken into consideration separately. There are residual positive charges on the nanofibers collected on the gap, while a continuous negative charge is applied on the plates. Residual positive charges on the nanofibers move towards negative charges on the plates. This movement causes the nanofibers to be stretched in both directions, thus the diameters of the nanofibers are reduced. As the gap distance increases, the density of these charges will increase, so the stretching forces will increase. Similar to the alignment results, it can be said that plate width changes the effect of the gap distance on the nanofiber diameters (Table 4.16). That explains the

different results about the effect of gap distance on the nanofiber diameter in literature [39,41].

Table 4.16 The average PVA nanofiber diameters (nm) and standard deviations

Plate Width (mm)	Gap Distance (cm)				
	1	**2**	**3**	**4**	**5**
1,5	197 ± 23	169 ± 17	190 ± 26	151 ± 17	153 ± 20
5	183 ± 27	216 ± 27	190 ± 26	199 ± 30	157 ± 18
8	183 ± 30	192 ± 16	197 ± 21	207 ± 19	205 ± 27
10	219 ± 21	190 ± 32	181 ± 29	188 ± 21	218 ± 22
15	214 ± 26	191 ± 33	176 ± 22	205 ± 22	193 ± 29
20	203 ± 32	167 ± 30	217 ± 26	179 ± 33	191 ± 26
30	184 ± 18	197 ± 20	165 ± 21	177 ± 31	162 ± 22

4.2.3 The Results of Charge Density Study (Study-II)

We know that the effect of the electric field on the spun nanofiber alignment and diameter is extremely important. Figure 4.33 and 4.34 show SEM micrographs of electrospun PVA nanofibers according to charge density values for 15 mm of plate width / 4 cm of gap distance and 20 mm of plate width / 3 cm of gap distance. The best alignment formations are obtained the lowest CD for both of the selected gap distance and plate width values according to SEM micrographs given in Figure 4.33 and Figure 4.35. It is obviously seen that increasing of charge density negatively affects the orientation of the nanofibers.

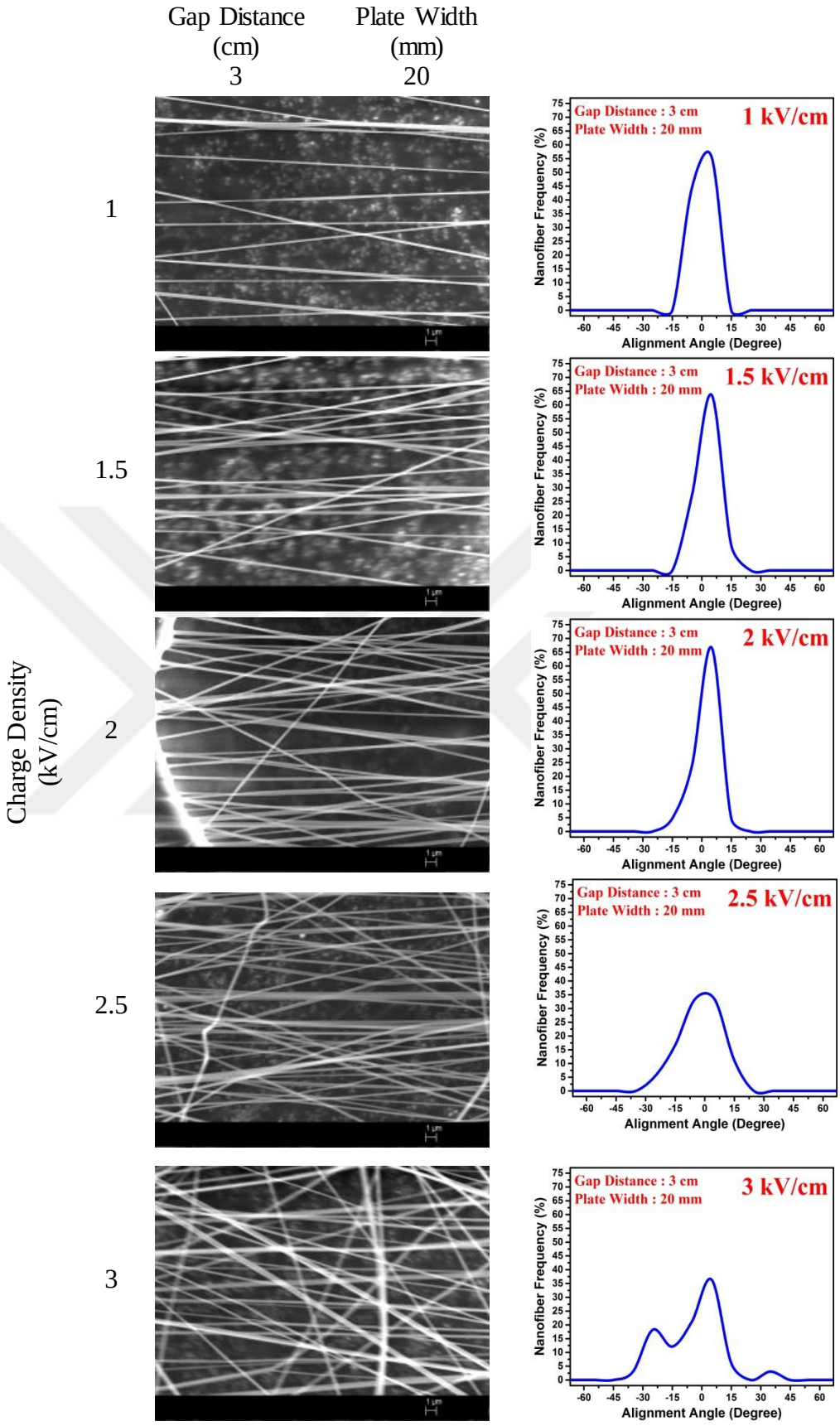


Figure 4.33 SEM micrographs and distributions of nanofibers for 20 mm of plate width / 3 cm of gap distance according to CD values.

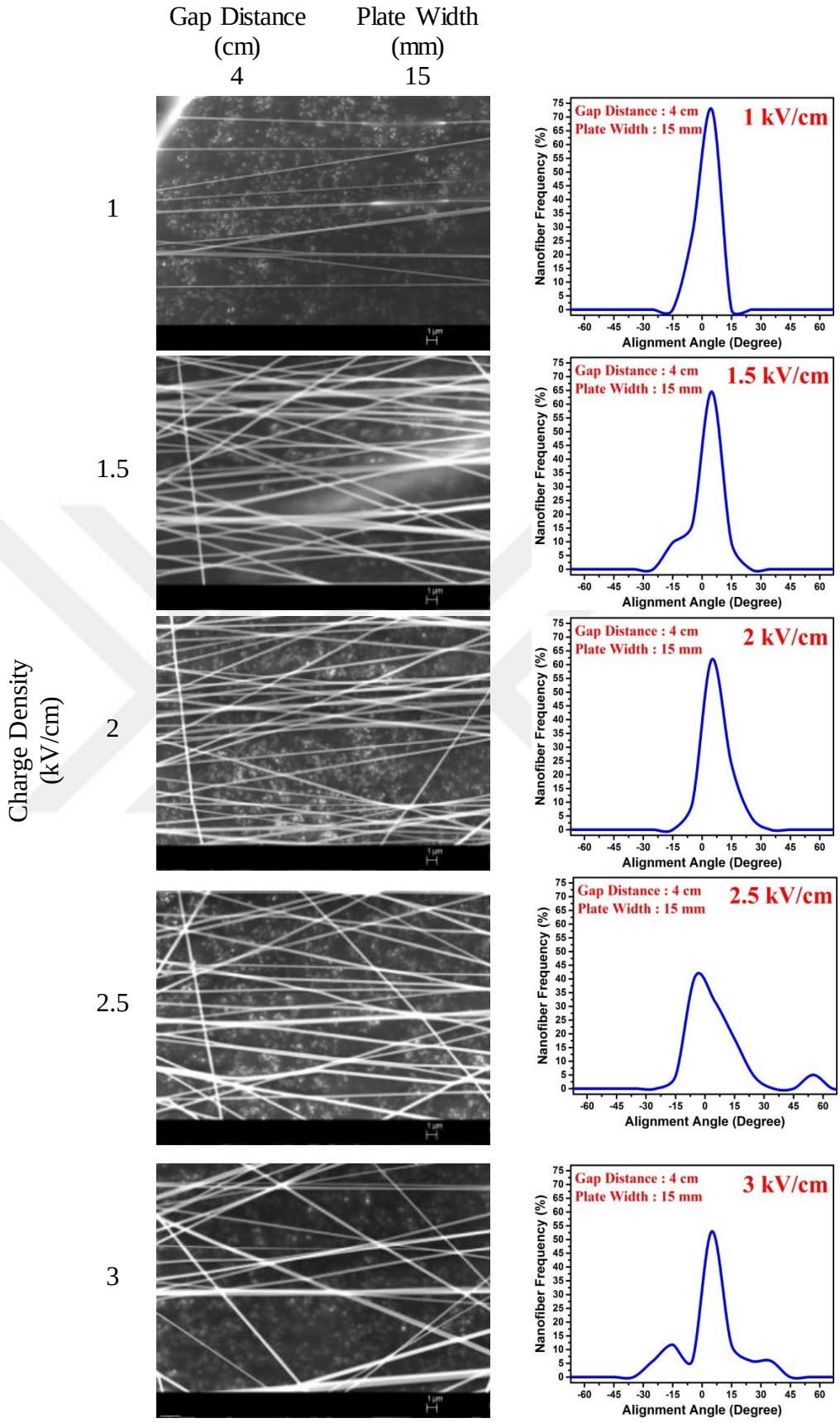


Figure 4.34 SEM micrographs and distributions of nanofibers for 15 mm of plate width / 4 cm of gap distance according to CD values.

4.2.3.1 Nanofiber Alignment Results

The voltage applied on the parallel collectors shows a big effect on the fiber orientation same as PAN polymer.

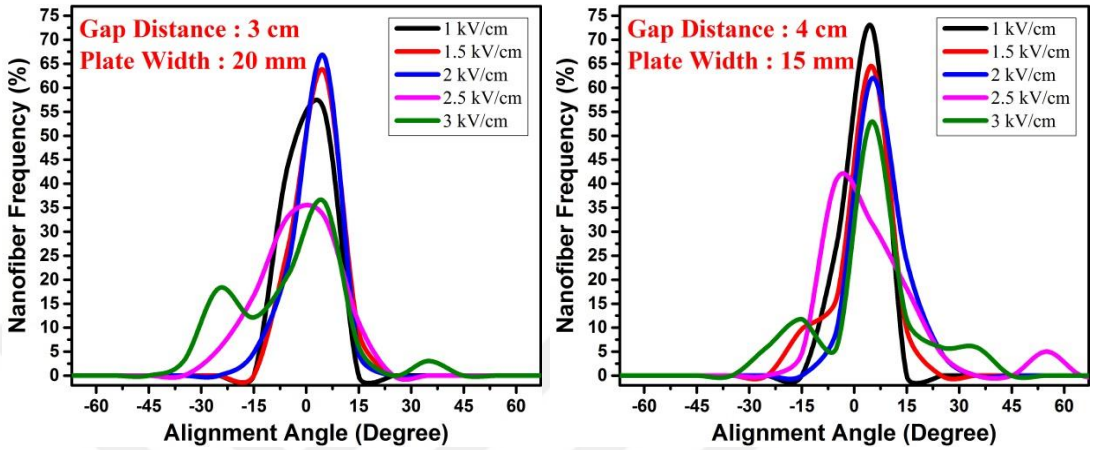


Figure 4.35 Distributions of nanofiber alignment of electrospun PVA nanofibers according to charge density.

Distributions of nanofiber alignment of electrospun PVA nanofibers according to charge density for 15 mm of plate width, 4 cm of gap distance and 20 mm of plate width and 3 cm of gap distance are given in Figure 4.35. While higher frequencies of nanofiber alignment are seen at lower CD values, lower frequencies of that are seen at higher CD values for both of the selected gap distance and plate width values (Figure 4.35). The angular standard deviation values are given according to CD values for better evaluation on the alignment of electrospun PVA nanofibers. Table 4 shows the angular standard deviations of electrospun PVA nanofibers as a function of the charge density.

Table 4.17 The angular standard deviations as a function of CD.

Plate Dimension		**Charge Density (kV/cm)**				
Gap D.	**Width**	**1**	**1.5**	**2**	**2.5**	**3**
3cm	**20mm**	4.63	7.03	6.71	10.47	15.48
4cm	**15mm**	4.61	8.82	8.85	10.85	16.50

Table 4.17 shows the angular standard deviations (degree) of electrospun PVA nanofibers as a function of the charge density (TCD:15 cm). It is seen that there is obvious relationship between the alignment of nanofibers and CD for both of the selected gap distance and plate width values. Increasing CD causes to decrease in the alignment of nanofibers. According to statistical analysis results, the effect of CD on the alignment is statistically significant ($p=0.0001<0.05$). The similar results are seen in the previous studies [38,44]. The applied voltage produces an electrical field between the needle tip and the collector, and that controls strongly the motion of the polymer jet. When applied voltage is increased, stable motion of the polymer jet is decreased. That may cause to distortion of the nanofiber alignment directly.

4.2.3.2 Nanofiber Diameter Results

Table 4.18 shows the average PVA nanofiber diameters and standard deviations as a function of the charge density. According to Table 4.18, increasing CD causes to increase in the average diameter of nanofibers for both of the selected gap distance and plate width values. According to statistical analysis results, the effect of CD on the diameter is statistically significant ($p \leq 0.01$). When applied voltage at a fixed TCD is increased, the flight time of the polymer jet is decreased [1]. Therefore, less stretching is applied and thicker nanofibers can be obtained. When the flight time is reduced, the solvent in the solution may not completely evaporate, and consequently nanofiber diameters are increased.

Table 4.18 The average PVA nanofiber diameters and standard deviations as a function of CD.

Gap Distance (cm)	Plate Width (mm)	CD (kV/cm)				
		1	1,5	2	2,5	3
3	20	151 ± 29	216 ± 13	217 ± 26	220 ± 27	240 ± 50
4	15	187 ± 31	204 ± 21	205 ± 22	217 ± 26	243 ± 55

4.2.4 The Results of TCD Study (Study-III)

Figure 4.36 and Figure 4.37 show SEM micrographs of electrospun PVA nanofibers according to tip to collector distance (TCD) values for 15 mm of plate width / 4 cm of gap distance and 20 mm of plate width / 3 cm of gap distance. The best alignment formations are obtained the lowest TCD for both of the selected gap distance and plate width values according to SEM micrographs given in Figure 4.36 and Figure 4.37. It is obviously seen that increasing of tip to collector distance distorts the orientation of the nanofibers. Distributions of nanofiber alignment of electrospun PVA nanofibers according to TCD for 15 mm of plate width, 4 cm of gap distance and 20 mm of plate width and 3 cm of gap distance are given in Figure 4.38.

While higher alignment degrees of the nanofibers are seen at lower TCD values, the lower alignment degrees are seen at higher TCD values for both of the selected gap distance and plate width values (Figure 4.38).

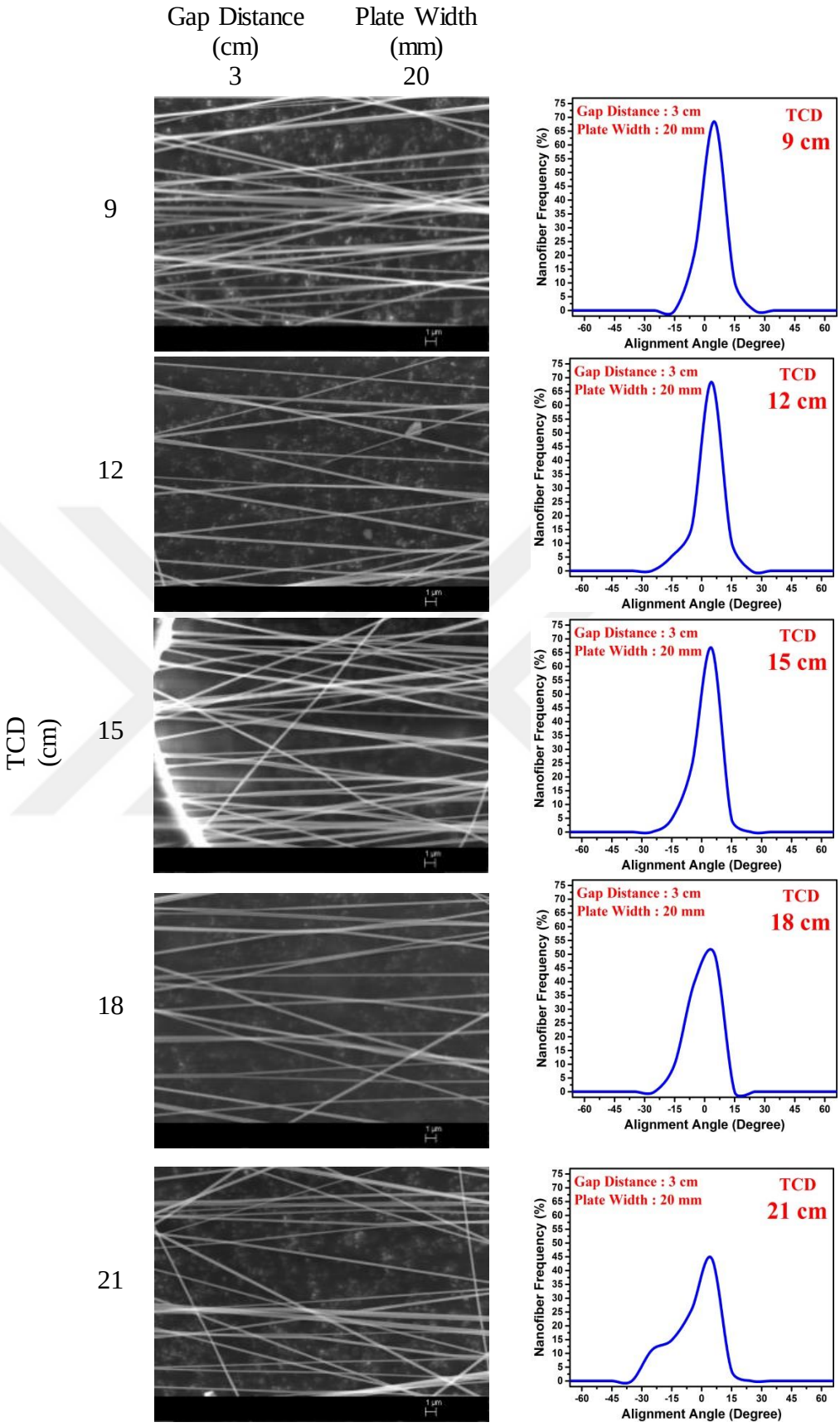


Figure 4.36 SEM micrographs and distributions for 20 mm of plate width / 3 cm of gap distance with all TCD values.

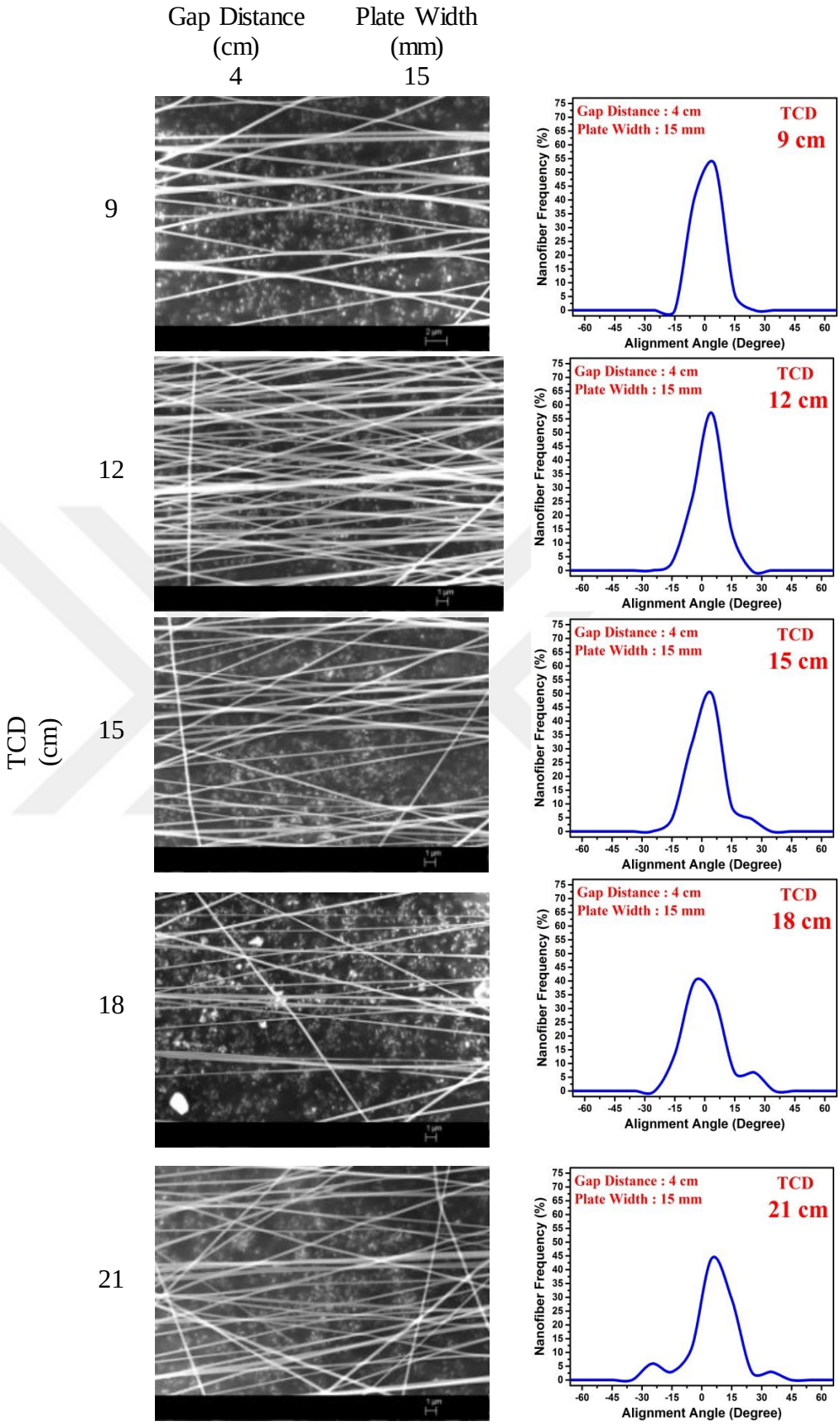


Figure 4.37 SEM micrographs and distributions 15 mm of plate width / 4 cm of gap distance according with all TCD values.

4.2.4.1 Nanofiber Alignment Results

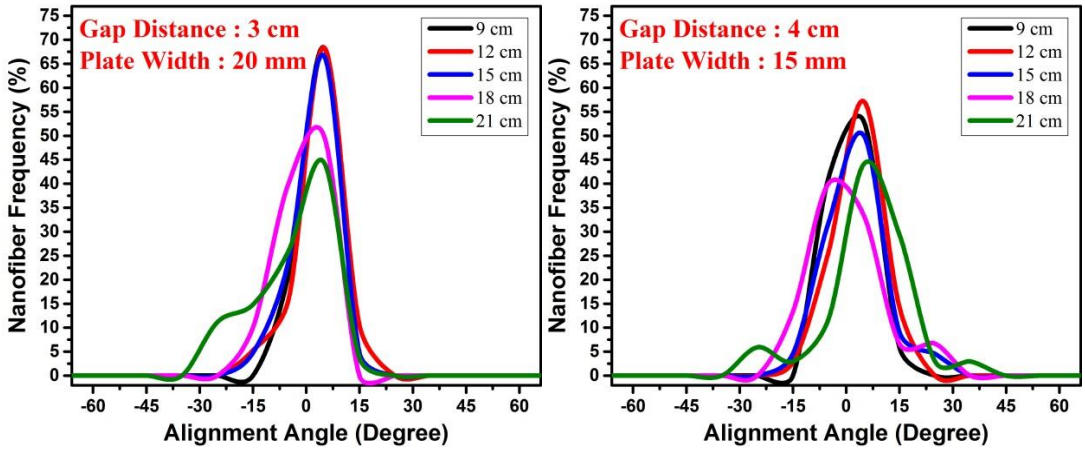


Figure 4.38 Distributions of nanofiber alignment of electrospun PVA nanofibers according to TCD.

Table 4.19 The angular standard deviations (degree) as a function of TCD (CD: 2 kV/cm).

Plate Dimension		TCD (cm)				
Gap D.	**Width**	**9**	**12**	**15**	**18**	**21**
3cm	**20mm**	6.06	6.31	6.71	6.93	10.51
4cm	**15mm**	8.19	8.30	8.85	9.50	13.20

The angular standard deviation values are given according to TCD values for better evaluation on the alignment of electrospun PVA nanofibers. Table 4.19 shows the angular standard deviations of electrospun PVA nanofibers as a function of the TCD. It is seen that there is obvious relationship between the alignment of nanofibers and TCD for both of the selected gap distance and plate width values. Increasing TCD causes to decrease in the alignment of nanofibers. According to statistical analysis results, the effect of TCD on the alignment is statistically significant ($p \leq 0.01$). The similar results are seen in the previous studies [38,46]. When TCD is increased for a fixed charge density, the polymer jet instability is increased due to the longer path of the jet. That may cause to distortion of the nanofiber alignment. This distortion is clearly seen when TCD becomes 21 cm (Table 4.19).

4.2.4.2 Nanofiber Diameter Results

Table 4.20 The average PVA nanofiber diameters (nm) and standard deviations as a function of TCD (CD: 2 kV/cm).

Gap Distance (cm)	Plate Width (mm)	TCD (cm)				
		9	12	15	18	21
3	20	189 ± 27	234 ± 29	217 ± 26	251 ± 22	224 ± 35
4	15	207 ± 22	206 ± 14	205 ± 22	197 ± 27	209 ± 28

Table 4.20 shows SEM micrographs of electrospun PVA nanofibers according to tip to collector distance (TCD) values for 15 mm of plate width, 4 cm of gap distance and 20 mm of plate width and 3 cm of gap distance. According to Table 4.20, there is no obvious relationship between the average nanofiber diameter and TCD. This may be related to fixed CD (2 kV/cm) applied for all TCD values. That means same electrostatic forces are applied to polymer jets during electrospinning process. According to statistical analysis results, the effect of TCD on the diameter is statistically significant ($p \leq 0.01$).

4.2.5 Statistical Analysis Results

Figure 4.39 and 4.40 shows the angle distribution and standard deviation of PVA nanofibers for plate width variance. According to Unequal variances results, interaction between gap distance and alignment of PVA nanofibers was found to be statistically insignificant ($p = .3678 > .05$) (see Table 4.20).

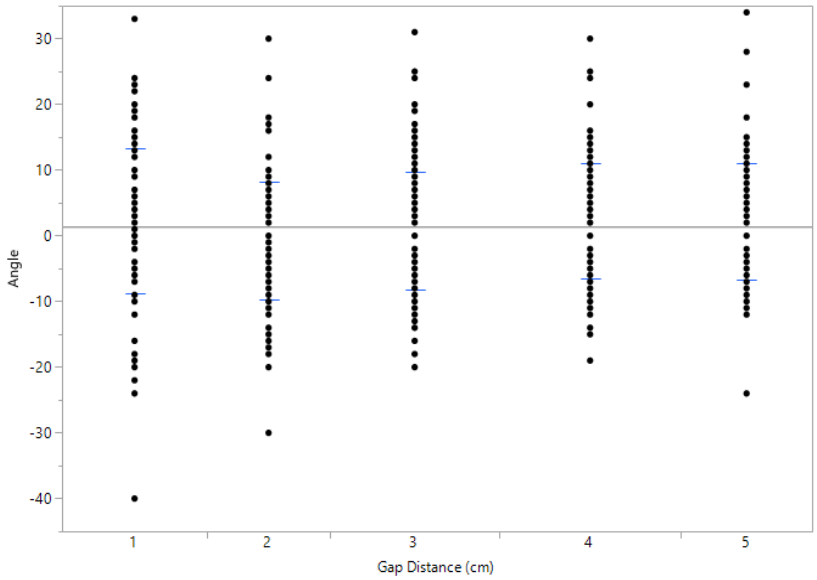


Figure 4.39 Effect of gap distance on angle distribution of PVA nanofiber

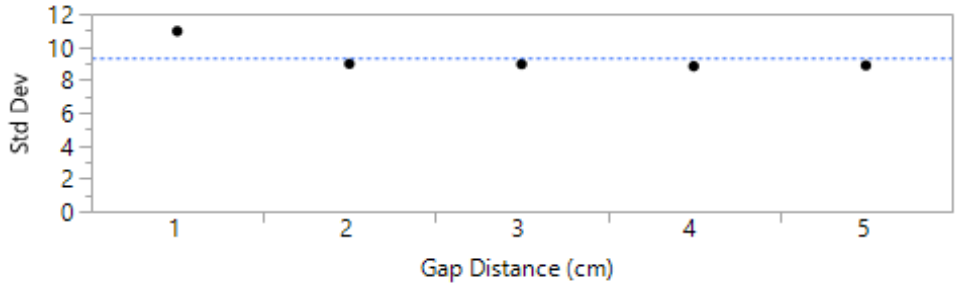


Figure 4.40 Standard deviation of nanofiber angles with variance of gap distance

Table 4.21 Probability result of the relationship between alignment and gap distance

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1,8006	4	647	0,1270
Brown-Forsythe	1,1110	4	647	0,3502
Levene	1,0752	4	647	0,3678
Bartlett	2,3628	4	.	0,0508

According to ANOVA results the interaction between gap distance and diameter of nanofibers was found to be statistically significant effects on diameter of PVA nanofibers (p = .0003< .05) (see Table 4.22)

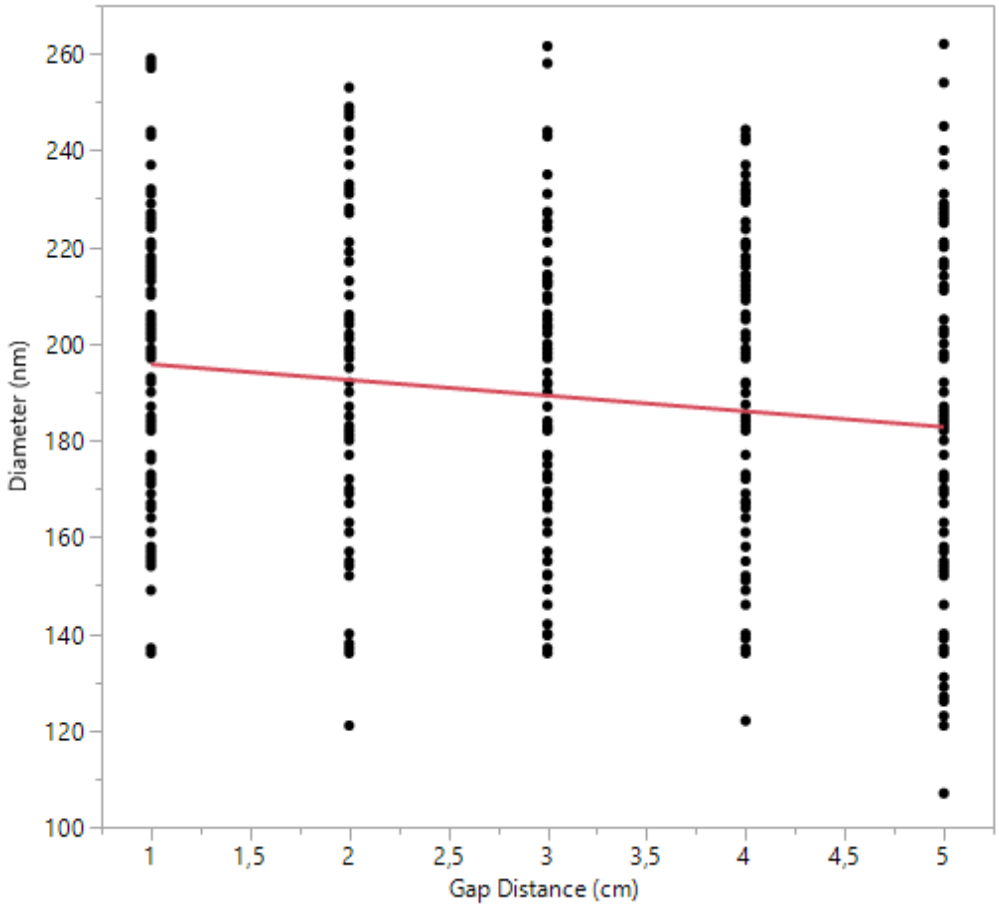


Figure 4.41 Effect of gap distance on diameter of PVA nanofiber

Table 4.22 Probability result of the relationship between diameter and gap distance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	11662,34	11662,3	13,0679
Error	557	497088,73	892,4	**Prob > F**
C. Total	558	508751,07		0,0003*

Figure 4.42 and 4.43 shows the angle distribution and standard deviation of PVA nanofibers for plate width variance. According to Unequal variances results, interaction between plate width and alignment of PVA nanofibers was found to be statistically significant ($p = .0196 < .05$) (see Table 4.22)

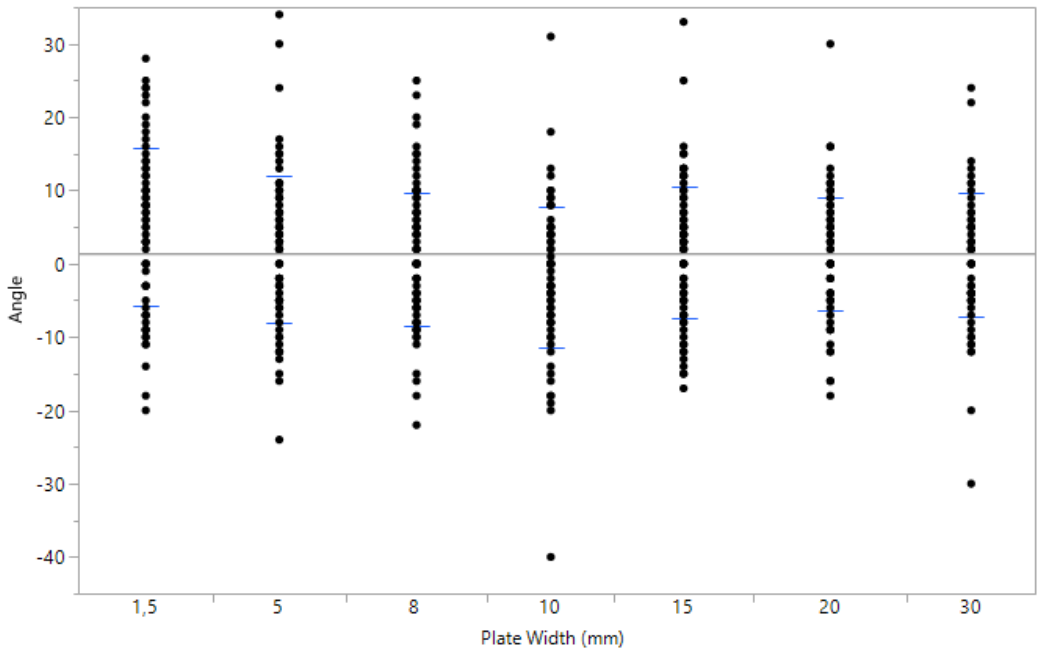


Figure 4.42 Effect of plate width on angle distribution of PVA nanofiber

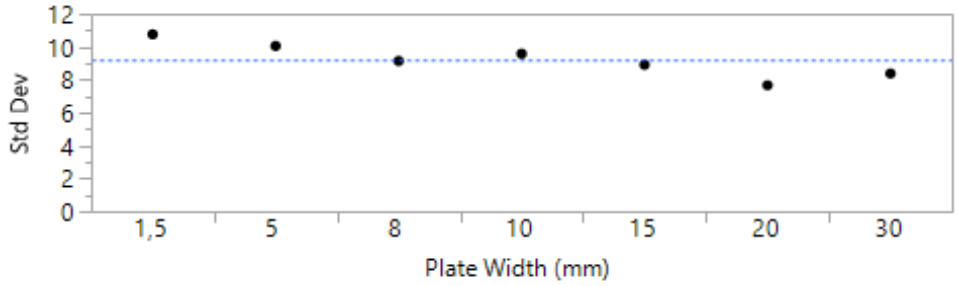


Figure 4.43 Standard deviation for effect of plate width on alignment

Table 4.23 Probability result of the relationship between alignment and plate width.

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	1,5948	6	645	0,1460
Brown-Forsythe	2,5531	6	645	0,0189*
Levene	2,5361	6	645	0,0196*
Bartlett	2,4062	6	.	0,0251*

According to ANOVA results the interaction between plate width and diameter of nanofibers was found to be statistically insignificant effects on diameter of PVA nanofibers (p = .4778 > .05) (see Table 4.23)

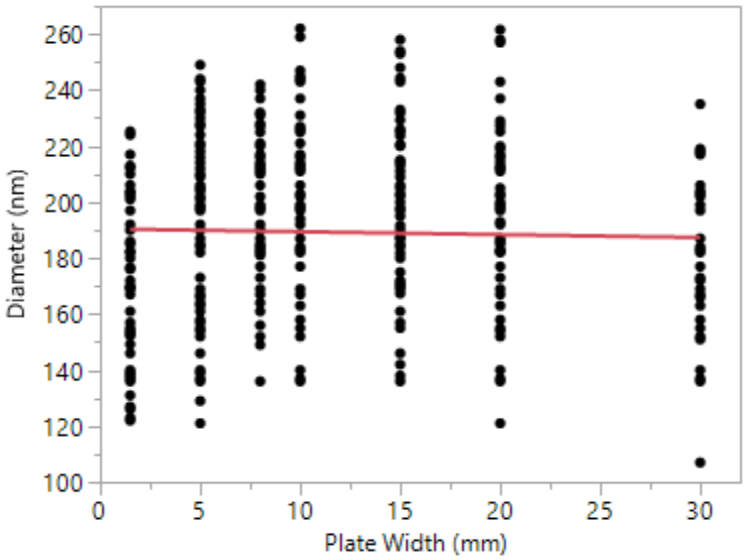


Figure 4.44 Effect of plate width on diameter of PVA nanofiber

Table 4.24 Probability result of the relationship between diameter and plate width

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	460,50	460,504	0,5046
Error	557	508290,57	912,550	**Prob > F**
C. Total	558	508751,07		0,4778

Figure 4.45 and 4.46 shows the angle distribution and standard deviation of PVA nanofibers for CD variance. According to Unequal variances results, interaction between CD and alignment of PVA nanofibers was found to be statistically significant (p = .0001 < .05) (see Table 4.24)

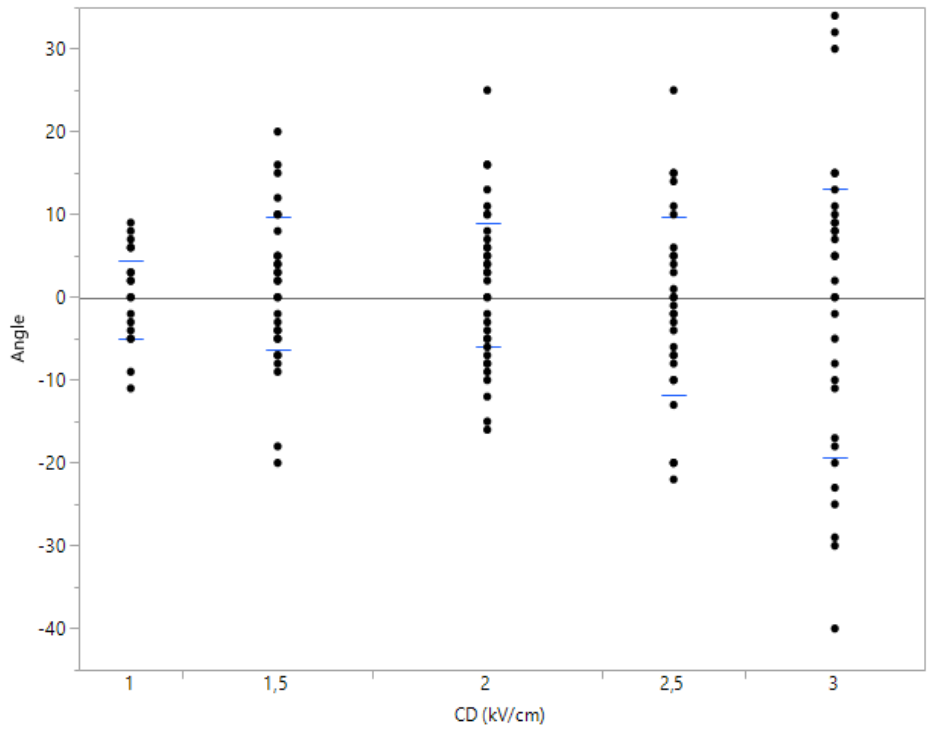


Figure 4.45 Effect of charge density on angle distribution of PVA nanofiber.

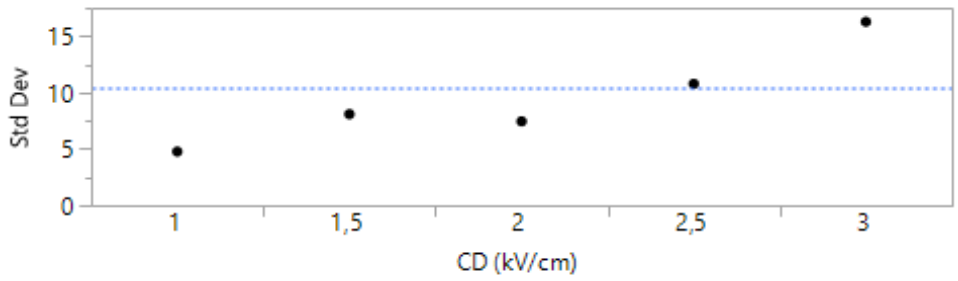


Figure 4.46 Standard deviation of nanofiber angles with variance of charge density.

Table 4.25 Probability result of the relationship between alignment and charge density.

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	10,6784	4	231	<,0001*
Brown-Forsythe	9,2072	4	231	<,0001*
Levene	11,5461	4	231	<,0001*
Bartlett	16,2550	4	.	<,0001*

According to ANOVA results the interaction between CD and diameter of nanofibers was found to be statistically highly significant effects on diameter of PVA nanofibers (p = . 0001 < .05) (see Table 4.25)

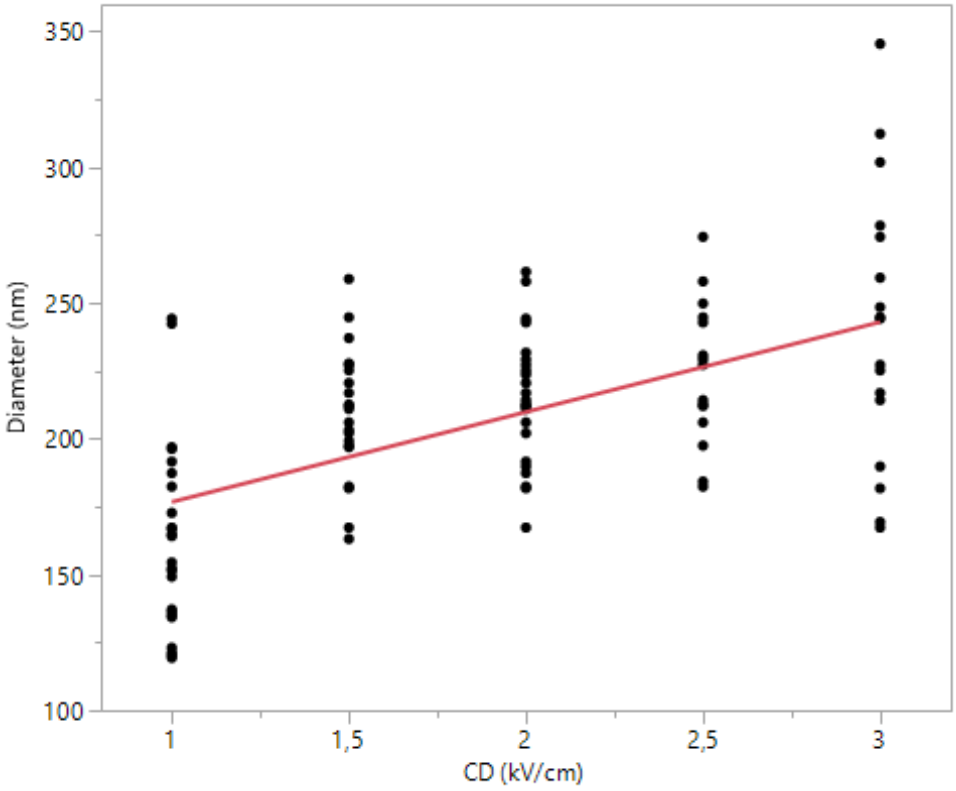


Figure 4.47 Effect of charge density on nanofiber diameter

Table 4.26 Probability result of the relationship between diameter and charge density.

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	64104,49	64104,5	66,6916
Error	138	132646,71	961,2	**Prob > F**
C. Total	139	196751,19		<,0001*

Figure 4.48 and 4.49 shows the angle distribution and standard deviation of PVA nanofibers for TCD variance. According to Unequal variances results, interaction between plate width and alignment of PVA nanofibers was found to be statistically significant (p = .0087 < .05) (see Table 4.26)

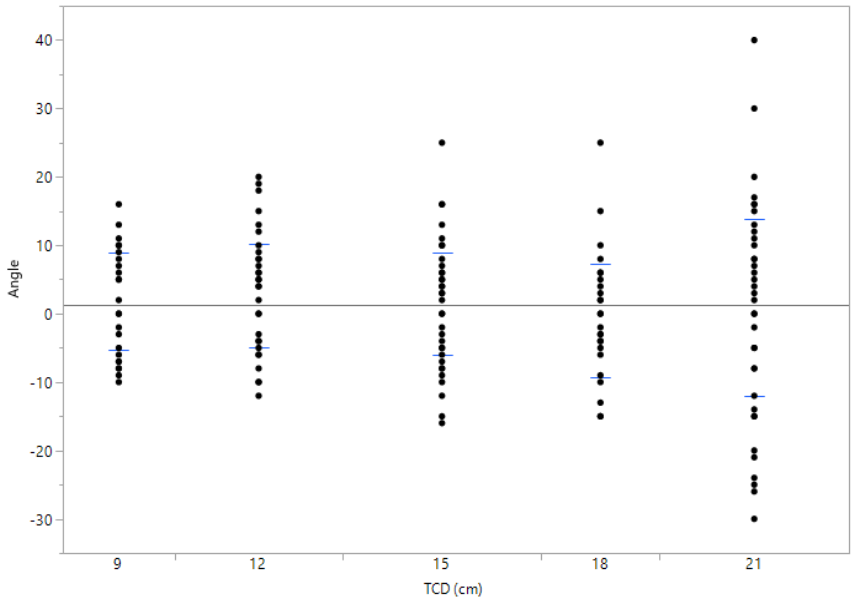


Figure 4.48 Effect of TCD on nanofiber alignment

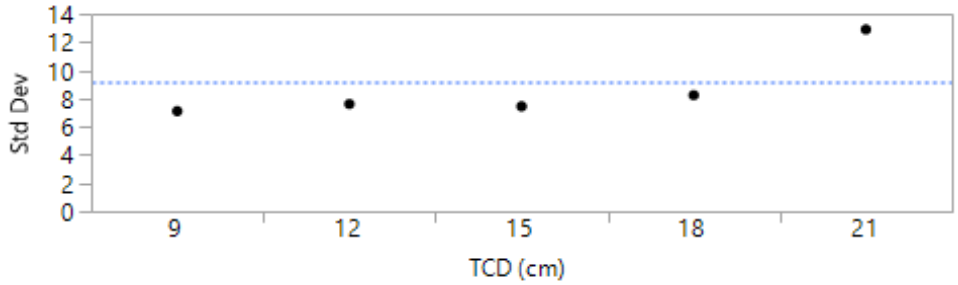


Figure 4.49 Standard deviation for effect TCD on alignment

Table 4.27 Probability result of the relationship between alignment and TCD

Test	F Ratio	DFNum	DFDen	Prob > F
O'Brien[.5]	5,2100	4	248	0,0005*
Brown-Forsythe	3,3479	4	248	0,0108*
Levene	3,4791	4	248	0,0087*
Bartlett	7,5398	4	.	<,0001*

According to ANOVA results the interaction between TCD and diameter of nanofibers was found to be statistically significant effects on diameter of PVA nanofibers (p = .0082 < .05) (see Table 4.27)

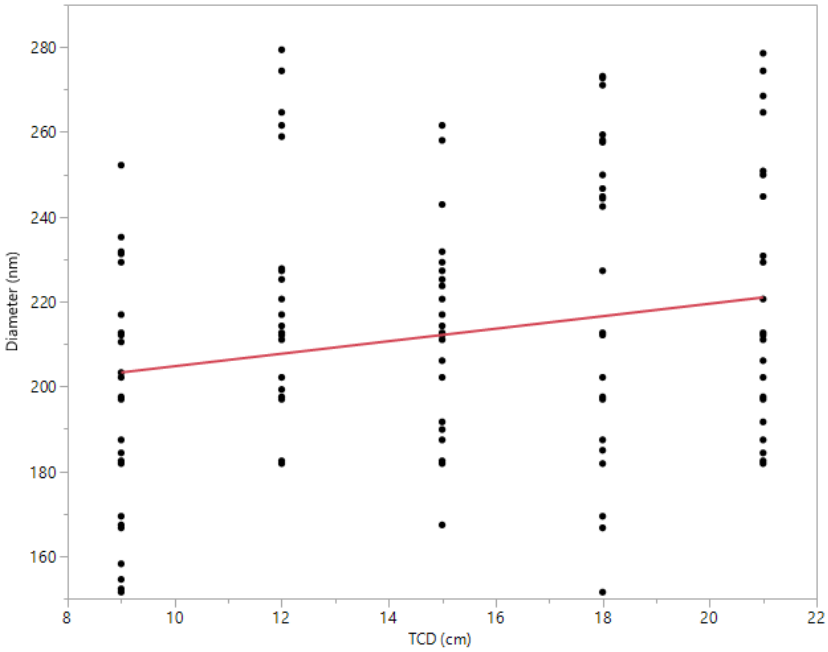


Figure 4.50 Standard deviation for effect TCD on alignment

Table 4.28 Probability result of the relationship between diameter and TCD

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	6024,03	6024,03	7,1817
Error	156	130852,90	838,80	**Prob > F**
C. Total	157	136876,93		0,0082*

Figure 4.50 and 4.51 shows the angle distribution and standard deviation of PAN and PVA nanofibers for polymer effect. According to Unequal variances results, interaction between polymer and alignment of nanofibers was found to be statistically highly significant (p = .0001 < .05) (see Table 4.28)

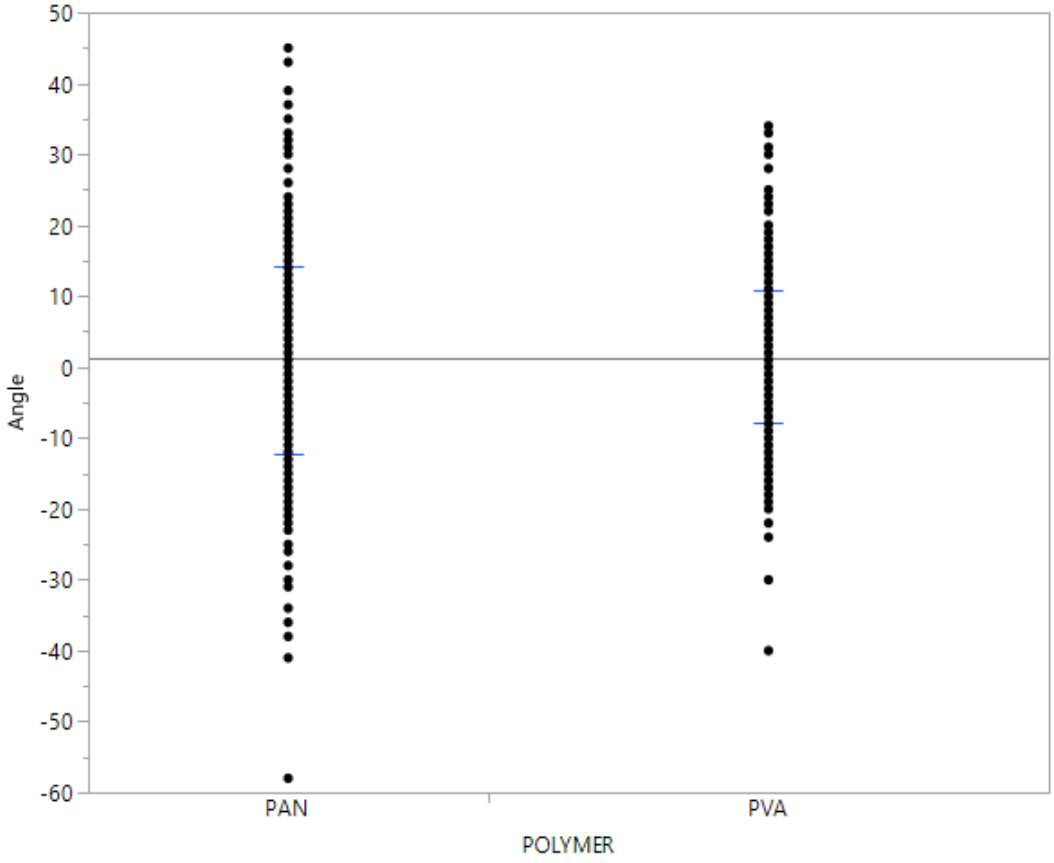


Figure 4.51 Effect of polymer on nanofiber alignment

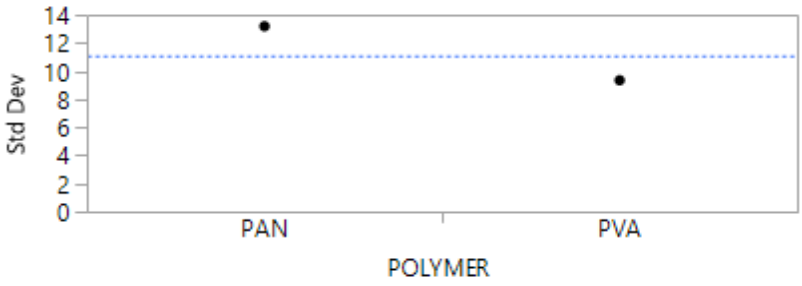


Figure 4.52 Standard deviation for effect polymer on alignment

Table 4.29 Probability result of the relationship between alignment and polymer

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	34,5317	1	1113	<,0001*
Brown-Forsythe	27,8444	1	1113	<,0001*
Levene	28,5296	1	1113	<,0001*
Bartlett	65,2672	1	.	<,0001*
F Test 2-sided	1,9908	463	650	<,0001*

According to ANOVA results the interaction between polymer type and diameter of nanofibers was found to be statistically significant effects ($p = .0001 < .05$) (see Table 4.29).

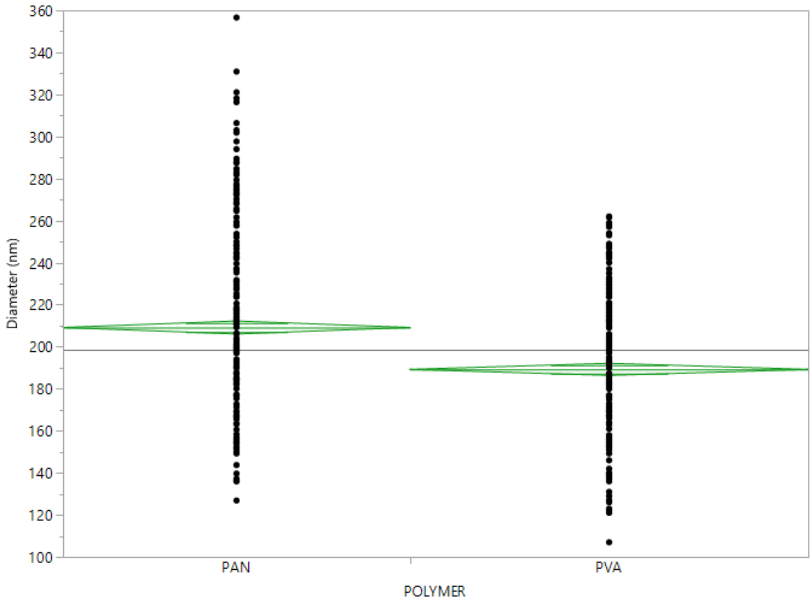


Figure 4.53 Effect of polymer on nanofiber diameter

Table 4.30 Probability result of the relationship between diameter and polymer

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
POLYMER	1	103081,0	103081	86,5183	<,0001*
Error	1042	1241475,6	1191		
C. Total	1043	1344556,5			

CHAPTER V

CONCLUSION AND RECOMMENDATIONS

In this thesis, effects of gap distance, plate width, charge density, tip to collector distance on the alignment and the average fiber diameter of PAN and PVA nanofibers in parallel electrode electrospinning are investigated. The conclusions of electrospun PAN nanofiber studies are given in the following.

It is seen that there is no obvious relationship between the alignment of PAN nanofibers and gap distance for narrower plate widths. Best alignment was reported for gap distance as 2 cm and plate width as 15 mm.. While there is no obvious relationship between the alignment of nanofibers and plate width for 1 cm, 4 cm and 5 cm of gap distance, alignment of nanofibers generally increases for 2 cm and 3 cm gap distances. There is no obvious relationship between the average nanofiber diameter and gap distances for all plate widths except 1.5 mm plate width. It shows an increasing diameter trend for 1.5 mm plate width.

It is seen that clearly there is a relationship between the alignment of PAN nanofibers and CD. Increasing CD causes decrease in the alignment of nanofibers. The best alignment formations are obtained the lowest CD for both of the selected gap distance and plate width values. Results also show that increasing CD causes increase in the average diameter of nanofibers.

It is obviously seen that increasing of tip to collector distance distorts the orientation of the nanofibers. The best alignment formations of PAN nanofibers are obtained the lowest TCD for both of the selected gap distance and plate width values.

The conclusions of electrospun PVA nanofiber studies are given in the following.

It is seen that there is no obvious relationship between the alignment of PVA nanofibers and gap distance for narrower plate widths. However, alignment of

nanofibers generally increases for wider plate widths (15-20-30 mm). Similar trend is seen for the effect of plate width on nanofiber alignment. While there is no obvious relationship between the alignment of nanofibers and plate width for 1 cm and 2 cm of gap distance, alignment of nanofibers generally increases for wider gap distances (3-4-5 cm). There is no obvious relationship between the average nanofiber diameter and gap distance for all plate width values.

The best alignment formations of PVA nanofibers are obtained the lowest CD for both of the selected gap distance and plate width values. It is seen that there is obvious relationship between the alignment of nanofibers and CD for both of the selected gap distance and plate width values. Increasing CD causes decrease in the alignment of nanofibers. Increasing CD causes increase in the average diameter of nanofibers for both of the selected gap distance and plate width values.

The best alignment formations are obtained the lowest TCD for both of the selected gap distance and plate width values. It is seen that there is obvious relationship between the alignment of PVA nanofibers and TCD for both of the selected gap distance and plate width values. Increasing TCD causes decrease in the alignment of nanofibers. There is no obvious relationship between the average nanofiber diameter and TCD.

For further studies;

Different polymers can be investigated in parallel electrode electrospinning.

Collector material type such as copper, gold, brass etc. can be investigated in parallel electrode electrospinning.

Larger gap distance values can be investigated in parallel electrode electrospinning.

The effect of the parameters investigated in this thesis on mechanical properties of electrospun nanofibers can also be investigated.

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